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Plastics — Biobased content —

Part 2: Determination of biobased carbon content

Plastiques — Teneur biosourcée —

Partie 2: Détermination de la teneur en carbone biosourcé

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Foreword

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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).

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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 61, *Plastics*, Subcommittee SC 14, *Environmental aspects*.

This second edition cancels and replaces the first edition (ISO 16620-2:2015), which has been technically revised.

The main changes compared to the previous edition are as follows:

— REF values for calculation of biobased carbon content from percent modern carbon vs. years are listed in Table 2.

A list of all parts in the ISO 16620 series can be found on the ISO website.

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

Increased use of biomass resources for manufacturing plastic products is effective in reducing global warming and the depletion of fossil resources.

Current plastic products are composed of biobased synthetic polymers, fossil-based synthetic polymers, natural polymers, and additives that can include biobased materials.

“Biobased plastics” refer to plastics that contain materials, wholly or partly of biogenic origin.

In the ISO 16620 series, the “biobased content” of biobased plastics refers to the amount of the biobased carbon content, the amount of the biobased synthetic polymer content, or the amount of the biobased mass content only.

Plastics — Biobased content —

Part 2: Determination of biobased carbon content

WARNING — The use of this document might involve hazardous materials, operations, and equipment. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine any restrictions prior to use.

1 Scope

This document specifies a calculation method for the determination of the biobased carbon content in monomers, polymers, and plastic materials and products, based on the ^{14}C content measurement.

This document is applicable to plastic products and plastic materials (e.g. plasticisers or modifiers), polymer resins, monomers, or additives, which are made from biobased or fossil-based constituents.

Knowing the biobased content of plastic products is useful when evaluating their environmental impact.

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 16620-1, *Plastics — Biobased content — Part 1: General principles*

3 Terms, definitions, symbols and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 16620-1 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/

3.1.1
percent modern carbon
pMC
normalized and standardized value for the amount of the ^{14}C isotope in a sample, calculated relative to the standardized and normalized ^{14}C isotope amount of oxalic acid standard reference material, NIST SRM 4990b or NIST SRM 4990c or Sucrose (NIST SRM 8542)[1)]

Note 1 to entry: The reference value of 100 % biobased carbon is given in Table 2.

1) NIST SRM 4990b or NIST SRM 4990c or Sucrose (NIST SRM 8542) is the trade name of a product supplied by the US National Institute of Standards and Technology. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products can be used if they can be shown to lead to the same results.

3.1.2
radiocarbon
radioactive isotope of the element carbon, ^{14}C, having 8 neutrons, 6 protons, and 6 electrons

Note 1 to entry: Of the total carbon on Earth, 1×10^{-10} % is ^{14}C. It decays exponentially with a half-life of 5 730 years and, as such, it is not measurable in fossil materials derived from petroleum, coal, natural gas, or any other source older than about 50 000 years.

[SOURCE: ISO 13833:2013, 3.7]

3.2 Symbols

^{14}C	carbon isotope with an atomic mass of 14
m	mass of a sample expressed in grams
pMC(s)	measured value, expressed in pMC, according to AMS method, of the sample
REF	reference value, expressed in pMC, of 100 % biobased carbon depending on the origin of organic carbon
x^{TC}	total carbon content, expressed as a percentage of the mass of the sample
x^{TOC}	total organic carbon content, expressed as a percentage of the mass of the sample
x_B	biobased carbon content by mass, expressed as a percentage of the mass of the sample
x_B^{TC}	biobased carbon content by total carbon content, expressed as a percentage of the total carbon content
x_B^{TOC}	biobased carbon content by total organic carbon content, expressed as a percentage of the total organic carbon content

NOTE 1 "Biobased carbon content by mass, x_B" used in this document corresponds to "biobased carbon content on mass" defined in 3.3.9 of ASTM D6866-18.

NOTE 2 "Biobased carbon content by total carbon content, x_B^{TC}" corresponds to "biogenic carbon content" defined in 3.3.8 of ASTM D6866-18.

NOTE 3 "Biobased carbon content by total organic carbon content, x_B^{TOC}" corresponds to "biobased carbon content" defined in 3.3.7 of ASTM D6866-18.

3.3 Abbreviated terms

AMS	accelerator mass spectroscopy
BI	beta-ionization
Bq	Bequerel (disintegrations per second)
cpm	counts per minute
dpm	disintegrations per minute
GM	Geiger-Müller
LLD	lower limit of detection
LSC	liquid scintillation-counter or liquid scintillation-counting

MOP 3-methoxy 1-propyl amine

pMC percentage of modern carbon

TC total carbon

TOC total organic carbon

4 Principle

The ^{14}C present in chemicals originates from recent atmospheric CO_2. Due to its radioactive decay, it is almost absent from fossil products older than 20 000 years to 30 000 years. Thus, the ^{14}C content might be considered as a tracer of chemicals recently synthesized from atmospheric CO_2 and particularly of recently produced bio-products.

The determination of the biomass content is based on the measurement of ^{14}C in polymers which allows the calculation of the biobased carbon fraction.

A large experience in ^{14}C determination and reference samples are available from dating of archaeological objects, on which the three methods described in this document are based:

— Method A: Liquid scintillation-counter method (LSC);

— Method B: Beta-ionization (BI);

— Method C: Accelerator mass spectrometry (AMS).

NOTE 1 The advantages and disadvantages of these test methods are given in Table 1.

Table 1 — Advantages and disadvantages of the methods

Method	Additional requests	Duration needed for measurement	Relative standard deviation	Instrumental costs
Method A (LSC)	Normal laboratory	4 h to 12 h	2 % to 5 %	Low
Method B (BI)	— Low background laboratory — Gas purification device	8 h to 24 h	0,2 % to 5 %	Low
Method C (AMS)	— Large installation — Graphite conversion device	10 min to 30 min	0,2 % to 2 %	High

For the ^{14}C LSC measurement, a low level counter should be used. The statistical scattering of the radioactive decay sets a limit, both for Method A and B. Thereby, both methods need a purified carbon dioxide, otherwise, oxides of nitrogen from the combustion in the calorific bomb will result in counting losses by quenching and adulteration of the cocktail in case of LSC measurement. When using Method A (LSC), samples with low bio-based carbon content (<10 %) can only be measured with sufficient precision using the benzene conversion procedure or, if applicable, direct LSC measurement, as described in Annex A.

NOTE 2 At this moment compact new AMS equipment has become available. In a number of cases, no graphite conversion is required anymore. CO_2 gas can be measured directly by these AMS.

5 Sampling

If there is a standard sampling procedure for the material or product to be evaluated that is widely accepted by the different parties, such a procedure can be used and the details of sampling recorded.

For any sampling procedure, the samples shall be representative of the material or product and the quantity or mass of sample shall be accurately established.

6 Determination of the ^{14}C content

6.1 General

A general sample preparation and three test methods for the determination of the ^{14}C content are described in this document. With this modular approach, it will be possible for normally equipped laboratories to prepare samples for the ^{14}C content and determine the ^{14}C content with own equipment or to outsource the determination of the ^{14}C content to laboratories that are specialized in this technique.

For the collection from the sample of the ^{14}C content, generally accepted methods for the conversion of the carbon present in the sample to CO_2 are described.

For the measurement of the ^{14}C content, methods are selected that are already generally accepted as methods for the determination of the age of objects.

6.2 Principle

The amount of biobased carbon in the biobased polymer is proportional to this ^{14}C content.

Complete combustion (see Annex A) is carried out in a way to comply with the requirements of the subsequent measurement of the ^{14}C content and shall provide the quantitative recovery of all carbon present in the sample as CO_2 in order to yield valid results. This measurement shall be carried out according to one of the two following methods:

— Liquid scintillation-counter method (LSC) (Method A): indirect determination of the isotope abundance of ^{14}C through its emission of beta-particles (interaction with scintillation molecules), specified in Annex B;

— Accelerator mass spectrometry (AMS) (Method C): direct determination of the isotope abundance of ^{14}C, specified in Annex D.

This measurement can also be carried out according to Method B [Beta-ionization (BI)]: indirect determination of the isotope abundance of ^{14}C, through its emission of beta-particle (Geiger-Müller type detector), described in Annex C.

6.3 Procedure for the conversion of the carbon present in the sample to a suitable sample for ^{14}C determination

The conversion of the carbon present in the sample to a suitable sample for the determination of the ^{14}C content shall be carried out according to the Annex A.

6.4 Measurement techniques

The $_{14}C$ content of the sample shall be determined using one of the methods as described in Annex B, Annex C, or Annex D.

When 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 in leak of CO_2 from air shall be performed by preparing laboratory blank's during the sampling stage.

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

For validation of the 100 % biomass content, the oxalic acid standard reference material NIST SRM 4990b or SRM 4990c or Sucrose (NIST SRM 8542) may be used. Mixing reference material NIST 4990 with a

known amount of fossil combustion aid improves its combustion behaviour, as oxalic acid is difficult to combust due to its low calorific value. For routine checks, a wood standard reference material calibrated against the oxalic acid is sufficient.

7 Determination of the total carbon content and total organic carbon content

The total carbon content and total organic carbon content shall be determined according to suitable methods.

Test methods as described in ISO 609, ISO 8245, ISO 10694, ISO 15350, ISO 17247, ASTM D5291-16, ASTM E1019 or EN 13137, can be used, as applicable.

8 Calculation of the biobased carbon content

8.1 General

The calculation of the biobased carbon content includes the following steps:

a) the determination of the total carbon content of the sample, x^{TC}, determined by one of the test methods specified in Clause 7, expressed as a percentage of the total mass or the determination of the total organic carbon content of the sample, x^{TOC}, determined by one of the test methods specified in Clause 7, expressed as a percentage of the total mass;

b) the calculation of the biobased carbon content by mass, x_B, using the ^{14}C content value, determined by calculation from one of the test methods specified in Clause 6, and applying the correction factors detailed in 8.2;

c) the calculation of the biobased carbon content as a fraction of the total carbon content, x_B^{TC} (see 8.3.2) or a fraction of the total organic carbon content, x_B^{TOC} (see 8.3.3).

8.2 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 year 1962 is 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 D6866-18 the 100 % bio-based C value of 100,5 pMC (for year 2018) 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.

The 100 % bio-based C value equates to decline of 0,5 pMC per year. Therefore, on January 1st of each year, the values given in Table 2 are used through 2019, reflecting the 0,5 pMC decrease per year.

Table 2 — 100 % biobased carbon values versus year

Year	100 % biobased carbon value REF (pMC, %)
2015	102,0
2016	101,5
2017	101,0
2018	100,5

Table 2 *(continued)*

Year	100 % biobased carbon value REF (pMC, %)
2019	100,0
2020	To be determined

NOTE These values are in accordance with ASTM D 6866-18.

From the 100,5 pMC value the correction factor of 0,995 (1/1,005) is derived. For the calculation of the bio-based carbon content, a ^{14}C content of 100/0,995 pMC or 13,56/0,995 dpm per gram C is considered as a 100 % biobased carbon content for biomass that is grown in year 2016.

The fraction of biomass content by mass shall be calculated using the biomass carbon in the biobased polymer as for other organic carbon materials.

8.3 Calculation method

8.3.1 Calculation of the biobased carbon content by mass, x_B

8.3.1.1 ^{14}C content determined by Method A (LSC) or Method B (BI)

Calculate the biobased carbon content by mass, x_B, expressed as a percentage, using Formula (1):

$$x_B = \frac{^{14}C_{activity}}{13{,}56 \times \frac{REF}{100} \times m} \times 100 \quad (1)$$

where

$^{14}C_{activity}$ is the ^{14}C activity, expressed in dpm, of the sample obtained by calculation when using Method A or Method B (see Annex B or Annex C);

REF is the reference value, expressed in pMC, of 100 % biobased carbon of the biomass from which the sample is constituted;

m is the mass, expressed in grams, of the sample.

8.3.1.2 ^{14}C content determined by Method C (AMS)

Calculate the biobased carbon content by mass, x_B, expressed as a percentage, using Formula (2):

$$x_B = x^{TC} \frac{\frac{pMC(s)}{100}}{\frac{REF}{100}} = x^{TC} \frac{pMC(s)}{REF} \quad (2)$$

where

x^{TC} is the total carbon content obtained by elemental analysis, expressed as a percentage, of the total mass, of the sample;

$pMC(s)$ is the measured value, expressed in pMC, of the sample;

REF is the reference value, expressed in pMC, of 100 % biobased carbon of the biomass from which the sample is constituted.

8.3.2 Calculation of the biobased carbon content, x_B^{TC}, as a fraction of TC

Calculate the biobased carbon content as a fraction of the total carbon content, x_B^{TC}, expressed as a percentage, using Formula (3):

$$x_B^{TC} = \frac{x_B}{x^{TC}} \times 100 \quad (3)$$

where

x_B is the biobased carbon content by mass, expressed as a percentage;

x^{TC} is the total carbon content, expressed as a percentage, of the sample.

8.3.3 Calculation of the biobased carbon content, x_B^{TOC}, as a fraction of TOC

Calculate the biobased carbon content as a fraction of the total organic carbon content, x_B^{TOC}, expressed as a percentage, using Formula (4):

$$x_B^{TOC} = \frac{x_B}{x^{TOC}} \times 100 \quad (4)$$

where

x_B is the biobased carbon content by mass, expressed as a percentage;

x^{TOC} is the total organic carbon content, expressed as a percentage, of the sample.

8.3.4 Examples

EXAMPLE 1 Calculation of biobased carbon content as a fraction of TC

Pure biobased polymer material

Sample made from PLA material: x^{TC} = 50,0 %; x_B = 50 %

$$x_B^{TC} = \frac{50,0}{50,0} \times 100 = 100\%$$

EXAMPLE 2 Calculation of biobased carbon content as a fraction of TOC

Mixed biobased polymer material

Sample made from PE material containing a mixture of fossil PE and PE produced from biogenic synthesis gas:

$$x^{TOC} = 86,0\%; x_B = 24,0\%$$

$$x_B^{TOC} = \frac{24,0}{86,0} \times 100 = 27,9\%$$

9 Test report

The test report shall include at least the following information:

a) a reference to this document, i.e. ISO 16620-2:2019;

b) all information necessary for complete identification of the biobased polymer material or product tested, including the origin of the biomass from which the material or product is constituted;

c) identification of the laboratory performing the test;

d) sample preparation;

e) storage conditions;

f) test method used for the determination of the ^{14}C content (Method A, B, or C, see Annex B, Annex C, or Annex D);

g) test methods used for the determination of the TC content and TOC content (see Clause 7);

h) results of the test including the basis on which they are expressed and application of the isotope correction, including a precision statement;

i) method for the conversion of the carbon (see A.4);

j) ^{14}C activity, expressed in dpm, of the sample or ^{14}C value, expressed in pMC;

k) total carbon content, x^{TC}, expressed as a percentage, of the sample;

l) REF value used;

m) total organic carbon content, x^{TOC}, expressed as a percentage, of the sample;

n) biobased carbon content by mass, x_B, expressed as a percentage, of the sample;

o) biobased carbon content by total carbon content, x_B^{TC}, expressed as a percentage, of the sample;

p) biobased carbon content by total organic carbon content, x_B^{TOC}, expressed as a percentage, of the sample;

q) any additional information, including details of any deviations from the test methods and any operations not specified in this document which could have had an influence on the results;

r) date of receipt of laboratory sample and dates of the test (beginning and end).

Annex A
(normative)

Procedure for the conversion of the carbon present in the sample to a suitable sample for ^{14}C determination

A.1 General

This annex describes the steps to prepare samples for ^{14}C determinations. The laboratories which are not equipped for ^{14}C analysis can prepare their samples for distribution to laboratories that are equipped for ^{14}C analysis.

For the determination of the ^{14}C content, carbon present in the sample shall be converted to CO_2. The conversion is performed by the combustion in oxygen. If necessary, a combustion aid can be used to ensure complete oxidation of carbon to CO_2.

For some liquid samples, no conversion to CO_2 is needed and a direct measurement of the ^{14}C content can be performed using LSC.

A.2 Preparation

A.2.1 General

The ^{14}C content of a biobased polymer is determined on CO_2 produced by the sample combustion. For the conversion of the sample to CO_2 used for the determination of the ^{14}C content, the following three methods are allowed:

— combustion in a calorimetric bomb (A.3.1);

— combustion in a tube furnace (A.3.2);

— combustion in a laboratory scale combustion apparatus (A.3.2).

In case of combustion, it depends on the method to be used for the determination of ^{14}C content how the formed CO_2 is collected and prepared for the measurement.

When Method C is used, the following are the three options:

a) direct collection of the formed CO_2 in a gas bag or a sealed quartz tube with CuO;

b) absorption of CO_2 in a 4 mol/l NaOH solution;

c) absorption in a solid absorber, developed for that purpose, usually NaOH or KOH fixed on a silica carrier (e.g. Carbotrap ®[2)]).

As Method C requires only a few milligrams of carbon containing matter, sample material containing CO_2 amounts of a few milligrams can be used.

In case of Method B, a direct collection of CO_2 in a gas bag, lecture bottle, or NaOH solution is allowed as well, provided the total amount of carbon present in the sample is at least 2 g.

2) Carbotrap is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

In case of Method A, the following three options are possible after combustion:

a) direct adsorption of the formed CO_2 in a carbamate solution [a suitable CO_2 absorption solution containing an amine, e.g. 1 mol/l 3-methoxypropylamine in ethanolamine, or Carbo-Sorb E®[3)]];

b) adsorption of the CO_2 in a 2 mol/l NaOH solution and transfer of CO_2 in NaOH to a carbamate solution;

c) direct conversion of CO_2 to benzene.

In some cases, the total carbonate content in the sampling solution shall be determined. For the direct sampling in carbamate solutions, the carbonate content can be determined by weighing the sample solution before and after sampling. For sampling in NaOH or KOH solutions, the carbonate content can be determined by standard methods using e.g. titrimetry. Guidance for such determination can be found in, for example, ISO 9963 (all parts) and ASTM D513-16. Carbamate solution was directly measured by Method A or B. CO_2 or graphite from CO_2 reproduced from carbamate solution was measured by Method C.

A.2.2 Reagents and materials

A.2.2.1 Carbamate solution.

A.2.2.2 Scintillation medium.

A.2.2.3 Glass bottles (standard glass sample bottles with plastic screw caps that are resistant to 4 mol/l NaOH).

A.2.2.4 4 mol/l NaOH, absorption liquid.

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

A.3 Combustion of the sample

A.3.1 Combustion of the sample in a calorimetric bomb

For the combustion of the sample in a calorimetric bomb, any suitable test method such as ISO 1716, ISO 1928 or EN 15400 can be used.

After the complete combustion in the oxygen bomb, the combustion gases are collected in a gas bag.

For biobased polymers that are difficult to combust, use a combustion aid to obtain complete combustion. Examples of combustion aids are polyethylene combustion bags, benzoic acid and glucose. Take care not to exceed the maximum amount of organic material allowable for the oxygen bomb that is used. Determine the amount of ^{14}C present in the combustion aid and correct for the contribution of the use of the combustion aid. (^{14}C content and total carbon content).

The determination of the carbonate content in the solution collected after combustion can be used to determine the yield of conversion. The carbonate content shall be equivalent to the amount of total carbon present in the combusted sample (including combustion aid).

3) Carbo-Sorb E is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

When Method A is used, the CO_2 shall be collected in a 4 mol/l NaOH solution prior to the conversion to benzene or collected in a cooled mixture of carbamate solution and a suitable scintillation liquid.

For the collection of CO_2 in 4 mol/l NaOH solution use a 250 ml washing bottle filled with 200 ml 4 mol/l NaOH solution, apply a flow of 50 ml/min.

For the collection of CO_2 in a carbamate solution the gas sample bag is connected to a pump with a connection line into a 20 ml glass vial, filled with a mixture of 10 ml of the carbamate sorption liquid and 10 ml of the scintillation cocktail, placed in an ice bath, to remove the heat of the exothermic carbamate formation reaction. The pumping speed is low, typically 50 ml·min^{-1} to 60 ml·min^{-1}. The transfer of the gas from the bag takes about 2 h to 3 h. After the sample has been collected, it is ready to be counted on a liquid scintillation counter. Blank samples shall 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 done as soon as possible after collection. At the latest, it shall be done within one week after sampling. 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. If the one week limit cannot be realized, collection of the CO_2 in a 4 mol/l NaOH solution is a good alternative.

When Method B or Method C is used, the CO_2 shall be collected in a 4 mol/l NaOH solution or on a suitable scintillation solid absorber.

For Method C, alternatively, approximately 2 ml of the CO_2 gas can be taken from the bag using a glass syringe and the gas can be transferred to the AMS target preparations system. As the bomb volume is released to atmospheric pressure, there will be a residual amount left over in the bomb that is directly related to the pressure in the bomb after the combustion.

NOTE With a residual pressure of 2,5 MPa, 4 % of the combustion gas will be left after release to atmospheric pressure.

To overcome this artefact:

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

b) use the vacuum pump to remove the residue;

c) flush the bomb with argon and collect the CO_2 in the rinsing gases as well.

A.3.2 Combustion of the sample in a tube furnace or a combustion apparatus

The tube furnace or the combustion apparatus shall be able to combust the biobased polymer with a complete conversion of the carbon present to CO_2. For the determination of the ^{14}C content by Method A, the CO_2 shall be collected using a suitable impinger filled with a cooled mixture of carbamate and a suitable scintillation liquid, a scintillation medium already containing a CO_2 absorber, or a 4 mol/l NaOH solution (see A.2.2.4). For the determination of the ^{14}C content by Method C or Method B, the CO_2 shall be collected using a suitable impinger filled with a 4 mol/l NaOH solution. As a result of the absorption of the CO_2, a large volume reduction of the gas volume will be observed after trapping. Therefore, the gas pump is to be positioned in front of the impinger and the gas pump used shall be gas tight.

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

A.3.3 Direct LSC measurement on the polymer

For liquid clear biobased polymers, direct measurement on the biobased polymer with the LSC technique is possible. This option is only allowed if equivalence with the methods with conversion to CO_2 can be demonstrated. This will, in general, be the case if no quenching is observed or if correction for quenching is performed using standard addition technique using the same, ^{14}C labelled, biobased polymer with known ^{14}C activity.

The dissolution method might not be appropriate to some biobased polymers, for instance when fillers are present.

For direct LSC measurements, DIN 51637 is recommended.

A.4 Standardization measurement results

A.4.1 LSC and BI methods

A liquid scintillation counter measures β-decay counts of ^{14}C (in counts per minute, cpm) indirectly by measuring the interaction signals of the β particles with scintillation molecules (emission of photons –light- proportional to the decay energy). For this measurement, sample CO_2 is either absorbed in a suitable absorbing solution to which also a scintillation reagent is added ("CO_2 -cocktail") or the CO_2 has been converted to benzene and is then mixed with liquid (scintillation) reagents to a 'benzene-cocktail'. The "benzene cocktail" method is more precise than the "CO_2-cocktail" method.

The same standardization as used for AMS and proportional gas counters shall be used for LSC measurement results. $^{14}C_{sampleC}$ shall be calculated by using Formula (A.1):

$$^{14}C_{sampleC}\,(pMC) = {}^{14}a_N^s \cdot 100 = \frac{{}^{14}A_N^s}{{}^{14}A_{RN}^0} \cdot 100 = \frac{\left({}^{14}A_{sample} - {}^{14}A_{bg}\right) \cdot \eta_{meas} \cdot \left[\frac{1 + {}^{13}\delta_N}{1 + {}^{13}\delta_{sample}}\right]^2}{{}^{14}A_{RN}^0} \cdot 100 \qquad \text{(A.1)}$$

where

$^{14}C_{sampleC}$ is the measured ^{14}C value (in pMC) of the investigated CO_2 sample;

$^{14}a_N^S$ is the standardized and normalized ^{14}C amount of the measured sample;

$^{14}a_N^S \cdot 100 = pMC$

$^{14}A_N^S$ is the normalized ^{14}C signal (isotope concentration or activity) of the measured sample;

$^{14}A_{RN}^0$ is the standardized and normalized ^{14}C amount of the primary reference standard, Oxalic acid (HOx-II, SRM 4990c);

$^{14}A_{sample}$ is the measured ^{14}C signal (isotope concentration or activity) of the sample;

$^{14}A_{bg\,sample}$ is the measured ^{14}C signal (isotope concentration or activity) of the background sample/blank sample, measured in the same batch as the sample and represents the background ^{14}C signal of the measured samples;

η_{meas} is the measuring efficiency of the used measurement technique;

$^{13}\delta_N$ is the standardized value for isotope fractionation. $^{13}\delta_N = -0{,}025$ (relative to VPDB);

$^{13}\delta_{sample}$ is the measured isotope fractionation value of the sample. It is obtained by measuring the $^{13}C/^{12}C$ ratio of the sample, relative to the measured $^{13}C/^{12}C$ ratio of a reference standard with known isotope fractionation value related to VPDB.

In the case that no primary or secondary reference standard has been measured, the measuring efficiency is not cancelled out and shall be determined using an internal standard. It is also necessary in that case to determine the activity of the sample in dpm/gC (disintegrations per minute) instead of cpm/gC. $^{14}A_{RN}^{0}$ = 13,56 ± 0,07 dpm/gC = 0,226 ± 0,001 Bq/gC.

A.4.2 AMS method

The AMS system measures the carbon isotopes ^{12}C, ^{13}C and ^{14}C of a carbon sample in the same sample run. A batch of samples shall also contain reference material samples. The measured ^{14}C amount (=^{14}C isotope concentration) in a sample is calculated relative to the measured (average) ^{14}C amount of the reference material samples in the same batch. If the reference material is the primary reference standard Oxalic Acid II (HOx-II, SRM 4990c), which is commonly used for this purpose, the standardized ^{14}C amount in the sample, $^{14}C_{sampleC}$ (= $^{14}a_N^S \cdot 100\%$ = pMC), shall be calculated by using Formula (A.2).

$$^{14}C_{sampleC}\,(pMC) = \frac{\left(^{14}A_{sample} - ^{14}A_{bg_{sample}}\right)\cdot\eta_{meas}\cdot\left[\frac{1+^{13}\delta_N}{1+^{13}\delta_{sample}}\right]^2}{0{,}7459\cdot\left(^{14}A_{OX2} - ^{14}A_{bg_{OX2}}\right)\cdot\eta_{meas}\cdot\left[\frac{1+^{13}\delta_N}{1+^{13}\delta_{OX2}}\right]^2}\cdot 100 \qquad \text{(A.2)}$$

where

$^{14}C_{sampleC}$ is the measured ^{14}C value (in pMC) of the investigated CO_2 sample;

$^{14}A_{sample}$ is the measured ^{14}C signal (isotope concentration or activity) of the sample;

$^{14}A_{bg_{sample}}$ is the measured ^{14}C signal (isotope concentration or activity) of the background sample/blank sample, measured in the same batch as the sample and represents the background ^{14}C signal of the measured samples;

$^{14}A_{OX2}$ is the measured (average) ^{14}C signal (isotope concentration or activity) of Oxalic acid reference standard samples (HOx-II, SRM 4990c), measured in the same batch as the unknown samples;

$^{14}A_{bg_{OX2}}$ is the measured (average) ^{14}C signal (isotope concentration or activity) of background samples, which represent the background signal of the measured Oxalic Acid reference standard (HOx-II, SRM 4990c), measured in the same batch as the Oxalic Acid samples;

η_{meas} is the measuring efficiency of the used measurement technique;

$^{13}\delta_N$ is the standardized value for isotope fractionation,

where $^{13}\delta_N$ = −0,025 (relative to VPDB);

$^{13}\delta_{sample}$ is the measured isotope fractionation value of the sample. It is obtained by measuring the $^{13}C/^{12}C$ ratio of the sample, relative to the measured $^{13}C/^{12}C$ ratio of a reference standard with known isotope fractionation value related to VPDB;

$^{13}\delta_{OX2}$ is the standardized isotope fractionation value of the Oxalic Acid reference standard; (HOx-II, SRM 4990c). $^{13}\delta_{OX2}$ = −0,017 6 (relative to VPDB). Decay rate of ^{14}C (in year). ^{14}C has a half-life of 5 730 years.

Annex B
(normative)

Method A — Determination by liquid scintillation-counter method (LSC)

B.1 General

This annex describes the method for the determination of the ^{14}C content by LSC in carbonate solutions or carbamate solutions obtained from the combustion of biobased polymer samples in a calorimetric bomb, a tube furnace, or a laboratory scale combustion device, as described in Annex A.

B.2 Principle

LSC determines the isotope abundance of ^{14}C indirectly through its emission of beta-particles due to the radioactive decay of the ^{14}C isotope. The beta-particles are observed through their interaction with scintillation molecules. The CO_2 formed by the combustion of a biobased polymer is trapped in an alkaline or carbamate solution. The CO_2 present in the alkaline solution is converted to benzene; the carbamate solution can directly be measured. The formed benzene or carbamate solution is mixed with the organic solution containing the scintillation molecules and the ^{14}C activity of this mixture is measured in a liquid scintillation counter.

B.3 Reagents and materials

B.3.1 Oxalic acid primary standard, e.g. SRM 4990c.

B.3.2 HCl solution, 5 mol/l.

B.3.3 Scintillation cocktail.

B.3.4 Carbamate solution.

B.3.5 ^{14}C labelled spike solutions for standard addition purposes.

B.3.6 Coal standard, e.g. BCR 181.

B.3.7 Reagent grade powdered lithium or lithium rod (each packed in Argon).

B.3.8 Reagent grade potassium chromate (in sulfuric or phosphoric acid).

B.3.9 Suitable catalyst (based on Cr_2O_3 or V_2O_5).

B.4 Apparatus

The low natural levels of radiocarbon-14 (^{14}C) in the earth's atmosphere (about 10^{-12} % volume fraction) require 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, and other factors. These background factors limit the accuracy,

precision, and range of the radiocarbon dating method as finite ages can only be calculated where sample activity is at least 3 standard deviations above background activity. Any liquid scintillation counter used shall meet these specifications.

B.5 Procedure

B.5.1 General

The best LSC performance characteristics are obtained by applying conversion of the collected CO_2 to benzene and direct counting of the benzene in a suitable scintillation cocktail, as for instance described in ASTM D 6866. For material with a high bio-based carbon content (>10 %), direct absorption of the CO_2 in a carbamate solution can be applied.

B.5.2 Benzene conversion

The collected CO_2 is reacted with a stoichiometric excess (3:1 lithium: carbon ratio) of molten lithium which has been preheated to 700 °C. Li_2C_2 is produced by slowly bleeding the CO_2 onto the molten lithium in a stainless steel vessel (or equivalent) while under a vacuum of < 135 mPa. The Li_2C_2 is heated to at least 640 °C and placed under vacuum for 15 min to 30 min to remove any unreacted gases and to complete the Li_2C_2 synthesis reaction. The Li_2C_2 is cooled to room temperature and gently hydrolysed with distilled or de-ionized water to generate acetylene gas (C_2H_2) by applying the water in a drop-wise fashion to the cartridge.

Passing it through dry ice traps dries the evolved acetylene, and the dried acetylene is subsequently collected in liquid nitrogen traps. The acetylene is purified by passing it through a phosphoric acid or potassium chromate (in sulphuric acid) trap to remove trace impurities, and by using dry ice traps to remove water. The C_2H_2 gas is catalysed to benzene (C_6H_6) by bleeding the acetylene onto a chromium catalyst which has been preheated to ≥ 90 °C applying a water jacket cooler to avoid decomposition from excessive heat generated during the exothermic reaction. As an alternative, a vanadium catalyst at ambient temperature can be used. The benzene is thermally evolved from the catalyst at 70 °C to 110 °C and then collected under vacuum at –78 °C. The benzene is then frozen until it is counted. Radon can be removed by pumping on the benzene while it is at dry ice temperature. Mix the benzene and scintillation cocktail in constant volume and proportion, if necessary benzene can be diluted with benzene from fossil origin (99,999 % pure, thiophene-free).

If ^{13}C isotope analysis is required, a representative subsample shall be taken extra for ^{13}C analysis.

B.5.3 Direct absorption of the CO_2 in a carbamate solution

An absorption flask is loaded with a known volume of CO_2 absorbent, e.g. with a suitable CO_2 absorption solution containing an amine, e.g. One mol/l 3-methoxypropylamine in ethanolamine, or Carbo-Sorb E.- The absorbing capacity of a suitable CO_2 absorption solution containing an amine, e.g. one mol/l 3-methoxypropyl in ethanolamine, or Carbo-Sorb E of about $4{,}8 \cdot 10^{-3}$ mol/ml shall be taken into account; no more than 80 % of this capacity shall be used. The flask shall be cooled in ice during the absorption process. After absorption of the CO_2, the absorbent is transferred to the measuring vial. An equal volume of the scintillation cocktail is added and the mixture is homogenized.

The CO_2 may also be absorbed in a scintillation cocktail already containing a CO_2 absorber, which shall be measured in the LSC without further handling.

Then the vial containing the mixture is placed in the LSC and measured. Typical counting times are 6 h to 24 h.

B.5.4 Measurement

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 (LSC) is related to the number of registrations of the reference sample under the same conditions.

Standard addition techniques shall 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.

For clear liquids direct LSC counting can be applied, e.g. as described in DIN 51637; mix 10 ml. of sample with 10 ml of a suitable scintillation cocktail and count after 12 h settling time. For each biobased polymer a quench curve shall be established before measurements can be done.

B.5.5 Blank correction

Measurement shall be performed together with a measurement of the "blank" sample, which is a scintillation vial filled with counting liquid 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.

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.

B.6 Calculation of the results

The background count rate of the counter is subtracted from the sample count rate to give the net count rate. The ^{14}C activity (dpm/gC) is obtained by normalizing the net count rate to the count rate of the reference standard (e.g. oxalic acid SRM 4990c).

Standardization of the LSC results shall be done as described in A.4.1.

Annex C
(informative)

Method B — ^{14}C determination by beta-ionization

C.1 General

This annex describes the procedure for the determination of the ^{14}C content by BI in basic carbonate solutions obtained from the combustion of biobased polymer samples in a calorimetric bomb, a tube furnace, or a laboratory scale combustion device, as described in Annex A.

C.2 Principle

The BI method determines the isotope abundance of ^{14}C indirectly. This method uses the emission of beta-particles by ^{14}C due to the radioactive decay of the ^{14}C isotope, like LSC. It detects beta-particles by means of discharging current pulses between high-voltage electrodes in a proportional gas counter. Those pulses are initiated by the beta-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 should be in the form of CO_2 or converted to CO_2. The carbonate, as obtained from the combustion of a biobased polymer, is converted to CO_2 by acidifying the NaOH solution with HCl. The CO_2 is purified to be suitable as a counting gas in a gas proportional counter, e.g. by removal of electron-negative impurities, such as oxygen, SO_2, or water vapour, through activated charcoal and radon. This step also removes radon. The purity of the gas is critical (e.g. O_2 levels need to be kept well below a few microlitres per litre).

The sample is counted for several days in a low-level counting system to reach the number of counts desired for statistical precision.

The CO_2 is held under pressure in the central tube (typically at 0,2 MPa to 0,3 MPa) and a high voltage is introduced between the central wire and the counter wall. An ionizing event, such as a β^- particle produced by a ^{14}C decay, creates an ionization trail and an avalanche of electrons. This avalanche is measured as an electrical pulse. Any impurities in the gas will quench the multiplication of electrons, leading to some decay events being undetected.

C.3 Reagents and materials

C.3.1 HCl solution, 5 mol/l.

C.3.2 NaOH solution, 4 mol/l.

C.3.3 Dry ice.

C.3.4 Organic solvent, acetone or ethanol.

C.3.5 Liquid nitrogen.

C.3.6 Oxalic acid primary standard, e.g. SRM 4990c.

C.3.7 Activated charcoal.

C.3.8 Coal standard, e.g. BCR 181.

C.4 Apparatus

C.4.1 System for the conversion of carbonate trapped in a 4 mol/l NaOH solution to CO_2.

C.4.2 CO_2 purification system, e.g. using activated charcoal.

C.4.3 System to obtain a fixed amount of sample, e.g. by adjusting the CO_2 pressure in a fixed volume and known gas temperature.

C.4.4 System to prepare standard and background samples.

C.4.5 Low-level counting system using a gas proportional counter.

The instruments used for the BI measurements are homemade high tech devices developed at several radiocarbon institutes. No commercial systems are available at the time of writing this document. For radiocarbon to be detectable, minimize background counts. Gas (in this case, purified CO_2 derived from the combustion gases) is loaded and counted in a copper counting tube (ultra-pure copper) and the desired low background is obtained applying heavy shielding with old lead and anticoincidence filtering of cosmic radiation. Usually, BI devices are located below ground level in cellars in order to obtain extra protection against cosmic radiation. Typical counting times are several days for low-level measurements.

C.5 Procedure

C.5.1 Transfer the carbonate solution to extraction bottle.

C.5.2 Attach the HCl solution dosing device.

C.5.3 Evacuate the bottle and dosing device (degassing, removal of dissolved N_2 and O_2 from air).

C.5.4 Add HCl solution to the carbonate solution.

C.5.5 Remove water vapour using a trap filled with acetone and dry ice.

C.5.6 Collect the formed CO_2 in a stainless steel trap that is submersed in liquid nitrogen.

C.5.7 Purify the CO_2, e.g. using activated carbon at 0° C.

C.5.8 Take a small sample for ^{13}C determination at this stage (optional).

C.5.9 Calculate the CO_2 volume by measuring the temperature and pressure and the known volume of the trapping system.

C.5.10 Transfer the CO_2 to the proportional counter (amounts up to 4 g of CO_2).

C.5.11 Count for several days until precision, as desired, is obtained.

C.5.12 Calculate the modern carbon value using the sample count rate and the blank count rate.

C.5.13 The statistical error of counting the sample, background, and standard is a result of the decay counting, following the statistical Poisson distribution. 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.

C.5.14 The total error is then the combination of the analytical errors and the errors of the standard and background determination. The latter errors usually are small compared to the sampling errors. With counting times of a few days, a typical overall (absolute) precision of 0,3 % to 0,4 % can be obtained. The estimated precision shall be reported in addition to the value declared.

C.5.15 When using activated charcoal for the purification of CO_2, the active carbon cartridge should be preheated for approximately 1 h in order to remove traces of radon (build-up of decay product of Uranium traces present in the activated charcoal). For other cleaning techniques, a waiting time of 2 days is sufficient to avoid any radon contribution.

C.6 Calculation of the results

From the sample count rate, the count rate of the NaOH blank solution is subtracted resulting in the net count rate. The ^{14}C activity (pMC) is obtained by normalizing the net count rate to the count rate of the reference standard (Oxalic acid SRM 4990c or materials that are traceable to this reference standard).

If correction for isotopic fractionation should be performed, then the $^{13}C/^{12}C$ isotopic ratio should be determined as well.

Standardization of the BI results shall be done as described in A.4.1.