

ICS 71.040.40; 13.020.55

English Version

Bio-based products- Use of stable isotope ratios of Carbon, Hydrogen, Oxygen and Nitrogen as tools for verification of the origin of bio-based feedstock and characteristics of production processes - Overview of relevant existing applications

Produits biosourcés - Utilisation des rapports isotopiques stables du carbone, de l'hydrogène, de l'oxygène et de l'azote comme outils de vérification de l'origine des matières premières biosourcées et des caractéristiques des procédés de production - Vue d'ensemble des applications existantes pertinentes

Biobasierte Produkte - Verwendung der Verhältnisse stabiler Isotope von Kohlenstoff, Wasserstoff, Sauerstoff und Stickstoff als Werkzeuge zur Überprüfung der Herkunft von biobasierten Rohstoffen und der Eigenschaften von Produktionsprozessen - Übersicht über relevante bestehende Anwendungen

This Technical Report was approved by CEN on 18 July 2021. It has been drawn up by the Technical Committee CEN/TC 411.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

Contents

Page

European foreword.....	3
Introduction	4
1 Scope.....	5
2 Normative references.....	5
3 Terms and definitions	5
4 Direct isotopic measurements	5
5 Assessment of the authenticity of natural products.....	6
6 Overview of feedstock isotopic fingerprint	8
6.1 C4 plant.....	8
6.2 Other raw materials: C3 plants	9
7 Determination of Biobased content for feedstocks and products.....	10
7.1 Bioplastics.....	10
7.2 Bio-rubbers	13
7.3 Biofuels – Bio-solvents	14
7.4 Biosurfactants	15
7.5 Other bio products.....	18
7.5.1 Biocosmetics	18
7.5.2 Bio-Flavours-Foods	20
7.5.3 Bio-pesticides	21
8 Monitoring industrial process approach.....	22
8.1 General.....	22
8.2 Synthesis of Isosorbide	22
8.3 Synthesis of a specific plastic.....	23
9 Supplementary benefits.....	25
9.1 Technical impacts	25
9.1.1 Bulk Stable Isotope Analysis	25
9.1.2 Compound Specific Isotope Analysis.....	26
9.1.3 Approach multi methods.....	27
9.2 Sustainability criteria	28
9.2.1 General.....	28
9.2.2 Agricultural and social impacts	28
9.2.3 Cosmetic issue	28
9.2.4 Religious impact	28
Bibliography	29

European foreword

This document (CEN/TR 17674:2021) has been prepared by Technical Committee CEN/TC 411 “Bio-based products”, the secretariat of which is held by NEN.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

Introduction

Part of **OPEN BIO Deliverable N°3.8** is used as starting point for the description given in this document. Bio-based products from forestry and agriculture have a long history of application, such as paper, board and various chemicals and materials. Over the last decades new bio-based products have emerged in the market. Some of the reasons for the increased interest lie in the bio-based products' benefits in relation to the depletion of fossil resources and climate change. Bio-based products may also provide additional product functionalities. This has triggered a wave of innovation with the development of knowledge and technologies allowing new transformation processes and product development.

Acknowledging the need for common standards for bio-based products, the European Commission issued Mandate M/492¹⁾, resulting in a series of standards developed by CEN/TC 411, with a focus on bio-based products other than food, feed and biomass for energy applications.

The standards of CEN/TC 411 "Bio-based products" provide a common basis on the following aspects:

- Common terminology
- Bio-based content determination
- Life Cycle Assessment (LCA)
- Sustainability aspects
- Declaration tools

It is important to understand what the term bio-based product covers and how it is being used. The term 'bio-based' means 'derived from biomass'. Bio-based products (bottles, insulation materials, wood and wood products, paper solvents, chemical intermediates, composite materials, etc.) are products which are wholly or partly derived from biomass. It is essential to characterize the amount of biomass contained in the product by, for instance, its bio-based content or bio-based carbon content.

The bio-based content of a product does not provide information on its environmental impact or sustainability, which may be assessed through LCA and sustainability criteria. In addition, transparent and unambiguous communication within bio-based value chains is facilitated by a harmonized framework for certification and declaration.

This document has been developed with the aim to specify the method for the determination of oxygen content in bio-based products using an elemental analyser. This document provides the reference test methods for laboratories, producers, suppliers and purchasers of bio-based product materials and products. It may be also useful for authorities and inspection organizations.

Part of the research leading to this document has been performed under the European Union Seventh Framework Programme OpenBio (see biobasedeconomy.eu)

¹⁾ A mandate is a standardization task embedded in European trade laws. Mandate M/492 is addressed to the European Standardization bodies, CEN, CENELEC and ETSI, for the development of horizontal European Standards for bio-based products.

1 Scope

This document provides an overview of existing applications of isotope ratio analysis of carbon, hydrogen, oxygen and nitrogen that are relevant to the analysis of bio-based feedstocks, products and production processes.

The stable isotope ratios of carbon, hydrogen, oxygen and nitrogen can be used to obtain information about the origin of bio-based feedstock and characteristics of production processes of bio-based products. However, no or limited attention for the use of the elements nitrogen and sulphur is given in this document due to the fact that these applications are not yet available.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 16575:2014, *Bio-based products - Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 16575:2014 apply

4 Direct isotopic measurements

As described previously in Direct Automation OPEN BIO Deliverable N°3.7, isotopic measurements are performed using an Isotope Ratio Mass Spectrometer (IRMS). In order to test various samples (solids, liquids), automatic elemental analysers (EA) are connected to isotope ratio mass spectrometer for whole sample material for Bulk Stable Isotope Analysis (BSIA). This methodology is easy to operate, carries out fast analyses (few minutes), and has relative low cost enabling multi isotopic determinations. EA-IRMS is very suitable for regular authenticity controls of pure raw materials. Usually isotopic instruments are able to give the isotopic values of all organic elements contained in the samples.

Isotopic ratio mass spectrometer can also be connected to chromatography devices (separate methods) combustion or pyrolysis interface for Compound Specific Isotope Analysis (CSIA). Two different processes are available (GC-C/P-IRMS or LC-co-IRMS) depending on the molecules to be investigated. This approach is extremely appropriate for regular authenticity control of natural mixture samples (flavour, honey, fruit juice, essential oils...) and is well used in this scheme.

Isotopic composition is reported in Delta notation (δ) (in this case the isotopic composition of carbon is used as an example, other isotopes can be easily replaced in the formula):

$$\delta(^{13}\text{C} / ^{12}\text{C}) = \left[\frac{R(^{13}\text{C} / ^{12}\text{C})_{\text{sample}}}{R(^{13}\text{C} / ^{12}\text{C})_{\text{standard}}} - 1 \right] * 1000$$

The uncertainty of measurements carried out on modern devices in continuous flow isotope analysis is good and enough to make difference on the difference origins of targeted compounds.

The uncertainties for BSIA are close to these values (in delta notation) depending on the supplier:

$\delta^{13}\text{C}$: $\pm 0,3 \text{ ‰}$ / $\delta^{15}\text{N}$: $\pm 0,3 \text{ ‰}$ / $\delta^2\text{H}$: $\pm 5 \text{ ‰}$ / $\delta^{18}\text{O}$: $\pm 1 \text{ ‰}$.

Performances and precision of the different devices must be verified using references standards. International reference standards are supplied by different organisations (International Agency of Atomic Energy, National Bureau of Standards...) and validated by inter-comparison assessments.