Customs training material

Date of document – November/2019 (M18)

D7.5:

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Monitoring the Bioeconomy

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N° 773297.

Technical References

Project Acronym	BIOMONITOR
Project Title	**Monitoring the Bioeconomy**
Project Coordinator	Justus Wesseler Wageningen University justus.wesseler@wur.nl
Project Duration	June 2018 – May 2022 (48 months)

Deliverable No.	D7.5
Dissemination level [1]	PU
Work Package	WP 7 – Trainings and overall stakeholder engagement
Task	T 7.2 – Customs Trainings
Lead beneficiary	Partner number 9 (TNO)
Contributing beneficiary(ies)	Partner number 11 (NEN)
Due date of deliverable	30 November 2019
Actual submission date	29 November 2019 (revised on 13 January 2020)

[1] PU = Public
PP = Restricted to other programme participants (including the Commission Services)
RE = Restricted to a group specified by the consortium (including the Commission Services)
CO = Confidential, only for members of the consortium (including the Commission Services)

Document history

V	Date	Beneficiary	Author
1	2-10-19	TNO	A. van Zomeren
2	23-10-19	TNO	A. van Zomeren
3	4-11-19	TNO	A. van Zomeren
4	11-11-2019	NEN	N. Planzer/ N. Krijger
5	29-11-2019	TNO	A. van Zomeren
6	13-01-2020	TNO	A. van Zomeren

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1 Summary

This deliverable describes the background of the Customs training workshops as part of Work Package 7 within the BioMonitor project. This deliverable contains three main sections:
The first section explains the role that customs laboratories can have within the European bioeconomy regarding collecting data and verifying the biobased content of products.
The second section explains the proposed method of determining biobased content to be used by customs officers. The last section describes planning, content, and materials to be used during the customs training workshops.

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2 Introduction

The bioeconomy covers all sectors and systems that rely on biological resources (animals, plants, micro-organisms and derived biomass, including organic waste), their functions and principles. It includes and interlinks: land and marine ecosystems and the services they provide; all primary production sectors that use and produce biological resources (agriculture, forestry, fisheries and aquaculture); and all economic and industrial sectors that use biological resources and processes to produce food, feed, bio-based products, energy and services[1]. The EU bio-economy includes the activities related to biomass production and conversion into food, feed, bioenergy and bio-based materials in textile, pulp & paper, biotechnological and chemical industries. It further captures farm and food processing streams like manure, post-harvest by-products and food waste (see e.g. Biomonitor Deliverable 1.1). Currently, the bio-economy generates about two trillion euros of annual turnover and twenty million jobs[2,3].

During the last twenty years, EU policymakers have placed a high priority on the expansion of bio-based value chains based on indigenous feedstocks to reduce the use of petrochemicals, mitigate climate change, reduce import dependency and promote local economies. Measuring the contribution of the bio-economy to reaching the societal objectives of the Bio-economy Strategy is well developed for sectors and products that belong to food, feed, pulp & paper and bioenergy chains. However, there is a confirmed lack of information for emerging innovative industries, such as chemistry and materials sectors that process biomass into bio-based intermediate and end products. This includes (i) a lack of a comprehensive database with statistics for industrial uses of biomass; (ii) a missing transparent methodology for data collection; and (iii) a lack of value chain integrated data illustrating the flow from raw materials to industrial end products.

In the context of the Horizon 2020 project Monitoring the Bio-economy (BioMonitor), the challenge is to close the data gaps by updating and enhancing currently used data sets and to assure quantitative monitoring of the new bio-based products and industries. BioMonitor will provide an enhanced toolbox that will be applicable to the monitoring of the development and assessment of the impacts of the whole bio-economy on societal goals in quantitative terms. This enhanced toolbox will facilitate future policy setting, encourage investment in the bio-economy and define possible trade-offs and synergies between various biomass uses.

BioMonitor will concentrate on a Eurostat consistent methodology to collect, improve and implement statistical data related to the use of biomass for bio-based intermediate and end products using NACE (Nomenclature statistique des Activités économiques dans la Communauté Européenne) class levels and CN (combined nomenclature) coding to create consolidated official data. Extension of the CN codes for specific bio-based products will be proposed to better categorize

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[1] European Bioeconomy strategy, European Comission, 2018, p. 4

[2] http://biconsortium.eu/sites/biconsortium.eu/files/newsimage/BIC_PressRelease_Bioeconomy2013_3March2016.pdf

[3] Ronzon, T. and M'Barek, R. (2018) 'Socioeconomic indicators to monitor the EU's bioeconomy in transition', Sustainability (Switzerland), 10(6). doi: 10.3390/su10061745.

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the different biobased products. The data collection methods will be identified and jointly selected in collaboration with industries that have to collect the data; statistical offices that have to implement and standardise the data in existing systems; and customs offices and laboratories that have to implement and standardise product codes in their systems.

However, there is currently a lack of expertise and equipment for the carbon-based test method within the Customs laboratories across the EU to properly collect and submit biobased product data in the existing systems. Therefore, the aim of Task 7.5 is to organise training sessions for these laboratories to increase the expertise and, hence, to obtain additional data sources for the monitoring of the bio-economy.

This deliverable describes the draft planning (dates/locations) of training workshops, the draft agenda of the workshops and the prepared training materials (Powerpoint presentations).

3 Role of Customs Laboratories in Monitoring the Bioeconomy

Additional codes for data collection
The innovative part of the BioMonitor project is to start with extending the Classification of Economic Activities in the European Community (NACE) and the National Accounting framework (SNA) to specifically collect data on bio-based sectors, for example, through a further breakdown of bio-based- and fossil-based parts in, for instance, the chemical and textile industries. It will be necessary for the consortium to define proposals for extending the Classification of Products by Activity (CPA) and the Combined Nomenclature (CN) codes (in cooperation with stakeholders) with specific bio-based products to add to the recently carried out introduction of CN codes for bio-based 1,4-Butanediol, Succinic acid and lubricants. In the future, customs laboratories will need to work with these codes. As such, our training will have an introductory character.

Moreover, the new CN codes, as will be proposed by the BioMonitor project, may have many more implications due to the likely different tax rates on these products. Experience from customs labs reveals that often large (justified and unjustified) shifts in labelling with certain CN codes take place after the introduction of new CN-codes. The policy aspect of this type of development (new measurement methods and new CN codes) should, therefore preferably be part of the intended training courses / workshops in the BioMonitor project.

The added value of customs lab data to the BioMonitor project
There seems to be a discrepancy between the assumptions made in the project description and the current practice of the Customs labs. The Biomonitor project proposal assumed that the Customs

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Labs can be an important source of data that can show how the EU bioeconomy is developing because of the assumption that they regularly check the quality of products. However, through interviews that have been conducted with customs labs, it was made clear that they only carry out checks in case there is a suspicion that something is wrong with goods that enter an EU Member State. Only in that case will the information be verified. This practice implies that only a relatively small part of the products are checked and that this population mainly consists of a specific selection of suspicious products (i.e., the samples are not random). This means that the data coming from Customs labs may not be a good indicator of the development of the EU bio-economy. This issue was discussed with Statistics Netherlands (CBS), and it was concluded that this potential problem can be solved by applying available methods for data extrapolation. By applying methods for data extrapolation, the biased data can be treated in such a manner that the data becomes more generically valid for the total population of goods/products. Many data sources that the Statistical Bureaus use, need to be extrapolated to be made generically valid. The data that comes from Customs laboratories can therefore still be a good basis for monitoring the development of the EU bio-economy. However, as with all extrapolations, the numbers will provide a better estimate of the situation but do not provide the factual status of all goods/products.

The importance of increased knowledge of bio-based carbon analyses for the customs labs and for the BioMonitor project lies mainly in the future introduction of new CN codes that specify certain levels of bio-based carbon as a specification in these products. The BioMonitor project also aims to propose new CN codes to improve discrimination in the data. If this is to happen, then the labs have to be ready, and sufficient knowledge and experience must be available as the labs would then need to perform these measurements routinely. That knowledge and experience are now still very limited as was shown in the 2017 Customs laboratory ring test of the bio-based carbon method where only five labs out of forty which could deliver bio-based carbon results (Personal communication, Maarten Schutter, Dutch Customs laboratory). The results of the ring test are not publicly available. We conclude that there is, among other things, a need for more knowledge and expertise on analyses of the bio-based carbon content of products. BioMonitor will organise courses for the (customs) test laboratories to assist them with the determination and interpretation of the bio-based content standard (EN 16640) for all bio-based products.

4 Method for determination of bio-based carbon in products

The selected method for the determination of bio-based carbon in products is the recently adopted European standard EN 16640. This standard uses the radiocarbon method to determine the bio-based content of a product and, hence, knowledge of total carbon and the ^{14}C are needed (direct method). The bio-based carbon content is then represented as a fraction of the radioactive carbon

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to the total carbon in the product. This standard was selected mainly because it represents an approved and validated method that is used in Europe for bio-based products.

The EN 16640 standard describes three possibilities for the determination of radiocarbon:
1) AMS - accelerator mass spectrometry
2) LSC - liquid scintillation counting
3) BI - beta-ionization technique

AMS and LSC techniques are considered to be equivalent. However, the LSC method was chosen as the preferred method for routine analysis within the Customs laboratories. The main reason for this choice is the fact that this method is already available within three Customs laboratories (NL, BE and DK). In addition, the equipment needed is widely commercially available at reasonable cost (investment around 300.000 euro). The AMS method is the most sensitive method but this method is not widely available, involves major investments in equipment and needs a high level of technical expertise. The analysis using BI measurements are not considered to be useful for Customs laboratories because (1) the method is not included in the normative part of CEN/TS 16640 (only informative) and (2) the use is limited to only few laboratories in the world.

5 Planning of training sessions

2.1 Number of training workshops

The EU Customs laboratories are coordinated inside the Customs Laboratories European Network (CLEN). The CLEN counts 89 laboratories and mobile laboratories at present. The project aims to train people from every Member State and can accommodate more Customs laboratories if needed based on the interest from those labs. The targeted audience are lab technicians and/or lab managers. As initial estimation, the training capacity needed was assumed on the presence of employees from 28 Member States. Every Member State is assumed to bring two people to the training sessions. This would imply that the capacity for the trainings is about 56 people.

The training sessions contain both a theoretical part and a practical part in the laboratory. The capacity for a group is highly limited by the amount of people that can be present and work in the laboratory. The reason for that is safety in the laboratory and the limitations on the use of equipment by the trainees (regardless of the chosen location). Therefore, the maximum number of trainees per training session is 15. This implies that the Biomonitor project is able to train all relevant Customs lab employees in 3-4 training sessions.

2.2 Training locations

The Netherlands, Belgium and Denmark are the only locations in the EU that have the necessary equipment to conduct the training workshops.

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The Dutch Customs laboratories in Amsterdam have already confirmed that they are willing to host a training session on their premises. This is an ideal location since it is well connected by train (10 minutes) to Amsterdam airport (Schiphol), and there are plenty of hotels nearby.

At the moment, the Dutch Customs laboratories are being renovated and they are ready for use around June 2020. It is agreed that the BioMonitor training in Amsterdam should be planned for October 2020. The exact planning of the date and sending invitations will start in April 2020.

The Danish Customs laboratory is also positive to hold a training workshop at their premises. The exact timing and planning is currently under discussion with the Danish Customs laboratory. The aim is to have the first training session around April 2020.

Contacts with the Belgian Customs laboratories have also been established. At the moment, it is unclear whether they can and are willing to offer their labs for additional training sessions.

6 Content training sessions

The objectives of this training session are to teach Customs labratories how to handle bio-based products and how to work with the EU standard to measure the bio-based carbon content. The training sessions will be organised in a 2-day workshop to be held at suitable locations across Europe. The general set-up for the training sessions was already developed in a former EU project and tested at the Dutch Customs laboratory in 2014. The training was well received by the participants. The training content is now renewed because the European standard EN 16640 was not yet in place at the time. In addition, the close relation to the BioMonitor objectives was also not in the focus before. Therefore, the general structure of the training will remain a 2-day session with both theoretical backgrounds and practical training in the laboratory.

The training will cover three parts:

1) Theoretical part: general explanation on the bio-based carbon content standard (EN 16640)

The theoretical part will contain an explanation of the EN 16640:2017 “Bio-based products - Bio-based carbon content - Determination of the bio-based carbon content using the radiocarbon method.” Currently, not many customs (can) use this method.

2) Practical part: testing the bio-based content in the laboratory

This part will contain the practical aspects of the determination of bio-based carbon in products and encompasses the sample pre-treatment, the conversion of the sample to CO_2, the collection of CO_2 and the analysis using LSC.

3) Policy discussion: implications of new CN codes

The policy part will focus on the implication of CN codes. New CN Codes are normally related to the differentiation of tax rates on these products. This often has the consequence that large shifts take place in the labelling of these CN-codes by the producers (justified and unfortunately also unjustified

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shifts). The policy aspect of this type of development (new measurement methods and new CN codes) is therefore, also part of the intended training courses / workshops.
The draft agenda for the sessions is outlined below.

Date/time	Activity	Presenter
Day 1, 9:30h	Welcome and registration	-
Day 1, 10:00h	Introduction to training and background	Andre van Zomeren
Day 1, 10:15h	Sample preparation for 14C analysis (including questions and discussion)	Karina Vogelpoel
Day 1, 11:00h	Coffee break	-
Day 1, 11:15h	Practical training in laboratory: sample preparation	Karina Vogelpoel/Marco Geusebroek
Day 1, 13:00h	Lunch break and group picture	-
Day 1, 14:00h	Analysis of 14C by Liquid scintillation counting (including questions and discussion)	Marco Geusebroek
Day 1, 14:45h	Practical training in laboratory: liquid scintillation counting	Karina Vogelpoel/Marco Geusebroek
Day 1, 15:30h	Coffee break	-
Day 1, 15:45h	Practical training in laboratory: liquid scintillation counting	Karina Vogelpoel/Marco Geusebroek
Day 1, 17:00h	Wrap-up	

Date/time	Activity	Presenter
Day 2, 9:30h	Data interpretation LSC analysis	Marco Geusebroek
Day 2, 11:00h	Coffee break	-
Day 2, 11:30h	Needs and consequences of new CN codes for biobased products: presentation and discussion	Ger Koomen
Day 2, 12:30h	Wrap up	Andre van Zomeren

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7 Training materials

The training materials have been prepared in Powerpoint presentations, Annex A, B and C. The training session is divided into three parts:

1. General introduction
2. Sample preparation (theory and practical training)
3. Analyses of ^{14}C by liquid scintillation counting (theory and practical training)

The part of the policy discussion will be mainly based on input from the Dutch Customs laboratory and will be prepared in due time. In addition, the necessary materials need to be available in the laboratory to be able to perform the practical part of the training sessions. The equipment and consumables needed are specified in detail in the EN 16640 standard and can be generally specified as:

-consumables
-standard laboratory equipment (e.g., balances, glassware)
-bomb calorimeter for the conversion of samples into CO_2 (alternatively, TNO can bring their calorimeter in case this is not present at the location)
-Liquid scintillation counter and scintillation liquids

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8 Annex A: Powerpoint presentation

Customs training, General introduction

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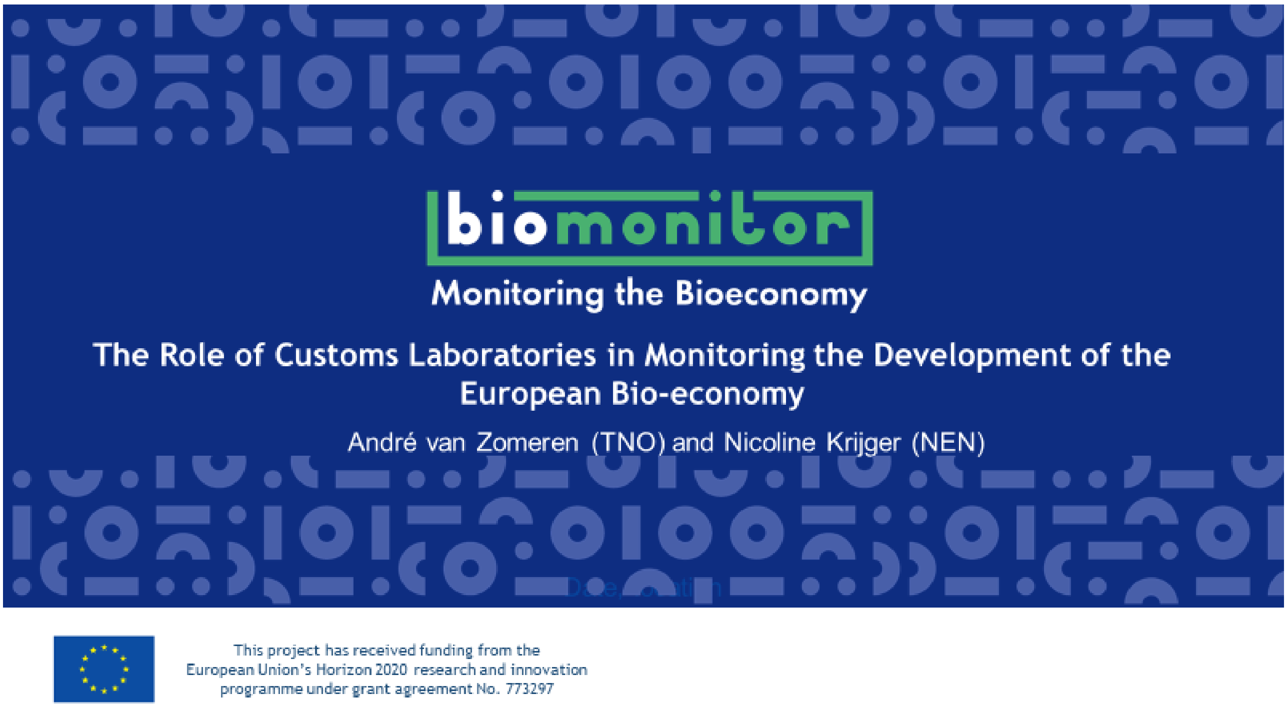

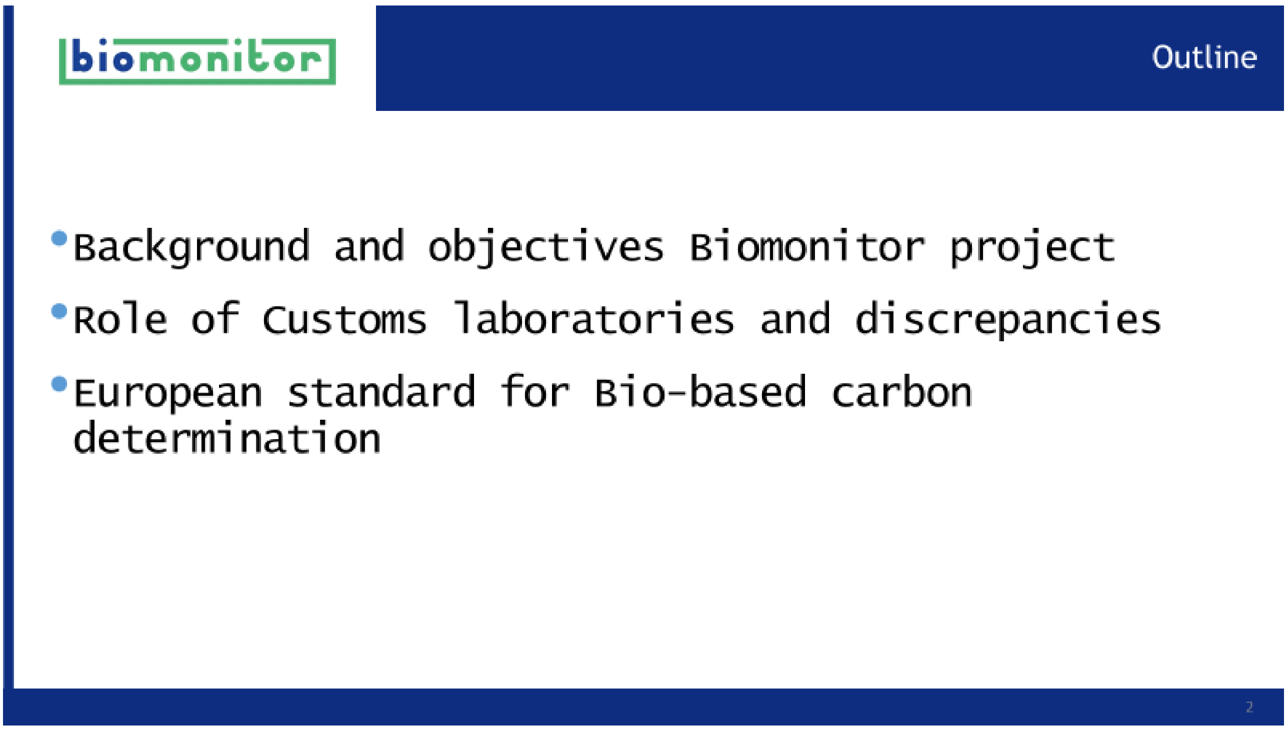

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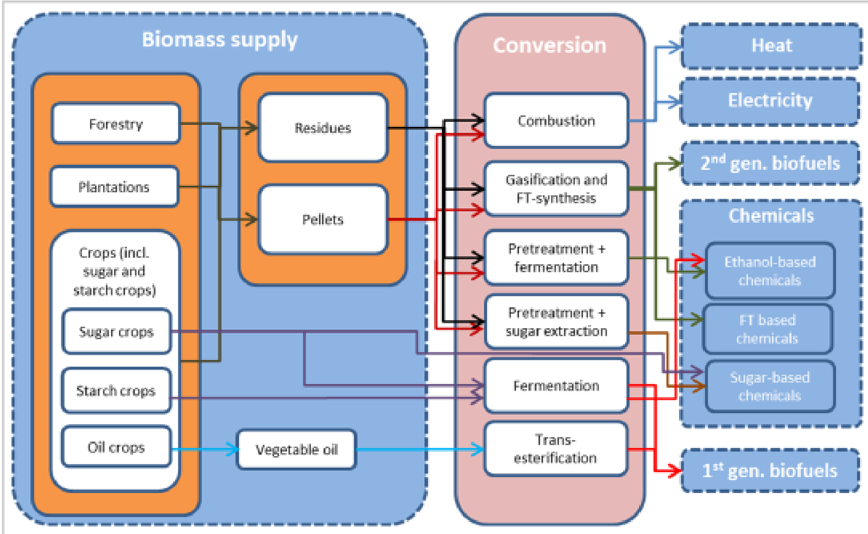
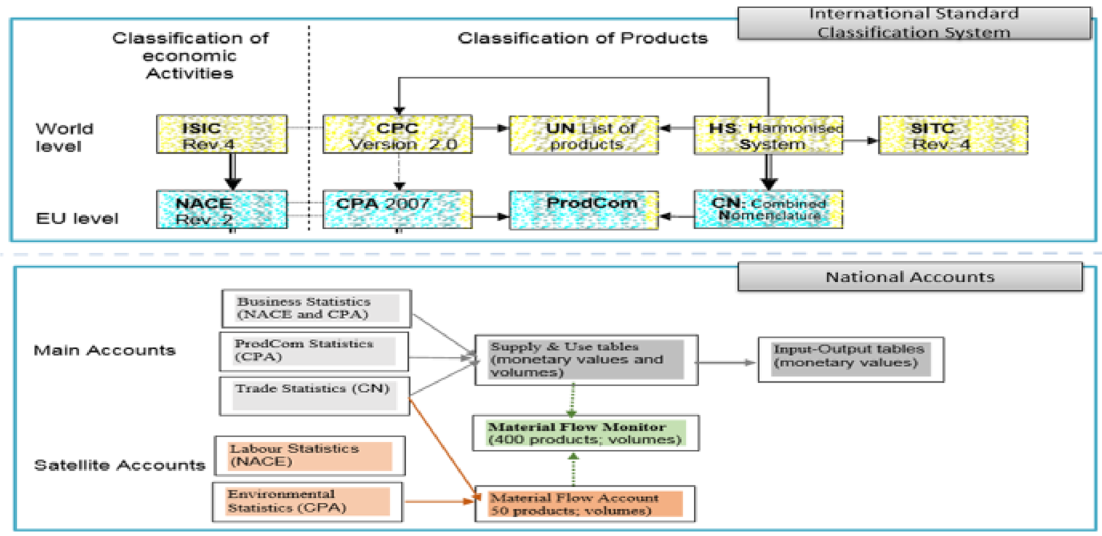
Examples of bio-based products in the value chain

- Feedstocks
- Conversion
- Products



3

International Standardized Classification Systems



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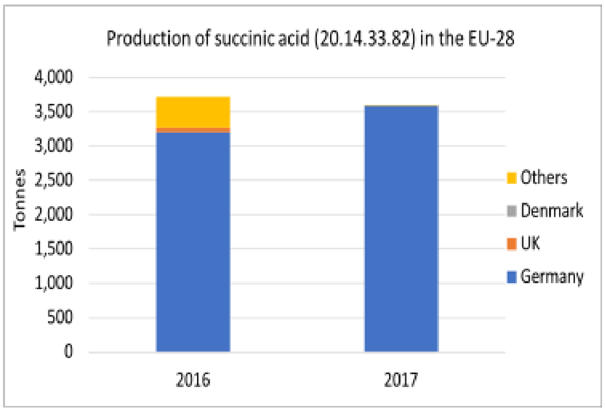
New bio-based products in PRODCOM - evaluation of first data

- **Succinic acid:**
  - New CN code for "Ethane-1,2-dicarboxylic acid or butanedioic acid (succinic acid) having a bio-based carbon content of 100 % by mass" (CN: 29.17.19.20, PRODCOM:20.14.33.82).
  - Succinic acid can be made chemically from fossil fuels or biologically from biomass.
  - Applications: pharmaceuticals, food ingredients, coatings & pigments, surfactants and detergents.
  - Succinic acid can be used as a building block for products in new applications such as polyurethanes, resins, polybutylene succinate (PBS) and plasticizers, as well as the precursor for other chemicals such as 1,4 butanediol (BDO).
  - **Production data in PRODCOM at least for some Member States estimated by national statistical offices due to national product classifications lagging behind (example: Germany)**

5

New bio-based products in PRODCOM - evaluation of first data



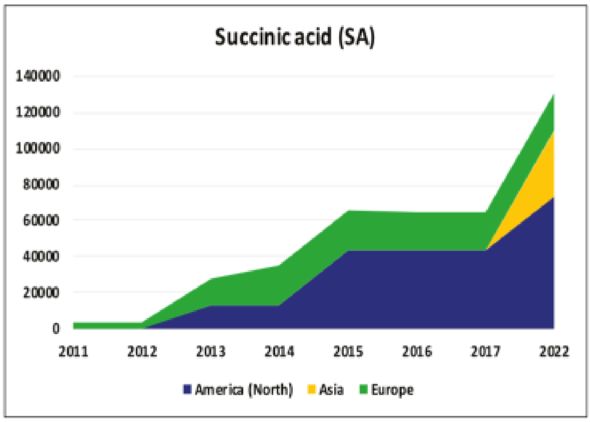


Figure 29: Worldwide production capacities of succinic acid in 2011– 2022 (in tonnes)

6

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Assumed role of Customs laboratories in project

- Customs laboratories can provide data for the national Statistics agencies
  - Monitoring of import and export flows of materials
  - CN codes to distinguish between bio-based and non bio-based

However,…

Only suspicious products are checked: no a-select sampling

7

Determination of bio-based carbon in products

- Developed in CEN/TC 411/WG3
- Why?
- Bio-based economy
- Stimulate market for bio-based products
- Certification of products

NEN-EN 16640:2017

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 16640

February 2017

ICS 13.020.55; 71.040.40; 83.040.01

Supersedes CEN/TS 16640:2014

English Version

Bio-based products - Bio-based carbon content - Determination of the bio-based carbon content using the radiocarbon method

biobased %

8

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Carbon-14 cycle: basis for biobased carbon content

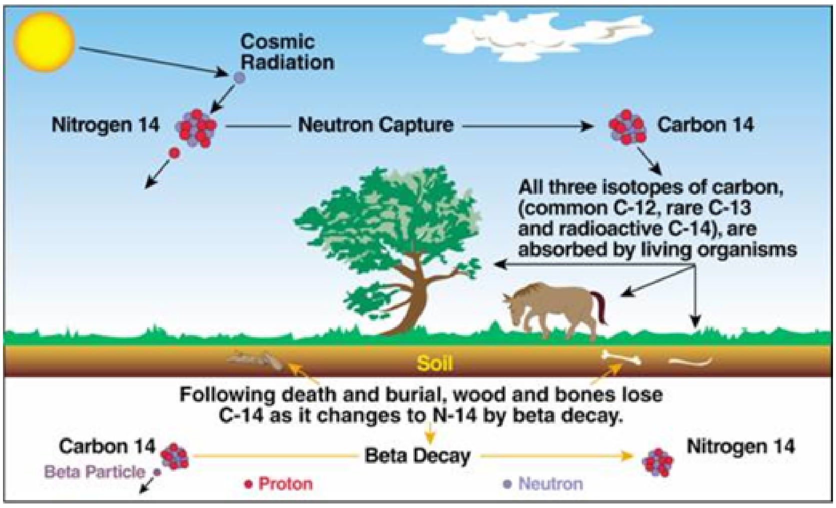
^{14}N + neutron = ^{14}C

$^{14}CO_2$ in biomass

Half-life= 5730 yr

Analyses of ^{14}C →

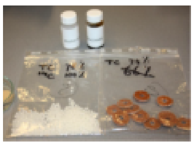
Bio-based content



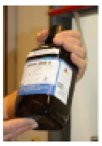
9

Bio-based carbon determination using liquid scintillation counting (EN 16640)

- Outline of procedure for bio-based carbon content using LSC:


Samples


Combustion in bomb calorimeter and gas collection


Collect CO2 in adsorbens (Carbosorb)


Transfer to scintillation vials


Analyses in LSC: 14C counting

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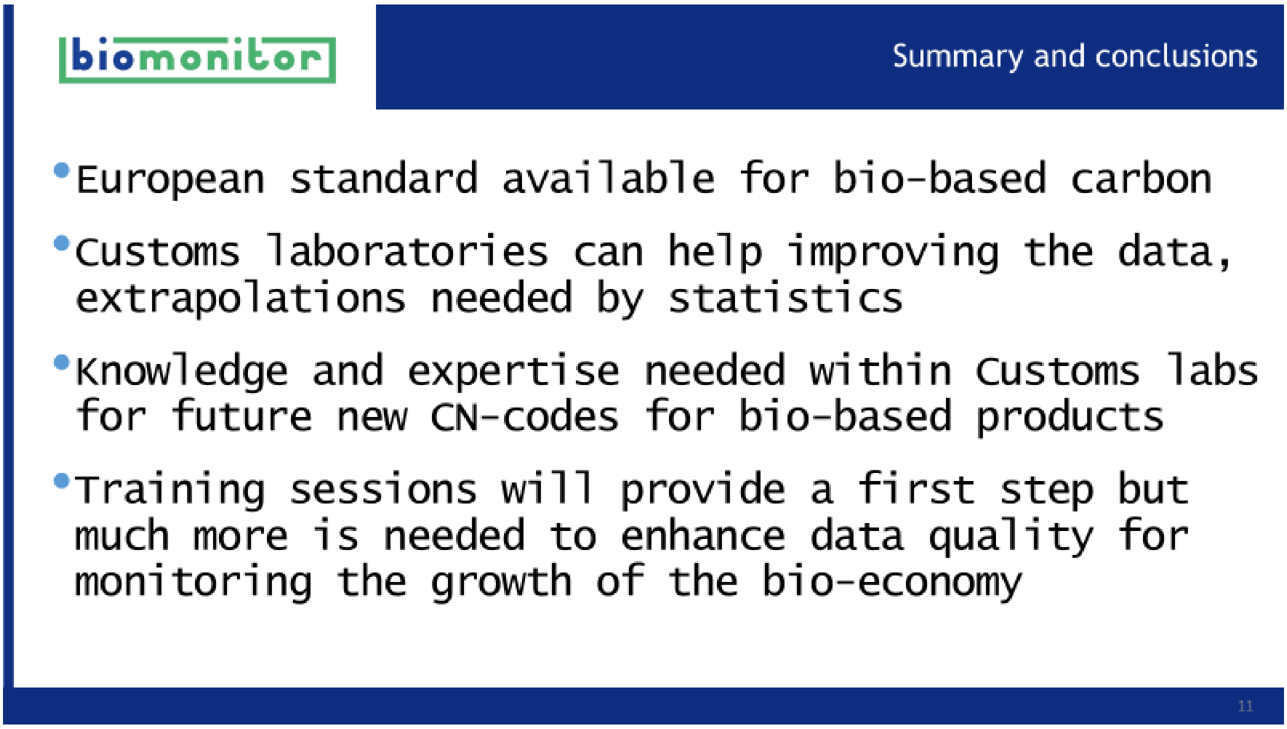
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Summary and conclusions
European standard available for bio-based carbon
Customs laboratories can help improving the data, extrapolations needed by statistics
Knowledge and expertise needed within Customs labs for future new CN-codes for bio-based products
Training sessions will provide a first step but much more is needed to enhance data quality for monitoring the growth of the bio-economy
11


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Monitoring the Bioeconomy
Thanks for your attention
André van Zomeren, TNO
Andre.vanzomeren@tno.nl
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9 Annex B: Powerpoint presentation

Customs training, sample preparation

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Monitoring the Bioeconomy

Training for customs laboratories for the combustion of samples for the determination of the bio-based carbon content in products

Karina Vogelpoel, TNO

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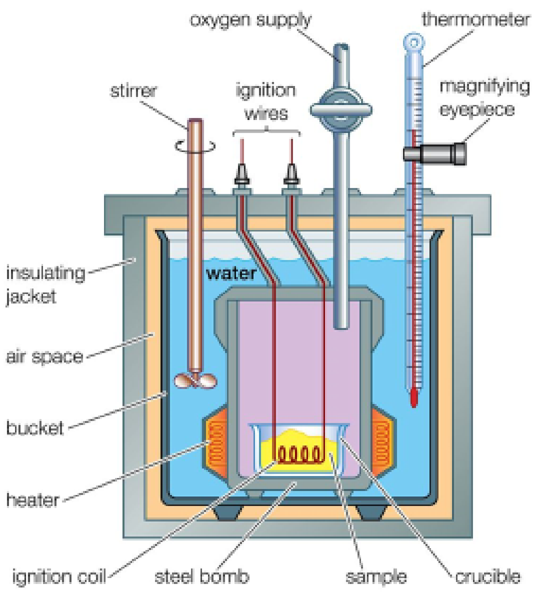
biomonitor

Principle bomb calorimeter

- Sample is burned in a 30 Bar oxygen filled pressure vessel
- Resulting gas is collected in a gas bag
- Gas is transfered into absorbing liquid (carbosorb) + counting cocktail (e.g. PermaFluorE+)
- Solution counted on a low level LSC



Presenter, date 2

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Examples of samples for bio-based carbon

Presenter, date 3

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Sample pans and sample holder

Several pans and the combustion unit (that will be place in the calorimeter)

Presenter, date 4

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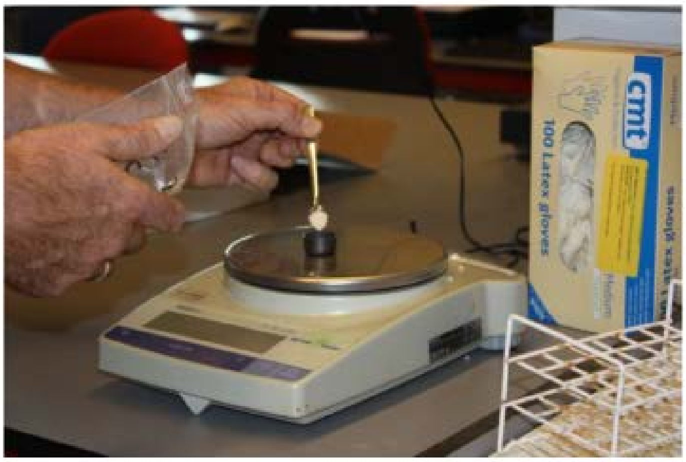
Sample weighing

Weighing 1 g sample in a pan

If temperature rises more than 11°C, the combustion process wil stop → use less sample weight



Presenter, date 5

Combustion unit bomb calorimeter

Setting the pan in the combustion unit

Presenter, date 6

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Ignition thread

Adding the ignition thread

Ignition thread is 10 mg, this is 1% of extra weight → no significant influence on results

Presenter, date 7

Placing sample holder in unit

Setting the combustion unit in the calorimeter

Presenter, date 8

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Parr bomb calorimeter

The calorimeter

Gas collection

Collecting CO_2 in the gas bag

(until combustion is completed; gas bag inflated)

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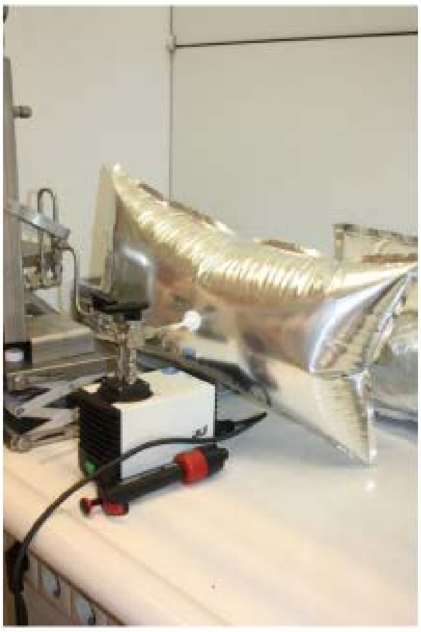
Transfer of collected gas

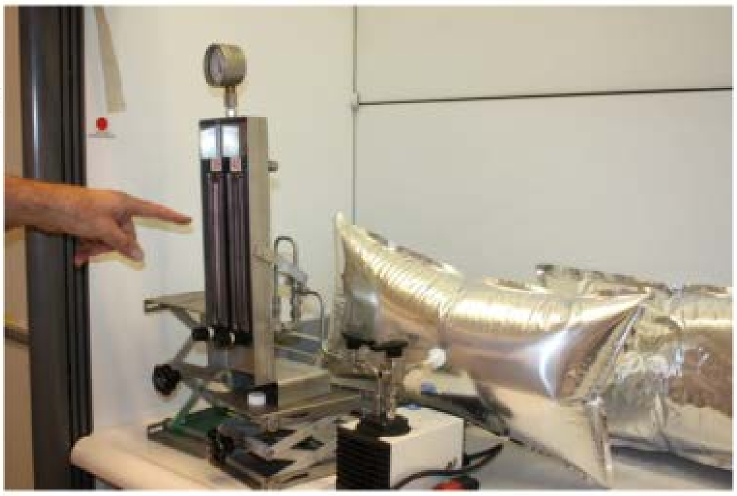
Fixing the filled gas bag to a pump

Quantitative transfer of CO_2 is important



Presenter, date 11

The gas from the bag goes from the pump through a gas flow controller…



Presenter, date 12

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…and from the gas flow controller the gas bubbles in a vial with 10mL of Carbo Sorb E collecting liquid.

Vial is placed in ice because the reaction is exotherm, and the absorption of CO2 is better by low temperature

Carbo Sorb E solution

Carbo Sorb E
(solution to trap the CO_2)

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Vial with Carbo Sorb collecting the Carbon of the sample (2h process under small regular flow)

Calculation

Bomb volume is 0.250 L, so if we fill to 30 Bar O_2:

$$P1 * V1 = P2 * V2$$

$$V2 = \frac{P1 * V1}{P2} = \frac{30 * 0,25}{1} = 7.5 \text{ L gas}$$

1 gram sample of 50% C gives: (0.50 / 12) x 44 = 1.83 gram CO2 (42 mmol)

Wood = Circa 50 % Carbon

Plastic = Circa 60 % Carbon

- Total mass (1.83 g) needs to be quantitatively transferred to Carbosorb solution (see presentation Marco)

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European Union's Horizon 2020 research and innovation
programme under grant agreement No. 773297

10 Annex C: Powerpoint presentation

Customs training, liquid scintillation counting

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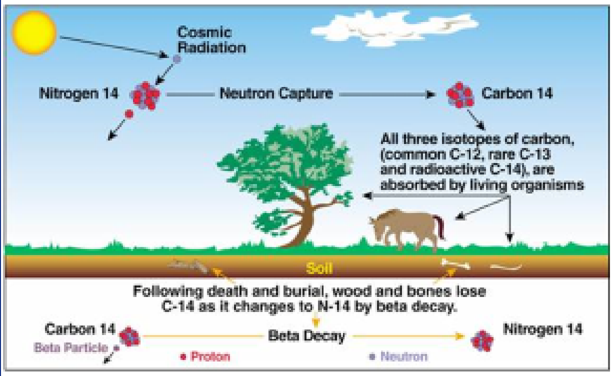
Principle

- How can we discriminate between fossil compounds (mainly derived from oil and coal) and biomass?
- Answer: Using isotope measurements!

- What are isotopes? Isotopes comes from the Greek root isos (ἴσος) = equal and tópos (τόπος) meaning place, thus the meaning behind the name is that different isotopes of a single element occupy the same position on the periodic table.
- In the world around us there are 3 types of isotopes for Carbon (C), $^{12}_{6}C$, $^{13}_{6}C$ and $^{14}_{6}C$ respectively.
- The atomic number is 6, which means that every carbon atom has 6 protons, so the neutron numbers of these isotopes are 6, 7 and 8 respectively.

Characteristics of carbon isotopes



1. $^{12}_{6}C$: abundance: 98,9% stable
2. $^{13}_{6}C$: abundance: 1,1% stable
3. $^{14}_{6}C$: abundance: 10^{-12} mol

Radioactive: T½ = 5730 years

Decay scheme: $^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}_{-1}\beta$

How does ^{14}C end up in our 'Carbon Cycle'?

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How can we measure the ^{14}C content? (1)

- By using 3 measurement techniques:

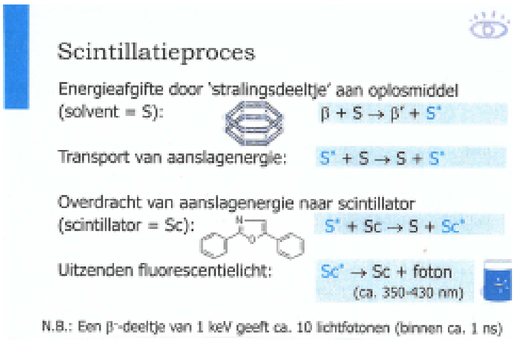
A. Liquid scintillation - counter method (LSC)

B. Accelerator Mass Spectrometry (AMS)

C. Beta-Ionization (BI)

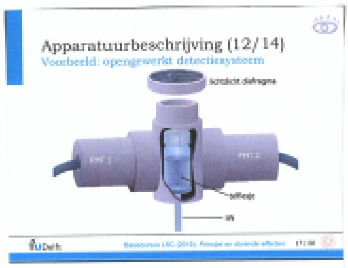
We will now focus on method A: LSC

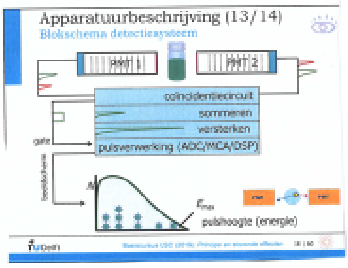
- LSC is an indirect determination of the isotope abundance of ^{14}C, through its emission of beta-particles after interaction with scintillation molecules



How can we measure the ^{14}C content? (2)

- Measuring equipment: ß-counting = light counting!
- LSC (Liquid scintillation counter method) 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 bio-based product 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.
- For material with a high bio-based carbon content (>10 %) direct absorption of the CO_2 in a carbamate solution can be applied.





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LSC measurement: samples

- Detailed operation of LSC instrument during practical training.
- The activity of a sample is compared with the activity of a reference material .
- Standard addition to check occurrence of chemical or optical quenching for each sampling or sample type. → 14C labelled component is added. Clear liquids can be counted directly.

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LSC measurement: blank correction

- Measure a ‘blank’ sample: a scintillation vial filled with counting liquid that is counted for at least the same period of time as the actual sample.
- Result is the background level for the whole system (apparatus and reagent).
- Then count the actual sample.

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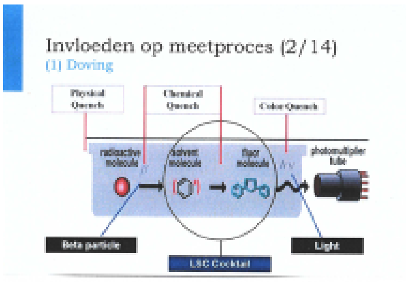
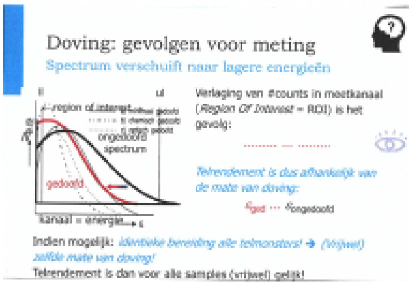
Influences on the counting process

- Process known as ‘quenching’:
- ‘Quenching is the phenomenon in which the conversion of the β-energy into light photons is disturbed and/or the produced light photons in the sample are absorbed.’
- The measurement efficiency is depending on the amount of quenching.
- Remedy: Identical treatment of all samples and standards!



→ Normal β-spectrum
→ Channel = Energy



^{14}C counting is low-level counting

$$Act\,(DPM) = \frac{CPM}{\varepsilon}$$

In which CPM = Counts Per Minute
ε = Measurement Efficiency
DPM = Desintegrations Per Minute

- β-counting is a statistical process which follows the ‘Poisson’ distribution in which N = number of counts and S = standard deviation $\sqrt{N}$
  If we state: R = counting rate (in CPM)
  t = counting time (in min)
  S = $\sqrt{R * t}$
- Low-level counting involves at least 2 counting processes, namely:
  - Sample counting
  - Background counting
- The combined error in the 2 processes will be $\sqrt{Sx^2 + Sy^2}$

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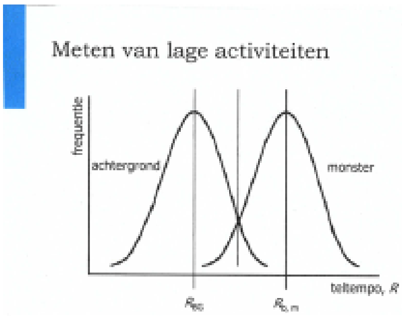
Measurements of low activities

- What is the lower limit of detection (LLD)?
- It is the minimal counting rate that can be detected just above the background counting rate at a certain probability.

Nnetto, sample ≥ $3\ Sn,\ BG$ →

Nnetto, sample ≥ $3\sqrt{N_{BG}}\ (counts)$



→ Counting rate, R

- If the measurement time = t, then

$$LLD = \frac{Nnetto}{t} = 3.\sqrt{\frac{R_{BG}}{t}}\ (CPM)$$

LLD (Lower Limit of detection)

- LLD = $({}^k\alpha + {}^k\beta) * \sqrt{2} * \sqrt{\frac{A_0}{t*\eta}}$

In which: ${}^k\alpha$ = one-sided significance level equivalent to 1-α (type I error)

${}^k\beta$ = one-sided significance level equivalent to 1-β (type II error)

A_0 = background counts

t = measurement time sample and blank

η = counting efficiency (0 ≥ η ≥ 1)

If significance level is 5%, the ${}^k\alpha = {}^k\beta$ = 1,65

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Example calculation lower limit of detection

Eg1: Wallac guardian 1414 LSC

T = 16000 s → 266,67 min   η = 80% = 0,8

14 C : 16 DPM/gC * 0,8 = 14 CPM

Background is 14 CPM

14 * 261,67 = 3733 counts

$LLD = (1.65 + 1.65) * \sqrt{2} * \sqrt{3733/(16000 * 0{,}8)}$ = 2,0 DPM

Eg2: Quantulus

T = 16000 s →   266,67 min   η = 80% = 0,8

Background is 1 CPM

$LLD = (1.65 + 1.65) * \sqrt{2} * \sqrt{267/(16000 * 0{,}8)}$ = 0,54 DPM

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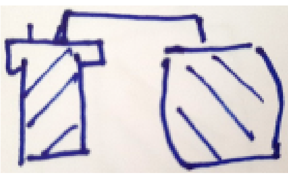
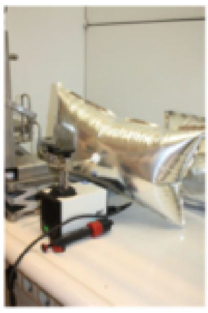
Now in practice: the combustion of 1g wood

- From table 2 (EN-16640:2017) P. 11 Wood contains 48% C, PMC = 112
- PMC is percent modern carbon (NIST SRM 4990 is set at 100 PMC = 13,56 dpm/g C)
- 1 g of wood is being combusted in a calorimeter with 30 bar O_2 (Karina's work!)
- 0,5 g C = $\frac{0{,}5}{12}$ = 0,0417 mol C = 0,0417 mol CO_2 = 42 mmol CO_2
- Now the produced gas from the bomb must be transferred into a gas-bag:
- A



bomb   gas bag (10L)



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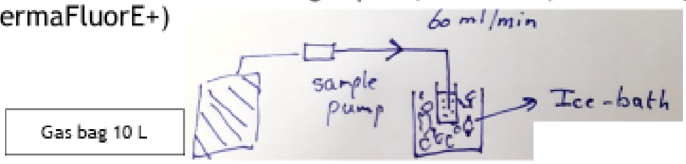
Transfer of the gas volume into the absorbing liquid

- Bomb volume is 0,250 L, so if we fill to 30 Bar O_2:

$$\boxed{P1 * V1 = P2 * V2}$$

$$V2 = \frac{P1 * V1}{P2} = \frac{30 * 0{,}25}{1} = 7{,}5 \text{ L gas}$$

- Transfer this into absorbing liquid (carbosorb) + counting cocktail (PermaFluorE+)



- Bubbling flow = 60 ml/min → transfer time = $\frac{7500\ [ml]}{60\ [ml/min]}$ = 125 min = 2,1 hrs

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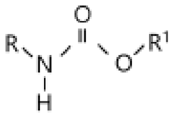
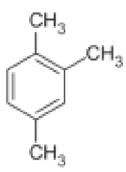
- Carbosorb is a carbamate



- They can take up CO_2, about 4.8 mmol CO_2/ml, therefore 10 ml of carbosorb is able to take up 48 mmol of CO_2 → we need to capture 42 mmol CO_2
- PermaFluor E+ is counting cocktail, a pseudocumene* based cocktail and designed for counting $^{14}CO_2$ samples that are trapped in Carbosorb E.
- * 1, 2, 4 trimethylbenzene



- After 2 hrs of bubbling the flow is stopped, solutions are shaken and counted for 6 to 24 hours on a low level LSC at a window setting of 20-200 KeV
- 3 Blanc solutions are counted under the same conditions to determine the background level

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Calculation counting results

- Netto CPM = CPM_{sample} - CPM blank
- $DPM_{netto} = \frac{CPM_{netto}}{(0 \geq \varepsilon \geq 1)}$
- In this case 100% biomass (wood) should give 7,3 DPM, so a counting rate of 7,3*0,8 = 5,8 CPM
- Eg.1: Wallac 1414 LSC: LLD = 2,0 DPM → Biogenic content: $\frac{2{,}0}{7{,}3}$ x 100% = 27% or more
- Eg. 2: Quantulus LLD = 0,54 DPM → Biogenic content $\frac{0{,}54}{7{,}3}$ x 100% = 7,4% or more

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Thank you for your attention

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