Open-Bio – Opening bio-based markets via standards, labelling and procurement: Deliverable 3.3: Performance characteristics for horizontal bio-based content standard – round robin assessment results

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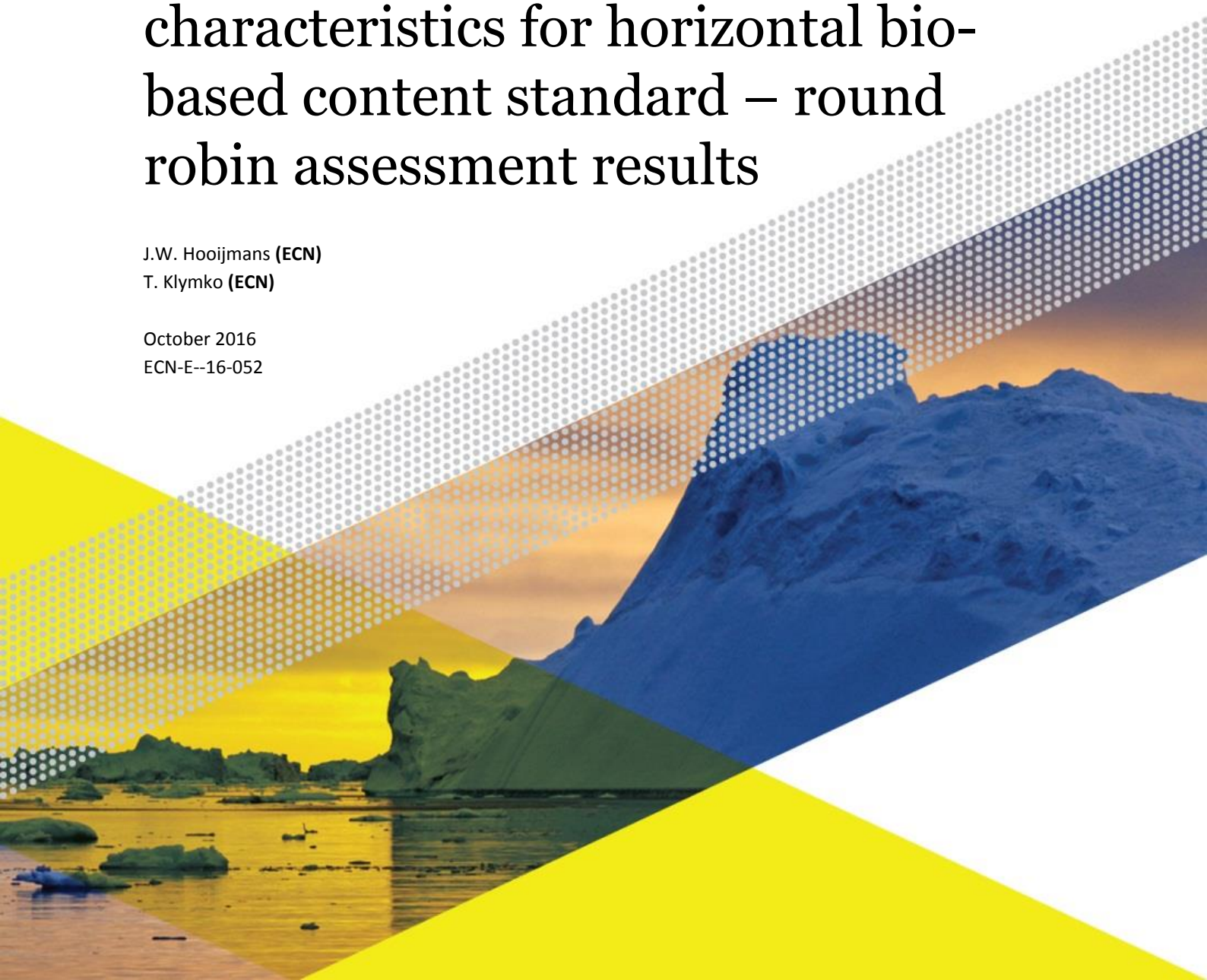

Open-Bio

Opening bio-based markets via standards, labelling and procurement

Work package 3

Bio-based content

Deliverable N° 3.3:

Performance characteristics for horizontal bio-based content standard – round robin assessment results

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1 Summary

This report presents the results of the round robin assessment that was held in order to test the procedure proposed for determination and validation of total bio-based content. The round robin assessment was initiated in the frameworks of the European Open-Bio project (www.biobasedeconomy.eu)

Determination of total bio-based content is closely related to the determination of total bio-based carbon content. The latter is typically represented as a fraction of ^{14}C to the total carbon content of a product. For the determination of the total bio-based carbon content, CEN/TS 16640 shall be followed. The procedure described in CEN/TS 16640 for the bio-based carbon content determination has been proven by the results of a separate round robin assessment that were presented in Deliverable 3.1 of Open-Bio. It was concluded there that the ^{14}C analysis can be done using well known LSC (Liquid Scintillation Counting) or AMS (Accelerated Mass Spectrometry) techniques. No inconsistencies were observed for the results of the measurements when using AMS or LSC techniques.

Total bio-based content is not restricted only to the bio-based carbon content and can involve contribution from bio-based oxygen and/or hydrogen and/or nitrogen. For the determination of total bio-based content of a product, the knowledge of all its constituents that derived from biomass, are needed. Total bio-based content is normally expressed as a percentage of the total mass of the product. Typically the bio-based content of a product is claimed by the producer of the product. However, in practice the claimed values can be over- or underestimated. Therefore a separate procedure for the validation of the bio-based content was proposed by pr EN 16785.

For the determination of the total bio-based content, besides the fraction of bio-based carbon content, the knowledge on other possible bio-based elements (oxygen or/and hydrogen or/and nitrogen) is required. For that purpose, rules for allocation of elements (pr EN 16785) have to be applied. Generally, if oxygen or/and hydrogen or/and nitrogen are bound to a carbon that is derived from biomass, then the fractions of these elements that are linked to bio-based carbon, are also considered to be parts of the bio-based content. In practice, it is not always possible to distinguish between elements originating from biomass and from non-biomass by measurements. Therefore in most cases the knowledge from product suppliers are needed in order to calculate the total bio-based content.

This was reflected in the round robin assessment devoted to the validation of the bio-based content of various samples that was stated by the producers of these samples. Validation of stated total bio-based content of several various products was the ultimate goal of initiated round robin assessment. The assessment involved 11 independent laboratories to whom in total 66 samples were delivered (11 equivalent sets of samples, 6 samples each set). Together with the samples,

the so-called statements were provided by samples suppliers. Every statement included information about composition of a given sample, its bio-based carbon content and its total bio-based content. The information mentioned in the statements was checked by the measurements by each of participating laboratories. Then the stated values were validated or not, depending how big was the difference between stated and measured value for each of involved parameters. The validation procedure was described in pr EN 16785 and was sent to each participating laboratory together with the set of samples.

While the results of the first round robin assessment on the bio-based carbon content determination (Deliverable 3.1 of Open-Bio on CEN/TS 16640) indicated a good consistency, determination and validation of the total bio-based content was more challenging among participating laboratories. Therefore a number of suggestions and recommendations were included into pr EN 16785 and resulted in a new version pr EN 16785-1 and finally in EN 16785-1 that currently is official full standard. As a remark, the finalization of the EN 16785-1 has been awaited before this report was finalized. As one of adaptations to EN 16785-1, a clear distinction was made between the products where only ^{14}C analysis and where both ^{14}C and CHN-O analyses are needed in order to validate the bio-based content. For these two cases, two decision trees and two templates for the representation of the results were suggested in order to make the validation procedure more transparent and easy to apply. Furthermore, separate remarks are made for the situations when bio-based content stated by supplier is lower than the calculated one. In this case, even despite the absolute difference between these two can be larger than the permitted limit, nevertheless the number that is stated by the supplier shall be validated as stated. Finally, special care shall be taken when analysing water-containing samples: the analysis and reporting of the results is advised to do on the dry basis.

2 Introduction

Accordingly to the definition given in CEN/TS 16640, the term “bio-based content“ refers to the fraction of the product that is derived from biomass. The bio-based content is normally expressed as a percentage of the total mass of a product. For the determination of the total bio-based content, the knowledge of all its constituents derived from biomass, are needed. As the most investigated part, first of all it involves the determination of the total bio-based carbon content. The latter is typically expressed as a fraction of the biogenic carbon (^{14}C) to the total carbon in a product.

For the determination of the total bio-based content, besides the fraction of bio-based carbon content, the knowledge on other possible bio-based elements (oxygen or/and hydrogen or/and nitrogen) is required. For that purpose, rules for allocation of elements (described in pr EN 16785) are referred to. Accordingly to these rules, if oxygen and/or hydrogen and/or nitrogen are bound to carbon that is derived from biomass, then the fractions of these elements that are linked to bio-based carbon, are also considered to be part of the bio-based content. However, in practice it is not always possible to distinguish by measurements which elements originating from biomass and which from non-biomass. Therefore in most cases the information from product manufactures is needed in order to calculate the total bio-based content. A separate procedure for the calculation and validation of the bio-based content that is claimed by a producer of a product was proposed in pr EN 16785.

Next paragraphs of this report will describe in details how the total bio-based content can be calculated and validated. The report is written based on the results of the round robin assessment that aimed to test the applicability of the proposed procedure for the validation of the bio-based content. Based on the results of the round robin assessment, necessary changes were proposed to pr EN 16785. This resulted in pr EN-16785-1as a new edition of the previous prenorm. This report refers to pr EN 16785 (that was used in the round robin assessment), but also mentioning pr EN 16785-1 and the changes that have been made compared to the initial version. Since December 2015, pr EN 16785-1 became a full standard EN 16785-1.

The round robin assessment included 11 participating laboratories to whom 11 equivalent sets of samples were delivered. Each set of samples consisted of 6 samples and information on their composition, bio-based carbon content and total bio-based content. The information mentioned in the statements needed to be checked by the measurements independently by each laboratory. Then the stated values for the bio-based content were validated or not, depending on the difference between stated and measured values. The criteria for validation were described in pr EN 16785 that was received by each participating laboratory together with the set of samples.

Further in this report a brief description of each sample and the summarizing overview of the results on the total carbon content and on the biogenic carbon content will be presented. Performance characteristics (measured average for each sample, reproducibility standard deviation and coefficient of the variation of the reproducibility) will be presented both for total carbon content and for the biogenic carbon content, for each of analysed samples. Overview on the validation of the total bio-based content that was stated by the suppliers of the samples, is presented as well. More detailed reports on each individual sample are given in Appendix A (for total carbon content for each of Samples 1-6) and in Appendix B (for biogenic carbon content for each of Samples 1-6). Appendices A and B also present the Z-score plots for each individual sample. For a given sample, the Z-score plots illustrate the deviation of the results of each single laboratory from the calculated average. Appendix C prodives the details of the Grubbs analysis that was performed in order to identify possible straggler and outliers. Appendix D describes samples preparations and samples convertion to the carbon dioxide by each laboratory.

3 Participating laboratories and samples description

Below a list of participating laboratories is presented:

Agroisolab GmbH, Germany
Beta Analytic, USA
Centre de Datation par le RadioCarbone/Institute of Analytical Sciences, France
Energy Research center of the Netherlands, the Netherlands
SGS, France
SKZ, Germany
Silesian University of Technology, Institute of Physics, Radiocarbon Laboratory, Poland
Scion/GNS Science, National Isotope Centre, Rafter Radiocarbon, New Zealand
University of Wageningen, Food and Biobased Research, the Netherlands
University of Groningen, Center for Isotope Research (CIO), the Netherlands
University of York, Green Chemistry Centre of Excellence, United Kingdom

Due to the confidentiality agreements, the results obtained by each laboratory are presented in an anonymous way. Every laboratory was prescribed a number known only to the organiser of the assessment and to that specific laboratory. In the final report, the results are presented using these names (Lab 1, Lab 2, … Lab 11). In this manner each laboratory can have an overview of all results, but is able to recognise only its own results.

The following samples were involved in the round robin testing:

Sample 1. White surfactant granules that are used in cosmetics; non-hazardous.
Sample 2. Cosmetic emulsion with high water content; non-hazardous.
Sample 3. Multilayer packaging film; presents no hazard.
Sample 4. Silk paint; non-hazardous.
Sample 5. Bio-based binder used in paints; non-hazardous.
Sample 6. Wooden particle board ground to 0.5mm; presents no hazard.

These samples were sent to each participating laboratory. For validation, each laboratory was advised to follow prEN 16785 in order to perform the validation of the stated bio-based content of every sample. None of the samples demanded special storage conditions.

4 Total bio-based content: calculation and validation scheme

4.1 Bio-based content calculation

Calculation methods for the total bio-based content are described in Annex C of prEN 16785-1 (previously Annex A of prEN 16785).

Usually the calculation of the total bio-based content is linked to the calculation of the bio-based carbon content. Eq.1 is used in prEN 16785-1 for the **bio-based carbon content** calculation:

$$x_B = \frac{\sum_{i=1}^{n} W_i \cdot x_{B,i}}{W} \qquad \text{Eq. 1}$$

where

x_B is the bio-based carbon content, expressed as a percentage of the total mass of the sample;

$x_{B,i}$ is the bio-based carbon content of the constituent (i), expressed as a percentage of the mass of the constituent (i) and is typically determined by the method described in CEN/TS 16640;

W_i is the mass of the constituent (i), expressed in grams;

W is the total mass of the sample, expressed in grams;

n is the number of constituents of the sample.

In order to calculate the **total bio-based content**, Eq.2 (formula C.2 in Annex C of prEN 16785-1) is used.

$$m_B = \frac{\sum_{i=1}^{n} W_i \cdot m_{B,i}}{W} \qquad \text{Eq.2}$$

where

m_B is the bio-based content of the product expressed as a percentage of the total mass of sample;

$m_{B,i}$ is the bio-based content of the constituent (i), expressed as a percentage of the mass of the constituent (i);

W_i is the mass of the constituent (i), expressed in grams;

W is the total mass of the sample, expressed in grams.

n is the number of constituents of the sample.

For more details, Annex C of EN 16785-1 (it is a full standard from December 2015) can be followed.

4.2 Bio-based content validation

Procedure for the validation of the bio-based content is described in details in paragraph 7.4 of prEN 16785-1. Here only a schematic description of the procedure is given and only the most important moments are underlined.

PrEN 16785-1 recognises two groups of products: Group 1 – products obtained by chemical synthesis and Group 2 – formulated products. In general, in order to make a proper validation, the results of the measurements have to be compared with the numbers claimed by the producers (the so-called statements). However, in case of **products obtained by chemical synthesis** the results both of the of the ^{14}C analysis and elemental analysis should be compared with the data obtained by calculation (so called "statement"). In case of formulated products the high number of components makes it difficult to calculate its elemental composition. Therefore for **formulated products** only the ^{14}C analysis is requested – and not the content of the different elements in a product. The result of the ^{14}C analysis is then compared with the bio-based carbon content obtained from the statements.

The procedure for the bio-based content validation is the following:

1. Stated value for the bio-based *carbon* content, namely "B1" (from formulations provided by product supplier) has to be compared with the measured value of the bio-based *carbon* content, namely "B2" (the value measured by every laboratory laboratory)

2. Each laboratory calculates a gap between stated and measured values, B1-B2

3. Definition of confidence levels

3.1 Group 2: depending on the gap, a confidence level (CL) for the ^{14}C is assigned (CL1, if the gap is less than 3% , CL2 if the gap is between 3 and 4.5%, CL3 if the gap is between 4.5 and 6%). See also Table 2.

3.2 Group 1: for complex products obtained by chemical synthesis, besides the ^{14}C analysis, the CHN-O analysis is also requested. Criteria for defining the confidence levels for

Group 1 products are given in Table 1: the CHN-O composition has to be measured and the confidence levels for C, H, N and O have to be established*. As a result, one has confidence levels defined for ^{14}C – CL1, CL2 or CL3; for C - CL1, CL2 or CL3; for H - CL1, CL2 or CL3; for N - CL1, CL2 or CL3; and for O - CL1, CL2 or CL3. Next, a final confidence level is defined: the confidence levels for the ^{14}C and two other elemental components have to be considered and the lowest** confidence level among them has to be chosen. Validation of stated bio-based content is done accordingly to the final confidence level that is assigned.

**If nitrogen or oxygen is not present in the product, it is not taken into account.*

***Among confidence levels 1, 2 and 3, 1 is the highest, 3 is the lowest.*

4. Stated bio-based content, namely "A", is validated as "A" if a final confidence level is 1; is validated as "A" rounded down to the nearest multiple 5% if a final confidence level is 2; is validated as "A" rounded down to the nearest multiple 5% providing the difference between stated and rounded values is more than 5%, if a final confidence level is 3. No validation is possible if no criteria for any of confidence levels are fulfilled.

Table 1. Definition of confidence levels for Group 1 products according to initial pr EN 16785 (for comparison see Figure 1 in pr EN 16785-1)

	Gap between stated values and values resulting from measurements				
Confidence level	Bio-based carbon content, ^{14}C, %	Total carbon content, %	Total hydrogen content, %	Total oxygen content, %	Total nitrogen content, %
1 (High)	-3.0 to +3.0	-0.4 to +0.4	-0.2 to +0.2	-0.4 to +0.4	-0.4 to +0.4
2 (Medium)	-4.5 to +4.5	-1.0 to +1.0	-0.5 to +0.5	-1.0 to +1.0	-1.0 to +1.0
3 (Low)	-6.0 to +6.0	-2.0 to +2.0	-1.0 to +1.0	-2.0 to +2.0	-2.0 to +2.0

For products that belong to Group 2, only the ^{14}C analysis is requested in order to define a confidence level. The criteria for products that belong for Group 2 are presented in Table 2.

Table 2. Definition of confidence levels for Group 2 products according to pr EN 16785 (for comparison see Figure 2 in pr EN 16785-1)

Confidence level	Gap between stated values and values resulting from measurements
1 (High)	-3.0 to +3.0
2 (Medium)	-4.5 to +4.5
3 (Low)	-6.0 to +6.0

In the round robin assessment that is described in this report, two samples belong to Group 1 (Samples 1 and 5 - a surfactant that is used in cosmetics and a bio-based binder that is used in paints). For these samples, Table 1 shall be used by each laboratory for the definition of a proper confidence level. The rest of the samples (sample 2, sample 3, sample 4 and sample 6) belong to Group 2. For them the validation criteria given in Table 2 have to be applied. Results

based on the application of validation procedure to the total bio-based content stated by the suppliers of Samples 1-6 are presented in next paragraph of this report.

5 Results

5.1 Total carbon content

The total carbon content of the samples (Table 3), was measured using an elemental analyser. Red cells indicate an outlier based on the performed Grubbs test (see Appendix D). Orange cells indicate a straggler accordingly to the Grubbs test. Outliers and stragglers are excluded when calculating the average numbers and Z-scores (see Appendix A for explanations of the Z-score calculations). Grey cells indicate that no measurement on that sample was performed. The column “Supplier” represents data provided by the suppliers of the samples.

Table 3. Total carbon content

	Total C fraction, %										
	Supplier	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10
SAMPLE 1	77.4	77.8	76.8	77.8	76.6	76.9	70.8	55.9		76.1	76.3
SAMPLE 2	15.38	15.4	17.9	15.5	28.4	15.7		13.7		17.3	15.7
SAMPLE 3	69.5	64.2	63.5	66.0	64.6	63.3	47.0	68.0		64.2	68.1
SAMPLE 4	12.4	13.7	13.2	13.2	21.3	13.0		12.9		14.7	13.5
SAMPLE 5	39.6	39.9	38.8	39.3	62.5	39.8		34.4		43.7	40.2
SAMPLE 6	49.34	45.3	45.8	44.8	46.5	45.7	41.3	46.0		46.0	49.4

Performance characteristics

Table 4 presents the performance characteristics that are obtained based on the results of the measurements given in Table 3. For each sample, the performance characteristics include the total number of participating laboratories, the number of outliers and/or stragglers, the percentage of the outlying values with respect to the total number of measurements, the overall average and the reproducibility standard deviations (S_R). For every sample, the overall average is calculated as the mean value of all reported measured values excluding the numbers that based on the results of the Grubbs test were regarded as outliers and/or stragglers. Subsequently, the same set of reported measured values was taken for the calculations of the reproducibility standard deviation (indicates the deviation among the laboratories with respect to the calculated average value). The coefficient of the variation of the reproducibility (CV_R) is also presented. Typically the CV_R is calculated as a ratio between the S_R and the overall average. In this content, for a given sample, lower CV_R means less variation is present, indicating that the reproducibility is higher.

Table 4. Performance characteristics based on the results of round robin test for total carbon content in each sample. S_R is the reproducibility standard deviation, CV_R is the coefficient of the variation of the reproducibility

SAMPLE	No of laboratories	No of outliers and stragglers	No of outlier and straggler free	% of outlying values	The overall average, % total C	S_R, % total C	CV_R, %
SAMPLE 1	9	2	7	22.2	76.9	0.7	0.9
SAMPLE 2	8	1	7	12.5	15.9	1.4	8.8
SAMPLE 3	9	1	8	11.1	65.2	1.9	2.9
SAMPLE 4	8	2	6	25.0	13.3	0.3	2.3
SAMPLE 5	8	1	7	12.5	39.5	2.7	6.8
SAMPLE 6	9	0	9	0.0	45.6	2.1	4.6

In Appendix A, the results on the total carbon content are presented for each sample individually, including measured average, reproducibility standard deviation, min and max values.

As it can be seen from the calculated performance characteristics, the highest coefficients of the variation of the reproducibility are observed for Samples 2 and 5 (correspondingly 8.8% and 6.8%). This can be explained by the fact that these samples were relatively „difficult“ to combust as they contained large fraction of water. S_R for the samples from the round robin testing are of the same order as S_R of other materials reported in other standards (see Table 5), although the direct comparison may not be appropriate due to a very different nature of the samples.

Table 5. Some selected S_R for various materials reported in standards.

Standard	Material	S_R for total C, %	S_R for total H, %
EN 15104, ISO 16948	Solid biofuels/ wood chips	0.55	0.36
ASTM 5291	Oils and lubricants	1.47	1.91
ISO 12902	Solid mineral fuels	1.5	0.3

5.2 Total hydrogen, nitrogen and oxygen content

Results of the hydrogen, oxygen and nitrogen measurements presented in this sub-paragraph are obtained using an elemental analyser.

The complete CHN-O measurements were necessary only for Samples 1 and 5 (Group 1) in order to perform the validation as described in prEN 16785-1. No CHN-O analysis was requested for Samples 2, 3, 4 and 6. Below an overview of measurements that were performed is pre-

sented for Samples 1-6. Cells marked in red indicate outliers. Since the samples contained almost no nitrogen, calculating the performance characteristics for nitrogen was out of the scope in the round robin assessment. Due to the limited number of laboratories who performed the hydrogen (also oxygen) measurements on the provided samples, performance characteristics for hydrogen (oxygen) can not be derived within this round robin testing. However the calculated standard deviation(STD) of the reported H measurements (see Table 6 for total hydrogen content) are of the same order as reported in other standards (see Table 5). Similarly as for total carbon data, due to the different nature of sample, the calculated standard deviation when reporting hydrogen results can only be used as an estimation and can not be directly compared with the numbers presented in Table 5.

Table 6. Total hydrogen content

	Total H fraction, %												
	Supplier	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10	Average	STD
SAMPLE 1	13.40	13.82		13.40	13.44	13.78		9.82			13.64	12.98	1.56
SAMPLE 2	10.97	10.20			7.48	11.01		2.16				9.56	1.85
SAMPLE 3	-	9.53			8.57	9.32		9.44				9.22	0.44
SAMPLE 4	-	5.77			2.48	6.10		1.61				4.78	2.00
SAMPLE 5	10.70	10.15		10.00	9.57	10.51		5.02			9.87	10.02	2.06
SAMPLE 6	-	6.28			6.00	6.46		5.64				6.10	0.36

Table 7. Total nitrogen content

	Total N fraction, %												
	Supplier	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10	Average	STD
SAMPLE 1	0.00	0.04	0.00		0.13	<0.05		-0.01		0.01	<0.1		
SAMPLE 2	0.00	0.05	0.10		0.00	<0.05		0.02		0.01			
SAMPLE 3	-	0.24	0.40		0.00	0.20		0.18		0.28			
SAMPLE 4	-	0.04	0.00		0.00	<0.05		0.01		0.02			
SAMPLE 5	<0.05	0.05	0.10		0.00	<0.05		-0.01		0.04	<0.1		
SAMPLE 6	-	3.94	2.60		3.29	3.73		3.17		1.89		3.35	0.52

Table 8. Total oxygen content

	Total O fraction, %										
	Supplier	Lab 1	Lab 2	Lab 3	*Lab 4*	Lab 5	Lab 6	*Lab 7*	Lab 8	Lab 9	Lab 10
SAMPLE 1	8.55	8.55		9.30	*9.80*	9.31		*34.30*			8.90
SAMPLE 2	63.86	63.86			*64.17*	72.34		*6.20*			
SAMPLE 3	22.25	22.25			*26.85*	21.76		*20.40*			
SAMPLE 4	40.57	40.57			*76.20*	43.32		*44.30*			
SAMPLE 5	42.68	42.68		46.70	*27.95*	47.18		*11.90*			45.37
SAMPLE 6	41.51	41.51			*44.24*	41.49		*40.30*			

NOTE: no measurements on oxygen content were done by Lab 4 and Lab 7. The oxygen content that is reported by Lab 4 and Lab 7 is calculated as 100% - %C - %H - %N (calculated deviating results are marked in light red colour). *Formally, the oxygen content if calculated as 100% - %C - %H - %N can not be taken into account while performing the validation procedure, only measured values have to be considered. However, in order to check the applicability of the*

proposed validation procedure was understood correctly, these values were taken into account, provided they were not too much deviating from the measured values provided by other laboratories (cells marked in light red in Table 8 were not considered at all). Also, since the oxygen measurements were done only by 3 out of 10 laboratories, no average values are presented in Table 8.

5.3 Biogenic carbon content

In this paragraph, the results of the ^{14}C measurements are presented. The measurements were done by AMS and LSC techniques.

Prior to the ^{14}C analysis, all samples were converted to CO_2 via combustion of the sample accordingly to procedure that is described in CEN/TS 16640 and is based on the complete combustion of a sample. In case of high water content in the sample the combustion aids can be used. Then, the true ^{14}C content of the sample has to be corrected on the amount of the total carbon and the ^{14}C that is present in the combustion enhancer. Among the samples that are described in this report, combution enhancers were used to facilitate the combustion of Sample 1 and Sample 5. The results presented in Table 9 are recalculated with correction on the biogenic content originating from the combustion aids. The combustion aids that were used were polyethylene bags, benzoic acid and hexadecane. More details on the pretreatment are given in Appendix C for each sample.

Table 9 presents the results on the biogenic carbon content of each sample. Red cells indicate an outlier (based on the Grubbs test, see Appendix D). Orange cells indicate a straggler (based on the Grubbs test). Outliers and stragglers are excluded when calculating the average numbers and Z-scores (see Appendix B for explanations of Z-scores). Grey cells indicate that no measurement on that sample was performed. The column “Supplier” represents data provided by the suppliers of the samples. More details with the corresponding graphs can be found in Appendix B.

Lab 3, Lab 8 and Lab 10 did the ^{14}C analysis using the LSC technique, while the results reported by the rest of the laboratories are obtained by performing an AMS analysis on each sample. As can be seen from Table 5, the results obtained by these two different techniques are equivalent.

Table 9. Biogenic carbon content

	Biogenic carbon fraction, %											
	Supplier	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7	Lab 8	Lab 9	Lab 10	Lab 11
SAMPLE 1	100	99	98	96	98	99	99	98		97	98	98
SAMPLE 2	97	94	82	93	96	95		98	94	94	95	96
SAMPLE 3	14	14	11	10	13	11	12	13	25	12	13	13
SAMPLE 4	81	72	73	71	74	91		71	78	73	74	73
SAMPLE 5	99	92	93	93	86	95		98	95	93	93	95
SAMPLE 6	92	99	100	99	100	100	100	99	100	98	100	98

Performance characteristics

The performance characteristics for carbon-14 were already reported in Deliverable 3.1 of Open-Bio, but for convenience will be repeated also in this report. Similarly as to the results on the total carbon content, the performance characteristics of the bio-based carbon determination include the total number of participating laboratories, the number of outliers and/or stragglers, the percentage of the outlying values with respect to the total number of measurements, the overall average and the reproducibility standard deviations, S_R (see Table 10). For every sample, the overall average is calculated as the mean value of all reported measured values excluding the numbers that based on the results of the Grubbs test were regarded as outliers and/or stragglers. Subsequently, the same set of reported measured values was taken for the calculations of the reproducibility standard deviation (indicates the deviation among the laboratories with respect to the calculated average value). The coefficient of the variation of the reproducibility, CV_R, is also presented. Typically the CV_R is calculated as a ratio between the S_R and the overall average. For a given sample, lower CV_R means less variation is present, indicating that the reproducibility is higher.

Table 10. Performance characteristics based on the results of round robin test for biogenic carbon content in each sample. S_R is the reproducibility standard deviation, CV_R is the coefficient of the variation of the reproducibility

SAMPLE	No of laboratories	No of outliers and stragglers	No of outlier and straggler free	% of outlying values	**The overall average, % ^{14}C**	**S_R, % ^{14}C**	CV_R, %
SAMPLE 1	10	0	10	0	98.0	1.0	1.0
SAMPLE 2	10	1	9	10	95.0	1.4	1.5
SAMPLE 3	11	1	10	9	12.2	1.2	9.8
SAMPLE 4	10	1	9	10	73.2	2.0	2.7
SAMPLE 5	10	1	9	10	94.1	1.8	1.9
SAMPLE 6	11	0	11	0.0	99.3	0.8	0.8

As one can see from the calculated performance characteristics, the highest coefficients of the variation of the reproducibility (9.8%) is observed for Sample 3. For this sample (multilayer packaging film, consisting of parts of different colours with 1-2% difference in their carbon content), lower reproducibility can be related to the preparation of the representative sample (having a sample including all colours or burning the sample as a whole). This could explain the higher variation of the reproducibility among participating laboratories.

5.4 Total bio-based content determination and validation results

This section gives an overview of results on the validation of total bio-based content of Samples 1-6.

Validation involved two groups of samples: group 1 (samples 1 and 5) where both the ^{14}C analysis and CHN-O analysis were needed in order to validate total bio-based content stated by products suppliers; group 2: samples 2, 3, 4, 6 where only the ^{14}C analysis was necessary in order to validate total bio-based content stated by products suppliers). Therefore the overview of validated numbers is presented separately for each of these groups: Table 11 – for sample 1, Table 12 – for sample 5, and Table 13 – for samples 2, 3, 4, 6.

Table 11. Overview of total bio-based content validation of Sample 1 (all numbers are reported in %)

SAMPLE 1	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 7	Lab 8	Lab 9	Lab 10
Stated biobased content, A (from formulations provided by product supplier)	***100***	***100***	***100***	***100***	***100***	***100***	***100***	***100***	***100***
Stated value for biogenic carbon content, B1 (from formulations provided by product supplier)	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*	*100*
Measured value for biogenic carbon content, B2	99	97.9	95.6	98	99	98		97	98.2
Gap between stated and measured, B1-B2	1	2.1	4.4	2				3	1.8
Confidence level for biogenic carbon (based on the gap B1-B2)	1		2	1		1		1	1
Stated value for total carbon content, TC1 (from formulations provided by product supplier)	*77.4*	*77.4*	*77.4*	*77.4*	*77.4*	*77.4*	*77.4*	*77.4*	*77.4*
Measured value for total carbon content, TC2	77.8	76.8	77.8	76.6	76.9	55.9		76.1	76.3
Gap between stated and measured total carbon content, TC1-TC2	-0.4	0.6	-0.4	0.8					1.1
Confidence level for total carbon (based on the gap TC1-TC2)	1		1	2					
Stated value for hydrogen content, H1 (from formulations provided by product supplier)	*13.4*	*13.4*	*13.4*	*13.4*	*13.4*	*13.4*	*13.4*	*13.4*	*13.4*
Measured value for hydrogen content, H2	13.8	-	13.4	13.4	13.8	9.8		-	13.6
Gap between stated and measured hydrogen content, H1-H2	-0.4		0	0					-0.2
Confidence level for hydrogen (based on the gap H1-H2)	2		1	1					
Stated value for nitrogen content, N1 (from formulations provided by product supplier)	-	-	-	-	-	-	-	-	-
Measured value for nitrogen content, N2	0.04	0	-	0.13		-		0.01	<0.1
Gap between stated and measured hydrogen content, N1-N2			-						
Confidence level for nitrogen (based on the gap N1-N2)									
Stated value for oxygen content, O1 (from formulations provided by product supplier)	*9.2*	*9.2*	*9.2*	*9.2*	*9.2*	*9.2*	*9.2*	*9.2*	*9.2*
Measured value for oxygen content, O2	8.6	-	9.3	9.8	9.3			-	8.9
Gap between stated and measured hydrogen content, O1-O2	0.6		-0.1	-0.6					0.3
Confidence level for oxygen (based on the gap O1-O2)	2		1	2					
Assigned FINAL confidence level (chosen among confidence levels for C14 and confidence levels for C, H, N, O)	**2**		**2**	**2**	**2**	**1**		**1**	**1**
Validated value accordingly to assigned FINAL confidence level (A, or A that is round down depending on the confidence level)	**95**		**95**	**95**	**95**	**100**		**100**	**100**
						Only 14C was used for validation		Only 14C was used for validation	Only 14C was used for validation

Remarks to Table 11:

1. Cells marked in green in Table 11 indicate that the validation rules were applied correctly accordingly to prEN 16785.

2. Lab 7, Lab 9 and Lab 10 used only the ^{14}C measurements to validate the bio-based content for Sample 1, while the CHN-O analysis was also required, accordingly to prEN 16785. Therefore this validation cannot be considered as complete (marked as blue for Lab 7, Lab 9 and Lab 10 in Table 11)

3. Grey cells (for Lab 2 and Lab 8) indicate that no measurements were done (Lab 8) or no validation was performed (Lab 2)

4. n.a – not assigned; n.v – not validated; "-" indicates that no measurement was reported/done; Empty cells indicate that no calculations were performed

5. Lab 6 did not participate in the validation part of the round robin.

Table 12. Overview of total bio-based content validation of Sample 5 (all numbers are reported in %)

Remarks to Table 12:

SAMPLE 5	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 7	Lab 8	Lab 9	Lab 10
Stated biobased content, A (from formulations provided by product supplier)	*99*	*99*	*99*	*99*	*99*	*99*	*99*	*99*	*99*
Stated value for biogenic carbon content, B1 (from formulations provided by product supplier)	*99*	*99*	*99*	*99*	*99*	*99*	*99*	*99*	*99*
Measured value for biogenic carbon content, B2	92	93.2	92.3	86 - straggler	95	98	95	93	93
Gap between stated and measured, B1-B2	7	5.8	6.7		4	1	4	6	6
Confidence level for biogenic carbon (based on the gap B1-B2)	n.a		n.a	n.a	2	1	2	3	3
Stated value for total carbon content, TC1 (from formulations provided by product supplier)	*39.6*	*39.6*	*39.6*	*39.6*	*39.6*	*39.6*	*39.6*	*39.6*	*39.6*
Measured value for total carbon content, TC2	39.9	38.8	39.3	62.48 - outlier	39.8	34.4	-	43.7	40.24
Gap between stated and measured total carbon content, TC1-TC2	-0.3	0.8	0.3		0.2				-0.64
Confidence level for total carbon (based on the gap TC1-TC2)	1		1		1				
Stated value for hydrogen content, H1 (from formulations provided by product supplier)	*10.7*	*10.7*	*10.7*	*10.7*	*10.7*	*10.7*	*10.7*	*10.7*	*10.7*
Measured value for hydrogen content, H2	10.2	-	10	9.57	10.51	5.02	-	-	9.87
Gap between stated and measured hydrogen content, H1-H2	0.5		0.7		0.19				0.83
Confidence level for hydrogen (based on the gap H1-H2)	2		3		1				
Stated value for nitrogen content, N1 (from formulations provided by product supplier)	<=0.05	<=0.05	<=0.05	<=0.05	<=0.05	<=0.05	<=0.05	<=0.05	<=0.05
Measured value for nitrogen content, N2	0.05	0.1	0	0		-	-	0.04	<0.1
Gap between stated and measured hydrogen content, N1-N2									
Confidence level for nitrogen (based on the gap N1-N2)	1		1						
Stated value for oxygen content, O1 (from formulations provided by product supplier)	*45.2*	*45.2*	*45.2*	*45.2*	*45.2*	*45.2*	*45.2*	*45.2*	*45.2*
Measured value for oxygen content, O2	42.7	-	46.7	27.95 - outlier	47.18		-	-	45.37
Gap between stated and measured hydrogen content, O1-O2	2.5		-1.5		-1.98				-0.17
Confidence level for oxygen (based on the gap O1-O2)	n.a		3		3				
Assigned FINAL confidence level (chosen among confidence levels for C14 and confidence levels for C, H, N, O)	**n.a**		**n.a**	**n.a**	**2**	**1**			
Validated value accordingly to assigned FINAL confidence level (A, or A that is round down depending on the confidence level)	**n.v**		**n.v**	**n.v**	**95**	**100**	**90**	**90**	**95**
					Correct based on measured values	Only 14C was used for validation	Only 14C was used for validation	Only 14C was used for validation	
n.a - can not be assigned									
n.v - can not be validated									

1. Green color is Table 12 indicated that validation rules were applied correctly accordingly to prEN 16785.

2. Lab 8 used only the ^{14}C measurement for the validation of the bio-based content stated by the product supplier. The stated value was 99%. The ^{14}C as measured was 95%. A gap between these two is 4% that falls into the confidence level 2. Accordingly to the rules defined in prEN 16785, for confidence level 2 the stated value has to be round down to the nearest multiple 5% value. Thus 99% have to be round down to 95% and not to 90%.

3. In case of Lab 10, a gap between measured and stated values is 6% that falls into the confidence level 3. Accordingly to the rules defined in prEN 16785, for confidence level 3 the stated value has to be round down to the nearest multiple 5% value providing the difference between the stated and the rounded values is larger than 5%. In such cases, 99% have to be round down to 90% and not to 95%.

4. Lab 7, Lab 8, Lab 9 and Lab 10 used only the ^{14}C measurements to validate the bio-based content for Sample 11, while the CHN-O analysis was also expected to be used accordingly to prEN 16785-1. Therefore this validation cannot be considered as complete (marked as blue for Lab 7, Lab 8, Lab 9 and Lab 10 in Table 12)

5. Grey cells (for Lab 2) indicate no validation was performed.

6. n.a – not assigned; n.v – not validated; "-" indicates that no measurement was reported/done; Empty cells indicate that no calculations were performed

7. Lab 6 did not participate in the validation part of the round robin.

Table 13. Overview of total bio-based content validation of Samples 2,3,4 and 6

Green cells in Table 13 (column "Total bio-based content validated by laboratory") indicate that the validation rules were applied correctly. Cell marked in red indicate that validation (or some steps of it) was not performed. Remarks on validation can be seen in the last column of Table 13. Lab 6 did not participate in the validation part of the round robin.

		14C measured, %	14C stated by sample supplier, %	Gap between stated ands measured, %	Confidence level assigned by laboratory	Total bio-based content stated by sample supplier, %	Total bio-based content validated by laboratory, %	Remark of the round robin organiser
Lab 1	SAMPLE 8	94	97	3	1	97	97	
	SAMPLE 9	14	14	0	1	22.3	22.3	
	SAMPLE 10	72	81	9	no confidence level could be assigned	21.7	not validated	
	SAMPLE 12	99	92	-7	1	92	92	
Lab 2	SAMPLE 8	82	97	15		97	can not be considered since measured value is an outlier	Measured value is an outlier. Was not done by the laboratory
	SAMPLE 9	11	14	3		22.3		
	SAMPLE 10	73	81	8		21.7		
	SAMPLE 12	100	92	-8		92		
Lab 3	SAMPLE 8	93.2	97	4	2	97	95	
	SAMPLE 9	10.2	14	4	2	22.3	20	
	SAMPLE 10	71.2	81	10	no confidence level could be assigned	21.7	not validated	
	SAMPLE 12	99.3	92	-7	1	92	92	
Lab 4	SAMPLE 8	96	97	1	1	97	97	
	SAMPLE 9	13	14	1	1	22.3	22.3	
	SAMPLE 10	74	81	7	no confidence level could be assigned	21.7	not validated	
	SAMPLE 12	100	92	-8	1	92	92	
Lab 5	SAMPLE 8	95	97	2	1	97	97	
	SAMPLE 9	11	14	3	1	22.3	22	
	SAMPLE 10	91	81	-10	not assigned	21.7	can not be considered since measured value is an outlier	Measured value is an outlier. Was not validated by the laboratory
	SAMPLE 12	100	92	-8	not assigned	92	not validated	Formally it is right not to validate accordingly to the distributed version of the standards, but it was mentioned by the laboratory 92% should be validated because measured value is higher that stated
Lab 7	SAMPLE 8	98	97	-1	1	97	97	
	SAMPLE 9	13	14	1	1	22.3	22.3	
	SAMPLE 10	98	81	-17	no confidence level could be assigned	21.7	not validated	
	SAMPLE 12	99	92	-7	no confidence level could be assigned	92	not validated	Was mentioned by the laboratory that, since stated bio-based content is lower than measured, then the rounding as for the confidence level 1 shall be applied. Formally the rules were applied correctly.
Lab 8	SAMPLE 8	94	97	3	1	97	94.4	97% should be validated based on the assigned confidence level
	SAMPLE 9	25	14	-11	1	22.3	can not be considered since measured value is an outlier	Measured value is an outlier
	SAMPLE 10	78	81	3	2	21.7	75	Validation should be applied to total bio-based content and not to bio-based carbon content
	SAMPLE 12	100	92	-8	1	92	100	Supplier claimed 92% bio-based content. 92% therefore shall be validated, not 100%
Lab 9	SAMPLE 8	94	97	3	1	97	97	
	SAMPLE 9	12	14	2	1	22.3	22	
	SAMPLE 10	73	81	8	3	21.7	15	Since the calculated gap exceeds 6%, no confidence level can be assigned.
	SAMPLE 12	98	92	-6	1	92	92	
Lab 10	SAMPLE 8	95	97	2		97	97	
	SAMPLE 9	13	14	1		22.3	20	22% should be validated since the gap of 1% is within the confidence level 1
	SAMPLE 10	74	81	7		21.7	15	No validation can be done since the gap of 7% is beyond the confidenece level 3
	SAMPLE 12	100	92	-8		92	92	Formally accordingly to the distributed version of the standard can not be validated, but since the stated value for the 14C is lower than measured, 92% of biobased content can be validated

6 Conclusions based on the round robin assessment results

This report presents the results of the round robin assessment that was organised to investigate the applicability of procedure described prEN 16785 for the determination and validation of the total bio-based content in various products. The round robin assessment was initiated in the frameworks of the European Open-Bio project (www.biobasedeconomy.eu). Determination of the total carbon content and the biogenic carbon content is part of the validation procedure.

Statistical evaluation of the results on total carbon and on biogenic carbon content was done by performing Grubbs test for the results on each sample reported by each laboratory. Outliers and stragglers that were defined based on the results of Grubbs analysis, were excluded from calculations of measured average numbers and the reproducibility standard deviations among all laboratories.

Total carbon content as reported in Table 3 was measured using an elemental analyser. For the ^{14}C analysis, the known LSC (Liquid Scintillation Counting) or the AMS (Accelerated Mass Spectrometry) techniques were used in this round robin assessment. 3 of 11 laboratories did the ^{14}C analysis using the LSC method (no direct LSC was performed on any samples). By 8 laboratories the AMS analysis was used in order to determine the ^{14}C amount in the delivered samples. The results of the round robin assessment indicates that no inconsistencies are observed for the results of the measurements when using AMS (Accelerated Mass Spectrometry) and LSC (Liquid Scintillation Counting) techniques and thus proves the equivalence of these two techniques.

From the calculated performance characteristics for the biogenic carbon content can be seen that the highest coefficient of the variation of the reproducibility (9.8%) is observed for Sample 3. In case of this sample (multi-layer packaging film, consisting of parts of different colours with 1-2% difference in their carbon content), lower reproducibility can be related to the preparation of the representative sample (having a sample including all colours or burning the sample as a whole). This could explain higher variation of the reproducibility among participating laboratories.

For the determination of the total bio-based content, besides the fraction of bio-based carbon content, the knowledge on other possible bio-based elements (oxygen or/and hydrogen or/and nitrogen) is required. For that purpose, rules for allocation of elements (prEN 16785-1) have to be applied: if oxygen or/and hydrogen or/and nitrogen are bound to a carbon that is derived from biomass, then the fractions of these elements that are linked to bio-based carbon, are also considered to be parts of the bio-based content. In practice, it is not always possible to distinguish between elements originating from biomass and from non-biomass by

measurements. Therefore in most cases the knowledge from product suppliers are needed in order to calculate the total bio-based content. Therefore, together with the samples, the so-called statements were provided by the suppliers of Samples 1-6. Every statement included information about composition of a given sample, its bio-based carbon content and its total bio-based content. The information mentioned in the statements was checked by the measurements in each of participating laboratories. Then the stated values were validated or not, based on the difference between stated and measured value for each of involved parameters. Validation of provided data on bio-based contenet presented a largest part in this round robin assessment and is summarized in Table 11, 12 and 13 of this report.

The results of the round robin assessment (application of the proposed validation procedure to validate the bio-based content stated by a product supplier) were carefully analysed and resulted in a number of improvement to the initial version of prEN 16785-1. The changes that are introduced to the the final document compared to its initial edition, are listed in the next section.

7 Necessary adaptations to prEN 16785

While the results of the first round robin assessment (Deliverable 3.1 of Open-Bio on CEN/ TS 16640) indicated reasonably good consistency, determination and validation of the total bio-based content in its initial edition was somewhat less understood among participating laboratories. This resulted in a number of suggestions and recommendations to prEN 16785 that were incorporated in a newer version prEN 16785-1. Here we list the most important moments that are incorporated in the final document:

- As one of adaptations, a clear distinction is now made between the products where only ^{14}C analysis and where both ^{14}C and CHN-O analysis are needed in order to validate the bio-based content. For these two cases, two decision trees (figure 1 and Figure 2 in pr EN 16785-1) and two templates (Table B1 and Table D1) are suggested in order to make the validation procedure more straightforward.
- Furthermore, separate remarks are made for the situations when the bio-based content stated by supplier is lower than the calculated one. In this case, even despite the absolute difference between these two is larger than a gap value permitted in prEN 16785, the number that is stated by the supplier shall be validated as stated.
- It is also mentioned that a special attention shall be paid when reporting the results from the water-containing samples with a high fraction of water: the analysis and reporting of results is advised to do on dry basis.

As a final remark to this document, the modified version prEN 16785-1 since December 2015 became a full European stardard EN 16785-1.

Appendix A. Total carbon content and Z-scores for Samples 1-6

Below the results of the measurements of the total carbon content are presented separately for each sample from 1 to 6. For each sample, the bar-plots give a comparison of the total carbon content reported by all participating laboratories. Outliers and stragglers that are defined by the Grubbs test, are included in the bar plots as well. The data from product suppliers are included as well in the graphs as well.

Z-score

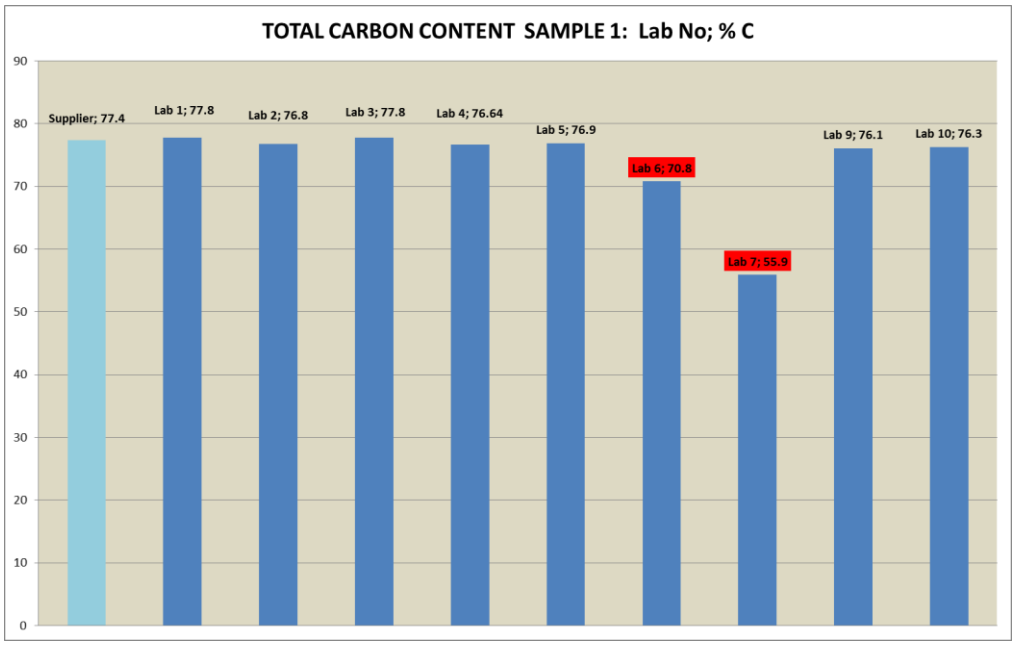
For graphical representation of consistency among all participating laboratories, the so-called Z score figures were used. The Z -score plots are presented separately for each sample. The Z-scores were calculated accordingly to the formula:

$Z\text{-score} = (X_{measured} - X_{mean}) / STD$

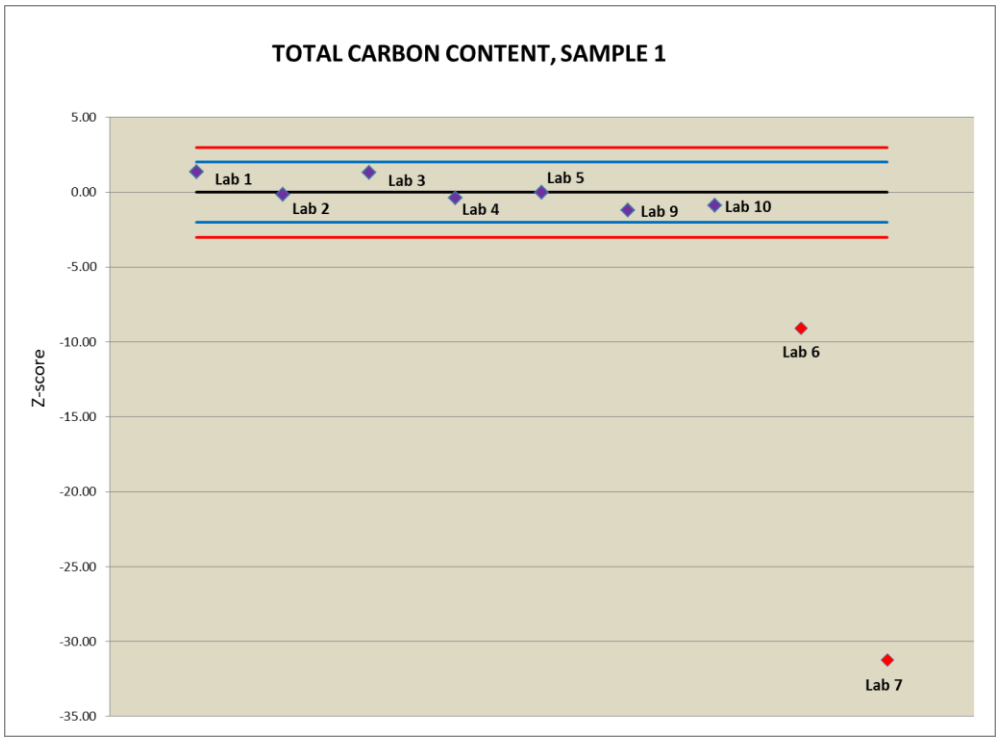
where $X_{measured}$ is the reported value, by each participating laboratory;
X_{mean} - mean value of all reported values (excluding straggles and outliers),
STD - reproducibility standard deviation.
Outliers and stragglers were excluded when calculating the average numbers and the Z-scores

Separately for each sample, the Z-score plots are given in Appendix A for the representation of the results on the total carbon content, and Appendix B when representing the results on the biogenic carbon content. **In Appendices A and B, for each individual sample, the Z-score plots indicate how far is each laboratory from calculated average number**. Blue and red lines in the Z-score plots correspondingly indicate $2 \cdot S_R$ and $3 \cdot S_R$ borders, where S_R is the reproducibility standard deviation.

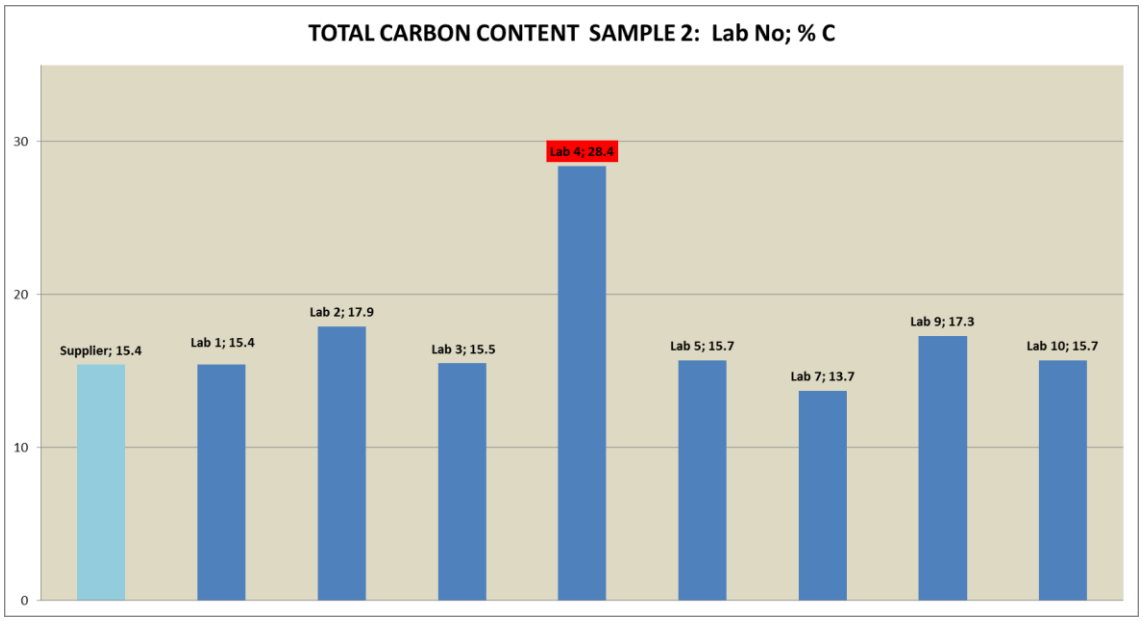
SAMPLE 1. White surfactant granules



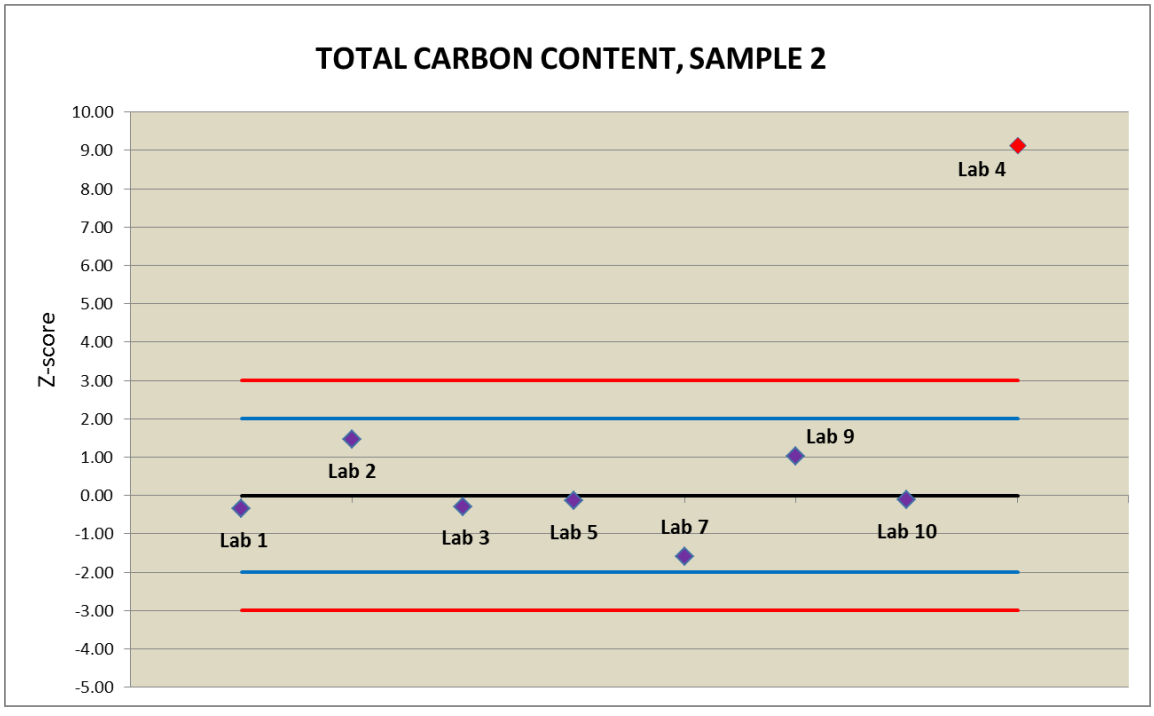
AVERAGE	76.9%
STD	0.7%
Min	76.1%
Max	77.8%



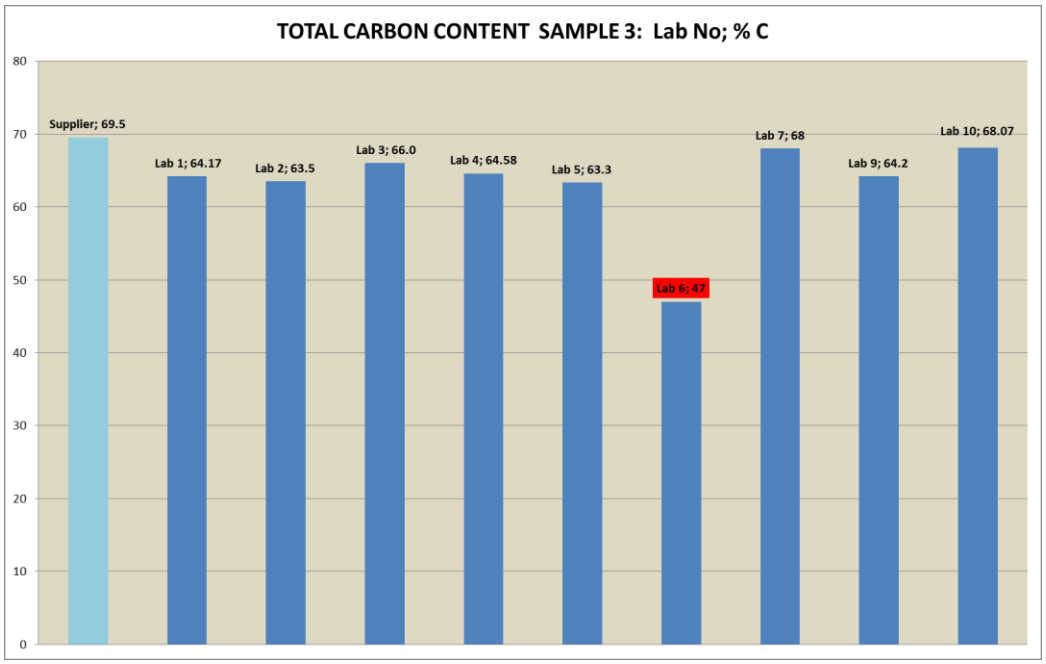
SAMPLE 2. Cosmetic emulsion with high water content



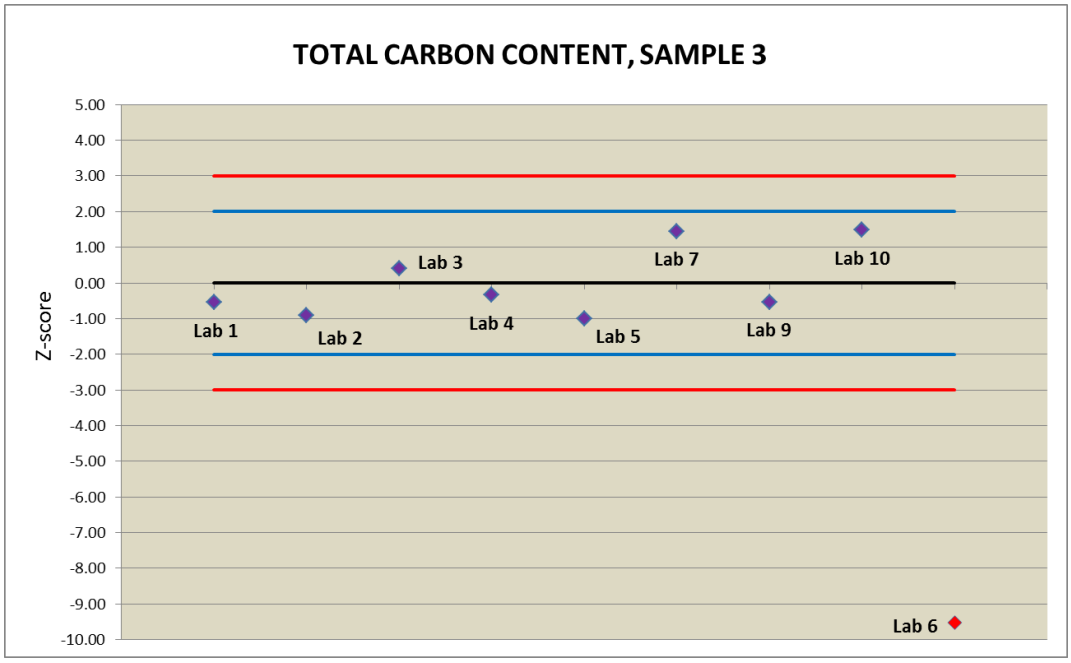
AVERAGE	15.9%
STD	1.4%
Min	13.7%
Max	17.9%



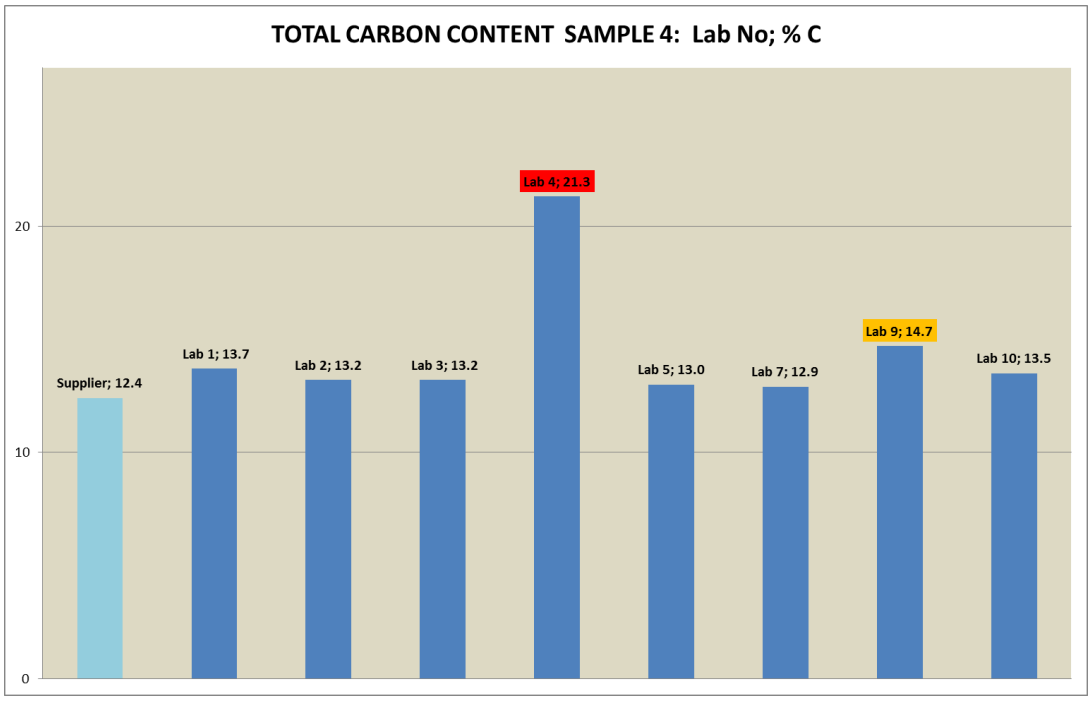
SAMPLE 3. Multilayer packaging film



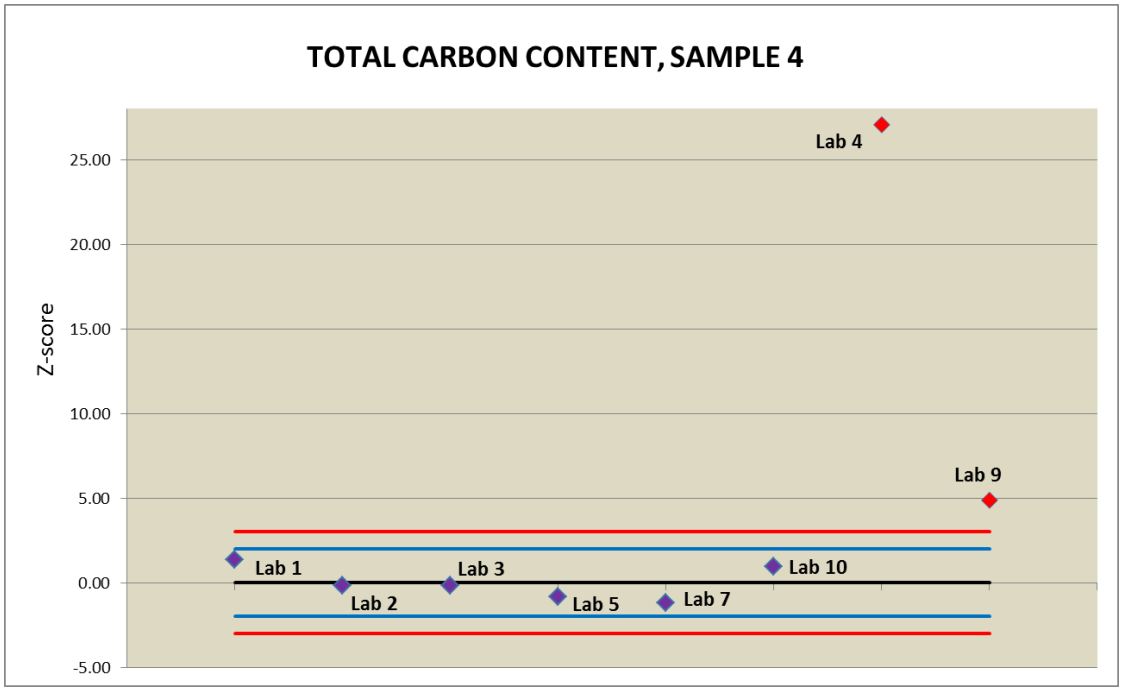
AVERAGE	65.2%
STD	1.9%
Min	63.3%
Max	68.1%



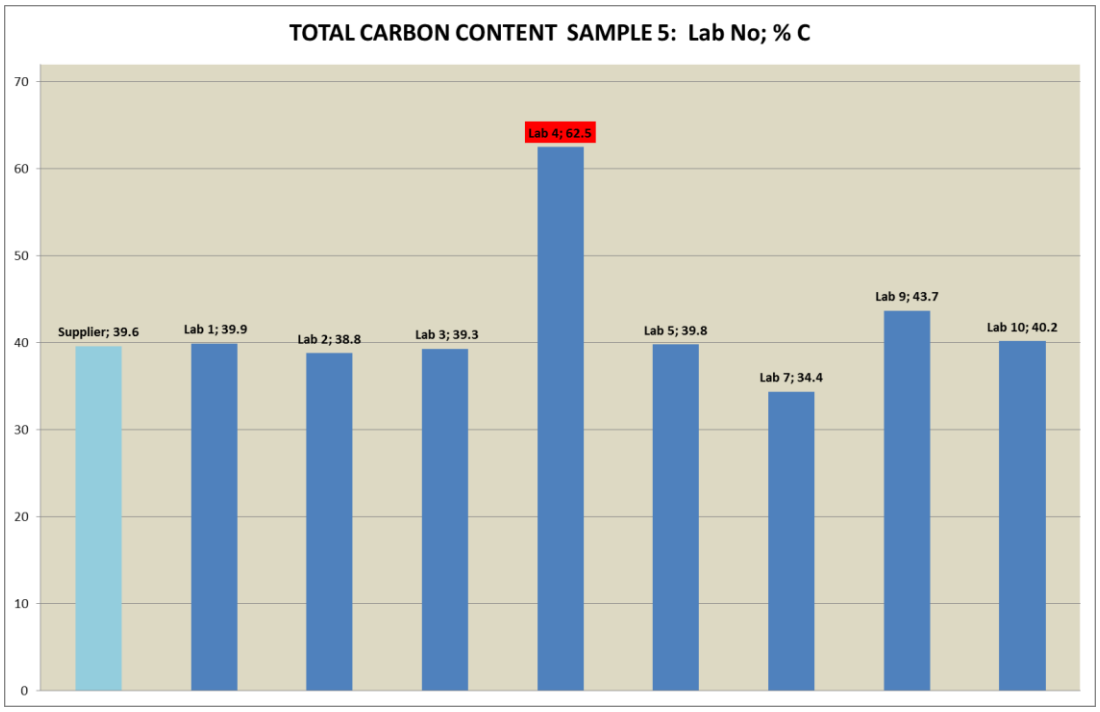
SAMPLE 4. Silk paint



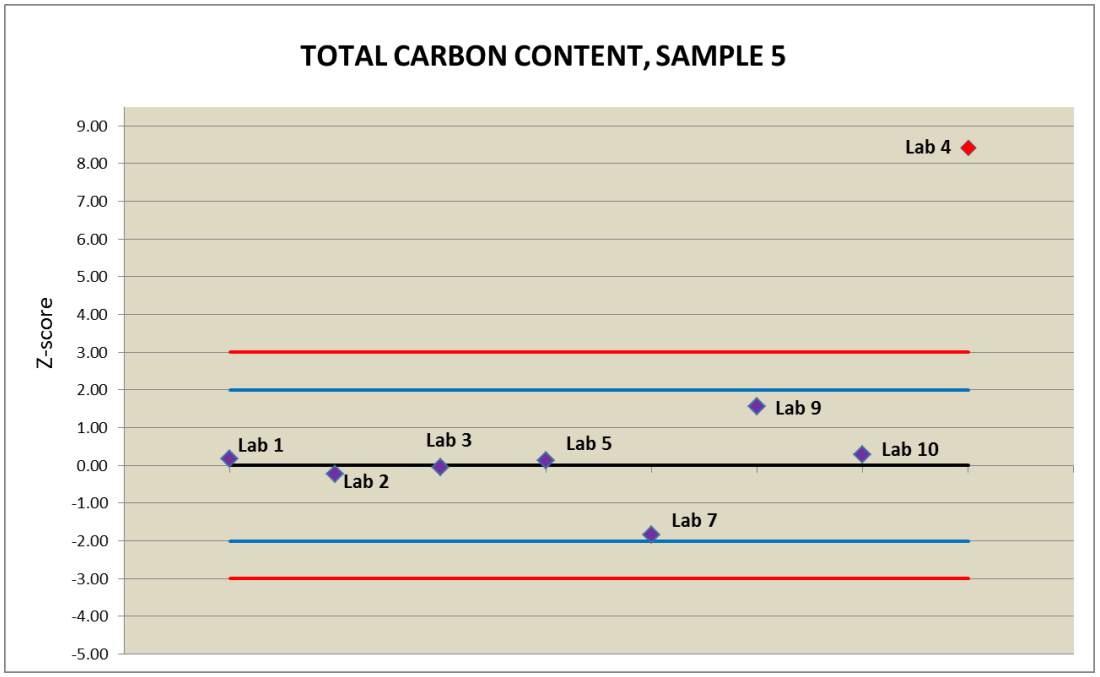
AVERAGE	13.5%
STD	0.6%
Min	12.9%
Max	14.7%



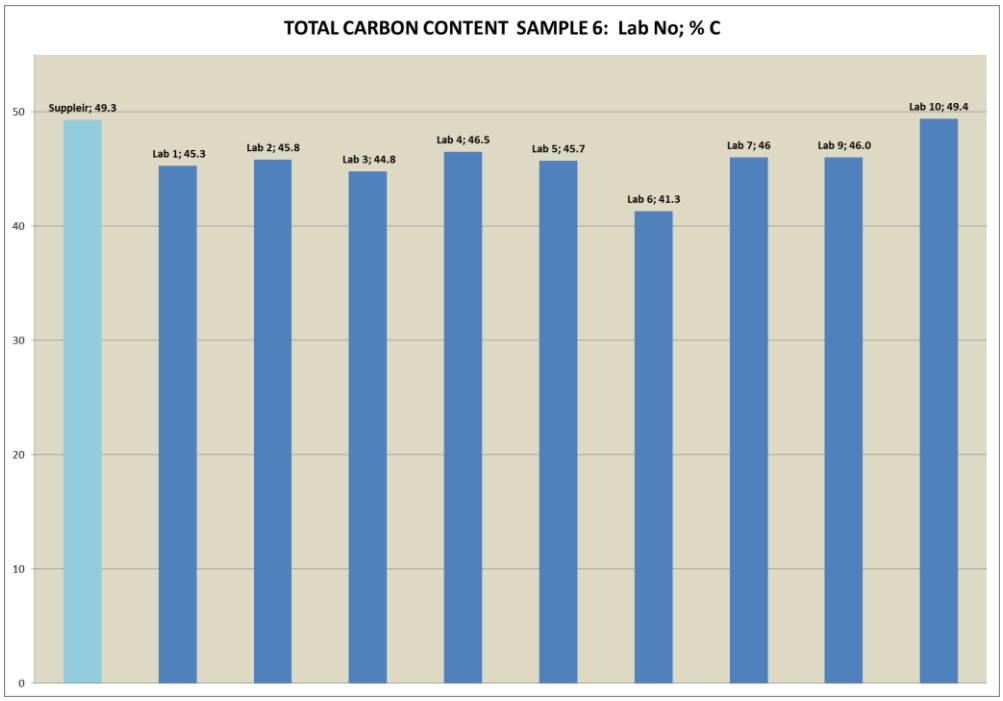
SAMPLE 5. Bio-based binder for paint



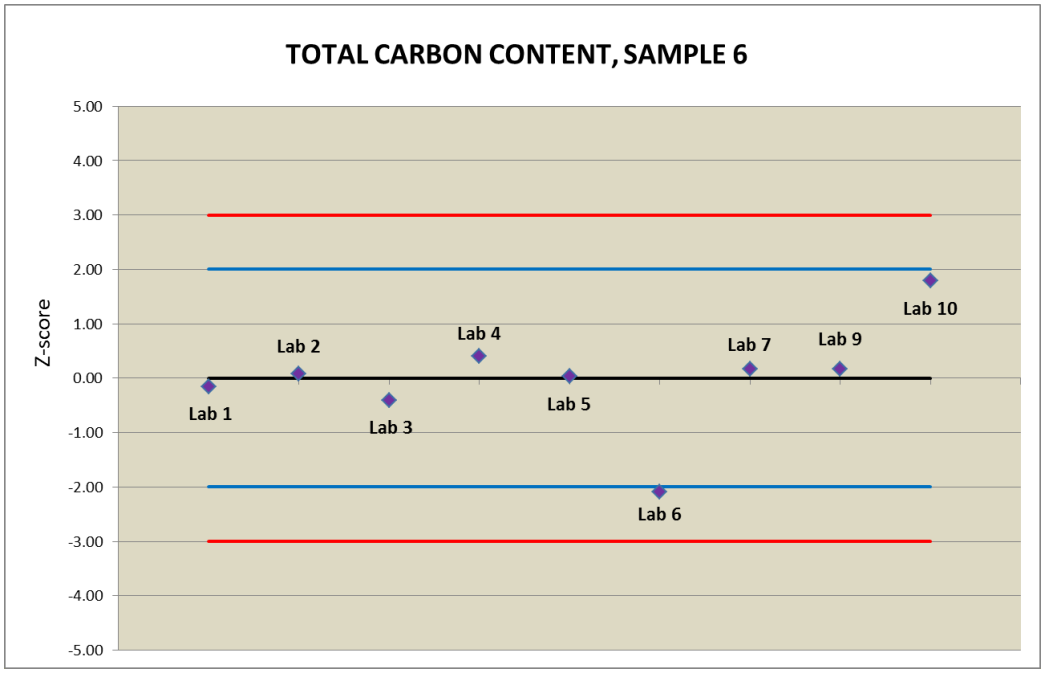
AVERAGE	39.5%
STD	2.7%
Min	34.4%
Max	43.7%



SAMPLE 6. Wooden particle board



AVERAGE	45.6%
STD	2.1%
Min	41.3%
Max	49.4%



Appendix B. Biogenic carbon content and Z-scores for Samples 1-6

In this appendix, the results of the measurements of the biogenic carbon content (as fraction of the total carbon content) are presented separately for Samples 1-6. For each sample, the bar-plots give a comparison of the biogenic carbon content reported by all partic-ipating laboratories. Outliers and stragglers were determined based on the Grubbs test (see Appendix D) and are shown in these plots by different colors. The data from product suppliers (when available) are included as well.

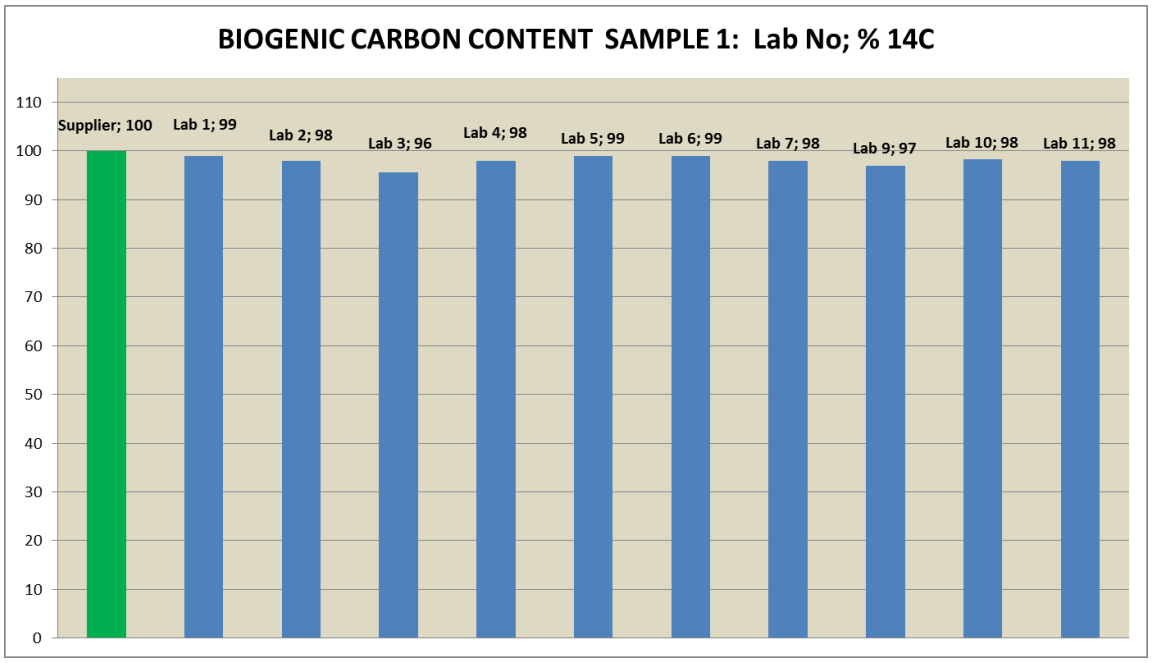
For graphical representation of consistency among all participating laboratories, the so-called Z score figures were used. The Z -score plots are presented separately for each sample. The Z-scores were calculated accordingly to the formula:

$$Z\text{-score} = (X_{measured} - X_{mean}) / STD$$

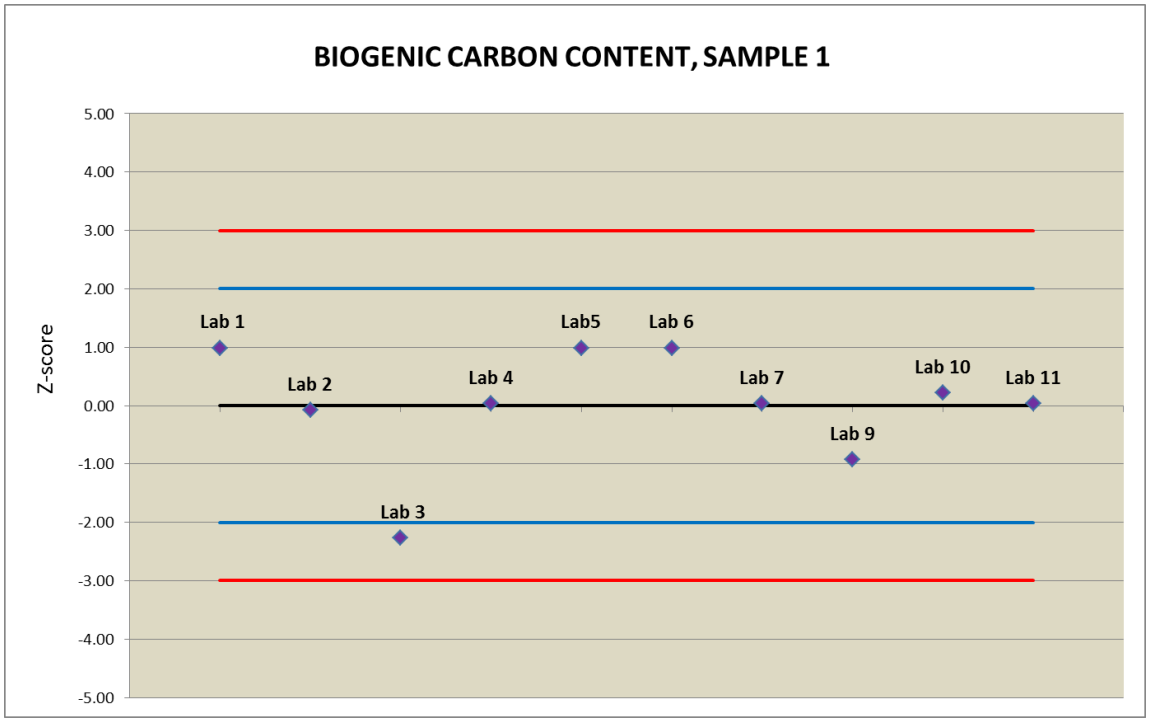
where $X_{measured}$ is the reported value, by each participating laboratory;
X_{mean} - mean value of all reported values (excluding straggles and outliers),
STD - reproducibility standard deviation.
Outliers and stragglers were excluded when calculating the average numbers and the Z-scores

Separately for each sample, the Z-score plots are given to present the results on the biogen-ic carbon content. **For each individual sample, the Z-score plots indicate how far is each laboratory from calculated average number.** Blue and red lines in the Z-score plots correspondingly indicate $2 \cdot S_R$ and $3 \cdot S_R$ borders, where S_R is the reproducibility standard deviation.

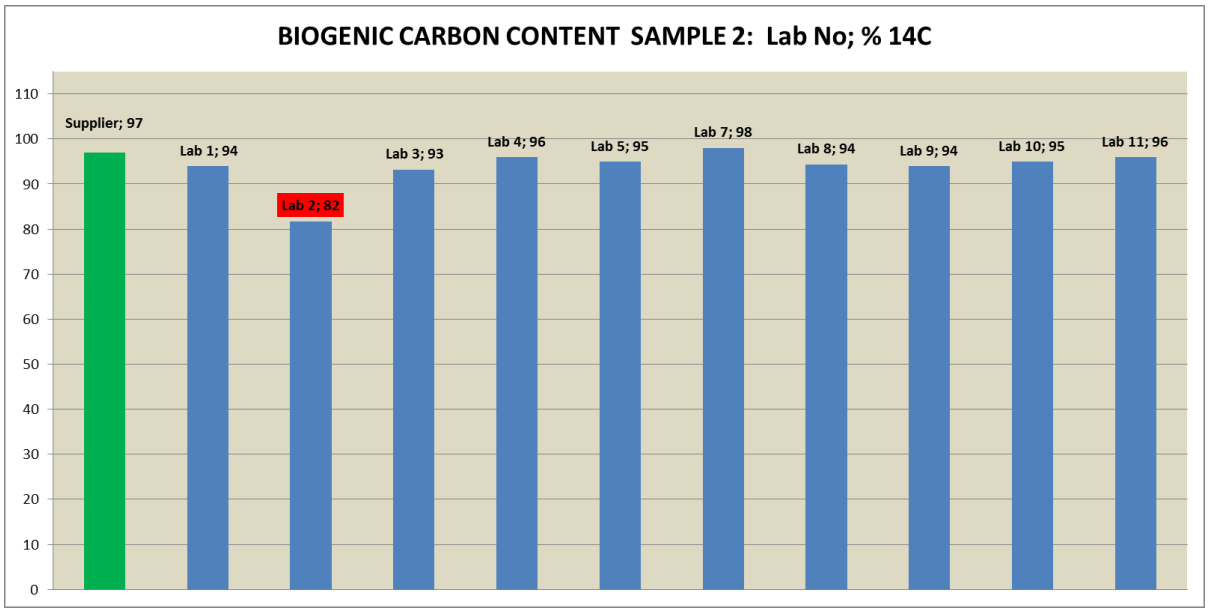
SAMPLE 1. White surfactant granules



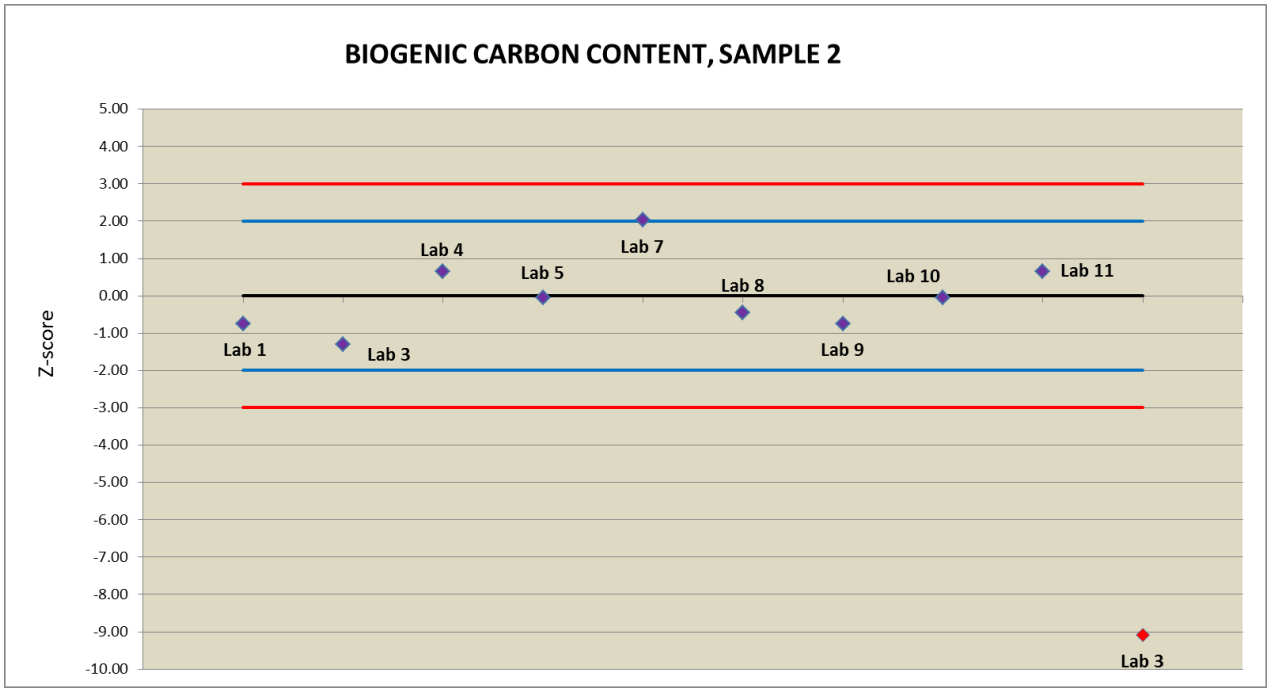
AVERAGE	97.9%
STD	1.0%%
Min	95.6
Max	99.0%



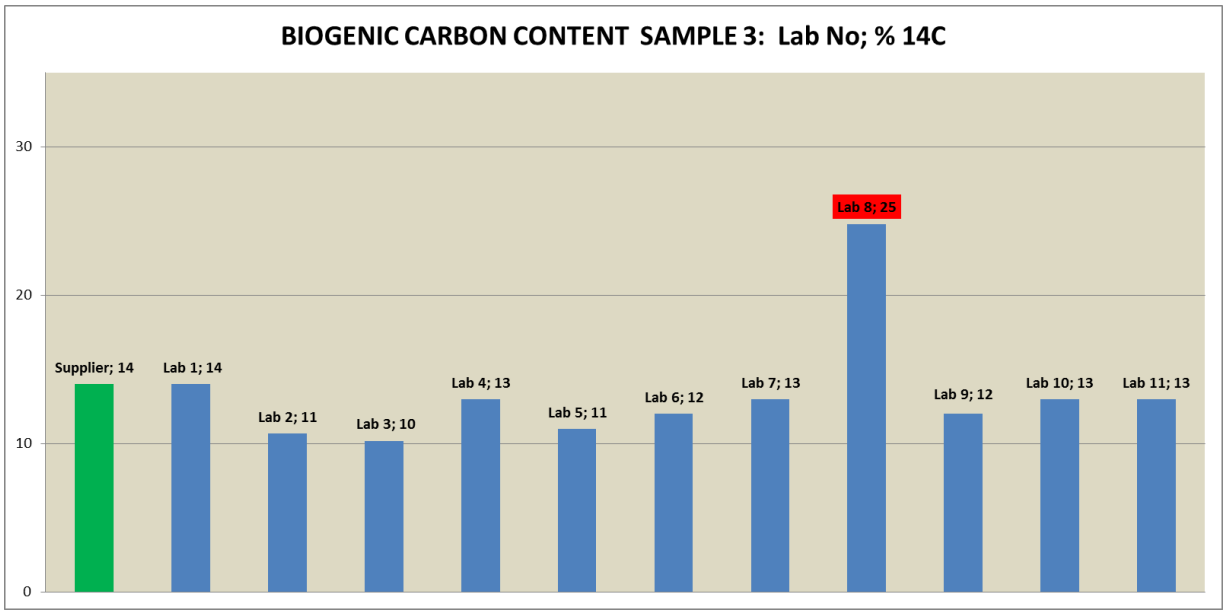
SAMPLE 2. Cosmetic emulsion with high water content



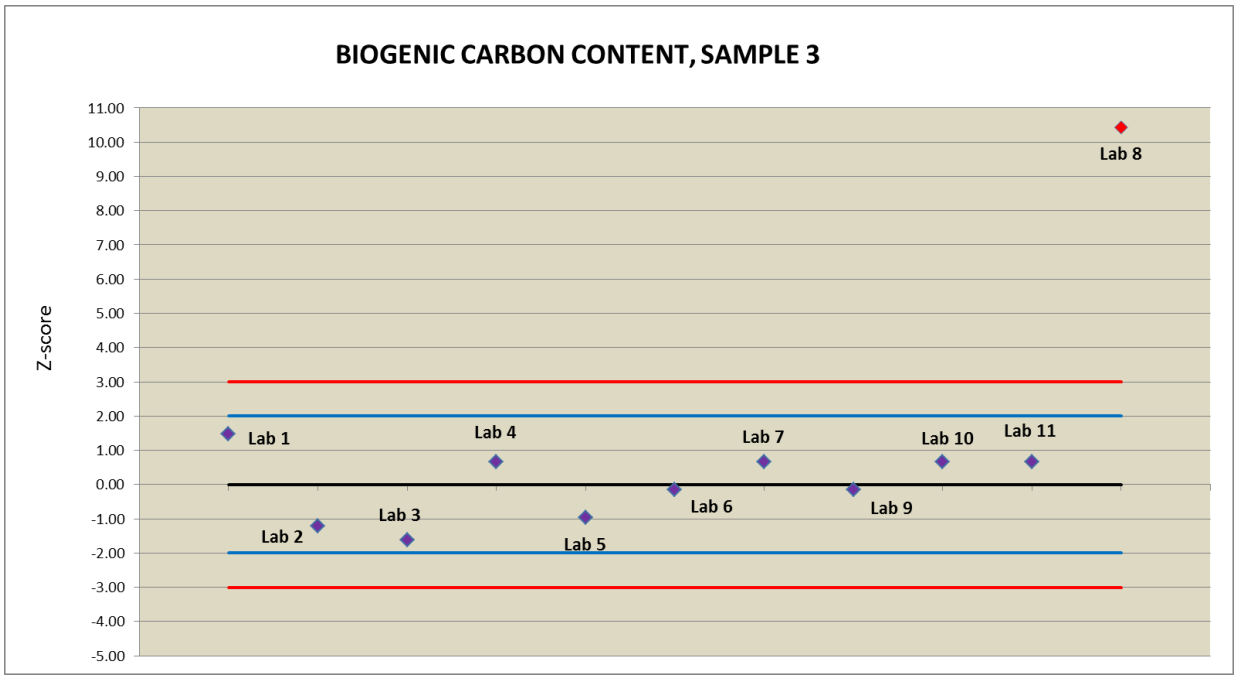
AVERAGE	95.1%
STD	1.4%
Min	93.2%
Max	98.0%



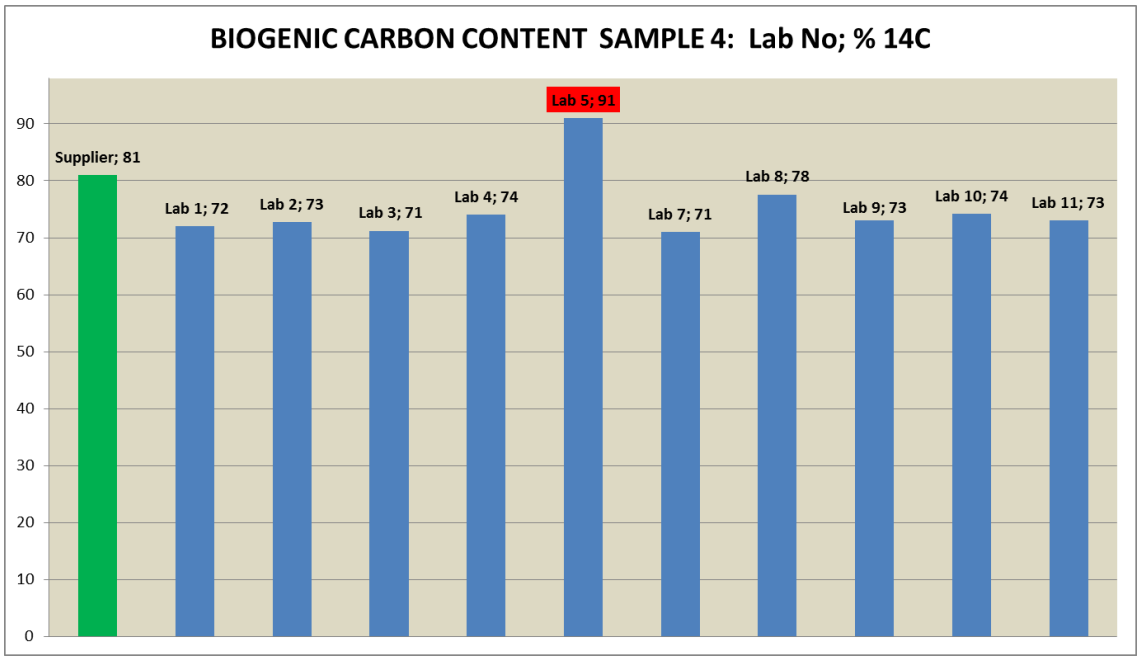
SAMPLE 3. Multilayer packaging film



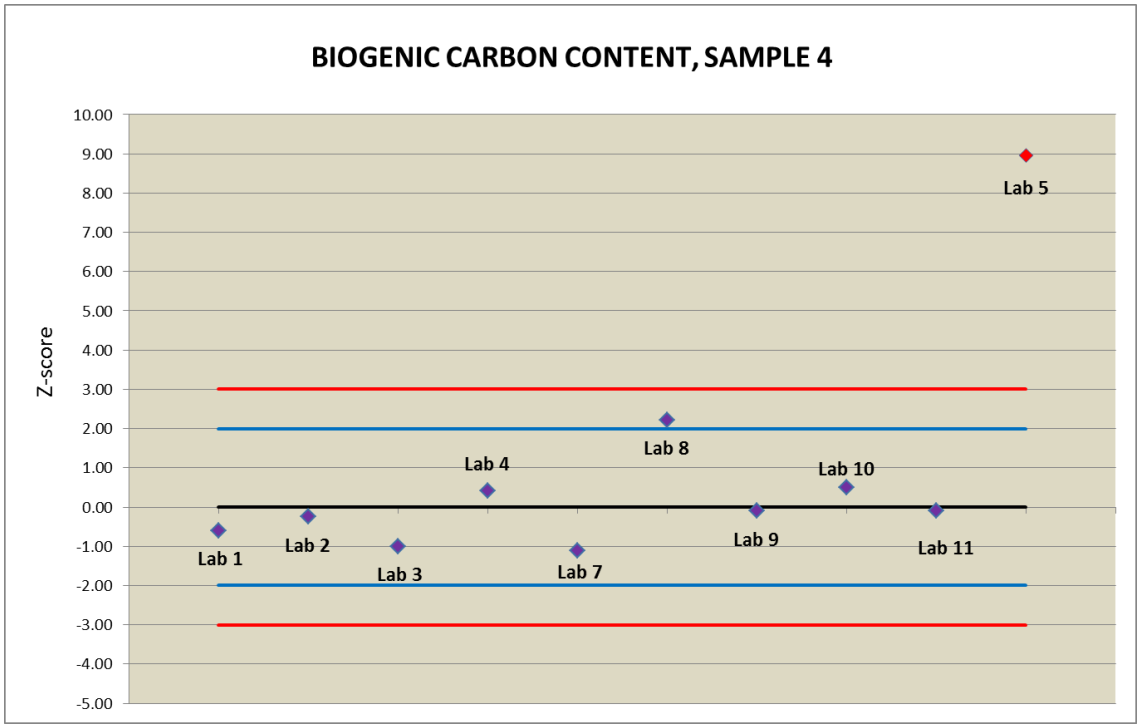
AVERAGE	12.2%
STD	1.2%
Min	10.0%
Max	14.0%



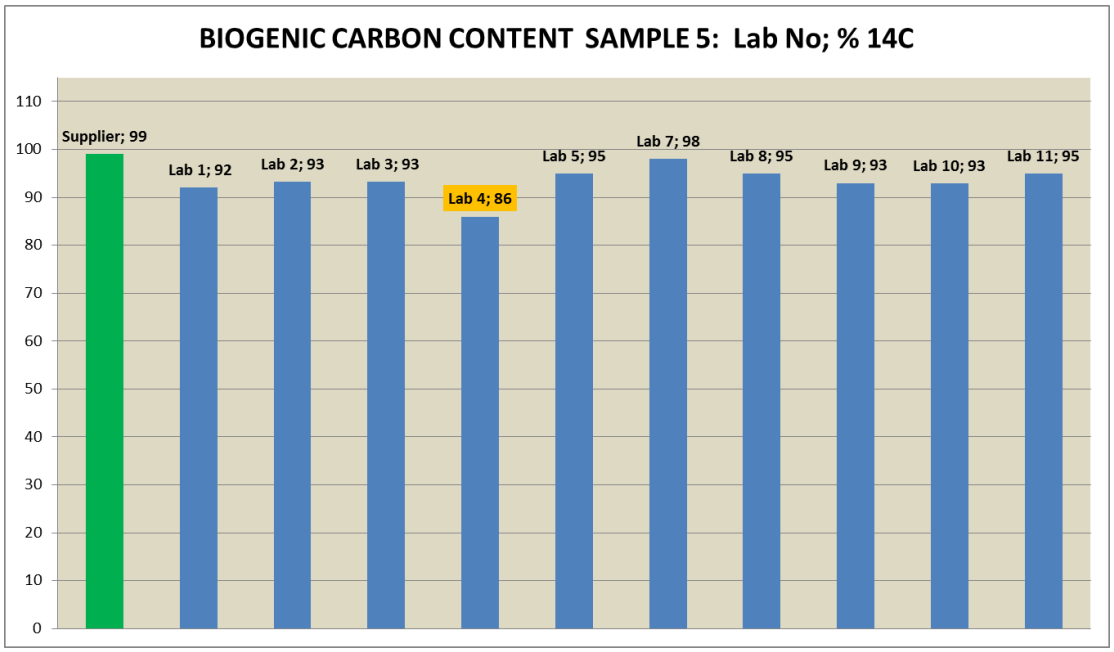
SAMPLE 4. Silk paint



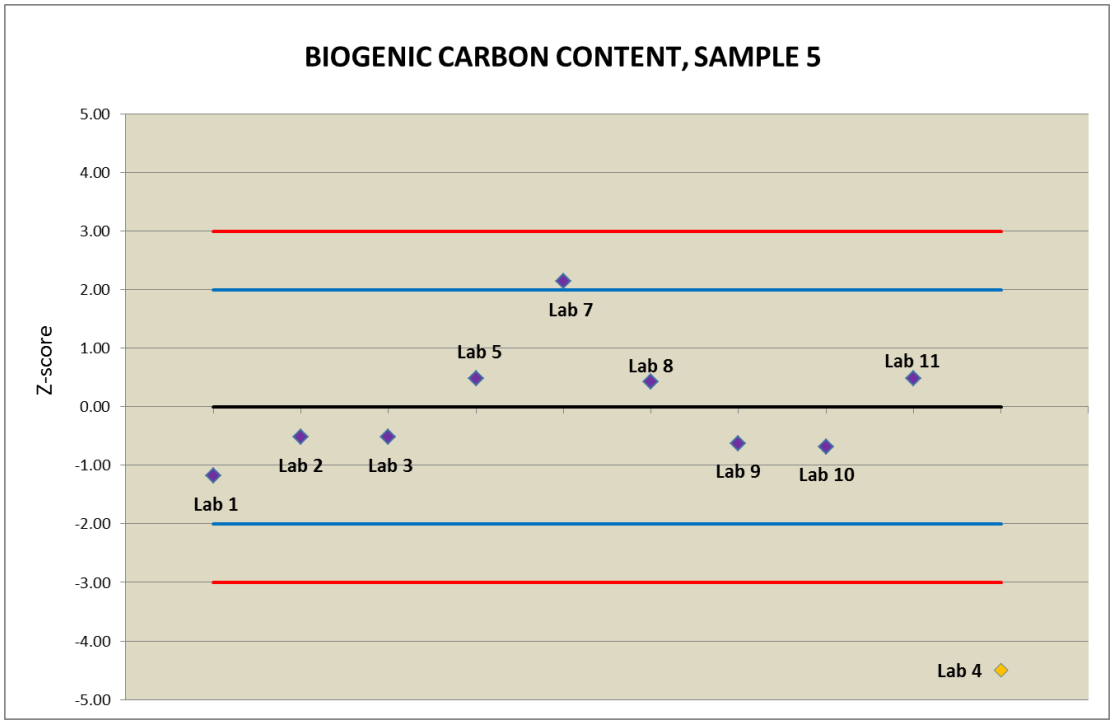
AVERAGE	73.2%
STD	1.9%
Min	71.0%
Max	78.0%



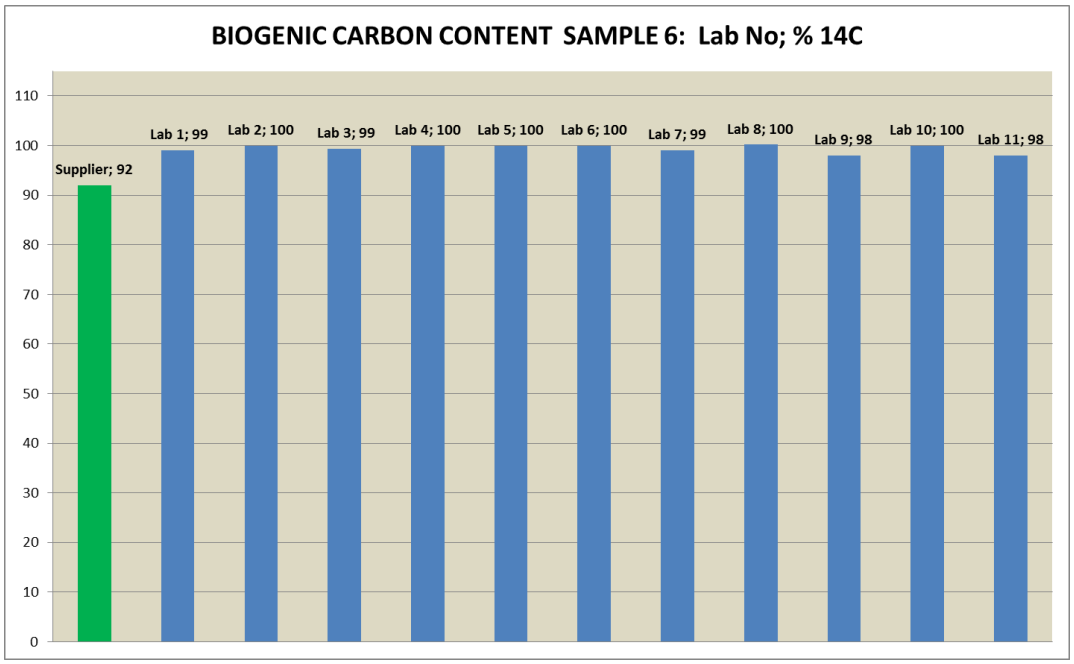
SAMPLE 5. Bio-based binder for paint



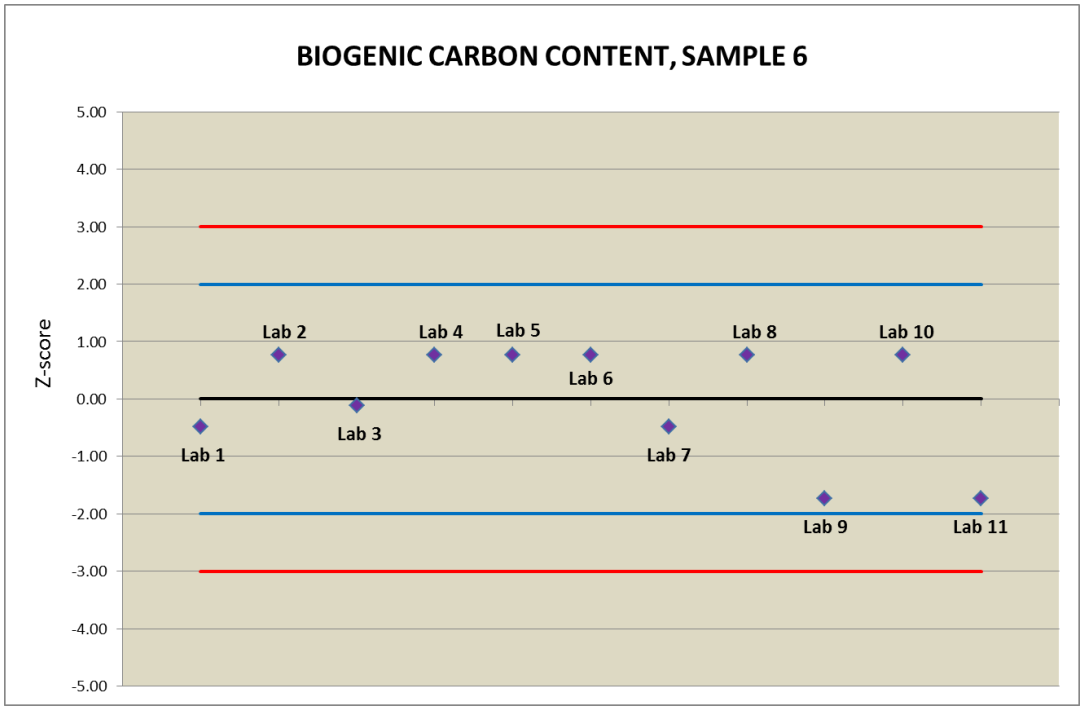
AVERAGE	94.1%
STD	1.8%
Min	92.0%
Max	98.0%



SAMPLE 6. Wooden particle board



AVERAGE	99.4%
STD	0.8%
Min	98.0%
Max	100.0%



Appendix C. Pre-treatment of the samples

As it was already mentioned in the introduction, CEN TS 16640 specifies several possibilities for the conversion of the samples to CO_2-form ready for the ^{14}C analysis. In this paragraph, the conversion that was done by each laboratory, is described.

Lab 1 and **Lab 7** used a calorimetric bomb for combustion of the samples. Where it was necessary, different catalysts to enhance the combustion were used (see further in the report for information for each sample).
In **Lab 2**, different subsamples were combusted to CO_2 and also measured on delta13C value with a combined Elementar Isotope Cube-Isoprime100 system (Isotope Ratio Mass Spectrometry, IRMS). The percentages of carbon and nitrogen were also (automatically) determined with this system. The obtained CO_2 of each sample was cryogenically trapped in a flask.
Lab 3 used a specific Macro-Element analyser to convert the samples into carbon dioxide, with subsequent with trapping and purifying of the CO_2.
In **Lab 4**, a tin capsule with a sample was placed in a nickel sleeve, injected into a high temperature furnace (975°C) and burnt in high purity oxygen under static conditions. The tin capsules used for the sample container allow an initial exothermic reaction to occur, raising the temperature of combustion to over 1800°C. A further dynamic burst of oxygen was added at the end of the combustion process, to ensure total combustion of all inorganic and organic substances. The resulting combustion products pass through specialised reagents to ensure full combustion of any methane produced and to remove halogens, sulphur and phosphorous. This process ultimately results in the production of CO_2 from the elemental carbon, H_2O from the hydrogen, and nitrogen (N_2) and N-oxides. The combustion gases are then passed, using helium as a carrier gas, through a tube packed with pure copper wire at 620°C, to remove excess oxygen and to reduce the N-oxides to elemental nitrogen. After this stage the gases enter a mixing chamber, to ensure a homogeneous mixture at constant temperature and pressure is delivered to the detectors. The mixture then passes through a series of high-precision thermal conductivity detectors, each containing a pair of thermal conductivity cells. Between the first two cells was a water trap, the differential signal between the cells is proportional to the water concentration, which is a function of the amount of hydrogen in the original sample. Between the next two cells was a carbon dioxide trap for measuring carbon.
Lab 5 followed EN 13137 for the combustion of the samples where the total carbon present in the undried sample is converted to carbon dioxide in an oxygen containing gas flow, free of carbon dioxide.
Lab 8 used equipment which consisted of a tube furnace and a purification line for the conversion of the samples into carbon dioxide.
Lab 9: liquid samples and emulsions (samples 2, 4 and 5) were converted to CO_2 using sealed tube combustion. The carbon dioxide was converted to graphite by reduction with

hydrogen over iron catalyst. Samples 1, 3 and 6 were converted to carbon dioxide by combustion in an elemental analyser.
Lab 10 used an elemental analyser with combustion furnaces maintained at 1000° C for conversion of samples into carbon dioxide.
No information was available from the rest of participating laboratories.

Most samples were analysed by all laboratories in „as received" conditions with no special preparations. Only for few samples the pre-treatment was done and is describes below:

SAMPLE 1

Lab 9

Description of sample when received: plastic jar with small spherical off white plastic granules. Sub sample was taken out; approximately 20mg was needed to be ground up for combustion. Pre-treatment description: beads were crushed up to coarse powder. Carbon dioxide was generated by elemental analyser combustion and 0.8mgC was obtained.

SAMPLE 2

Lab 1

Because of ignition and combustion difficulties, polyethylene bags with known carbon content (85.19%) and with known ^{14}C content (3%) were used as combustion aids. The sample was combusted together with a bag and then the collected CO_2 gas was analysed on its ^{14}C content. This resulted in 37% of biogenic carbon from collected CO_2. In turn, recalculated value for the true biogenic content of the sample itself equals 94%.

Lab 4

The elemental analysis and combustion experiments for the sample was performed on air-dried sample. Lab 4 found that combustion of the sample was not possible without the addition of benzoic acid. The true biogenic carbon content of the sample itself was recalculated accordingly and was determined to be 96%. The laboratory considered that for the samples presented as aqueous solutions it is of need to remove the water to get combustion to work, yet not evaporate any volatile components of each formulation. Therefore the sample was literately painted onto the inside of a glass vial and left the vial unsealed overnight. This was done for smaller and bigger subsamples. The data from the mass loss before and after evaporation were used to estimate the evaporated volatile part:

Sample (small subsample)
Sample mass, g 1.32
Dry mass, g 0.90
Fraction dry mass 68%
Sample (bigger subsample)

Sample mass, g	10.73
Dry mass, g	8.14
Fraction dry mass	76%

Lab 7

The sample was vacuum dried at 40ºC for 17 hours (solid after drying). On order to facilitate the combustion of the sample, the combustion enhancer $C_{16}H_{34}$ was used, with total carbon fraction of 85%. The biogenic carbon fraction was 3% as determined by an AMS for a pure enhancer. Both wet sample and vacuum dried sample gave no combustion at 30bar oxygen environment using a bomb calorimeter. Combustion of the wet sample was only possible after adding drying material ($MgSO_4$) and a fire enhancer (hexadecane). The biogenic carbon content of the sample itself was the recalculated to be 98%.

SAMPLE 4

Lab 1

Because of ignition and combustion difficulties, polyethylene bags with known carbon content (85.19%) and with known ^{14}C content (3%) were used as combustion aids. The sample was combusted together with a bag and then the collected CO_2 gas was analyzed on its ^{14}C content. This resulted in 28% of biogenic carbon from collected CO_2. In turn, recalculated value for the true biogenic content of the sample itself equals 72%.

Lab 4

The same as for Sample 2.

Lab 7

The sample was vacuum dried at 40ºC for 17 hours (solid after drying). On order to facilitate the combustion of the sample, the combustion enhancer $C_{16}H_{34}$ was used, with total carbon fraction of 85%. The biogenic carbon fraction was 3% as determined by an AMS for a pure enhancer. Both wet sample and vacuum dried sample gave no combustion at 30bar oxygen environment using a bomb calorimeter. Combustion of the wet sample was only possible after adding drying material ($MgSO_4$) and a fire enhancer (hexadecane). The biogenic carbon content of the sample itself was the recalculated to be 71%.

SAMPLE 5

Lab 1

Because of ignition and combustion difficulties, polyethylene bags with known carbon content (85.19%) and with known ^{14}C content (3%) were used as combustion aids. The sample was combusted together with a bag and then the collected CO_2 gas was analysed on its ^{14}C content. This resulted in 59% of biogenic carbon from collected

CO_2. In turn, recalculated value for the true biogenic content of the sample itself equals 92%.

Lab 4

The same as for Sample 2. Only 36.4% of CO_2 originated from benzoic acid, the remaining 63.6% of CO_2 resulted from the sample itself. The carbon content and the recovery values were corrected for this. The biogenic carbon fraction was found to be 55% of ^{14}C when uncorrected and 86% after the corresponding correction on the carbon from benzoic acid.

Lab 7

The sample was vacuum dried at 40ºC for 17 hours (solid after drying). On order to facilitate the combustion of the sample, the combustion enhancer $C_{16}H_{34}$ was used, with total carbon fraction of 85%. The biogenic carbon fraction was 3% as determined by an AMS for a pure enhancer. Both wet sample and vacuum dried sample gave no combustion at 30bar oxygen environment using a bomb calorimeter. Combustion of the wet sample was only possible after adding drying material ($MgSO_4$) and a fire enhancer (hexadecane). The biogenic carbon content of the sample itself was the recalculated to be 98%.

Appendix D. Grubbs test and Z-score analyses

Grubbs test

In the current study, the Grubbs test was used for the statistical evaluation of the results that were reported for each sample by every participating laboratory.

This test is used to detect the outliers and/or stragglers. The Grubbs test always checks the value whether the extreme value (high or low) that shows the largest absolute deviation from the mean, is an outlier or a straggler. In the current study, the tested data were the minimum and maximum measured values reported by all participating laboratories for each of the samples.

The application of the test is the following:

- the maximum (X_{max}) and the minimum (X_{min}) among the reported measured values have to be determined.
- The average among all measured values X_{mean} (for the same sample) and the reproducibility standard deviation (SD) have to be calculated.
- Then the ratio $|X_{min} - X_{mean}|/SD$ and $|X_{max} - X_{mean}|/SD$ is calculated and the results are compared to the critical values given by the Grubbs table (see Table D1). If for a given number of measurements, the resulting value is greater than the critical value, then the corresponding minimal (or maximum) value can be regarded as an outlier or a strag-gler, depending on the reliability interval. An observation is considered an outlier if the reliability is 99%. For stragglers the limit of 95% reliability applies.

Table D1. Critical values for the Grubbs test depending on the number of measurements.

GRUBBS TABLE		
No of measurements	Critical values	
	1% - outlier	5% - straggler
3	1.155	1.155
4	1.496	1.481
5	1.764	1.715
6	1.973	1.887
7	2.139	2.020
8	2.274	2.126
9	2.378	2.215
10	2.482	2.290
11	2.564	2.355
12	2.636	2.412
13	2.699	2.462

14	2.755	2.507
15	2.806	2.549
16	2.852	2.585
17	2.894	2.620
18	2.932	2.651
19	2.968	2.681
20	3.001	2.709
21	3.031	2.733
22	3.060	2.758
23	3.087	2.781
24	3.112	2.802
25	3.135	2.822
26	3.157	2.841
27	3.178	2.859
28	3.199	2.876
29	3.218	2.893
30	3.236	2.908

All outliers (cells that marked in red in the previous paragraphs when representing the results) and the stragglers (marked in orange) that were defined based on the results of Grubbs analysis, were excluded from calculations of performance characteristics (final average numbers and the final reproducibility standard deviations among all laboratories).

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