Evaluation of results of ILC BIOREMA biodiesel

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Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel
Belgium

National Institute of Metrology, Standardization and Industrial Quality
Av. Nossa Senhora das Graças, 50, Prédios 6 e 4
Xerém, Duque de Caxias, Rio de Janeiro
25250-020
Brazil

National Institute of Standards and Technology
100 Bureau Drive, Stop 8392
Gaithersburg
MD 20899-8392
United States of America

NPL
Hampton Road
Teddington, Middlesex
TW11 0LW
United Kingdom

LGC
Queens Road
Teddington, Middlesex
TW11 0LY
United Kingdom

VSL
Thijsseweg 11
2629JA Delft
The Netherlands

Summary

The main objective of the project BIOREMA (Reference Materials for Biofuel Specifications) is the development of two test materials (one bio-ethanol material and one biodiesel material) with well-established reference values.

In this interlaboratory comparison, two NIST Standard Reference Materials (SRM 2772 and SRM 2773) have been used alongside the biodiesel material “B” developed during this project, specifically for this interlaboratory comparison.

The objective of the BIOREMA biodiesel interlaboratory comparison is to compare measurement results from testing laboratories with reference values obtained during this project. The emphasis in this interlaboratory comparison is therefore not on the performance rating of the laboratories, but in recognising and interpreting systematic differences if they occur. The information gathered about the methods used is an important element in the interpretation of the data.

Results of the BIOREMA interlaboratory comparison (ILC) were discussed during the BIOREMA Workshop, which took place in Brussels, Belgium, on the 27th of October 2010. Present during this workshop were many of the ILC-participants and also representatives of the BIOREMA project partners.

The agreement of results between the laboratories, and between the consensus and reference values, as far as available, was perceived as satisfactory. The results of the content measurements of mono–, di– and triacylglyceride suffer from inconsistencies in the interpretation of the gas chromatograms.

The lack of suitable reference materials (RMs) was noted in various instances and for different applications. The use of pure substances for flash point is regarded as unsatisfying, because the vapour pressure of pure substances behaves quite differently from that of complex mixtures such as biodiesel. A clear demand was expressed for RMs of biodiesel from the various feedstocks, as it is deemed impossible to select a single biodiesel that will accommodate all aspects relevant in quality control and method validation.

One laboratory expressed explicitly the need for the use of target uncertainties and independent reference values in proficiency testing schemes in biodiesel. Furthermore, a need for harmonising the frequency of participation in such schemes was identified, as the requirements now range from once a year to once every four years.

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k	coverage factor
$\bar{n}$	average number of observations of the laboratories
n_i	number of observations of laboratory *i*
p	number of laboratories
u_{bb}	standard uncertainty due to between-bottle homogeneity
u_{char}	standard uncertainty from characterisation
U_i	expanded uncertainty associated with result of laboratory *i*
u_{ref}	standard uncertainty associated with the reference value
u_{lts}	standard uncertainty due to long-term stability
s_i	standard deviation of laboratory *i*
s_L	between-laboratory standard deviation
s_R	reproducibility standard deviation
s_r	repeatability standard deviation
y_{ij}	laboratory result
$\bar{y}_i$	laboratory average
y_{ref}	reference value

1 Introduction

The main objective of the project BIOREMA (Reference Materials for Biofuel Specifications) is the development of two test materials with well-established reference values. One material (A) consists of bio-ethanol, the other material (B) is a biodiesel material from the feedstock rapeseed. These materials have been used in an interlaboratory comparison. This report describes the results of the biodiesel interlaboratory comparison. This intercomparison covers, apart from the previously mentioned material B, also two NIST Standard Reference Materials, namely SRM 2772 and SRM 2773.

The objective of the BIOREMA biodiesel interlaboratory comparison is to compare measurement results from testing laboratories with reference values obtained during this project. The emphasis in this interlaboratory comparison is therefore not on the performance rating of the laboratories, but in recognising and interpreting systematic differences if they occur. The participating laboratories can compare their performance against that of their peers, and to reference values obtained independently from the interlaboratory comparison study. Another aspect is to find out how well established these reference values are. For many method-specific parameters, for both the reference value and the reported values, the same or similar measurement methods are used.

Notwithstanding the fact that biofuels testing takes place for more than 10 years now, this field of testing still has all the characteristics of an emerging field. This status is reflected in, e.g., the very limited availability of certified reference materials (CRMs) and the use of consensus values in proficiency testing, whereas for many parameters better alternatives are available. Consequently, some of the reference values obtained are not as coherent as for similar parameters in for example the petroleum industry, which have a much longer record. Nevertheless, the reference values reveal to some extent what currently can be expected from national metrology institutes and reference material producers in this important field.

2 Design of the comparison

2.1 Sample preparation

The test material (B) was obtained by IRMM (Institute for Reference Materials and Measurements) in the beginning of August 2009 [1]. The material is a rapeseed oil fatty acid methyl ester material with the addition of an antioxidant, butylhydroxytoluene (BHT). A certificate of analysis was provided by the producer proving the suitability of the material, i.e. fulfilling the specification limits as laid down in EN 14214. The processing of 5100 units (2339 units with 20 mL and 2761 units with 25 mL) took place in the middle of August 2009 and was finished by end of August 2009 [1]. Test material B has been subjected to a homogeneity, stability and characterisation study [2-4] prior to the interlaboratory comparison.

2.2 Measurement programme

The 26 participating laboratories (Asia: 6, Europe: 16, North America: 1, South America: 3) received one package containing three different batches of test samples labelled as:

- BIOREMA Test Material B (40 ampoules each containing 20-25 mL sample = batch 1),
- BIOREMA Test Material C (6 ampoules each containing 10 mL sample = batch 2) and
- BIOREMA Test Material D (2 ampoules each containing 10 mL sample = batch 3).

Laboratories were instructed to store the materials received at 4°C and re-homogenise them prior to use. Unfortunately one laboratory did not receive the samples because their package was withheld by their customs office.

The following parameters were supposed to be determined (tables 1-3).

Table 1: Parameters to be determined (material B)

Lot	Parameter	No. of ampoules	No. of analyses
1	Sodium content, mg/kg	2	4
2	Potassium content, mg/kg	2	4
3	Sulfur content, mg/kg	2	4
4	Methanol content, 10^{-2} g/g	2	4
5	Water content, mg/kg	2	4
6	Density at 15 °C, kg/m^3	4	4
7	Viscosity at 40 °C, mm^2/s	4	4
8	Ester content (total), 10^{-2} g/g	2	4
	Linolenic acid (C18:3 n-3) methyl ester, 10^{-2} g/g		4
	Palmitic acid (C16:0) methyl ester, 10^{-2} g/g		4
	Stearic acid (C18:0) methyl ester, 10^{-2} g/g		4
	Total sum of C18:1 methyl ester isomers, 10^{-2} g/g		4
	Total sum of C18:2 methyl ester isomers, 10^{-2} g/g		4
	Total sum of C18:3 methyl ester isomers, 10^{-2} g/g		4
9	Monoacylglyceride content (total), 10^{-2} g/g	2	4
	Diacylglyceride content (total), 10^{-2} g/g		4
	Triacylglyceride content (total), 10^{-2} g/g		4
	Total glycerol content, 10^{-2} g/g		4
	Monolein content, 10^{-2} g/g		4
	Diolein content, 10^{-2} g/g		4
	Triolein content, 10^{-2} g/g		4
	Free glycerol content, 10^{-2} g/g		4

Lot	Parameter	No. of ampoules	No. of analyses
10	FAME content with ≥ 4 double bonds, 10^{-2} g/g	2	4
11	Iodine value, 10^{-2} g/g	2	4
12	Flash point, °C	2	4
13	Oxidation stability (110 °C), hours	2	4
14*	Acid value, mg/g	4	4

* For the determination of the acid value the participants should only take samples of Test Material B from number 3039 onwards, as they contain 25 mL sample material.

Table 2: Parameters to be determined (material C)

Lot	Parameter	No. of ampoules	No. of analyses
1	Methanol content, 10^{-2} g/g	4	4
2	Ester content (total), 10^{-2} g/g	2	4
	Linolenic acid (C18:3 n-3) methyl ester, 10^{-2} g/g		4
	Palmitic acid (C16:0) methyl ester, 10^{-2} g/g		4
	Stearic acid (C18:0) methyl ester, 10^{-2} g/g		4
	Total sum of C18:1 methyl ester isomers, 10^{-2} g/g		4
	Total sum of C18:2 methyl ester isomers, 10^{-2} g/g		4
	Total sum of C18:3 methyl ester isomers, 10^{-2} g/g		4
	Monoacylglyceride content (total), 10^{-2} g/g		4
	Diacylglyceride content (total), 10^{-2} g/g		4
	Triacylglyceride content (total), 10^{-2} g/g		4
	Total glycerol content, 10^{-2} g/g		4
	Monolein content, 10^{-2} g/g		4
	Diolein content, 10^{-2} g/g		4
	Triolein content, 10^{-2} g/g		4
	Free glycerol content, 10^{-2} g/g		4

Table 3: Parameters to be determined (material D)

Lot	Parameter	No. of ampoules	No. of analyses
1	Sulfur content, mg/kg	2	4

2.3 Schedule

The schedule of this comparison was as follows (table 4).

Table 4: Schedule

Event	Date
Enrolment	until 30 April 2010
Sample dispatch	18 May 2010
Deadline for submission of results	2 July 2010
Workshop and report of the comparison	27 October 2010

2.4 Consensus values

The consensus values are obtained using the following approach. The laboratory averages are scrutinised as follows. From the entire dataset, the median (y_{med}) is determined, as well as the median of the absolute deviations (MAD). These deviations are defined as

$$d_i = \left| \bar{y}_i - y_{med} \right| \quad (1)$$

The criterion for marking a laboratory average ($\overline{y}_i$) as outlier is the following

$$d_i \geq 3s \tag{2}$$

where the standard deviation *s* is given by

$$s = 1.4826 \cdot MAD \tag{3}$$

Laboratory results, for which $2s \leq d_i < 3s$ are considered stragglers and kept in the dataset. No outlier testing is performed on the laboratory standard deviations.

After removing the outliers, the one-way ANOVA based statistics of ISO 5725 [5,6] are used to obtain the mean (*m*), the repeatability standard deviation (s_r), the between-laboratory standard deviation (s_L) and the reproducibility standard deviation (s_R).

The consensus value is defined according to:

$$\hat{m} = \overline{\overline{y}} = \frac{\sum_{i=1}^{p} n_i \overline{y_i}}{\sum_{i=1}^{p} n_i} \tag{4}$$

where n_i equals the number of results reported by laboratory *i*, $\overline{y}_i$ the average result of this laboratory and *p* is the total number of laboratories. The repeatability standard deviation follows from:

$$s_r^2 = \frac{\sum_{i=1}^{p} (n_i - 1) s_i^2}{\sum_{i=1}^{p} (n_i - 1)} \tag{5}$$

The between-laboratory standard deviation is calculated according to:

$$s_L^2 = \frac{s_d^2 - s_r^2}{\overline{\overline{n}}} \tag{6}$$

where

$$s_d^2 = \frac{1}{p-1} \sum_{i=1}^{p} n_i \left(\overline{y_i} - \overline{\overline{y}} \right)^2 \tag{7}$$

$\overline{\overline{n}}$ is defined as

$$\overline{\overline{n}} = \frac{1}{p-1} \left[\sum_{i=1}^{p} n_i - \frac{\sum_{i=1}^{p} n_i^2}{\sum_{i=1}^{p} n_i} \right] \tag{8}$$

The reproducibility standard deviation is calculated according to:

$$s_R^2 = s_L^2 + s_r^2 \quad (9)$$

2.5 Reference values

The test material B has been subjected to a homogeneity, stability and characterisation study [2-4] prior to this interlaboratory comparison. The results are given in table 5. The table lists the reference value (y_{ref}), the standard uncertainty due to between-bottle homogeneity (u_{hom}), the standard uncertainty due to long-term stability (u_{lts}), the standard uncertainty due to characterisation (u_{char}), and the expanded uncertainty associated with the reference value, using a coverage factor k = 2 (U_{ref}). The standard uncertainty associated with the reference value is obtained by combining u_{hom}, u_{lts} and u_{char}.

Table 5: Reference values for material B

Parameter	n	Unit	y_{ref}	u_{hom}	u_{lts}	u_{char}	U_{ref}
Density	3	kg/m^3	883.466	0.008	0.003	0.016	0.035
Viscosity	3	mm²/s	4.4498	0	0.0013	0.0020	0.0048
Sulfur content	1	mg/kg	2.26	0.09	0.07	0.16	0.39
Methanol content[1]	2	10^{-2} g/g	0.027	0.007	0.002	0.004	0.016
Water content	3	mg/kg	218	15	8	6	36
Iodine value[1,3]	11	10^{-2} g/g	114.30	0.57	0.73	0.40	2.02
Flash point[1,4]	8	°C	175.9	3.3	1. 3	2.1	8.3
Oxidation stability[1,5]	10	h	12.2	0.04	0.17	0.18	0.49
Acid value[1,6]	12	mg/g	0.2020	0.0003	0.0032	0.0045	0.0111
Total ester content[2]	3	10^{-2} g/g	98.34	0.12	0.14	0.33	0.76
Linolenic acid methyl ester[2]	2	10^{-2} g/g	10.009	0	0.003	0.030	0.061
C16:0	3	10^{-2} g/g	4.742	0	0.001	0.046	0.091
C18:0	3	10^{-2} g/g	1.732	0	0.001	0.017	0.035
Total C18:1	3	10^{-2} g/g	57.97	0	0.02	0.63	1.27
Total C18:2[1]	3	10^{-2} g/g	20.544	0	0.006	0.601	1.203
Total C18:3[1]	3	10^{-2} g/g	10.101	0	0.003	0.290	0.583

Notes:
1. Value determined as arithmetic mean
2. In accordance with EN 14103 [33]
3. In accordance with EN 14111 [35]
4. In accordance with EN ISO 3679 [15]
5. In accordance with EN 14112 [31]
6. In accordance with EN 14104 [42]

For the remaining parameters, as listed in Table 1, no reference values were assigned

Materials C (table 6) and D (table 7) are NIST SRMs.

Table 6: Reference values material C

Parameter	Unit	y_{ref}	U_{ref}	k	Remarks
Methanol content	10^{-2} g/g	0.0587	0.0044	*2*	Coverage factor based on *t*–distribution[1]
Linolenic acid methyl ester	10^{-2} g/g	7.82	0.2	3	
Palmitic acid methyl ester	10^{-2} g/g	10.7	0.2	2	
Stearic acid methyl ester	10^{-2} g/g	4.3	0.27	3	
Monolein, monolinolein and monolinolenin	10^{-2} g/g	0.1994	0.0098	*2*	Coverage factor based on *t*–distribution[1]

Parameter	Unit	y_{ref}	U_{ref}	k	Remarks
Diolein and diolinolein	10^{-2} g/g	0.0707	0.0031	*2*	Coverage factor based on *t*–distribution[1]
Triolein	10^{-2} g/g	0.0241	0.0017	*2*	Coverage factor based on *t*–distribution[1]
Free glycerol	10^{-2} g/g	0.0164	0.0016	*2*	Coverage factor based on *t*–distribution[1]

Note:

1. no information is provided with regard to the (effective) number of degrees of freedom; if necessary $k = 2$ is used to convert the expanded uncertainty into a standard uncertainty

Table 7: Reference value material D

Parameter	Unit	y_{ref}	U_{ref}	k	Remarks
Sulfur content	mg/kg	7.39	0.39	2	

The use of the reference values is limited to a comparison with the consensus value, and if applicable, means of groups of laboratories.

3 Results per parameter

3.1 General

In the figures, the reference value is given as a solid line. For each parameter, the text indicates what value has been used for the performance rating. The 95% coverage limits are denoted by dashed lines. The laboratory results are indicated with different markers, depending on the method used. The uncertainty bars of these values denote $2 \cdot s_i$.

In some figures, in absence of a reference value, the consensus value is given by a solid line. In those cases, the standard uncertainty associated with the consensus value is estimated to be s_R / p , where s_R denotes the reproducibility standard deviation and p the number of laboratories (after removal of outliers, if any).

3.2 Density at 15°C

The results for density (at 15°C) are shown in figures 1 and 2. One value is totally off (L001).Three other laboratories (L015, L018, and L021) are also flagged as outliers for the consensus value calculation. Two laboratories did not report their measurement method.

The mean value is 883.467 kg m^{-3} and based on 19 results. The repeatability standard deviation is 0.027 kg m^{-3}, the between-laboratory standard deviation is 0.083 kg m^{-3}, and the reproducibility standard deviation is 0.087 kg m^{-3}. The consensus value and the reference value (883.466 kg m^{-3}) agree well. There are no meaningful influences of the methods used.

Figure 1 presents the complete dataset, whereas figure 2 presents a more detailed overview of the measurement results close to the reference value (i.e. not showing the measurement results of laboratories L001 and L018).

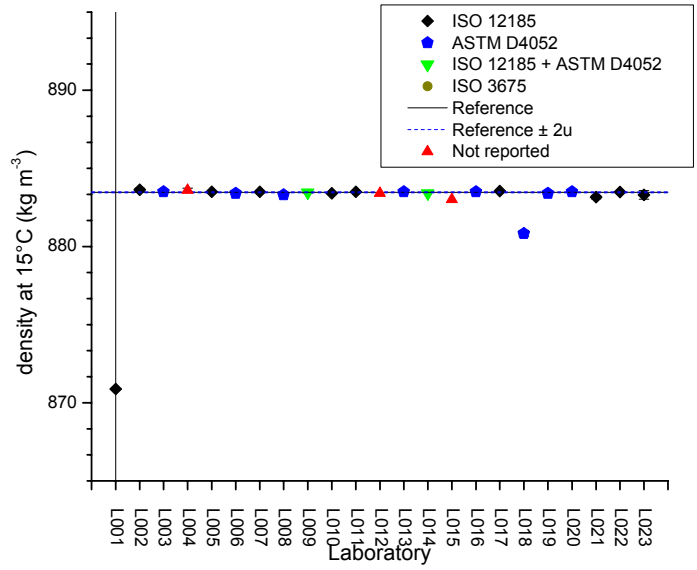

Figure 1: Results for density (complete dataset; material B)

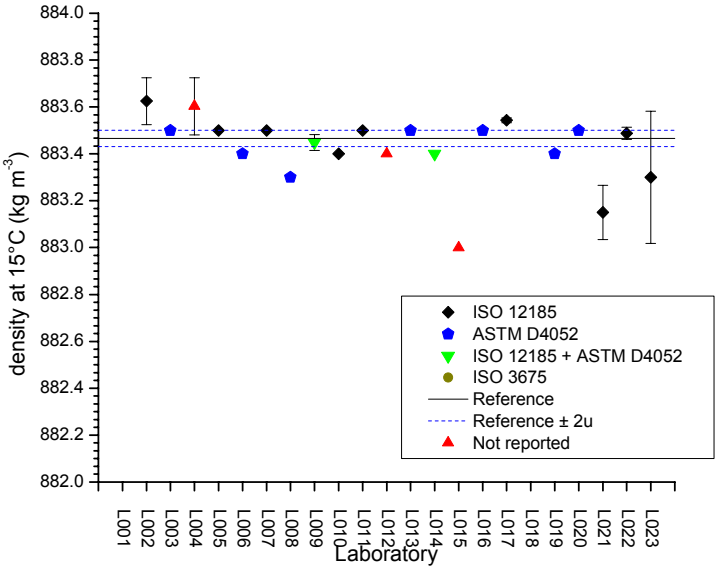

Figure 2: Results for density (detail; material B)

3.3 Viscosity at 40°C

The results for viscosity (at 40°C) are given in figure 3.

In the calculation of the consensus value, three results are flagged as outlier: L012, L015, and L016. The precision (within–laboratory standard deviation) differs appreciably between the laboratories.

Neither with respect to the measurement values, nor with respect to the within–laboratory standard deviations, differences are found between the methods used, as far as can be judged from the dataset.

The mean is 4.4492 mm^2s^{-1}, based on 18 results. The repeatability standard deviation is 0.0078 mm^2s^{-1}, the within–laboratory standard deviation 0.0149 mm^2s^{-1}, and the reproducibility standard deviation is 0.0168 mm^2s^{-1}. A good agreement exists between the reference value (4.4498 mm^2s^{-1}) and the consensus value.

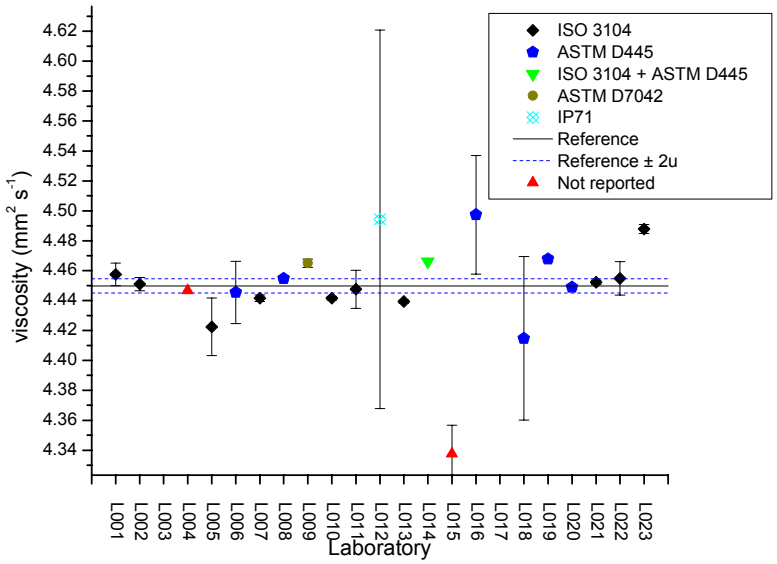

Figure 3: Results for viscosity (material B)

3.4 Flash point

The results for flash point are given in figure 4.

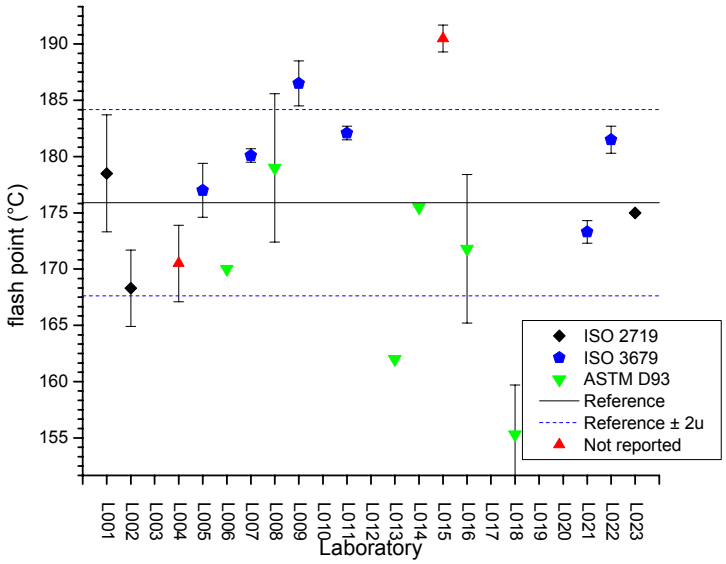

Figure 4: Results for flash point (material B)

No outliers were identified. Most reported values agree with the reference value (175.9 °C) within the respective uncertainties. The values from laboratories using ASTM D93 are en group somewhat lower than those using ISO 3679.

The mean 175.7 °C is computed from 17 results. The repeatability standard deviation is 1.8°C, the within–laboratory standard deviation is 8.9°C, and the reproducibility standard deviation is 9.1°C.

During the BIOREMA Workshop, it was noted that presently EN 3679 and EN ISO 2719 suggest using pure substances (e.g. dodecane or hexadecane) as the reference material (RM). However, as the vapour pressure of these pure substances is different from typical biofuel samples, it seems that these substances are not suitable in the field of biofuels. As such reference materials have to be developed composed of several compounds having different vapour pressures. These reference materials also should be inexpensive as up to 150 mL per test is needed.

3.5 Sodium content

The results for sodium content are given in figure 5. No reference value is available, because the content was below the limit of quantification of the methods used by the National Metrology Institutes participating in the characterisation study. For many participants, the same is true. A wide variety of methods have been used.

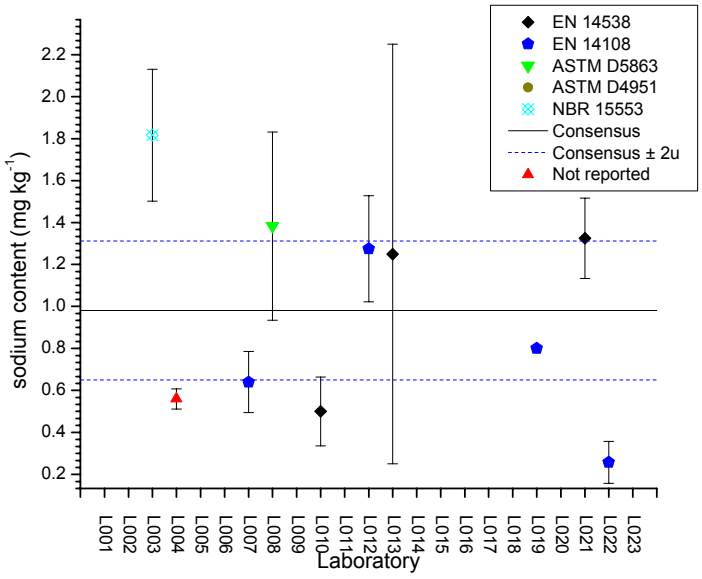

Figure 5: Results for sodium content (material B)

The consensus value will inevitably be affected by the vicinity of the limit of quantification. The consensus mean is 0.981 mg kg^{-1} computed from 10 results. The repeatability standard deviation is 0.191 mg kg^{-1}, the between-laboratory standard deviation is 0.487 mg kg^{-1} and the reproducibility standard deviation is 0.523 mg kg^{-1}.

3.6 Potassium content

The results for potassium content are given in figure 6. No reference value is available, because the content was below the limit of quantification of the methods used by the National Metrology Institutes participating in the characterisation study. The same is true for the vast majority of the participating laboratories. Three results agree quite well among each other, whereas one result is quite off (L005) and flagged as outlier.

The consensus value is 0.121 mg kg^{-1} computed from 3 results. This value is likely to be biased due to the large number of non-numeric results ignored (i.e., the statements that the value is below the limit of quantification/detection).

The repeatability standard deviation is 0.009 mg kg^{-1}, the between-laboratory standard deviation is 0.071 mg kg^{-1}, and the reproducibility standard deviation is 0.072 mg kg^{-1}.

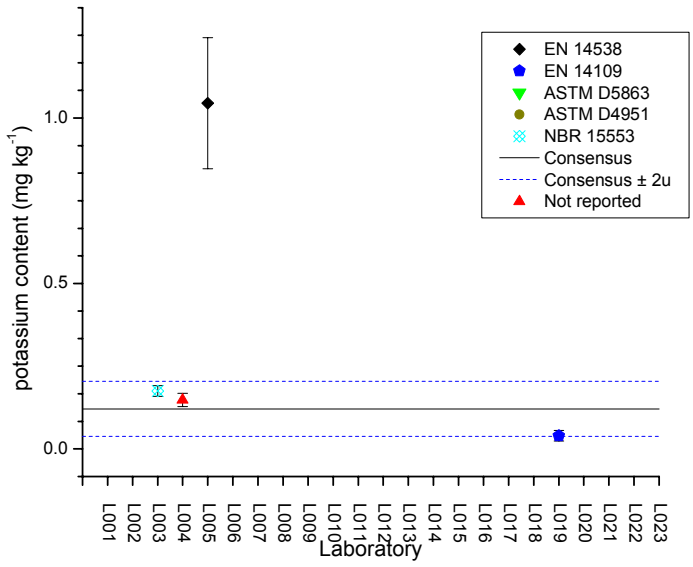

Figure 6: Results for potassium content (material B)

3.7 Sulfur content

The results for sulfur content are shown in figures 7 and 8. There is a good agreement for both ILC test materials (B and D) between their reference values and the laboratory results. The precision (within–laboratory standard deviation) is quite different among the participants. A wide variety of methods have been used.

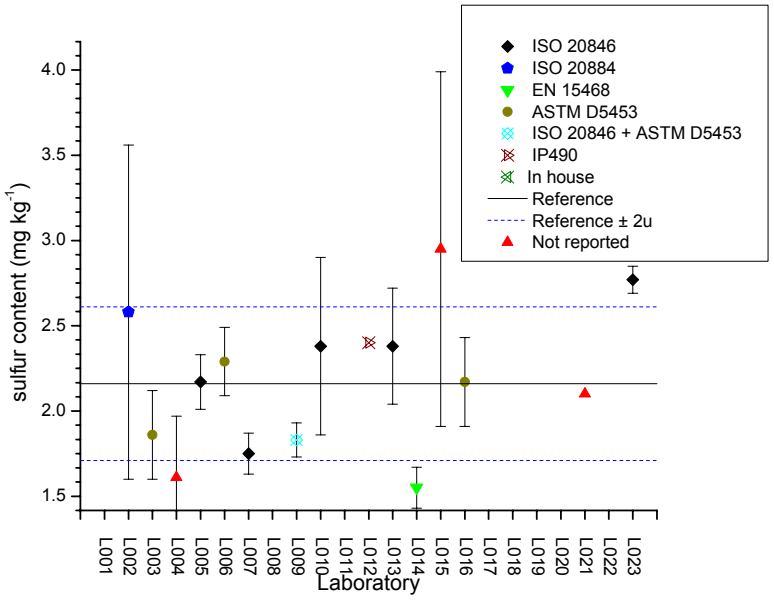

Figure 7: Results for sulfur content (material B)

With respect to the measurement results reported for sulfur content in material B, no outliers have been found (figure 7). The consensus mean is 2.16 mg kg^{-1}, based on 15 results. The repeatability standard deviation is 0.22 mg kg^{-1}, the between-laboratory standard deviation is 0.39 mg kg^{-1}, and the reproducibility standard deviation is 0.45 mg kg^{-1}. The reference value for sulfur content in material B is 2.26 mg kg^{-1}.

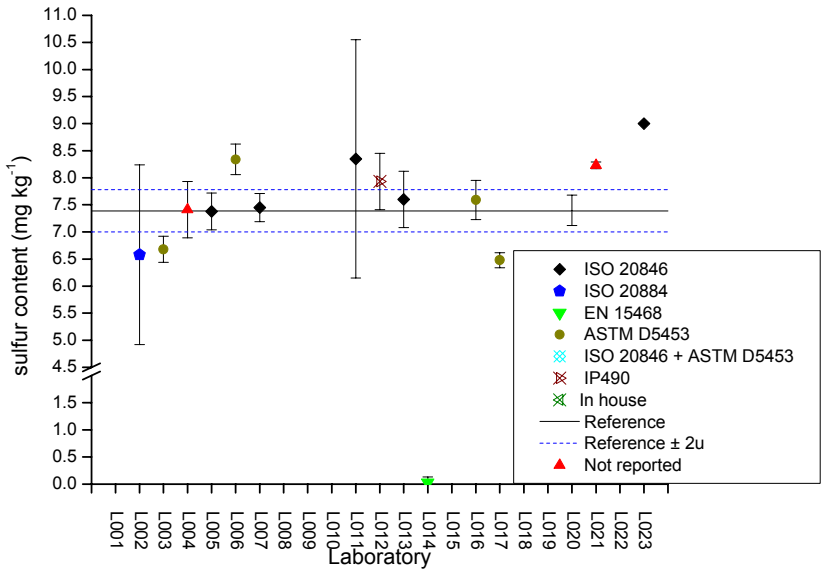

Figure 8: Results for sulfur content (material D)

The sulfur content in material D (see figure 8) is much higher than the sulfur content in material B. Concerning the measurement results reported for material D one laboratory result is flagged as outlier (L014). The consensus value is 7.53 mg kg^{-1} and based on 14 measurement results. The repeatability standard deviation is 0.42 mg kg^{-1}, the between-laboratory standard deviation is 0.63 mg kg^{-1}, and the reproducibility standard deviation is 0.76 mg kg^{-1}. The agreement with the reference value (7.39 mg kg^{-1}) is good.

3.8 Water content

The results for water content are given in figure 9. One laboratory reports a result that is quite off (L012) and this result is flagged as outlier in the consensus value calculation. As far as can be judged from the data, no big differences in results from the various methods can be observed.

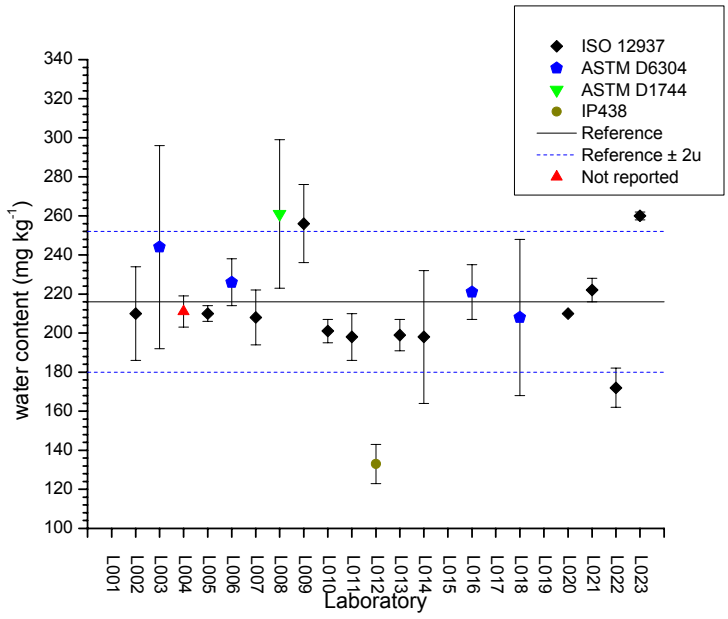

Figure 9: Results for water content (material B)

The consensus value is 216 mg kg^{-1}, based on 18 results. The repeatability standard deviation is 11 mg kg^{-1}, the between-laboratory standard deviation is 22 mg kg^{-1}, and the reproducibility standard deviation is 25 mg kg^{-1}. There is a good agreement between the reference value (218 mg kg^{-1}) and the consensus value.

3.9 Oxidation stability at 110°C

The results for oxidation stability are given in figure 10. Most results agree well with the reference value (12.2 h), which is also method-based. Two results are flagged as outliers (L007 and L022) in the calculation of the consensus value.

The consensus value is 12.0 h computed from 15 measurement results. The repeatability standard deviation is 0.1 h, the between-laboratory standard deviation is 0.4 h, and the reproducibility standard deviation is 0.5 h.

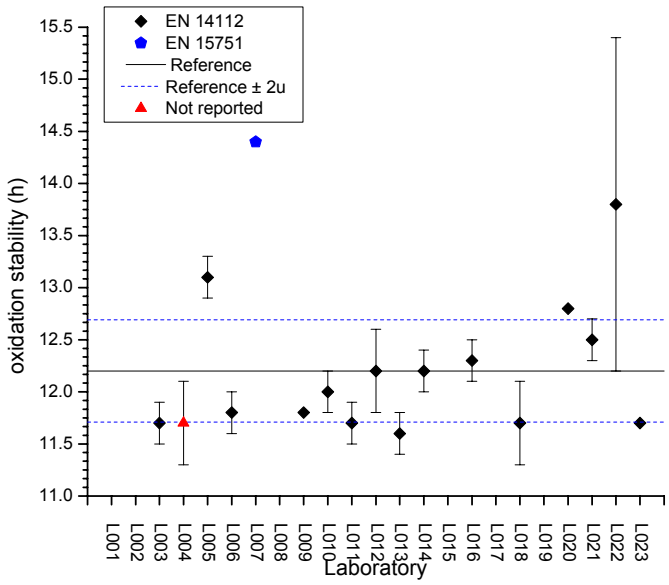

Figure 10: Results for oxidation stability (material B)

3.10 Acid value

The results for acid value are given in figure 11.

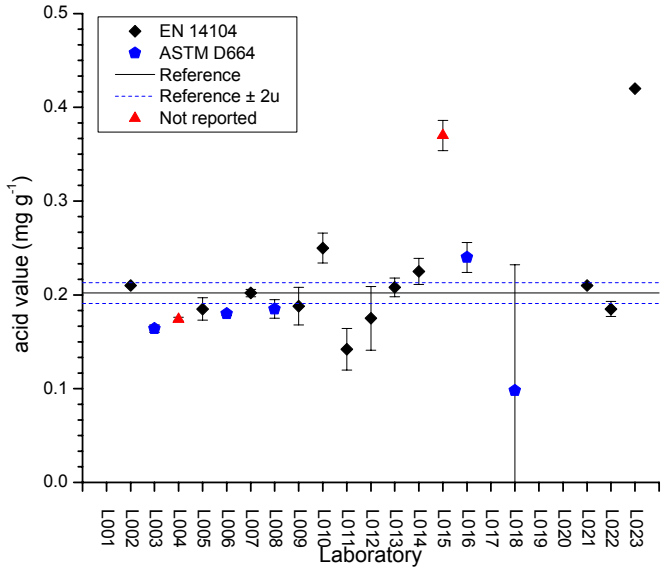

Figure 11: Results for acid value (material B)

Two results are flagged as outlier (L015 and L023). The consensus mean is 0.188 mg g^{-1} and based on 17 measurement results. The repeatability standard deviation 0.018 mg g^{-1}, the between-laboratory standard deviation is 0.035 mg g^{-1} and the reproducibility standard deviation is 0.039 mg g^{-1}. The consensus value is lower than the reference value (0.202 mg g^{-1}), which is obtained from a group of 12 laboratories. Both values agree still within their respective uncertainties.

3.11 Iodine value

The results for iodine value are shown in figure 12. Two results are flagged as outliers in the consensus value calculation (L012 and L015). Almost all laboratories use EN 14111 [35].

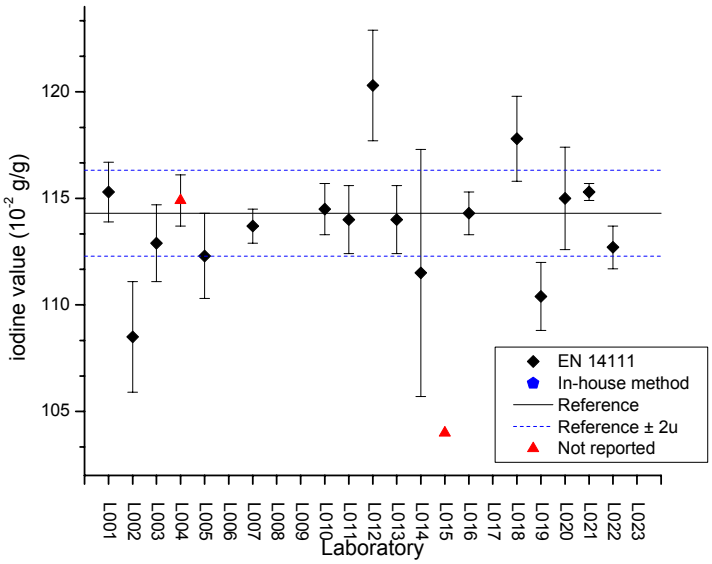

Figure 12: Results for iodine value (material B)

The consensus value is $113.5 \cdot 10^{-2}$ g/g and is based on 16 measurement results. The repeatability standard deviation is $1.1 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $2.1 \cdot 10^{-2}$ g/g and the reproducibility standard deviation is $2.4 \cdot 10^{-2}$ g/g. There is good agreement between the reference value ($114.3 \cdot 10^{-2}$ g/g) and the consensus value.

3.12 Polyunsaturated fatty acid methyl ester content

The results for polyunsaturated fatty acid methyl ester content (PUFA content) are given in figure 13. No reference value is available.

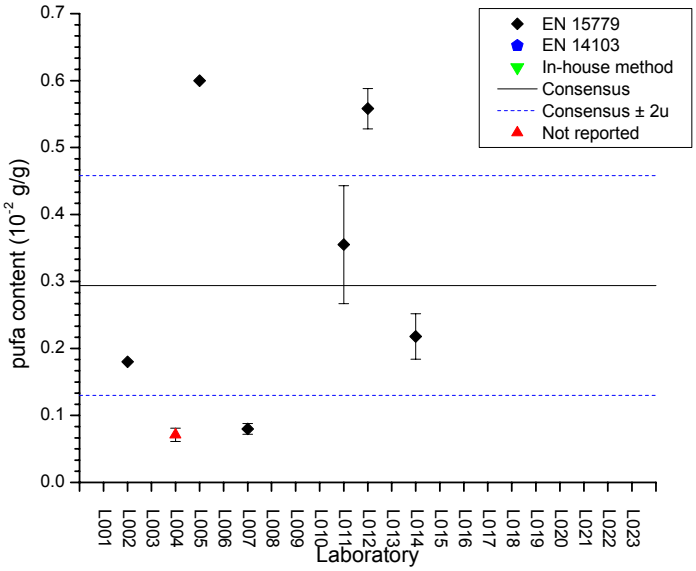

Figure 13: Results for polyunsaturated fatty acid methyl ester content (material B)

There are not that many results, and those reported show quite some scatter. Some laboratories report that the content is below their limit of quantification (detection). No outliers are found. The consensus mean is $0.294 \cdot 10^{-2}$ g/g based on 7 measurement results. The repeatability standard deviation is $0.019 \cdot 10^{-2}$ g/g, the within–laboratory standard deviation is $0.216 \cdot 10^{-2}$ g/g and the reproducibility standard deviation is $0.217 \cdot 10^{-2}$ g/g.

During the BIOREMA Workshop one of the ILC participants commented that the EN method is not suitable for high PUFA contents. A better alternative for high PUFA contents is quantifying using GC-MS.

3.13 Methanol content

The results for methanol content are given in figure 14 for material B and in figure 15 for material C.

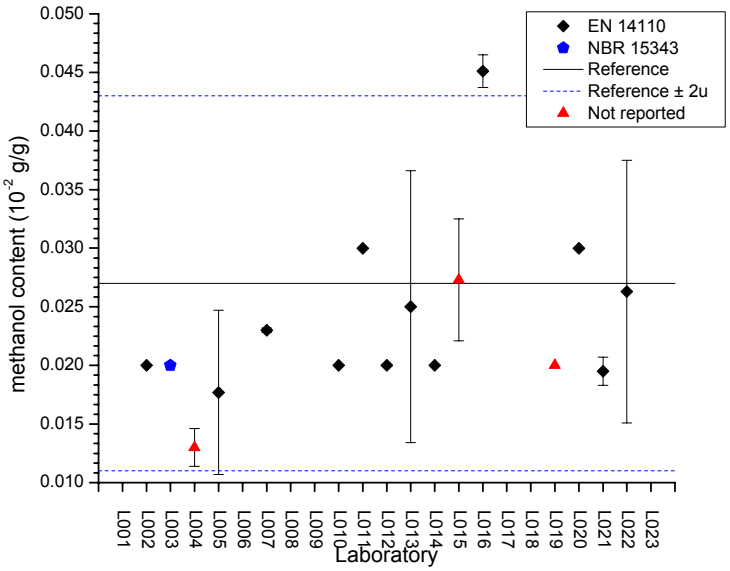

Figure 14: Results for methanol content (material B)

With respect to the measurement results for material B one outlier is removed (L016). The consensus value is $0.0216 \cdot 10^{-2}$ g/g based on 15 measurement results. The repeatability standard deviation is $0.0025 \cdot 10^{-2}$ g/g, the within–laboratory standard deviation is $0.0041 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.0048 \cdot 10^{-2}$ g/g. The consensus value is lower than the reference value of $0.027 \cdot 10^{-2}$ g/g, but they agree within the respective uncertainties.

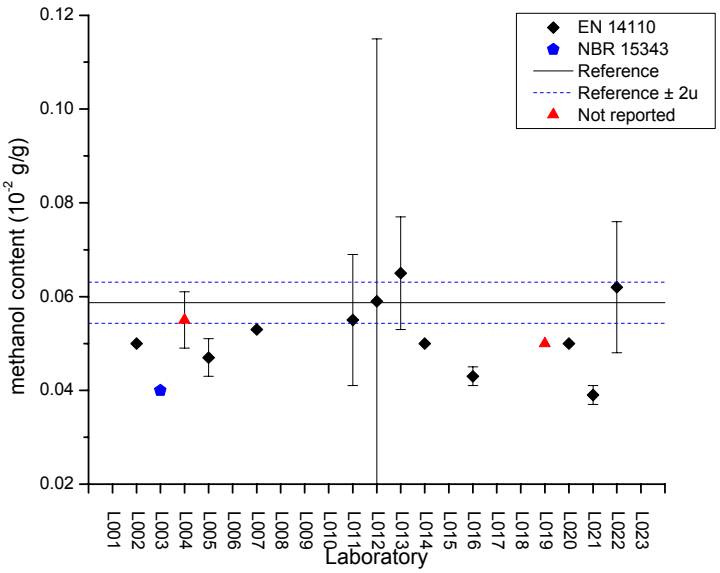

Figure 15: Results for methanol content (material C)

The results for methanol content for material C are shown in figure 15. No outliers are found. The consensus value is $0.051 \cdot 10^{-2}$ g/g based on 14 results; the repeatability standard deviation is $0.008 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is 0.007 g/100 g and the reproducibility standard deviation is $0.011 \cdot 10^{-2}$ g/g. The consensus value is considerably lower than the reference value of $0.0587 \cdot 10^{-2}$ g/g.

3.14 Monoacylglycerides content

The results for monoacylglycerides content in material B are given in figure 16. Three outliers are identified in the calculation of the consensus value (L012, L015, and L019). The consensus mean is $0.660 \cdot 10^{-2}$ g/g, based on 15 laboratories. The repeatability standard deviation is $0.017 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.069 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.071 \cdot 10^{-2}$ g/g. As far as can be judged, the results from the EN and ASTM methods used agree.

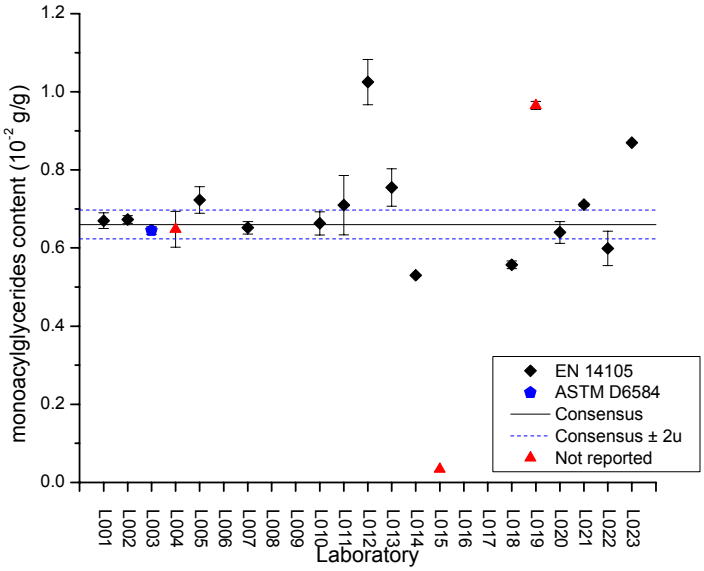

Figure 16: Results for monoacylglycerides content (material B)

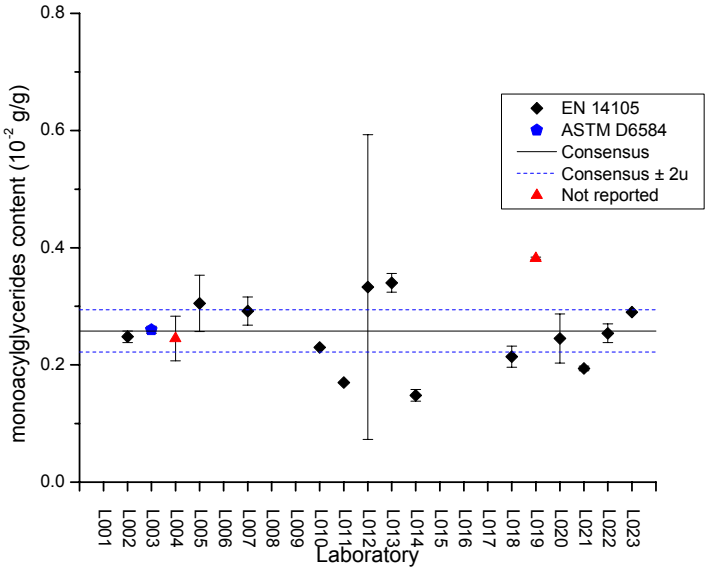

Figure 17: Results for monoacylglycerides content (material C)

The results for monoacylglycerides content for material C are given in figure 17. The consensus value is based on 16 laboratory results. The mean is $0.258 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $0.036 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.062 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.072 \cdot 10^{-2}$ g/g. There is no reference value.

3.15 Diacylglycerides content

The results for diacylglycerides content in material B are given in figure 18.

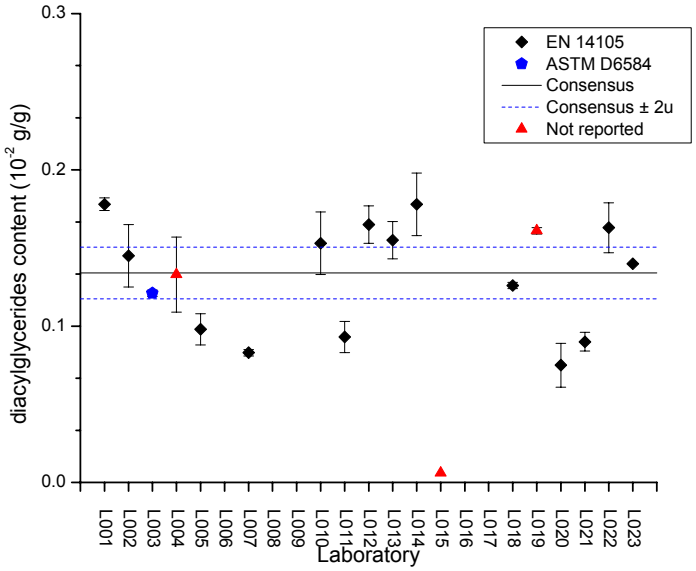

Figure 18: Results for diacylglycerides content (material B)

One outlier is detected (L015). The consensus value is $0.134 \cdot 10^{-2}$ g/g, based on 17 results. The repeatability standard deviation is $0.006 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation and reproducibility standard deviation are $0.034 \cdot 10^{-2}$ g/g.

The results for diacylglycerides content in material C are given in figure 19. No outliers are detected.

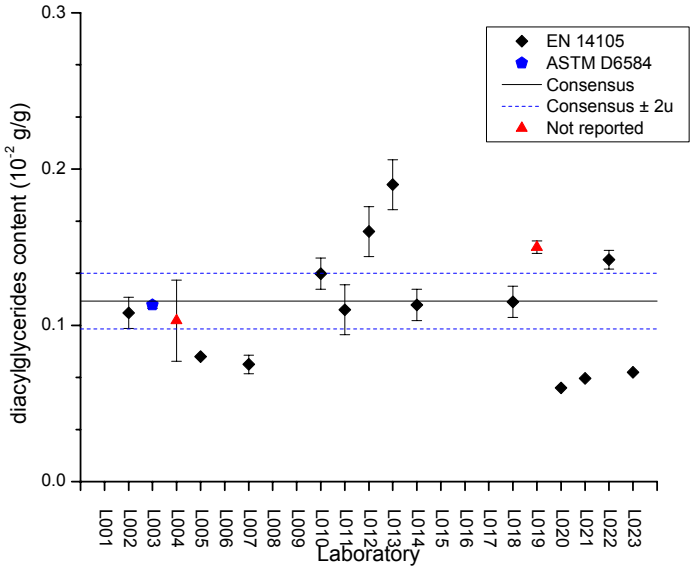

Figure 19: Results for diacylglycerides content (material C)

The consensus value is $0.1155 \cdot 10^{-2}$ g/g and based on 16 measurement results. The repeatability standard deviation is $0.0059 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.0354 \cdot 10^{-2}$ g/g, and the reproducibility is $0.0358 \cdot 10^{-2}$ g/g.

3.16 Triacylclycerides content

The results for triacylglycerides content in material B are given in figure 20.

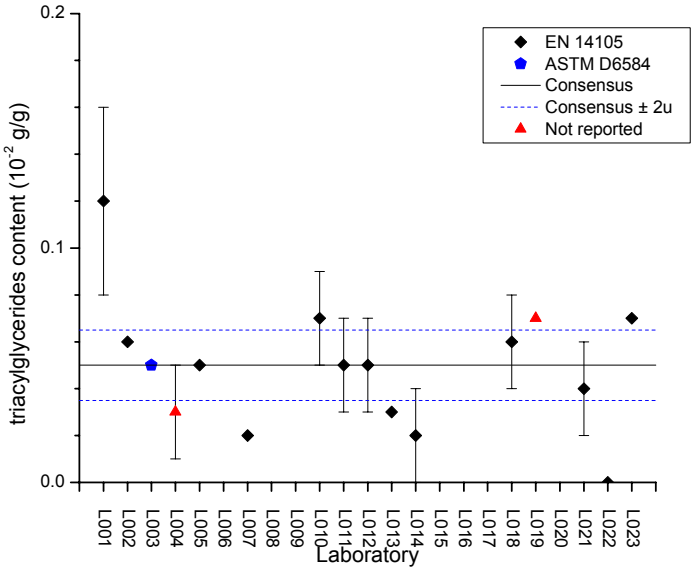

Figure 20: Results for triacylglycerides content (material B)

No outliers have been found. The consensus value is $0.05 \cdot 10^{-2}$ g/g and based on 16 results. The repeatability standard deviation is $0.01 \cdot 10^{-2}$ g/g, the within–laboratory and reproducibility standard deviations are $0.03 \cdot 10^{-2}$ g/g.

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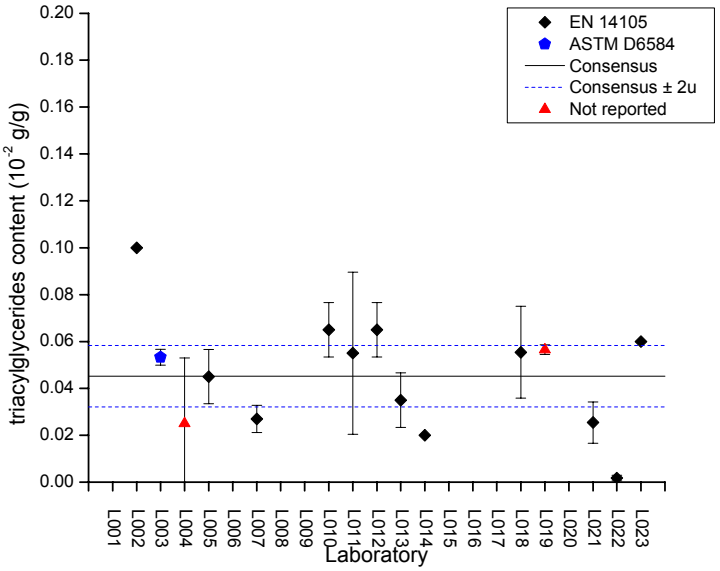

Figure 21: Results for triacylglycerides content (material C)

The results for triacylglycerides content in material C are given in figure 21.

The consensus value is $0.0452 \cdot 10^{-2}$ g/g and based on 15 laboratory results (no outliers are found). The repeatability standard deviation is $0.0074 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.0243 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.0254 \cdot 10^{-2}$ g/g.

3.17 Monolein content

The results for monolein content in material B are given in figure 22.

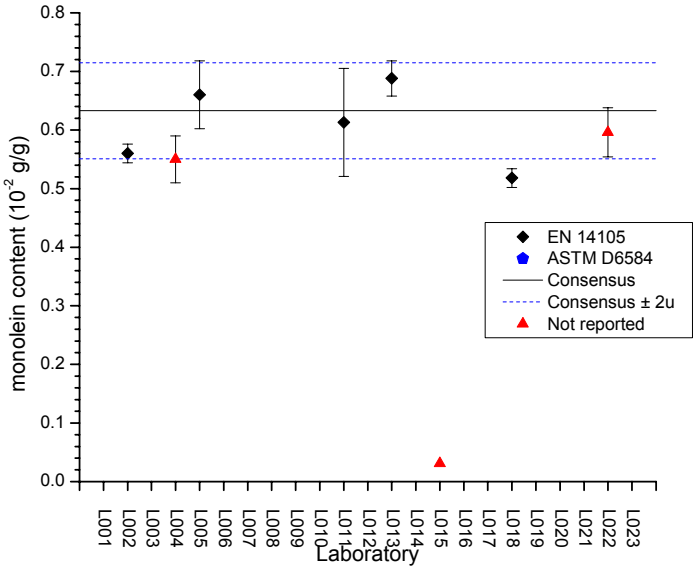

Figure 22: Results for monolein content (material B)

The result of laboratory L015 is flagged as outlier. The consensus value, based on 8 results, is $0.633 \cdot 10^{-2}$ g/g. The repeatability standard deviation is $0.023 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.113 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.115 \cdot 10^{-2}$ g/g.

The results for monolein content in material C are given in figure 23.

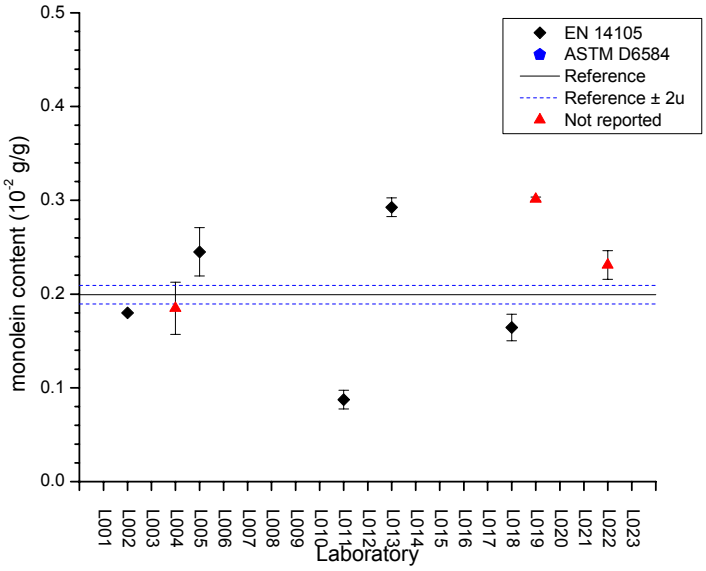

Figure 23: Results for monolein content (material C)

No outliers were found. The consensus value is based on 8 measurements. The mean is $0.2108 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $0.0081 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.0710 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.0715 \cdot 10^{-2}$ g/g. The reference value of $0.1994 \cdot 10^{-2}$ g/g (for monolein, monolinolein and monolinolenin) is slightly lower than the consensus value, but within the respective uncertainties the values agree.

3.18 Diolein content

The results for diolein content in material B are given in figure 24.

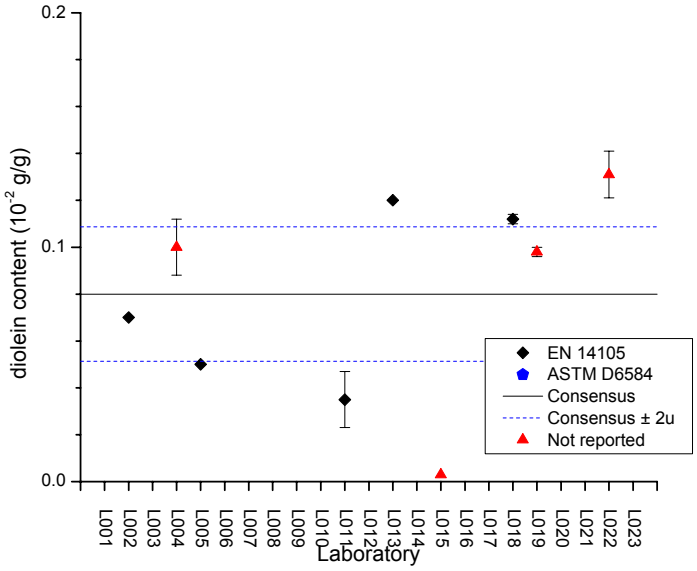

Figure 24: Results for diolein content (material B)

No outliers have been found. The dataset may be considered to be of poor quality. The consensus value is $0.080 \cdot 10^{-2}$ g/g and based on 9 results. The repeatability standard deviation is $0.003 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.043 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.043 \cdot 10^{-2}$ g/g.

The results for diolein content in material C are given in figure 25. No outliers were removed.

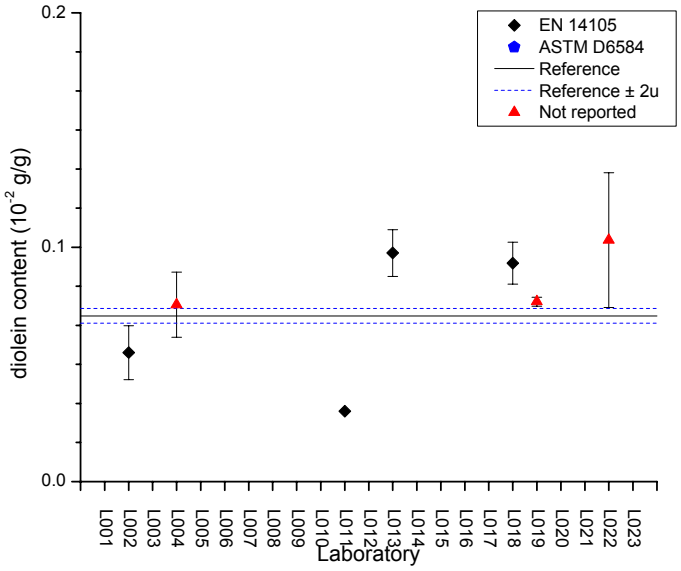

Figure 25: Results for diolein content (material C)

The consensus value is based on 7 measurement results. The mean is $0.0758 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $0.0069 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.0257 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.0266 \cdot 10^{-2}$ g/g. The reference diolein content (diolein and dilinolein) of $0.0707 \cdot 10^{-2}$ g/g is slightly lower than the consensus value.

3.19 Triolein content

The results for triolein content in material B are given in figure 26.

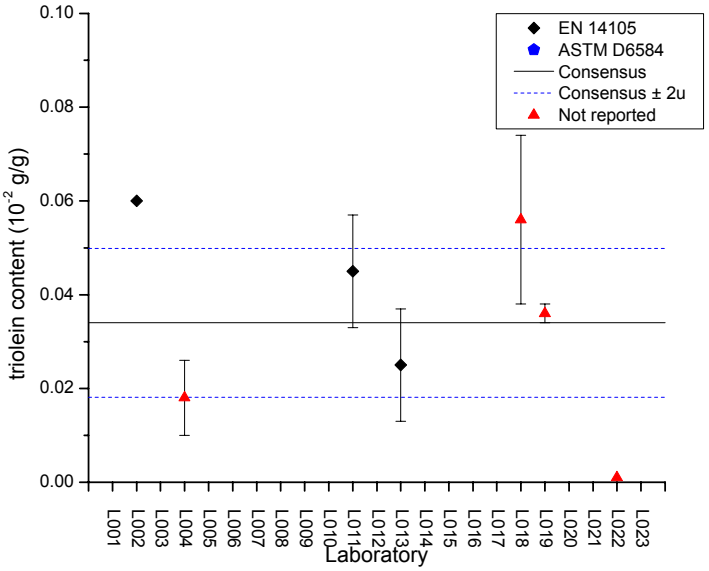

Figure 26: Results for triolein content (material B)

No outliers have been identified. Several laboratories report that the content is below their limit of quantification (detection). The dataset is of a rather poor quality. The consensus value is $0.034 \cdot 10^{-2}$ g/g and based on 7 measurement results. The repeatability standard deviation is $0.005 \cdot 10^{-2}$ g/g, and the between-laboratory and reproducibility standard deviations are $0.021 \cdot 10^{-2}$ g/g.

The results for triolein content in material C are given in figure 27.

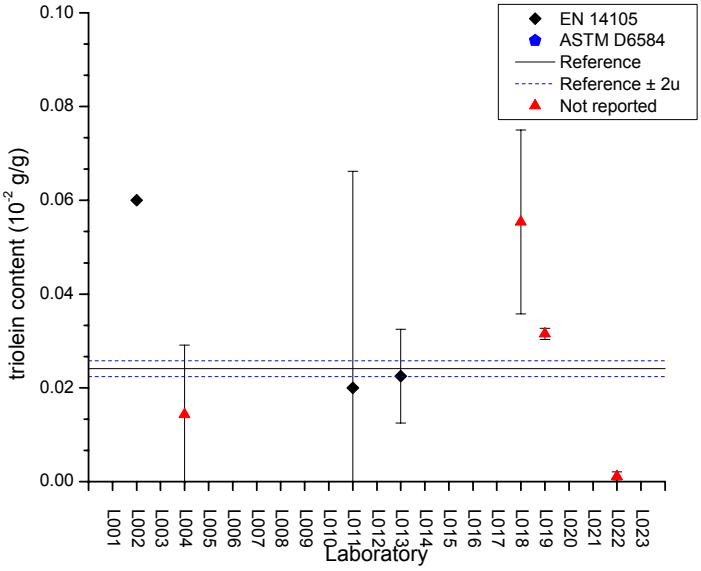

Figure 27: Results for triolein content (material C)

No outliers are detected. The mean is $0.0303 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $0.0103 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.0205 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.0229 \cdot 10^{-2}$ g/g. The consensus value is considerably higher than the reference value of $0.0241 \cdot 10^{-2}$ g/g.

3.20 Free glycerol content

The results for free glycerol content in material B are given in figure 28.

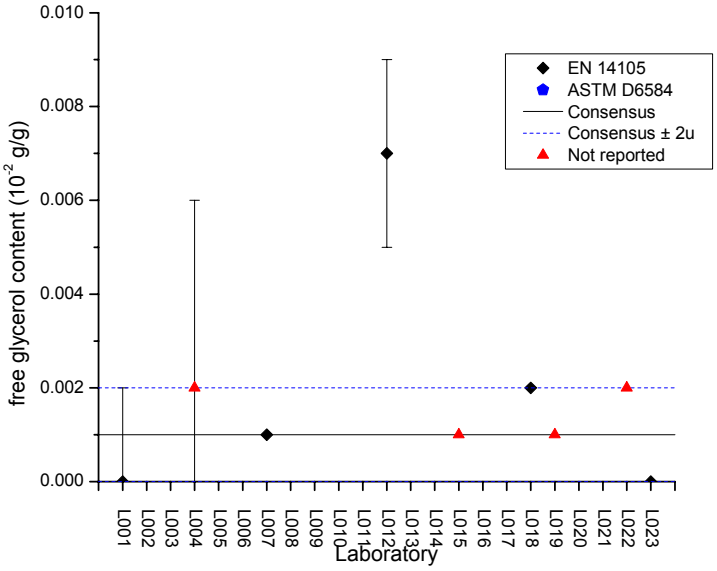

Figure 28: Results for free glycerol content (material B)

The content of free glycerol is quite low, which results in a poor dataset. Several laboratories report that the content is below their limit of quantification. The result of laboratory L012 is flagged as outlier, but it is hard to tell whether the statistical approach chosen is telling the whole truth.

The consensus value is $0.001 \cdot 10^{-2}$ g/g and based on 8 measurement results. All three standard deviations (repeatability, between-laboratory, and reproducibility) are $0.001 \cdot 10^{-2}$ g/g.

The results for free glycerol content in material C are given in figure 29.

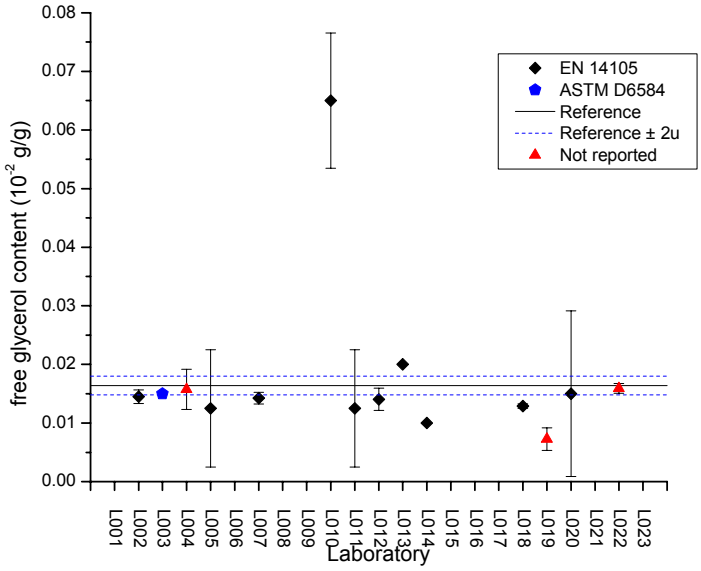

Figure 29: Results for free glycerol content (material C)

The content of free glycerol is appreciably higher in material C than in material B. The dataset of material C therefore gives a much better view on the laboratory performance. Two outliers have been removed (L010 and L019). The mean is 0.0143 g/100 g and based on 12 laboratories.

The repeatability standard deviation is $0.0025 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.0021 \cdot 10^{-2}$ g/g and the reproducibility standard deviation is $0.0033 \cdot 10^{-2}$ g/g.

3.21 Total glycerol content

The results for total glycerol content in material B are given in figure 30. One result (L015) is probably a reporting error. In addition to this result, there is one more result flagged as outlier (L012).

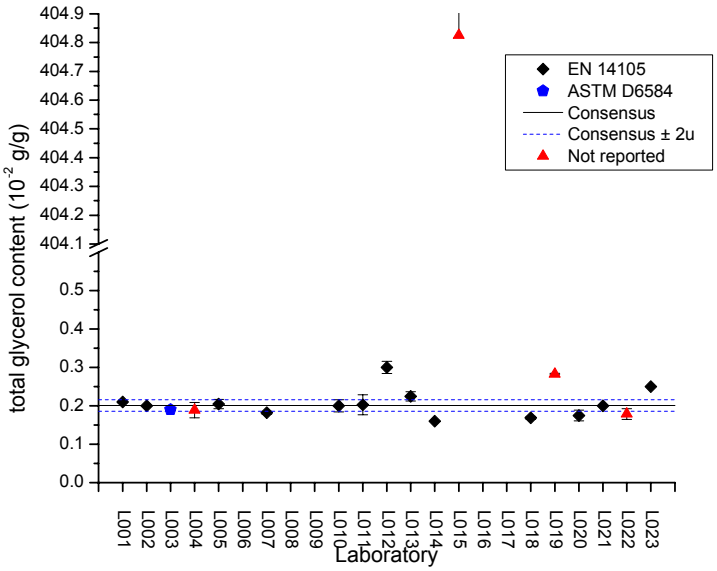

Figure 30: Results for total glycerol content (material B)

The consensus value is based on 16 measurement results and is $0.201 \cdot 10^{-2}$ g/g. The repeatability standard deviation is $0.006 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.029 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.030 \cdot 10^{-2}$ g/g.

The results for total glycerol content in material C are given in figure 31.

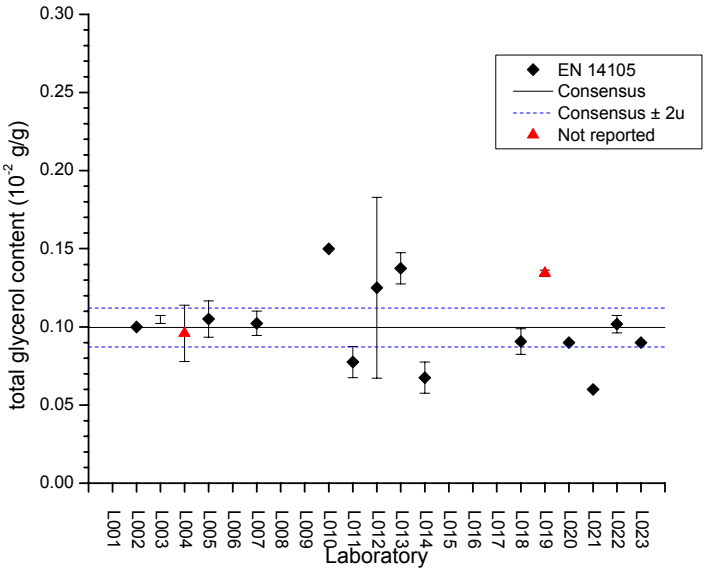

Figure 31: Results for total glycerol content (material C)

One laboratory result (L010) is flagged as outlier. The mean is $0.0996 \cdot 10^{-2}$ g/g and based on 15 laboratories. The repeatability standard deviation is $0.0089 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.0222 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.0240 \cdot 10^{-2}$ g/g.

3.22 Total ester content

The results for total ester content in material B are given in figure 32. No outliers are found. The consensus value is $97.61 \cdot 10^{-2}$ g/g and based on 18 measurement results. The repeatability standard deviation is $0.38 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $1.16 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $1.22 \cdot 10^{-2}$ g/g. There is fair agreement between the reference value of $98.34 \cdot 10^{-2}$ g/g and the consensus value.

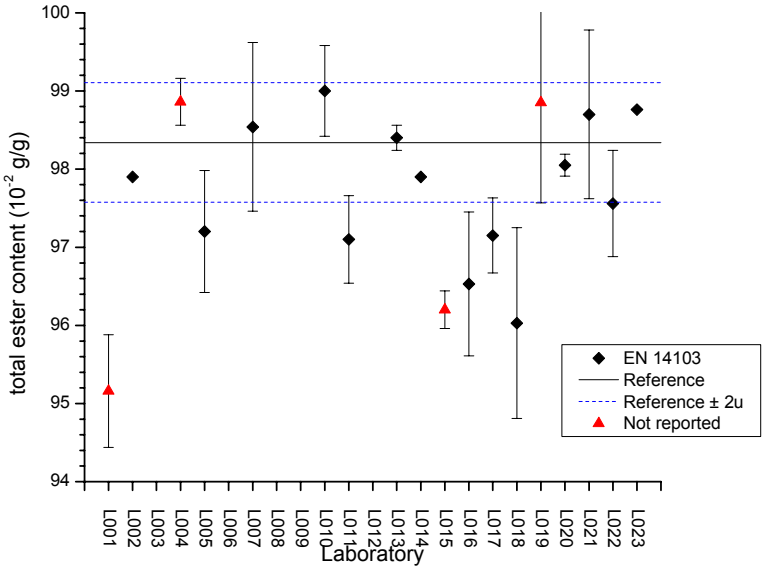

Figure 32: Results for total ester content (material B)

The results for total ester content in material C are given in figure 33.

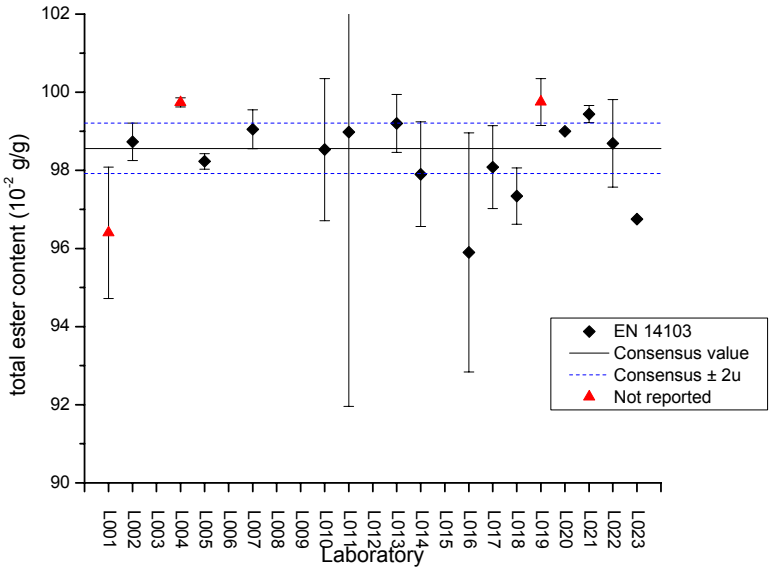

Figure 33: Results for total ester content (material C)

One laboratory result is flagged as outlier (L016). The mean is $98.56 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $1.04 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.77 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $1.29 \cdot 10^{-2}$ g/g. The value of the repeatability standard deviation is relatively large because of several laboratories with a relative high within–laboratory standard deviation.

3.23 Linolenic acid methyl ester content

The results for linolenic acid methyl ester content in material B are given in figure 34. Three outliers are found (L001, L002, and L011). The consensus value is $9.90 \cdot 10^{-2}$ g/g and based on 13 measurement results. The repeatability standard deviation is $0.09 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.14 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.17 \cdot 10^{-2}$ g/g. The consensus value is somewhat lower than the reference value of $10.009 \cdot 10^{-2}$ g/g, but both values are consistent within the respective uncertainties.

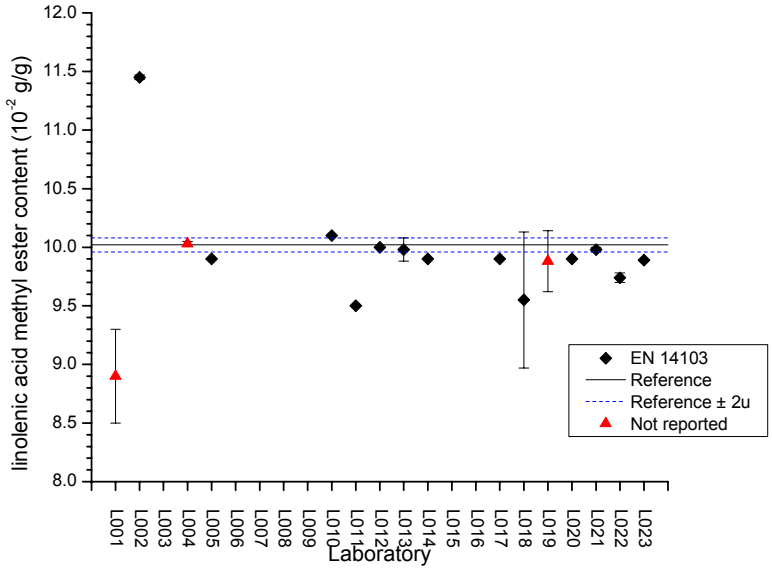

Figure 34: Results for linolenic acid methyl ester content (material B)

The results for linolenic acid methyl ester content in material C are given in figure 35.

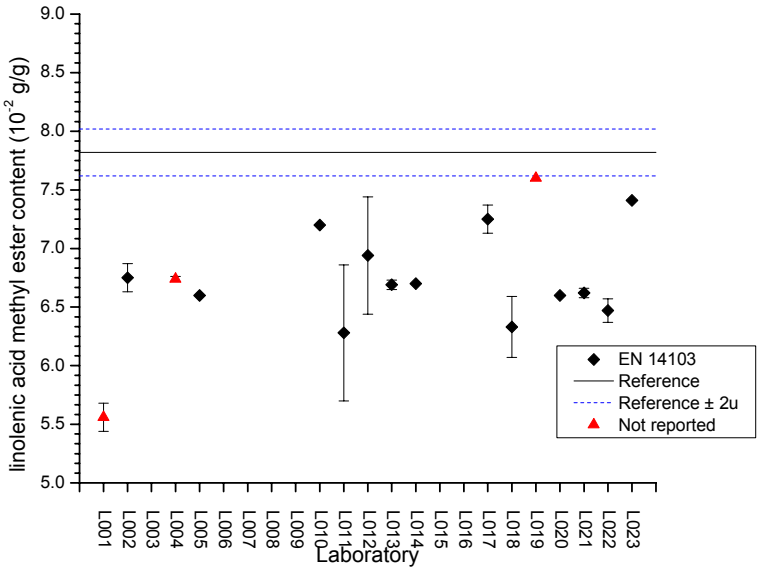

Figure 35: Results for linolenic acid methyl ester content (material C)

One laboratory result is flagged as outlier (L001). The mean is $6.79 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $0.11 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.37 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.39 \cdot 10^{-2}$ g/g. The reference value of $7.82 \cdot 10^{-2}$ g/g is significantly higher than the consensus value.

3.24 Palmitic acid methyl ester content

The results for palmitic acid methyl ester content in material B are given in figure 36.

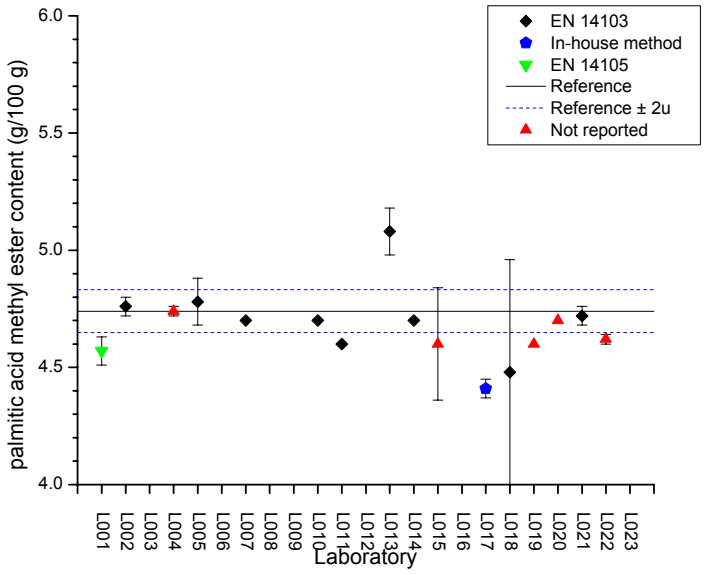

Figure 36: Results for palmitic acid methyl ester content (material B)

One laboratory (L001) claims to have used EN 14105, which is quite unusual for this parameter. The measurement result of L013 is flagged as outlier. The consensus value is based on 15 laboratories and is $4.64 \cdot 10^{-2}$ g/g. The repeatability standard deviation is $0.07 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.10 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.12 \cdot 10^{-2}$ g/g. The consensus value is somewhat lower than the reference value of $4.74 \cdot 10^{-2}$ g/g, but both values are consistent.

The results for palmitic acid methyl ester content in material C are given in figure 37.

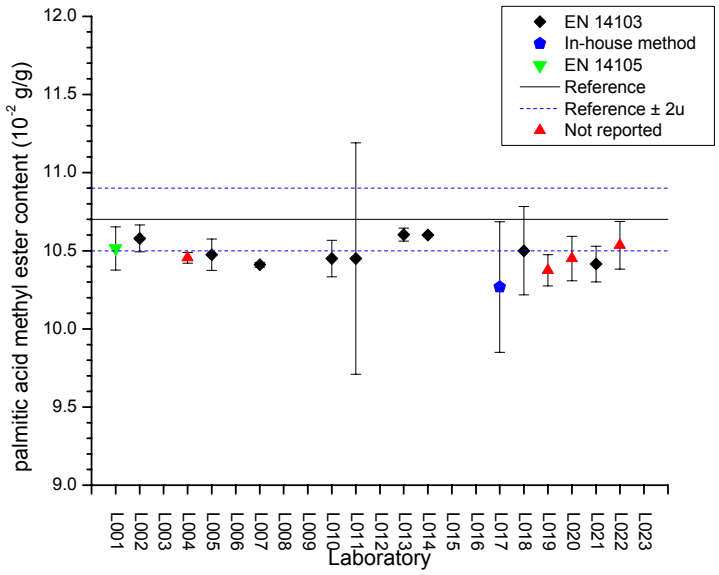

Figure 37: Results for palmitic acid methyl ester content (material C)

All reported values are below the reference value of $10.7 \cdot 10^{-2}$ g/g. Many of them fall within the limits of the interval given by the value ± the expanded uncertainty. No outliers are found. The mean is $10.473 \cdot 10^{-2}$ g/g, and based on 15 laboratory results. The repeatability standard deviation is $0.126 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.064 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.141 \cdot 10^{-2}$ g/g.

3.25 Stearic acid methyl ester content

The results for stearic acid methyl ester content in material B are given in figure 38. One result is flagged as outlier (L013). The consensus value is based on 15 measurement results and is $1.70 \cdot 10^{-2}$ g/g. The repeatability standard deviation is $0.04 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.09 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.10 \cdot 10^{-2}$ g/g. The consensus value and the reference value ($1.73 \cdot 10^{-2}$ g/g) agree well.

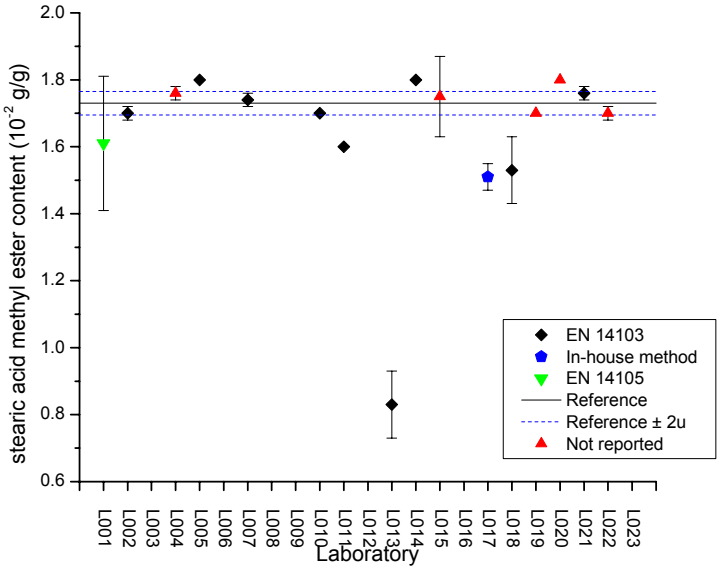

Figure 38: Results for stearic acid methyl ester content (material B)

The results for stearic acid methyl ester content in material C are given in figure 39.

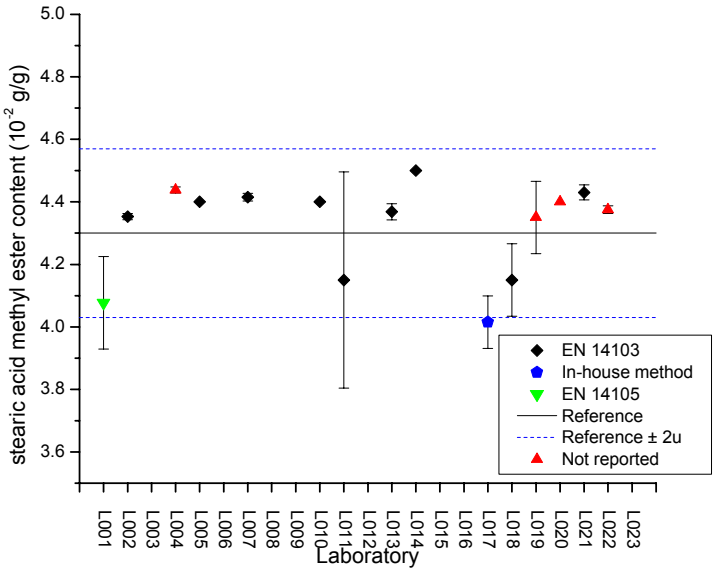

Figure 39: Results for stearic acid methyl ester content (material C)

Four results are flagged as outliers (L001, L011, L017 and L018). The mean is $4.40 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $0.02 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.04 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.05 \cdot 10^{-2}$ g/g. The consensus and reference value ($4.3 \cdot 10^{-2}$ g/g) agree well.

3.26 Total of C18:1 methyl ester content

The results for C18:1 methyl ester content in material B are given in figure 40.

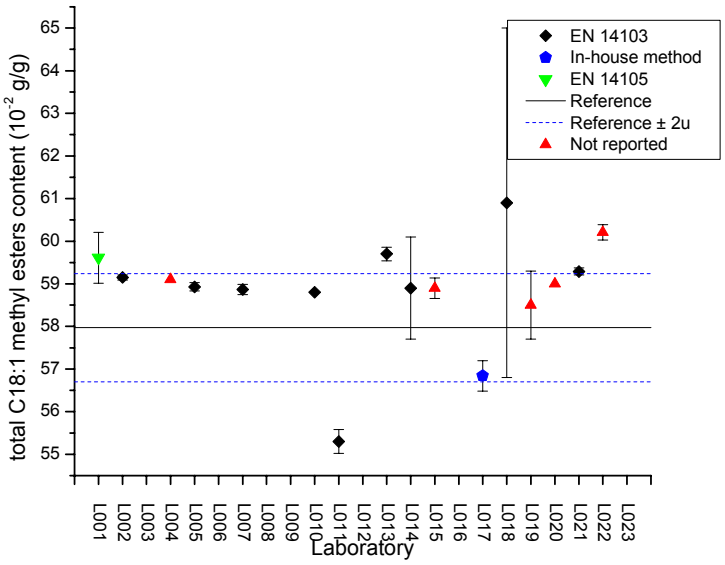

Figure 40: Results for total C18:1 methyl esters content (material B)

Four results are flagged as outliers: L011, L017, L018, and L022. The consensus value is $59.06 \cdot 10^{-2}$ g/g, based on 12 laboratories. The repeatability standard deviation is $0.24 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.32 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.40 \cdot 10^{-2}$ g/g. The reference value for total C18:1 methyl esters is $57.97 \cdot 10^{-2}$ g/g.

The results for C18:1 methyl ester content in material C are given in figure 41.

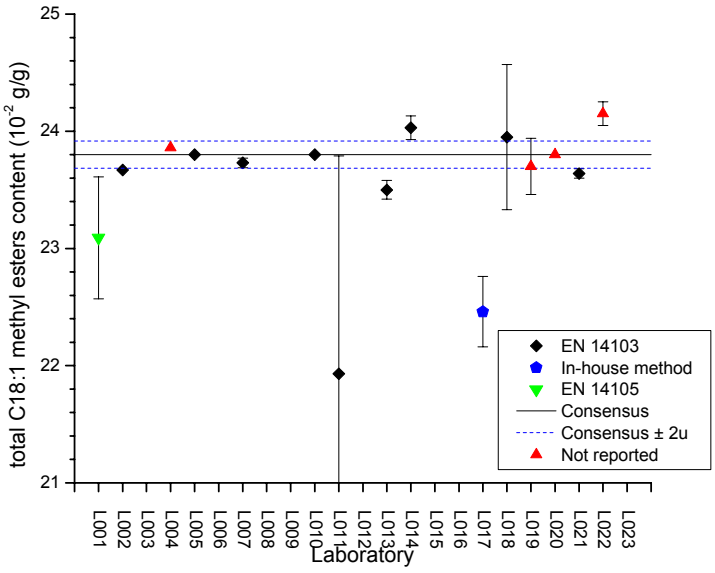

Figure 41: Results for total C18:1 methyl esters content (material C)

Two outliers are found (L011 and L017). The mean is $23.80 \cdot 10^{-2}$ g/g and based on 12 values. The repeatability standard deviation is $0.10 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.17 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.20 \cdot 10^{-2}$ g/g.

3.27 Total of C18:2 methyl ester content

The results for C18:2 methyl ester content in material B are given in figure 42.

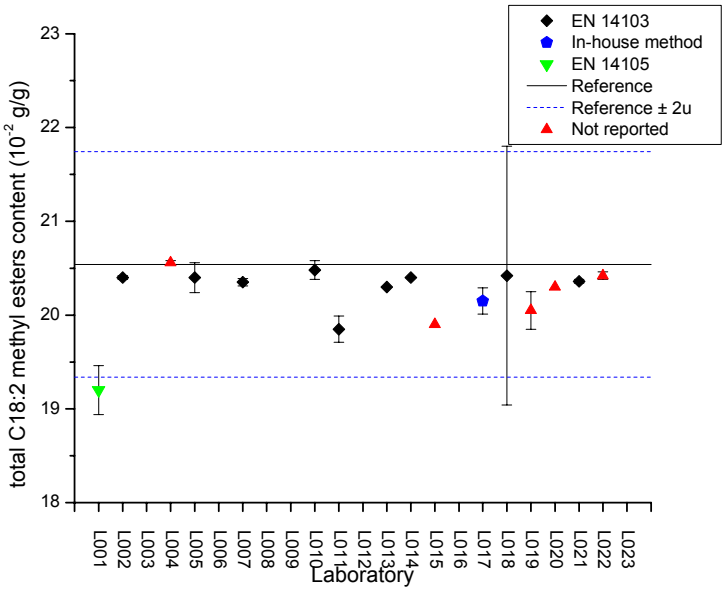

Figure 42: Results for total C18:2 methyl esters content (material B)

Four results are flagged as outliers: L001, L011, L015, and L019. The consensus value is $20.38 \cdot 10^{-2}$ g/g and based on 12 measurement results. The standard deviations are $0.21 \cdot 10^{-2}$ g/g, $0.00 \cdot 10^{-2}$ g/g, and $0.21 \cdot 10^{-2}$ g/g, for repeatability, between-laboratory, and reproducibility respectively. The consensus value and the reference value ($20.54 \cdot 10^{-2}$ g/g) agree well.

The results for C18:2 methyl ester content in material C are given in figure 43.

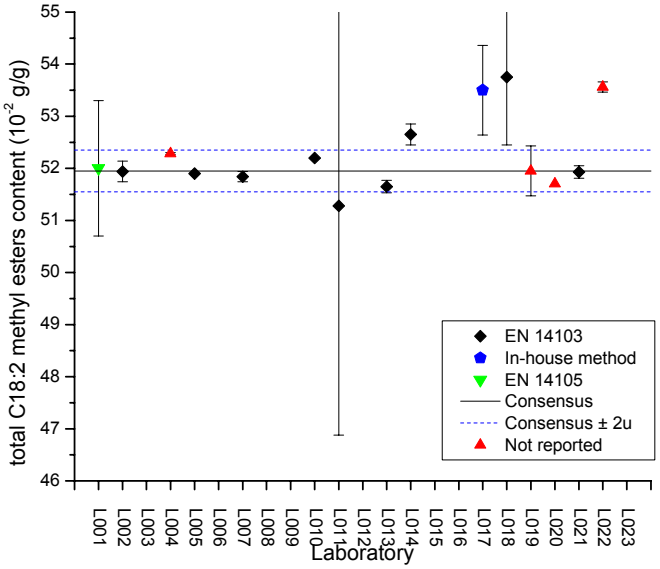

Figure 43: Results for total C18:2 methyl esters content (material C)

The dataset is quite heterogeneous in terms of within–laboratory standard deviations. Three outliers are found (L17, L018, L022). The mean is $51.95 \cdot 10^{-2}$ g/g. The repeatability standard deviation is $0.69 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.69 \cdot 10^{-2}$ g/g. The between-laboratory standard deviation is zero because of the heterogeneity of the dataset.

3.28 Total of C18:3 methyl ester content

The results for C18:3 methyl ester content in material B are given in figure 44.

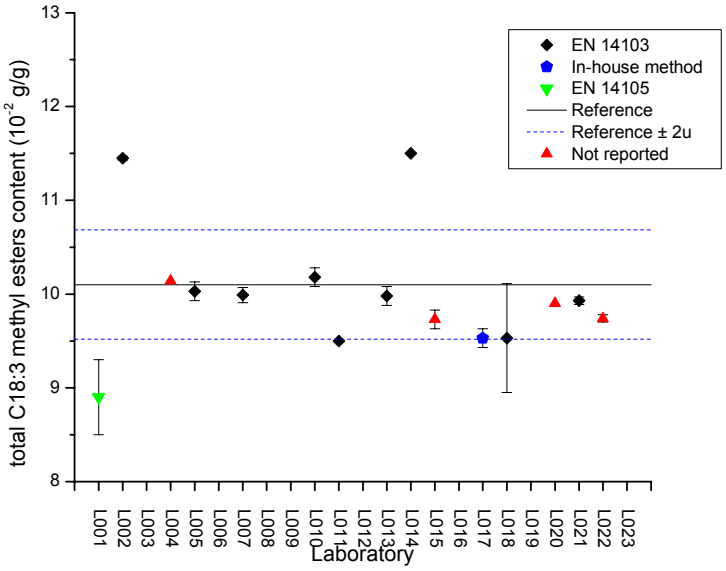

Figure 44: Results for total C18:3 methyl esters content (material B)

Three results are flagged as outliers: L001, L002, and L014. The consensus value is $9.86 \cdot 10^{-2}$ g/g (12 laboratories). The repeatability standard deviation is $0.10 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.23 \cdot 10^{-2}$ g/g, and the reproducibility standard deviation is $0.25 \cdot 10^{-2}$ g/g. The consensus value and the reference value ($10.1 \cdot 10^{-2}$ g/g) agree within their respective uncertainties.

The results for C18:3 methyl ester content in material C are given in figure 45.

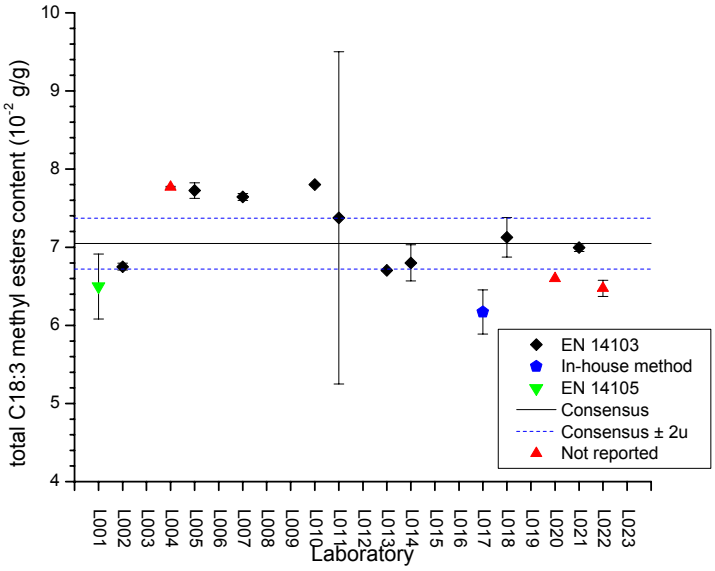

Figure 45: Results for total C18:3 methyl esters content (material C)

The mean is $7.046 \cdot 10^{-2}$ g/g and based on 14 laboratory values. The repeatability standard deviation is $0.304 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.528 \cdot 10^{-2}$ g/g and the reproducibility standard deviation is $0.609 \cdot 10^{-2}$ g/g.

3.29 Consensus values

The consensus values for material B are summarised in table 8.

Table 8: Consensus values after outlier removal (material B)

Parameter	Unit	*m*	*p*	s_r	s_L	s_R
Density at 15 °C	kg m^{-3}	883.467	19	0.027	0.083	0.087
Viscosity at 40 °C	mm^2 s^{-1}	4.4492	18	0.0078	0.0149	0.0168
Flash point	°C	175.7	17	1.8	8.9	9.1
Sodium content	mg kg^{-1}	0.981	10	0.191	0.487	0.523
Potassium content	mg kg^{-1}	0.121	3	0.009	0.071	0.072
Sulfur content	mg kg^{-1}	2.16	15	0.22	0.39	0.45
Water content	mg kg^{-1}	216	18	11	22	25
Oxidation stability (110 °C)	h	12.0	15	0.1	0.4	0.5
Acid value	mg g^{-1}	0.188	17	0.018	0.035	0.039
Iodine value	10^{-2} g/g	113.5	16	1.1	2.1	2.4
FAME content	10^{-2} g/g	0.294	7	0.019	0.216	0.217
Methanol content	10^{-2} g/g	0.0216	15	0.0025	0.0041	0.0048
Monoacylglyceride content (total)	10^{-2} g/g	0.660	15	0.017	0.069	0.071
Diacylglyceride content (total)	10^{-2} g/g	0.134	17	0.006	0.034	0.034
Triacylglyceride content (total)	10^{-2} g/g	0.05	16	0.01	0.03	0.03
Monolein content	10^{-2} g/g	0.633	8	0.023	0.113	0.115
Diolein content	10^{-2} g/g	0.080	9	0.003	0.043	0.043
Triolein content	10^{-2} g/g	0.034	7	0.005	0.021	0.021
Free glycerol content	10^{-2} g/g	0.001	8	0.001	0.001	0.001
Total glycerol content	10^{-2} g/g	0.201	16	0.006	0.029	0.030
Ester content (total)	10^{-2} g/g	97.61	18	0.38	1.16	1.22
Linolenic acid (C18-3 n-3)	10^{-2} g/g	9.90	13	0.09	0.14	0.17
Palmitic acid (C16-0)	10^{-2} g/g	4.64	15	0.07	0.10	0.12
Stearic acid (C18-0)	10^{-2} g/g	1.70	15	0.04	0.09	0.10
Total of C18:1 methyl esters content	10^{-2} g/g	59.06	12	0.24	0.32	0.40
Total of C18:2 methyl esters content	10^{-2} g/g	20.38	12	0.21	0.00	0.21
Total of C18:3 methyl esters content	10^{-2} g/g	9.86	12	0.10	0.23	0.25

The consensus values for material C are summarised in table 9.

Table 9: Consensus values after outlier removal (material C)

parameter	Unit	*m*	*p*	s_r	s_L	s_R
Methanol content	10^{-2} g/g	0.051	14	0.008	0.007	0.011
Monoacylglyceride content	10^{-2} g/g	0.258	16	0.036	0.062	0.072
Diacylglyceride content	10^{-2} g/g	0.1155	16	0.0059	0.0354	0.0358
Triacylglyceride content	10^{-2} g/g	0.0452	15	0.0074	0.0243	0.0254
Monolein content	10^{-2} g/g	0.2108	8	0.0081	0.0710	0.0715
Diolein content	10^{-2} g/g	0.0758	7	0.0069	0.0257	0.0266
Triolein content	10^{-2} g/g	0.0303	7	0.0103	0.0205	0.0229
Free glycerol content	10^{-2} g/g	0.0143	12	0.0025	0.0021	0.0033
Total glycerol content	10^{-2} g/g	0.0996	15	0.0089	0.0222	0.0240
Total ester content	10^{-2} g/g	98.56	16	1.04	0.77	1.29
Linolenic acid (C18-3 n-3)	10^{-2} g/g	6.79	15	0.11	0.37	0.39
Palmitic acid (C16-0)	10^{-2} g/g	10.473	15	0.126	0.064	0.141
Stearic acid (C18-0)	10^{-2} g/g	4.40	11	0.02	0.04	0.05
Total of C18:1 methyl esters content	10^{-2} g/g	23.80	12	0.10	0.17	0.20
Total of C18:2 methyl esters content	10^{-2} g/g	51.95	12	0.69	0.00	0.69

parameter	Unit	*m*	*p*	s_r	s_L	s_R
Total of C18:3 methyl esters content	10^{-2} g/g	7.046	14	0.304	0.528	0.609

The consensus values for material D are summarised in table 10.

Table 10: Consensus value after outlier removal (material D)

parameter	Unit	*m*	*p*	s_r	s_L	s_R
Sulfur content	mg kg^{-1}	7.53	14	0.42	0.63	0.76

4 Discussion and conclusions

For most parameters, there is good agreement among methods, and between the consensus and reference values (if available). None of the datasets permits going into the calculation of method-specific characteristics for repeatability and reproducibility, as for this purpose the datasets are too unbalanced.

The ILC-participants present during the BIOREMA Workshop expressed their happiness with the outcome (measurement results) of the BIOREMA biodiesel ILC. It was considered that biodiesel forms a very difficult matrix for which a lot of research and development work is still required, especially with regard to improving the quantification of the monoacylglyceride, diacylglyceride and triacylglyceride contents. For monoacylglyceride, diacylglyceride, triacylglyceride, monolein, diolein and triolein content chromatographic peak identification problems persist. A consistent identification of all peaks, belonging to the individual groups, would have lead to a better agreement of the results. Furthermore, the aging of the column, especially when EN 14105 is followed, proves to be an issue in the measurement of the di- and triacylglyceride contents.

Although it was understood by the ILC-participants that the BIOREMA ILC especially aimed at finding generic problems, they still stressed the importance of receiving *Z*-scores. As proficiency testing (PT) results are also used during laboratory accreditation assessments, it was noted as a weak point by one of the laboratories that current biofuel PTs only provide consensus values, whereas reference values would provide real “anchor points”. Considerable effort is being put in current PT participation, without revealing whether the measurement capabilities for these parameters are proved to be fit-for-purpose. Last but not least, some accreditation bodies allegedly demand PT participation every year for each parameter accredited, whereas others seem satisfied with participation once every four years.

Flash point measurement results are measurement method specific. Currently no appropriate reference materials (RMs) are available for the calibration and checking of the equipment and method. The pure compounds usually used have rather different vapour pressures than biofuels, so that this use of these RMs is not regarded as sufficiently representative for the behaviour of the method under real conditions..

For the fatty acid analysis, the use of C17 as the internal standard/surrogate leads to complications, as C17 is present in some feedstocks, e.g., animal fat-based and also soy-based biodiesel. The current version of EN 14103 is not suited for dealing with this coelution however.

For glyceryol analysis, it was noted that instead of butanetriol butanediol might be used as internal standard. Butanediol is less expensive, and its availability is better than the triol.

For EN 14105 and other biodiesel written standards it is recommended to convert these standards from prescriptive standards into performance-based standards, giving performance criteria for various parts of the standard test methods.

The analysis of trace metals is very difficult at the typical levels present in biodiesel. Another difficult parameter is the measurement of phosphorous content. Not only are the levels often low, but they can be further reduced due to adsorbance on glass walls of the polar phosphorous compounds present in a non polar biofuel matrix.

Concerning analyses for methanol (and ethanol) content, the use of headspace analysis was discouraged by the audience during the BIOREMA workshop. The direct injection was preferred for obtaining better measurement results.

With respect to the animal fat-based biodiesel material (“material D”) not all laboratories seemed to have warmed up this material sufficiently before use, as they observed the presence of particles.

It was also noted that using 100% animal fat-based material sometimes material remains on filter material, but that currently used written standards do not give any indication how this material should be washed away (i.e., specifying “how much solvent volume” should be used).

During the BIOREMA workshop it was noted that there is a lack of (C)RMs available for biofuel analyses. Currently, ILC test materials are often used over time as quality control materials. When deviations are found however, it cannot be concluded whether the result deviates due to a wrong measurement or stability problems of this control material.

Requirements for reference materials as brought forward by one of the field laboratories present:

- A “known” true value
- Homogeneous
- Long-term stability (of the specified property)
- Same or similar composition as the real sample
- A value either close to an average sample or close to the specification limit
- Suited for checking of the method
- Availability (sufficient amount)
- Affordable price (per measurement)

As the feedstocks for biofuels are diverse it was considered best to prepare (more) suitable RMs with respect to those feedstocks most frequently used. Furthermore it does not seem feasible to develop “a single reference material for all applications”. As such it is recommended developing RMs tailored to specific measurement methods and feedstocks. To avoid stability issues, the use of an anti-oxidant is becoming the norm. Furthermore oxygen (from air) is as much as possible to be removed or replaced (e.g., by argon) in the CRM storage container to further improve the long-term stability of the RM.

In the ILC, measurement uncertainty was reported by only a few of the participating laboratories. Usually (for other types of test material) at least half of ILC participating laboratories report their measurement uncertainty. During the workshop the reporting of measurement uncertainty was seen by many field laboratories as being too much effort in this setting, and only done when specifically asked for.

5 Recommendations from the BIOREMA workshop

The needs & recommendations for the analysis of biofuel parameters from the BIOREMA Workshop can be summarised as follows:

- Describe commutability of material (closeness to real field testing sample)
- Provide a variety of CRMs tailored to specific measurement methods and feedstocks
- Provide CRMs that can be used as “pure” calibration standards for specific measurement methods
- Define properly the quantity to be measured in written standards
- Explore the possibility of introducing structurally defined measurands into biofuels standards
- Further harmonize accreditation requirements for laboratories such as ILC participation and uncertainty estimation
- Facilitate further understanding of different performance evaluation techniques
- Do performance rating in proficiency testing based on a reference value and target uncertainty where feasible

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