Evaluation of results of ILC BIOREMA Test Material A – bio-ethanol

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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. This report describes the results of the interlaboratory comparison for bio-ethanol.

The objective of the BIOREMA bio-ethanol 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.

Only 13 participants provided data, resulting in a small data set for evaluation. Further, it appeared that for a number of laboratories the availability of the material was not sufficient for the analysis of all requested parameters. Nevertheless, the evaluation of the measurement results of the BIOREMA ILC for material A “Bio-ethanol fuel” has lead to interesting conclusions.

In most cases, as far as the data permit, it can be concluded that the consensus values, based on participant’s results, are in good agreement with the reference or the BIOREMA values.

For three parameters, namely ethanol and water content, and density, there is good agreement between the reference and consensus value. For these parameters, the reproducibility standard deviation is close to or even smaller than the expanded uncertainty associated with the reference value. A number of parameters show very poor reproducibility: pH_e, electrolytic conductivity, and acidity. The same applies to sodium and copper content, which are very low and therefore challenging parameters.

The results of the ILC underpin the demand for certified reference materials, if not for quality control, then for facilitating the improvement of the precision and trueness of the results from testing laboratories.

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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
ICP-MS	Inductively coupled plasma mass spectrometry
IC	Ion chromatography
GC	Gas Chromatography

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) is a bio-ethanol, the other (B) a bio diesel material. These materials have been used in an interlaboratory comparison. This report describes the results of the interlaboratory comparison for bio-ethanol.

The objective of the BIOREMA bio-ethanol 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 possible. 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 samples of bio-ethanol from sugar cane (approximately 99.6 % ethanol content) were provided by a Brazilian producer in a 200 L container. The ethanol was bottled in about five thousand amber glass ampoules of 10 mL that had been preevacuated with argon and were flame-sealed, and in about one hundred amber glass bottles of 100 mL. The sample preparation was performed by INMETRO.

The test material was subjected to a homogeneity, stability and characterisation study prior to this ILC (see section 2.6 for details).

2.2 Measurement programme

The participating laboratories received a package of 46 samples labelled “BIOREMA Test material A”. The samples should be handled as regular samples. Samples could be combined if necessary. The code numbers of the samples used to measure each parameter should be indicated on the reporting sheet.

The following parameters were supposed to be determined:

1. Iron content, µg/kg
2. Sodium content, mg/kg
3. Acidity, mg/L
4. Copper content, µg/kg
5. Sulfate content, mg/kg
6. Conductivity, µS/cm
7. Chloride content, mg/kg
8. Water content, 10^{-2} g/g
9. pHe
10. Sulfur content, mg/kg
11. Ethanol content, 10^{-2} g/g
12. Density[1], g/mL

2.3 Schedule

The schedule of this comparison was as follows (table 1).

Table 1: 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 Participants

The sample material available for the interlaboratory comparison (ILC) was sufficient for 30 applications. Although more than 100 laboratories were invited to paricipate free of charge in the comparison, only 15 organizations

[1] Laboratories were requested to indicate the applicable temperature.

submitted their application. One laboratory did not receive the samples. 13 laboratories reported results. These laboratories are biofuel producers and testing and customs labs based in Europe, Asia and America.

2.5 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

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

The criterion for marking a laboratory average ($\bar{y}_i$) 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 [4,5] 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:

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

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

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

where

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

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

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

The reproducibility standard deviation is calculated according to:

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

2.6 Reference values

The test material was subjected to a characterisation [1] prior to this interlaboratory comparison. The results are given in table 2.

Table 2: Overview results characterisation bio-ethanol [1]

Parameter	Unit	y_{ref}	$u(y_{ref})$	n	Basis
Copper content	µg/kg	149.10	1.11	1	laboratory result
Iron content	µg/kg	18.557	0.183	1	laboratory result
Sodium content	mg/kg	0.8248	0.0095	1	laboratory result
Chloride content	mg/kg	0.09598	0.00115	1	laboratory result
Sulfate content	mg/kg	1.288	0.014	1	laboratory result
Water content	10^{-2} g/g	0.3926	0.0017	3	weighted mean
Ethanol content	10^{-2} g/g	99.504	0.076	2	weighted mean
Density (at 20°C)	g/mL	0.790630	0.000017	2	weighted mean
pHe		3.543	0.094	2	weighted mean
Acidity	mg/L	8.216	0.101	1	laboratory result
Electr. conductivity	µS/cm	1.520	0.026	1	laboratory result

The values obtained as weighted mean are referred to as "reference value". The other results are referred to as "BIOREMA value".

The uncertainty budget of the property values given in table 2 are based on the characterisation measurements only. These budgets need be supplemented by the uncertainty contributions due to between-bottle homogeneity (s_{bb}) and stability (u_{lts}), which are given in tables 3 and 4 respectively.

Table 3: Summary of the homogeneity study [2]

Parameter	*unit*	s_{bb}
Copper content	µg/kg	3.2
Iron content	µg/kg	0.6
Sodium content	mg/kg	0.029
Chloride content	mg/kg	0.014
Sulfate content	mg/kg	0.012
Water content	g/100 g	0.005
Ethanol content	g/100 g	0.18
Density	g/mL	0.00007

Parameter	*unit*	s_{bb}
pHe		0.04
Acidity	mg/L	0
Electrolytic conductivity	µS/cm	0

Table 4: Uncertainty evaluation long-term stability study

Parameter	Unit	u_{lts}
Copper content	µg/kg	3.24
Iron content	µg/kg	0.46
Sodium content	mg/kg	0.0064
Chloride content	µg/kg	0.0114
Sulfate content	mg/kg	0.0179
Water content	10^{-2} g/g	0.0043
Ethanol content	10^{-2} g/g	0.14
Density	g/mL	$5.0 \cdot 10^{-6}$
pHe		0.0156
Acidity	mg/L	0.0305
Electrolytic conductivity	µS/cm	0.0149

The reference and BIOREMA values and associated combined standard uncertainties are given in table 5.

Table 5: Reference and BIOREMA values and associated uncertainties[2]

Parameter	Unit	y_{ref}	u_{char}	u_{bb}	u_{lts}	U_{ref}
Copper content	µg/kg	149.1	1.1	3.2	3.3	9.4
Iron content	µg/kg	18.6	0.2	0.6	0.5	1.6
Sodium content	mg/kg	0.825	0.010	0.029	0.006	0.062
Chloride content	mg/kg	0.0960	0.0012	0.014	0.012	0.036
Sulfate content	mg/kg	1.288	0.014	0.012	0.018	0.052
Water content	**10^{-2} g/g**	**0.393**	0.002	0.005	0.005	**0.014**
Ethanol content	**10^{-2} g/g**	**99.50**	0.08	0.18	0.14	**0.48**
Density (at 20°C)	**g/mL**	**0.79063**	$1.7 \cdot 10^{-5}$	0.00007	$5.0 \cdot 10^{-6}$	**0.00015**
Density (at 15°C)	**g/mL**	**0.79490**	$1.7 \cdot 10^{-5}$	0.00007	$5.0 \cdot 10^{-5}$	**0.00015**
pHe		**3.54**	0.10	0.04	0.016	**0.21**
Acidity	mg/L	8.22	0.10	0	0.03	0.21
Electr. conductivity	µS/cm	1.52	0.026	0	0.0149	0.060

NOTE: the values in bold are "reference values". The other results are referred to as "BIOREMA value".

The table lists the reference values (in bold) and the BIOREMA values (y_{ref}), the standard uncertainty due to characterisation (u_{char}), the standard uncertainty due to between-bottle homogeneity (u_{bb}), the standard uncertainty due to long-term stability (u_{lts}), 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_{char}, u_{bb}, and u_{lts}.

The use of the reference and BIOREMA values in this comparison is solely for comparing with the consensus value, and if applicable, means of groups of laboratories.

[2] Expanded uncertainty of the reference or BIOREMA value established using a coverage factor $k = 2$.

3 Results and discussion

3.1 General

In the figures, the reference or BIOREMA 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 $2 \cdot s_i$.

3.2 Iron content

The results for iron content are given in figure 1. There are only five laboratories reporting iron content, of which one reports below 0.05 µg/kg. The visual representation includes the BIOREMA value which was obtained by measuring iron content using an ICP-OES based method.

The reason why only few measurements results were reported is not known. A possible explanation is that iron content in this biomaterial is very low. Participants did not indicate however whether this parameter was below their quantification or detection limit, or below specifications. Only one participant reported the uncertainty associated with the result.

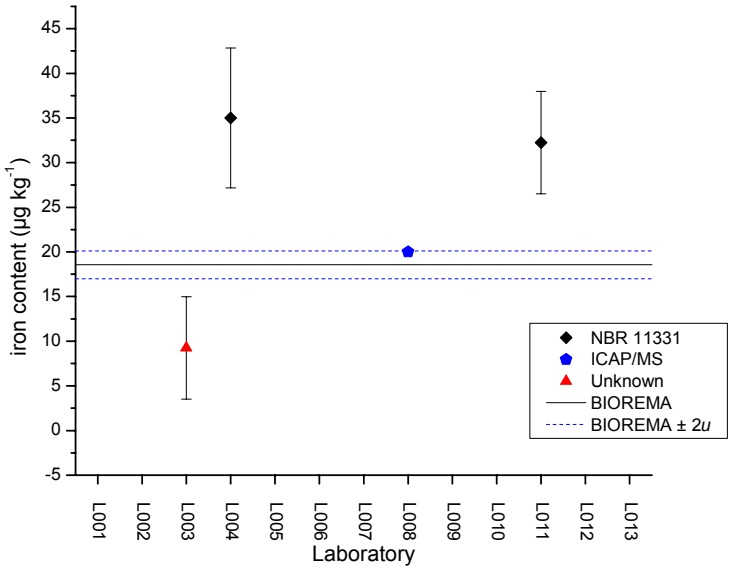

Figure 1: Results for iron content

No outliers are detected. The consensus mean is 24.1 µg/kg and based on 4 measurement results. The repeatability standard deviation is 2.8 µg/kg, the between-laboratory standard deviation is 11.8 µg/kg, and the reproducibility standard deviation is 12.1 µg/kg. Both the between-laboratory and reproducibility standard deviations are quite large. There is good agreement between the consensus and the BIOREMA value(18.56 ± 1.56 µg/kg), which is mainly due to the large uncertainty associated with the consensus value.

Because of the poor quality of the few data available, it is not recommended to evaluate the laboratory performance based on the consensus value for this parameter.

3.3 Copper content

The results for copper content are shown in figure 2.

Five of the thirteen laboratories reported results. The visual representation includes the BIOREMA value which was obtained by measuring copper content using an ICP-OES.

The reason why only few laboratories reported measurements results is not known. Copper content in this biomaterial is above bio-ethanol specifications and therefore it should be possible to measure it with methods provided in written standards.

It should also be noted that only two participants reported the uncertainty associated with their results.

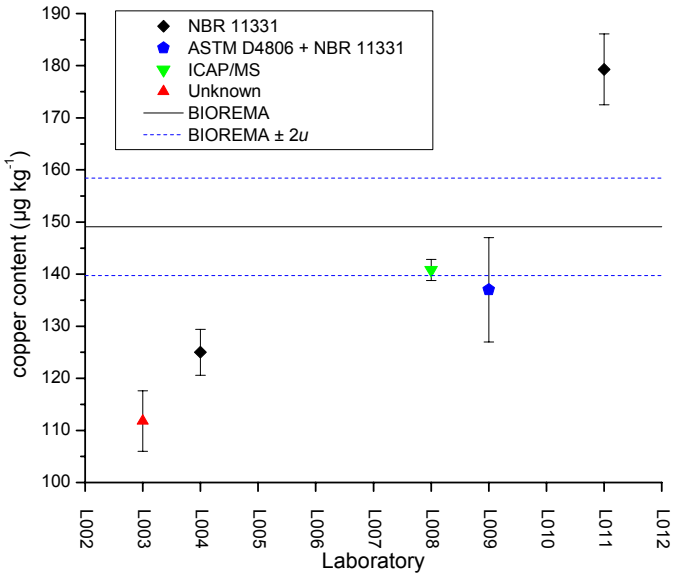

Figure 2: Results for copper content

For this parameter, the reported results are very spread indicating the difficulty of analysis of copper. No conclusions can be drawn on the comparability of the methods used.

No outliers are found. The consensus value is 138.8 µg/kg and computed from 5 measurement results. The repeatability standard deviation is 3.2 µg/kg, the between-laboratory standard deviation is 25.3 µg/kg and the reproducibility standard deviation is 25.5 µg/kg. As for iron, there is good agreement between the consensus and the BIOREMA value (149.1 ± 9.4 µg/kg), which is mainly due to the large uncertainty associated with the consensus value.

3.4 Chloride content

The results for chloride content are shown in figure 3.

Six of the thirteen laboratories reported results, of which two reported the content to be below 1 mg/kg. The visual representation includes the BIOREMA value which was obtained by measuring chloride content using Ion Chromatography (IC).

The reason why only approximately half of the laboratories reported the measurements results is unknown. Chloride content in this biomaterial is well below bio-ethanol specifications and therefore possibly below the limit of quantification or detection of most methods.

Only one participant reported the uncertainty associated with its result.

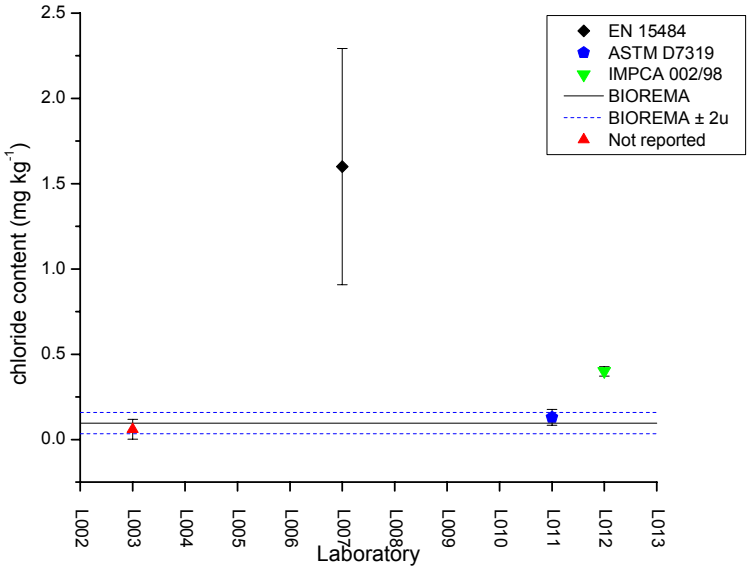

Figure 3: Results for chloride content

For this parameter, the reported results are very spread indicating the difficulty of analysis of copper. No conclusions can be drawn on the comparability of the methods used.

One result (L007) is flagged as outlier. The consensus value is based on 3 measurement results, and is 0.156 mg/kg. The repeatability standard deviation is 0.025 mg/kg, the between-laboratory standard deviation is 0.157 mg/kg, and the reproducibility standard deviation 0.159 mg/kg. The agreement between the consensus and BIOREMA value (0.096 ± 0.037 mg/kg) is fair. The between-laboratory standard deviation and reproducibility standard deviation are larger than the consensus value.

Because of the poor quality of the few data available, it is not recommended to evaluate the laboratory performance based on the consensus value for this parameter.

3.5 Sulfur content

The results for sulfur content are shown in figure 4.

Six out of thirteen laboratories reported results. No reference or BIOREMA value is available.

For this parameter, four labs used ASTM method and one the EN method (both Ultraviolet Fluorescence). One laboratory did not report the measurement method. No conclusions can be drawn on the comparability of the methods used.

The reason why only approximately half of the laboratories reported the measurements results is not known. Although no laboratories reported below method detection limits or below specifications, the sulfur content in this biomaterial is well below bio-ethanol specifications.

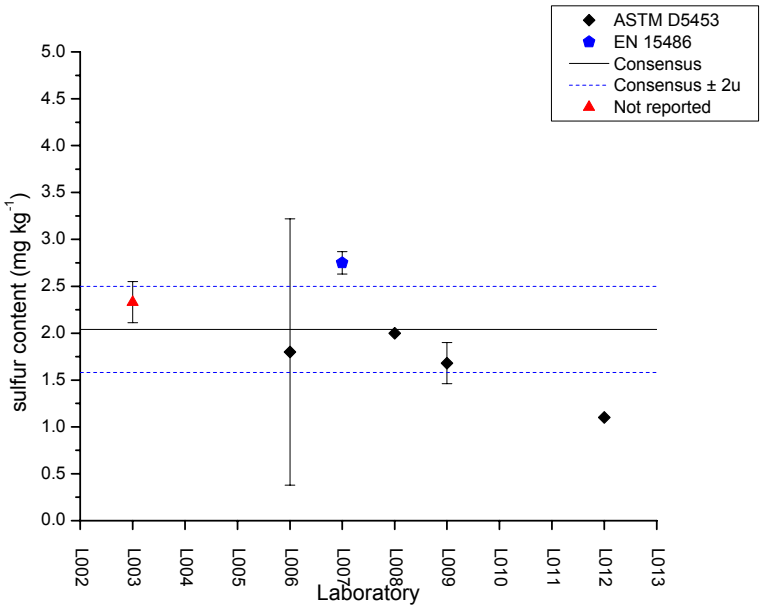

Figure 4: Results for sulfur content

No outliers were identified. The consensus value is 2.04 mg/kg and based on 6 results. The repeatability standard deviation is 0.20 mg/kg, the between-laboratory standard deviation is 0.53 mg/kg and the reproducibility standard deviation is 0.56 mg/kg.

3.6 Sodium content

The results for sodium content are shown in figure 5.

Seven laboratories reported sodium content. The visual representation includes the BIOREMA value which was obtained by measuring sodium content using flame atomic absorption spectrometry.

The sodium content in this biomaterial is low. No conclusions can be drawn on the comparability of the methods used. It should be noted that the uncertainty of the measurement results was reported by two participants.

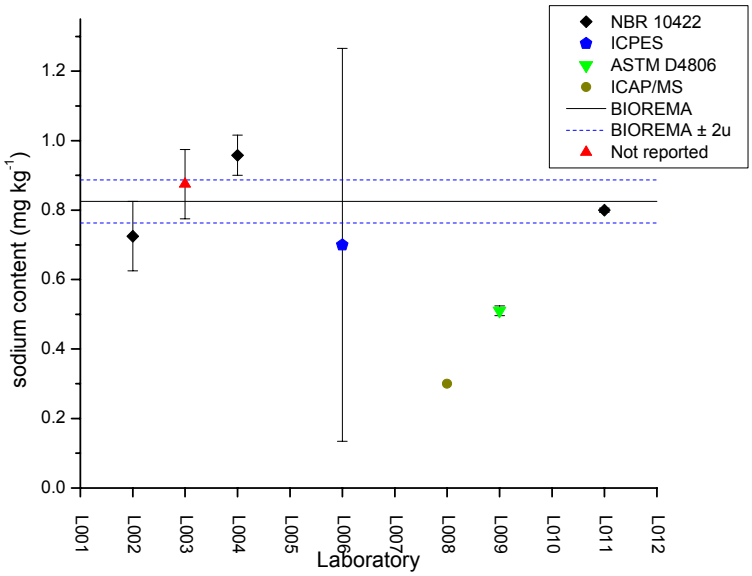

Figure 5: Results for sodium content

No outliers are identified. The dataset is quite heteroscedastic. The consensus value is 0.695 mg/kg, the repeatability standard deviation is 0.072 mg/kg, the between-laboratory standard deviation is 0.231 mg/kg and the reproducibility standard deviation is 0.242 mg/kg. There is good agreement between the consensus and BIOREMA value (0.825 ± 0.062 mg/kg).

3.7 Sulfate content

The results for the sulfate content are shown in figure 6. Only three laboratories out of thirteen reported the results. The visual representation includes the BIOREMA value which was obtained by measuring sulfate content using Ion Chromatography (IC). The reason why few laboratories report results is unknown. A possible explanation is that sulfate content in this biomaterial is lower than specifications values. Participants did not indicate however whether this parameter was below their quantification or detection limit, or below specifications.

Only one participant reports the uncertainty associated with its result.

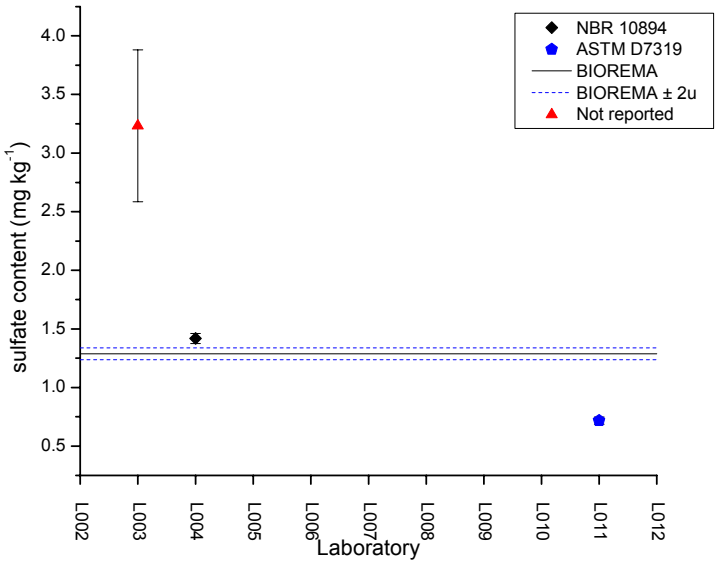

Figure 6: Results for sulfate content

The consensus value is based on all measurements and is 1.79 mg/kg, the repeatability standard deviation is 0.19 mg/kg, the between-laboratory standard deviation is 1.30 mg/kg, and the reproducibility standard deviation is 1.31 mg/kg. There is good agreement between the consensus and the BIOREMA value (1.288 ± 0.051 mg/kg), which is mainly due to the large uncertainty associated with the consensus value.

Because of the poor quality of the few data available, it is not recommended to evaluate the laboratory performance based on the consensus value for this parameter.

3.8 Water content

The results for water content are shown in figure 7. All thirteen laboratories have reported results. The visual representation includes the reference value which was obtained using coulometric Karl Fischer titration..

With one exception, all laboratories reported the method used. Although the methods are widely different, ranging from using density tables to Karl Fischer titration, results are in general well comparable (two results were flagged as outliers and removed from the calculation of the consensus value).

Furthermore, as shown in figure 7, seven results are within the expanded uncertainty of the reference value and four just above the upper uncertainty boundary of the 95% coverage interval, indicating good agreement of the laboratory results with the reference value.

Only three laboratories reported the measurement uncertainties of their results.

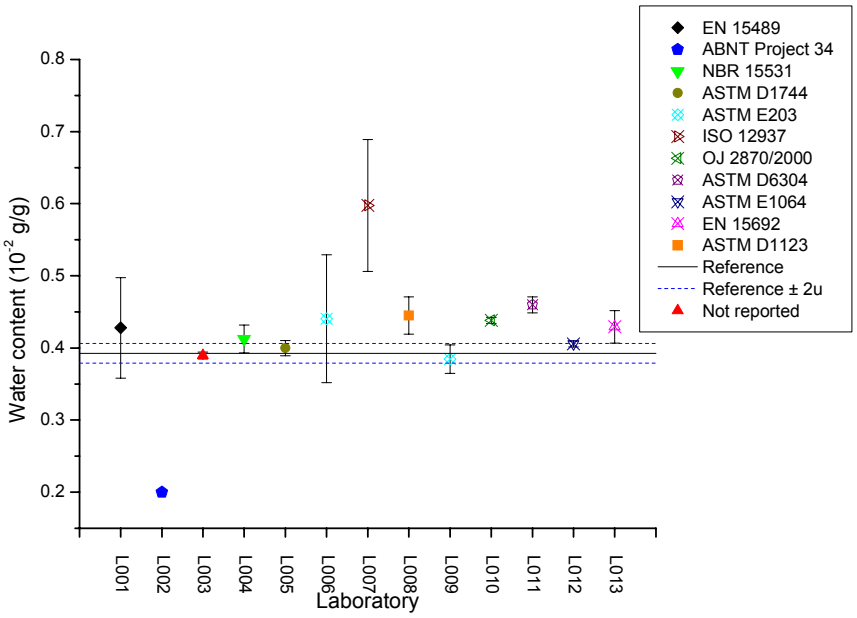

Figure 7: Results for water content

Two results are flagged as outliers (L002 and L007). The consensus value is $0.422 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $0.019 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.023 \cdot 10^{-2}$ g/g and the reproducibility standard deviation is $0.030 \cdot 10^{-2}$ g/g. The consensus value and reference value ($0.393 \pm 0.014 \cdot 10^{-2}$ g/g) agree within their respective uncertainties.

In conclusion, irrespective of the methods used or of the specifications set for water content in the various regions, results of the measurements of the water content in bio-ethanol agree well.

3.9 Ethanol content

The results for ethanol content are shown in figure 8. Eleven of the thirteen laboratories have reported results. The visual representation includes the reference value which was obtained by measuring the ethanol content using Gas Chromatography (GC).

With exception of one laboratory, all labs reported the method used. Like for water content, the results for ethanol content are well comparable (no flagged results for the calculation of the consensus value). Furthermore, as shown in figure 8, all results are within the expanded uncertainty of the reference value, indicating good agreement between laboratory results and the reference value. It is remarkable that also indirect measurements of ethanol, done by conversion of density data into ethanol content (OIML R22) lead to good results.

Only two laboratories reported the measurement uncertainty of their results.

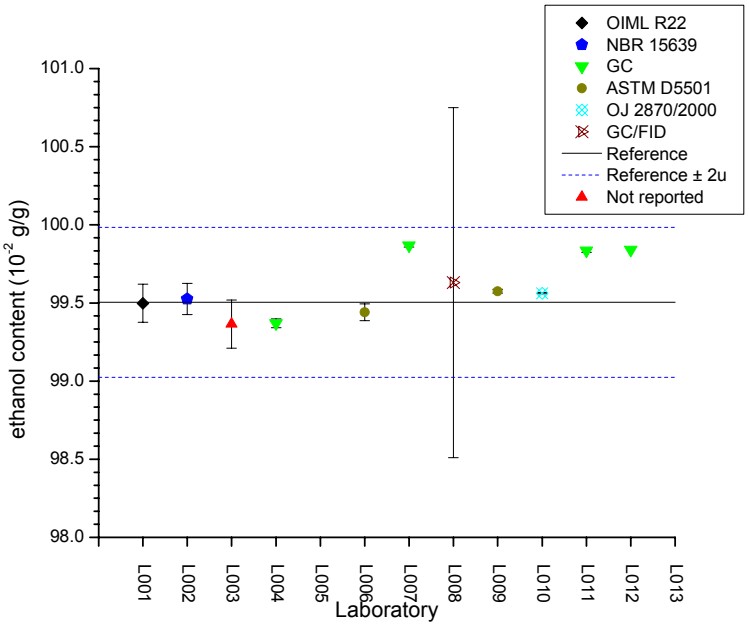

Figure 8: Results for ethanol content

No outliers are found. The consensus value is $99.58 \cdot 10^{-2}$ g/g, the repeatability standard deviation is $0.18 \cdot 10^{-2}$ g/g, the between-laboratory standard deviation is $0.15 \cdot 10^{-2}$ g/g and the reproducibility standard deviation is $0.24 \cdot 10^{-2}$ g/g. The consensus and reference value ($99.50 \pm 0.48 \cdot 10^{-2}$ g/g) agree well.

In conclusion, independent of the method used, measurements of the ethanol content in anhydrous bio-ethanol agree well.

3.10 Acidity

The results for acidity are shown in figure 9. Seven laboratories reported acidity. The visual representation includes the BIOREMA value which was obtained by measuring acidity using volumetric titration with potentiometric end-point detection. With exception of one laboratory, all labs reported the method used. Only two participants reported the uncertainty of the measurement results.

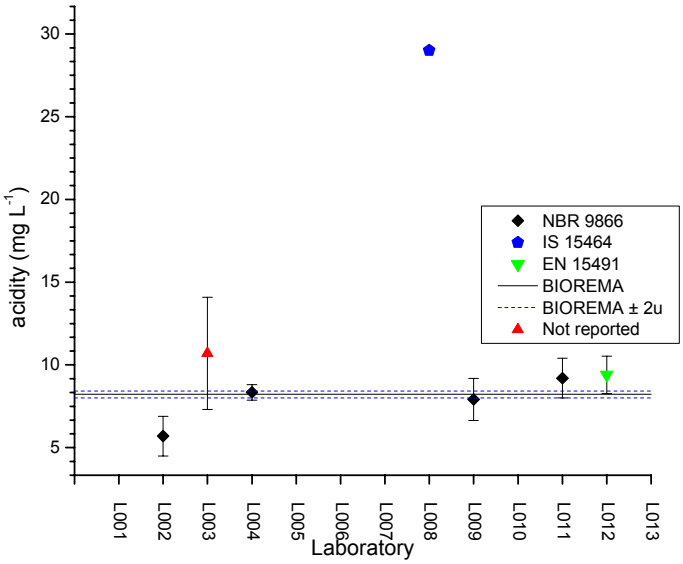

Figure 9: Results for acidity

One result (L008) is flagged as outlier. The consensus value is 8.24 mg/L, based on 6 results. The repeatability standard deviation is 0.69 mg/L, the between-laboratory standard deviation is 1.61 mg/L, and the reproducibility standard deviation is 1.75 mg/L. There is a good agreement between the consensus and BIOREMA value. The good agreement is partly due to the large uncertainty associated with the consensus value.

3.11 Electrolytic conductivity

The results for electrolytic conductivity are shown in figure 10. Five laboratories reported the results. The visual representation includes the BIOREMA value which was obtained by measuring the electrolytic conductivity using a conductivity meter.

For this parameter, four labs used NBR 10547 ”potentiometric method” and one laboratory did not report the method. The spread of the results indicates the difficulty in implementing the same measurement method for electrolytic conductivity. This is probably due to temperature issues. Certainly, the presence of Certified Reference Materials for this parameter would help improving the comparability of the measurement results.

The reason why only few laboratories reported is not known. Possibly this is due to the lack of of EN or ASTM specifications for this parameter. Because more attention is growing in Europe for this parameter (rather pHe) special efforts should be dedicated to in the future to develop non-aqueous reference materials to be used for the quality control of standard methods.

Only two participants reported the uncertainty of the measurement results.

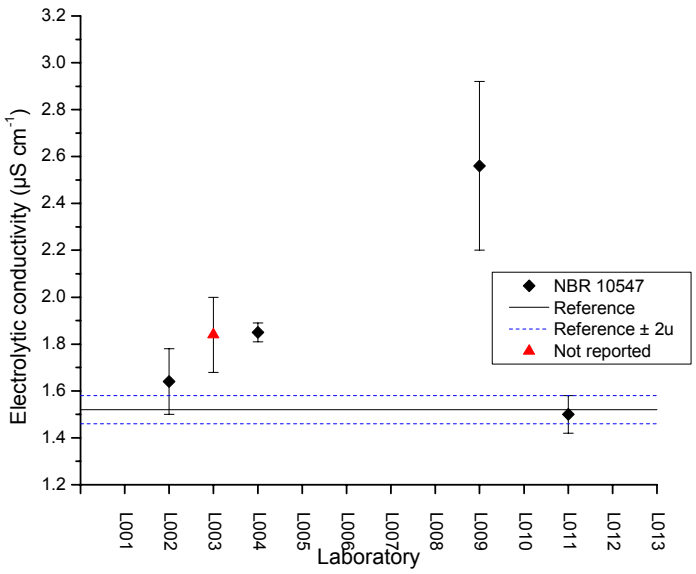

Figure 10: Results for electrolytic conductivity

Among the 5 results, there are no outliers. The agreement between the values is poor. The consensus value for electrolytic conductivity is 1.88 µS/cm, the repeatability standard deviation is 0.10 µS/cm, the between-laboratory standard deviation is 0.40 µS/cm, and the reproducibility is 0.42 µS/cm. The consensus value and BIOREMA value (1.52 ± 0.06 µS/cm) agree, taking into account the appreciable uncertainty associated with the consensus value.

3.12 pHe

The results for pHe are shown in figure 12.

Seven of the thirteen laboratories have reported results and those that measured electrolytic conductivity measured also pHe. The visual representation includes the reference value which was obtained using the ASTM D6423 method. Three participants did not report the measurement methods and the rest used the same method as that used for the assignment of the reference value.

As for electrolytic conductivity, the application of the standard method shows poor reproducibility. In fact, participant's results are spread and not in agreement with the reference value. This effect could be explained by the difficulty in following closely the requirements of the ASTM method. The presence of non-aqueous reference materials for this parameter would facilitate the improvement of the quality of the results.

It must be noted that in Europe, the measurement of pHe is complicated by the fact that the content of water in bio-ethanol, as set in the specifications, is very low. Only one laboratory reported the measurement uncertainty associated with its result.

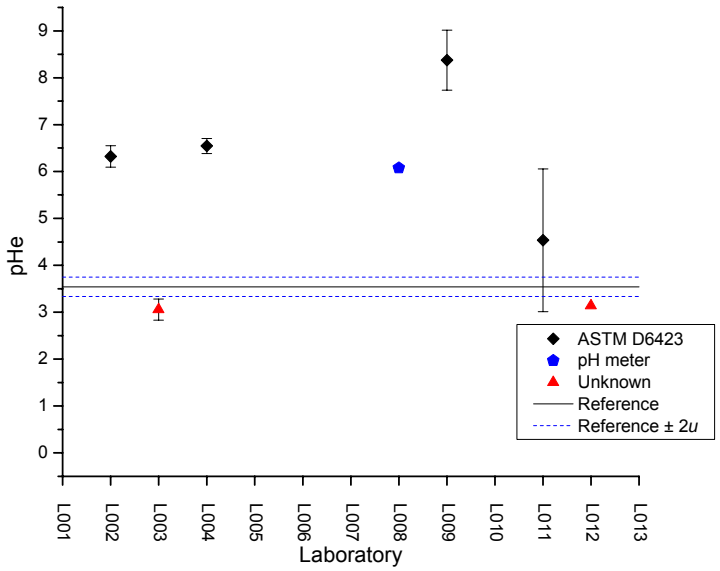

Figure 11: Results for pHe

The dataset for pHe is very poor. Nevertheless, no outliers were identified. The consensus value is 5.709, based on 7 measurement results. The repeatability standard deviation is 0.345, the between-laboratory standard deviation is 1.858 and the reproducibility standard deviation is 1.889. There is a large gap between the consensus value and reference value (3.543 ± 0.207). Furthermore, the between-laboratory and reproducibility standard deviations are unacceptably large.

It should be noted that pH_e shall have a value around 6.5 according to specifications (fiscal reasons). Considering the reference value, the material should have been flagged as "non-compliant" by the field labs. However, some of the laboratories would have identified the material as compliant.

3.13 Density

The results for density are shown in figure 12.

With the exception of L005, participants reported their results, at 20°C. 5 participants did not mention the temperature conditions during measurement (L003, L006, L007, L008, L012) and therefore no clear conclusions could be drawn at the time of evaluation of the data on the fact that two groups of results for density were present. After presentation and discussion of the results at the BIOREMA workshop, those 5 laboratories were asked to provide such information. L003, L006, L007 and L008 reported that their density measurements were carried out at 15°C. Assuming that also L012 has measured at 15 °C, the presence of two groups of results is then explained.

Considering that the distribution of the results at the two measuring temperature was balanced, it should be concluded that special attention has to be paid to the specification of the temperature used to report the density of bio-ethanol. In the evaluation of proficiency testing data such distribution of results may lead to the calculation of meaningless consensus values and inappropriate performance rating.

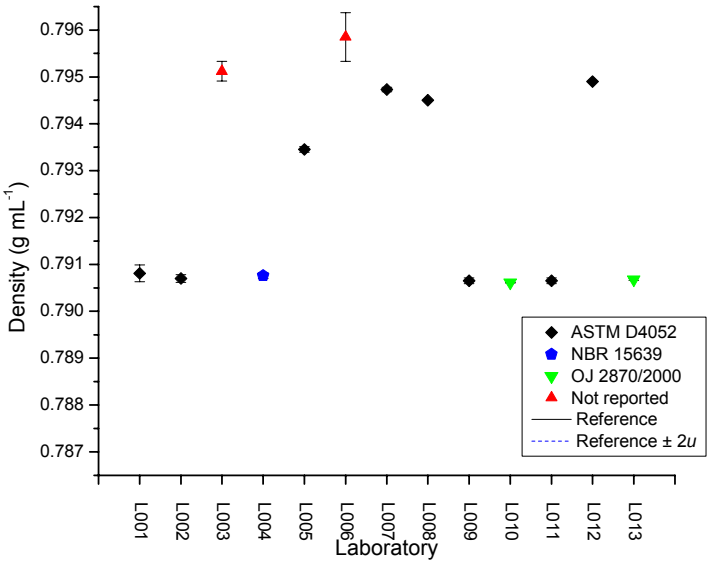

Figure 12: Results for density (complete dataset)

The results can be split into two groups: laboratories L001, L002, L004, L009, L010, L011, and L013 determine the density at 20°C, whereas the others report the density at 15°C. It is worth noting that the results at 15°C scatter substantially more than those at 20°C. This increased scatter is due to the fact that the density measurement at temperatures below room temperature is trickier, because of possible condensation of air moisture in the liquid.

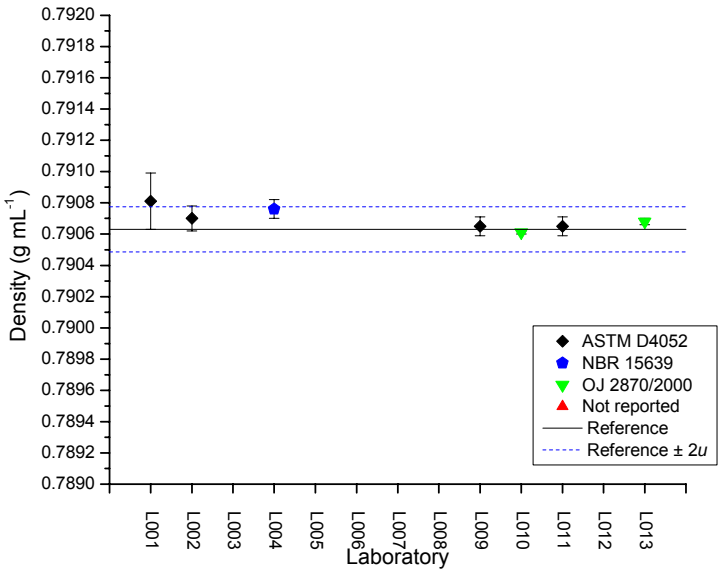

Figure 13: Results for density (20°C)

The consensus value is 0.790693 g/mL, based on 7 laboratories measuring at 20°C. The repeatability standard deviation is 0.000085 g/mL, the between-laboratory standard deviation is 0.000056 g/mL, and the reproducibility standard deviation 0.000101 g/mL. The consensus and reference values(0.790630 ± 0.000144 g/mL) agree well indicating no problems in the measurement of density at this temperature.

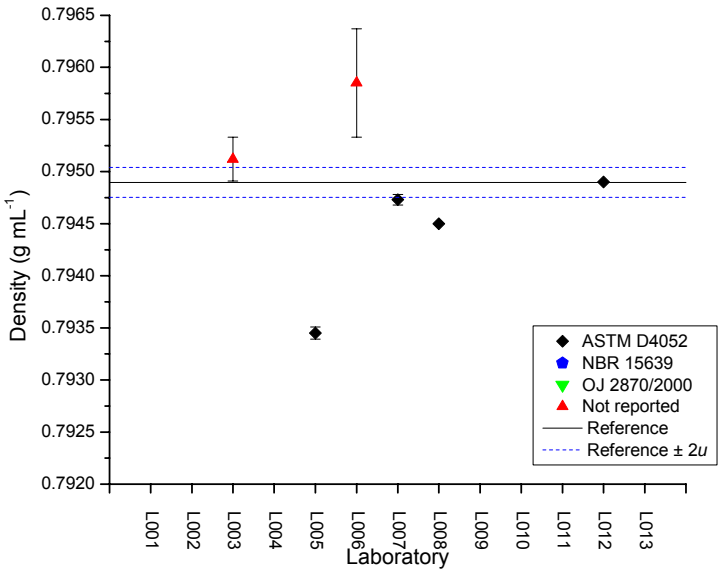

Figure 14: Results for density (15°C)

For the dataset at 15°C, the consensus value is 0.794745 g/mL, the repeatability standard deviation is 0.000245 g/mL, the between-laboratory standard deviation is 0.000818 g/mL and the reproducibility standard deviation is 0.000853 g/mL. All results are based on 6 observations. There is good agreement between the consensus and reference value (0.794900 ± 0.000144 g/mL).

3.14 Consensus values

The consensus values are summarised in table 6.

Table 6: Consensus values after outlier removal

Parameter	Unit	m	p	s_r	s_L	s_R
Iron content #	µg/kg	24.1	4	2.8	11.8	12.1
Copper content	µg/kg	138.8	5	3.2	25.3	25.5
Chloride content #	mg/kg	0.156	3	0.025	0.157	0.159
Sulfur content	mg/kg	2.04	6	0.20	0.53	0.56
Sodium content	mg/kg	0.695	7	0.072	0.231	0.242
Sulfate content #	mg/kg	1.79	3	0.19	1.30	1.31
Water content	10^{-2} g/g	0.422	11	0.019	0.023	0.027
Ethanol content	10^{-2} g/g	99.58	11	0.18	0.15	0.24
Acidity	mg/L	8.24	6	0.69	1.61	1.75
Electrolytic conductivity	µS/cm	1.88	5	0.10	0.40	0.42
pHe		5.71	7	0.35	1.86	1.89
Density (20°C)	g/mL	0.790693	7	0.000085	0.000056	0.000101
Density (15°C)	g/mL	0.794745	6	0.000245	0.000818	0.000853

The consensus value reported for this parameter is based on a very small dataset of poor quality.

4 Conclusions

Only 13 participants provided data resulting in a small data set for evaluation. Further, it appeared that for a number of laboratories the availability of the material was not sufficient for the analysis of all requested parameters. Nevertheless, the evaluation of the measurement results of the BIOREMA ILC for material A “Bio-ethanol fuel” has lead to interesting conclusions.

Many assigned values are based on the result of a single National Metrology Institute (called BIOREMA value, to distinguish them from a ‘true’ reference value), but in most cases, as far as the data permit, it can be concluded that they are in good agreement with the consensus values.

For four parameters of biomaterial A, namely, water, ethanol, pHe and density, it was possible to establish a reference value and an expanded uncertainty.

For the three parameters: density, ethanol and water, the consensus values are in very good agreement with the reference values. Furthermore, the reproducibility standard deviation of the laboratories results for these parameters is in line or even better than the expanded uncertainty of the reference value. These results indicate that laboratories can measure these parameters satisfactorily and no further need for improvement of the measurement methods is identified. Reference materials are of course still needed as a quality control tool for laboratories.

A number of parameters: pH_e, electrolytic conductivity and acidity, where mostly the same measurement method is used, have poor measurement reproducibility. For these specifications there is an urgent need for (Certified) Reference Materials to improve the reproducibility of the measurement methods. As it regards pH_e, the method for the determination of the reference value and the method used by (most of) the participants was the same. Laboratories overestimate pHe appreciably. The main issue concerns however the reproducibility of the participant’s results, which is poor when compared to the expanded uncertainty associated with the reference value.

For sodium and copper, further work should be aiming at the improvement of the reproducibility of the measurement results obtained. The existence of (Certified) Reference Materials could facilitate this work.

For the remaining parameters: iron, chloride and sulfate, too few laboratories reported the measurement data, probably due to the low concentration values in the material. For these parameters no conclusions can be drawn.

In addition, this ILC highlighted the following issues:

1- Density measurement of bio-ethanol is performed by laboratories at 15 °C or 20 °C. Laboratories should clearly specify the temperature used when reporting their results. Furthermore, the measurement of density at 15 °C shows poorer reproducibility when compared to the measurement of the same material at 20 °C.

2- Laboratories, in particular those that have an accreditation as testing laboratory, should be stimulated to report uncertainties of their measurement results. In this scheme, only few accredited laboratories reported their uncertainty estimates.

3- Measurement uncertainties should be properly estimated. In several cases, the order of magnitude of the uncertainties values for the same measured parameters is not comparable.

4- More attention should be paid to the correct use of the measurement units when reporting measurement results.

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