Executive summary

BIOREMA

REference MAterials for BIOfuel specifications

SEVENTH FRAMEWORK PROGRAMME

Introduction

Within the framework of the EU funded BIOREMA (REference MAterials for BIOfuel specifications, FP7 contract grant 219081) project, reference materials for bio-ethanol and biodiesel have been examined. The aim of this project was to demonstrate the feasibility of preparing and characterizing reference materials for biofuels. The focus was on providing SI-traceable reference values for the materials studied. Furthermore, the project has established the current level of measurement capability in the end user community by means of a worldwide interlaboratory comparison using these test materials.

Background

With the introduction of the European Directives on renewable energies (RED 2009/28/EC) and on fuel quality (FQD 2009/30/EC), and with the increasing addition of biological products to gasoline and diesel (e.g. bio-ethanol and biodiesel) the quality of these products becomes more important. There is, however, up to now no international consensus on the technical specifications of biofuels. Neither is it fully clear what measurement standards, reference materials and measurement techniques are needed to support the legislative infrastructure.

Needs

Reference materials for biofuels with well-characterized property values are essential for the development and validation of measurement methods. Also, these materials are an important tool in the quality assurance of routine measurements, and in obtaining reliable, traceable measurement results.

Objectives

The main objective of the project was to establish whether the preparation of biodiesel and bio-ethanol reference materials with traceable reference values was feasible. To that end, test materials were prepared and tested for homogeneity and stability, followed by a value assignment procedure using high-level measurement methods. Additionally, the long-term stability of the reference values has been assessed.

Another important objective of the study was to establish the level of measurement capability of field laboratories. Information on the quality (repeatability, reproducibility, bias of measurement) has been obtained from interlaboratory comparisons that were organized using the characterized test materials.

Summary description of project context and objectives

In the framework of the EU funded project with the acronym BIOREMA, REference MAterials for BIOfuel specifications, test materials for bio-ethanol and biodiesel were examined. The aim was to demonstrate the feasibility of preparing and characterizing reference materials for biofuels. Further, the project established the current quality of measurement practice by means of interlaboratory comparisons using these test materials.

Introduction

With the increased addition of biological products to gasoline and diesel, e.g. bio-ethanol and biodiesel, the quality of these products becomes more important. There is however up to now no international consensus on the technical specifications of biofuel. Neither is it fully clear what measurement standards, reference materials and measurement techniques are needed.

Needs

Reference materials for biofuels with well-characterized reference values are essential for pre-normative research and standardization, *i.e.*, in the development and validation of measurement methods. They are also fundamental during testing to proof reliability and quality of the measurement data.

BIOREMA project

Within the framework of the EU funded BIOREMA (REference MAterials for BIOfuel specifications, FP7 contract grant 219081) project, reference materials for bio-ethanol and biodiesel have been examined. The aim of this project was to demonstrate the feasibility of preparing and characterizing reference materials for biofuels. The focus was on providing SI-traceable reference values for the materials studied. Furthermore, the project has established the current level of measurement capability in the end user community by means of a worldwide interlaboratory comparison using these test materials.

Project partners

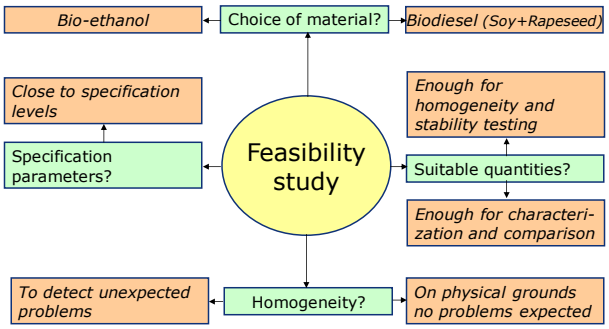
- VSL (the Netherlands), project coordinator
- IRMM (European Commission)
- NPL (United Kingdom)
- Inmetro (Brazil)
- NIST (USA)

Objectives

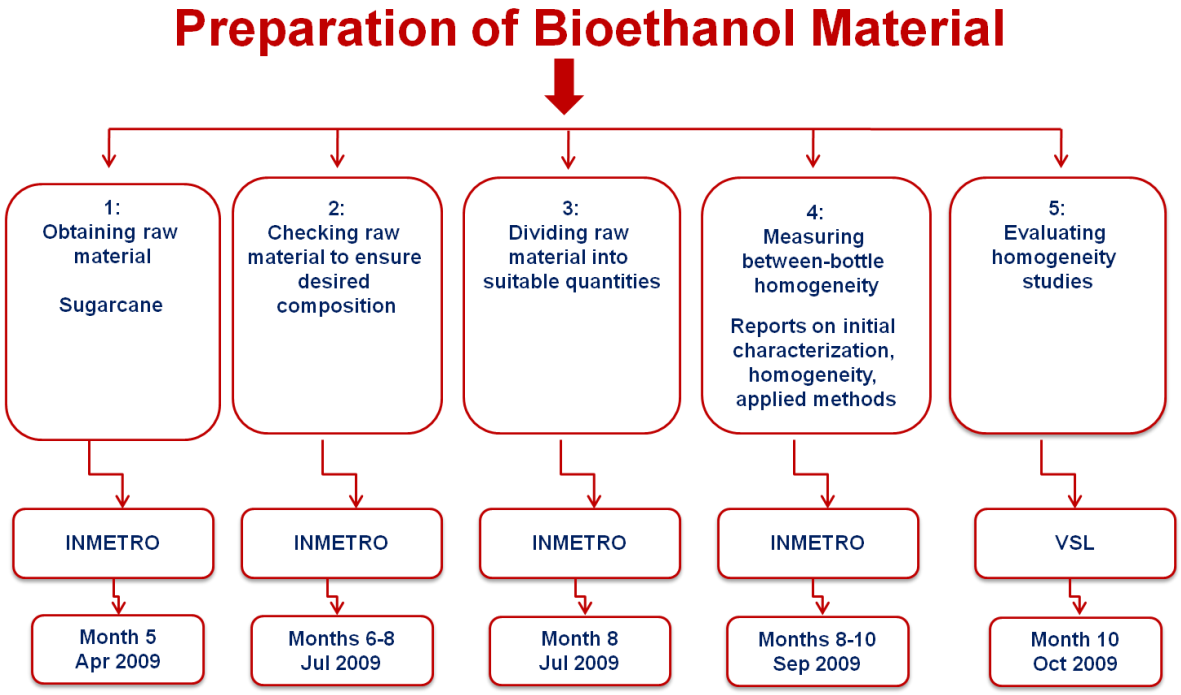
- Feasibility study for the preparation of bio-ethanol and biodiesel reference materials
- Characterization and stability measurements of reference materials
- Establishing the current quality of measurement practice by means of a questionnaire and interlaboratory comparisons

Feasibility study for the preparation of bio-ethanol and biodiesel reference materials

The feasibility study was held from April until October 2009. The next figure gives a schematic overview of the study.



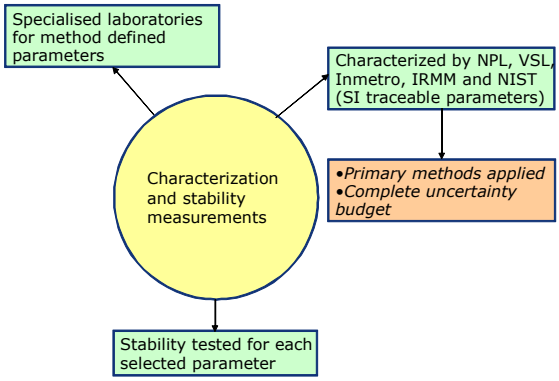
The samples of bio-ethanol from sugar cane (approximately 99.6 % ethanol content) were provided by a Brazilian producer in a 200 L container. The ethanol was bottled in about five thousand amber glass ampoules of 10 mL that had been pre-evacuated with argon and were flame-sealed, and in about one hundred amber glass bottles of 100 mL. The sample preparation was performed by Inmetro.
The test material was subjected to a homogeneity and stability study.



The biodiesel test material was obtained by IRMM (Institute for Reference Materials and Measurements) in the beginning of August 2009. 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. The test material has been subjected to a homogeneity and stability study.

Characterization and stability measurements

The characterization and stability measurements were held from August 2009 until October 2010.



At the start of the project, the characterization study of each analyte was supposed to be performed by at least two project partners in order to obtain at least two independent measured values. In some cases the concentration range of the analyte or the complexity of its measurement did not allow more than one institute to perform the measurement. Each partner performed the characterization of an agreed number of analytes. The characterization of the analyte was based on the measurement of 3 different ampoules. For each ampoule, two independent measurements were performed by using a reference measurement method able to provide SI traceable results. A large volume of solution was needed for the measurement of viscosity and acid value in biodiesel, so more units were combined in order to obtain the required number of independent measurements results.
For a number of parameters (total ester content and glycerides content) a primary method was not available, though it could be developed if joint efforts are made. In this case, a first step towards a metrological approach was made by measuring individual, or a selected group of, analytes representative of the class. The same parameters were also measured according to the appropriate EN test methods to be able to provide an assigned value to be used in the interlaboratory comparison. Furthermore, for a third group of analytes no traceable primary methods exist and currently measurement results may be biased by method dependency. For this group, test methods described in EN or ASTM standards were used. The short-term and long-term stability studies proved that the test materials were stable under the test conditions, except for some parameters.
Therefore it could be shown that it is feasible to produce stable and homogenous reference materials for bioethanol and biodiesel, and that it will be possible to certify such materials for many parameters under discussion.

Establishing current quality of measurement practice by means of a questionnaire and interlaboratory comparisons

Questionnaire
In January 2010, 68 laboratories active in the field of biofuel analyses (57 accredited laboratories in Europe, 4 labs in South America, 4 labs in North America, and 3 labs in Asia) were approached to take part in the

BIOREMA's Biofuel intercomparison mentioned above, that would start May 2010. Later on another 21 laboratories were approached with the same message (11 in Europe, 7 in North America, and 3 in Asia) to further support a worldwide coverage of the potential ILC participation candidates.

Each of the laboratories was asked to answer their willingness in participation in BIOREMA's bio-ethanol and/or biodiesel ILC, together with their interest in the BIOREMA workshop that would deal with the ILC measurement results. Furthermore each laboratory was asked to fill out the BIOREMA questionnaire, which aimed to establish current measurement practices for biofuels and the problems commonly encountered.

The response to the questionnaire was 35% (31 laboratories). Thanks to this high return rate the BIOREMA questionnaire has produced a detailed overview, presenting a lot of information about the types of biofuels most commonly analysed worldwide, the measurement methodologies used for these analyses, whether reference materials are employed, and whether laboratories participate in intercomparison exercises.

Interlaboratory comparisons

The test materials prepared were used in two worldwide interlaboratory comparisons (ILCs), held in 2010. These ILCs covered, apart from the two previously mentioned materials, also two NIST Standard Reference Materials, namely SRM 2772 and SRM 2773. In the bio-ethanol ILC 13 laboratories provided their measurement data. In the biodiesel ILC 26 participants reported data. The objective of the ILCs consisted of gathering information on the current quality of analytical measurements by field laboratories with respect to current biofuel specifications.

BIOREMA Workshop

The BIOREMA Workshop on the measurement of biofuel characteristics was held in the Conference Center Albert Borchette, Brussels, of the European Commission on the 27th of October 2010. The workshop focused on the presentation and discussion of the measurement results of the two world-wide ILCs.
The BIOREMA workshop was attended by ILC participants from Europe, Asia and Brazil. The first session of the workshop was dedicated to the introduction of the BIOREMA project activities and to the experience of the Metrology Institutes in preparing Certified Reference Materials for biofuels. The next two sessions focused on the presentation of the ILC results, where a number of measurement results from field laboratories could be compared with the reference values obtained by the national metrology institutes participating in this project. The presentation part concluded with two field laboratories giving their experiences in measuring bio-ethanol and biodiesel, and the measurement problems they are facing in this field.
A lively discussion followed. Main discussion points dealt with concerned: i) The difficulty of measuring specific parameters such as density, pHe and electrolytic conductivity in bio-ethanol, and FAME content in biodiesel, ii) Needs with respect to "fit for purpose" Certified Reference Materials for biofuel measurements, and iii) Requirements in the ISO/IEC 17025 standard for the accreditation of testing laboratories relative to the quotation of uncertainty estimates in measurement results and to the frequency in participation to ILCs.
A final session, presenting both the results of a questionnaire sent to laboratories and the needs and recommendations identified during the workshop:

- 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 biofuel 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

In general laboratories were pleased with the organization and outcome of the ILCs and workshop. The feed-back received was also positive because participants could exchange contact details and their experience on analyzing biofuels.

Conclusion

The Biorema project has demonstrated the feasibility of preparing and characterizing reference materials for biofuels. However, further research is needed for a number of parameters like EC/pH_e in bio-ethanol and the glycerides in biodiesel. The interlaboratory comparisons have shown that in general the measurement capabilities of field laboratories are good for measuring biodiesel specifications, although the availability (and use) of reference materials certainly would enhance the comparability of measurement results for parameters like flash point, phosphorous content, glycerides and trace metals.

Description of the main S&T results/foregrounds

Although slight delays occurred, the overall progress of the BIOREMA project has been according to the deliverable and milestone schedule.

Work Package 1 "Inventory" had its focus during the second year of the project. All preparations to accomplish the targets set during this second year were performed. The address list of worldwide biofuel laboratories was completed and a questionnaire circulated.

Work Package 2 "Preparation of a bio-ethanol material" led to ampoules with stable and homogeneous bio-ethanol. A problem with bio-ethanol interaction with the cap material of bottled bio-ethanol caused part of the material to be discarded. However, enough material in ampoules was available.

Work Package 3 "Preparation of biodiesel material" took a month extra (and extra material and time) as the first batch did not prove to be stable. The second batch fulfilled the criteria and could be used. The month of delay did not cause any problem as the following steps were carried out a bit faster.

Work Package 4 and Work Package 5 "Characterization and stability measurements of a bio-ethanol and biodiesel reference material" were carried out according to plan as the materials were available and tested on homogeneity and (short term) stability.

Work Package 6 and Work Package 7 "Interlaboratory comparison for the characterization of bio-ethanol and biodiesel" were run in 2010. During the October 2010 BIOREMA Workshop the results were highlighted as well as the results of the stability and characterization study by the BIOREMA partners.

WP 1 Inventory

The objective of this WP was to obtain an overview of i) the specifications of biogas and advanced biofuels, ii) the measurement methods applied for biogas and advanced biofuels and their performance characteristics, and iii) the availability of reference materials for traditional as well as advanced biofuels, including the identification of parameters for which no suitable reference materials exist.
The information abovementioned was gathered by means of a questionnaire, distributed in month 14, to laboratories performing biofuel analyses.
Addresses of these laboratories were gathered trying to achieve a worldwide coverage. A draft questionnaire was developed by the project partners, distributed for the third BIOREMA meeting, and tested by three Brazilian companies involved in biofuel measurements. A modified draft questionnaire was open for suggestions during month 13 and then updated with the suggestions received.

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Europe, 7 in North America, and 3 in Asia) to further support a worldwide coverage of the potential ILC participation candidates.

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The outcome of the questionnaire, deliverable 1.2, was also presented during the October 2010 BIOREMA workshop.

WP 2 Preparation of a bio-ethanol material

The preparation of the bio-ethanol samples, the study of their homogeneity, and the sending of the bio-ethanol samples for characterization were performed by Inmetro.
The samples of bio-ethanol, from the feed stock sugar cane (approximately 99.6 % ethanol content), were provided by a Brazilian producer in a barrel of 200 L. The ethanol was partly bottled in amber glass ampoules of 10 mL (after blanketing with argon) and flame sealed, and partly in amber glass bottles of 100 mL.
The homogeneity study was carried out for the parameters sodium content, copper content, iron content, chloride content, sulphate content, water content, ethanol content, density, pHe, electrolytic conductivity and acidity.
A problem occurred for the determination of the following parameters: acidity, pHe and electrolytic conductivity. These measurements were started, but a colour change (from colourless to yellow) was noticed for the bio-ethanol samples contained in the glass bottles. Due to this problem, probably caused by the cap material used, all the samples in bottles were discarded. The parameters abovementioned were then determined with samples only stored in the ampoules.
The chronogram of the road map was revised related to the period for homogeneity and short-term studies, and this version was sent to all participants of this project.
The results of the homogeneity study, carried out by Inmetro, were sent to VSL for evaluation. Results of the homogeneity assessment have been summarised in deliverable 2.3.
In December 2009 the samples were sent to NIST, LGC and NPL for characterization, in order to perform their measurements until March, 2010.

WP 3 Preparation of biodiesel material

The objective of WP 3 was the preparation of a rapeseed FAME (Fatty Acid Methyl Ester) biodiesel material to be characterized in WP 5 and for use in the intercomparison of WP 7. This objective has been achieved within the duration of the project.

Task 3.1, 3.2 and 3.3:

In month 6 a batch of rapeseed FAME biodiesel was obtained from a biodiesel manufacturer. The material was delivered with a certificate of analysis, indicating that the biodiesel batch

was within specifications of EN 14214. The certificate of analysis also showed that this batch was typical for rapeseed biodiesel, as its specifications were quite similar to that of other batches. The material was further processed at IRMM and filled in amber glass ampoules of 25 mL in month 7. After processing, some deposits were observed in the ampoules. It was decided that this material was unsuitable for further use within the project, as the observed deposits could affect the stability and homogeneity of the material. Immediately a replacement was sought and a new batch of biodiesel was obtained from the manufacturer. Also this batch was within specifications of EN 14214 and typical for a rapeseed biodiesel. With this material 5100 ampoules (2339 units with 20 mL and 2761 units with 25 mL) were filled with one month delay (i.e. month 9) compared to the planning. This month delay caused a shift of one month in the planning of the homogeneity and short-term stability testing; other work was rescheduled to compensate for this delay, by shortening the time allocated to the measurement of the long-term stability samples and the characterisation. By strict adherence to the revised schedule, the delay could be compensated in the further work and did not result in a delay of the intercomparison (WP7) which depended on the timely delivery of the material (see Table 1). The problems with the first batch of the material resulted in additional work to be carried out at JRC for the processing of the second batch and additional resources for the purchase of the additional ampoules.

Table 1: Revised time schedule for the homogeneity, stability and characterisation of the rape seed biodiesel test material

Study	Time table	Storage	Distribution	Measurements	Evaluation
Homogeneity	Old	-	AUG 09	AUG 09	SEP 09
Homogeneity	New	-	SEP 09	SEP 09	OCT 09
Short term stability	Old	AUG 09	SEP 09	SEP 09	OCT 09
Short term stability	New	SEP 09	OCT 09	OCT 09	NOV 09
Long term stability	Old	AUG 09 - JAN 10	FEB 10	FEB - MAR 10	APR 10
Long term stability	New	SEP 09 - FEB 10	MAR 10	MAR 10	APR 10
Characterization	Old	-	NOV 09	NOV 09 - MAR 10	APR 10
Characterization	New	-	DEC 09	DEC 09 - MAR 10	APR 10

Task 3.4 and 3.5:

Almost all measurements required for the homogeneity assessment of the rapeseed test material had been carried out by the project partners and a subcontracted laboratory as foreseen within year 1 of the project except for the parameters methanol, free glycerol and total glycerol. Results for the three parameters had been delayed, caused by a delay in the delivery of the samples to the responsible project partner due to a delay in customs clearance in Brazil. A report containing the homogeneity assessment using the available data up to that point had been submitted to the project coordinator in month 11. The report was amended as

the remaining data became available and was submitted to the project coordinator in month 13. The rapeseed test material was found sufficiently homogeneous for the purpose of the project for the parameters investigated and the project proceeded with the characterisation of the material (WP5). Results of the homogeneity assessment have been summarised in deliverable 3.3.

WP 4 Characterization and stability measurements of a bio-ethanol reference material

The objectives of this WP were i) establishing the feasibility of the production of a bio-ethanol reference material for relevant parameters, ii) establishing the parameters for which reference values can be established and iii) identification of parameters for which research is required.
The start of this WP was month 9 of the project. A start was made identifying the relevant parameters and, for each parameter, two national metrology institutes that have capabilities for obtaining SI-traceable measurement results for the parameters they would be measuring. Furthermore the results of a short term stability study were discussed. Based upon these results it was decided that only the ampoules with numbers 3000 – 5000 could be used for the characterization and stability measurements for all bio-ethanol parameters, including density, water and ethanol content. The ampoules available outside this range could be used for all parameters except water content, ethanol content and density.
As such enough ampoules were available for the characterization and stability measurements.

Characterization study

The bio-ethanol test material, bottled in ampoules containing 10 mL was sent by the material provider (Inmetro) to the project partners for characterisation early December 2009.
The number of samples provided to the partners was enough to allow preliminary test measurements on the materials before characterisation. Where previously agreed, the material supplied would also be measured for stability purposes.
For the characterisation study of ethanol content, water content and density in the bio-ethanol test material only the samples in the ampouling sequence range from 3000 to 5000 were used. Ampoules from the same sequence range would also be used later for the interlaboratory comparison.

The results of the characterisation of test material A (bio-ethanol) are given in Table 2.

The result *y* is given, its associated standard uncertainty, and the number of observations *n*. In most cases, only one result was available. In that case, the BIOREMA value represents the value from the laboratory and the standard uncertainty is calculated from the expanded uncertainty stated by the laboratory. For sulfur, no results were reported. Later on (October 2010) the sulfur value was determined (sub-contract) by LGC (UK).

Table 2: Overview results characterisation bio-ethanol

Parameter	Unit	*y*	*u*(*y*)	*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
Sulfur content	mg/kg	2.73	0.3	1	laboratory result
Chloride content	mg/kg	0.09598	0.00115	1	laboratory result
Sulphate content	mg/kg	1.288	0.014	1	laboratory result
Water content	wt-%	0.3926	0.0017	3	weighted mean
Ethanol content	wt-%	99.504	0.076	2	weighted mean
Electr. conductivity	µS/cm	1.520	0.026	1	laboratory result
Density (at 20°C)	g/mL	0.790630	0.000017	2	weighted mean
pHe	1	3.543	0.094	2	weighted mean
Acidity	mg KOH/L	8.216	0.101	1	laboratory result

For most of the parameters in the characterisation of bio-ethanol, only one result was available. For those parameters, for which multiple results were available, these results are consistent within their respective uncertainties. These reference values (water content, ethanol content, density and pHe) are weighted means. The associated standard uncertainties have been obtained by duly propagating the uncertainties stated with the results from the participating laboratories.

Results of the characterization measurements have been summarised in deliverable 4.1

Short-term stability study

The short-term stability study of test material A (bio-ethanol) in the BIOREMA project was carried out using the isochronous design. In this design, all measurements are taken under repeatability conditions, providing more definitive results. In order to further enhance the performance of the design, generalised distance regression was used for the trend analysis, which provides results with smaller uncertainties at no extra cost.
The material is unstable in the short-term for electrolytic conductivity and to a lesser extent for pHe. For the contents of copper, sodium, chloride, iron, sulphate, water, and ethanol as well as for density and pHe, the material is stable for 28 days at 50°C. The recommended temperature for transport is the reference temperature, 4°C.

The results of this short-term stability study are summarised in Table 3.

Table 3: Summary of results of the short-term stability study

Parameter	Result trend analysis		
	k = 2	*t*(95%)	*t*(99%)
Chloride content	Trend (k=2)	No trend	No trend
Copper content	No trend	No trend	No trend
Iron content	Trend (k=2)	No trend	No trend
Sulphate content	No trend	No trend	No trend
Water content	No trend	No trend	No trend
Ethanol content	No trend	No trend	No trend
Density	No trend	No trend	No trend
pHe	Trend (k=2)	Trend (95%)	No trend
Acidity	Trend (k=2)	No trend	No trend
Electrolytic conductivity	Trend (k=2)	Trend (95%)	Trend (99%)
Sodium content	No trend	No trend	No trend

The material is fairly stable under the harsh conditions of this short-term stability study, except for electrolytic conductivity and to a lesser extent, pHe.

The results of the (short term) stability study have been summarized in deliverable 4.2.

Long-term stability study

The results of the long-term stability study are summarised in Table 4.

Table 4: Summary of results of the long-term stability study

Parameter	Result trend analysis			Verdict
	k = 2	*t*(95%)	*t*(99%)	
Chloride content	Trend (k=2)	Trend (95%)	Trend (99%)	Unstable
Copper content	Trend (k=2)	Trend (95%)	Trend (99%)	Stable
Iron content	Trend (k=2)	No trend	No trend	Stable
Sulfate content	Trend (k=2)	Trend (95%)	Trend (99%)	Stable
Water content	Trend (k=2)	Trend (95%)	Trend (99%)	Stable
Ethanol content	Trend (k=2)	Trend (95%)	Trend (99%)	Stable
Density	Trend (k=2)	Trend (95%)	No trend	Stable
pHe	No trend	No trend	No trend	Stable
Acidity	No trend	No trend	No trend	Stable
Electrolytic conductivity	Trend (k=2)	Trend (95%)	Trend (99%)	Stable
Sodium content	No trend	No trend	No trend	Stable

The material is stable under the conditions of this long-term stability study, except chloride.

The results of the long term stability study have been summarized in deliverable 4.2a.

WP 5 Characterization and stability measurements of a FAME biodiesel reference material

The objective of WP 5 was to investigate the feasibility of producing a rapeseed FAME biodiesel reference material. The stability of the test material produced in WP 3 has been investigated and the material has been characterized for a range of parameters.

Task 5.1:

The distribution of measurement tasks for the characterization was agreed with the project partners. The sulfur measurements have been subcontracted by the project coordinator. The execution of task 5.1 started in month 13, and the last results of the characterisation were received by IRMM in month 19. Results of the characterization have been reported in deliverable 5.1 which was finally sent to the coordinator, with 2 months delay, in month 19.

Task 5.2:

The samples for the assessment of the short term stability have been subjected to a 4 week isochronous storage scheme to test the influence of different temperatures which may occur during transport of the material. After the finalisation of this isochronous storage scheme the samples have been dispatched to the project partners in the beginning of month 11. Measurement results were due after 4 weeks, at the end of month 11. Most results were received in due time except for methanol, free glycerol, total glycerol and viscosity. Those results were received with some delay. Suitable dispatch conditions could be established for all parameters investigated.

The long term stability (i.e stability during storage) was assessed in a 6 month isochronous storage scheme which finished in month 15. Samples were dispatched to the project partners for measurements in the beginning of month 16 and results were received by the end of month 16, as planned. Evaluation of the data obtained allowed to draw conclusions about the stability of the produced rapeseed material during the time scale needed for the project. Results of the long term stability are reported in deliverable 5.2 and an additional report on the short term stability study was submitted.

Results of WP3 (homogeneity study), and WP5 (characterization and stability study), are summarised and evaluated in the milestone 5 report "Feasibility of the production of certified reference materials for FAME characterisation". This report was submitted after the finalisation of the characterization study (deliverable 5.1) in month 21 (with some delay due to the delay of deliverable 5.1) and revised again at the end of the project to include further insights and findings.

WP 6 Interlaboratory comparison for the characterization of bio-ethanol

The objective of the BIOREMA bio-ethanol interlaboratory comparison was to compare measurement results from testing laboratories with reference values obtained during this project. The emphasis in this interlaboratory comparison was therefore not on the performance rating of the laboratories, but in recognising and interpreting systematic differences if they occurred. The information gathered about the methods used was 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, 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 for quality control purposes as well as improving the precision and trueness during method validation.

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 was not comparable.

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

The results of the interlaboratory comparison have been summarized in deliverable 6.1.

WP 7 Interlaboratory comparison for the characterization of biodiesel

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

The results of the interlaboratory comparison have been summarized in deliverable 7.1.

Potential impact

With the introduction of the European Directives on renewable energies (RED 2009/28/EC) and on fuel quality (FQD 2009/30/EC), and with the increasing addition of biological products to gasoline and diesel (e.g. bio-ethanol and biodiesel) the quality of these products becomes more important. There is, however, up to now no international consensus on the technical specifications of biofuels. Neither is it fully clear what measurement standards, reference materials and measurement techniques are needed to support the legislative infrastructure.
Reference materials for biofuels with well-characterized property values are essential for the development and validation of measurement methods. Also, these materials are an important tool in the quality assurance of routine measurements, and in obtaining reliable, traceable measurement results.
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.

BIOREMA Questionnaire

The response to the BIOREMA questionnaire was 35% (31 laboratories). Thanks to this high return rate the BIOREMA questionnaire has produced a very detailed overview, presenting a lot of information about the types of biofuels most commonly analysed worldwide, the measurement methodologies used for these analyses, whether reference materials are employed, and whether laboratories participate in intercomparison exercises. The majority of the measurement methods used is EN standard methods. However, because most of the questionnaire submitters are based in Europe, the questionnaire results may be biased. From the questionnaire results it appears that the participation in Interlaboratory Comparisons (ILCs) is good practice and there is a good correlation between ILC participation and measurement frequency of the various specifications. As it regards the use of SI traceable (Certified) Reference Materials (CRMs), there is a clear request for suitable CRMs for biodiesel for most of the measured specifications and for bio-ethanol for some of them. In general, laboratories use different commercial reference materials or biofuel from previous interlaboratory comparisons whose specifications are known.

BIOREMA Workshop

The BIOREMA Workshop was attended by 31 persons in total.
Biofuel field laboratories from the following countries attended the workshop:

- Brazil
- India, Thailand
- Belgium, France, Germany, Greece, The Netherlands, Spain, Sweden, Turkey, United Kingdom

The Agenda of the BIOREMA workshop can be found on the next pages.

BIOREMA Workshop 2010
27th of October 2010
Brussels, Belgium

European Commission
Room AB-4A, Centre Albert Borschette
rue Froissart 36, 1040 Brussels

PROGRAMME

08:30 - 09:00	Registration	
09:00 - 10:30	Session 1	
	09:00 - 09:10	Welcome by Kyriakos Maniatis, DG ENER, European Commission
	09:10 - 09:30	Introduction of the Biorema project - Annarita Baldan (VSL)
	09:30 - 10:30	Production of biofuel Reference Materials used for the ILCs
		09:30 - 09:50 Bio-ethanol RMs – Romeu Daroda (Inmetro)
		09:50 - 10:15 Biodiesel RMs – Manuela Buchgraber (IRMM)
		10:15 - 10:30 NIST Biodiesel CRMs – Michele Schantz (NIST)
10:30 - 11:00	Coffee break	
11:00 - 12:15	Session 2	
	11:00 - 12:15	ILC Bio-ethanol measurement results & discussion
		Chair: Romeu Daroda (Inmetro)
		Rapporteur: Paul Brewer (NPL)
		11:00 - 11:25 Presentation of ILC bio-ethanol results – Valnei Cunha (Inmetro)
		11:25 - 11:35 Experiences in measuring bio-ethanol – Juliana Belincanta (PETROBRAS – CENPES; Brazil)
		11:35 - 12:15 Discussion
12:15 - 13:15	Lunch break	
13:15 - 15:15	Session 3	
	13:15 - 15:15	ILC Biodiesel measurement results & discussion
		Chair: Hendrik Emons/Andrea Held (IRMM)
		Rapporteur: Gavin O'Connor (LGC)
		13:15 - 14:00 Presentation of ILC biodiesel results – Manuela Buchgraber (IRMM)
		14:00 - 14:10 Experiences in measuring biodiesel – Klaus Redlich (ASG Analytik – Service GmbH; Germany)
		14:10 - 15:15 Discussion
15:15 - 15:45	Coffee break	
15:45 - 17:00	Session 4	
	15:45 - 16:05	Presentation of Questionnaire results - Hugo Ent (VSL)

	16:05 - 16:10	Main issues and problems identified in Session 2 – Paul Brewer (NPL)
	16:10 - 16:15	Main issues and problems identified in Session 3 – Gavin O'Connor (LGC)
	16:15 - 16:50	Needs and recommendations – Annarita Baldan (VSL)
	16:50 - 17:00	Conclusion and point of view of the European Commission regarding biofuel developments - Kyriakos Maniatis (EC)
17:00 - 18:00	Closure and farewell drinks	

Press release

After the BIOREMA Workshop the following press release was publicised:

The BIOREMA Workshop on the measurement of biofuel characteristics was held in the Brussels' Conference Center of the European Commission on the 27th of October 2010. The BIOREMA Workshop concluded the two-year EU funded 7th Framework project "Reference Materials for Biofuels Specifications" BIOREMA (grant agreement 219081).
The workshop was organized by the JRC Institute of Reference Materials and Measurements (IRMM) of the European Commission in cooperation with the following National Metrology Institutes: VSL, The Netherlands; Inmetro, Brazil; NIST, USA; NPL, UK; and LGC, UK.
The workshop focused on the presentation and discussion of the measurement results of two world-wide biofuel interlaboratory comparisons (ILCs) held in 2010.
The objective of the ILCs consisted of gathering information on the current quality of analytical measurements by field laboratories with respect to current biofuel specifications. Therefore two homogenous and stable materials were prepared and characterized within the BIOREMA project: a sugar cane based bioethanol – E100 and a rapeseed based FAME – B100. Furthermore NIST provided two biodiesel Standard Reference Materials which were also used in the biodiesel ILC.
The BIOREMA workshop was attended by ILC participants from Europe, Asia and Brazil. The first session of the workshop was dedicated to the introduction of the BIOREMA project activities and to the experience of the Metrology Institutes EC-JRC-IRMM, Inmetro and

NIST in preparing Certified Reference Materials for biofuels. The next two sessions focused on the presentation of the ILC results, where a number of measurement results from field laboratories could be compared with the reference values obtained by the national metrology institutes participating in this project. The presentation part concluded with two field laboratories giving their experiences in measuring bioethanol and biodiesel, and the measurement problems they are facing in this field.
A lively discussion followed. Main discussion points dealt with concerned:

- The difficultly of measuring specific parameters such as density, pHe and electrolytic conductivity in bioethanol, and FAME content in biodiesel
- Needs with respect to “fit for purpose” Certified Reference Materials for biofuel measurements
- Requirements in the ISO/IEC 17025 standard for the accreditation of testing laboratories relative to the quotation of uncertainty estimates in measurement results and to the frequency in participation to ILCs.

A final session, presenting both the results of a questionnaire sent to laboratories and the needs and recommendations identified during the workshop concluded the workshop. In general laboratories were pleased with the organization and outcome of the ILCs and workshop. The feed-back received was also positive because participants could exchange contact details and their experience on analyzing biofuels. This event gave a good opportunity to discuss the measurement issues of field laboratories and define needs for future investigations.
The workshop presentations, the ILC reports of the measurement results of bioethanol and biodiesel, and the report on the questionnaire results will be available online soon.

Annarita Baldan,
Chair of BIOREMA
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Needs & recommendations identified during 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

BIOREMA Presentations

Besides Powerpoint presentations about the BIOREMA project, a flyer, and a Press Release after the BIOREMA Workshop, also two posters were prepared, e.g. for the conference "The Future of Reference Materials - Science and Innovation", IRMM, Geel (Belgium), 23 - 25 November 2010.

Follow-up

It is intended to continue the “BIOREMA activities” in this field, e.g. in the EMRP projects on biofuels and biogas.
A presentation of the results of the BIOREMA Bio-ethanol and Biodiesel interlaboratory comparisons was given to CEN members during the CEN TC 19 WG24 “Specification of automotive diesel” meeting in Rotterdam, held the 30th of November 2010.
Furthermore the outcome of the BIOREMA project is intended to be published in peer reviewed articles.

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