19ENG09 BIOFMET

D5: Report on certification of liquid and solid biofuel reference materials

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BIODIESEL
UME BIOFMET CRM 01

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ABBREVIATIONS

ANOVA	analysis of variance
α	significance level
BAM	Bundesanstalt für Materialforschung und -prüfung, Germany
BRML-INM	National Metrology Institute, Bucharest, Romania
CRM	certified reference material
DTI	Danish Technological Institute, Denmark
EMPIR	European Metrology Programme for Innovation and Research
FAME	Fatty Acid Methyl Ester
GUM	Central Office of Measures, Poland
HR ICP-MS	High resolution ICP-MS
ICP-MS	Inductively coupled plasma mass spectrometry
ID MS	Isotope Dilution Mass Spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IMBIH	Institute of Metrology, Sarajevo, Bosnia and Herzegovina
IS	internal standard
ISO	International Organization for Standardization
LGC	LGC Paragon Scientific Ltd. Prenton, Wirral, United Kingdom
$MS_{between}$	mean square between-bottle from ANOVA
MS_{within}	mean square within-bottle from ANOVA
n	number of replicates per unit
QC	quality control
PTB	Physikalisch Technische Bundesanstalt, Braunschweig, Germany
RME	rapeseed methyl ester
RSD	relative standard deviation
s	standard deviation
s_{bb}	between-bottle standard deviation
SGT	single Grubbs' test
SI	International System of Units
SME	soy methyl ester
s_{wb}	within-bottle standard deviation
U_{AV}	expanded uncertainty of assigned value
u_{bb}	standard uncertainty related to possible between-bottle heterogeneity
u^*_{bb}	standard uncertainty of heterogeneity that can be hidden by method repeatability
U_{CRM}	expanded uncertainty of certified value
UME	TÜBİTAK National Metrology Institute, Türkiye
u_{char}	standard uncertainty related to characterisation
u_{lts}	standard uncertainty related to long term stability

The subscript "rel" is added when a variable is expressed in relative terms (e.g. as percent)

ABSTRACT

Biomass is a key element in biofuels. It can be defined as a fuel produced through contemporary biological processes, and its increased use can support the EU's aims of reducing greenhouse gas emissions. Information on the nature and the quality of the biomass or biofuel is important in order to support the optimization of their combustion with respect to realizing higher efficiencies and lower emissions during energy production.

BIOFMET project aims to establish advanced traceable measurement standards for the determination of the calorific value and impurities.

This report describes the production of a biodiesel reference material: UME BIOFMET CRM 01, certified for calorific value, density, viscosity and mass fractions of Ca, K, Mg, Na, P, S elements. The material was produced in accordance with requirements of ISO 17034 standard.

The raw material for the CRM is Biodiesel (B100 composed of 80% RME [rapeseed methyl ester] and 20% SME [soy methyl ester]) which was produced in Romania. The material was spiked with Ca, K, Mg, Na, P standards in mineral oil.

Homogeneity and stability of the material were assessed in accordance with ISO Guide 35. The material was characterized by an interlaboratory comparison among competent laboratories.

Uncertainties of the certified values were calculated in accordance with GUM "Guide to the Expression of Uncertainty in Measurement" and includes characterization, homogeneity, stability components.

The material is intended for method development and validation in determination of calorific value, density, viscosity and mass fractions of Ca, K, Mg, Na, P, S elements and for quality control purposes. The CRM is available in glass bottles containing approximately 500 mL of material.

INTRODUCTION

Energy has a crucial role in life which is needed for heating, lighting, cooking in households and for every transport activity. Fossil fuels (coal, gas, and oil) currently account for about 79% of world energy consumption, nuclear energy for 7%, and renewable energy sources for 14% [1]. One of the renewable energy source is biomass and a definition adopted by EU legislation for biomass is "the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries". When biomass is burned or digested, the organic carbon is recycled in a global process known as the carbon cycle. In this process, the CO_2 that was absorbed as the plants grew is simply returned to the atmosphere when the biomass is burned. Therefore, if the growth and harvest cycle is maintained, there will be no net release of CO_2, therefore biomass is regarded as a carbon neutral energy source that does not emit CO_2 into the atmosphere when burned. Biomass can be used as feedstock for energy production either by direct combustion or through conversion to biofuels such as biodiesel, ethanol or biogas.

Biodiesel is produced by a chemical process called the esterification of fatty acids produced from vegetable oils. Rapeseed oil is the most commonly used feedstock for the production of biodiesel whereas sunflower oil or used cooking oils are also used as feedstock. All diesel engines can run on biodiesel or blends of biodiesel with normal diesel. Emissions of carbon dioxide are less for biodiesel than they are for fossil fuel diesel. Emissions of hydrocarbons and soot are also lower for biodiesel than for fossil-fuel-derived diesel. In addition, biodiesel releases fewer solid particles and, because it contains less sulfur, does not create too much SO_2, which contributes to acid rain.

FAME (Fatty Acid Methyl Ester) is the generic chemical term for biodiesel derived from renewable sources. Relevant characteristics, requirements and test methods for FAME to define the product to be used as automotive diesel fuel and in heating applications are given in EN 14214:2012+A2:2019 standard [2].

Laboratories performing sampling and tests in this field need matrix CRMs enabling appropriate quality control. National metrology institutes and designated institutes with proven metrological capabilities for the production and certification of such materials are necessary for the provision of quality data. The EMPIR joint research project BIOFMET [3] developed capacity to produce CRMs for biofuel analysis by transferring the theoretical and practical know-how between the partners and combining their skills to focus on biofuel CRM production according to ISO 17034:2016 [4] and ISO Guide 35:2017 [5].

UME BIOFMET CRM 01, the production of which was carried out by a project consortium described in this report, is intended to be used as a quality assurance and quality control tool especially by the laboratories involved in the quality control of the biodiesel used for automotive diesel fuel and in heating applications.

The parameters aimed to be certified in UME BIOFMET CRM 01 are the following: calorific value, density, viscosity, water and mass fractions of Ca, K, Mg, Na, P, S elements. The target concentration levels for elements were decided to meet laboratories' needs.

PARTICIPANTS

Laboratory/organizations involved in the production and their contributions are presented in Table 1.

Table 1. Laboratory/organisations involved and their contributions

Activity	Laboratory / Organization
Project management and data evaluation	TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye
Preliminary measurements	TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye
Processing	TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye
Homogeneity and Stability studies	PTB, Physikalisch Technische Bundesanstalt, Braunschweig, Germany BRML-INM, National Metrology Institute, Bucharest, Romania IMBIH, Institute of Metrology of Bosnia and Herzegovina, Sarajevo, Bosnia and Herzegovina TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye
Characterization Study (in alphabetical order)	BAM - Bundesanstalt für Materialforschung und prüfung, Berlin, Germany BRML-INM, National Metrology Institute, Bucharest, Romania DTI-Danish Technological Institute, Aarhus, Denmark GUM - Central Office of Measures, Warszawa, Poland

Activity	Laboratory / Organization
Characterization Study (in alphabetical order)	IMBIH, Institute of Metrology of Bosnia and Herzegovina, Sarajevo, Bosnia and Herzegovina
	LGC Paragon Scientific Ltd. Prenton, Wirral, United Kingdom
	PTB, Physikalisch Technische Bundesanstalt, Braunschweig, Germany
	TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye

MATERIAL PROCESSING

The raw material for the CRM Biodiesel (B100 composed of 80% RME [rapeseed methyl ester] and 20% SME [soy methyl ester]) was produced in Romania. Collected samples (total of 350 Liters in 70 x 5-liter metal canisters) were transported from Romania to TÜBİTAK UME for further processing.

For preliminary elemental content measurements, subsamples from 3 different canisters were taken and analyzed by TÜBİTAK UME. Results of this measurement are summarized in Table 2.

Table 2. Mass fraction levels of elements in biodiesel material

Parameter	Preliminary Measurement Result (mg/kg)	Target Range Level (mg/kg)
Ca	0.036	0.5-2.5
K	0.15	0.5-2.5
Mg	0.0023	0.2-1.0
Na	0.33	1.0-5.0
P	0.56	1.0-5.0
S	6.47	6.5-10

Results showed that the candidate raw material has low level of the target elements except sulfur, thus it was decided to spike calcium, potassium, magnesium, sodium and phosphorus elements to this material to reach target levels.

Material in canisters were filtered (0.7 µm, glass fiber) and combined in homogenization tank (320 L, HDPE). Spike mixture (prepared from Ca, K, Mg, Na and P element standards in mineral oil, Conostan) was added and the tank was filled with filtered biodiesel. Homogenization is performed by drawing and filling the content to the tank.

Filling and capping were done manually. A total of 553 units, each ~500 mL was filled and capped to amber colored glass bottles. All bottles were labelled following the filling order using automated labelling machine (Farmatek, Türkiye).

After this step, the bottles were stored at 4 °C in the dark. All stages of processing are summarized as a flow diagram in Annex 1. Details of the processing is also documented as a video: https://www.youtube.com/watch?v=DDnfvmhP20Y

HOMOGENEITY

Homogeneity study between the units is performed to show that the assigned values are valid for all units within the stated uncertainty. Homogeneity study between the units is performed with a number of samples representing the whole batch. In this project, 10 units were selected by using random stratified sampling for each of the participant laboratories. Homogeneity tests were carried out by measuring 2 or 3 sub-samples under repeatability conditions. The samples to be analysed were introduced to the instruments by random order to find out any trend arising from analytical and/or filling sequences. For Ca, Mg and P, data supplied for homogeneity samples by BRML was evaluated as technically invalid due to high variance on some of the individual units. Alternatively short-term stability sample data was used to evaluate the homogeneity of these parameters.

Grubbs test (one sided) was applied to all data for the presence of outlier at 99% confidence level and outliers were detected for two parameters. Two of the outliers detected for one parallel measurement result out of three measurements of one unit for Tri-Glycerides and density parameters are excluded from the calculations. Data was visually checked whether all individual data follow a unimodal distribution using histograms and normal probability plots. It was found that the distribution was normal and unimodal. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations. The results of all statistical evaluations are given in Table 3.

Table 3. Statistical Evaluation of Homogeneity Results for Biodiesel

Parameter	Is there a Trend?		Number of Outliers		Distribution
(Lab)	Analytical sequence	Filling sequence	All data	Unit averages	All data
Calorific Value (PTB)	No	No	-	-	Normal/unimodal
Mono-Glycerides (BRML)	No	No	-	-	Normal/unimodal
Di-Glycerides (BRML)	No	No	-	-	Not Normal/unimodal
Tri-Glycerides (BRML)	No	No	2	-	Not Normal/unimodal
Free Glycerol (BRML)	No	No	-	-	Normal/unimodal
Total Glycerol (BRML)	No	No	-	-	Not Normal/unimodal
Methyl Linoleate (IMBIH)	No	No	-	-	Normal/unimodal
Methyl Palmitoleate (IMBIH)	No	No	-	-	Normal/unimodal
Methyl Palmitate (IMBIH)	No	No	-	-	Normal/unimodal
Methyl 11-Octadecenoate (IMBIH)	No	No	-	-	Not Normal/unimodal
Methyl Stearate (IMBIH)	No	No	-	-	Normal/unimodal
Methyl cis-11-Eicosenoate (IMBIH)	No	No	-	-	Normal/unimodal

Table 3. (Continued) Statistical Evaluation of Homogeneity Results for Biodiesel

Parameter (Lab)	**Is there a Trend?**		**Number of Outliers**		**Distribution**
	Analytical sequence	**Filling sequence**	**All data**	**Unit averages**	**All data**
Calcium (BRML)	No	No	-	-	Normal/unimodal
Magnesium (BRML)	No	No	-	-	Not Normal/unimodal
Phosphorus (BRML)	No	No	-	-	Not Normal/unimodal
Potassium (BRML)	No	No	-	-	Normal/unimodal
Sodium (BRML)	Yes	No	-	-	Normal/unimodal
Sulfur (BRML)	No	No	-	-	Normal/unimodal
Viscosity (PTB)	No	No	-	-	Normal/unimodal
Density (PTB)	No	No	3	1	Normal/unimodal
Methanol (TÜBİTAK UME)	Yes	No	-	-	Normal/unimodal
Water (TÜBİTAK UME)	No	No	-	-	Normal/unimodal

Regression analyses were used to evaluate potential trends in each analytical run at 95% and 99% confidence levels. It is observed that there was significant analytical trend at 95% confidence level for the measurements of Na and Methanol. As the analytical sequence and the unit numbers were not correlated, mathematical correction of the dataset for the significant analytical trend of the measurements was performed using the Equation (1) where trends were significant:

$$C_{Corrected} = C_{Measured} - b \cdot i \quad (1)$$

where;

b : slope of the linear regression,

i : position of the result in the analytical sequence.

The ANOVA allowed the calculation of the within- (s_{wb}) and between-unit homogeneity (s_{bb}), estimated as standard deviations, according to the equations (2) and (3):

$$s_{wb} = \sqrt{MS_{within}} \quad (2)$$

MS_{within} : Mean squares within-unit

s_{wb} is equivalent to the s of the method, provided that subsamples are representative for the whole unit.

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (3)$$

$MS_{between}$: Mean squares between-unit

n : Number of replicates per unit

When MS_{between} is smaller than MS_{within}, s_{bb} cannot be calculated. Instead, u^*_{bb}, the heterogeneity that can be hidden by the method repeatability [6], is calculated according to the equation (4):

$$u^*_{bb} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}} \quad (4)$$

$\nu_{MSwithin}$: Degrees of freedom of MS_{within}

The occurrence of $MS_{between} < MS_{within}$ can be seen, if material heterogeneity is smaller than that can be detected by the analytical methodology used.

For density parameter an outlying bottle mean was observed, and in this case alternative data evaluation was applied and between unit homogeneity was modeled as a rectangular distribution and equation (5) was applied for rectangular standard uncertainty (u_{rect}) of homogeneity.

$$u_{rect} = \frac{|Outlier\ value - Average\ value|}{\sqrt{3}} \quad (5)$$

For the parameters for which ANOVA was applied, the larger value of s_{bb} or u^*_{bb} is taken as uncertainty contribution for homogeneity, u_{bb} (Table 4).

Table 4. Results of the homogeneity study

Parameter	$s_{wb,rel}$, %	$s_{bb,rel}$, %	$u^*_{bb,rel}$, %	$u_{rec,rel}$, %	$u_{bb,rel}$,%
Calorific Value	0.042	0.023	0.02	-	0.023
Mono-Glycerides	0.18	0.28	0.06	-	0.28
Di-Glycerides	0.49	0.45	0.16	-	0.45
Tri-Glycerides	0.90	1.18	0.30	-	1.18
Free Glycerol	0.50	0.84	0.16	-	0.84
Total Glycerol	0.26	0.22	0.08	-	0.22
Methyl Linoleate	1.7	0.78	0.54	-	0.78
Methyl Palmitoleate	9.1	1.5	2.96	-	2.96
Methyl Palmitate	5.1	MS_{between}<MS_{within}	1.66	-	1.66
Methyl 11-Octadecenoate	0.84	0.82	0.17	-	0.82
Methyl Stearate	4.6	MS_{between}<MS_{within}	1.49	-	1.49
Methyl cis-11-Eicosenoate	5.1	3.25	1.69	-	3.25

Table 4. (Continued) Results of the homogeneity study

Parameter	$s_{wb,rel}$, %	$s_{bb,rel}$, %	$u^*_{bb,rel}$, %	$u_{rec,rel}$, %	$u_{bb,rel}$,%
Calcium	12	$MS_{between}$<MS_{within}	3.8	-	3.8
Magnesium	8.6	3.5	2.9	-	3.5
Phosphorus	13	$MS_{between}$<MS_{within}	4.2	-	4.2
Potassium	11	6.5	3.7	-	6.5
Sodium	25	2.9	8.2	-	8.2
Sulfur	3.4	$MS_{between}$<MS_{within}	1.1	-	1.1
Viscosity	0.024	0.031	0.011	-	0.031
Density	0.00086	0.00068	0.00029	0.0013	0.0013
Methanol	4.2	2.2	1.4	-	2.2
Water	1.2	3.2	0.57	-	3.2

The plotted data used for the evaluation of homogeneity can be found in Annex 2.

STABILITY

The stability of the units which are exposed to different environmental conditions that may occur during shipment and shelf life is tested and evaluated at defined storage conditions by reference material producers.

Stability studies were performed with isochronous design. For the short term stability (STS) test +45°C temperature and five time points (0, 1, 2, 3, and 4 weeks) were tested. 10 units were selected for each laboratory by using a stratified sampling scheme covering whole batch. 32 samples were subjected to the test temperature for the specified time intervals. For the long-term stability test (LTS), 10 units for each laboratory were tested at +22 °C for 0, 2, 4, 6, and 8 months' time points.

Units were moved to +4 °C (reference temperature) after completion of the test time. All units were analyzed at the same time. Samples were analyzed under the repeatability conditions to determine the values for the parameters of interest.

Short Term Stability Results:

The results obtained from isochronous measurements were first grouped according to the time period and then evaluated for each time point.

The data for each parameter was first examined by single Grubbs test for both 95% and 99% confidence intervals to find out outliers. Number of detected outliers are given in the Table 5. Two outlying (one out of three parallel results of two different units) results were removed from the dataset for methyl palmitate reported by IMBIH.

Values calculated for each time point were plotted against the time. The relationship between variables were analyzed in order to determine if any significant change exists with the testing time (regression analysis). It was found that the slopes were significant for free glycerol reported by BRML and methanol reported by TÜBİTAK UME. The trend graphs of short term stability are shown in Annex 3. The relative short term stability uncertainty, $u_{sts,rel}$ for each parameter is calculated using Equation (6) for the required transfer time as described in [7], and results are given in Table 5:

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum (t_i - \bar{t})^2}} \times t \tag{6}$$

where,

RSD : relative standard deviation of the points on the regression line as described in B.17 [7],

t_i : time point for each replicate expressed in weeks ,

$\bar{t}$: mean of all time points expressed in weeks,

t : maximum time suggested for transfer (2 weeks).

Table 5. Short Term Stability (STS) test results

Parameter (Lab)	**45 °C $u_{sts,rel}$ for 2 week (%)**	**Number of outliers in 95% confidence interval** [1]	**Number of outliers in 99% confidence interval** [1]	**Any significant trend in 95% confidence interval?**	**Any significant trend in 99% confidence interval?**
Calorific Value (PTB)	0.023	-	-	No	No
Mono-Glycerides (BRML)	0.23	-	-	No	No
Di-Glycerides (BRML)	0.36	-	-	No	No
Tri-Glycerides (BRML)	1.1	-	-	No	No
Free Glycerol (BRML)	0.63[2]	-	-	Yes	Yes
Total Glycerol (BRML)	0.16	-	-	No	No
Methyl Linoleate (IMBIH)	0.46	-	-	No	No
Methyl Palmitoleate (IMBIH)	1.5	-	-	No	No
Methyl Palmitate (IMBIH)	0.69	2	2	No	No
Methyl 11-Octadecenoate (IMBIH)	0.41	-	-	No	No
Methyl Stearate (IMBIH)	1.4	-	-	No	No
Methyl cis-11-Eicosenoate (IMBIH)	1.6	-	-	No	No

[1] Single Grubbs Test

[2] u_{sts} is calculated by taking into account the degradation (u_{sts}= slope of reg. line/√3)

Table 5. (Continued) Short Term Stability (STS) test results

Parameter (Lab)	45 °C $u_{sts,rel}$ for 2 weeks (%)	Number of outliers in 95% confidence interval [1]	Number of outliers in 99% confidence interval [1]	Any significant trend in 95% confidence interval?	Any significant trend in 99% confidence interval?
Calcium (BRML)	2.8	-	-	No	No
Magnesium (BRML)	3.1	-	-	No	No
Phosphorus (BRML)	3.3	-	-	No	No
Potassium (BRML)	2.8	-	-	No	No
Sodium (BRML)	4.8	-	-	No	No
Sulfur (BRML)	1.9	-	-	No	No
Viscosity (PTB)	0.13	1	-	Yes	No
Density (PTB)	0.0029	-	-	No	No
Methanol (TÜBİTAK UME)	2.5[2]	-	-	Yes	Yes
Water (TÜBİTAK UME)	2.5	-	-	No	No

[1] Single Grubbs Test
[2] u_{sts} is calculated by taking into account the degradation (u_{sts}= slope of reg. line/√3)

The material is found to be stable at 45°C for up to 2 weeks. Thus, the samples can be safely dispatched under conditions where the temperatures do not exceed 45 °C for up to 2 week, i.e. at ambient temperature without applying any cooling elements.

Long Term Stability Results:

Shelf life of the CRM has been determined through long term stability measurements. For the measurements, for each partner two units for each of the months of 0, 2, 4, 6 and 8 have been stored at +22 °C and transferred to reference temperature (+4 °C) after each period of time to be measured isochronously afterwards. Eight units, designated as reference units, of the month 0 was stored at +4 °C. Detected outlying results were removed since they were observed only in one parallel measurement result out of three measurements of a unit.

The relative long term stability uncertainty, $u_{lts,rel}$ for each parameter is calculated using equation (7) for the required shelf life as [7]:

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \times t \tag{7}$$

where

RSD : the relative standard deviation of the points on the regression line as described in B.17 [7],
t_i : the time point for each replicate expressed in months,
$\bar{t}$: the average of all time points expressed in months,
t : the proposed shelf life at 18 °C (12 months).

The uncertainty contribution u_{lts} was calculated for 12 months (t) at 22 °C. The graphs for long term stability are given in Annex 4.

Table 6. Long Term Stability (LTS) test results

Parameter (Lab)	22 °C $u_{lts,rel}$ for 12 months (%)	Number of outliers in 95% confidence interval [1]	Number of outliers in 99% confidence interval [1]	Any significant trend in 95% confidence interval?	Any significant trend in 99% confidence interval?
Calorific Value (PTB)	0.076	1	-	No	No
Mono-Glycerides (BRML)	0.79	-	-	No	No
Di-Glycerides (BRML)	1.3	-	-	No	No
Tri-Glycerides (BRML)	1.4	-	-	No	No
Free Glycerol (BRML)	1.6	-	-	No	No
Total Glycerol (BRML)	0.61	-	-	No	No
Methyl Linoleate (IMBIH)	1.1	1	-	No	No
Methyl Palmitoleate (IMBIH)	6.4	1	1	No	No
Methyl Palmitate (IMBIH)	3.5	-	-	No	No
Methyl 11-Octadecenoate (IMBIH)	1.2	1	-	No	No
Methyl Stearate (IMBIH)	2.8	-	-	No	No
Methyl cis-11-Eicosenoate (IMBIH)	4.0	2	-	No	No
Calcium (BRML)	5.3	-	-	No	No
Magnesium (BRML)	5.7	-	-	No	No
Phosphorus (BRML)	9.4	-	-	No	No
Potassium (BRML)	11.3	-	-	No	No
Sodium (BRML)	12.4	-	-	No	No
Sulfur (BRML)	6.3	-	-	No	No
Viscosity (PTB)	0.39[2]	-	-	Yes	Yes
Density (PTB)	0.019[2]	-	-	Yes	Yes
Methanol (TÜBİTAK UME)	8.4[2]	-	-	Yes	Yes
Water (BRML)	11.7[2]	-	-	Yes	Yes

[1] Single Grubbs Test

[2] u_{lts} is calculated by taking into account the degradation (u_{lts}= slope of reg. line/√3)

CHARACTERIZATION

According to ISO 17034, the characterization and the value assignment can be carried out in different ways. The approach chosen in this project is; characterization of a non-operationally and operationally defined measurands using two or more methods of demonstrable accuracy in two or more competent laboratories. The participating laboratories were partners and collaborators of the BIOFMET project consortium [3]. The detailed information about the laboratories is given in the participants section. The participating laboratories used validated methods for the characterization.

Each laboratory received 2 units of samples which were selected from the whole set of samples to represent the whole produced batch. The samples were selected randomly from the set of samples by the random stratified sampling technique. Each laboratory was asked to report at least three independent measurement results for each unit, together with their associated measurement uncertainty values and the approach used for the estimation of measurement uncertainty. In the reports, the details of the reference materials used in the calibration were also requested in order to assure the traceability of the reported results.

Measurement uncertainties were calculated according to the “Guide to the Expression of Uncertainty in Measurements (GUM)” and “EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement” documents or estimated in accordance with ISO 17034:2016 and ISO Guide 35:2017. Equations (8, 9, 10) were used to calculate characterization standard uncertainty (u_{char}) stated by M. S. Lenson et al [8] for the cases where two method/laboratory results were available. In cases where more than two method/laboratory results were available, characterization standard uncertainty (u_{char}) is calculated using Equation (11) by taking into account the uncertainties and the standard deviation of the means reported by the participating laboratories. Value assignment of the material performed by arithmetic averaging two or more method results.

$$u(B) = \frac{|x_{Method\ 1} - x_{Method\ 2}|}{2\sqrt{3}} \quad (8)$$

$$u(X) = \sqrt{(\tfrac{1}{2})^2 u^2(\text{Method 1}) + (\tfrac{1}{2})^2 u^2(\text{Method 2})} \quad (9)$$

$$u_{char} = \sqrt{u^2(X) + u^2(B)} \quad (10)$$

here,
$u(B)$: the standard uncertainty based on the difference on the difference of results of two methods,
$u(X)$: the standard uncertainty obtained by combining uncertainties of two methods,
u_{char} : the standard uncertainty of characterization by two methods.

$$u_{\text{char}} = \sqrt{\bar{u}^{\,2}_{\text{labs}} + \left(\frac{SD}{\sqrt{n}}\right)^2} \quad (11)$$

where;

u_{char} : Standard uncertainty arising from characterization,
$\bar{u}_{labs}$: Arithmetic mean of standard uncertainties reported by the participating laboratories,
SD : Standard deviation of accepted means of participating laboratories,
n : Number of laboratories with accepted results.

A list of laboratories with their abbreviations and their corresponding methodologies used for the measurements are summarized in Table 7. More details about the measurement methods are given in Annex 5. Characterization plots are given in Annex 6.

Table 7. Techniques used by participating laboratories

Parameter	BAM	BRML	DTI	IMBIH	GUM	LGC	PTB	UME
Calorific Value	-	ISOP-CAL	ISOP-CAL	-	-	-	ISOP-CAL	ISOP-CAL
Mono-Glycerides	-	GC-FID	-	-	-	-	-	-
Di-Glycerides	-	GC-FID	-	-	-	-	-	-
Tri-Glycerides	-	GC-FID	-	-	-	-	-	-
Free Glycerol	-	GC-FID	-	-	-	-	-	-
Total Glycerol	-	GC-FID	-	-	-	-	-	-
Methyl Linoleate	-	-	-	GC-MS	-	-	-	-
Methyl Palmitoleate	-	-	-	GC-MS	-	-	-	-
Methyl Palmitate	-	-	-	GC-MS	-	-	-	-
Methyl 11-Octadecenoate	-	-	-	GC-MS	-	-	-	-
Methyl Stearate	-	-	-	GC-MS	-	-	-	-
Methyl cis-11-Eicosenoate	-	-	-	GC-MS	-	-	-	-
Calcium	-	ICP-MS	-	-	-	-	-	ICP-OES
Magnesium	-	-	-	-	ICP-MS	-	-	HR ICP-MS ICP-OES
Phosphorus	-	-	-	-	-	-	-	HR ICP-MS ICP-OES
Potassium	-	-	-	-	ICP-MS	-	-	ICP-OES
Sodium	-	ICP-MS	-	-	ICP-MS	-	-	HR ICP-MS ICP-OES
Sulfur	ID ICP-MS	ICP-MS	-	-	-	-	-	ID ICP-MS HR ICP-MS ICP-OES
Viscosity	-	-	-	-	-	SVM	SVM	-
Density	-	-	-	-	-	DM	DM	-
Methanol	-	-	-	-	-	-	-	GC-FID
Water	-	COU-KFT	-	-	-	-	-	COU- o-KFT

COU-KFT : Coulometric Karl Fischer Titrimetry
COU-o-KFT : Coulometric Karl Fischer Titrimetry with Oven
DM : Density Meter
GC-FID : Gas Chromatography Flame İonization Detector
GC-MS : Gas Chromatography Mass Spectrometry
ICP-MS : Inductively Coupled Plasma Mass Spectrometry
ICP-OES : Inductively Coupled Plasma Optical Emission Spectrometry
ID ICP-MS : Isotope Dilution ICP-MS
ISOP-CAL : Isoperibol Calorimetry
SVM : Stabinger Viscometer

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

Assigned values and uncertainties of the CRM were evaluated by applying approach in the characterization and uncertainty data that contribute to the homogeneity and stability assessments.

Data obtained in the characterization study were checked for normal distribution and outliers. Distributions were found to be normal, and no outlier was detected.

Unweighted mean value of characterization results is assigned as the property value of the reference materials.

Equation (11) is used to calculate the combined expanded uncertainty of the CRM:

$$\mathrm{U_{CRM}} = k\sqrt{\mathrm{u}_{\mathrm{char}}^2 + \mathrm{u}_{\mathrm{bb}}^2 + \mathrm{u}_{\mathrm{lts}}^2 + \mathrm{u}_{\mathrm{sts}}^2} \qquad (11)$$

Uncertainty value on CRM certificate includes uncertainty contribution from characterization (u_{char}), homogeneity (u_{bb}), long term stability (u_{lts}) and short-term stability (u_{sts}). Expansion of uncertainty value of CRM was done with a coverage factor (k = 2) representing 95 % confidence level. Certified values, uncertainties and relative percent contribution of each component on uncertainty is given in Table 7.

Table 7. Certified values and uncertainties

Parameter	Certified value [1]	U_{CRM} (k=2) [1,2]	$U_{CRM,rel}$ (%, k=2)	$u_{char,rel}$ (%)	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)
Gross Calorific Value [$q_{V,gr}$] [3] (J/g)	39901	97	0.25	0.089	0.023	0.023	0.076
Density at 15 °C [4] (g/cm^3)	0.88353	0.00035	0.040	0.0025	0.0013	0.0029	0.019
Kinematic Viscosity at 40 °C [5] (mm^2/s)	4.419	0.039	0.89	0.18	0.031	0.13	0.39
Ca [6] (mg/kg)	1.03	0.31	30	13	3.8	2.8	5.3
K [6] (mg/kg)	1.01	0.28	28	10	6.5	2.8	11
Mg [7] (mg/kg)	0.48	0.10	21	11	3.5	3.1	5.7
Na [8] (mg/kg)	1.70	0.56	33	5.1	8.2	4.8	12
P [9] (mg/kg)	2.13	0.51	24	2.6	4.2	3.2	10
S [10] (mg/kg)	8.7	1.4	16	4.0	1.1	1.9	6.3
Water [11] (mg/kg)	339	89	26	4.1	3.2	1.8	12

[1] The certified values and the uncertainties are traceable to the International System of Units (SI).

[2] The expanded uncertainty of the certified value includes characterization, homogeneity, stability components and is stated as the standard uncertainty of measurement multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with GUM "Guide to the Expression of Uncertainty in Measurement".

[3] Calculated from the arithmetic mean of the accepted results of gross calorific value at constant volume submitted by four laboratories applying DIN 51900-2 method.

[4] Calculated from the arithmetic mean of the accepted results submitted by two laboratories applying ASTM D4052 and EN ISO 12185 methods.

[5] Calculated from the arithmetic mean of the accepted results submitted by two laboratories applying ASTM D7042 and EN ISO 3104 methods.

[6] Calculated from the arithmetic mean of the accepted results submitted by two laboratories applying ICP-MS and ICP-OES methods.

[7] Calculated from the arithmetic mean of the accepted results submitted by two laboratories applying ICP-MS, HR ICP-MS and ICP-OES methods.

[8] Calculated from the arithmetic mean of the accepted results submitted by three laboratories applying ICP-MS, HR ICP-MS and ICP-OES methods.

[9] Calculated from the arithmetic mean of the accepted results submitted by one laboratory applying HR ICP-MS and ICP-OES methods.

[10] Calculated from the arithmetic mean of the accepted results submitted by four laboratories applying ICP-MS, HR ICP-MS, ID ICP-MS and ICP-OES methods.

[11] Calculated from the arithmetic mean of the accepted results submitted by two laboratories applying EN ISO 12937 method with direct and oven sample introduction systems.

INFORMATIVE VALUES

Parameters for which a consensus value cannot be assigned due to lack of multiple laboratory measurement methods or results are given as informative value. Results for these measurements are given in Table 8 and Table 9.

Table 8. Informative values and uncertainties for Biodiesel

Parameter	Assigned value (g/100g)*	U_{AV} (k=2) (g/100g)*	$U_{AV,rel}$ (%, k=2)	$u_{char,rel}$ (%)	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)
Net Calorific Value [$q_{V,net}$] [1] (J/g)	37361	91	0.25	0.089	0.023	0.023	0.076
Mono-Glycerides[2]	0.566	0.019	3.3	1.4	0.28	0.23	0.79
Di-Glycerides[2]	0.1752	0.0080	4.6	1.8	0.45	0.36	1.2
Tri-Glycerides[2]	0.1432	0.0089	6.2	2.2	1.2	1.1	1.4
Free Glycerol[2]	0.0193	0.0027	14	6.5	0.84	0.63	1.6
Total Glycerol[2]	0.204	0.019	9.0	4.5	0.22	0.16	0.61
Methyl Linoleate[3]	28.7	2.2	7.7	3.6	0.78	0.46	1.1
Methyl Palmitoleate[3]	0.248	0.069	28	12	3.0	1.5	6.4
Methyl Palmitate[3]	8.67	0.93	11	3.6	1.7	0.69	3.5
Methyl 11-Octadecenoate[3]	58.4	3.1	5.3	2.2	0.82	0.41	1.2
Methyl Stearate[3]	2.40	0.31	13	5.4	1.5	1.4	2.8
Methyl cis-11-Eicosenoate[3]	1.09	0.21	19	7.8	3.3	1.6	4.0
Methanol[4]	0.176	0.035	20	3.6	2.2	2.5	8.4

*Except for Net calorific value

[1] Calculated from the certified gross calorific value at constant volume [$q_{V,gr}$] by substracting 206 x measured hydrogen content, in percentage by mass .

[2] Calculated from the arithmetic mean of the accepted results submitted by one laboratory applying EN 14105 method.

[3] Calculated from the arithmetic mean of the accepted results submitted by one laboratory applying GC-MS method aiming quantification of relative amount based on total area of the methyl esters.

[4] Calculated from the arithmetic mean of the accepted results submitted by one laboratory applying GC-FID method.

Table 9. Informative values for Carbon and Hydrogen element content

Element	Measurement Result [1] (g/100g)
C	77.29 ± 0.23
H	12.33 ± 0.16

* Values written with "±" sign represents standard deviation

[1] Arithmetic mean of the accepted analysis results (n = 12) by TÜBİTAK UME.

COMMUTABILITY

Commutability is defined as the mathematical relationship of the equation between the reference material and the results produced by the different measurement methods that can be used to measure the routine samples it represents [9]. UME BIOFMET CRM 01 was produced from a regular biodiesel (80% RME, 20% SME) produced in Romania by spiking with a mixture of Ca, K, Mg, Na, P standards in mineral oil. The analytical behavior is expected to be the same as for a routine sample of biodiesel of similar content. It should be noted that the extractability of the five spiked elements (Ca, K, Mg, Na, P) from this CRM can be different to the extractability from an unspiked biodiesel sample tested by the user's laboratory due to the possibility that these elements might exist in different chemical forms.

TRACEABILITY

The metrological traceability of the CRM was ensured by using SI traceable calibration standards and using reference methods i.e., ID ICP MS by the participating laboratories. The laboratories were asked to provide detailed information about the calibration standards and reference methods used in the measurements. Details about the measurement methods, calibration standards and quality control materials used by the participating laboratories are given in Annex 5.

INSTRUCTIONS FOR USE

Shipping conditions

This material can be safely dispatched under conditions where the temperature does not exceed 45 °C for up to two weeks, i.e. at ambient temperature without applying any cooling elements.

Storage conditions

The material should be stored at (22 ± 4) °C in a dark and clean environment. The bottle should be shaken before opening. In order to prevent contamination, it is recommended that the bottle should be opened in a clean environment and pipette should not be inserted into the bottle. TÜBİTAK UME cannot be held responsible for changes that might happen to the material at the customer’s premises due to noncompliance with the instructions for use, and the storage conditions given.

Safety precautions

For laboratory use only. The usual laboratory safety measures apply.

Minimum sample intake

The minimum sample intake is defined by the required sample volume stipulated in the respective standard methods.

Use of Certified Value

For assessing the method performance, the measured values of the CRM are compared with the certified values [10]. The procedure can be described briefly as:

- Calculate the absolute difference between mean measured value and the certified value (Δ_m).

- Combine measurement uncertainty (u_{meas}) with the standard uncertainty of the certified value (u_{CRM}) using Equation (9):

$$u_{\Delta}=\sqrt{u_{meas}^2+u_{CRM}^2} \quad (9)$$

- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty (u_{Δ}) using a coverage factor of two ($k = 2$), corresponding to a confidence level of approximately 95 %.

If $\Delta m \leq U\Delta$, then it is assumed that there is no significant difference between the measurement result and the certified value at a confidence level of approximately 95%.

An online application: CRM Result Evaluation-CRM RE to evaluate your measurement results and automatically create quality control charts is available through the link: https://rm.ume.tubitak.gov.tr/en/crm_re/

ACKNOWLEDGEMENTS

The work of this study is part of the 19 ENG09 BIOFMET project, which was funded within the framework of the EMPIR. The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States. Intern and scholar students; Berke Can, Elif Nur Kırbaş, Beyzanur Çobanoğlu, Rana Yaldız, Hikmet Küçük, Ayşenur Düzgün, Feyzanur Şentürk, Muhammed Faruk Kıran and Selina Turunç are acknowledged for their contribution to the project. TUBITAK BIDEB 2247-C Intern Researcher Scholarship Program (STAR) is acknowledged for financial support of scholar students.

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[2] Liquid petroleum products — Fatty acid methyl esters (FAME) for use in diesel engines and heating applications — Requirements and test methods, EN 14214:2012+A2:2019

[3] BIOFMET project homepage; http://biofmet.eu/

[4] ISO 17034:2016. General requirements for the competence of reference materials producers

[5] ISO Guide 35:2017. Reference materials — Guidance for characterization and assessment of homogeneity and stability

[6] T. P. J. Linsinger, J. Pauwels, A. M. H. Van der Veen, H. Schimmel, A. Lamberty, Homogeneity and stability of reference materials, Accred. Qual. Assur. 6:20-25 (2001)

[7] A. Lamberty, H. Schimmel, J. Pauwels, The study of the stability of reference materials by isochronous measurements, Fres. J. Anal. Chem. 360:359-361 (1998)

[8] Lenson,M.S. An Approach to Combining Results From Multiple Methods Motivated by the ISO GUM, *Journal of Research of the National Institute of Standards and Technology*, *105*, 57 (2000)

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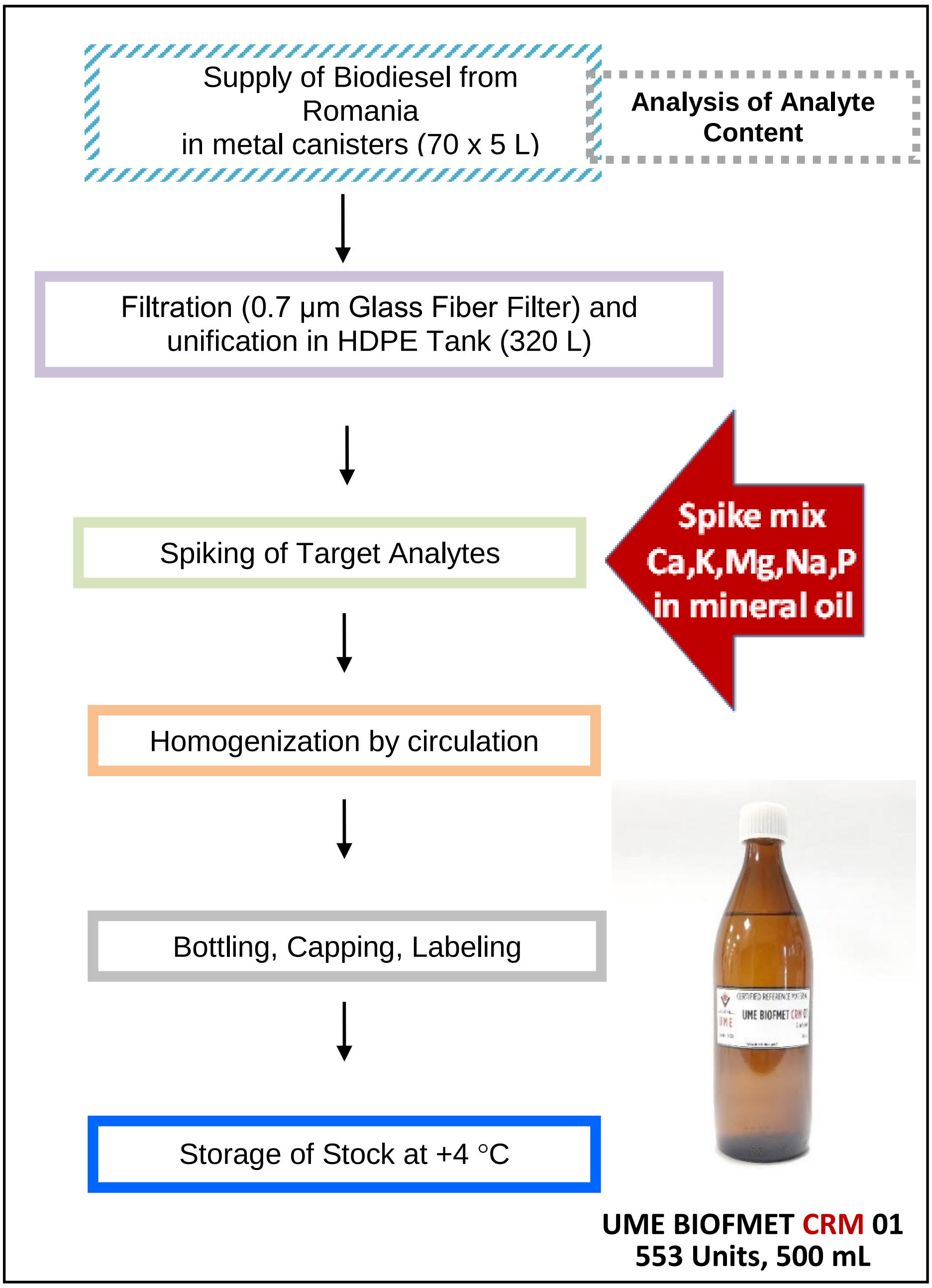
[10] For more information about comparison of a measurement result with the certified value please see ERM Application Note 1 https://crm.jrc.ec.europa.eu/e/132/User-support-Application-Notes

REVISION HISTORY

Date	Remarks
XX.YY.2023	First issue.

ANNEX 1. Flow Diagram for the Preparation of the Biodiesel CRM



Details of the processing is documented as a video:
https://www.youtube.com/watch?v=DDnfvmhP20Y

ANNEX 2. Graphs for Homogeneity Studies

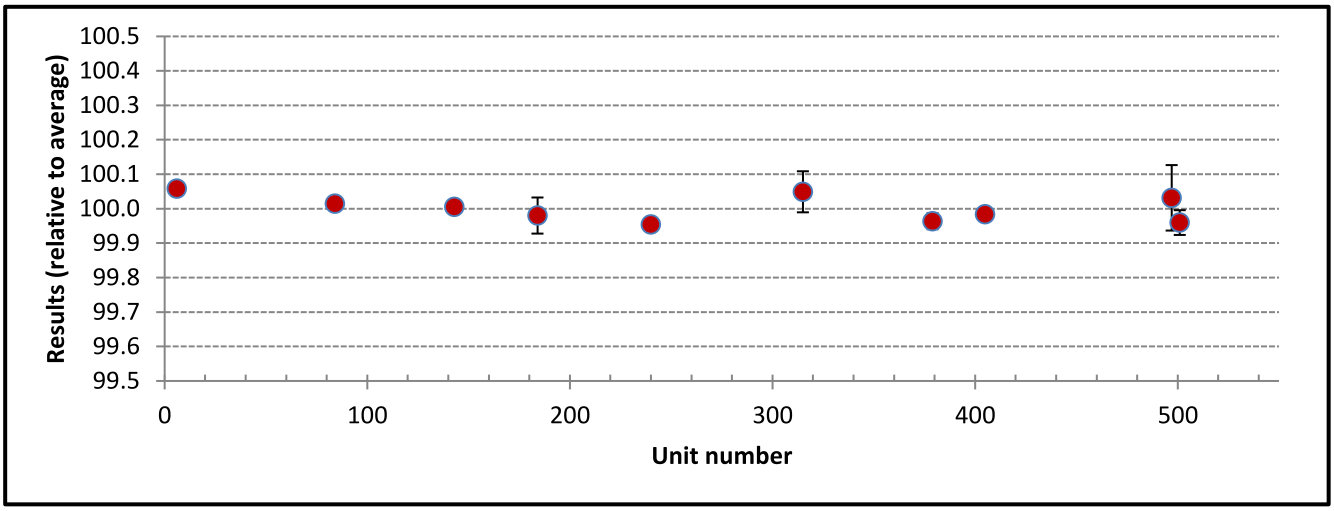


Figure A2.1. Between units homogeneity plot for Calorific Value by PTB

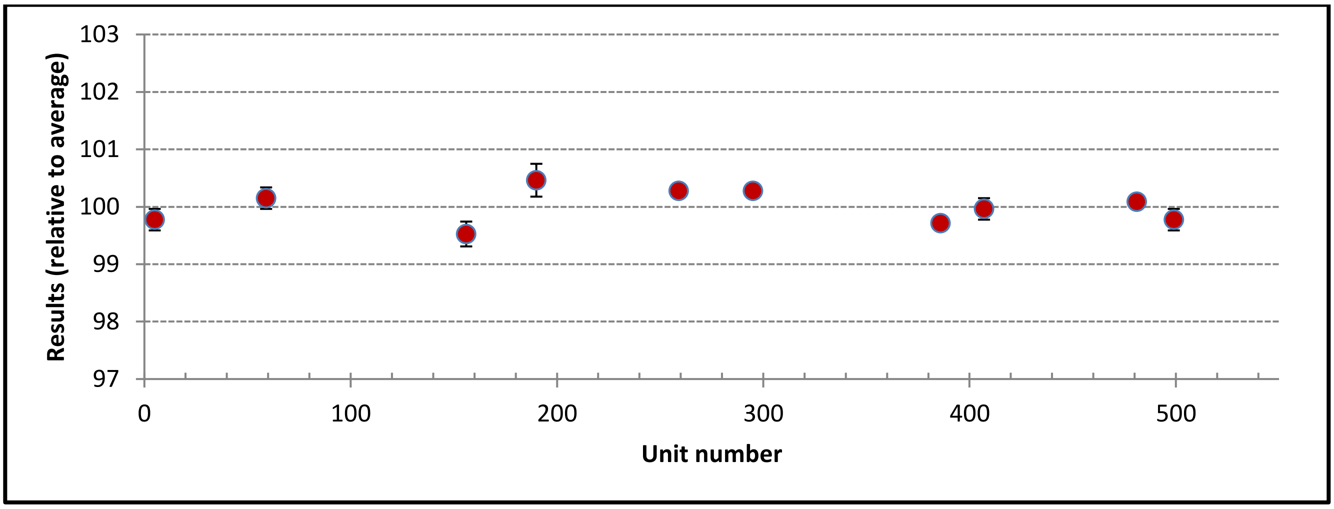


Figure A2.2. Between units homogeneity plot for Mono-Glyceride by BRML

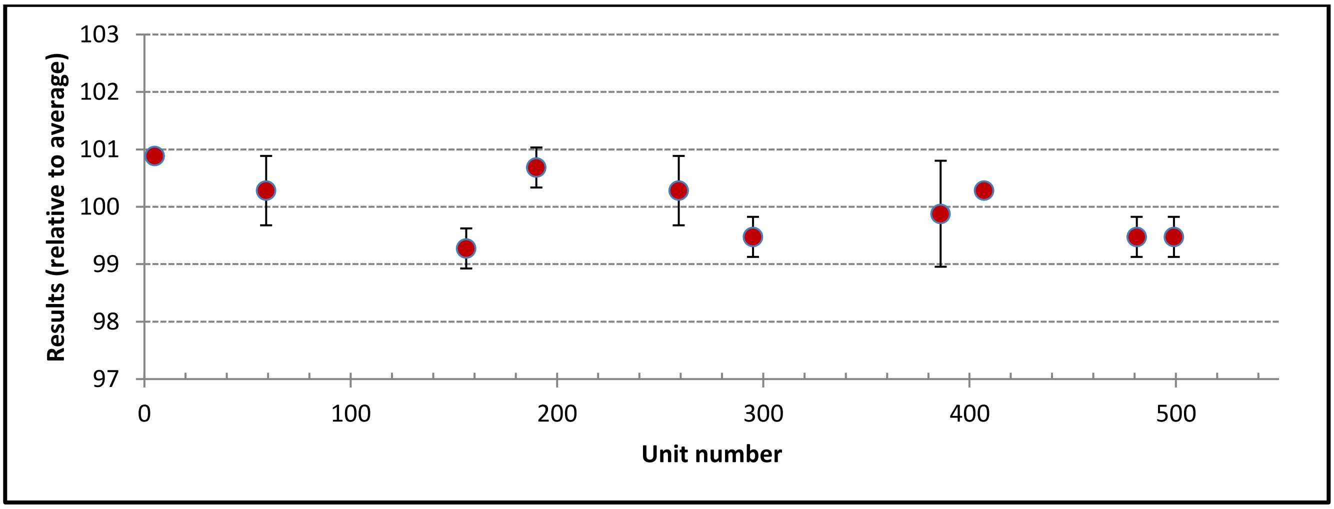


Figure A2.3. Between units homogeneity plot for Di-Glyceride by BRML

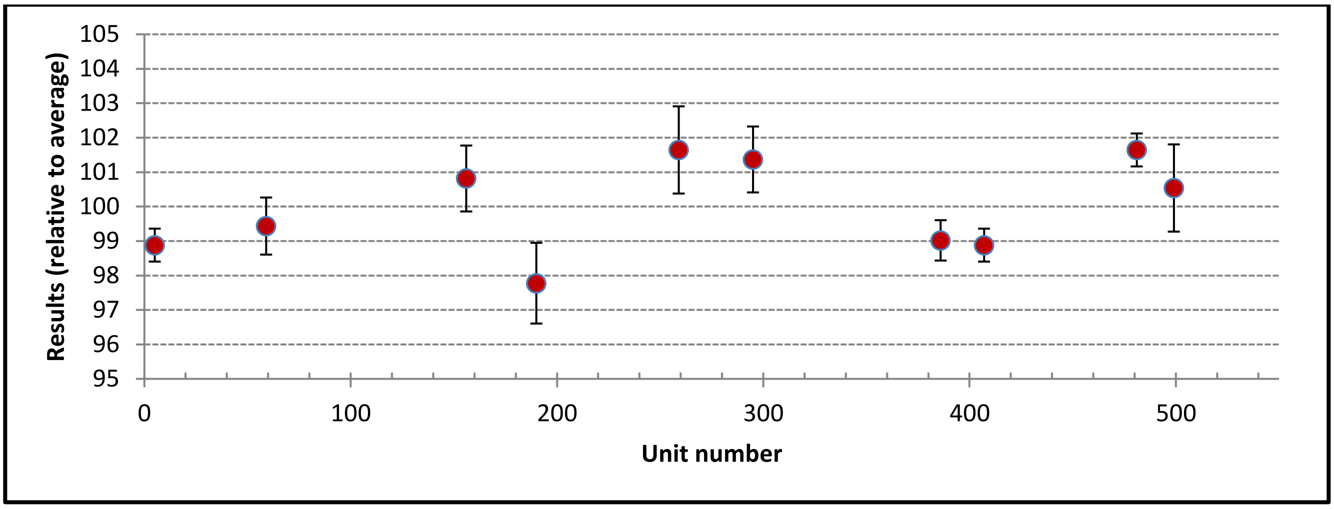


Figure A2.4. Between units homogeneity plot for Tri-Glyceride by BRML

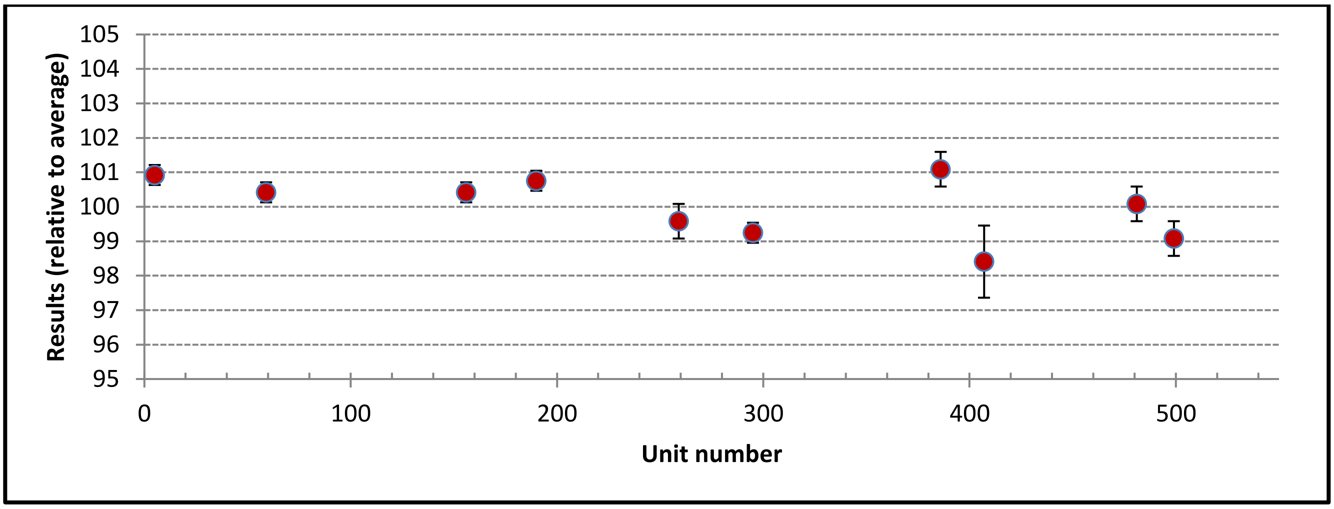


Figure A2.5. Between units homogeneity plot for Free Glycerol by BRML

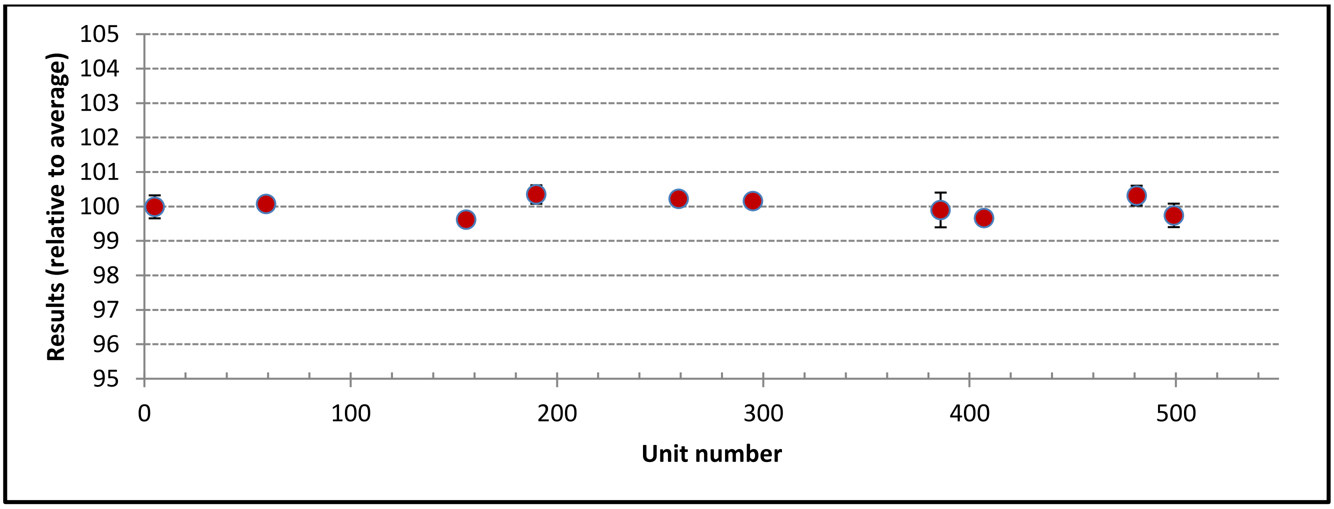


Figure A2.6. Between units homogeneity plot for Total Glycerol by BRML

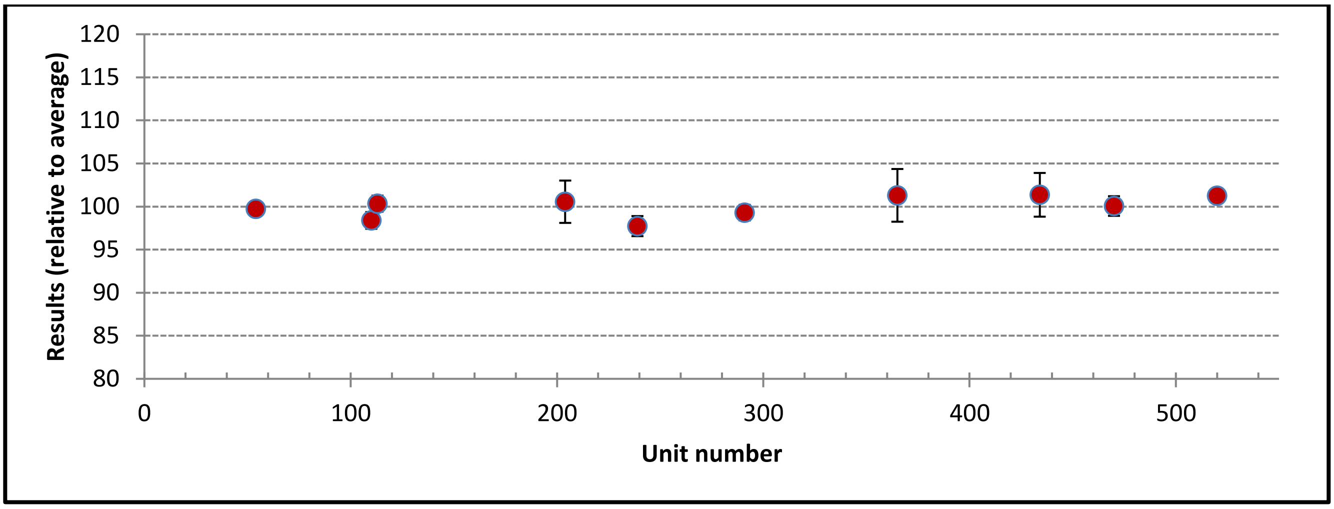


Figure A2.7. Between units homogeneity plot for Methyl Linoleate by IMBIH

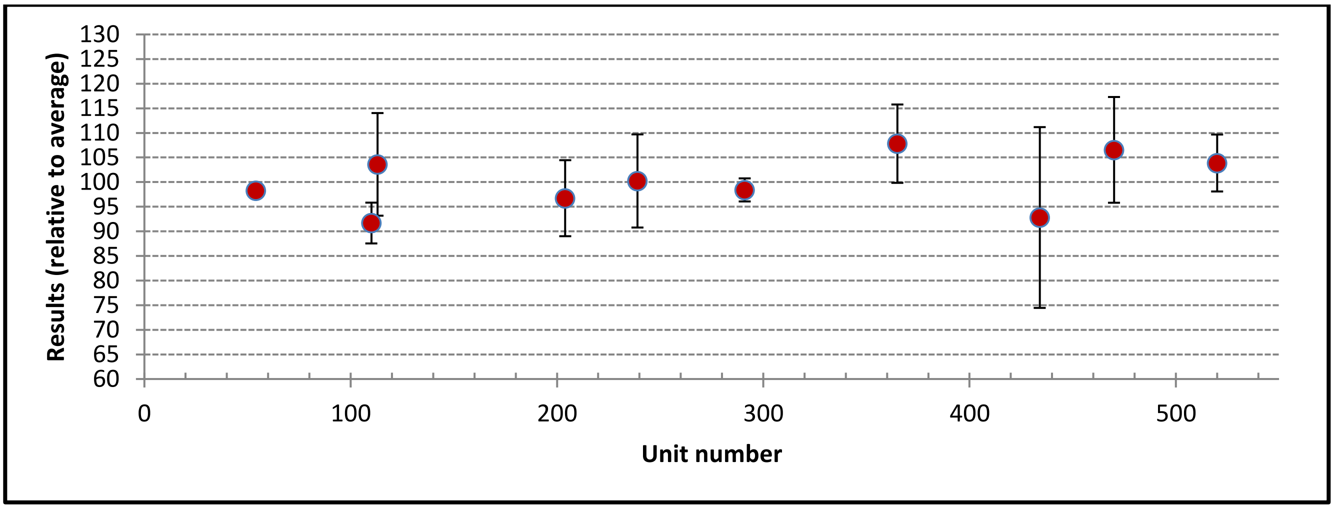


Figure A2.8. Between units homogeneity plot for Methyl Palmiteolate by IMBIH

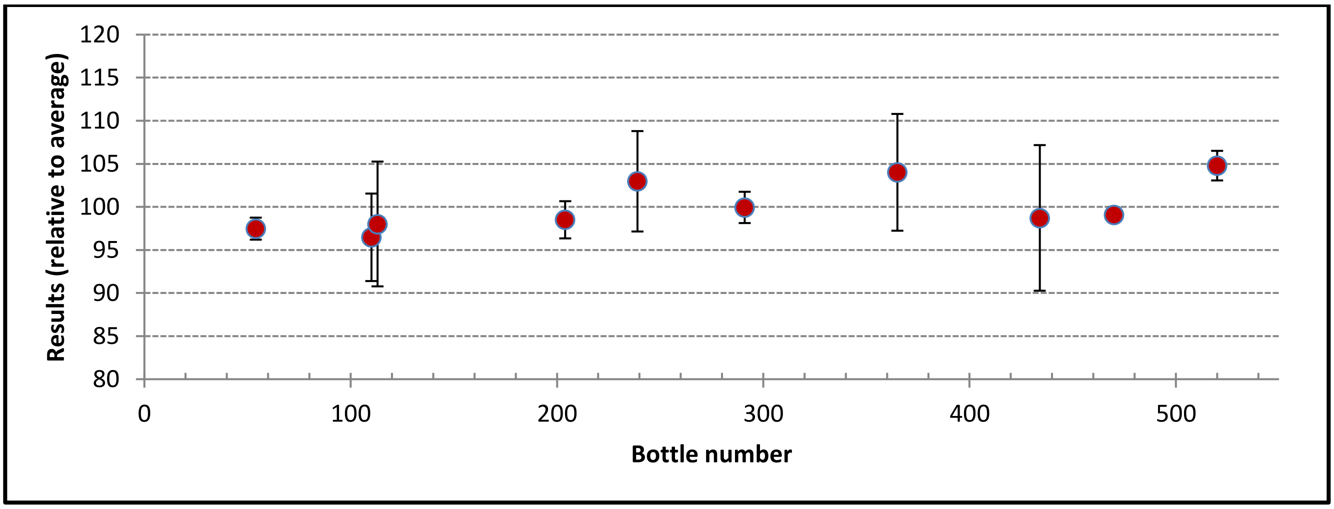


Figure A2.9. Between units homogeneity plot for Methyl Palmitate by IMBIH

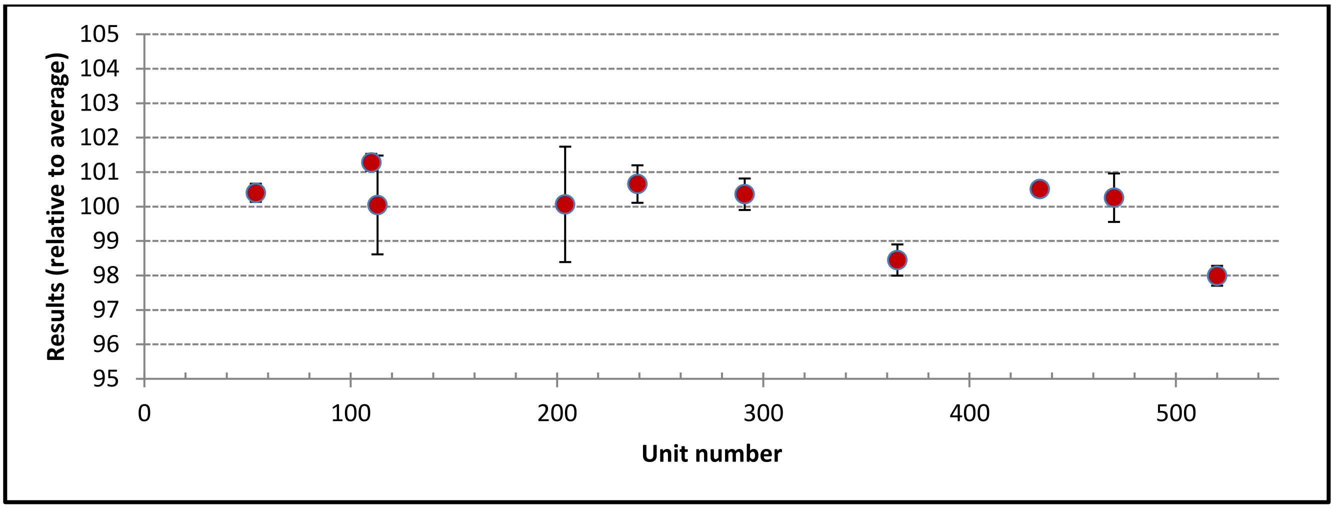


Figure A2.10. Between units homogeneity plot for Methyl 11-Octadecenoate by IMBIH

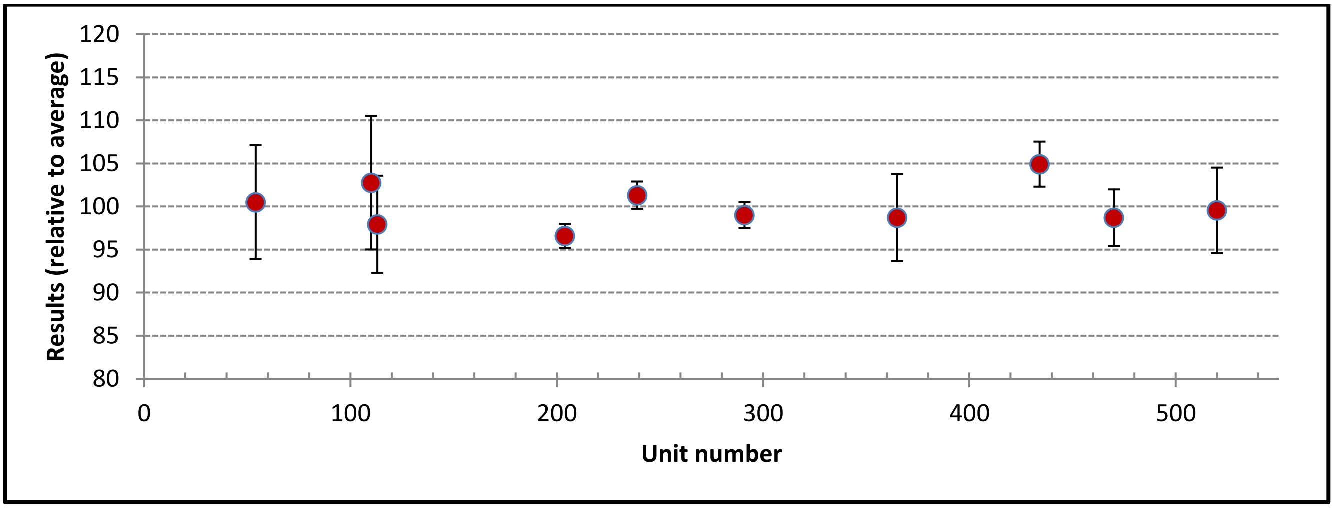


Figure A2.11. Between units homogeneity plot for Methyl Stearate by IMBIH

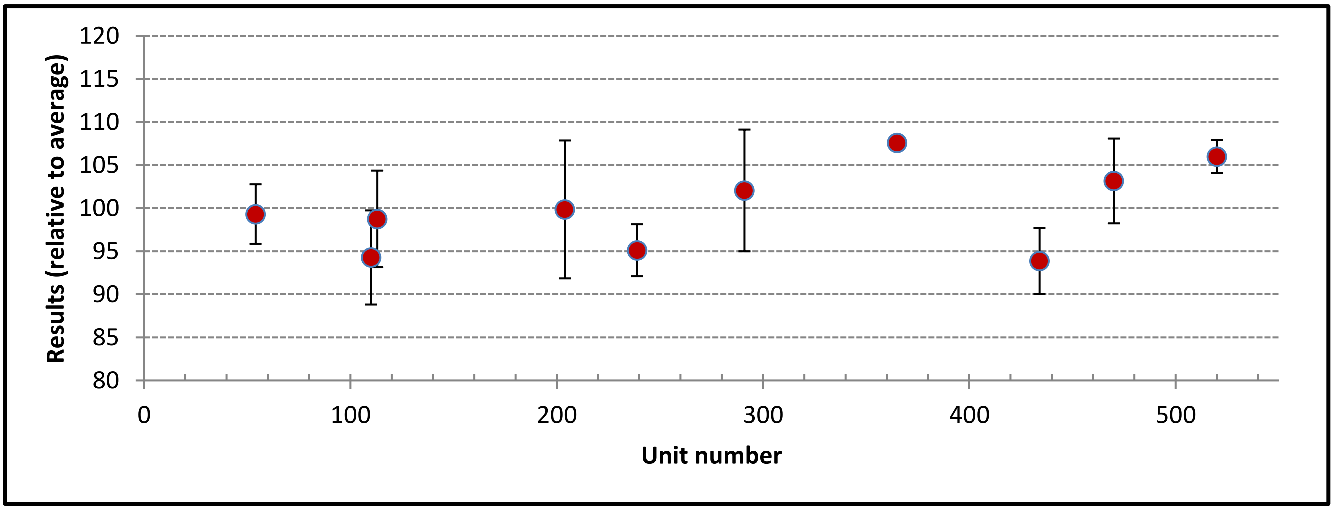


Figure A2.12. Between units homogeneity plot for Methyl cis-11-Eicosenoate by IMBIH

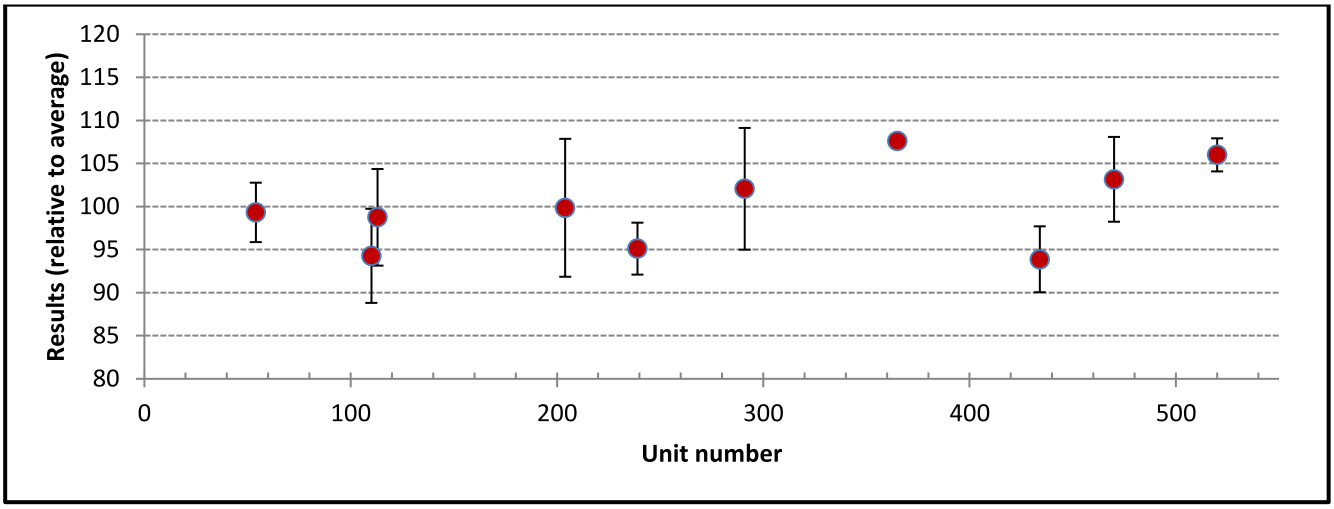


Figure A2.13. Between units homogeneity plot for Calcium by BRML

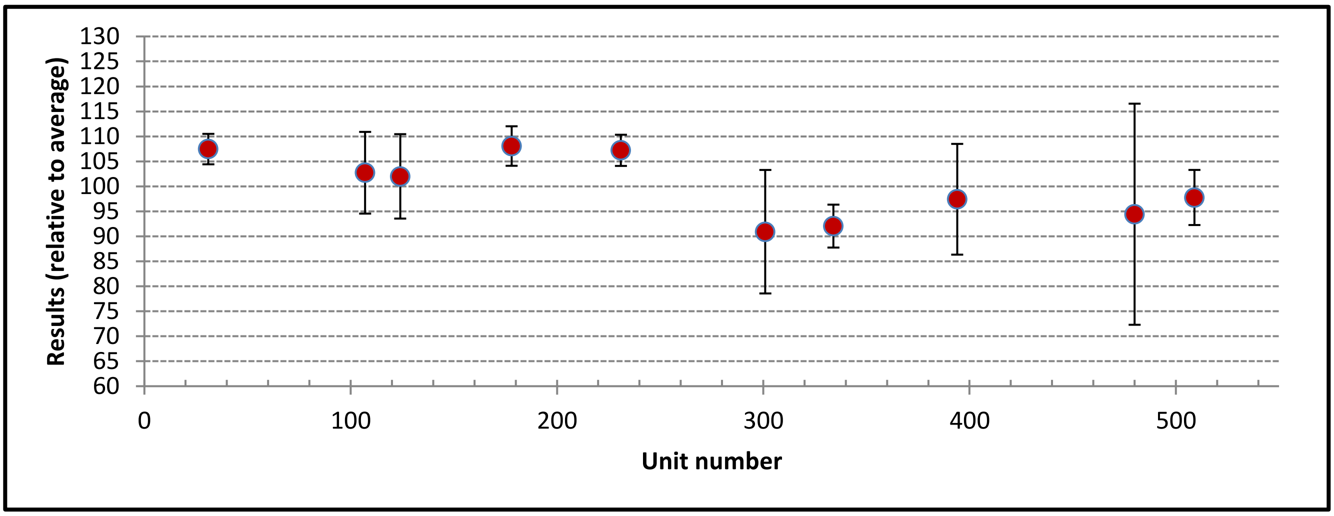


Figure A2.14. Between units homogeneity plot for Magnesium by BRML

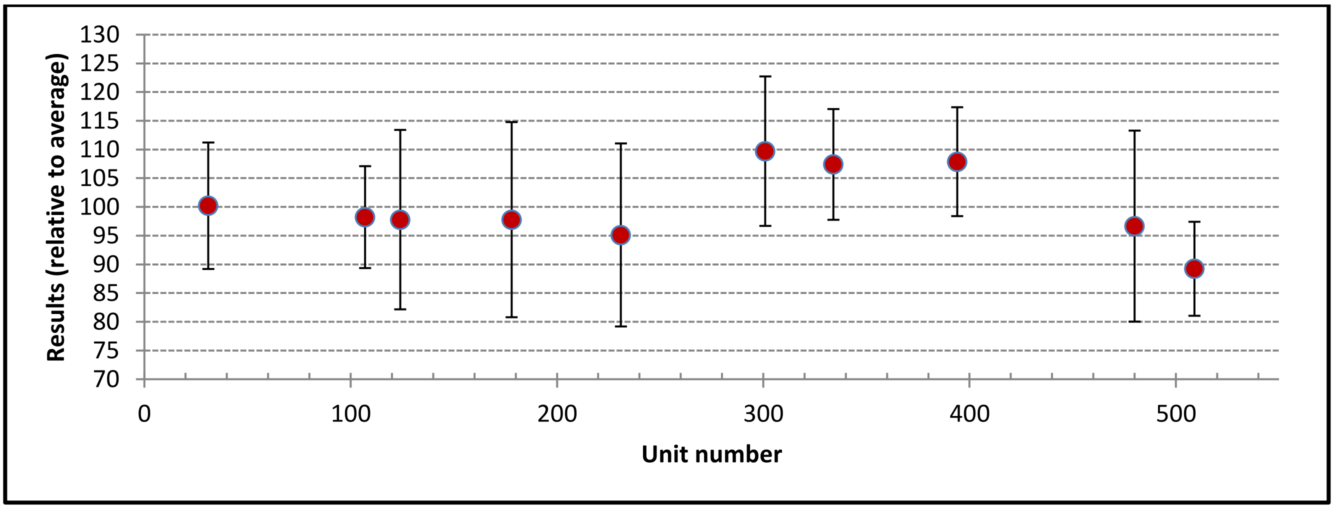


Figure A2.15. Between units homogeneity plot for Phosphorus by BRML

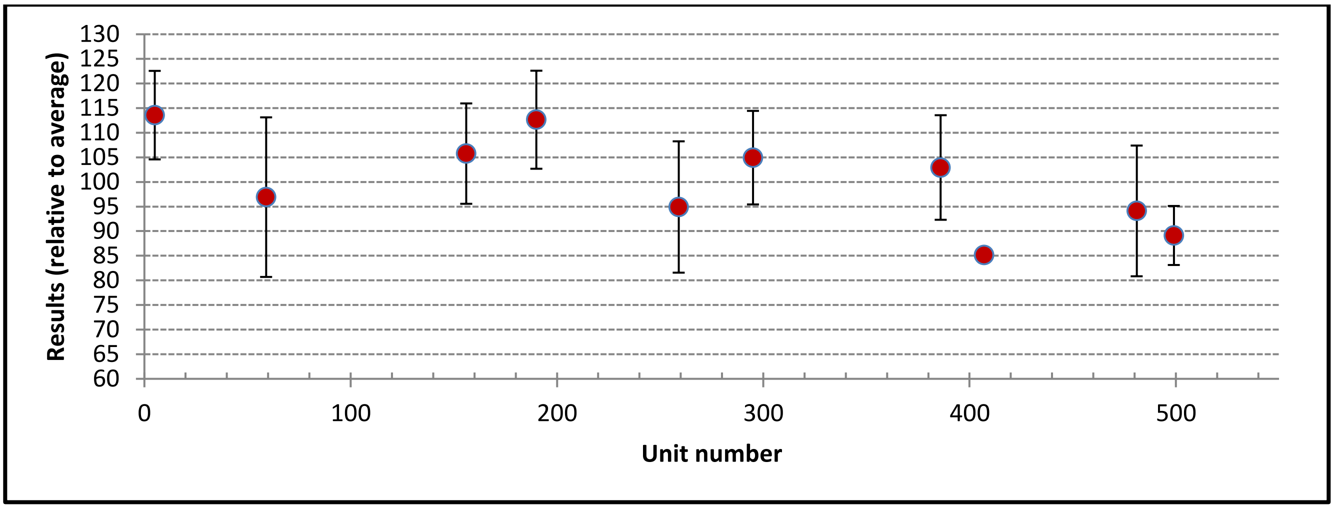


Figure A2.16. Between units homogeneity plot for Potassium by BRML

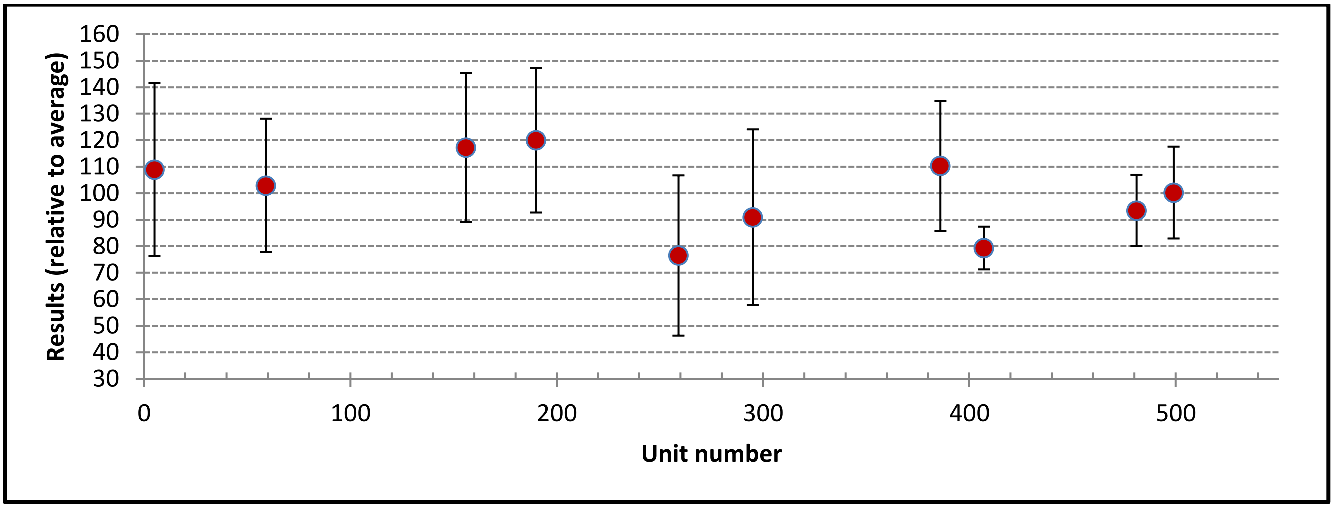


Figure A2.17. Between units homogeneity plot for Sodium by BRML

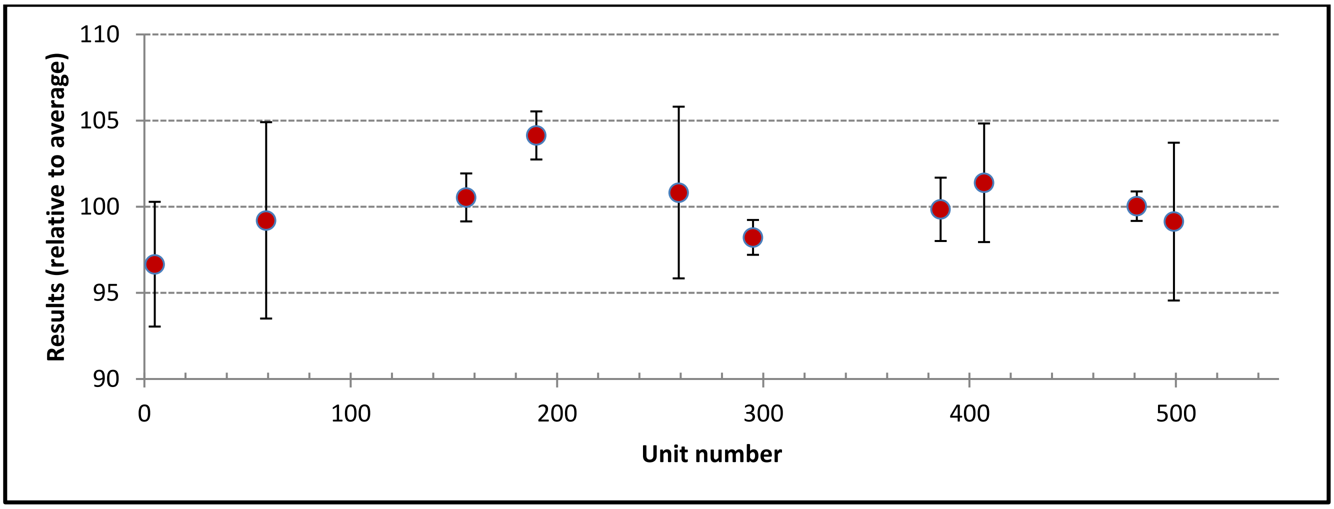


Figure A2.18. Between units homogeneity plot for Sulfur by BRML

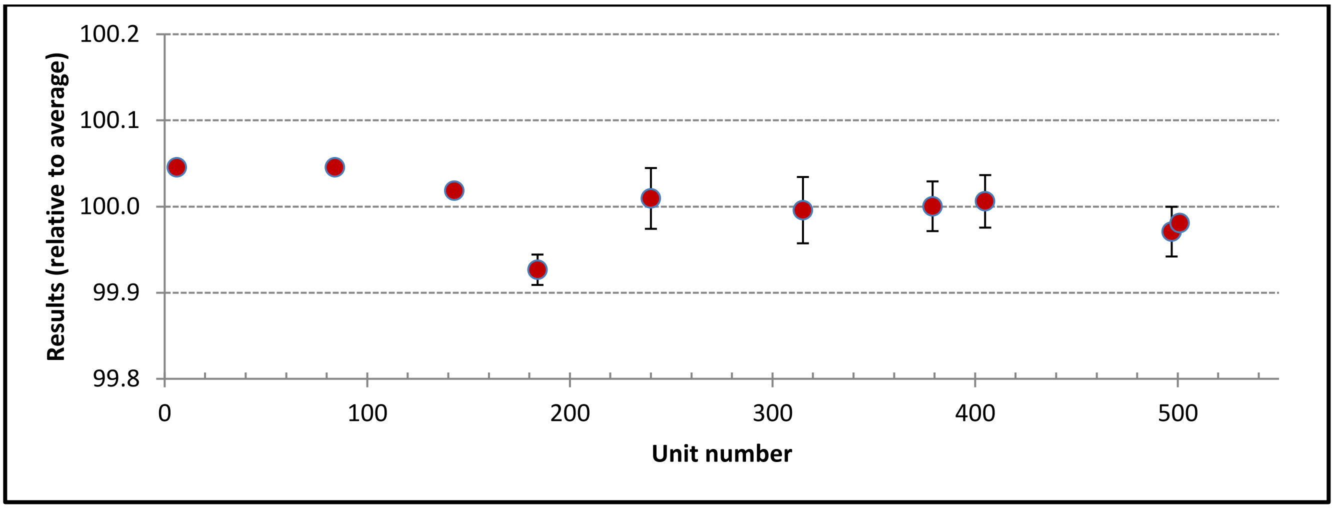


Figure A2.19. Between units homogeneity plot for Viscosity by PTB

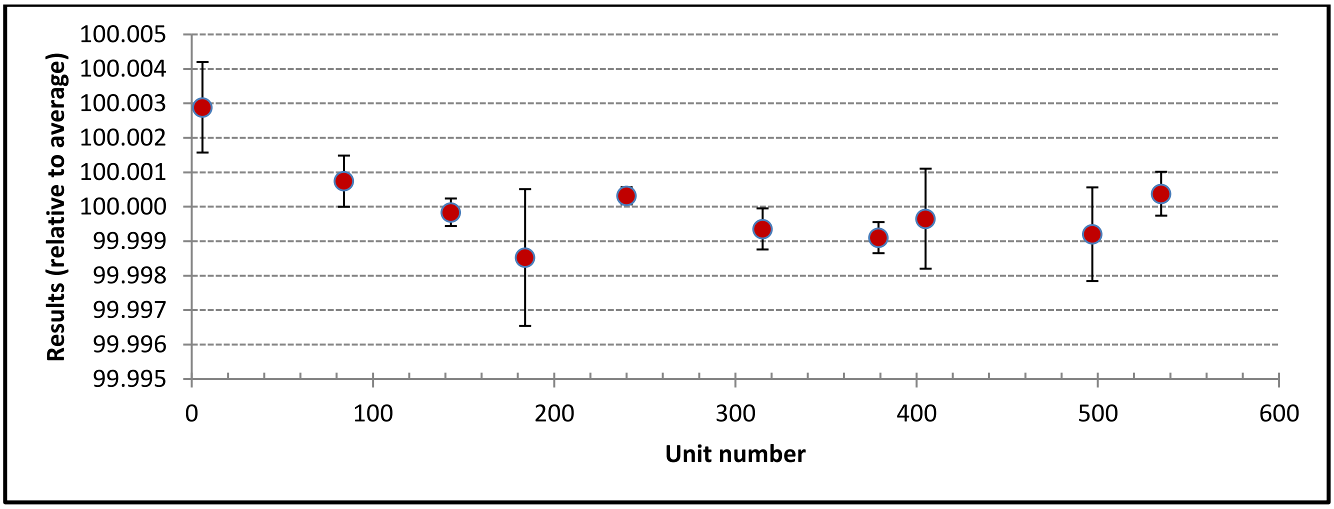


Figure A2.20. Between units homogeneity plot for Density by PTB

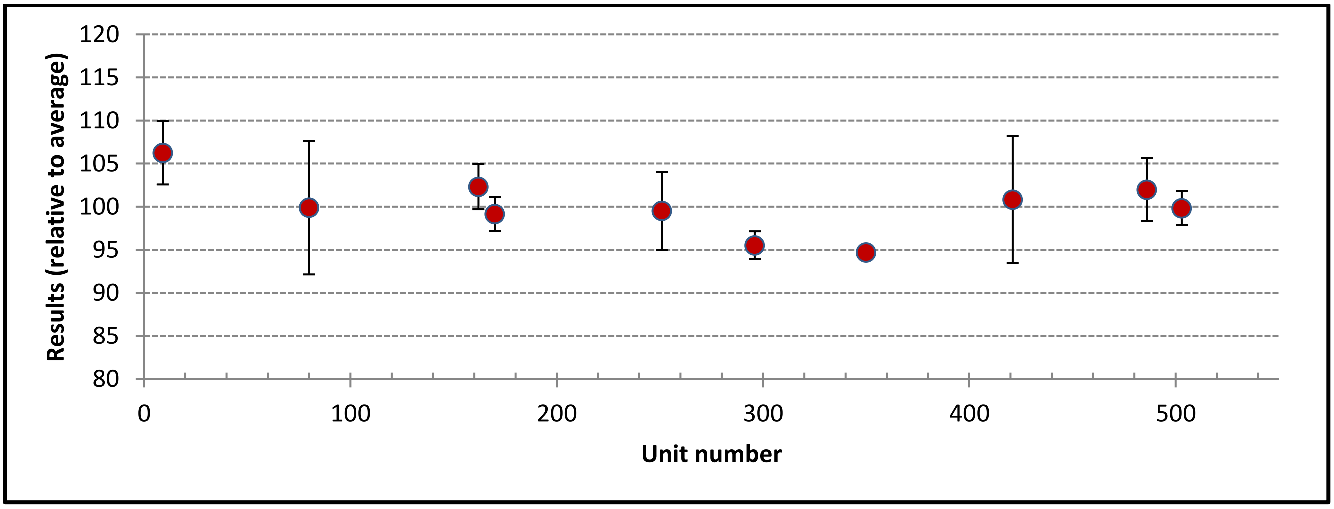


Figure A2.21. Between units homogeneity plot for Methanol by UME

ANNEX 3. Graphs for Short Term Stability Studies

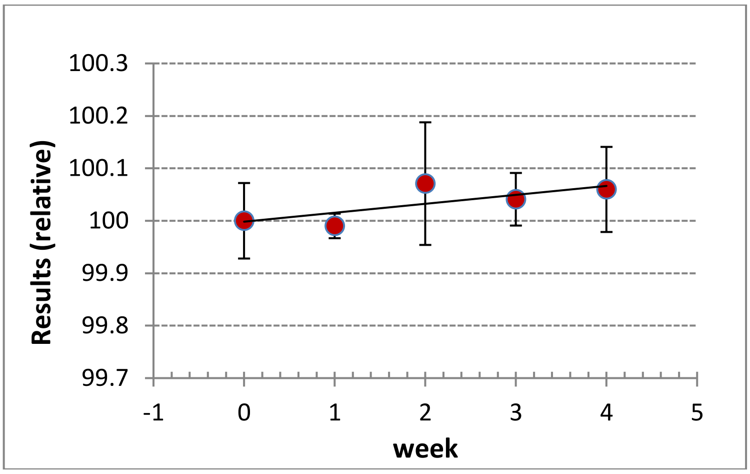


Figure A3.1. Short Term Stability Plot for Calorific Value at 45 °C by PTB

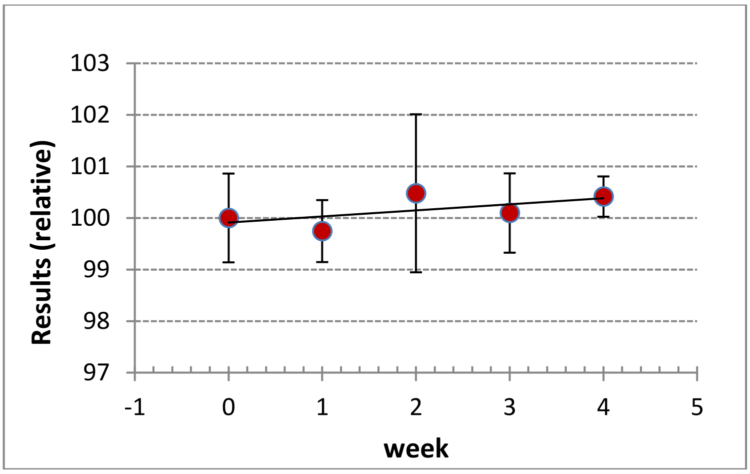


Figure A3.2. Short Term Stability Plot for Mono-Glyceride at 45 °C by BRML

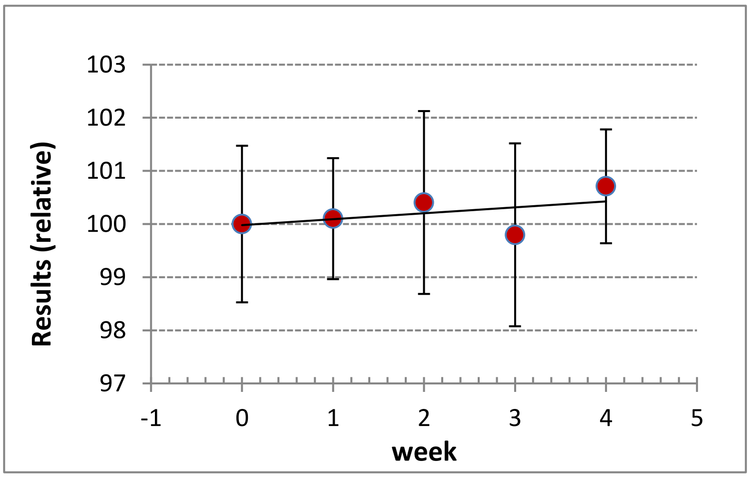


Figure A3.3. Short Term Stability Plot for Di-Glyceride at 45 °C by BRML

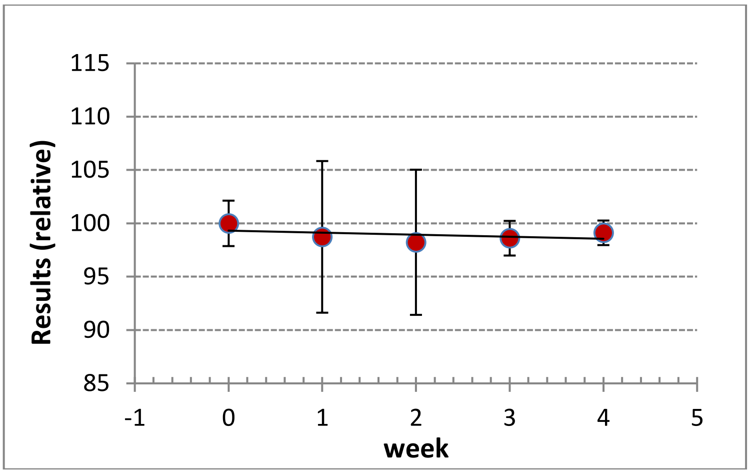


Figure A3.4. Short Term Stability Plot for Tri-Glyceride at 45 °C by BRML

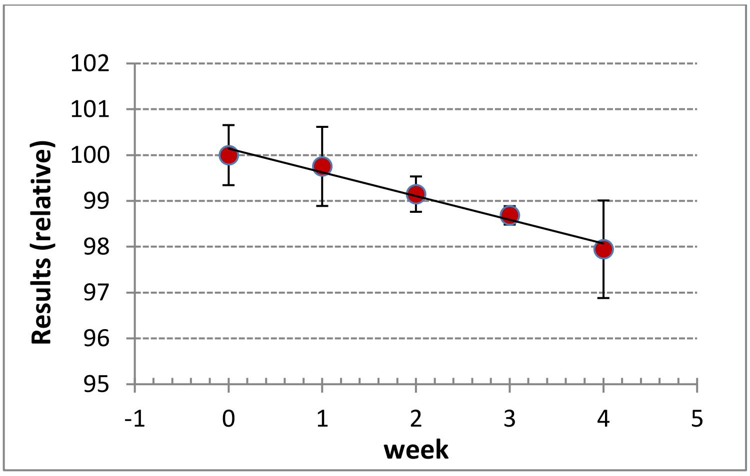


Figure A3.5. Short Term Stability Plot for Free Glycerol at 45 °C by BRML

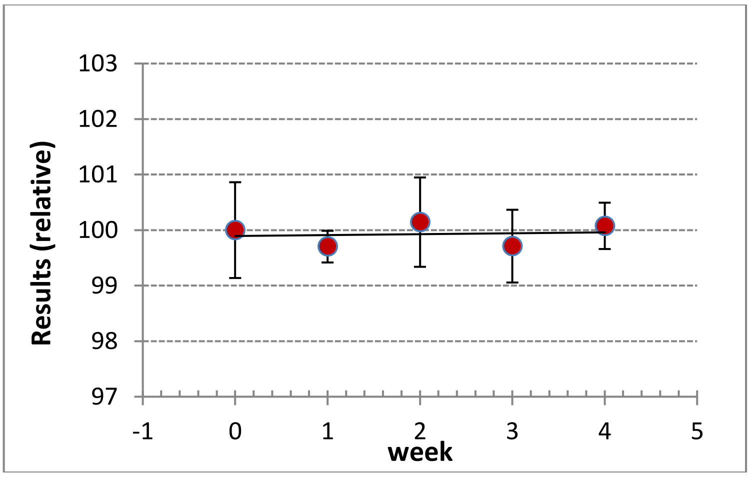


Figure A3.6. Short Term Stability Plot for Total Glycerol at 45 °C by BRML

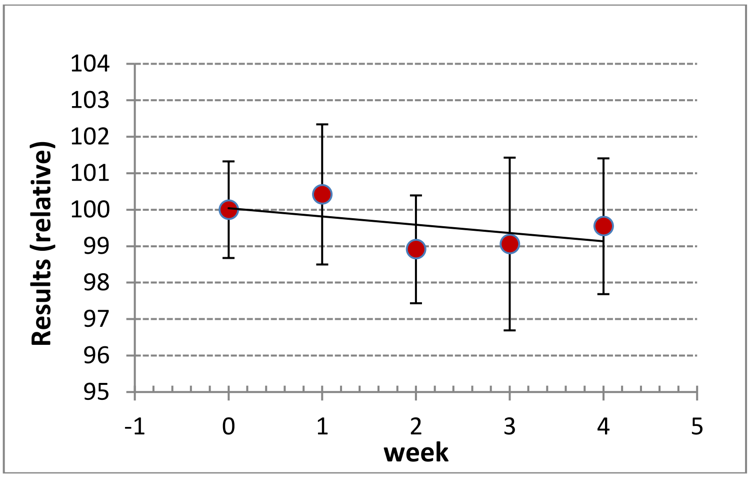


Figure A3.7. Short Term Stability Plot for Methyl Linoleate at 45 °C by IMBIH

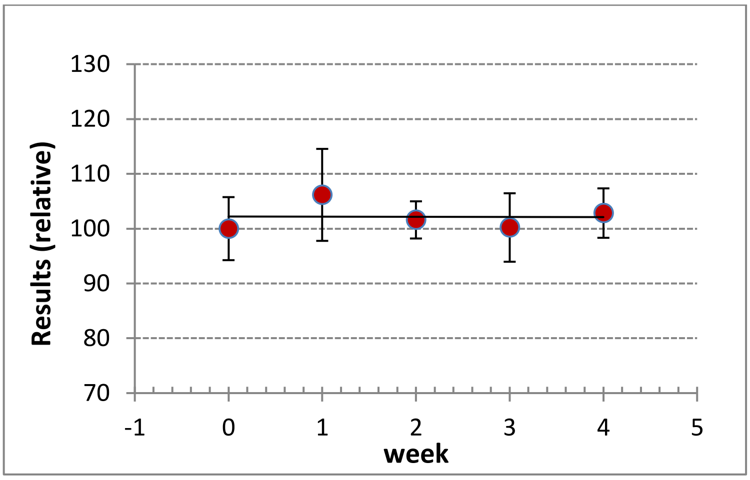


Figure A3.8. Short Term Stability Plot for Methyl Palmitoleate at 45 °C by IMBIH

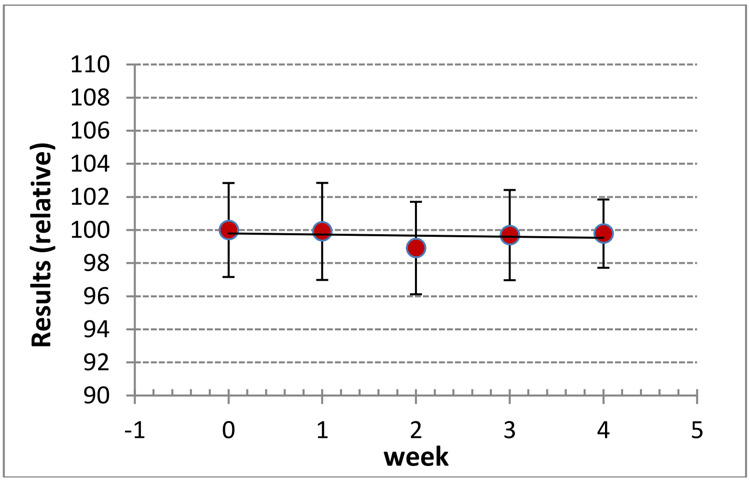


Figure A3.9. Short Term Stability Plot for Methyl Palmitate at 45 °C by IMBIH

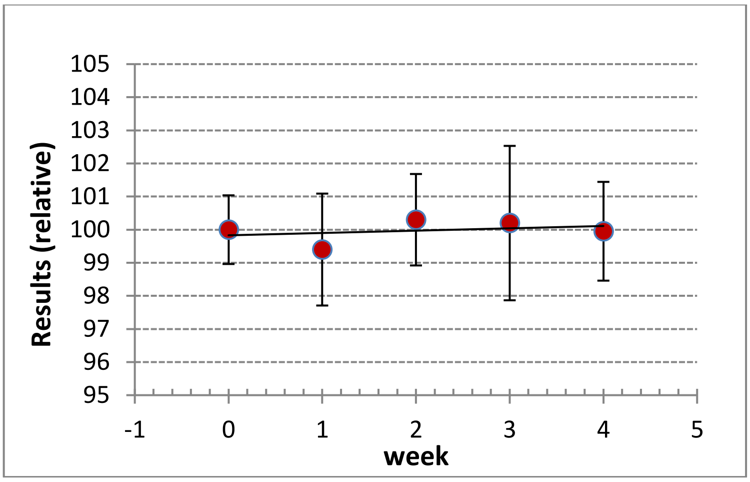


Figure A3.10. Short Term Stability Plot for Methyl 11-Octadecenoate at 45 °C by IMBIH

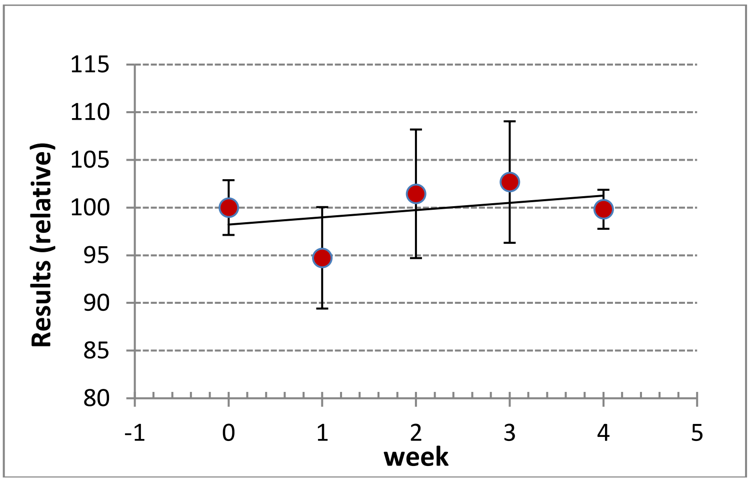


Figure A3.11. Short Term Stability Plot for Methyl Stearate at 45 °C by IMBIH

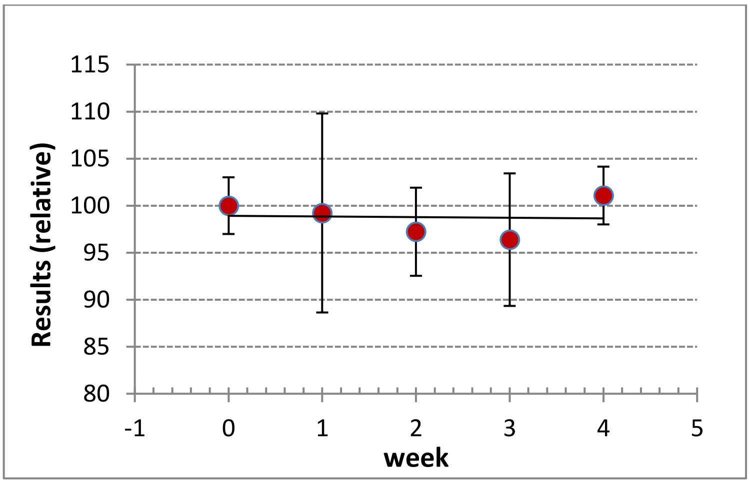


Figure A3.12. Short Term Stability Plot for Methyl cis-11-Eicosenoate at 45 °C by IMBIH

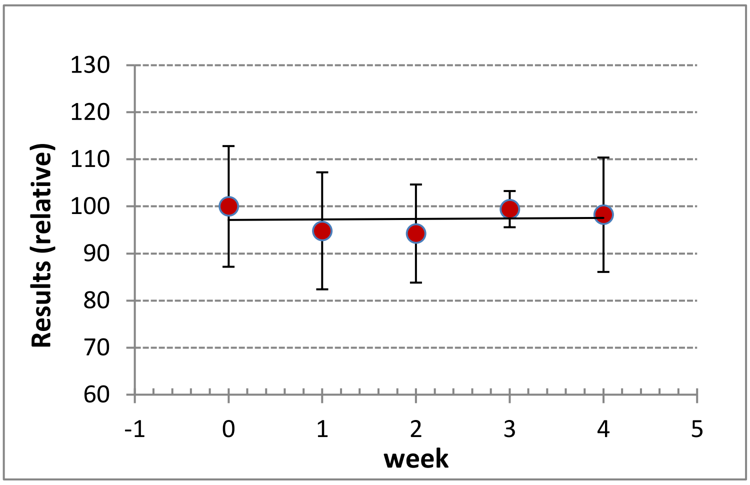


Figure A3.13. Short Term Stability Plot for Calcium at 45 °C by BRML

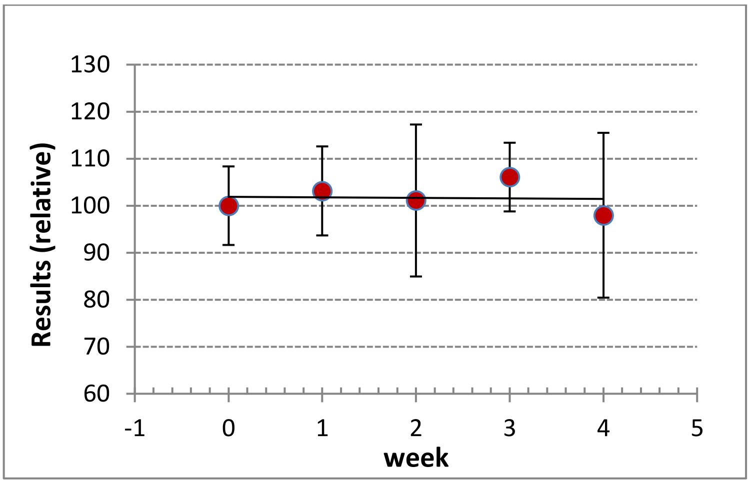


Figure A3.14. Short Term Stability Plot for Magnesium at 45 °C by BRML

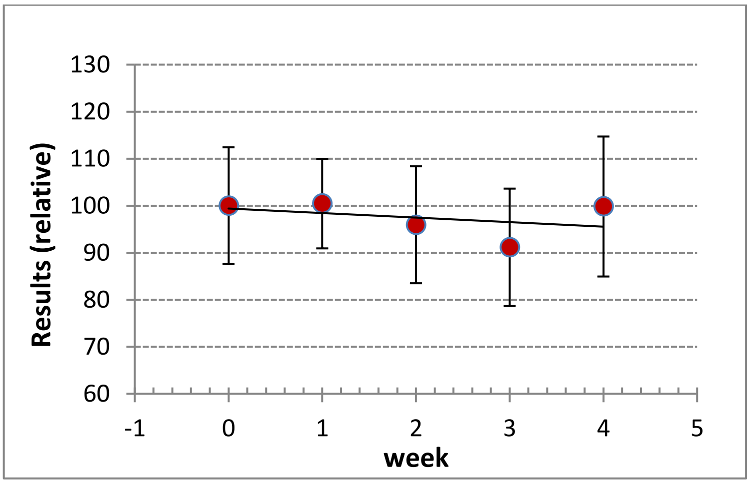


Figure A3.15. Short Term Stability Plot for Phosphorus at 45 °C by BRML

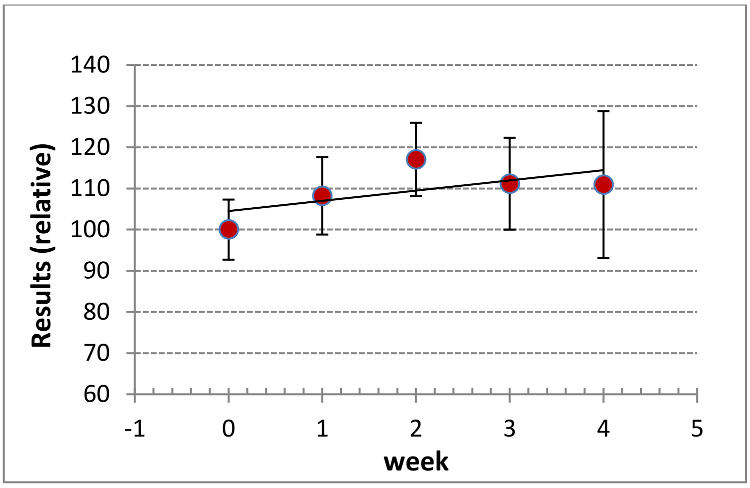


Figure A3.16. Short Term Stability Plot for Potassium at 45 °C by BRML

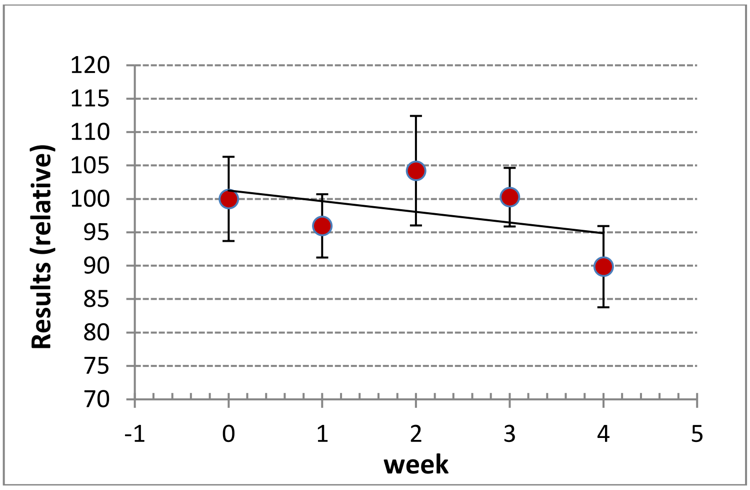


Figure A3.17. Short Term Stability Plot for Sodium at 45 °C by BRML

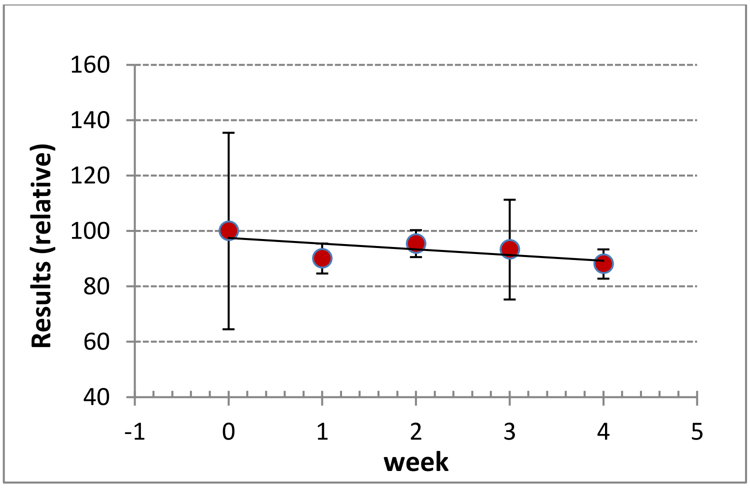


Figure A3.18. Short Term Stability Plot for Sulfur at 45 °C by BRML

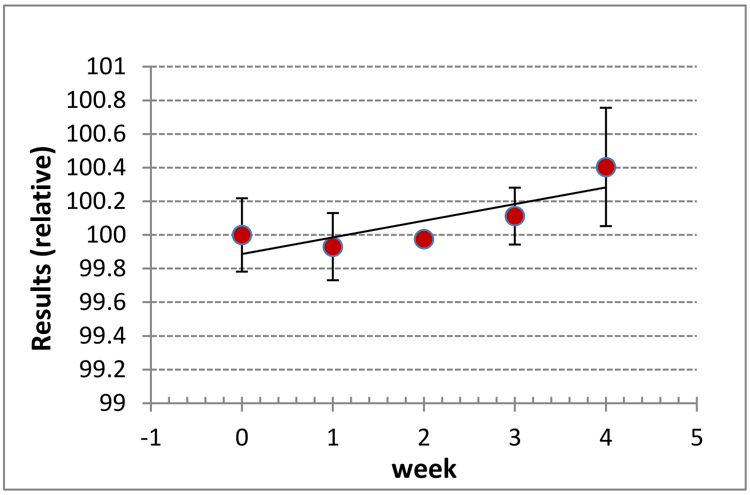


Figure A3.19. Short Term Stability Plot for Viscosity at 45 °C by PTB

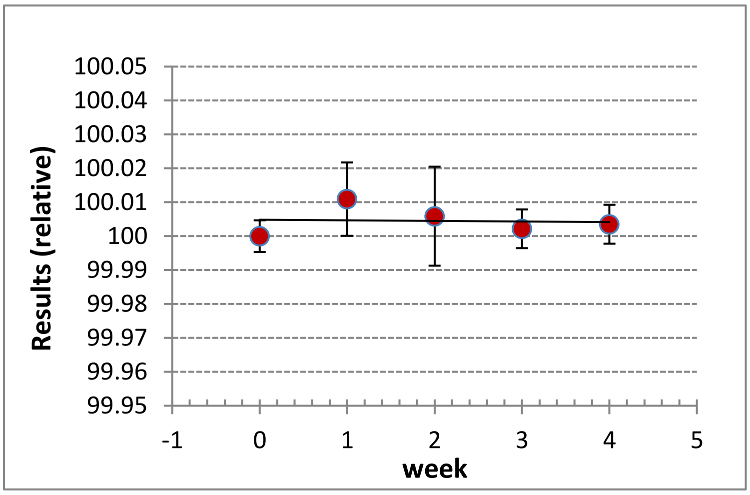


Figure A3.20. Short Term Stability Plot for Density at 45 °C by PTB

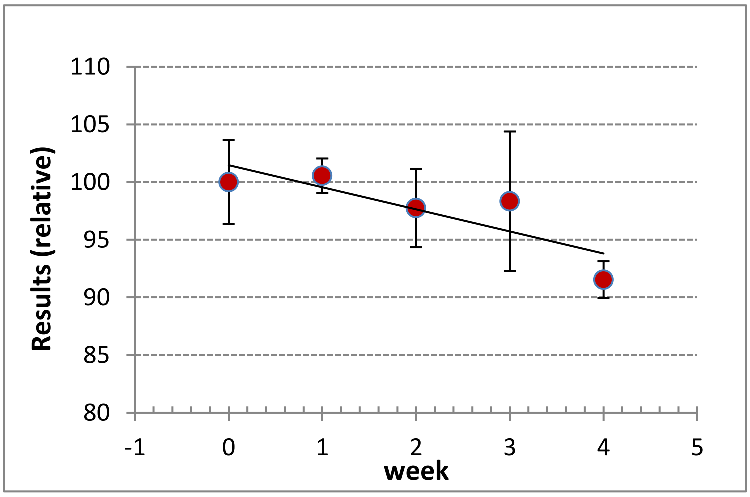


Figure A3.21. Short Term Stability Plot for Methanol at 45 °C by UME

ANNEX 4. Graphs for Long Term Stability Studies

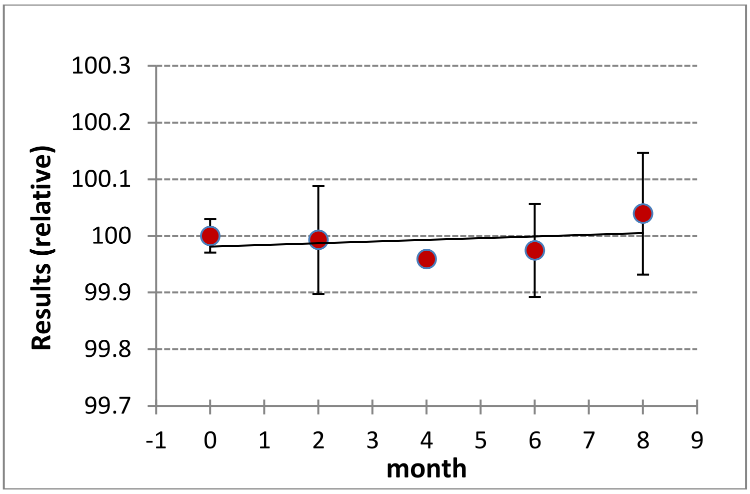


Figure A4.1. Long Term Stability Plot for Calorific Value at 22 °C by PTB

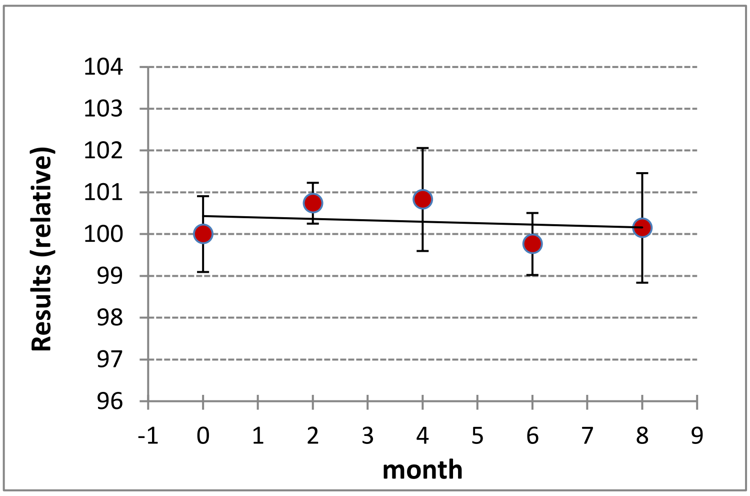


Figure A4.2. LongTerm Stability Plot for Mono-Glyceride at 22 °C by BRML

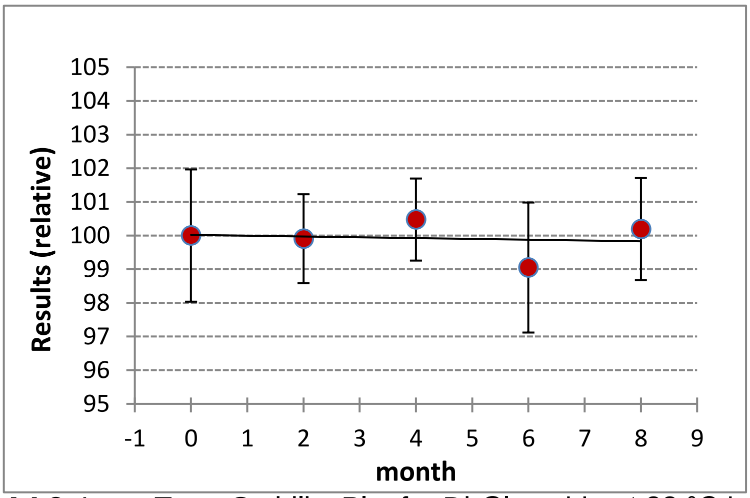


Figure A4.3. Long Term Stability Plot for Di-Glyceride at 22 °C by BRML

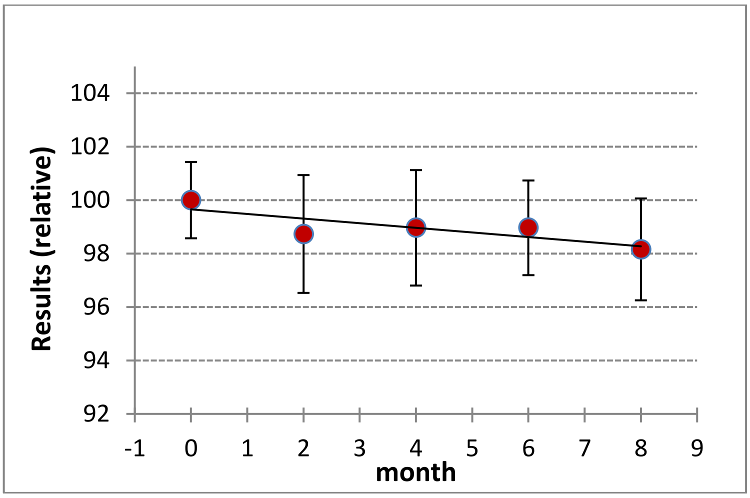


Figure A4.4. Long Term Stability Plot for Tri-Glyceride at 22 °C by BRML

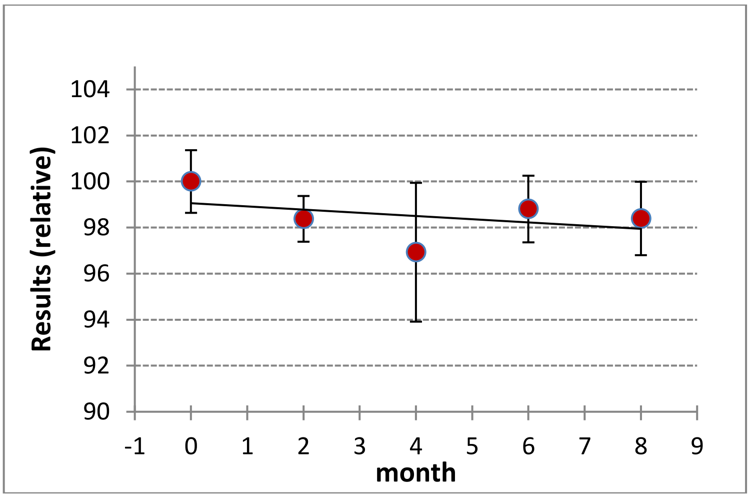


Figure A4.5. Long Term Stability Plot for Free Glycerol at 22 °C by BRML

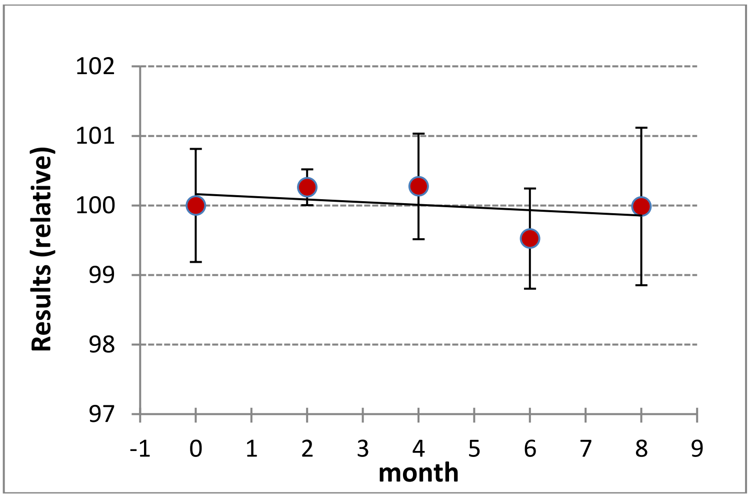


Figure A4.6. Long Term Stability Plot for Total Glycerol at 22 °C by BRML

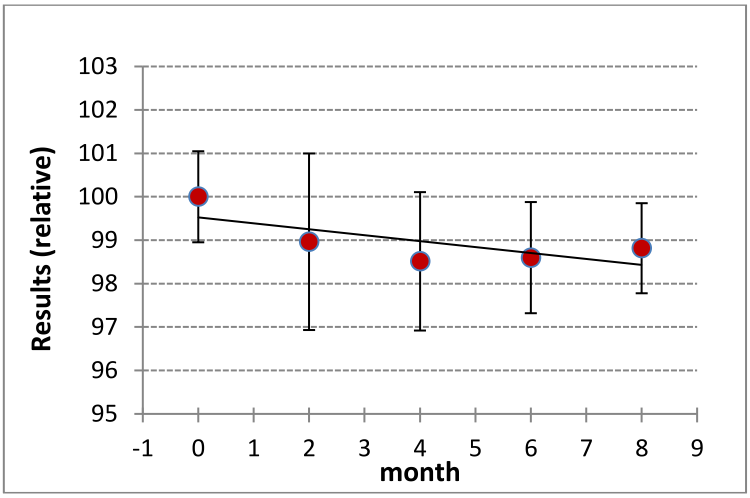


Figure A4.7. Long Term Stability Plot for Methyl Linoleate at 22 °C by IMBIH

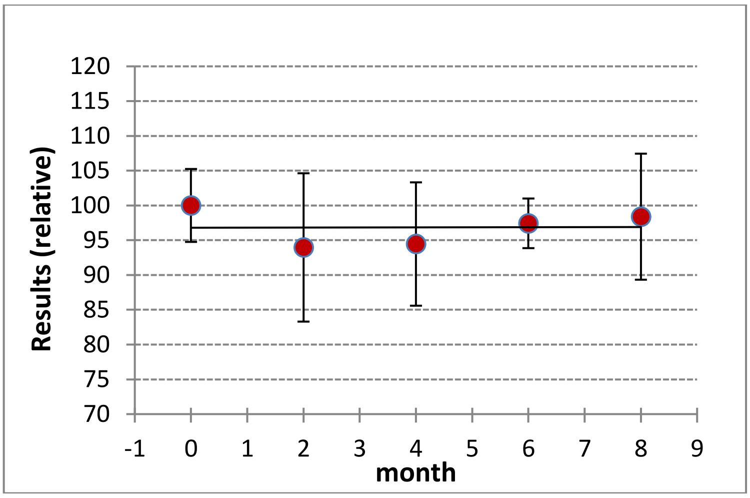


Figure A4.8. Long Term Stability Plot for Methyl Palmitoleate at 22 °C by IMBIH

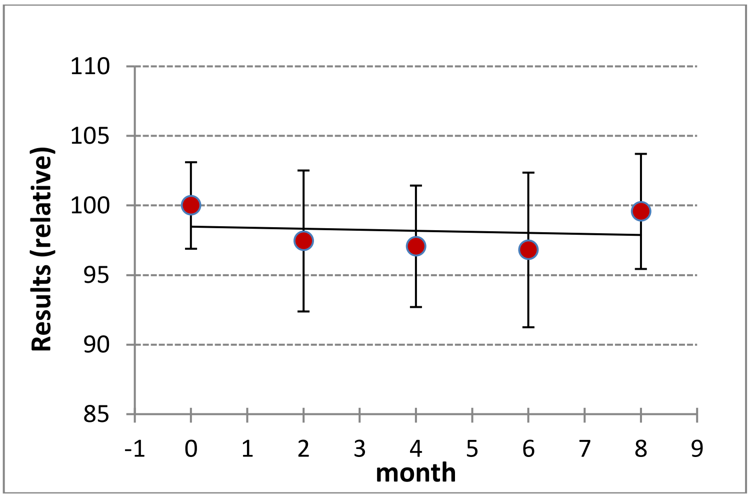


Figure A4.9. Long Term Stability Plot for Methyl Palmitate at 22 °C by IMBIH

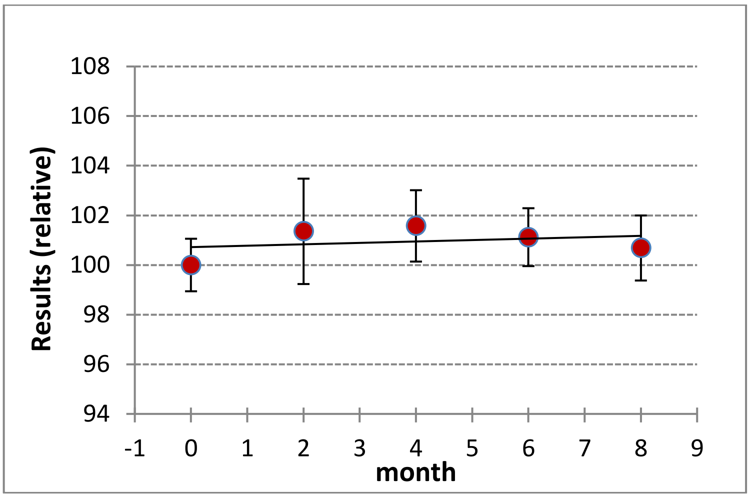


Figure A4.10. Long Term Stability Plot for Methyl 11-Octadecenoate at 22 °C by IMBIH

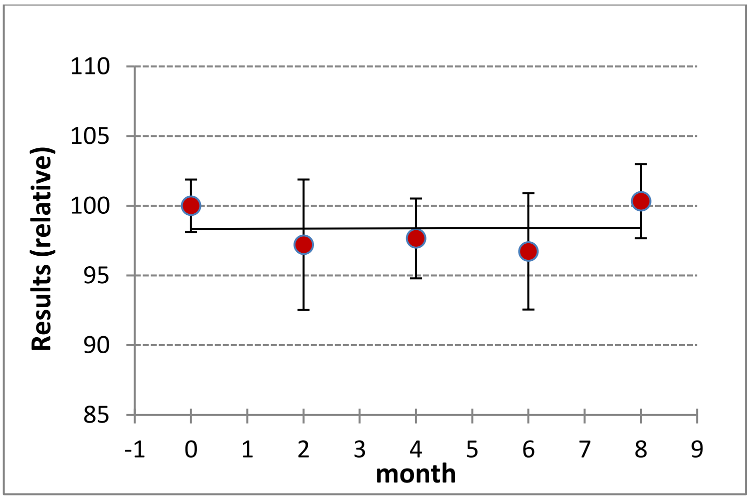


Figure A4.11. Long Term Stability Plot for Methyl Stearate at 22 °C by IMBIH

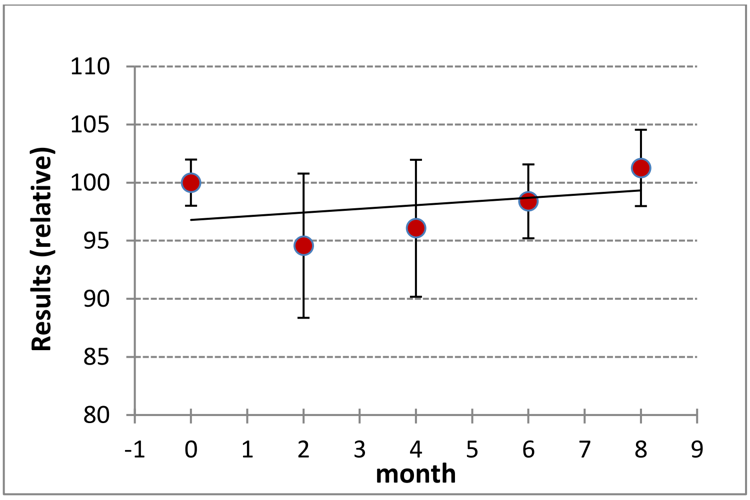


Figure A4.12. Long Term Stability Plot for Methyl cis-11-Eicosenoate at 22 °C by IMBIH

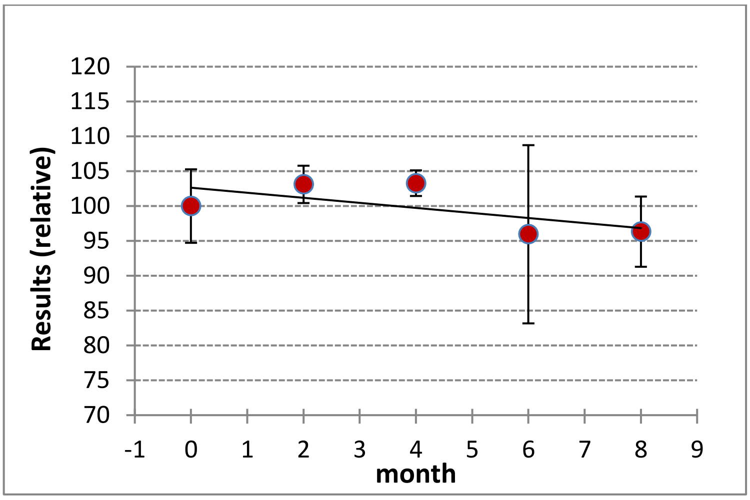


Figure A4.13. Long Term Stability Plot for Calcium at 22 °C by BRML

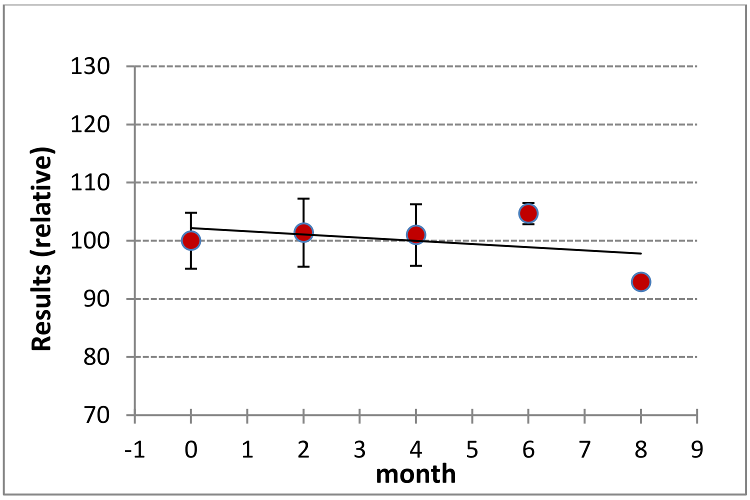


Figure A4.14. Long Term Stability Plot for Magnesium at 22 °C by BRML

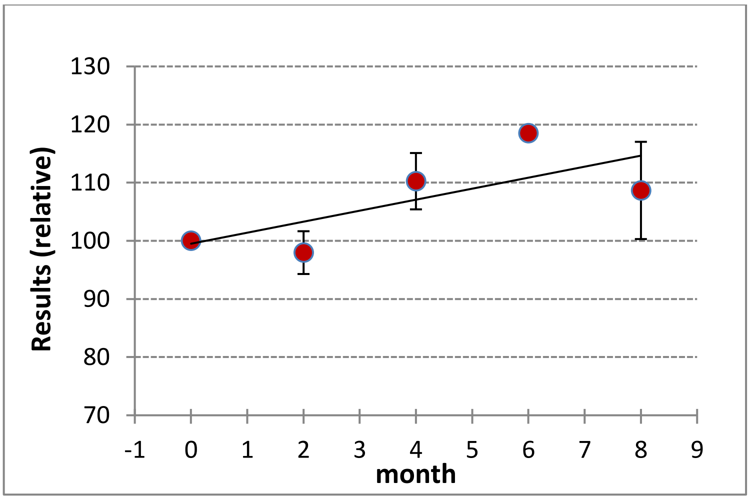


Figure A4.15. LongTerm Stability Plot for Phosphorus at 22 °C by BRML

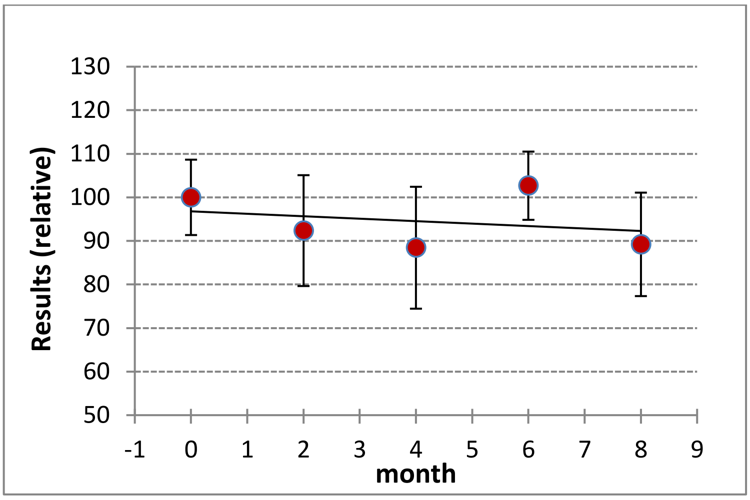


Figure A4.16. Long Term Stability Plot for Potassium at 22 °C by BRML

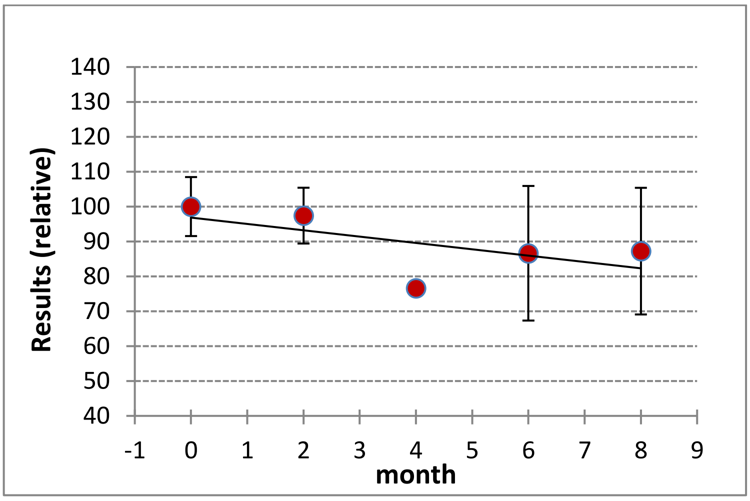


Figure A4.17. Long Term Stability Plot for Sodium at 22 °C by BRML

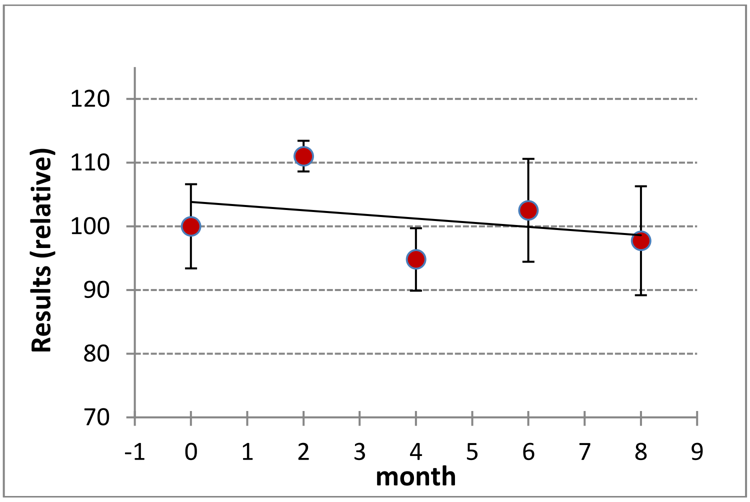


Figure A4.18. Long Term Stability Plot for Sulfur at 22 °C by BRML

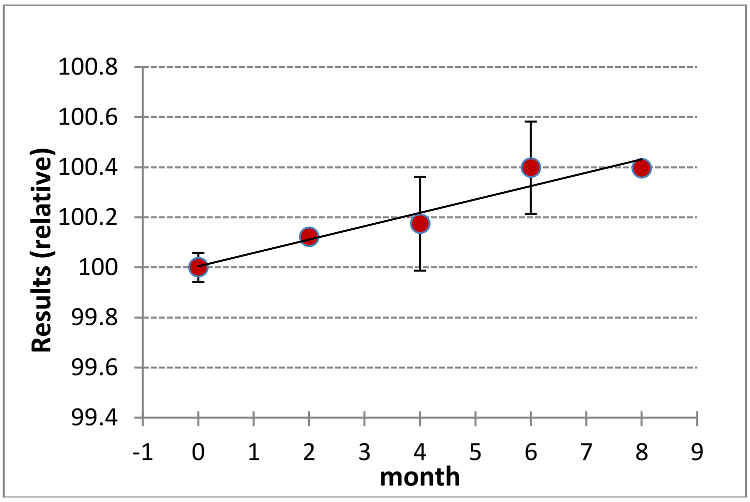


Figure A4.19. Long Term Stability Plot for Viscosity at 22 °C by PTB

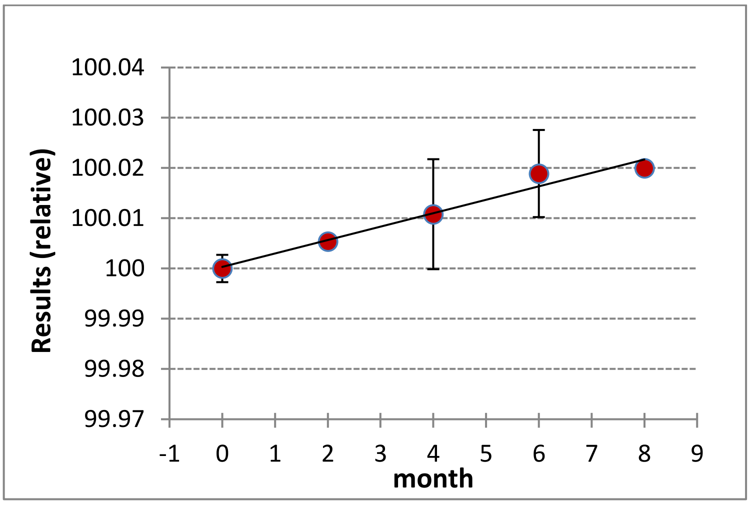


Figure A4.20. Long Term Stability Plot for Density at 22 °C by PTB

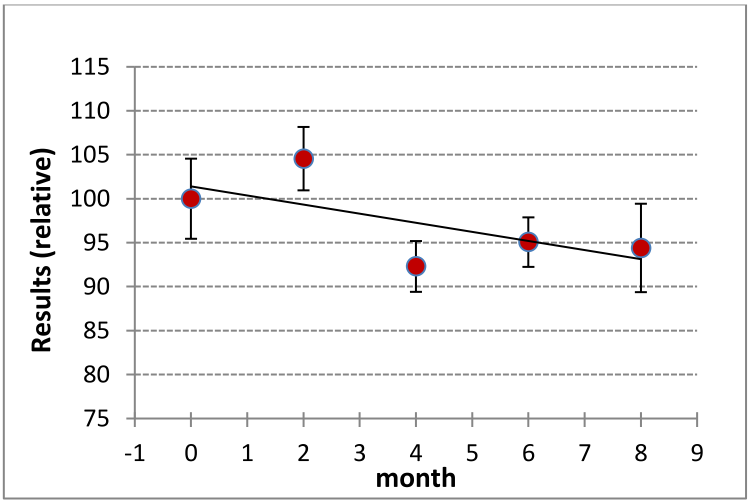


Figure A4.21. Long Term Stability Plot for Methanol at 22 °C by UME

ANNEX 5. Information about the Methods Used for the Characterization Study

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
BAM	Sulfur	Decomposition: Closed digestion with HNO_3 (5 mL) and H_2O_2 (1 mL) using a high pressure asher with T_{max} ≈ 300°C and P_{max} ≈ 130 bar Separation: Ion exchange chromatography with AG 1X8 resin filled in Eichrom columns, sample loading with dilute HNO_3 (0.028 mol/L), elution of matrix with water, and elution of S with HNO_3 (0.25 mol/L)	IDMS with inhouse calibrated ^{34}S-spike, as backspike NIST SRM 3181 was used to establish SI traceablity; isotopes measured: ^{32}S & ^{34}S, Ratio: $^{32}S/^{34}S$	Isotope dilution mass spectrometry	Inhouse calibrated ^{34}S-spike NIST SRM 3181 ERM-EF213 Sulfur in petrol
BRML	Calorific Value	No pretreatment	According to international standard ASTM D240-19	Isoperibol Oxygen Bomb Calorimetry	Standard Reference Material 39j Benzoic Acid (NIST)
	Calcium Magnesium Phosphorus Potassium Sodium Sulfur	500 mg of homogenized sample is mixed with 3 mL H_2O_2 30%, 8 mL HNO_3 65% and 1 mL HF 40% in a closed Teflon digestion container. The mixture is allowed to react for 5 minutes before closing the container. The heating was done using a microwave digestion system, according to the following temperature program: heating for 15 minutes to 190 °C; holding for 20 minutes at 190 °C. After cooling to the room temperature, HF is neutralized by addition of 10 mL H_3BO_3 4%. After neutralization, the samples are re-digested in the microwave according to the program: heating for 15 minutes to 150 °C; holding for 20 minutes at 150 °C.After cooling down to the room temperature, the digest is transferred into a 50 mL volumetric flask by gravimetric filtration.	5 point external calibration	ICP-MS with dynamic reaction cell	Multi-element ICP-MS Calibration Std. 3, 10µL/mL, Al, As, Ba, Be, Ci, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, k, Li, Mg, Mn, Ni, Pb, Rb, Se, Na, Ag, Sr, Ti, V, U, Zn, 5% HNO3, Merck, Germany; -ICP Multi-element standard solution IV, 1000 mg/L Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn 6.5% HNO3, Merck, Germany; -Multi-element calibration standard 5, 10µL/mL B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr H2O / 0.2% HF / Tr. HNO3, PerkinElmer, United States.
	-Mono-Glycerides -Di-Glycerides -Tri-Glycerides	Weigh approximately 100 mg of the homogenized sample into a 10 ml volumetric flask. Add 80 µl of the 1,2,4-butanetriol stock solution, 200 µl of the internal standard stock solution for glycerides, 200 µl of pyridine and 200 µl of MSTFA. Contact with moisture must be avoided. Close the volumetric flask hermetically and shake vigorously. Keep the mixture for 15 min. at room temperature, then make up to the mark with n-heptane. 1 µl of the reaction mixture is analyzed by gas chromatography	Single point calibration by using internal standards of glycerides	GC-FID EN 14105	For mono-, di-, and triglycerides, it is considered that, within the concentration range, the response of the detector is linear For each analysis, the relative RRF response factor of dinonadecanoate (Di C38) is evaluated according to trinonadecanoate (Tri C57) RRF<1.8

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
BRML	Free Glycerol Total Glycerol	Free glycerol from biodiesel is transformed into a more volatile and stable silyl derivative in the presence of pyridine and N-methyl-N-trimethylsilylfluoroacetamide (MSTFA). After silanization, the samples are analyzed by gas chromatography on a short capillary column with a low stationary phase deposition, with the introduction of the sample directly into the capillary column (on-column) and the detection of the compound with a flame ionization detector (FID). The quantitative determination of free glycerin is carried out in the presence of the internal standard 1,2,4-butanetriol (ISBT).	4 point external calibration	GC-FID EN 14105	For calibration: Glycerol, analytical standard,and 1,2,4-butanetriol For Quality Control: CRM4 4892 Glycerin
	Water	Measurement was done in accordance with ISO 12937:2000.,ASTM240-19,EN14105/2011,EN14214/2014. Cou-Lo Formula "A" Coulometric Anode Solution, Cou-Lo Formula "C" Coulometric Cathode Solution for the diaphragm titration cell of the Karl Fischer coulometric titrator were used	N/A	Coulometric Karl Fischer Titrimetry	MRC Aquastar Water Standard 0.01 % for the intermediate control of the titrator. SRM 2890 NIST USA was used for verification of measurements.
DTI	Calorific Value	No pretreatment	Specific heat capacity of the calorimeter is determined using benzoic acid reference material.	Isoperibol oxygen bomb calorimetry	Benzoic acid IKA C723, ID nr 32 430 00 EU index 607 705 – 00-8
GUM	Sodium Potassium Magnesium	An amount of 0,5 g of the sample was weighted directly in the mineralization PFTE vessel. Then 6 mL of HNO_3 and 2,5 mL H_2O_2 were added gradually to avoid sample losses. After around 1 h vessel was capped (vessel was covered by a watch glass before) and then sample was mineralised by Anton Paar Multiwave 3000 (programme for 4 vessels: (1) ramp 525 W, 20 min; (2) hold 525 W, 40 min; (3) cooling until 40 ℃ reached. After mineralisation sample was quantitatively transferred into the 50 mL vessel, diluted with high-purity deionized water water to 50 mL and weighted.	Calibration curve with internal standardization, the following ratios were measured $^{23}Na/^{45}Sc$, $^{24}Mg/^{45}Sc$, $^{39}K/^{45}Sc$	ICP-MS with collision gas (He) mode	Monoelemental aqueous solutions provided by Slovak Institute of Metrology: sodium SMU B23, potassium SMU B18, magnesium SMU B20. Samples were spiked with the known amount of mixed standard to determine recovery of the added element. Quality Control samples were measured to control the instrument drift.

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
IMBIH	-Methyl Linoleate -Methyl Palmitoleate -Methyl Palmitate -Methyl 11-Octadecenoate -Methyl Stearate -Methyl cis-11-Eicosenoate	Samples were diluted in 2 steps in pure n-hexane (HPLC/GC grade) to achieve readable concentrations of corresponding compounds step1 - 30 µL of biodiesel sample in 3,5 mL of n-hexane step2 - 30 µL of diluted sample from step1 in 1 mL of n-hexane"	Individual peaks of chemical components biodiesel samples were identified by comparison of their retention indices (RI) with those of authentic compounds or literature data and computer matching between samples mass spectra and mass spectra from spectrometer database libraries (Wiley7NIST05 and NIST14).	GC/MS	-
LGC	Density at 15 °C	No pretreatment	Calibrated Instrument for the range of measurement is used	ASTM D4052 Density Meter	Paragon Scientific D1480 Certified sample N8.
	Kinematic Viscosity at 40 °C	No pretreatment	Calibrated Instrument for the range of measurement is used	ASTM D7042 Stabinger Viscometer	Paragon Scientific D1480 Certified sample N8.
PTB	Calorific Value	No pretreatment	Specific heat capacity of the calorimeter is determined using benzoic acid reference material.	Isoperibol oxygen bomb calorimetry	UME CRM 1504 Benzoic Acid
	Density at 15 °C	No pretreatment	Calibrated instrument is used	Oscillation-type densimeter	High Purity Water
	Kinematic Viscosity at 40 °C	No pretreatment	Calibrated instrument is used	Stabinger Viscosimeter	-

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
UME	Calorific Value	No pretreatment	Specific heat capacity of the calorimeter is determined using benzoic acid reference material.	Isoperibol oxygen bomb calorimetry	UME CRM 1504 was used as certified reference material (benzoic acid) in instrument calibration
	Calcium Magnesium Phosphorus Potassium Sodium	1 mL sample was diluted with 2 mL ICP solvent (Conostan) All solutions were prepared by weighing	Standard addition calibration, Conostan 15-100-115 for Na, 15-100-125 for Mg, 15-100-155 for P, 15-100-195 for K, 15-100-205 for Ca were used to establish SI traceablity; Wavelenghts measured: Na 589.592, Na 588.995, Mg 279.553, Mg 280.270, P 177.495, P 178.287, K 766.491, Ca 396.847, Ca 315.887, Ca 422.673, Ca 396.847	ICP-OES	Conostan 15-100-115 for Na, 15-100-125 for Mg, 15-100-155 for P, 15-100-195 for K, 15-100-205 for Ca, NMIJ 8302a Biodiesel Fuel
	Magnesium Phosphorus Sodium	0,6 mL sample was digested with 4 mL HNO_3 (Suprapur, Merck) The sample was mineralised by microwave digestion system. Temperature programme : (1) ramp 25 min. up to 150 °C; (2) hold 30 min at 150 °C . After mineralisation sample was transferred into the 50 mL PP vessel, diluted with high-purity deionized water up to 50 mL. All solutions were prepared by weighing	Standard addition calibration, NIST SRM 3152a for Na, NIST SRM 3131a for Mg, NIST SRM 3139a for P were used to establish SI Isotopes measured: 23Na, 24Mg, 31P	HR ICP-MS	, NIST SRM 3152a for Na, NIST SRM 3131a for Mg, NIST SRM 3139a for P, NMIJ 8302a Biodiesel Fuel
	Sulfur	99.26% ^{34}S enriched material (ISOFLEX) was dissolved in ICP solvent (Conostan) ^{34}S spiked solution: 65 mg/kg sulfur Sample blend : 300 uL sample was mixed with 70 uL ^{34}Spiked solution Calibration blend 1 : 300 uL NIST SRM 1616b was mixed with 50 uL ^{34}Spiked solution Calibration blend 2 : 300 uL NIST SRM 1616b was mixed with 80 uL ^{34}Spiked solution The blend solutions were diluted with ICP solvent up to 1,8 mL. All solutions were prepared by weighing	IDMS with in-house ^{34}S-spike, NIST SRM 1616b was used to establish SI traceablity; Isotopes measured: 32S & 34S, Ratio: 32S/34S	ID-ICP MS	NIST SRM 1616b NMIJ 8302a Biodiesel Fuel

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
UME	Sulfur	0,6 mL sample was digested with 4 mL HNO_3 (Suprapur, Merck) The sample was mineralised by microwave digestion system. Temperature programme : (1) ramp 25 min. up to 150 °C; (2) hold 30 min at 150 °C . After mineralisation sample was transferred into the 50 mL PP vessel, diluted with high-purity deionized water up to 50 mL. All solutions were prepared by weighing	Standard addition calibration, NIST SRM 3181 was used to establish SI traceablity Isotopes measured: : 32S & 34S	HR ICP-MS	NIST SRM 3181 NMIJ 8302a Biodiesel Fuel
	Sulfur	1 mL sample was diluted with 2 mL ICP solvent (Conostan). All solutions were prepared by weighing	Standard addition calibration, NIST SRM 1616b was used to establish SI traceablity; wavelenghts measured: S180.731 & S182.034	ICP OES	NIST SRM 1616b NMIJ 8302a Biodiesel Fuel
	Methanol	980 µl biodiesel sample and 20 µl IS was mixed to the headspace sample bottle.	3 point internal standard calibration. 2-propanol solution was prepared as an internal standard.	Headspace GC-FID	-
	Water	Approximately 2.5-3.0 mL sample is weighed and sealed. Oven is adjusted to 140 °C. Sample is heated for 7 min. Hydranal® 34836 - Coulomat Ag Reagent For Coulometric Kf Titration (Anolyte Solution) was used in the cell.	N/A	COU- o-KFT	NIST 2890 Water Saturated Octanol

ANNEX 6. Graphs for Characterization Study

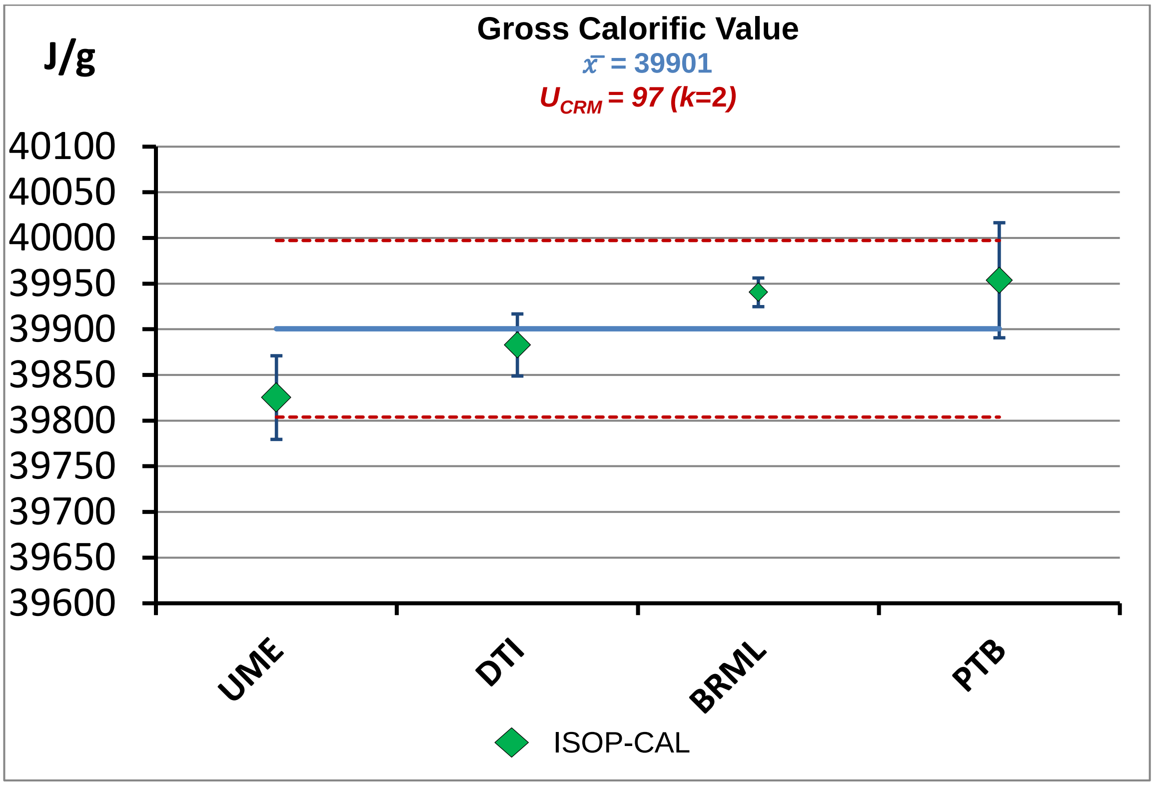


Figure A6.1. Characterization Study Plot for Calorific Value

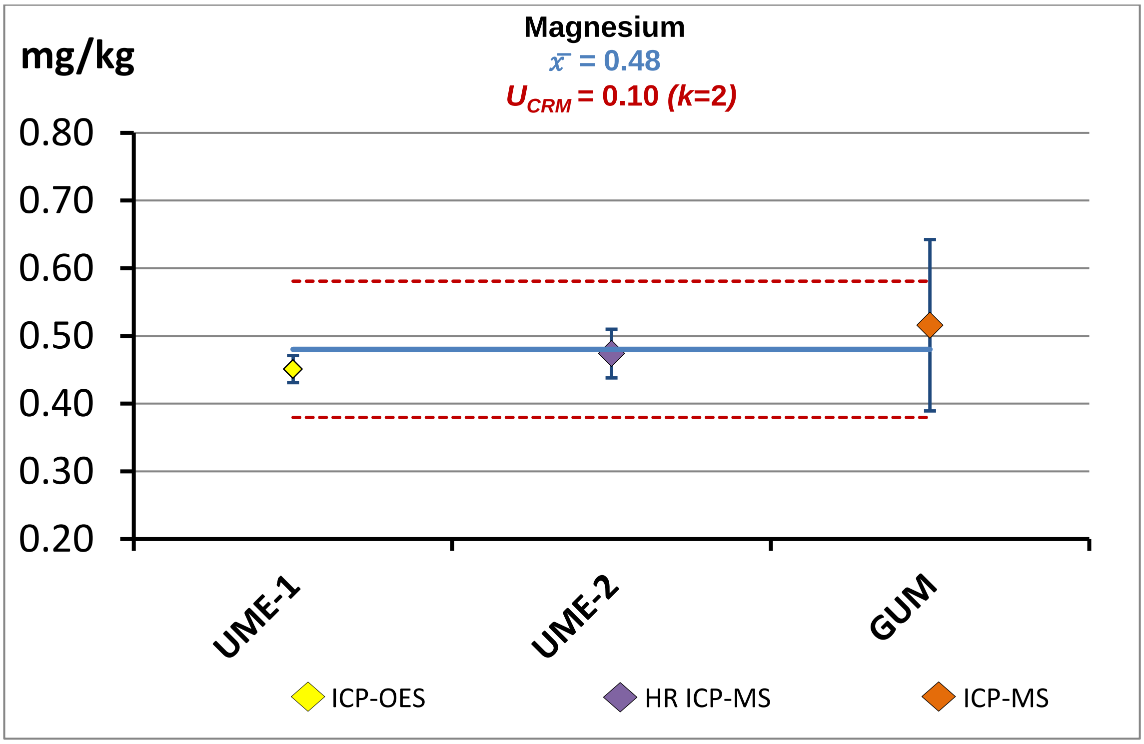


Figure A6.2. Characterization Study Plot for Magnesium

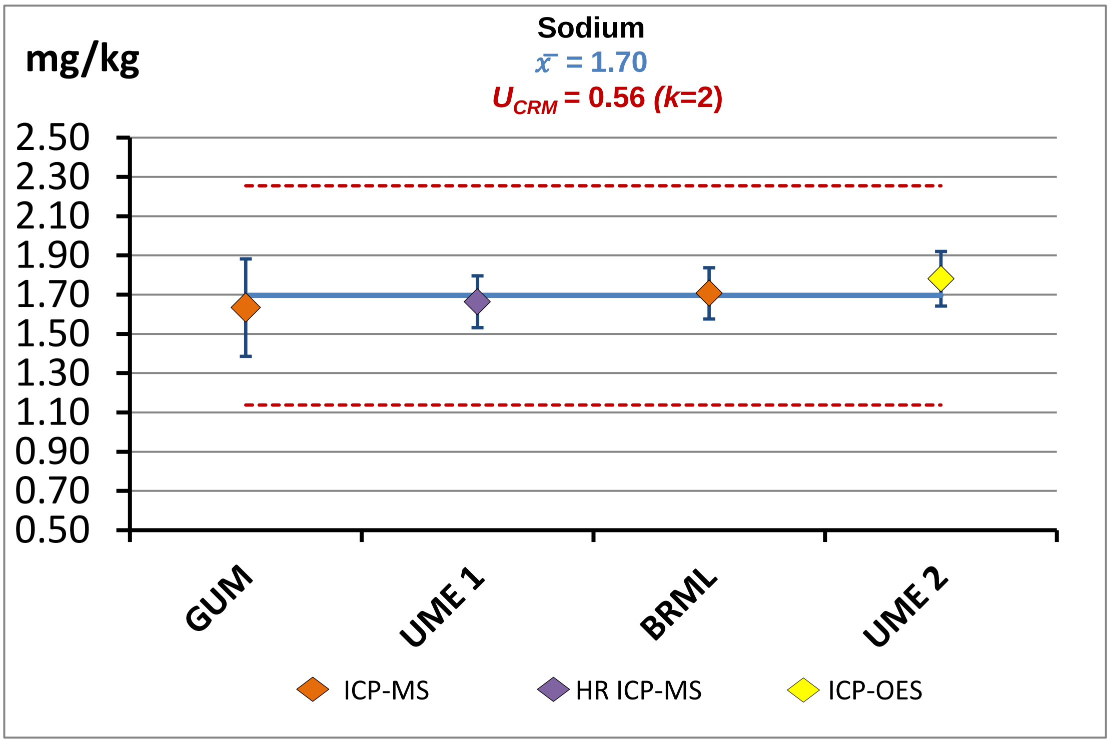


Figure A6.3. Characterization Study Plot for Sodium

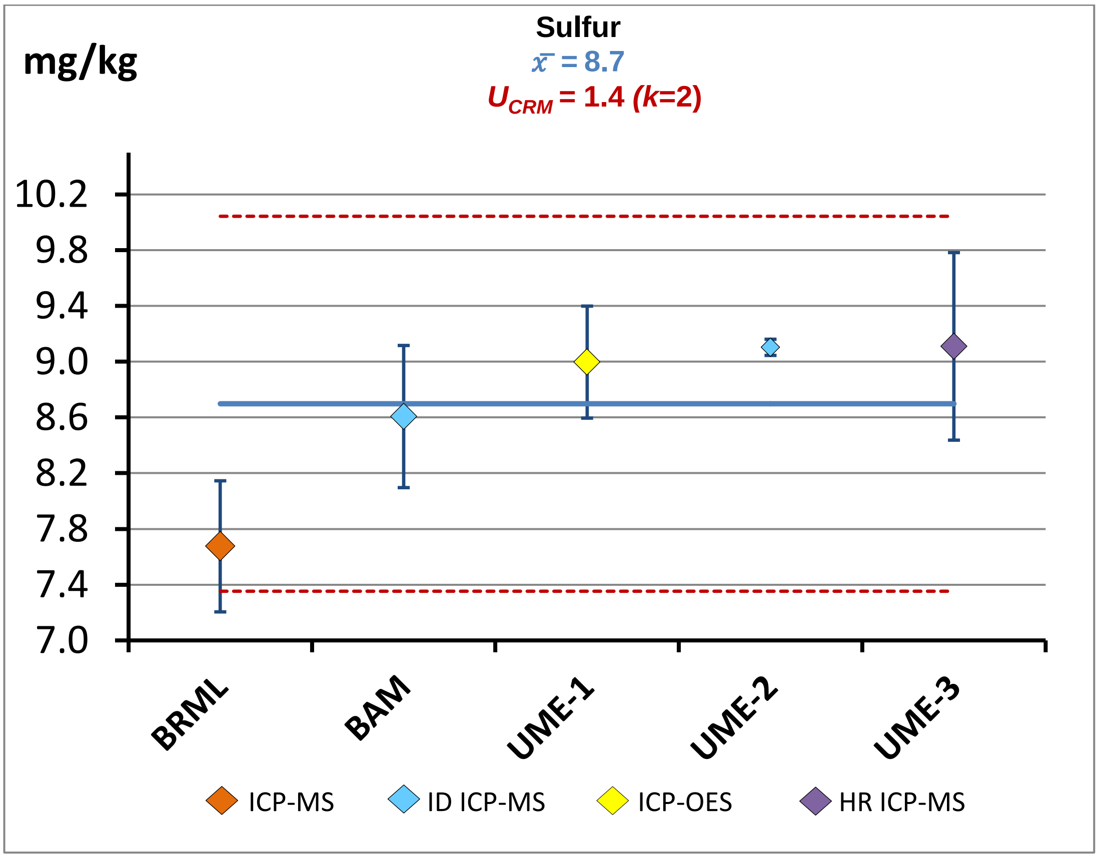


Figure A6.4. Characterization Study Plot for Sulfur

WOOD PELLET POWDER
UME BIOFMET CRM 02
&
WOOD PELLET
UME BIOFMET CRM 03

Alper İşleyen
Kemal Özcan
Murat Tunç
Aylin Boztepe
Fatma Gonca Coşkun
Adnan Şimşek
Dilara Kurt
Gökhan Aktaş
Hatice Altuntaş

Kai Moshammer
Moaaz Shehab
Katarina Hafner-Vuk
Dijana Coric
Milica Krajisnik
Camelia Stratulat
Adriana Bratu
Raluca Ginghina
Mihail Radu
George Victor Ionescu

Jochen Vogl
Maren Koenig
Strzelec Michał
Anna Bojanowska-Czajka
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Anne Mette Frey
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Date
XX.YY.2023

Assoc. Prof. Mustafa Çetintaş
Acting Director

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ABBREVIATIONS

ANOVA	analysis of variance
α	significance level
BAM	Bundesanstalt für Materialforschung und -prüfung, Germany
BRML-INM	National Metrology Institute, Bucharest, Romania
CRM	certified reference material
DTI	Danish Technological Institute, Denmark
EMPIR	European Metrology Programme for Innovation and Research
EU	European Union
GUM	Central Office of Measures, Poland
HDPE	High density polyethylene
HR ICP-MS	High resolution ICP-MS
ICP-MS	Inductively coupled plasma mass spectrometry
ID MS	isotope dilution Mass Spectrometry
IMBIH	Institute of Metrology, Sarajevo, Bosnia and Herzegovina
IS	internal standard
ISO	International Organization for Standardization
LOQ	Limit of Quantification
MPAES	Microvawe plasma atomic emission spectroscopy
$MS_{between}$	mean square between-bottle from ANOVA
MS_{within}	mean square within-bottle from ANOVA
n	number of replicates per unit
PTB	Physikalisch Technische Bundesanstalt, Braunschweig, Germany
RSD	relative standard deviation
s	standard deviation
s_{bb}	between-bottle standard deviation
SGT	single Grubbs' test
SI	International System of Units
s_{wb}	within-bottle standard deviation
U_{AV}	expanded uncertainty of assigned value
u_{bb}	standard uncertainty related to possible between-bottle heterogeneity
u^*_{bb}	standard uncertainty of heterogeneity that can be hidden by method repeatability
U_{CRM}	expanded uncertainty of certified value
UME	TÜBİTAK National Metrology Institute, Türkiye
u_{char}	standard uncertainty related to characterisation
u_{lts}	standard uncertainty related to long term stability
u_{sts}	standard uncertainty related to short term stability

The subscript "rel" is added when a variable is expressed in relative terms (e.g. as percent)

ABSTRACT

Biomass is a key element in biofuels. It can be defined as a fuel produced through contemporary biological processes, and its increased use can support the EU's aims of reducing greenhouse gas emissions. Information on the nature and the quality of the biomass or biofuel is important in order to support the optimisation of their combustion with respect to realising higher efficiencies and lower emissions during energy production.

BIOFMET project aims to establish advanced traceable measurement standards for the determination of the calorific value and impurities.

This report describes the production of two solid biofuel reference materials: UME BIOFMET CRM 02, certified for calorific value, moisture, ash and mass fractions of Al, Cr, Cu, Mg, Mn, Ni, Pb, S, Zn elements and UME BIOFMET CRM 03, certified for calorific value and moisture. These materials were produced in accordance with requirements of ISO 17034 standard.

The raw material for the CRMs is wood pellet (property class labelled as A1 according to ISO 17225-2 by the manufacturer) which was produced in Poland. For UME BIOFMET CRM 02, the material was spiked with As, Cr, Ni, Pb, Hg and milled to obtain a powder material whereas UME BIOFMET CRM 03 was bottled as it is, in pellet form after homogenization without further processing except gamma irradiation which was applied to both materials.

Homogeneity and stability of the material were assessed in accordance with ISO Guide 35. The material was characterized by an interlaboratory comparison among competent laboratories.

Uncertainties of the certified values were calculated in accordance with GUM "Guide to the Expression of Uncertainty in Measurement" and includes characterization, homogeneity, stability components.

UME BIOFMET CRM 02-Wood Pellet Powder material is intended for method development and validation in determination of calorific value, moisture, ash and mass fractions of Al, Cr, Cu, K, Mg, Mn, Ni, Pb, S, Zn elements and for quality control purposes. The CRM is available in glass bottles containing approximately 50 g of powder material. UME BIOFMET CRM 03 material is intended for method development and validation in determination of calorific value and moisture and for quality control purposes. The CRM is available in glass bottles containing approximately 100 g of pellet material.

INTRODUCTION

Energy has a crucial role in life which is needed for heating, lighting, cooking in households and for every transport activity. Fossil fuels (coal, gas, and oil) currently account for about 79% of world energy consumption, nuclear energy for 7%, and renewable energy sources for 14% [1]. One of the renewable energy source is biomass and a definition adopted by EU legislation for biomass is "the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries". When biomass is burned or digested, the organic carbon is recycled in a global process known as the carbon cycle. In this process, the CO_2 that was absorbed as the plants grew is simply returned to the atmosphere when the biomass is burned. Therefore, if the growth and harvest cycle is maintained, there will be no net release of CO_2, therefore biomass is regarded as a carbon neutral energy source that does not emit CO_2 into the atmosphere when burned. Biomass can be used as feedstock for energy production either by direct combustion or through conversion to biofuels such as biodiesel, ethanol or biogas.

Wood pellets are a type of biomass fuel made from compressed sawdust or other wood by-products. They are small, cylindrical pellets typically measuring up to 25 millimeters in diameter and 5-40 millimeters in length. Wood pellets are widely used as a renewable energy source for heating and power generation. They have a high energy density, low moisture content, and consistent size, which makes them efficient and convenient to use in pellet stoves, boilers, and furnaces. Wood pellets are considered a sustainable alternative to fossil fuels because they are made from renewable resources and emit fewer greenhouse gases when burned.

Relevant characteristics, requirements and test methods for graded wood pellets for non-industrial and industrial use are given in EN ISO 17225-2 standard [2].

Laboratories performing sampling and tests in this field need matrix CRMs enabling appropriate quality control. National metrology institutes and designated institutes with proven metrological capabilities for the production and certification of such materials are necessary for the provision of quality data. The EMPIR joint research project BIOFMET [3] developed capacity to produce CRMs for biofuel analysis by transferring the theoretical and practical know-how between the partners and combining their skills to focus on biofuel CRM production according to ISO 17034:2016 [4] and ISO Guide 35:2017 [5].

UME BIOFMET CRM 02 and UME BIOFMET CRM 03, the production of which were carried out by a project consortium described in this report, is intended to be used as a quality assurance and quality control tool especially by the laboratories involved in the quality control of the solid biofuels used for heating applications.

The parameters aimed to be certified in UME BIOFMET CRM 02 are the following: calorific value, moisture, ash and mass fractions of Al, Cr, Cu, K, Mg, Mn, Ni, Pb, S, Zn elements. The target concentration levels for elements were decided to meet laboratories' needs. The parameters aimed to be certified in UME BIOFMET CRM 03 are calorific value and moisture.

PARTICIPANTS

Laboratory/organisations involved in the production and their contributions are presented in Table 1.

Table 1. Laboratory/organizations involved and their contributions

Activity	Laboratory / Organization
Project management and data evaluation	TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye
Preliminary measurements	TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye
Processing	TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye

Activity	Laboratory / Organization
Homogeneity and Stability studies	PTB, Physikalisch Technische Bundesanstalt, Braunschweig, Germany BRML-INM, National Metrology Institute, Bucharest, Romania IMBIH, Institute of Metrology of Bosnia and Herzegovina, Sarajevo, Bosnia and Herzegovina TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye
Characterization Study (in alphabetical order)	BAM - Bundesanstalt für Materialforschung und prüfung, Berlin, Germany BRML-INM, National Metrology Institute, Bucharest, Romania DTI-Danish Technological Institute, Aarhus, Denmark GUM - Central Office of Measures, Warszawa, Poland IMBIH, Institute of Metrology of Bosnia and Herzegovina, Sarajevo, Bosnia and Herzegovina PTB, Physikalisch Technische Bundesanstalt, Braunschweig, Germany TÜBİTAK UME, National Metrology Institute, Gebze - Kocaeli, Türkiye

MATERIAL PROCESSING

The raw material for the CRMs is wood pellet (property class labelled as A1 according to ISO 17225-2 by the manufacturer) which was produced in Poland. Approximately 150 kg of raw pellet material was transferred from DTI (Denmark) to TÜBİTAK UME (Türkiye) in plastic packages (15 kg x 10).

UME BIOFMET CRM 03 – Wood Pellet:

Packages content were first evaluated for moisture and the ones with closest moisture values (15 kg x 4) were selected to be used for the production of wood pellet CRM. Selected pellets were gently homogenized by transfering the content in between 120 L and 60 L HDPE containers. Homogenized pellets were split into 5 L vacuumed HDPE containers. After control of the homogeneity of the moisture content in different containers, material was decided to be split in to bottles. Filling and capping of the pellets into amber colored glass bottles were done manually using a balance (Sartorius, MSA524S-100-DA, Germany). 100 g material was filled per unit, and total 571 units were filled. The candidate CRM was sterilized by γ-irradiation with a ^{60}Co source at a minimum dose of 25 kGy. After this step, all bottles were labelled following the filling order using automated labelling machine (Farmatek, Türkiye) and stored at 4 °C in the dark. All stages of processing of UME BIOFMET CRM 03 – Wood Pellet are summarized and presented as a flow diagram in Annex 2b. Details of the processing is also documented as a video: https://www.youtube.com/watch?v=hwYNEMSBFYM

UME BIOFMET CRM 02 – Wood Pellet Powder:

First 80 kg of wood pellet was first milled with a cutting mill equipped with perforated sieve (Fritsch Pulverisette-19, Germany) to reduce the size below 1 mm. Then the obtained material smaller than 1 mm was milled second time to reduce the size below 0.5 mm.

Results of preliminary elemental analysis of this wood pellet powder by ICP-MS after microwave assisted acidic digestion are summarized in Table 2.

Table 2. Natural and target mass fraction levels of elements in wood pellet powder

Element	Preliminary Measurement Result (mg/kg)	Target Range (mg/kg)
As	< LOQ	0.1-0.5
Cd	0.216	0.1-0.5
Cr	0.098	2.0-10.0
Cu	0.664	0.2-1.0
Hg	< LOQ	0.1-0.5
Mg	175	100-500
Mn	71.2	50-250
Ni	0.024	2.0-10.0
Pb	0.081	2.0-10.0
S	73	20-100
Zn	8.8	2.0-10.0

Results showed that the candidate raw material has low level of As, Cr, Pb, Hg and Ni elements, thus it was decided to spike these elements to reach the target levels in the reference material.

A mixture of As, Cr, Pb, Hg and Ni elements was prepared (~ 8 L). 430 g of wood pellets were soaked with the 330 mL of mixture of elements in a 5 L plastic container. Mixing process repeated 24 times to soak approximately 10 kg of pellet with the five element containing mixture. All containers were placed in an oven (BINDER, Germany) at 35 °C, equipped with hepa filtered air flow and allowed to dry for 7 days. Dried pellet residue was milled to give powder < 0.5 mm particle size (Fritsch Pulverisette-19, Germany). Spiked powder was further sieved (Retsch SA 200, Germany) and powder > 0.5 mm particle size was successively milled to ensure the particle size reduction < 0.5 mm. Particle size distribution (MALVERN, Mastersizer 2000, United Kingdom) was measured with laser diffraction method. The particle size analysis was consistent with the milling and sieving steps as the > 83% of the top particles were below 550 µm for the spiked powder (Annex 1). All particles < 0.5 mm were combined in a 30 L HDPE drum and then homogenized using a three dimensional (3-D) mixer (HKTM Megamix, Türkiye). 72 kg of wood pellet powder (element unspiked) and 8 kg of five element spiked powder were blended in 350 L stainless steel tank and allowed to homogenize for 16 hours using the 3-D mixer. 71% of the top particles were measured to be below 550 µm for the final CRM (Annex 1). Homogenized content was transferred to sealed plastic bags (0.5 L) to prevent moisture uptake until bottling. Material was bottled using semiautomatic auger type filling machine (AUGAPAC-Vecto-fill, Belgium). 50g material was filled per unit, and total 1463 units were filled. The candidate CRM was sterilized by γ-irradiation with a ^{60}Co source at a minimum dose of 25 kGy. After this step, all bottles were labelled following the filling order using automated labelling machine (FARMATEK, Türkiye) and stored at 4 °C in the dark. All stages of processing are summarized and presented as a flow diagram in Annex 2a. Details of the processing is also documented as a video: https://www.youtube.com/watch?v=ohAJMLEJI0Q

HOMOGENEITY

Homogeneity study between the units is performed to show that the assigned values are valid for all units within the stated uncertainty. Homogeneity study between the units is performed with a number of samples representing the whole batch. In this project, 12 units were selected for wood pellet powder material and 10 units were selected for wood pellet material by using random stratified sampling for each of the participant laboratories. Homogeneity tests were carried out by measuring 2 or 3 sub-samples under repeatability conditions. The samples to be analysed were introduced to the instruments by random order to find out any trend arising from analytical and/or filling sequences. For Al, As, Cd, Cu and Hg, data supplied for homogeneity samples was missing or evaluated as technically invalid due to high variance on some of the individual units. Alternatively short-term or long-term stability sample data was used to evaluate the homogeneity of these parameters.

Grubbs test (one sided) was applied to all data for the presence of outlier at 99% confidence level and outliers were detected for Fe and K parameters. Data was visually checked whether all individual data follow a unimodal distribution using histograms and normal probability plots. It was found that the distribution was normal and unimodal except for As, Hg, K, P, Si parameters. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations. The results of all statistical evaluations are given in Table 3a and Table 3b for the wood pellet powder and wood pellet, respectively.

Table 3a. Statistical Evaluation of Homogeneity Results for Wood Pellet Powder

Parameter	**Is there a Trend?**		**Number of Outliers**		**Distribution**
(Lab)	**Analytical sequence**	**Filling sequence**	**All data**	**Unit averages**	**All data**
Calorific Value (PTB)	No	No	-	-	Normal/unimodal
Moisture (TÜBİTAK UME)	No	No	-	-	Normal/unimodal
Ash (TÜBİTAK UME)	Yes	No	-	-	Normal/unimodal
Al (IMBIH)	No	No	2	-	Normal/unimodal
As (BRML)	No	No	-	-	Not Normal/unimodal
Ca (IMBIH)	Yes	No	-	-	Normal/unimodal
Cd (BRML)	No	No	-	-	Normal/unimodal
Cr (IMBIH)	No	Yes	-	-	Normal/unimodal
Cu (BRML)	No	No	-	-	Normal/unimodal
Fe (IMBIH)	Yes	No	1	-	Normal/unimodal
Hg (BRML)	No	No	-	-	Not Normal/unimodal
K (IMBIH)	Yes	No	1	-	Not Normal/unimodal
Mg (BRML)	No	No	-	-	Normal/unimodal
Mn (IMBIH)	No	No	-	-	Normal/unimodal
Na (IMBIH)	No	No	-	-	Normal/unimodal

Table 3a. (Continued) Statistical Evaluation of Homogeneity Results for Wood Pellet Powder

Parameter (Lab)	Is there a Trend?		Number of Outliers		Distribution
	Analytical sequence	Filling sequence	All data	Unit averages	All data
Ni (IMBIH)	No	Yes	-	-	Normal/unimodal
P (BRML)	No	No	-	-	Not Normal/unimodal
Pb (IMBIH)	Yes	No	-	-	Normal/unimodal
S (BRML)	No	No	-	-	Normal/unimodal
Si (IMBIH)	No	No	-	-	Not Normal/unimodal
Ti (BRML)	No	Yes	-	-	Normal/unimodal
Zn (IMBIH)	No	No	-	-	Normal/unimodal

Table 3b. Statistical Evaluation of Homogeneity Results for Wood Pellet

Parameter (Lab)	Is there a Trend?		Number of Outliers		Distribution
	Analytical sequence	Filling sequence	All data	Unit averages	All data
Calorific Value (BRML)	No	No	-	-	Normal/unimodal
Moisture (TÜBİTAK UME)	No	No	1	-	Normal/unimodal

Regression analyses were used to evaluate potential trends in each analytical run at 95% and 99% confidence levels. It is observed that there was significant analytical trend at 95% confidence level for the measurements of Ash, Ca, Fe, K and Pb. As the analytical sequence and the unit numbers were not correlated, mathematical correction of the dataset for the significant analytical trend of the measurements was performed using the Equation (1) where trends were significant:

$$C_{Corrected} = C_{Measured} - b \cdot i \qquad (1)$$

where;

b : slope of the linear regression,

i : position of the result in the analytical sequence.

The ANOVA allowed the calculation of the within- (s_{wb}) and between-unit homogeneity (s_{bb}), estimated as standard deviations, according to the equations (2) and (3):

$$s_{wb} = \sqrt{MS_{within}} \qquad (2)$$

MS_{within} : Mean squares within-unit

s_{wb} is equivalent to the *s* of the method, provided that subsamples are representative for the whole unit.

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (3)$$

$MS_{between}$: Mean squares between-unit

n : Number of replicates per unit

When MS_{between} is smaller than MS_{within}, s_{bb} cannot be calculated. Instead, $u*_{\text{bb}}$, the heterogeneity that can be hidden by the method repeatability [6], is calculated according to the equation (4):

$$u^*_{bb} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}} \quad (4)$$

$\nu_{MSwithin}$: Degrees of freedom of MS_{within}

The occurrence of $MS_{between} < MS_{within}$ can be seen, if material heterogeneity is smaller than that can be detected by the analytical methodology used.

For Cr, Ni and Ti, filling trend was observed, and in these cases alternative data evaluation was applied and between unit homogeneity was modeled as a rectangular distribution and equation (5) was applied for rectangular standard uncertainty (u_{rect}) of homogeneity.

$$u_{rect} = \frac{|highest\ value - lowest\ value|}{2\sqrt{3}} \quad (5)$$

For the parameters for which ANOVA was applied, the larger value of s_{bb}, $u*_{bb}$ or u_{rec} is taken as uncertainty contribution for homogeneity, u_{bb} (Table 4a and Table 4b).

Table 4a. Results of the homogeneity study for wood pellet powder

Parameter	$s_{wb,rel}$, %	$s_{bb,rel}$, %	$u*_{bb,rel}$, %	$u_{rec,rel}$, %	$u_{bb,rel}$, %
Calorific Value	0.23	0.059	0.071	-	0.071
Moisture	1.3	0.65	0.40	-	0.65
Ash	8.2	2.4	2.5	-	2.5
Al	6.0	$MS_{between} < MS_{within}$	2.0	-	2.0
As	17	27	5.6	-	27
Ca	4.8	$MS_{between} < MS_{within}$	1.5	-	1.5
Cd	9.5	9.1	3.0	-	9.1
Cr	1.3	3.1	0.39	6.4	6.4
Cu	8.9	4.3	2.8	-	4.3
Fe	11	$MS_{between} < MS_{within}$	3.6	-	3.6
Hg	4.9	18	1.6	-	18
K	14	$MS_{between} < MS_{within}$	4.4	-	4.4
Mg	1.3	10	0.4	-	10
Mn	3.5	$MS_{between} < MS_{within}$	1.1	-	1.1
Na	25	$MS_{between} < MS_{within}$	7.8	-	7.8

Table 4a. (Continued) Results of the homogeneity study for wood pellet powder

Parameter	$s_{wb,rel}$, %	$s_{bb,rel}$, %	$u^*_{bb,rel}$, %	$u_{rec,rel}$, %	$u_{bb,rel}$,%
Ni	2.8	2.4	0.86	4.0	4.0
P	1.8	8.8	0.57	-	8.8
Pb	11	5.6	3.3	-	5.6
S	0.31	1.1	0.10	-	1.1
Si	23	$MS_{between}$<MS_{within}	7.0	-	7.0
Ti	6.2	8.4	1.9	12	12
Zn	5.9	2.8	1.8	-	2.8

Table 4b. Results of the homogeneity study for wood pellet

Parameter	$s_{wb,rel}$, %	$s_{bb,rel}$, %	$u^*_{bb,rel}$, %	$u_{rec,rel}$, %	$u_{bb,rel}$,%
Calorific Value	0.16	0.0088	0.052	-	0.052
Moisture	0.40	0.25	0.19	-	0.25

The plotted data used for the evaluation of homogeneity can be found in Annex 3A and Annex 3B for the wood pellet powder and wood pellet, respectively.

STABILITY

The stability of the units which are exposed to different environmental conditions that may occur during shipment and shelf life is tested and evaluated at defined storage conditions by reference material producers.

Stability studies were performed with isochronous design. For the short term stability (STS) test +45°C temperature and five time points (0, 1, 2, 3 and 4 weeks) were tested. 10 units were selected for each laboratory by using a stratified sampling scheme covering whole batch. 32 samples were subjected to the test temperature for the specified time intervals. For the long term stability test (LTS), 10 units for each laboratory were tested at +22 °C for 0, 2, 4, 6 and 8 months' time points.

Units were moved to +4 °C (reference temperature) after completion of the test time. All units were analyzed at the same time. Samples were analyzed under the repeatability conditions to determine the values for the parameters of interest.

Short Term Stability Results:

The results obtained from isochronous measurements were first grouped according to the time period and then evaluated for each time point. The data for each parameter was first examined by single Grubbs test for both 95% and 99% confidence intervals to find out outliers. Number of detected outliers are given in the Table 5a and 5b. All outlying results were removed from the datasets.

Values calculated for each time point were plotted against the time. The relationship between variables were analyzed in order to determine if any significant change exists with the testing time (regression analysis). It was found that the slope was significant for moisture parameter of wood pellet powder. The trend graphs of short term stability are shown in Annex 3a and Annex 3b for wood pellet powder and wood pellet, respectively. The relative short term stability uncertainty, $u_{sts,rel}$ for each parameter is then calculated using Equation (6) for the required transfer time as described in [7] and results are given in Table 5a and Table 5b for wood pellet powder and wood pellet, respectively:

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum (t_i - \bar{t})^2}} \times t \qquad (6)$$

where,

RSD : relative standard deviation of the points on the regression line as described in B.17 [7],

t_i : time point for each replicate expressed in weeks ,

$\bar{t}$: mean of all time points expressed in weeks,

t : maximum time suggested for transfer (2 weeks).

Table 5a. Short Term Stability (STS) test results for wood pellet powder

Parameter (Lab)	45 °C $u_{sts,rel}$ for 2 week (%)	Number of outliers in 95% confidence interval [1]	Number of outliers in 99% confidence interval [1]	Any significant trend in 95% confidence interval?	Any significant trend in 99% confidence interval?
Calorific Value (PTB)	0.082	-	-	No	No
Moisture (TÜBİTAK UME)	1.44[2]	-	-	Yes	Yes
Ash (TÜBİTAK UME)	2.0	-	-	No	No
Al	1.6	1	1	No	No
As	n.a.	n.a.	n.a.	n.a.	n.a.
Ca (IMBIH)	4.5	-	-	No	No
Cd (BRML)	6.8	-	-	No	No
Cr (IMBIH)	0.56	-	-	No	No
Cu (BRML)	2.1	-	-	No	No
Fe (IMBIH)	5.5	1	-	No	No
Hg	n.a.	n.a.	n.a.	n.a.	n.a.
K (IMBIH)	1.7	-	-	No	No
Mg (BRML)	2.6	-	-	No	No
Mn (IMBIH)	0.99	-	-	No	No
Na (BRML)	3.8	3	-	No	No

[1] Single Grubbs Test

[2] u_{sts} is calculated by taking into account the degradation (u_{lts}= slope of reg. line/√3)

n.a.: Data not available

Table 5a. (Continued) Short Term Stability (STS) test results for wood pellet powder

Parameter (Lab)	45 °C $u_{sts,rel}$ for 2 week (%)	Number of outliers in 95% confidence interval [1]	Number of outliers in 99% confidence interval [1]	Any significant trend in 95% confidence interval?	Any significant trend in 99% confidence interval?
Ni (IMBIH)	0.82	-	-	No	No
P (BRML)	2.0	3	-	No	No
Pb (BRML)	2.1	1	-	No	No
S (BRML)	0.21	-	-	No	No
Si (BRML)	5.0	-	-	No	No
Ti (BRML)	1.7	1	-	No	No
Zn (IMBIH)	2.2	1	-	No	No

[1] Single Grubbs Test

Table 5b. Short Term Stability (STS) test results for wood pellet

Parameter (Lab)	45 °C $u_{sts,rel}$ for 2 week (%)	Number of outliers in 95% confidence interval [1]	Number of outliers in 99% confidence interval [1]	Any significant trend in 95% confidence interval?	Any significant trend in 99% confidence interval?
Calorific Value (PTB)	0.036	1	1	No	No
Moisture (BRML)	0.25	-	-	No	No

[1] Single Grubbs Test

Both wood pellet powder and wood pellet are found to be stable at 45°C for up to 2 weeks. Thus, the samples can be safely dispatched under conditions where the temperatures do not exceed 45 °C for up to 2 week, i.e. at ambient temperature without applying any cooling elements.

Long Term Stability Results:

Shelf life of the CRM has been determined through long term stability measurements. For the measurements, for each partner two units for each of the months of 0, 2, 4, 6 and 8 have been stored at +22 °C and transferred to reference temperature (+4 °C) after each period of time to be measured isochronously afterwards. Eight units, designated as reference units, of the month 0 was stored at +4 °C. Detected outlying results were removed from the datasets.

The relative long term stability uncertainty, $u_{lts,rel}$ for each parameter is calculated using equation (7) for the required shelf life as [7] and results are given in Table 6a and Table 6b for wood pellet powder and wood pellet, respectively:

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \times t \quad (7)$$

where,

RSD : the relative standard deviation of the points on the regression line as described in B.17 [7],
t_i : the time point for each replicate expressed in months,
$\bar{t}$: the average of all time points expressed in months,
t : the proposed shelf life at 18 °C (12 months).

The uncertainty contribution u_{lts} was calculated for 12 months (*t*) at 22 °C. The graphs for long term stability are given in Annex 4a and Annex 4b.

Table 6a. Long Term Stability (LTS) test results for wood pellet powder

Parameter (Lab)	22 °C $u_{lts,rel}$ for 12 months (%)	Number of outliers in 95% confidence interval [1]	Number of outliers in 99% confidence interval [1]	Any significant trend in 95% confidence interval?	Any significant trend in 99% confidence interval?
Calorific Value (PTB)	0.24	-	-	No	No
Moisture (TÜBİTAK UME)	0.81	-	-	No	No
Ash (BRML)	6.4	-	-	No	No
Al (IMBIH)	4.1	1	-	No	No
As (BRML)	11.3	-	-	No	No
Ca (IMBIH)	5.2	-	-	No	No
Cd (BRML)	16.3	-	-	No	No
Cr (IMBIH)	2.4	1	1	No	No
Cu (BRML)	12	-	-	No	No
Fe (IMBIH)	11.4	2	2	No	No
Hg (BRML)	14	-	-	No	No
K (IMBIH)	6.0	4	4	No	No
Mg (IMBIH)	6.5	-	-	No	No
Mn (IMBIH)	3.9	-	-	No	No
Na (IMBIH)	8.8	-	-	No	No

[1] Single Grubbs Test

Table 6a. (Continued) Long Term Stability (LTS) test results for wood pellet powder

Parameter (Lab)	22 °C $u_{lts,rel}$ for 12 months (%)	Number of outliers in 95% confidence interval [1]	Number of outliers in 99% confidence interval [1]	Any significant trend in 95% confidence interval?	Any significant trend in 99% confidence interval?
Ni (IMBIH)	3.0	1	-	No	No
P (BRML)	11	-	-	No	No
Pb (IMBIH)	12	-	-	No	No
S (BRML)	6.2	-	-	No	No
Si (BRML)	23	-	-	No	No
Ti (BRML)	7.8	-	-	No	No
Zn (IMBIH)	4.7	-	-	No	No

[1] Single Grubbs Test

Table 6b. Long Term Stability (LTS) test results for wood pellet

Parameter (Lab)	22 °C $U_{lts,rel}$ for 12 months (%)	Number of outliers in 95% confidence interval [1]	Number of outliers in 99% confidence interval [1]	Any significant trend in 95% confidence interval?	Any significant trend in 99% confidence interval?
Calorific Value (PTB)	0.24	-	-	No	No
Moisture (BRML)	0.44	-	-	No	No

[1] Single Grubbs Test

CHARACTERIZATION

According to ISO 17034, the characterization and the value assignment can be carried out in different ways. The approach chosen in this project is; characterization of a non-operationally and operationally defined measurands using two or more methods of demonstrable accuracy in two or more competent laboratories. The participating laboratories were partners and collaborators of the BIOFMET project consortium [3]. The detailed information about the laboratories is given in the participants section. The participating laboratories used validated methods for the characterization.

Each laboratory received 2 units of samples which were selected from the whole set of samples to represent the whole produced batch. The samples were selected randomly from the set of samples by the random stratified sampling technique. Each laboratory was asked to report at least three independent measurement results for each unit, together with their associated measurement uncertainty values and the approach used for the estimation of measurement uncertainty. In the reports, the details of the reference materials used in the calibration were also requested in order to assure the traceability of the reported results.

Measurement uncertainties were calculated according to the “Guide to the Expression of Uncertainty in Measurements (GUM)” and “EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement” documents or estimated in accordance with ISO 17034:2016 and ISO Guide 35:2017. Equations (8, 9, 10) were used to calculate characterization standard uncertainty (u_{char}) stated by M. S. Lenson et al [8] for the cases where two method/laboratory results were available. In cases where more than two method/laboratory results were available, characterization standard uncertainty (u_{char}) is calculated using Equation (11) by taking into account the uncertainties and the standard deviation of the means reported by the participating laboratories. Value assignment of the material performed by arithmetic averaging two or more method results.

$$u(B) = \frac{|x_{Method\ 1} - x_{Method\ 2}|}{2\sqrt{3}} \tag{8}$$

$$u(X) = \sqrt{(\frac{1}{2})^2 u^2(\text{Method 1}) + (\frac{1}{2})^2 u^2(\text{Method 2})} \tag{9}$$

$$u_{char} = \sqrt{u^2(X) + u^2(B)} \tag{10}$$

here,
$u(B)$: the standard uncertainty based on the difference on the difference of results of two methods,
$u(X)$: the standard uncertainty obtained by combining uncertainties of two methods,
u_{char} : the standard uncertainty of characterisation by two methods.

$$u_{\text{char}} = \sqrt{\bar{u}^2_{\text{labs}} + \left(\frac{SD}{\sqrt{n}}\right)^2} \tag{11}$$

where;

u_{char} : Standard uncertainty arising from characterization,
$\bar{u}_{labs}$: Arithmetic mean of standard uncertainties reported by the participating laboratories,
SD : Standard deviation of accepted means of participating laboratories,
n : Number of laboratories with accepted results.

A list of laboratories with their abbreviations and their corresponding methodologies used for the measurements are summarized in Table 7a and Table 7b for wood pellet powder and wood pellet, respectively. More details about the measurement methods are given in Annex 7A and Annex 7B for wood pellet powder and wood pellet, respectively.

Additional comparative data for moisture (Oven drying at 105 °C for 3 h, 5 h and Halogen Lamp Moisture Analyser Analyser drying at 175 °C for 9 min) and water (Evolved Water Vapor Thermo-Coulometer and Acoustic Methods) content of wood pellet is presented as a plot in Annex 8.

Table 7a. Techniques used by participating laboratories for wood pellet powder

Parameter	BAM	BRML	DTI	IMBIH	GUM	PTB	UME
Calorific Value	-	ISOP-CAL	ISOP-CAL	-	-	ISOP-CAL	ISOP-CAL
Moisture	-	OD	OD	-	-	-	-
Ash	-	AA	-	-	-	-	AA
Al	-	ICP-MS	-	MPAES	-	-	-
As	-	-	-	-	ICP-MS	-	ICP-MS
Ca	-	ICP-MS	-	MPAES	-	-	-
Cd	-		-	-	ICP-MS	-	ICP-MS
Cr	-	ICP-MS	-	MPAES	ICP-MS	-	ICP-MS
Cu	-	ICP-MS	-	MPAES	ICP-MS	-	ICP-MS
Fe	-	ICP-MS	-	MPAES	-	-	-
Hg	-	-	-		ICP-MS	-	ICP-MS
K	-	ICP-MS	-	MPAES	-	-	-
Mg	-	ICP-MS	-	MPAES	-	-	-
Mn	-	ICP-MS	-	MPAES	-	-	-
Na	-	ICP-MS	-	MPAES	-	-	-
Ni	-	ICP-MS	-	MPAES	ICP-MS	-	ICP-MS
P	-	ICP-MS	-	-	-	-	-
Pb	-	ICP-MS	-	MPAES	ICP-MS	-	ICP-MS
S	ID ICP-MS	ICP-MS	-	-	-	-	ID ICP-MS ICP-MS
Si	-	ICP-MS	-	-	-	-	-
Ti	-	ICP-MS	-	-	-	-	-
Zn	-	ICP-MS	-	MPAES	ICP-MS	-	ICP-MS

AA : Ash Analysis based on gravimetry
ICP-MS : Inductively Coupled Plasma Mass Spectrometry
ICP-OES : Inductively Coupled Plasma Optical Emission Spectrometry
ID ICP-MS : Isotope Dilution ICP-MS
ISOP-CAL : Isoperibol Calorimetry
MPAES : Microwave Plasma Atomic Emission Spectroscopy
OD : Oven Drying based on gravimetry

Table 7b. Techniques used by participating laboratories for wood pellet

Parameter	BRML	DTI	PTB	UME
Calorific Value	ISOP-CAL	ISOP-CAL	ISOP-CAL	ISOP-CAL
Moisture	OD	OD	-	-

ISOP-CAL : Isoperibol Calorimetry
OD : Oven Drying based on gravimetry

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

Assigned values and uncertainties of the CRM were evaluated by applying approach in the characterization and uncertainty data that contribute to the homogeneity and stability assessments.

Data obtained in the characterization study were checked for normal distribution and outliers. Distributions were found to be normal, and no outlier was detected.

Mean value of characterization results is assigned as the property value of the reference materials.

Equation (12) is used to calculate the combined expanded uncertainty of CRMs:

$$U_{CRM} = k\sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2 + u_{sts}^2} \quad (12)$$

Uncertainty value on CRM certificate includes uncertainty contribution from characterization (u_{char}), homogeneity (u_{bb}), long term stability (u_{lts}) and short-term stability. Expansion of uncertainty value of CRMs was done with a coverage factor (k = 2) representing 95 % confidence level. Certified values, uncertainties and relative percent contribution of each component on uncertainty is given in Table 7a and Table 7b for wood pellet powder and wood pellet, respectively.

Table 7a. Certified values and uncertainties for wood pellet powder

Parameter (unit)	Certified value [1]	U_{CRM} [1,2] (*k*=2)	$U_{CRM,rel}$ (%, *k*=2)	$u_{char,rel}$ (%)	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)
Gross Calorific Value [$q_{V,gr,d}$] [3] (J/g)	20690	136	0.66	0.19	0.071	0.082	0.24
Moisture [4] (g/100g)	7.30	0.34	4.6	1.47	0.65	1.44	0.81
Ash [5] (g/100g)	0.231	0.044	20	6.4	2.5	1.7	6.4
Al [#] (mg/kg)	IN PREPARATION				2.0	1.6	4.1
Cr [#] (mg/kg)					6.4	0.56	2.4
Cu [#] (mg/kg)					4.3	2.1	12
Fe[#] (mg/kg)					3.6	5.5	12
K [#] (mg/kg)					4.4	1.7	6.0
Mg [#] (mg/kg)					10	2.6	6.5
Mn [#] (mg/kg)					1.1	0.99	3.9
Ni [#] (mg/kg)					4.0	0.82	3.0
Pb [#] (mg/kg)					5.6	2.1	12
S [6] (mg/kg)	68.3	9.3	14	2.5	1.1	0.21	6.2
Zn [#] (mg/kg)	IN PREPARATION				2.8	2.2	4.7

[1] The certified values and the uncertainties are traceable to the International System of Units (SI). Certified value is corrected for dry mass except the moisture parameter. Moisture content is determined at (105 ± 2) °C until constant weight as defined in ISO 18134-3 method.

[2] The expanded uncertainty of the certified value includes characterization, homogeneity, stability components and is stated as the standard uncertainty of measurement multiplied by the coverage factor *k* = 2, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with GUM "Guide to the Expression of Uncertainty in Measurement".

[3] Calculated from the arithmetic mean of the accepted results of the gross calorific value at constant volume of the dry fuel submitted by four laboratories applying ISO EN 18125 method.

[4] Calculated from the arithmetic mean of the accepted results submitted by two laboratories applying ISO 18134-3 method.

[5] Calculated from the arithmetic mean of the accepted results submitted by two laboratories applying ISO 18122 method.

[6] Calculated from the arithmetic mean of the accepted results submitted by four laboratories applying ICP-MS, HR ICP-MS and ID ICP-MS methods.

Table 7a. Certified values and uncertainties for wood pellet

Parameter (unit)	**Certified value** [1]	**U_{CRM}**[1,2] **(*k*=2)**	**$U_{CRM,rel}$ (%, *k*=2)**	**$u_{char,rel}$ (%)**	**$u_{bb,rel}$ (%)**	**$u_{sts,rel}$ (%)**	**$u_{lts,rel}$ (%)**
Gross Calorific Value [$q_{V,gr,d}$] [3] (J/g)	20793	128	0.62	0.20	0.052	0.036	0.22
Moisture [4] (g/100g)	8.46	0.24	2.8	1.3	0.25	0.25	0.44

[1] The certified values and the uncertainties are traceable to the International System of Units (SI).

[2] The expanded uncertainty of the certified value includes characterization, homogeneity, stability components and is stated as the standard uncertainty of measurement multiplied by the coverage factor *k* = 2, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with GUM "Guide to the Expression of Uncertainty in Measurement".

[3] Calculated from the arithmetic mean of the accepted results of the gross calorific value at constant volume of the dry fuel submitted by four laboratories applying ISO 18125 method.

[4] Calculated from the arithmetic mean of the accepted results submitted by two laboratories applying modified 18134-3 method (3 gram pellet samples were used as received in pellet form without reducing the top size to below 1 mm).

INFORMATIVE VALUES

Parameters for which a consensus value cannot be assigned due to lack of multiple laboratory measurement results or high uncertainty are given as informative value. Results for these parameters are given in Table 8, Table 9 and Table 10.

Table 8. Informative values and uncertainties for wood pellet powder

Parameter (unit)	**Assigned value**	**U_{AV}**[1] **(*k*=2)**	**$U_{AV,rel}$ (%, *k*=2)**	**$u_{char,rel}$ (%)**	**$u_{bb,rel}$ (%)**	**$u_{sts,rel}$ (%)**	**$u_{lts,rel}$ (%)**
Net Calorific Value [$q_{V,net,m}$] [1] (J/g)	17992	119	0.66	0.19	0.071	0.082	0.24
As [#] (mg/kg)					27	n.a	11.3
Ca [#] (mg/kg)					1.5	4.5	5.2
Cd [#] (mg/kg)					9.1	6.8	16
Hg [#] (mg/kg)	IN PREPARATION				18	n.a	14
Na [#] (mg/kg)					7.8	3.8	8.8
P [#] (mg/kg)					8.8	2.0	11
Si [#] (mg/kg)					7.0	5.0	19
Ti [#] (mg/kg)					12	1.7	7.8

[1] Calculated for as received moisture from the certified gross calorific value at constant volume of dry fuel using the following equation: $q_{V,net,m} = [q_{V,gr,d} - 206 \times$ hydrogen content of moisture free biofuel, in percentage by mass$] \times (1 - 0.01 \times$ moisture, in percentage by mass$) - (23.0 \times$ moisture, in percentage by mass$)$ as described in ISO 18125.

Table 9. Informative value and uncertainty for wood pellet

Parameter (unit)	Assigned value	U_{AV}[1] (k=2)	$U_{AV,rel}$ (%, k=2)	$u_{char,rel}$ (%)	$u_{bb,rel}$ (%)	$u_{sts,rel}$ (%)	$u_{lts,rel}$ (%)
Net Calorific Value [$q_{V,net,m}$] [2] (J/g)	17815	111	0.62	0.20	0.052	0.036	0.22

[1] The expanded uncertainty of the certified value includes characterization, homogeneity, stability components and is stated as the standard uncertainty of measurement multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with GUM "Guide to the Expression of Uncertainty in Measurement".

[2] Calculated for as received moisture from the certified gross calorific value at constant volume of dry fuel using the following equation: $q_{V,net,m}$ = [$q_{V,gr,d}$ – 206 x hydrogen content of moisture free biofuel, in percentage by mass] x (1 – 0.01 x moisture, in percentage by mass) – (23.0 x moisture, in percentage by mass) as described in ISO 18125.

Table 10a. Informative values for Carbon, Hydrogen and Nitrogen content in wood pellet powder

Element	Measurement Result [1] (g/100g)
C	50.35 ± 0.38
H	5.34 ± 0.10
N	0.330 ± 0.034

* Values written with "±" sign represents standard deviation

[1] Arithmetic mean of the accepted analysis results (n = 12) by TÜBİTAK UME.

Table 10b. Informative values for Carbon, Hydrogen and Nitrogen content in wood pellet

Element	Measurement Result [1] (g/100g)
C	50.79 ± 0.34
H	5.43 ± 0.20
N	0.209 ± 0.022

* Values written with "±" sign represents standard deviation

[1] Arithmetic mean of the accepted analysis results (n = 12) by TÜBİTAK UME.

COMMUTABILITY

Commutability is defined as the mathematical relationship of the equation between the reference material and the results produced by the different measurement methods that can be used to measure the routine samples it represents [10]. UME BIOFMET CRM 02 and UME BIOFMET CRM 03 were produced from regular wood pellet (property class labelled as A1 according to ISO 17225-2 by the manufacturer) produced in Poland. UME BIOFMET CRM 02- wood pellet powder was produced by spiking with a mixture containing As, Cr, Pb, Hg, Ni elements. The analytical behavior is expected to be the same as for a routine sample of wood pellet of similar content. It should be noted that the extractability of the five spiked elements (As, Cr, Pb, Hg, Ni) from this CRM can be different to the extractability from an unspiked wood pellet powder sample tested by the user's laboratory due to the possibility that these elements might exist in different chemical forms.

TRACEABILITY

The metrological traceability of the CRM was ensured by using SI traceable calibration standards and using reference methods i.e., ID ICP MS by the participating laboratories. The laboratories were asked to provide detailed information about the calibration standards and reference methods used in the measurements. Details about the measurement methods, calibration standards and quality control materials used by the participating laboratories are given in Annex 6A and Annex 6B for wood pellet powder and wood pellet, respectively.

INSTRUCTIONS FOR USE

Shipping conditions

These materials can be safely dispatched under conditions where the temperature do not exceed 45 °C for up to two weeks, i.e. at ambient temperature without applying any cooling elements.

Storage conditions

Materials should be stored at (22 ± 4) °C in dark and clean environment. The bottle should be shaken before opening (for the powder material). In order to prevent contamination, it is recommended that the bottle should be opened in a clean environment. TÜBİTAK UME cannot be held responsible for changes that might happen to the material at customer's premises due to noncompliance with the instructions for use, and the storage conditions given.

Safety precautions

For laboratory use only. The usual laboratory safety measures apply as in the case of similar powders. It is strongly recommended that the material must be handled and disposed according to the safety guidelines where applicable. It is recommended to avoid inhalation of powder material and work under appropriate ventilation conditions. No special precaution is necessary to work with the wood pellet material.

Minimum sample intake

The minimum sample intake is defined by the required sample mass stipulated in the respective standard methods. For UME BIOFMET CRM 03-Wood pellet, homogeneity of the material for moisture was tested on 3 g sub-samples directly in the form of pellet, without further size reduction, therefore minimum sample intake amount for wood pellet is 3g for the moisture measurements.

For elemental analysis, during the measurements performed for homogeneity, characterization, stability studies, the lowest amount used was 0.2 g for and no sign of heterogeneity have been observed. Therefore, this can be considered as the minimum sample amount to be used in the elemental analysis.

Before opening and taking sample, bottle should be shaken to re-homogenize the content. After use, the bottle should be immediately and tightly recapped.

It should be noted that the moisture content of the materials can decrease or increase after several use depending on the relative humidity (RH) of the laboratory. For moisture analysis, it is recommended to open the cap of the bottle under 50 ± 5 RH condition and/or close the cap as quick as possible to minimize moisture uptake or loss.

Use of Certified Value

For assessing the method performance, the measured values of the CRM are compared with the certified values [11]. The procedure can be described briefly as:

- Calculate the absolute difference between mean measured value and the certified value (Δ_m).
- Combine measurement uncertainty (u_{meas}) with the standard uncertainty of the certified value (u_{CRM}) using Equation (13):

$$u_\Delta = \sqrt{u_{meas}^2 + u_{CRM}^2} \qquad (13)$$

- Calculate the expanded uncertainty (U_Δ) from the combined uncertainty (u_Δ) using a coverage factor of two (k = 2), corresponding to a confidence level of approximately 95 %.

If $\Delta m \leq U\Delta$, then it is assumed that there is no significant difference between the measurement result and the certified value at a confidence level of approximately 95%.

An online application: CRM Result Evaluation-CRM RE to evaluate your measurement results and automatically create quality control charts is available through the link: https://rm.ume.tubitak.gov.tr/en/crm_re/

ACKNOWLEDGEMENTS

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[10] For more information about comparison of a measurement result with the certified value please see ERM Application Note 1 https://crm.jrc.ec.europa.eu/e/132/User-support-Application-Notes

REVISION HISTORY

Date	Remarks
XX.YY.2023	First issue.

ANNEX 1. Particle Size Analysis of Wood Pellet Powder Samples

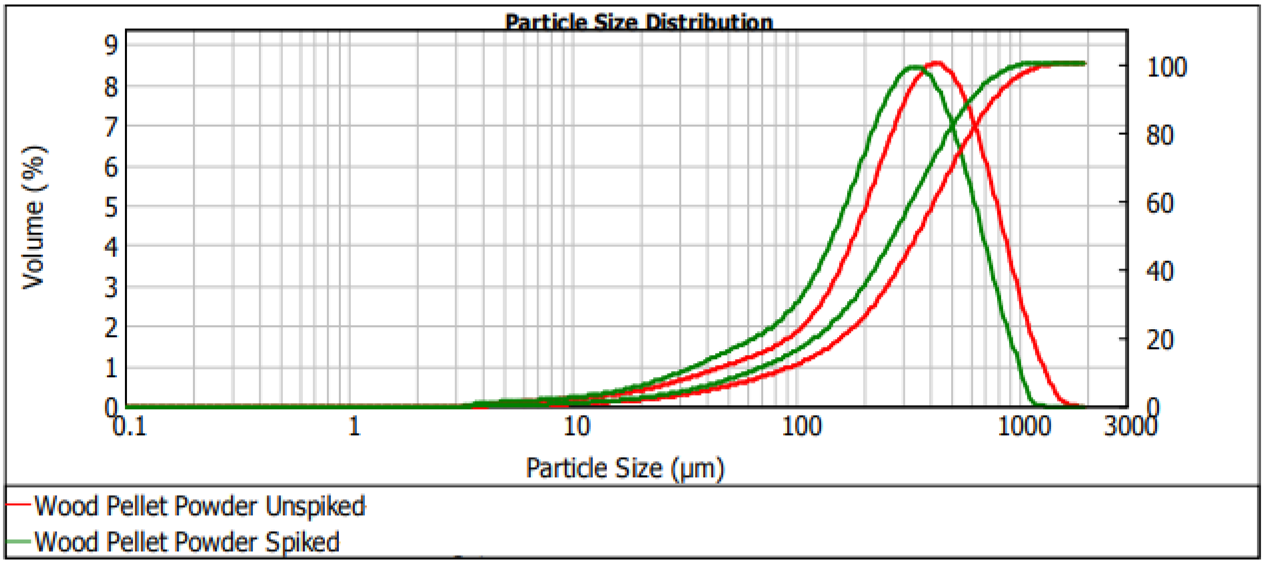


Figure A1.1. Comparative particle size distribution analysis of unspiked and spiked wood pellet powder by laser diffraction

d(0.1): 70.386 um   d(0.5): 358.145 um   d(0.9): 904.380 um

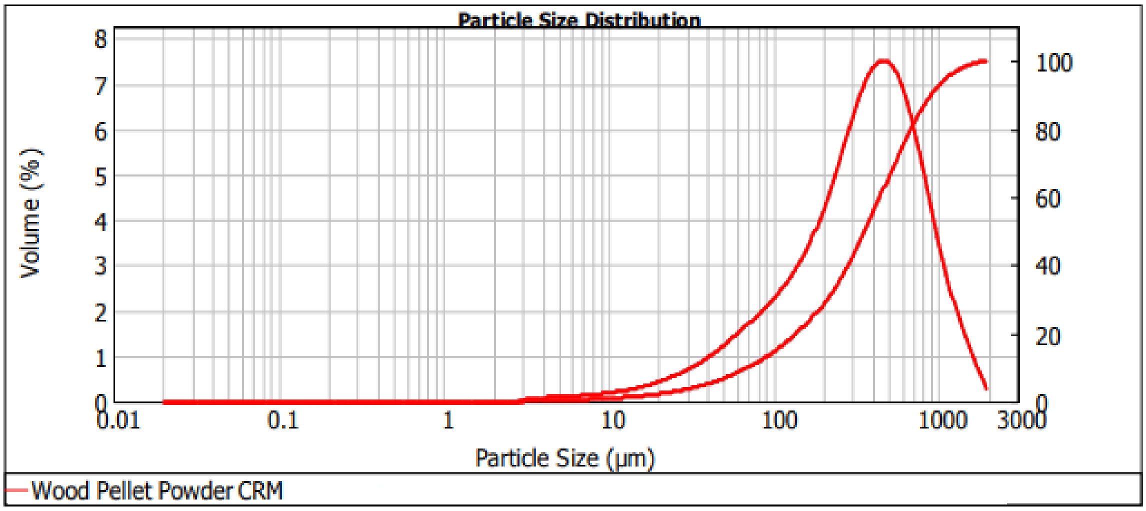
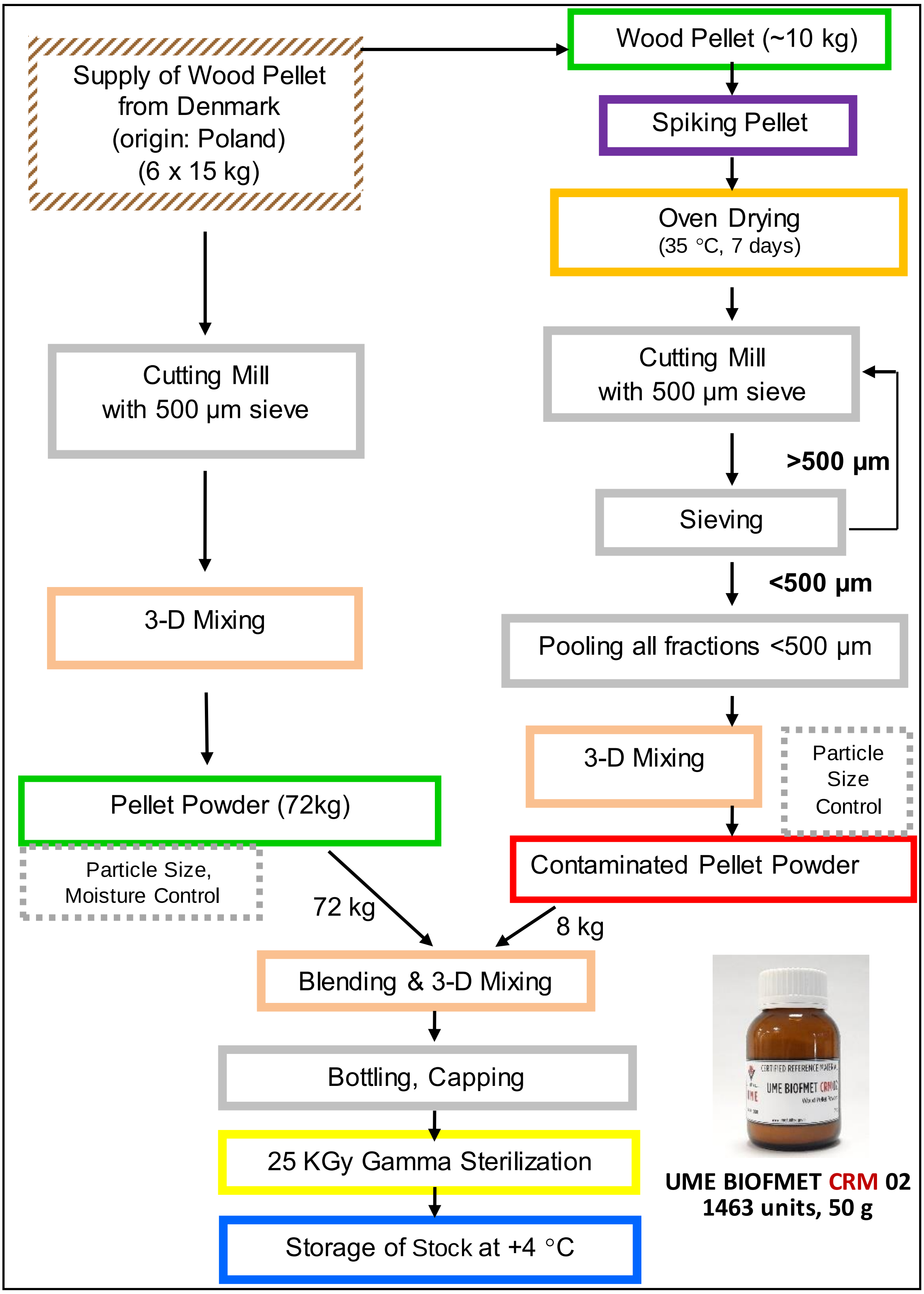


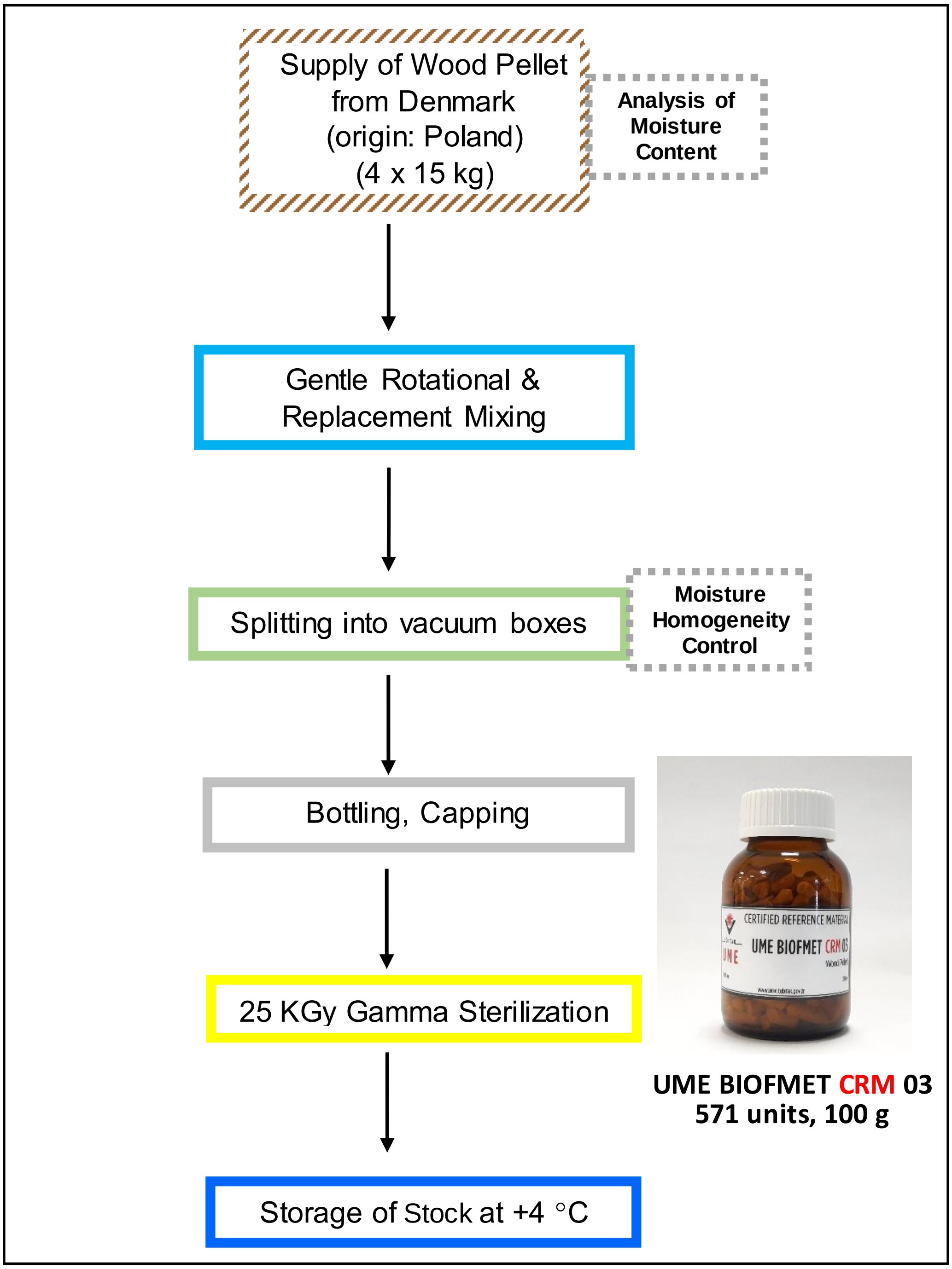
Figure A1.2. Particle size distribution analysis of wood pellet powder CRM by laser diffraction

ANNEX 2a. Flow Diagram for the Preparation of the Wood Pellet Powder CRM



Details of the processing is also documented as a video:
https://www.youtube.com/watch?v=ohAJMLEJI0Q

ANNEX 2b. Flow Diagram for the Preparation of the Wood Pellet CRM



Details of the processing is also documented as a video:
https://www.youtube.com/watch?v=hwYNEMSBFYM

ANNEX 3A. Graphs for Homogeneity Studies for Wood Pellet Powder

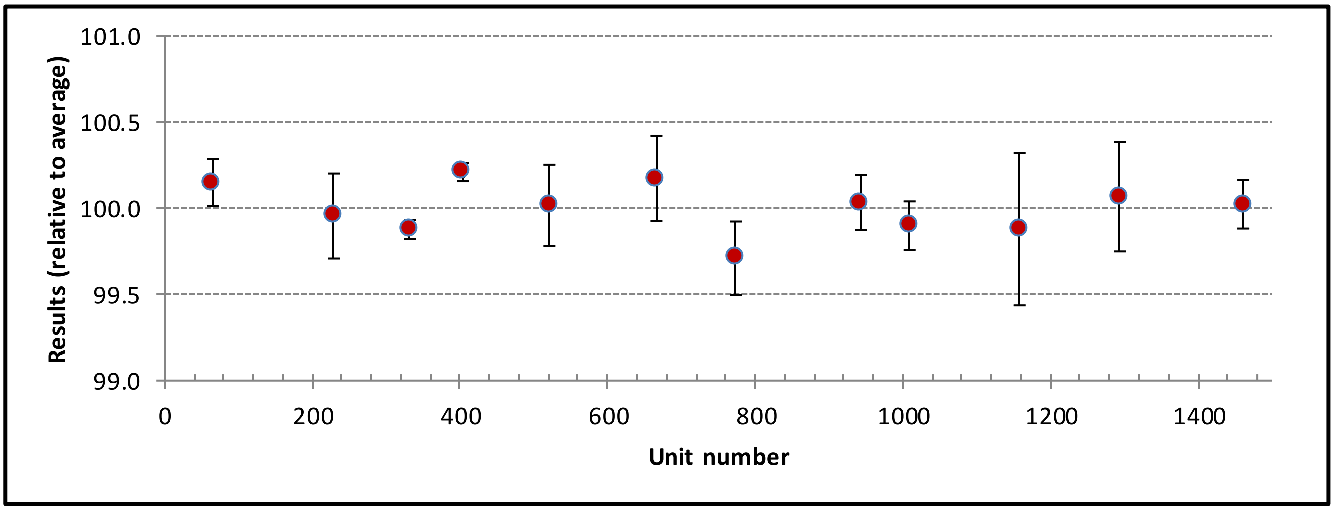


Figure A3A.1. Between units homogeneity plot for Calorific Value by PTB

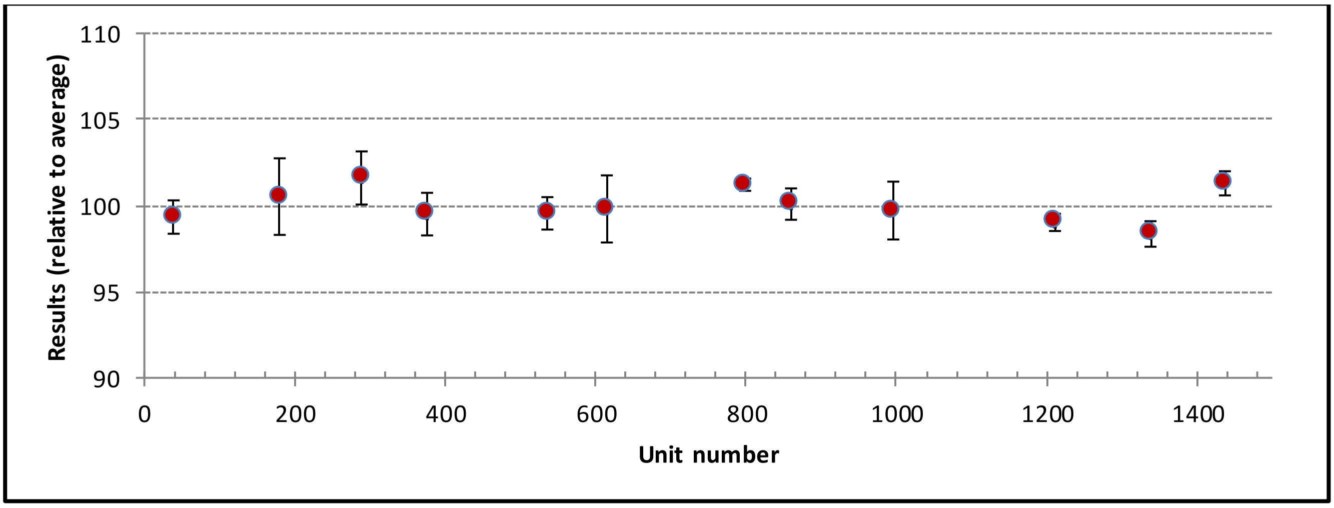


Figure A3A.2. Between units homogeneity plot for Moisture by UME

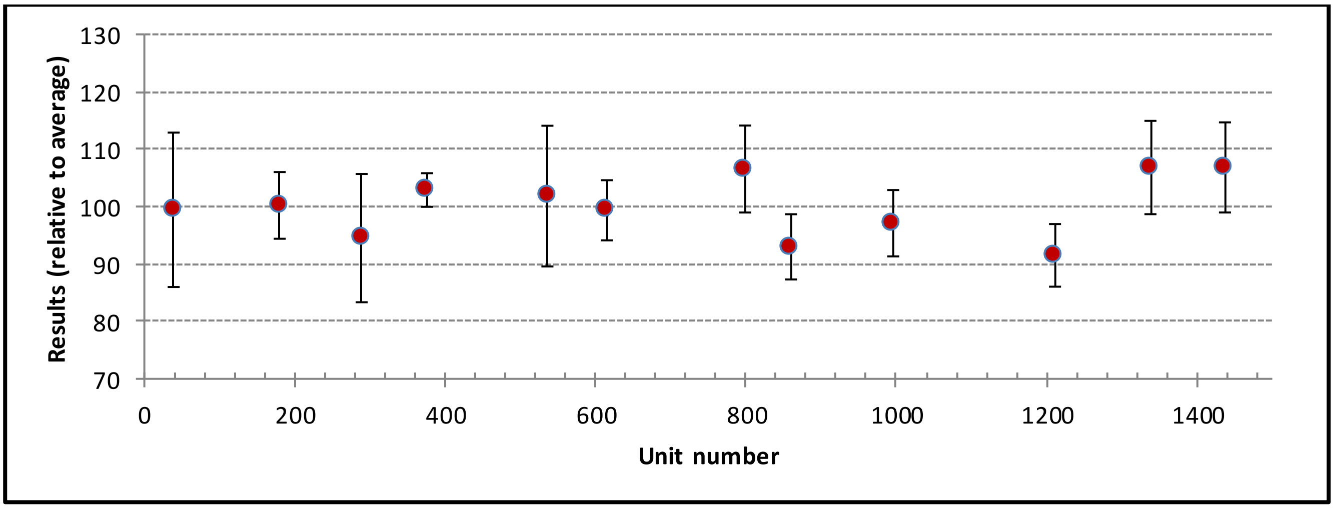


Figure A3A.3. Between units homogeneity plot for Ash by UME

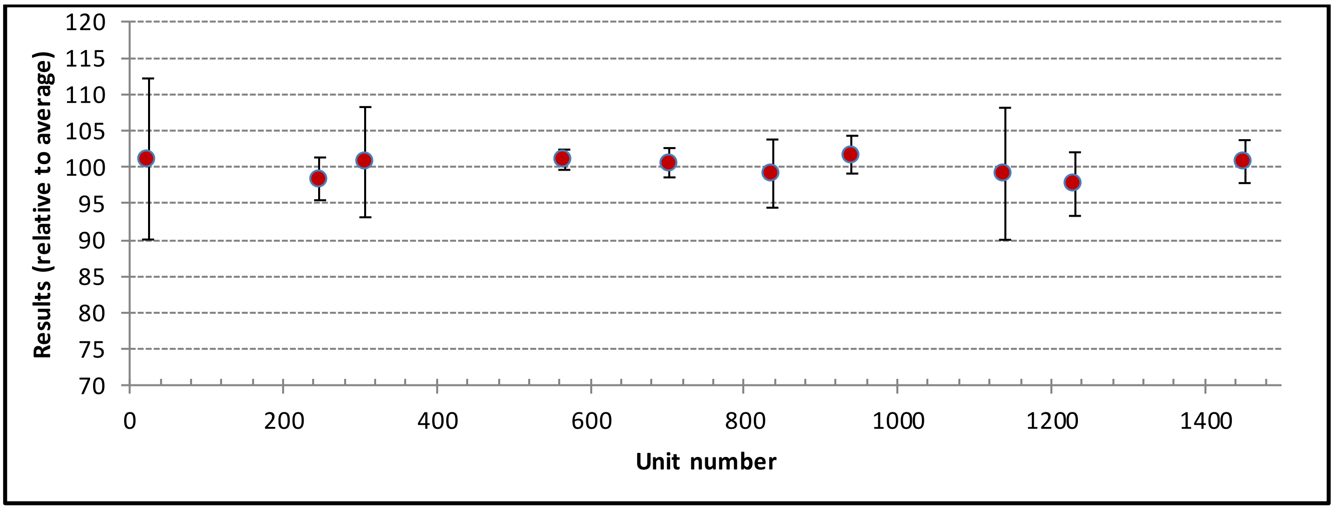


Figure A3A.4. Between units homogeneity plot for Aluminum by IMBIH

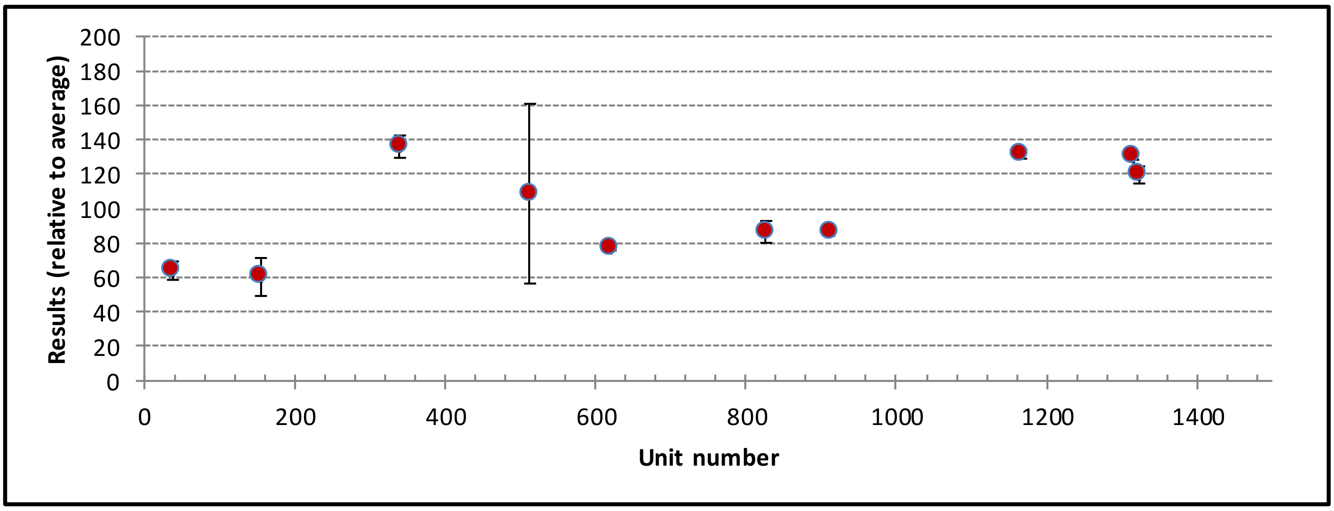


Figure A3A.5. Between units homogeneity plot for Arsenic by BRML

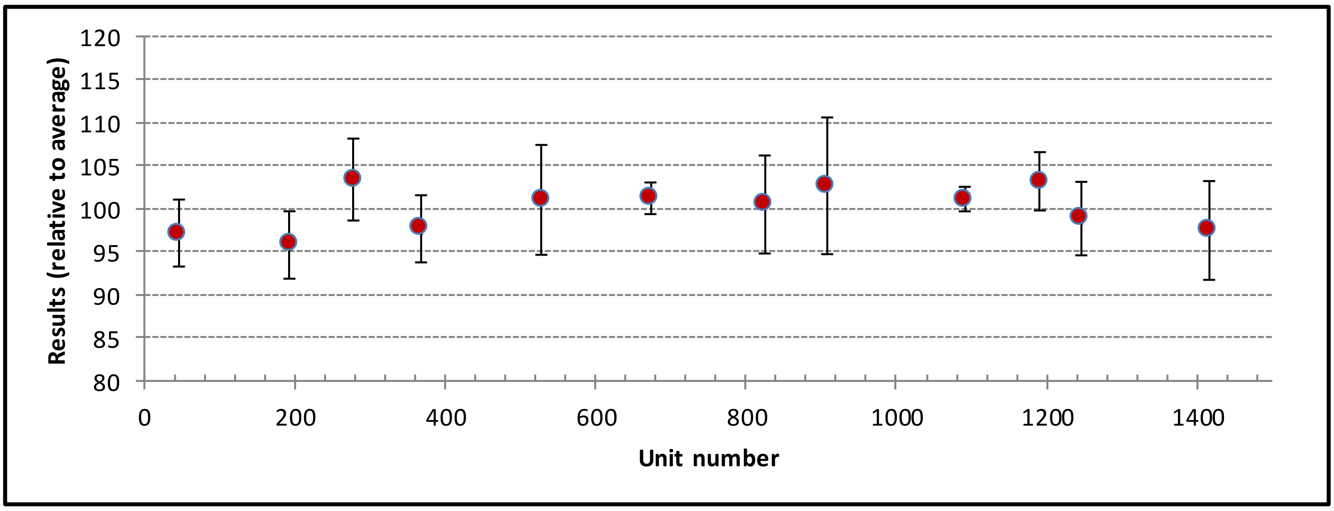


Figure A3A.6. Between units homogeneity plot for Calcium by IMBIH

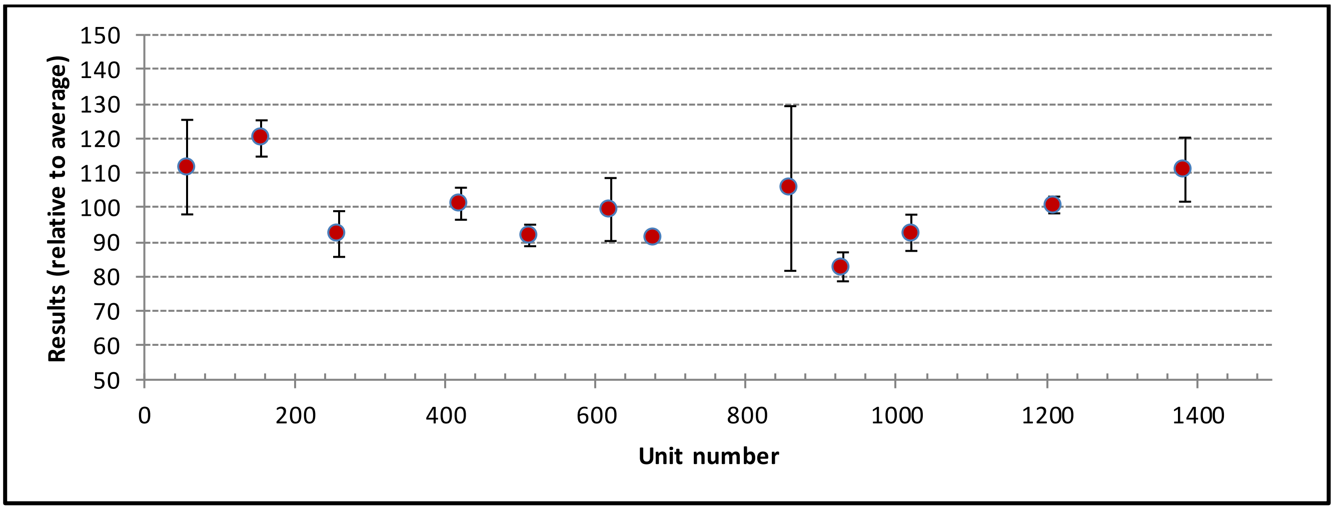


Figure A3A.7. Between units homogeneity plot for Cadmium by BRML

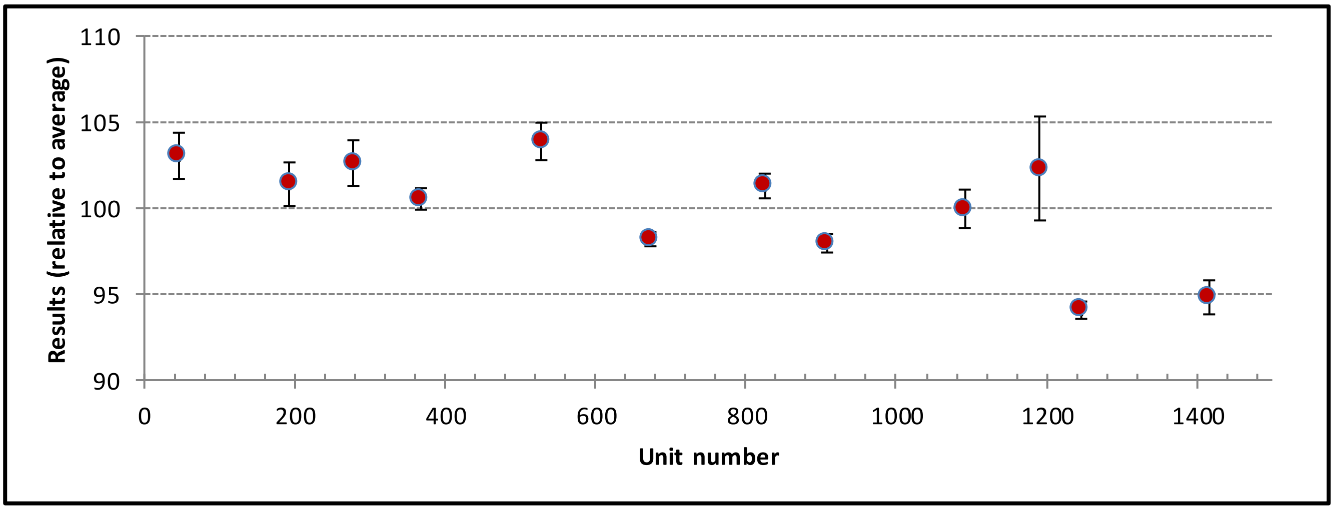


Figure A3A.8. Between units homogeneity plot for Chromium by IMBIH

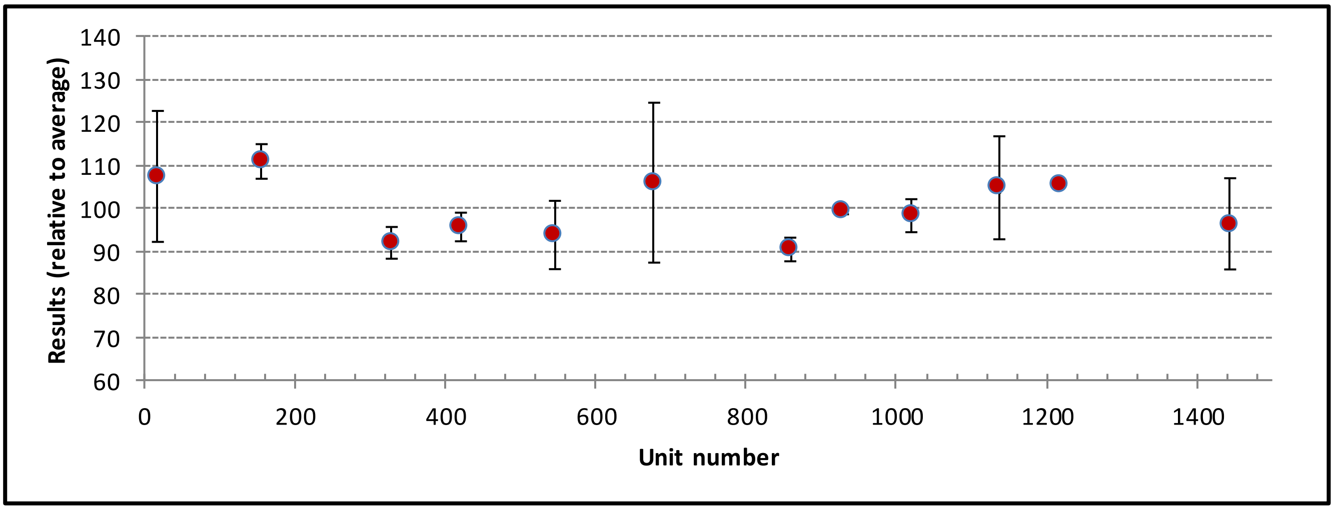


Figure A3A.9. Between units homogeneity plot for Copper by BRML

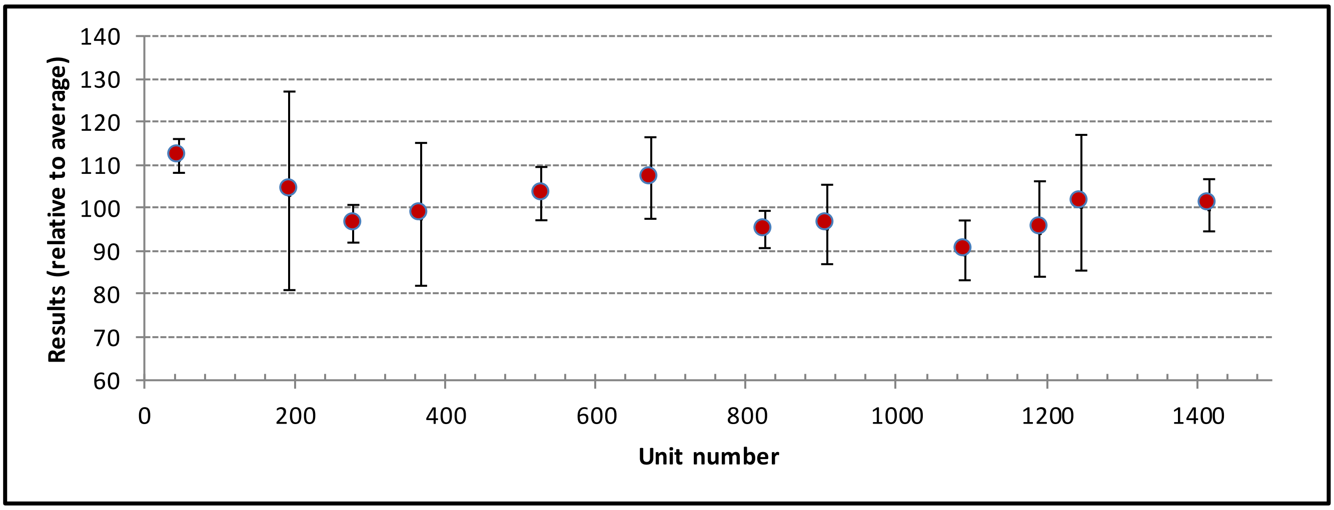


Figure A3A.10. Between units homogeneity plot for Iron by IMBIH

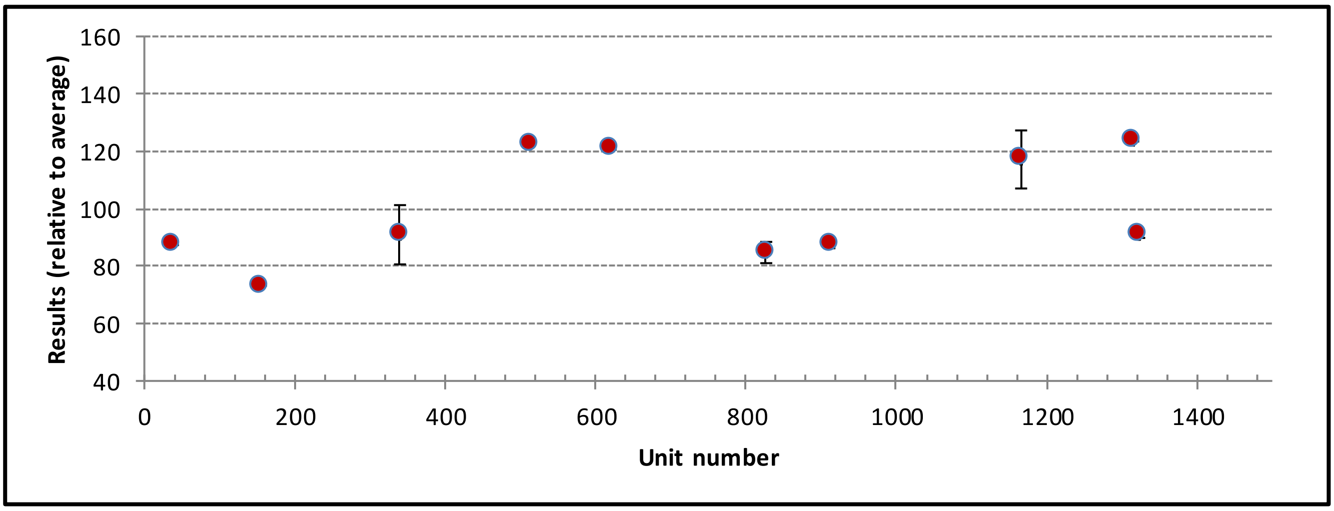


Figure A3A.11. Between units homogeneity plot for Mercury by BRML

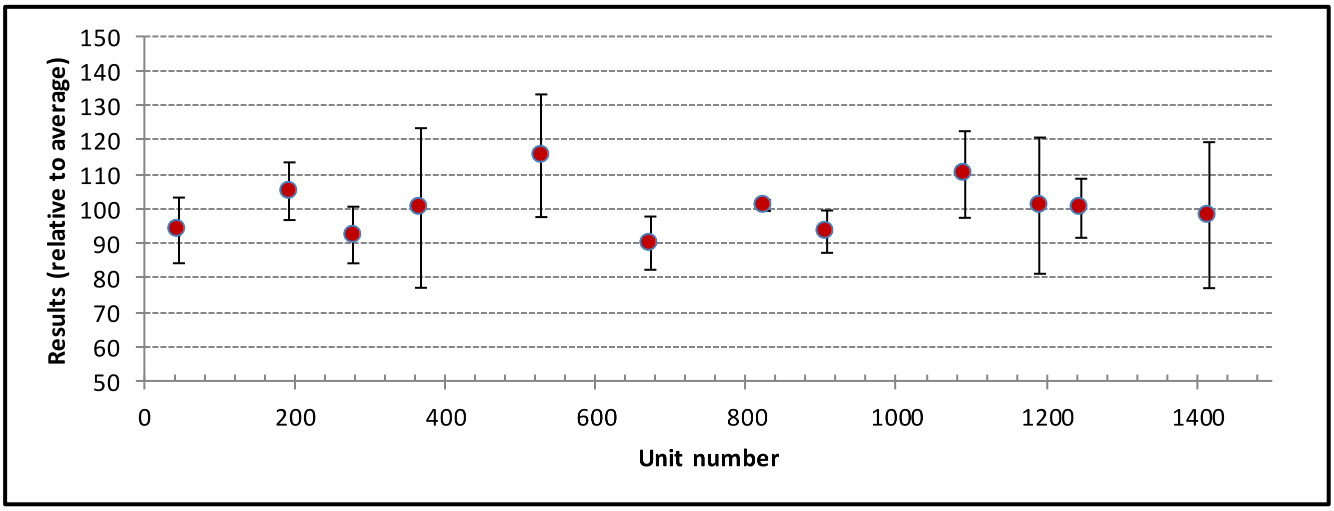


Figure A3A.12. Between units homogeneity plot for Potassium by IMBIH

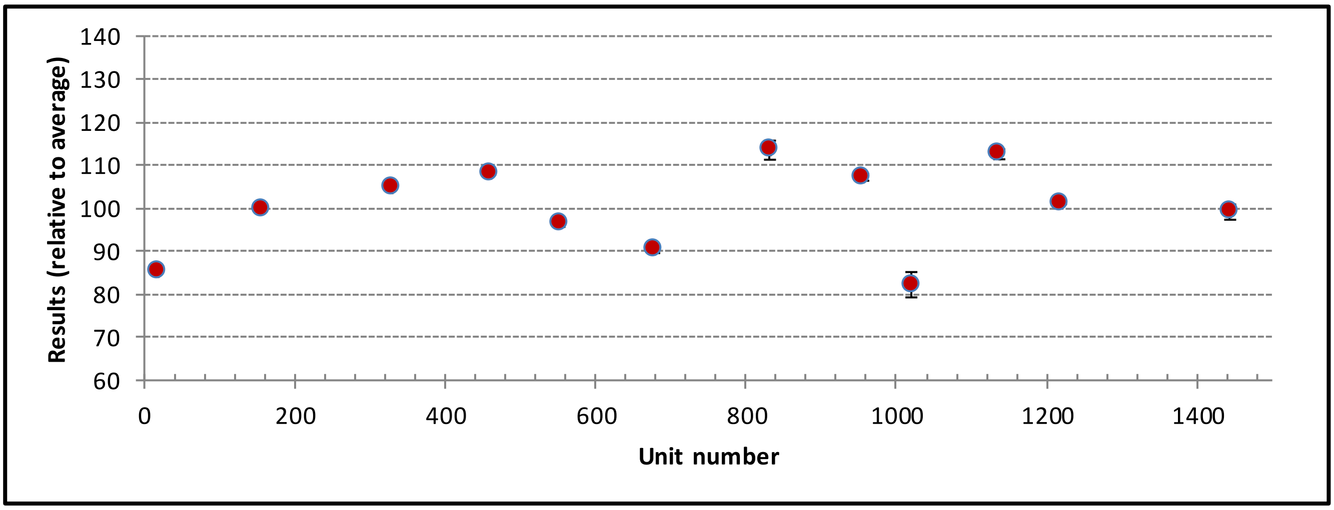


Figure A3A.13. Between units homogeneity plot for Magnesium by BRML

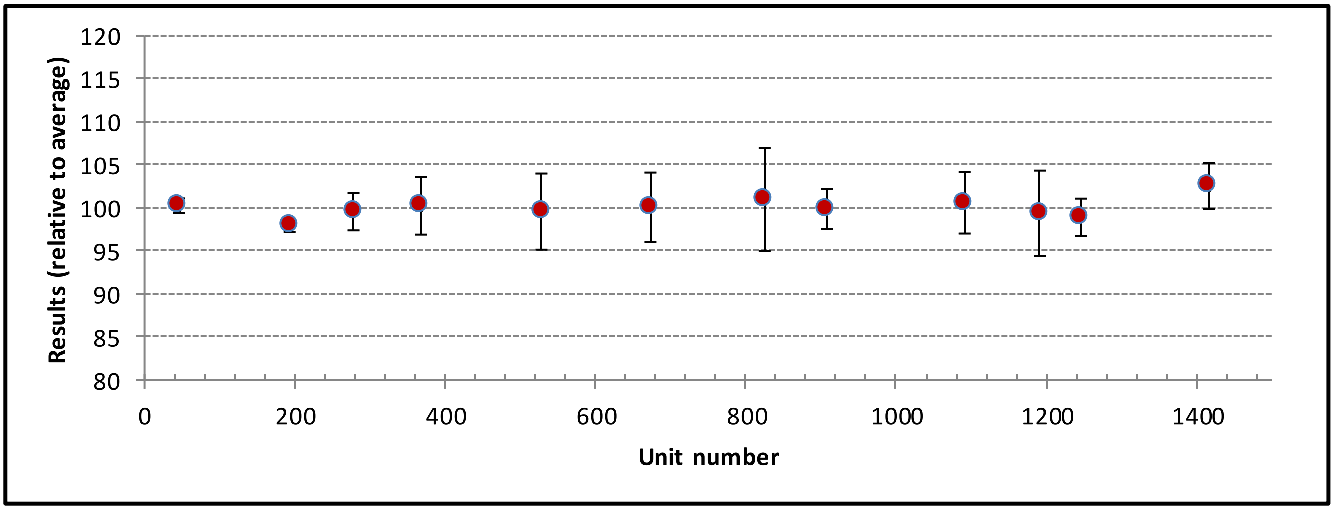


Figure A3A.14. Between units homogeneity plot for Manganese by IMBIH

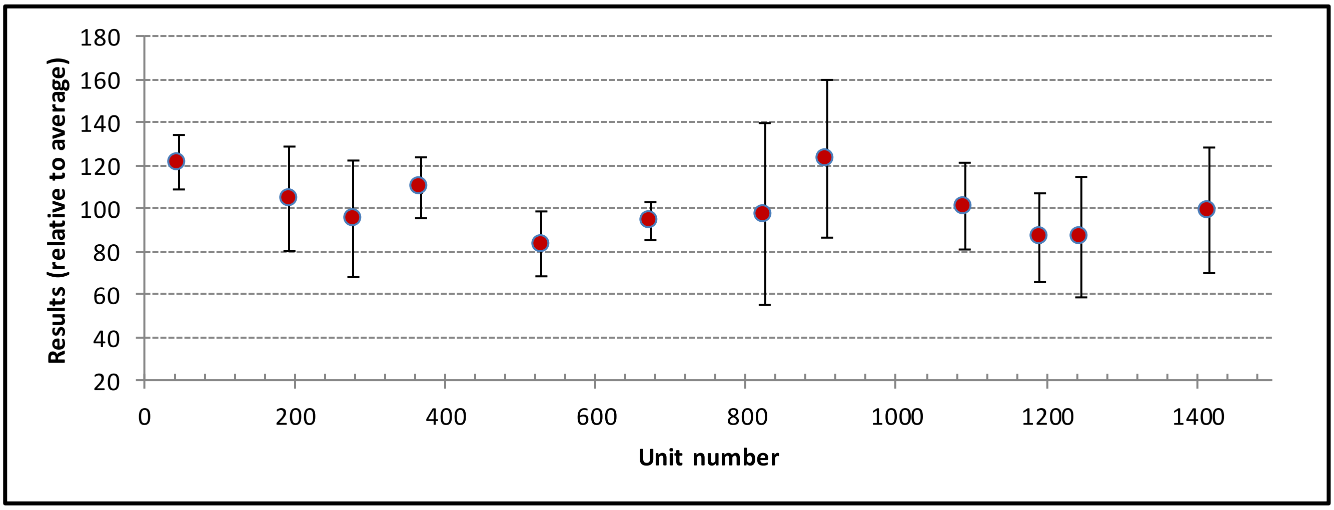


Figure A3A.15. Between units homogeneity plot for Sodium by IMBIH

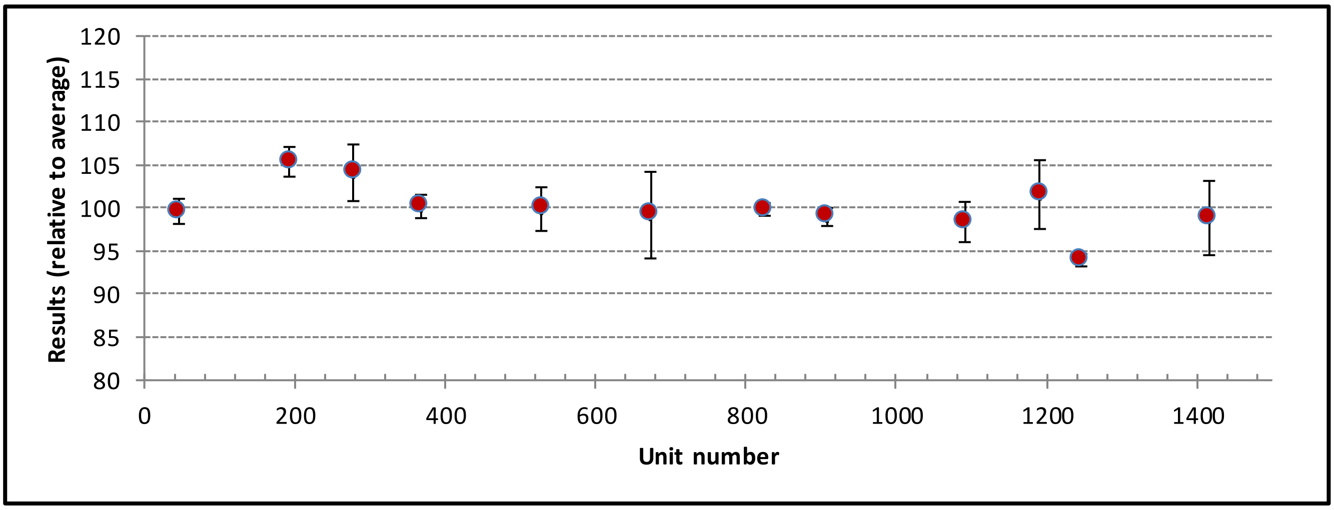


Figure A3A.16. Between units homogeneity plot for Nickel by IMBIH

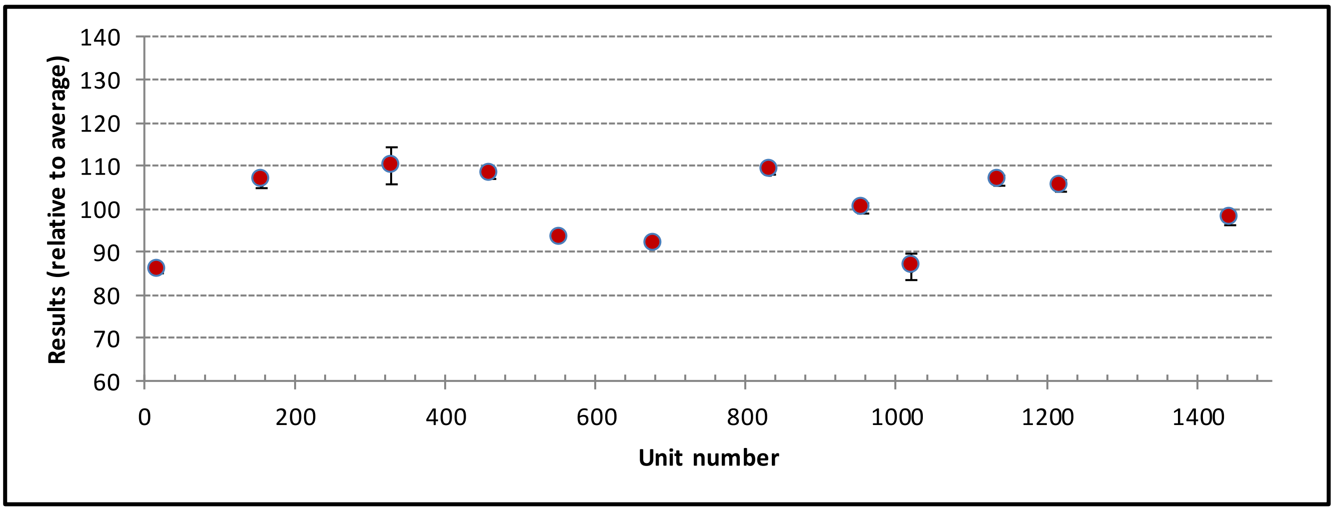


Figure A3A.17. Between units homogeneity plot for Phosphorus by BRML

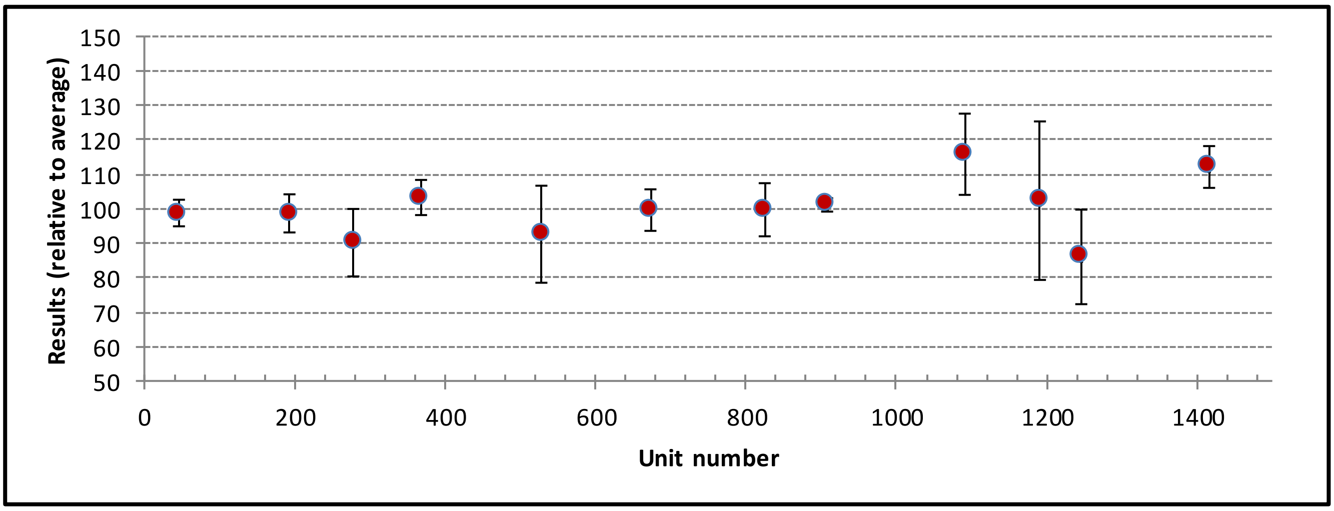


Figure A3A.18. Between units homogeneity plot for Lead by IMBIH

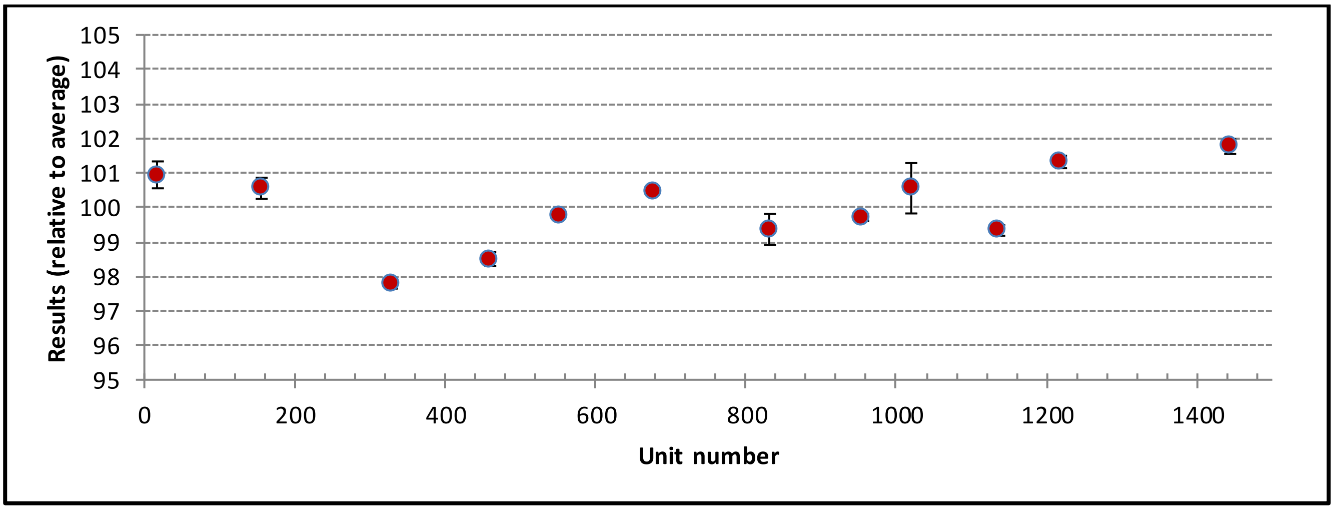


Figure A3A.19. Between units homogeneity plot for Sulfur by BRML

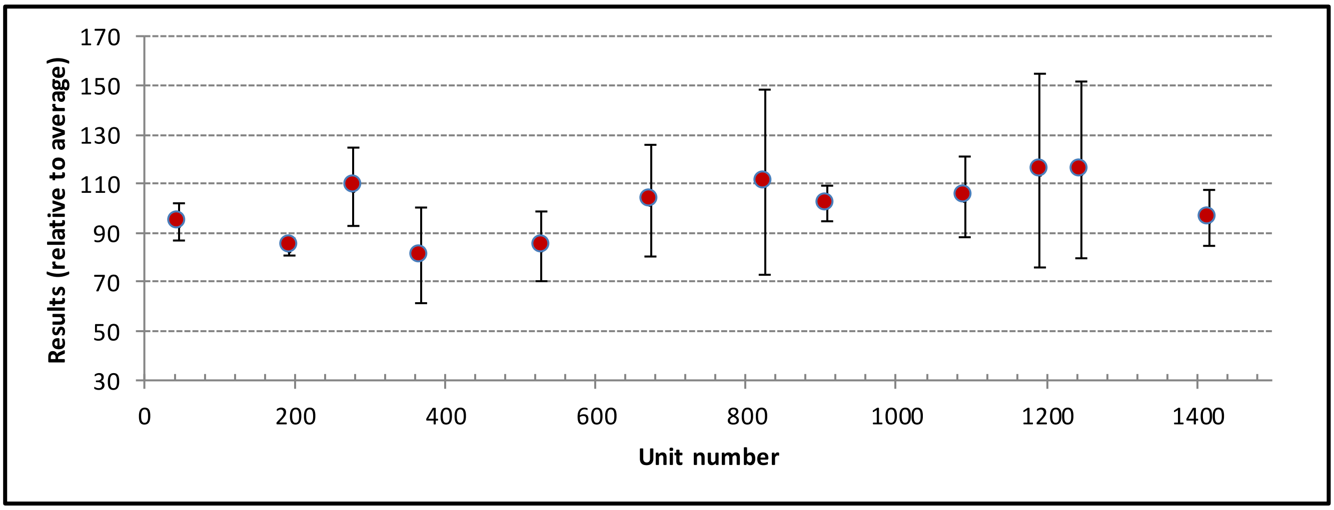


Figure A3A.20. Between units homogeneity plot for Silicon by IMBIH

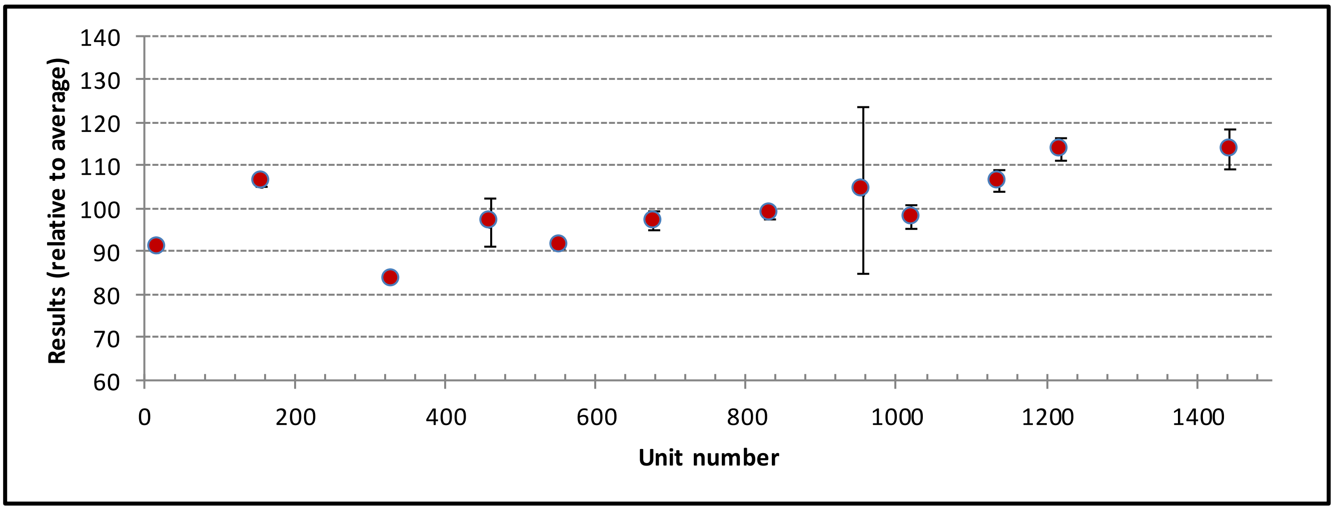


Figure A3A.21. Between units homogeneity plot for Titanium by BRML

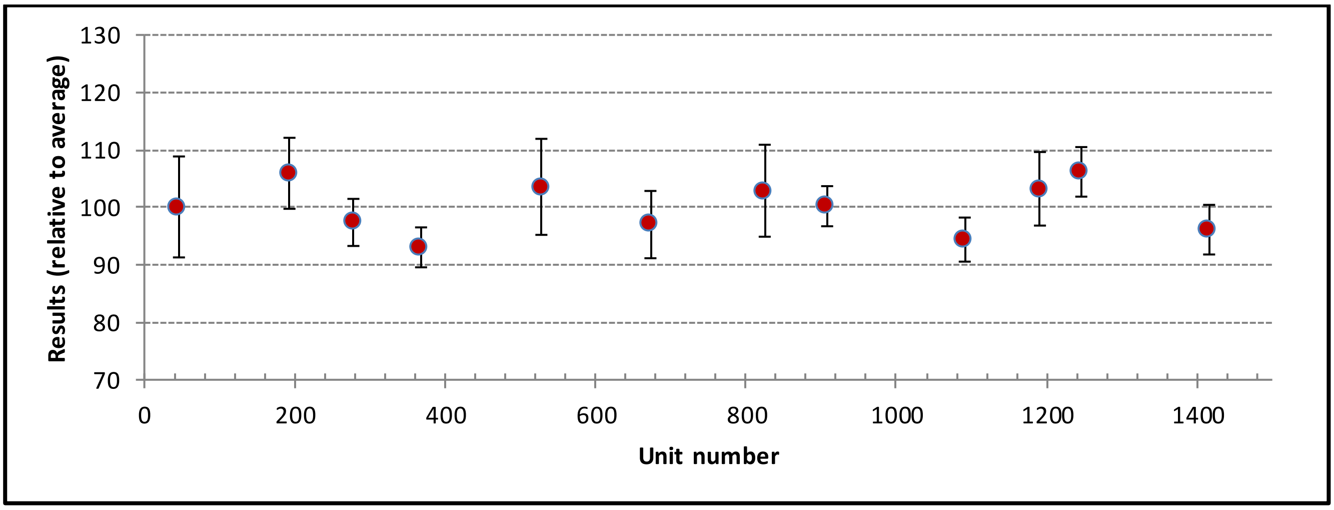


Figure A3A.22. Between units homogeneity plot for Zinc by IMBIH

ANNEX 3B. Graphs for Homogeneity Studies for Wood Pellet

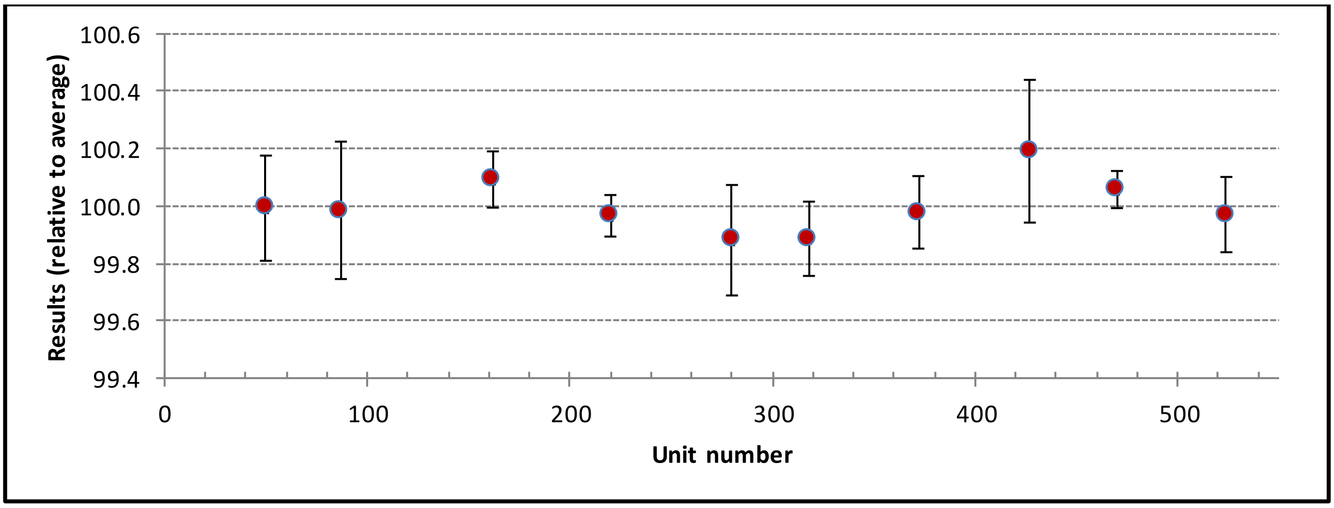


Figure A3B.1. Between units homogeneity plot for Calorific Value by BRML

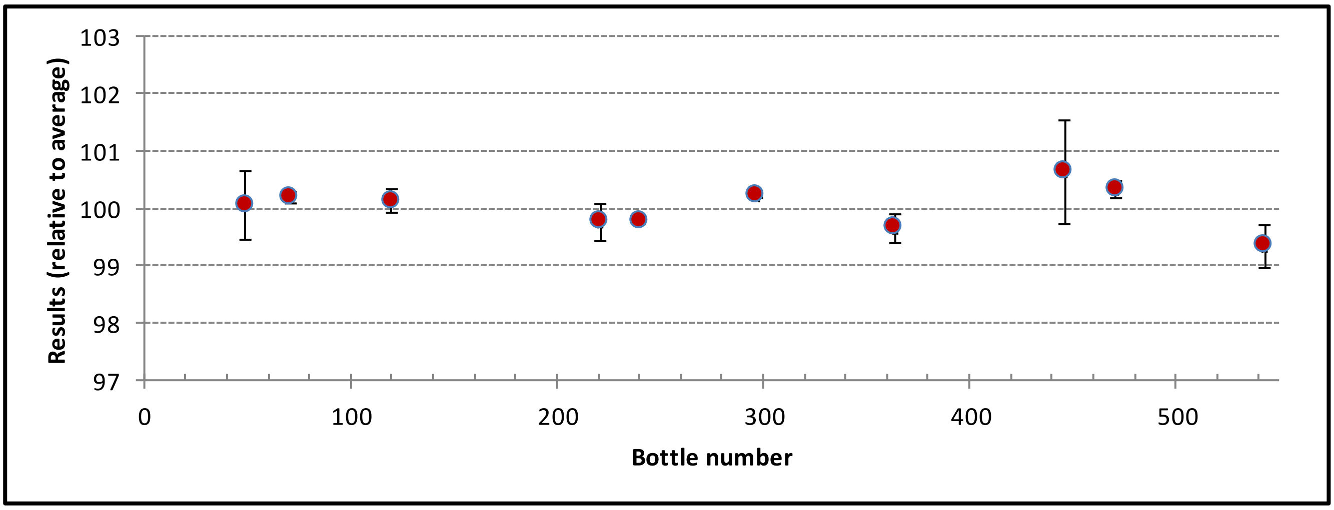


Figure A3B.2. Between units homogeneity plot for Moisture by UME

ANNEX 4A. Graphs for Short Term Stability Studies for Wood Pellet Powder

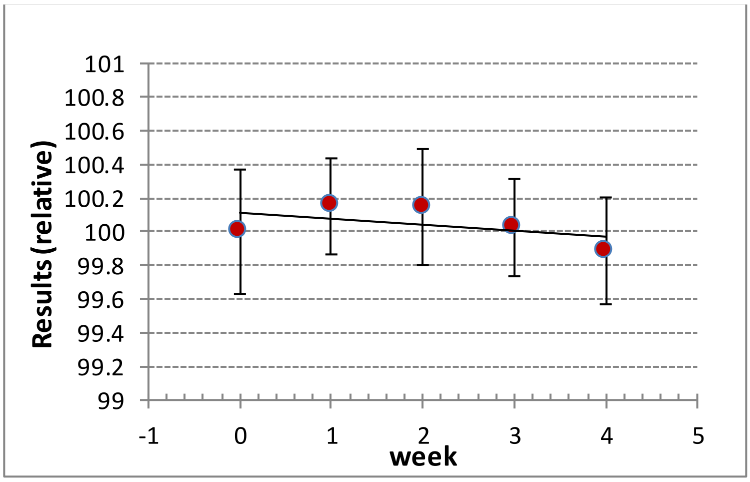


Figure A4A.1. Short Term Stability Plot for Calorific Value at 45 °C by PTB

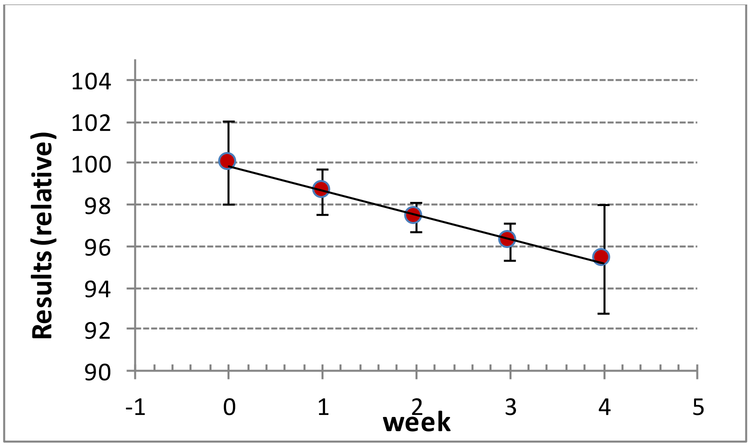


Figure A4A.2. Short Term Stability Plot for Moisture at 45 °C by UME

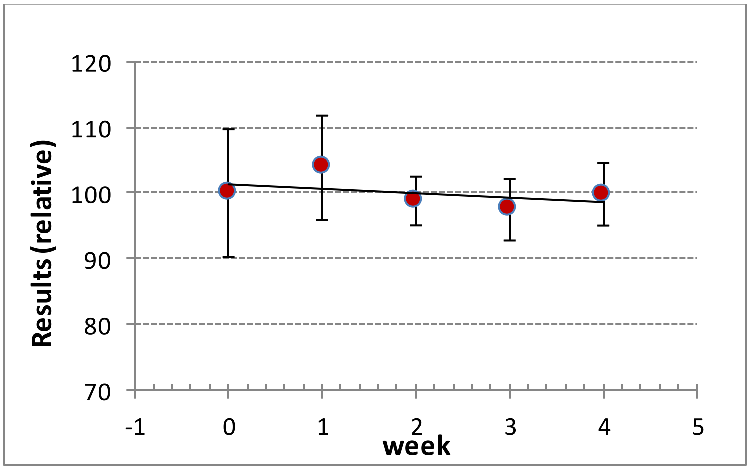


Figure A4A.3. Short Term Stability Plot for Ash at 45 °C by UME

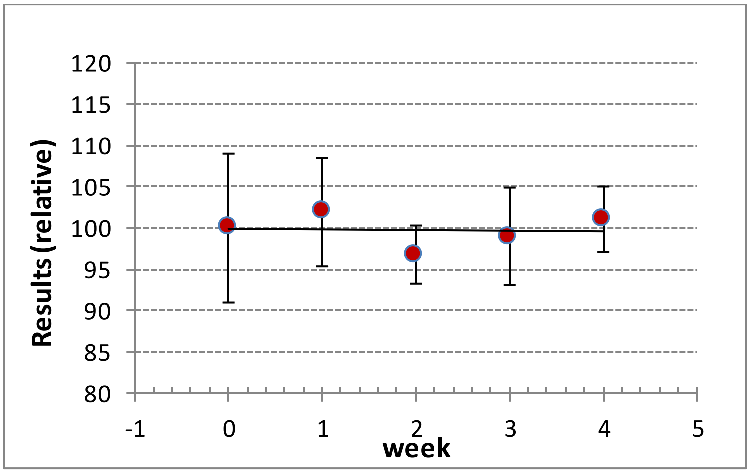


Figure A4A.4. Short Term Stability Plot for Aluminum at 45 °C by IMBIH

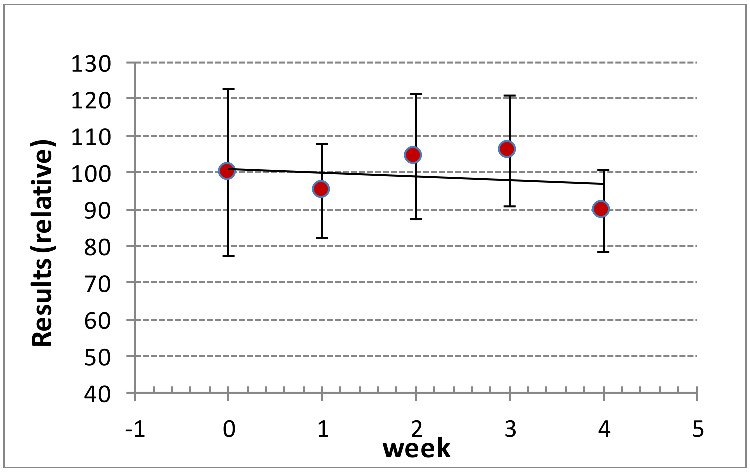


Figure A4A.5. Short Term Stability Plot for Calcium at 45 °C by IMBIH

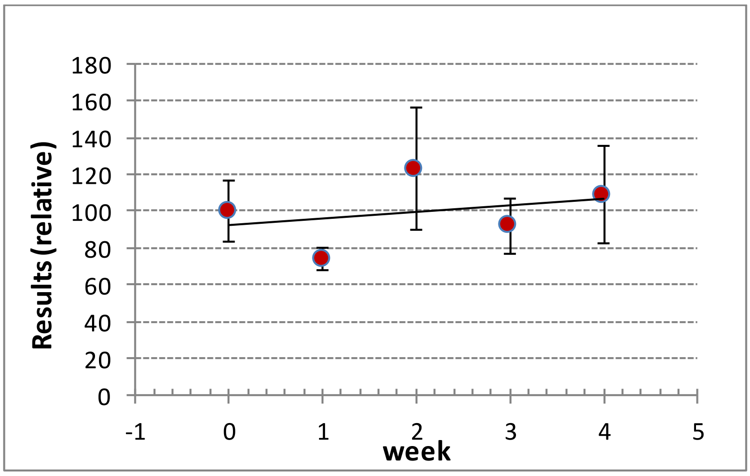


Figure A4A.6. Short Term Stability Plot for Cadmium at 45 °C by BRML

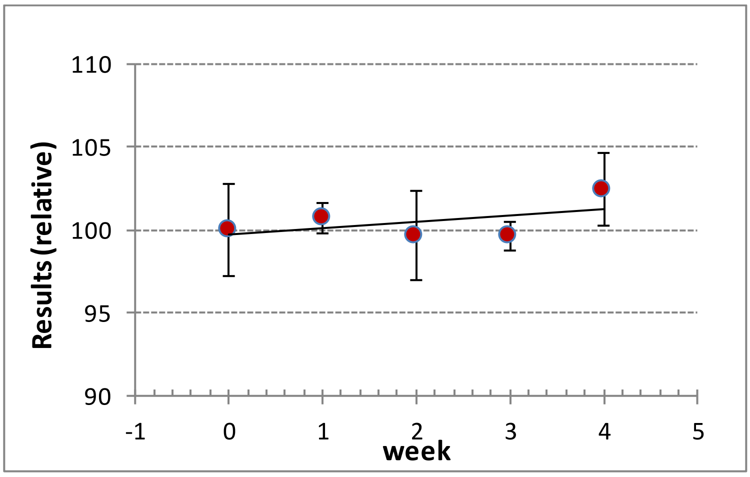


Figure A4A.7. Short Term Stability Plot for Chromium at 45 °C by IMBIH

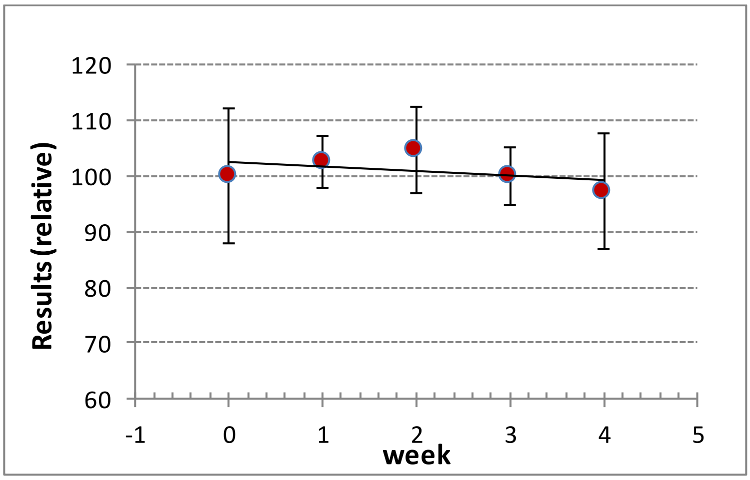


Figure A4A.8. Short Term Stability Plot for Copper at 45 °C by BRML

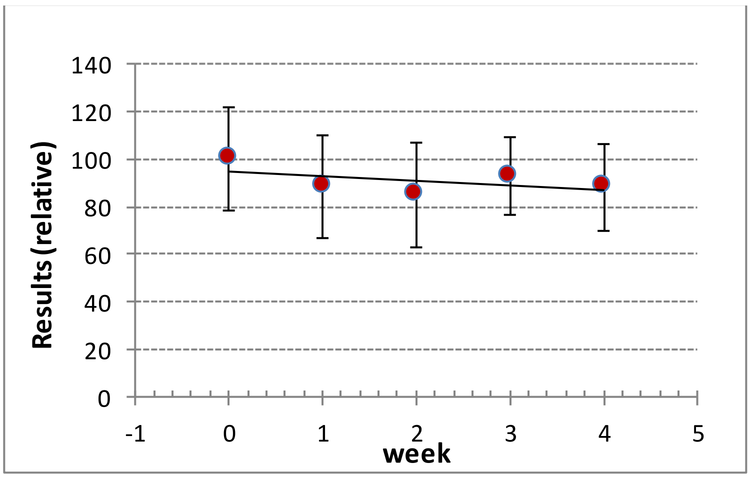


Figure A4A.9. Short Term Stability Plot for Iron at 45 °C by IMBIH

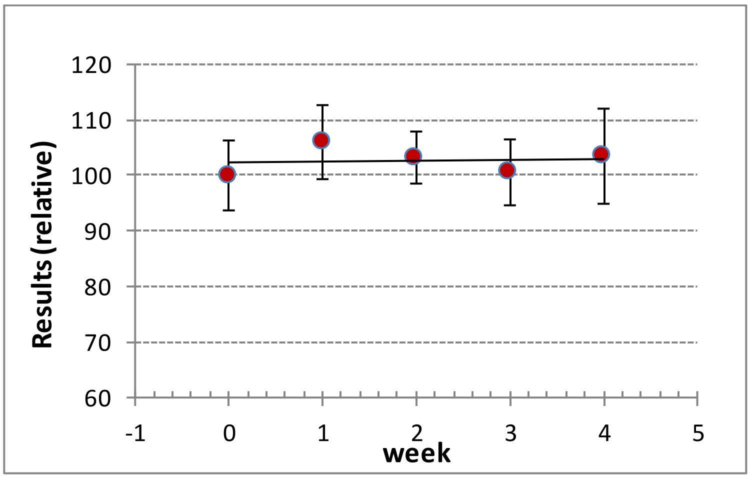


Figure A4A.10. Short Term Stability Plot for Potassium at 45 °C by IMBIH

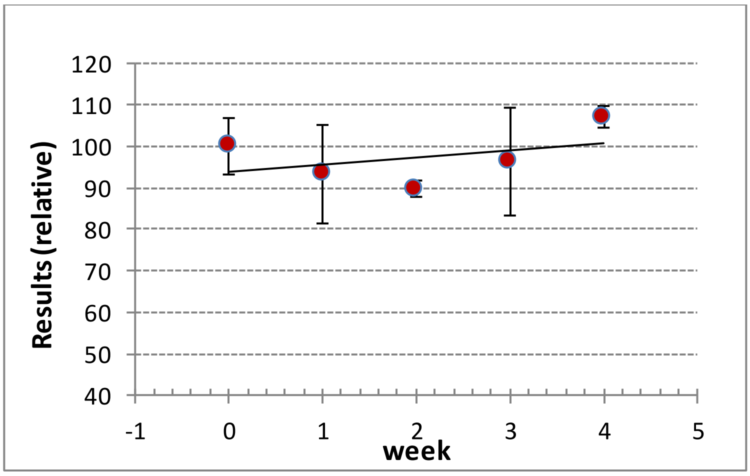


Figure A4A.11. Short Term Stability Plot for Magnessium at 45 °C by BRML

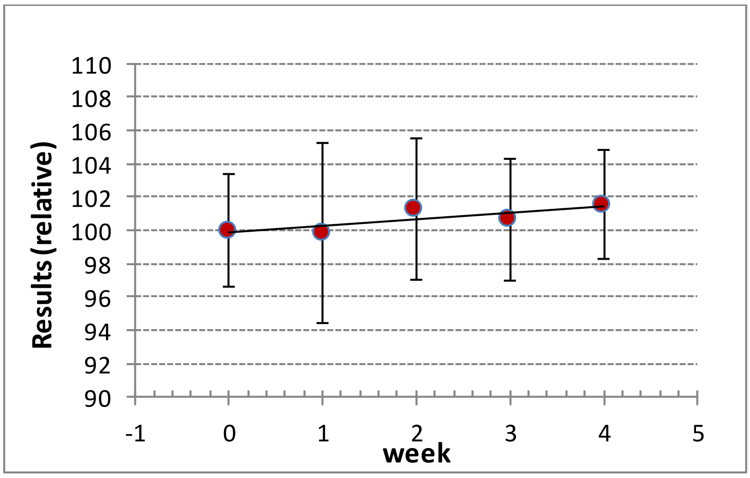


Figure A4A.12. Short Term Stability Plot for Manganese at 45 °C by IMBIH

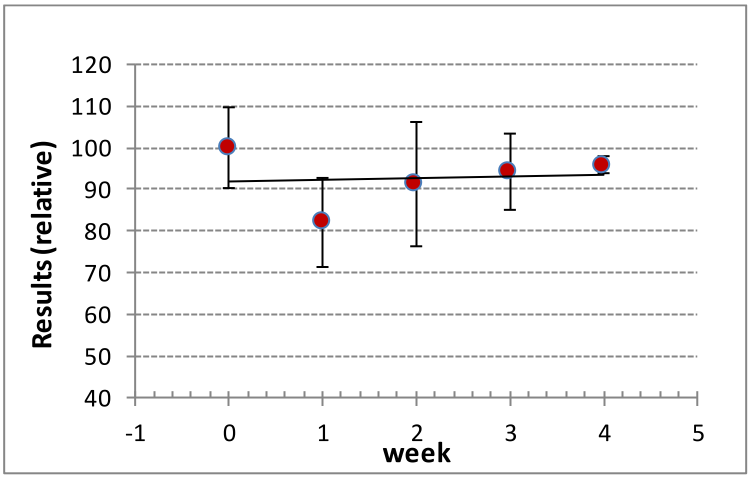


Figure A4A.13. Short Term Stability Plot for Sodium at 45 °C by BRML

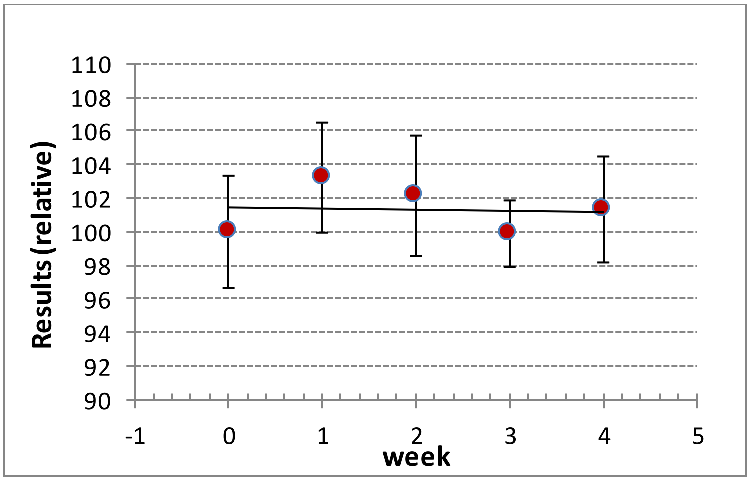


Figure A4A.14. Short Term Stability Plot for Nickel at 45 °C by IMBIH

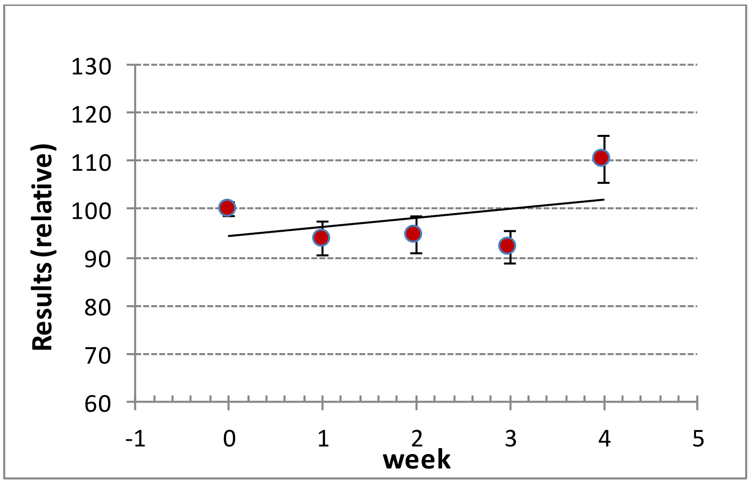


Figure A4A.15. Short Term Stability Plot for Phosphorus at 45 °C by BRML

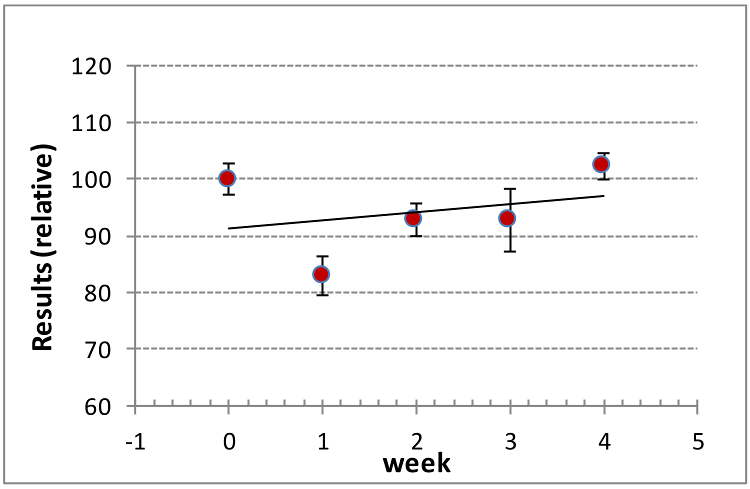


Figure A4A.16. Short Term Stability Plot for Lead at 45 °C by BRML

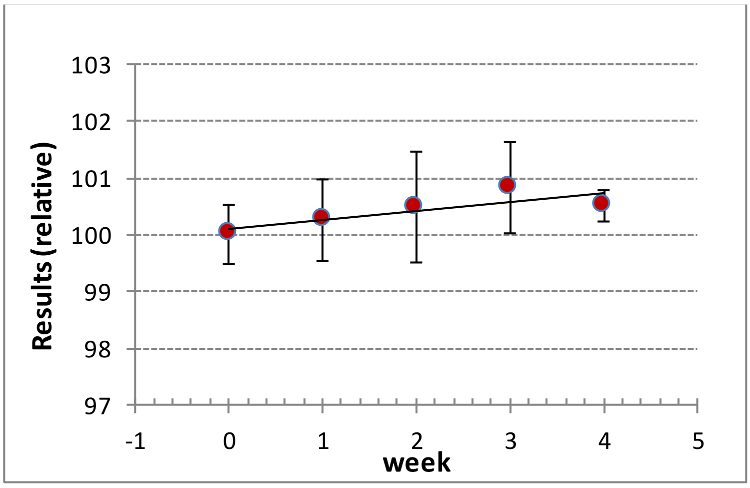


Figure A4A.17. Short Term Stability Plot for Sulfur at 45 °C by BRML

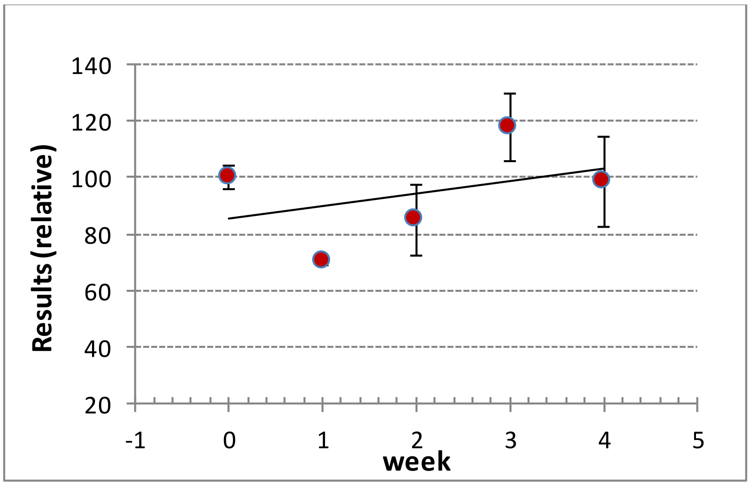


Figure A4A.18. Short Term Stability Plot for Silicon at 45 °C by BRML

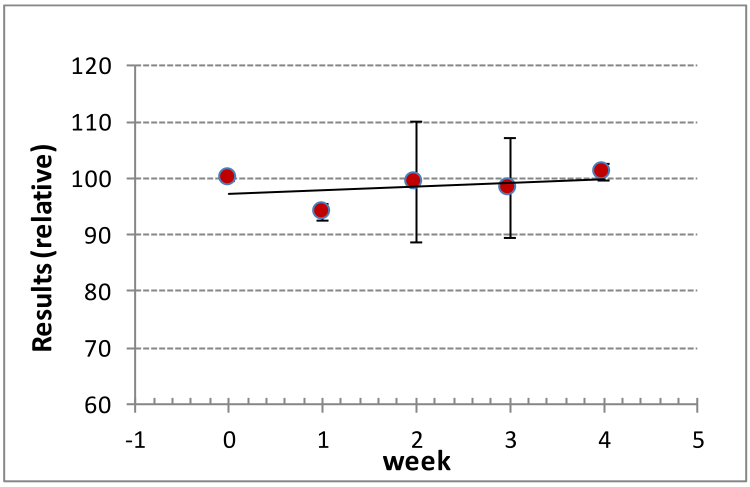


Figure A4A.19. Short Term Stability Plot for Titanium at 45 °C by BRML

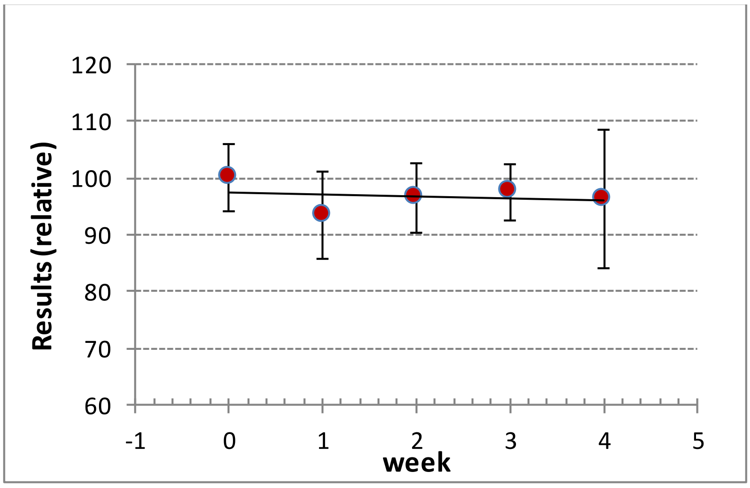


Figure A4A.20. Short Term Stability Plot for Zinc at 45 °C by IMBIH

ANNEX 4B. Graphs for Short Term Stability Studies for Wood Pellet

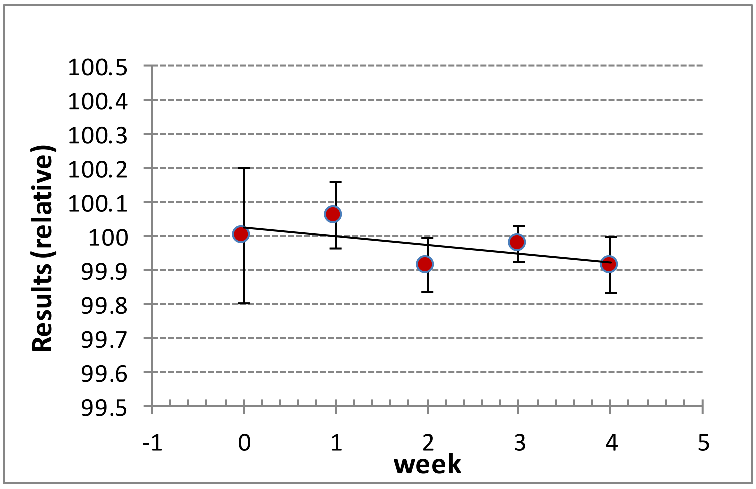


Figure A4B.1. Short Term Stability Plot for Calorific Value at 45 °C by BRML

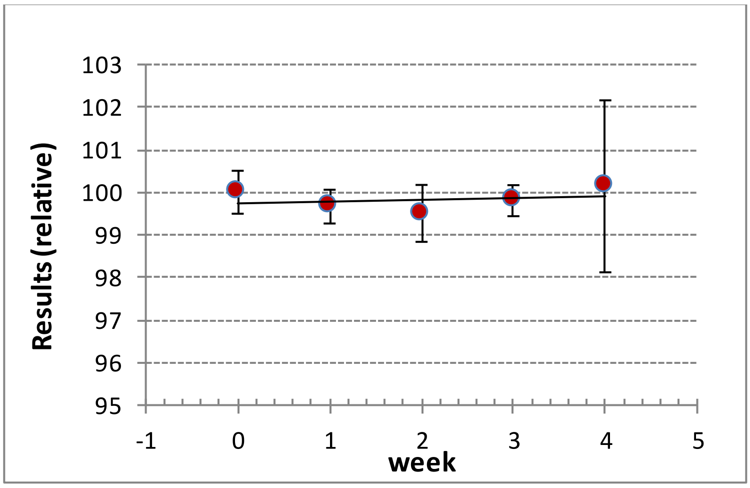


Figure A4B.2. Short Term Stability Plot for Moisture at 45 °C by UME

ANNEX 5A. Graphs for Long Term Stability Studies for Wood Pellet Powder

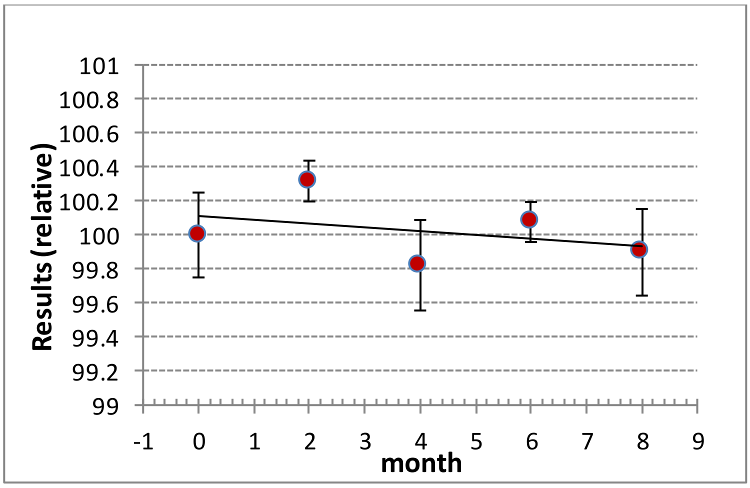


Figure A5A.1. Long Term Stability Plot for Calorific Value at 22 °C by PTB

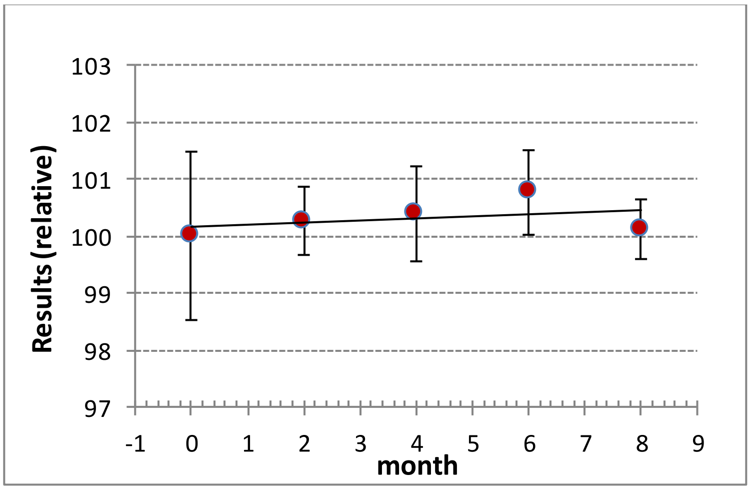


Figure A5A.2. Long Term Stability Plot for Moisture at 22°C by UME

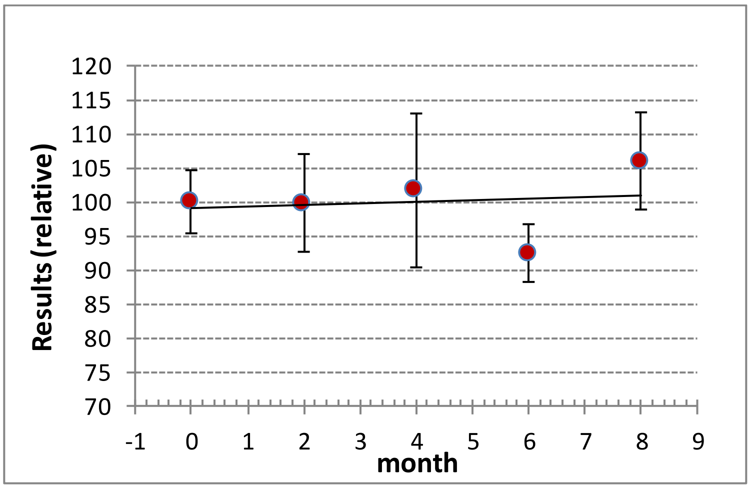


Figure A5A.3. Long Term Stability Plot for Ash at 22°C by BRML

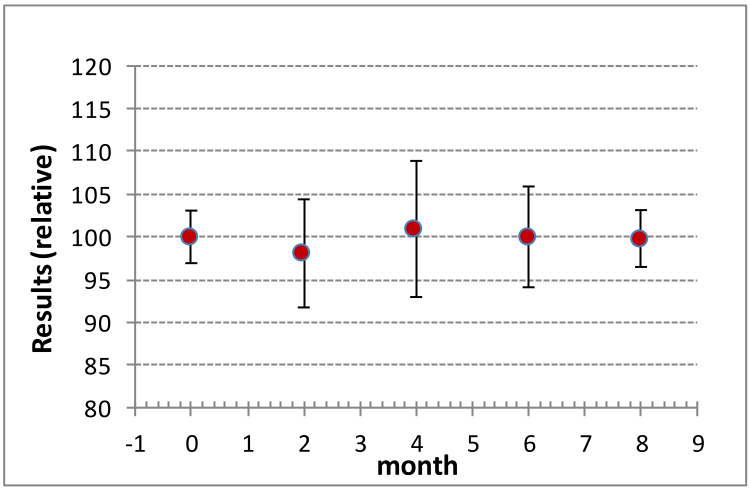


Figure A5A.4. Long Term Stability Plot for Aluminum at 22°C by IMBIH

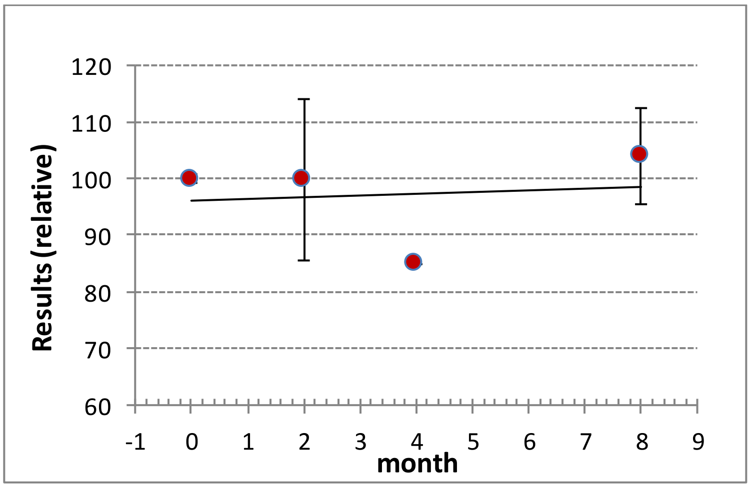


Figure A5A.5. Long Term Stability Plot for Arsenic at 22°C by BRML

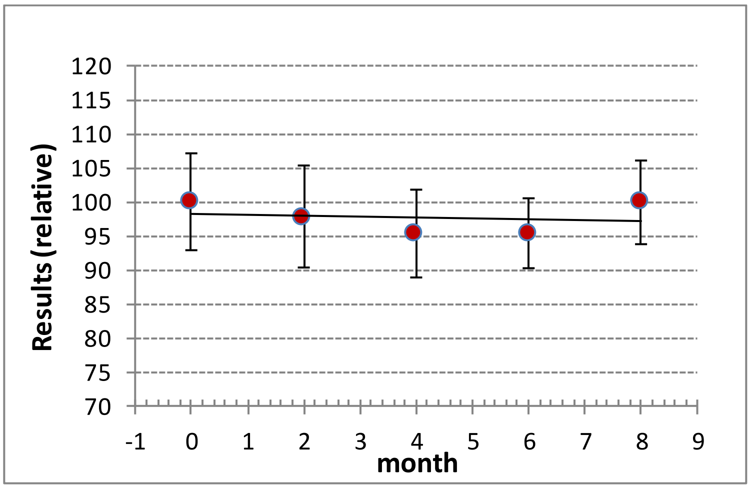


Figure A5A.6. Long Term Stability Plot for Calcium at 22°C by IMBIH

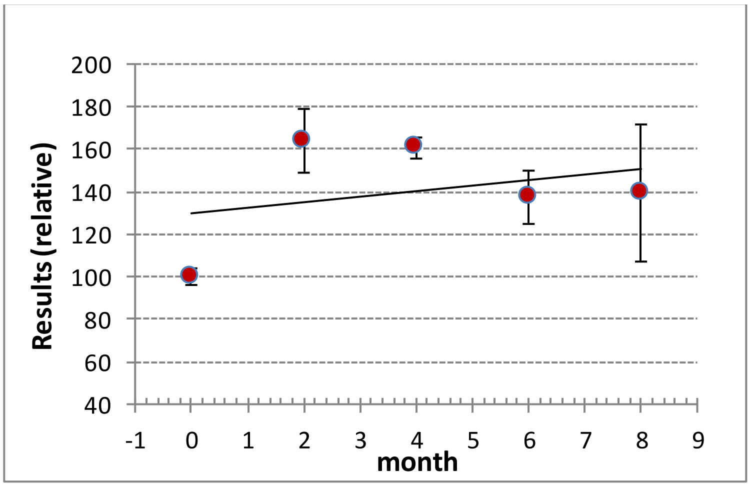


Figure A5A.7. Long Term Stability Plot for Cadmium at 22°C by BRML

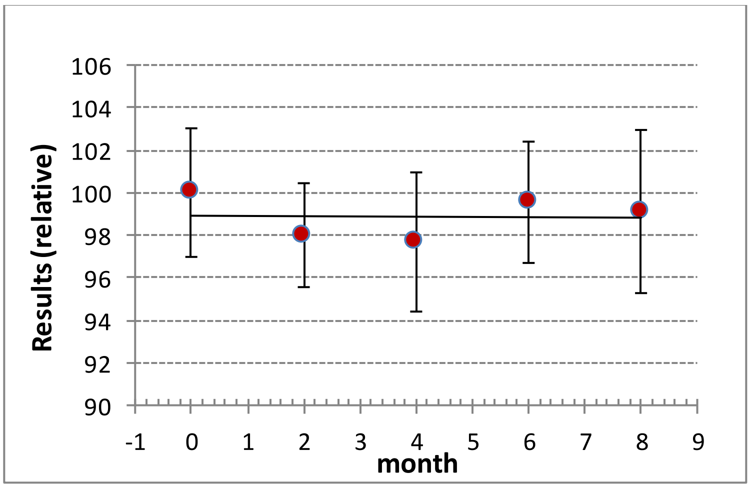


Figure A5A.8. Long Term Stability Plot for Chromium at 22°C by IMBIH

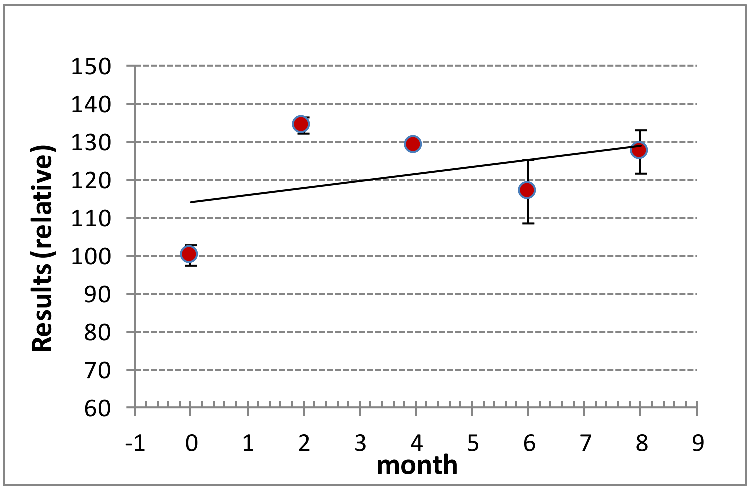


Figure A5A.9. Long Term Stability Plot for Copper at 22°C by IMBIH

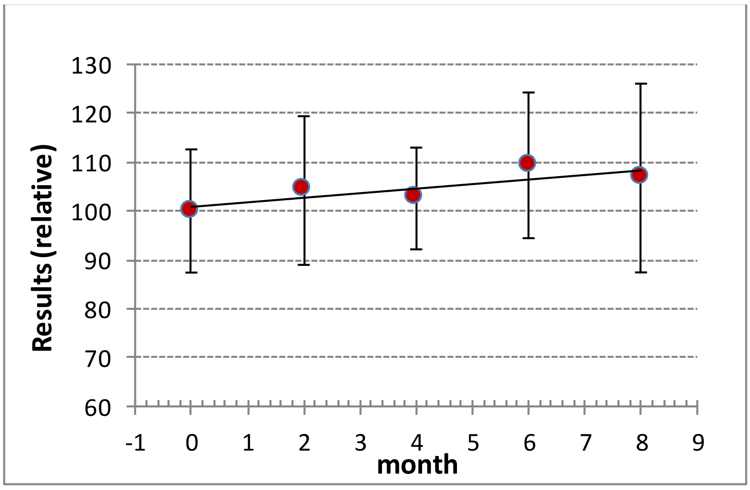


Figure A5A.10. Long Term Stability Plot for Iron at 22°C by IMBIH

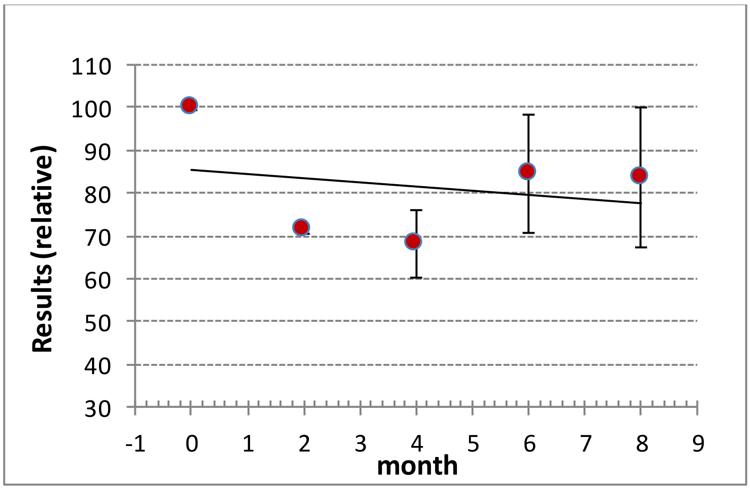


Figure A5A.11. Long Term Stability Plot for Mercury at 22°C by BRML

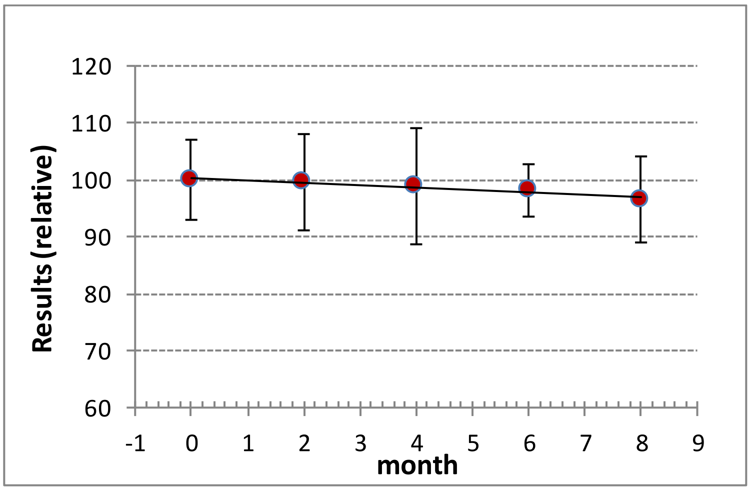


Figure A5A.12. Long Term Stability Plot for Potassium at 22°C by IMBIH

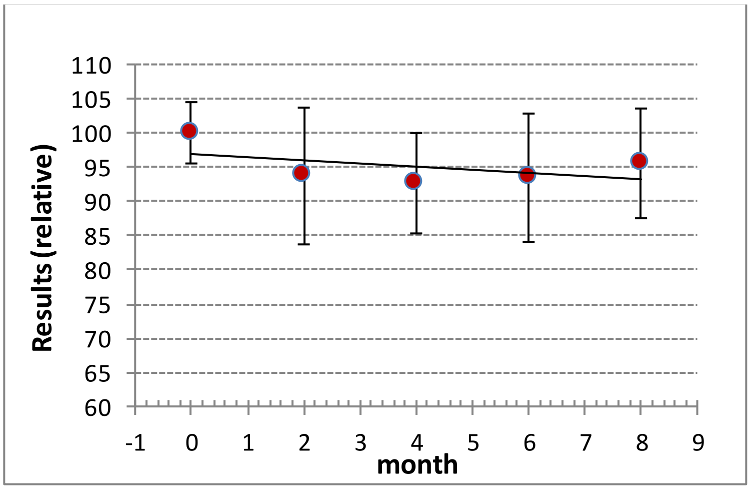


Figure A5A.13. Long Term Stability Plot for Magnessium at 22°C by IMBIH

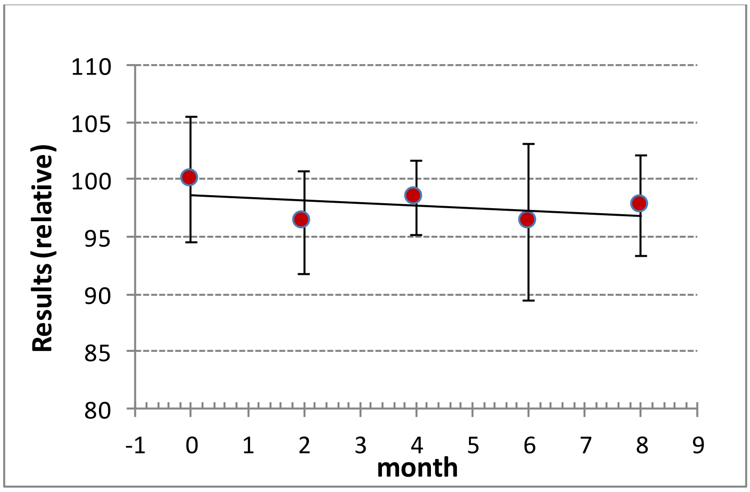


Figure A5A.14. Long Term Stability Plot for Manganese at 22°C by IMBIH

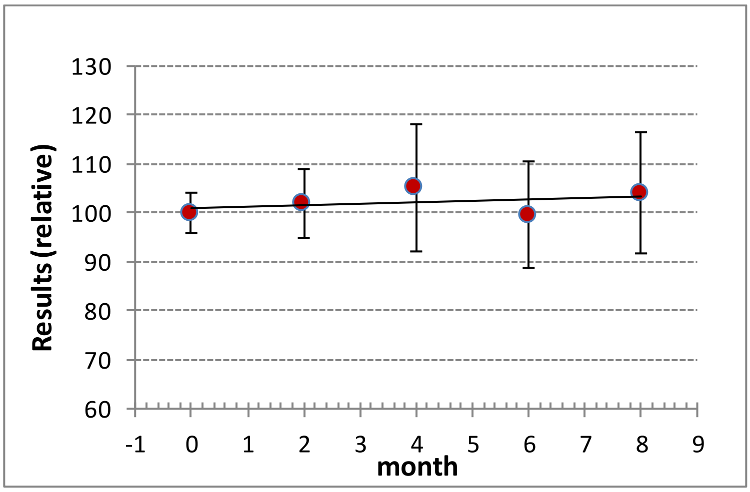


Figure A5A.15. Long Term Stability Plot for Sodium at 22°C by IMBIH

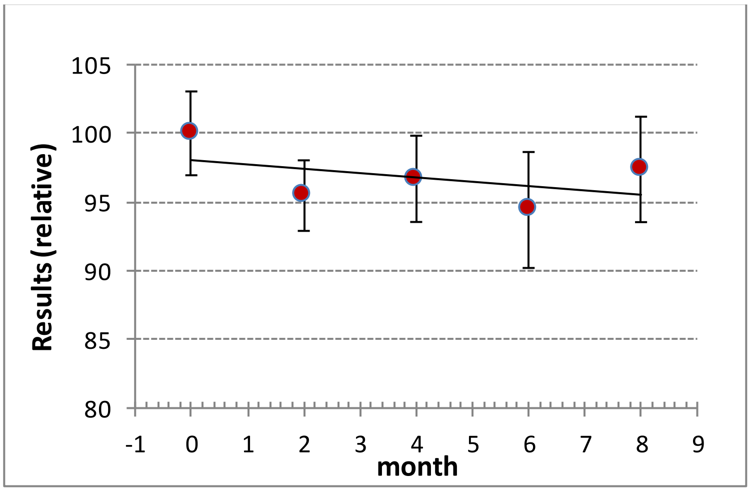


Figure A5A.16. Long Term Stability Plot for Nickel at 22°C by IMBIH

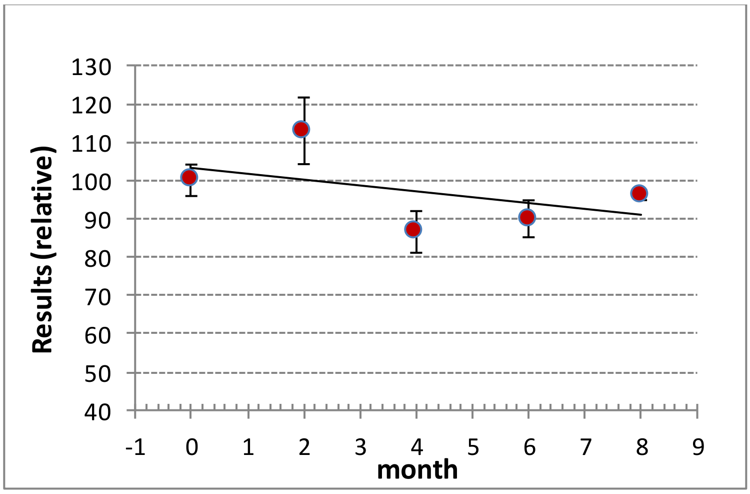


Figure A5A.17. Long Term Stability Plot for Phosphorus at 22°C by BRML

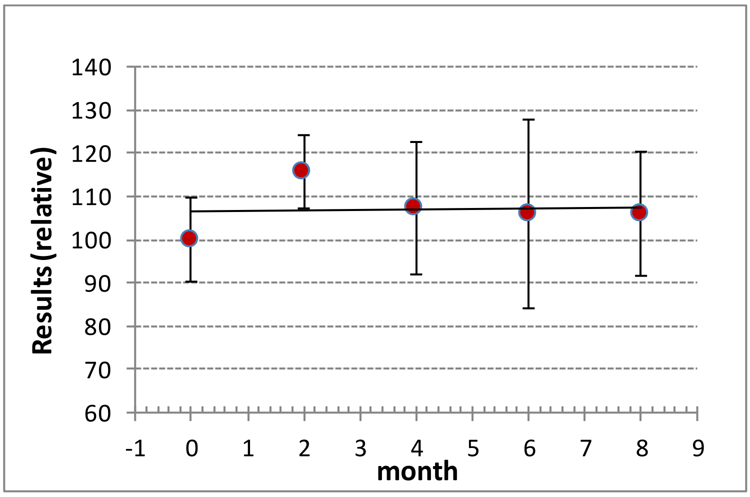


Figure A5A.18. Long Term Stability Plot for Lead at 22°C by IMBIH

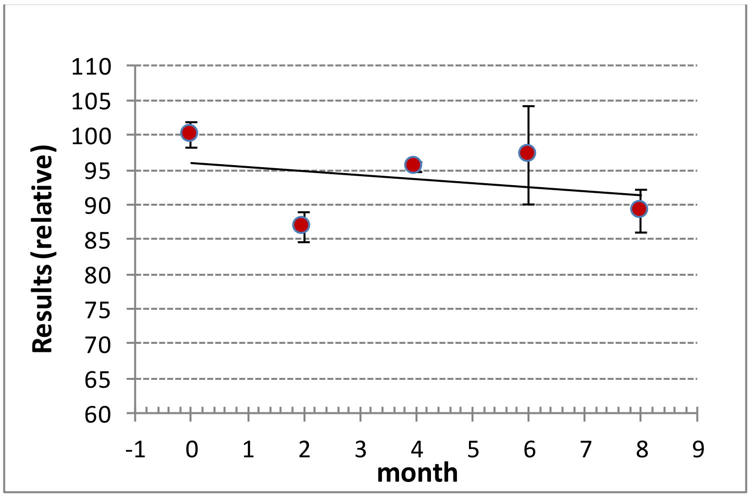


Figure A5A.19. Long Term Stability Plot for Sulfur at 22°C by BRML

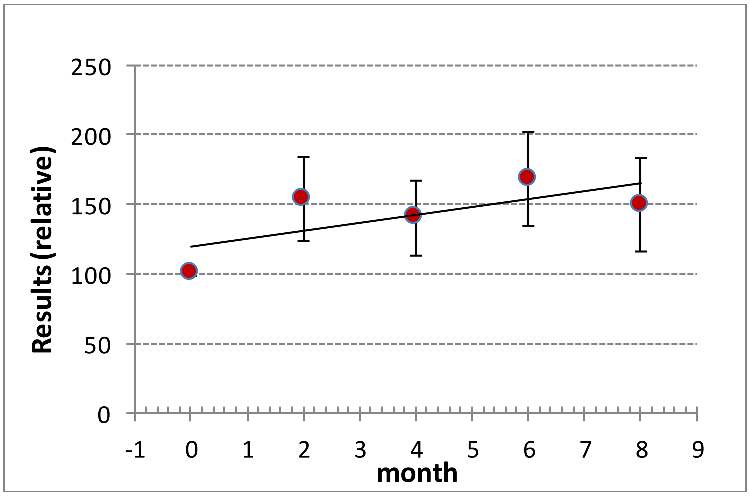


Figure A5A.20. Long Term Stability Plot for Silicon at 22°C by BRML

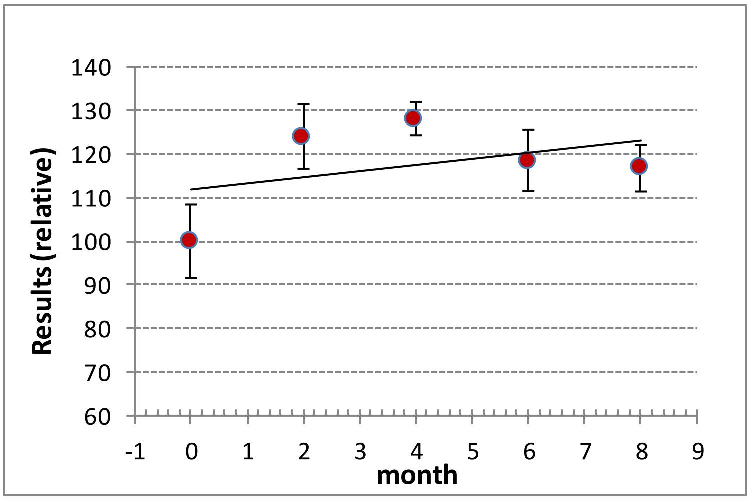


Figure A5A.21. Long Term Stability Plot for Titanium at 22°C by BRML

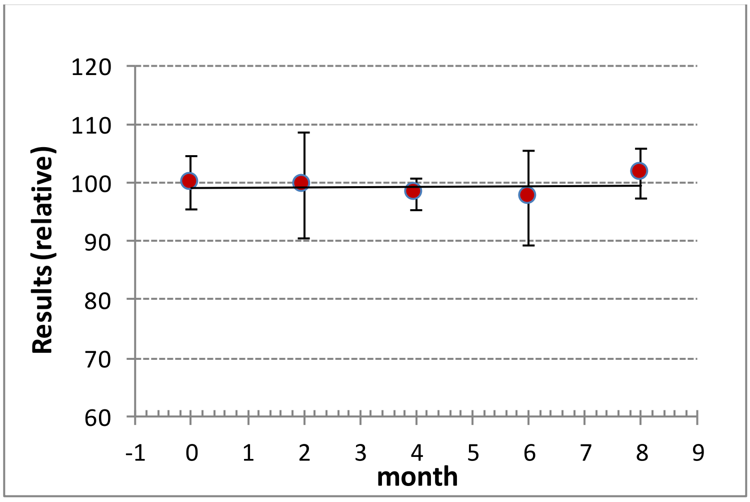


Figure A5A.22. Long Term Stability Plot for Zinc at 22°C by IMBIH

ANNEX 5B. Graphs for Long Term Stability Studies for Wood Pellet

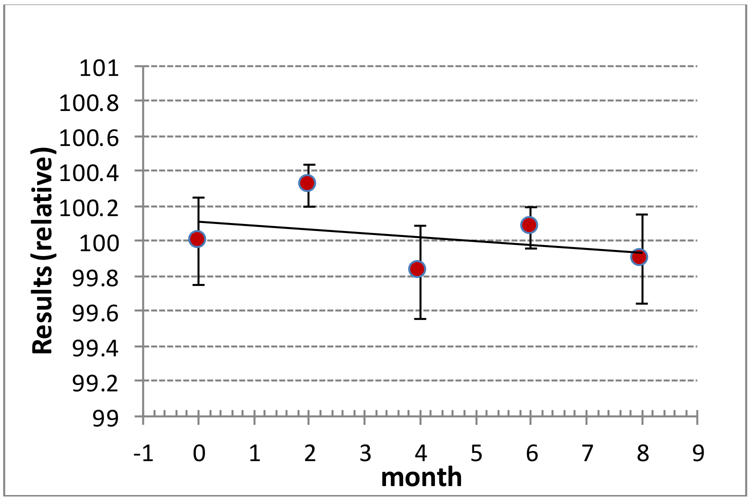


Figure A5B.1. Long Term Stability Plot for Calorific Value at 22 °C by BRML

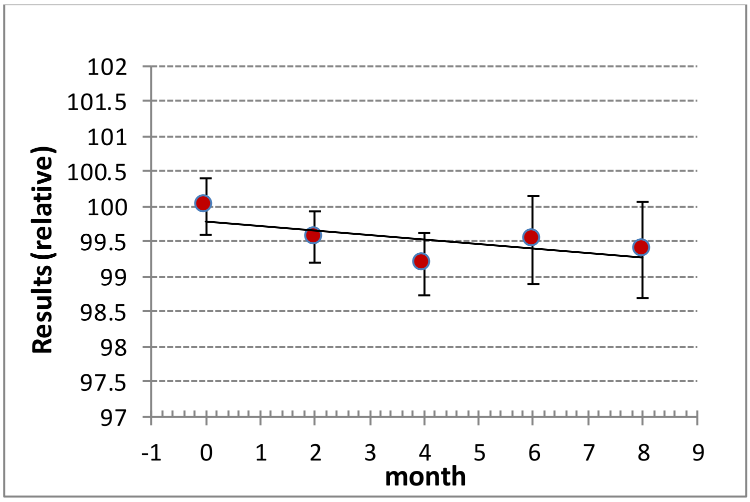


Figure A5B.2. Long Term Stability Plot for Moisture at 22°C by BRML

ANNEX 6A. Information about the Methods Used for the Characterization Study of Wood Pellet Powder

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
BAM	Sulfur	Decomposition: Closed digestion with HNO_3 (5 mL) and H_2O_2 (1 mL) using a high pressure asher with T_{max} ≈ 300°C and P_{max} ≈ 130 bar Separation: Ion exchange chromatography with AG 1X8 resin filled in Eichrom columns, sample loading with dilute HNO_3 (0.028 mol/L), elution of matrix with water, and elution of S with HNO_3 (0.25 mol/L)	IDMS with inhouse calibrated ^{34}S-spike, as backspike NIST SRM 3181 was used to establish SI traceablity; isotopes measured: ^{32}S & ^{34}S, Ratio: $^{32}S/^{34}S$	Isotope dilution mass spectrometry	Inhouse calibrated ^{34}S-spike NIST SRM 3181
BRML	Ash	No sample preparation	Calibrated balance used	ISO 18122 Gravimetry	Not applicable
	Moisture	No sample preparation	Calibrated balance used	ISO 18134-3 Gravimetry	Not applicable
	Calorific Value	~0.5 g sample is pelletized and used	Specific heat capacity is determined using benzoic acid reference material.	Isoperibol Oxygen Bomb Calorimetry ISO 18125	Standard Reference Material 39j Benzoic Acid (NIST)
	Calcium Chromium Copper Iron Potassium Magnessium Manganese Sodium Nickel Phosphorus Lead Sulfur Silicon Titanium Zinc	500 mg of homogenized sample is mixed with 3 mL H_2O_2 30%, 8 mL HNO_3 65% and 1 mL HF 40% in a closed Teflon digestion container. The mixture is allowed to react for 5 minutes before closing the container. The heating was done using a microwave digestion system, according to the following temperature program: heating for 15 minutes to 190 °C; holding for 20 minutes at 190 °C. After cooling to the room temperature, HF is neutralized by addition of 10 mL H_3BO_3 4%. After neutralization, the samples are re-digested in the microwave according to the program: heating for 15 minutes to 150 °C; holding for 20 minutes at 150 °C.After cooling down to the room temperature, the digest is transferred into a 50 mL volumetric flask by gravimetric filtration.	5 point external calibration	ICP-MS with dynamic reaction cell	Multi-element ICP-MS Calibration Std. 3, 10µL/mL, Al, As, Ba, Be, Ci, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, k, Li, Mg, Mn, Ni, Pb, Rb, Se, Na, Ag, Sr, Ti, V, U, Zn, 5% HNO_3, Merck, Germany; -ICP Multi-element standard solution 4, 1000 mg/L Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn 6.5% HNO_3, Merck, Germany; -Multi-element calibration standard 5, 10µL/mL B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr H_2O / 0.2% HF / Tr. HNO_3, PerkinElmer, United States.

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
DTI	Calorific Value	0.5 g powder was pelletized and used	Specific heat capacity of the calorimeter is determined using benzoic acid reference material.	Isoperibol oxygen bomb calorimetry ISO 18125	Benzoic acid IKA C723, ID nr 32 430 00 EU index 607 705 – 00-8
	Moisture	No pretreatment	Calibrated thermometer and balance were used	ISO 18134-3 Gravimetry	-
GUM	Arsenic Cadmium Chromium Copper Lead Mercury Nickel Zinc	An amount of 0,5 g of the sample was weighted directly in the mineralization PFTE vessel. Then 6 mL of HNO_3 and 2,5 mL H_2O_2 and 0,5 mL HCl were added gradually to avoid sample losses. After around 2 h vessel was capped (vessel was covered by a watch glass before) and then sample was mineralised by Anton Paar Multiwave 3000 (programme for 4 vessels: 1) ramp 525 W, 15 min; (2) hold 525 W, 20 min; (3) ramp 700 W, 10 min; (4) hold 700 W, 20 min; (5) cooling until 40 °C reached. After mineralisation sample was quantitatively transferred into the 50 mL vessel, diluted with water to 50 mL acidified with 0.5 mL of concentrated HCl and weighted. Standards and samples were prepared with high-purity deionized water (≥18 MΩ Milli-Q® water purification system)	Calibration curve with internal standarisation, the following ratios were measured 75As/72Ge, 114Cd/115In, 52Cr/72Ge, 65Cu/72Ge, 202Hg/209Bi, 62Ni/72Ge, (206Pb+207Pb+208 Pb)/Bi209, 66Zn/72Ge. Internal standard solution (VHG, LIS6, 25 µg/mL each of Bi, Ge, In, Tb) was diluted then added directly to all solutions at the same level. Integration time of 1s was applied for 114Cd and 202Hg while integration time 0.5s was applied for the rest of isotopes.	ICP-MS with collision gas (He) mode	Monoelemental aqueous solutions provided by Slovak Institute of Metrology (As B03, Cd B08, Cr B10, Cu B12, Hg B15, Ni B24, Pb B26, Zn B37) were used for calibration standard preparation. Certified Reference Material, Polish Virginia Tobacco Leaves (INCT-PVTL-6) was prepared for analysis together with the sample to check the method recovery. Quality Control samples were measured to control the instrument drift.

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
IMBIH	Calcium Chromium Copper Iron Lead Magnessium Manganese Potassium Sodium Zinc	Approximetely 0,5g of each sample/replicate w as w eighted on analytical balance (Sartorius AG, model MSE225S-OCE-DU, d=0,01g) directly to microw ave vessels. Digestion w as performed in Microw ave ow en Milestone ETHOsEasy using program for w ood material: 0.5 g of sample + 9 mL HNO3 + 1 mL H2O2 Temperature: 1. 20 min: 1800 W and 210° 2. 15 min: 1800 W and 210° Digested samples w ere quantitativelly transferred to prew eights plastic vessels and total mass of the digested sample w as obtained. samples w ere analysed directly or subjected to further dillution w ith 2% HNO3 for more concentrated elements.	Calibration i.e. mass fraction interval is covered by a minimum of 5 standards (excluding blank) Mn (403.076 nm); Zn (213.857 nm); Fe (371.993 nm); Ca (396.847 nm); K (766.491 nm); Mg (279.553 nm); Na (588.995 nm); Cr ((425.433 nm), Pb (405.781 nm), Ni (352.454 nm)	MP-AES	EPA Method 200.7 Mixed Calibration Std #1 - Calcium; 100.0 ± 0.5 µg/mL, Manganese; 20.0 ± 0.1 µg/mL, Copper; 20 ± 0.1 µg/mL EPA Method 200.7 Mixed Calibration Std #2 - Potassium; 200.0 ± 1.0 µg/mL, Sodium; 100.0 ± 0.5 µg/mL EPA Method 200.7 Mixed Calibration Std #4 - Zinc; 50.0 ± 0.3 µg/mL, Chromium; 50.0 ± 0.3 µg/mL EPA Method 200.7 Mixed Calibration Std #5 - Iron; 100.0 ± 0.5 µg/mL, Magnesium; 100.0 ± 0.5 µg/mL, Lead; 100.0 ± 0.5 µg/mL, Nickel; 20.0 ± 0.1 µg/mL AccuTrace Reference Standard - Manganese; 1000 µg/mL ± 5% AccuTrace Reference Standard - Iron; 1000 µg/mL ± 5% AccuTrace Reference Standard - Zinc; 1000 µg/mL ± 5%
PTB	Calorific Value	0.5 g of powder sample was pelletized applying 0.5 ton of pressure.	Specific heat capacity of the calorimeter is determined using benzoic acid reference material. After nitrate and sulfate analysis of combustion remainings by ion chromatography follow ing correction factors have been used: Q_N = 3.5 J/g, Q_S = 0.26 J/g	Isoperibol oxygen bomb calorimetry ISO 18125	UME CRM 1504 Benzoic acid

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
UME	Calorific Value	Pellet powder sample of 0.45-0.60 g was weighed on analytical balance (Mettler Toledo, model WXSS205, d=0.01 mg). The powder was then pelletized using a manual hydraulic press (Specac), and the pellets were dried in an oven at 105 °C for 4 hours. The dried pellets in bottles were kept in the desiccators.	Specific heat capacity of the calorimeter is determined using benzoic acid reference material. After nitrate and sulfate analysis of combustion remainings by ion chromatography following correction factors have been used: Q_N = 5.7 J/g, Q_S = 0.52 J/g	Isoperibol oxygen bomb calorimetry ISO 18125	UME CRM 1504 was used as certified reference material (benzoic acid) in instrument calibration
	Ash	No sample preparation	Calibrated balance used	ISO 18122 Gravimetry	-
	Arsenic Cadmium Chromium Copper Lead Mercury Nickel Zinc	IN PREPARATION			
	Sulfur	0.3 g of wood pellet samples were weighed into the microwave digestion vessels. 2.5 mL HNO_3 1.5 mL H_2O_2 and 0.2 mL HF were added to the vessels. Temperature programme : (1) ramp 30 min. up to 150 °C; (2) hold 25 min at 150 °C .	IDMS with IRMM 646 as ^{34}S-spike, NIST SRM 3181 was used to establish SI traceablity; Isotopes measured: 32S & 34S, Ratio: 32S/34S	Isotope Dilution High Resolution ICP-MS	NIST SRM 3181 IRMM 646 NJV-94-5 Wood Fuel
	Sulfur	0.3 g of wood pellet samples were weighed into the microwave digestion vessels. 2.5 mL HNO_3 1.5 mL H_2O_2 and 0.2 mL HF were added to the vessels. Temperature programme : (1) ramp 30 min. up to 150 °C; (2) hold 25 min at 150 °C . After mineralisation sample was transferred into the 50 mL PP vessel, diluted with high-purity deionized water up to 50 mL. All solutions were done by weighting	Standard addition calibration, NIST SRM 3181 was used to establish SI traceablity Isotopes measured: : 32S & 34S	High Resolution ICP-MS	NIST SRM 3181 NJV-94-5 Wood Fuel

ANNEX 6B. Information about the Methods Used for the Characterization Study of Wood Pellet

Lab	Parameter(s)	Sample Preparation	Calibration Strategy	Method/ Technique	CRM(s) used for Calibration and Quality Control
BRML	Calorific Value	No pretreatment	Specific heat capacity of the calorimeter is determined using benzoic acid reference material.	Isoperibol oxygen bomb calorimetry ISO 18125	Standard Reference Material 39j Benzoic Acid (NIST)
	Moisture	No pretreatment, 3 gram of pellet was used	Calibrated balance used	Modified ISO 18134-3 Gravimetry	-
DTI	Calorific Value	No pretreatment, 0.5 gram pellet was weighed and used	Specific heat capacity of the calorimeter is determined using benzoic acid reference material.	Isoperibol oxygen bomb calorimetry ISO 18125	Benzoic acid IKA C723, ID nr 32 430 00 EU index 607 705 – 00-8
	Moisture	No pretreatment, 3 gram of pellet was used	Calibrated thermometer and balance were used	Modified ISO 18134-3 Gravimetry (5 hours drying)	-
PTB	Calorific Value	No pretreatment, 0.5 gram pellet was used	Specific heat capacity of the calorimeter is determined using benzoic acid reference material. After nitrate and sulfate analysis of combustion remainings by ion chromatography following correction factors have been used: Q_N = 3.2 J/g, Q_S = 0.2 J/g	Isoperibol oxygen bomb calorimetry ISO 18125	UME CRM 1504 Benzoic acid
UME	Calorific Value	Pellet samples of 0.45-0.60 g were weighed on analytical balance (Mettler Toledo, model WXSS205, d=0.01 mg) and were dried in an oven at 105 °C for 4 hours. The dried pellets were placed in bottles and kept in the desiccators.	Specific heat capacity of the calorimeter is determined using benzoic acid reference material. After nitrate and sulfate analysis of combustion remainings by ion chromatography, following correction factors have been used: Q_N = 3.8 J/g, Q_S = 0.46 J/g	Isoperibol oxygen bomb calorimetry ISO 18125	UME CRM 1504 was used as certified reference material (benzoic acid) in instrument calibration

ANNEX 7A. Graphs for Characterization Study for Wood Pellet Powder

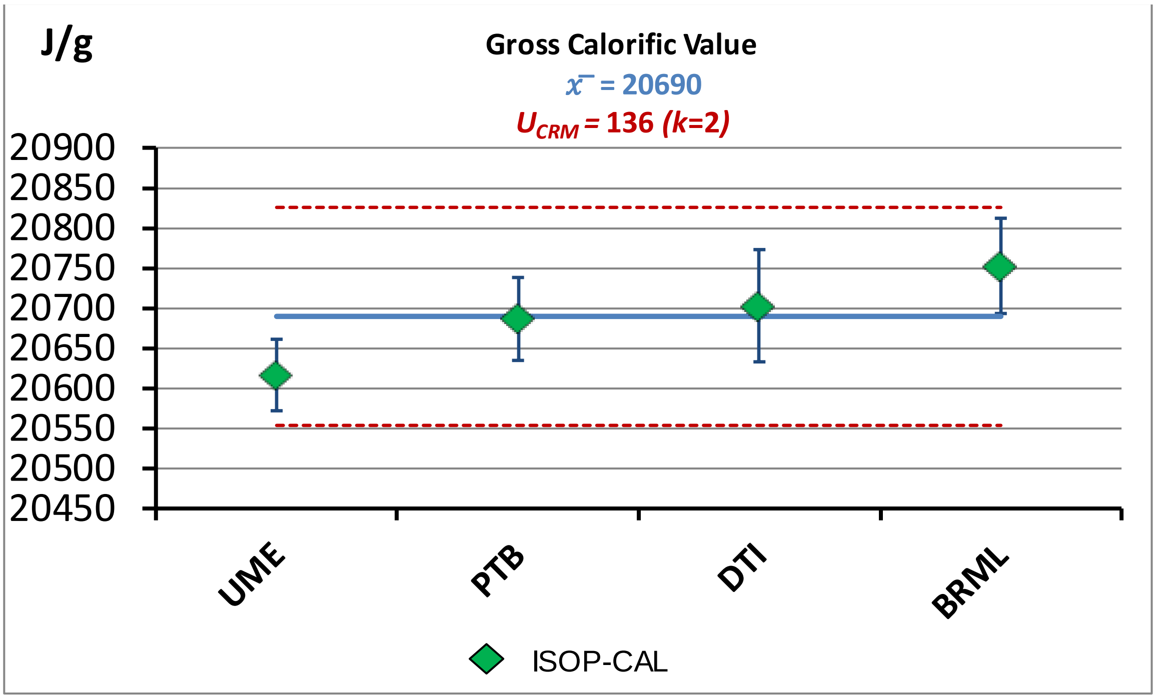


Figure A7A.1. Characterization Study Plot for Calorific Value of Wood Pellet Powder

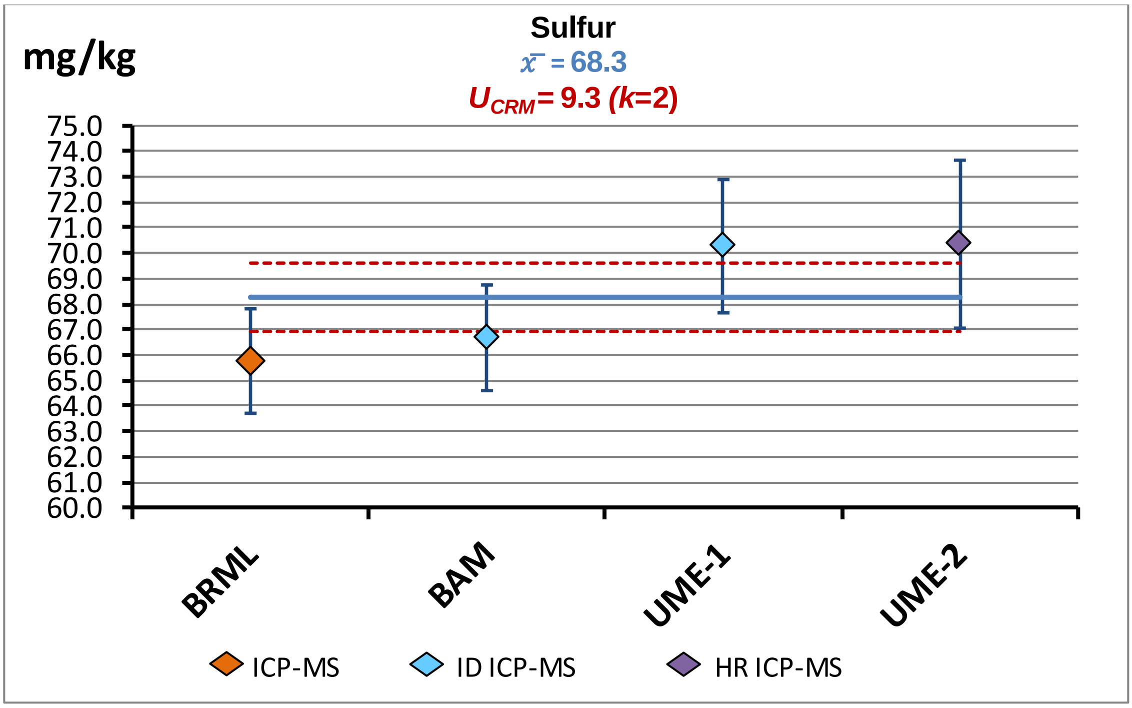


Figure A7A.2. Characterization Study Plot for Sulfur of Wood Pellet Powder

ANNEX 7B. Graphs for Characterization Study for Wood Pellet

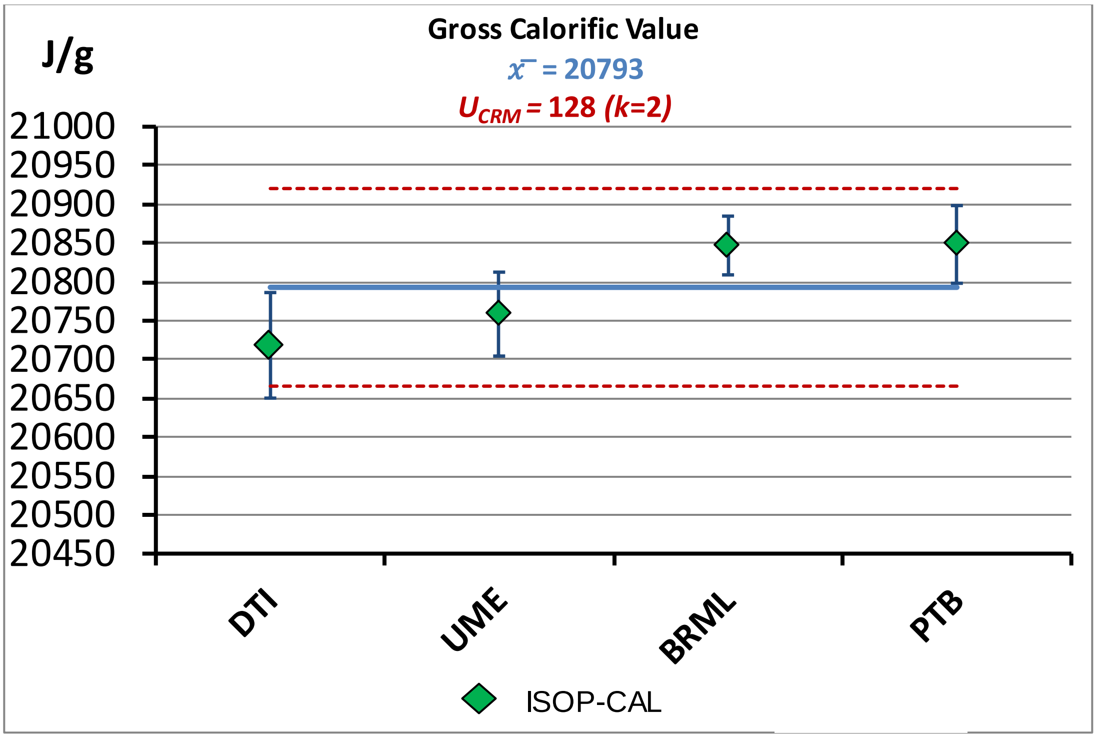


Figure A7B.1. Characterization Study Plot for Calorific Value of Wood Pellet

ANNEX 8. Additional Information on Wood Pellet Moisture and Water Content

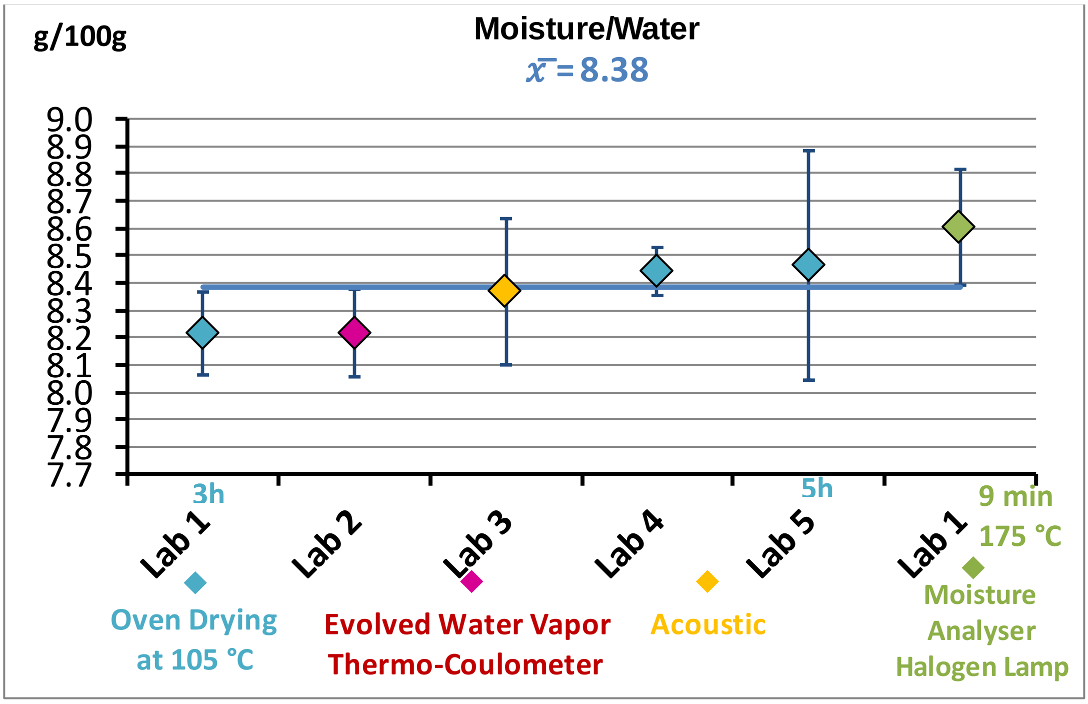


Figure A8.1 Plot for Moisture and Water content of wood pellet with different techniques