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ERM
European Reference Materials

CERTIFICATION REPORT

The certification of the gross calorific value and mass fractions of ash, C, H, N, S, Cl, major elements and trace elements in three coal materials: ERM®-EF411 (hard coal), ERM®-EF412 (brown coal) and ERM®-EF413 (furnace coke)

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The certification of the gross calorific value and mass fractions of ash, C, H, N, S, Cl, major elements and trace elements in three coal materials: ERM®-EF411 (hard coal), ERM®-EF412 (brown coal) and ERM®-EF413 (furnace coke)

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Disclaimer

Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the production of ERM-EF411, ERM-EF412 and ERM-EF413, three coal materials certified for proximates and trace elements. The materials have been produced following ISO Guide 34:2009 [1].

Industial hard coal, brown coal and furnace coke were obtained, dried, milled (ERM-EF411 and ERM-EF413) and filled into aluminium laminated sachets.

Between-unit homogeneity were quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006 [2]. Within-unit heterogeneity was quantified to determine the minimum sample intake.

The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.

Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [3] and include uncertainties related to possible heterogeneity and instability and to characterisation.

The materials are intended for quality control and assessment of method performance. As any reference material, they can be used for control charts or validation studies, as well. The CRMs are available in sachets containing 50 g of dried material. The minimum amount of sample to be used, depending on the analyte, varies from 30 mg to 1 g.

The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

The following certified values were assigned:

	ERM-EF411		ERM-EF412		ERM-EF413		Unit
	Value[2]	Uncert.[3]	Value[2]	Uncert.[3]	Value[2]	Uncert.[3]	
Gross calorific value[1]	29.0	0.4	26.02	0.22	29.5	0.4	MJ/kg
Net calorific value[1]	28.0	0.4	24.98	0.25	29.4	0.5	MJ/kg
Volatile matter[1]	38.1	1.0	50.1	0.7			g/100 g
Ash[1]	8.3	0.7	4.11	0.23			g/100 g
C[1]	71.4	1.0	66.2	0.7	87.8	1.9	g/100 g
H[1]	4.80	0.14	4.88	0.15			g/100 g
N[1]	1.43	0.10	0.74	0.06	1.10	0.07	g/100 g
S[1]	0.598	0.017	0.360	0.023	0.58	0.12	g/100 g
Cl	99	19					mg/kg
Ca			9.8	0.4	2.92	0.22	g/kg
Na			2.20	0.12	0.64	0.07	g/kg
K			229	18			mg/kg
Hg			0.070	0.011			mg/kg
Mn			48.6	1.9			mg/kg
Se	5.1	1.0	0.96	0.14	1.33	0.26	mg/kg
V			0.57	0.04			mg/kg
Zn					16.0	2.5	mg/kg

1) as determined by the procedures used

2) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified value and its uncertainty are traceable to the International System of Units (SI)."

3) The certified uncertainty is the expanded uncertainty with a coverage factor k = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

The following indicative values were assigned

Analyte	ERM-EF411		ERM-EF412		ERM-EF413		Unit
	Value[1]	Uncert.[2]	Value[1]	Uncert.[2]	Value[1]	Uncert.[2]	
Cl					0.35	0.13	g/kg
Cd			0.012	0.004			mg/kg
Co	3.5	0.8					mg/kg
Cu			0.68	0.22			mg/kg
Hg	0.079	0.015					mg/kg
Mg			3.73	0.16	1.23	0.19	g/kg
Pb			0.25	0.05	8.41	1.6	mg/kg
Sb	1.5	0.4	0.024	0.004			mg/kg
Tl	0.24	0.07					mg/kg
V	22	7					mg/kg
Zn	13	4	0.99	0.18			mg/kg

1) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The indicative value and its uncertainty are traceable to the International System of Units (SI).

2) The indicative uncertainty is the expanded uncertainty with a coverage factor k = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

The following information values were assigned

Analyte	ERM-EF411	ERM-EF412	ERM-EF413	Unit
Ash			10	g/100 g
S (ASTM D3177)	0.59	0.37	0.55	g/100 g
F	39	40	64	mg/kg
K			1.5	g/kg
Cu	7			mg/kg
Ni	15			mg/kg
Sn		0.1		mg/kg
Tl			0.15	mg/kg

1 Table of content

2 Glossary

AAS	Atomic absorption spectrometry
AES	Atomic emission spectrometry
ANOVA	Analysis of variance
ASTM international	ASTM international (formerly American Society for Testing and Materials)
b	Slope in the equation of linear regression $y = a + bx$
BCR®	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
CI	confidence interval
CRM	Certified reference material
CVAAS	Cold vapour atomic absorption spectrometry
CVAFS	Cold vapour atomic fluorescence spectrometry
DIN	Deutsches Institut fuer Normung
DMA	Direct Mercury Analyzer
ERM®	Trademark of European Reference Materials
EU	European Union
GCV	Gross calorific value
GFAAS	Graphite furnace atomic absorption spectrometry
GC-TCD	Gas chromatography with thermal conductivity detection
GUM	Guide to the Expression of Uncertainty in Measurements *[ISO/IEC Guide 98-3:2008]*
IC	Ion chromatography
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma-atomic emission spectrometry
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-SFMS	ICP-Sectorfield mass spectrometry
ID-TIMS	Isotope dilution thermal ionisation mass spectrometry
IEC	International Electrotechnical Commission
INAA	Instrumental neutron activation analysis
IRMM	Institute for Reference Materials and Measurements of the JRC
ISE	Ion selective electrode
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
k_0NAA	k_0-Neutron Activation Analysis
LOD	Limit of detection
LOQ	Limit of quantification
MS	Mass spectrometry
$MS_{between}$	Mean of squares between-unit from an ANOVA
MSDS	Material safety data sheet
MS_{within}	Mean of squares within-unit from an ANOVA
n	Number of replicates per unit
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
NCV	Net calorific value
NIST	National Institute of Standards and Technology (USA)
QC	Quality control
QCM	Quality control material
p	Number of accepted datasets in the characterisation study
rel	Index denoting relative figures (uncertainties etc.)
ret.	Retained

RM	Reference material
RSD	Relative standard deviation
r^2	Coefficient of determination of the linear regression
s	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added as appropriate
$s_{between}$	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added as appropriate
SI	International System of Units
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
t	Time
t_i	Time point for each replicate
TGA	Thermogravimmetryic analysis
$t_{\alpha, df}$	Critical *t*-value for a *t*-test, with a level of confidence of 1-α and df degrees of freedom
t_{sl}	Proposed shelf life
u	standard uncertainty
U	expanded uncertainty
u^*_{bb}	Standard uncertainty related to a maximum between-unit homogeneity that could be hidden by method repeatability; an additional index "rel" is added as appropriate
u_{bb}	Standard uncertainty related to a possible between-unit homogeneity; an additional index "rel" is added as appropriate
u_c	combined standard uncertainty; an additional index "rel" is added as appropriate
u_{cal}	Standard uncertainty of calibration
u_{char}	Standard uncertainty of the material characterisation; an additional index "rel" is added as appropriate
u_{CRM}	Combined standard uncertainty of the certified value; an additional index "rel" is added as appropriate
U_{CRM}	Expanded uncertainty of the certified value; an additional index "rel" is added as appropriate
u_{rec}	Standard uncertainty related to possible between-unit homogeneity modelled as rectangular distribution; an additional index "rel" is added as appropriate
u_{sts}	Standard uncertainty of the short-term stability
XRF	X-ray fluorescence spectrometry
α	significance level
ν_{smeas}	Degrees of freedom for the determination of the standard deviation s_{meas}
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}

3 Introduction

3.1 Background: need for the CRM

Conventional fuels are still the dominant energy source in the European Union. Moreover, burning of coal is a substantial source of toxic trace elements like mercury and plays an important role in the European mercury strategy. Therefore, measurement standards for fossil fuels can contribute to more resource efficiency and to a reduced introduction of these compounds into the environment. The measurements on the quality of fuels need to be comparable to protect the environment and to facilitate the free movements of these goods within the European Union, thus strengthening European competitiveness in the global economy.

For this reason, the Community Bureau of Reference (BCR) released a suite of certified reference materials named BCR-180, BCR-181 and BCR-182 in 1986 [4]. These materials are exhausted and need to be replaced.

3.2 Choice of the material

While the previous coal materials all consisted of hard coal with a similar content of volatile matter, it was decided to replace them with materials that cover a larger range of volatilie matter. Therefore, one hard coal, one brown coal and one coke were selected as raw materials. No particular emphasis was put on specific trace element levels, as the aim was to certify a material as similar to natural materials as possible.

Sampling, sample preparation and grinding are important steps in coal analysis and hence potentially important sources of error. For this purpose, the previous standards specified minimum sample intakes for dry mass determination of 2.5 kg [5]. This, however, is not feasible for a certified reference material. It was therefore decided to produce coarser materials than before, but with grain sizes small enough ensure that each 50 g sample would be representative for the whole batch.

3.3 Design of the project

After processing, homogeneity and stability testing, characterisation was based on intercomparison of expert laboratories. No results were to be excluded on statistical reasons alone. Such intercomparison requires clear definitions of the analytes. In coal analyses, analytes are commonly divided into minor and trace elements and proximates. Minor and trace elements are determined by instrumental methods or after complete digestion and are defined by their chemical nature alone. Proximates are generally operationally defined. To ensure comparability among laboratories, several standardisation organisations have developed standard methods for proximate analysis. The list below gives a short description of the methods considered for proximate analysis:

- **Gross calorific value (GCV)** is determined by measuring the heat produced by combustion of a sample in a bomb calorimeter. The heat capacity of the bomb calorimeter is tested by calibrating using the heat generated by benzoic acid. Differences consist in the setup: GCV can be measured at constant volume or at constant pressure. In the latter case, a part of the heat generated by combustion is used to expand the gas. ISO 1928 [6] and ASTM D5865 [7] prescribe the determination of GCV at constant volume. A closer look at the two standards indicates that the results should be equivalent. This expectation is confirmed by results in proficiency tests..
- **Net calorific value (NCV)** is calculated from the GCV applying a correction for the moisture and hydrogen content of the sample. These calculations are described in ISO 1928 and ASTM D5865, as well.
- **Volatile matter** is determined by heating the sample for a short time at a high temperature in a vessel with a closed lid. The closed lid prevents exaggerated

oxidation of the samples. Naturally, heating conditions and the vessel (shape and material) critically influence the result.
ISO 5071 [8] prescribes the application of two muffle furnaces. The sample is placed in a fused silica vessel with a lid and heated first for 7 minutes at 400 °C, followed by a second heating step of 7 minutes at 900 °C.
ISO 562 [9] prescribes the use of a fused silica vessel with lid, but restricts the heating to 7 minutes at 900 °C in one muffle furnace. The scope of the method is restricted to hard coal and coke, which contain less volatile matter than brown coal.
ASTM D3175 [10] prescribes the use of Pt crucibles with a lid. The sample is placed into a vertical tube furnace heated at 950 °C. The fast evaporating volatiles are burnt off and the total heating time is restricted to 7 minutes.
Due to the different crucible materials, different furnace setups and temperatures, values from the ASTM method and ISO methods are not comparable.

- The **ash content** is defined as the mass fraction of the residue after complete incineration of the sample.
  ISO 1171 [11] prescribes ashing of the sample at a temperature of 815 °C in air until constant mass is achieved.
  ASTM D3174 [12] prescribes a final ashing temperature of 700-750 °C for coals and 950 °C for coke.
  Due to this complete incineration, small deviations in the method parameters have less influence on the result and the results of the two methods are therefore in most cases equivalent.

- The **sulfur content** can be determined by various methods, each of them being based on a different quantification principle after combustion.
  ISO 351 [13], prescribes combustion in an oxygen stream at 1350 °C. The combustion gases are absorbed in a H_2O_2 solution and the resulting H_2SO_4 and HCl are titrated using Na_2BO_4. A correction for the Cl content is made.
  ISO 19579 [14] and ASTM D4239 [15] work according to the same principle. The sample is combusted in an oxygen stream at 1350 °C and the S mass fraction is determined by infrared (IR) absorption of the formed SO_2.
  ASTM D3177 [16] prescribes combustion in a bomb. The combustion gases are absorbed in water and the sulfate content is determined gravimetrically by precipitation as $BaSO_4$. This method was withdrawn in the meantime.
  While ISO 19579 and ASTM D4239 are leading to equivalent results, the results differ significantly from those obtained by ISO 351 and ASTM D3177.

- **Carbon, hydrogen and nitrogen** are quantified by analysis of the combustion gases.
  ISO 29541 [17] and ASTM D5373 [18], describe the instrumental method, in which the sample is burned in an oxygen atmosphere and the combustion products CO_2, H_2O and N_2 are determined by gas analysis procedures after calibration of the apparatus with, for example ethylene diamine tetra-acetic acid (EDTA).
  ISO 609 [19] describes very much the same approach: the samples are burnt at 1350 °C in a stream of oxygen and the amount of C and H are determined gravimetrically by absorption of H_2O and CO_2 in solutions of $Mg(ClO_4)_2$ and NaOH.
  ISO 333 [20] describes the semi-micro Kjeldahl method for the determination of N, in which the pulverised sample is boiled with sulphuric acid and a catalyst (a mixture of K_2SO_4, metallic Se and V_2O_5). The solution is made alkaline converting ammonium to ammonia, which is distilled, absorbed in boric acid and the amount of ammonia is determined by titration with sulphuric acid. These methods and their results are equivalent.

The goal of the project was to include all methods leading to equivalent results for analytes where several methods exist. In this way the applicability of the material to all of these methods can be demonstrated.

4 Participants

4.1 Project management and evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-RM)

4.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE

4.3 Homogeneity study

ALS Scandinavia AB, Luleå, SE
(measurements in the scope of ISO/IEC 17025 accreditation SWEDAC 1087)

GreenGas, Paskov, CZ
(measurements in the scope of ISO/IEC 17025 accreditation Czech Accreditation Institute 1091)

Nuon Power Generation NV, Utrecht, NL
(measurements in the scope of ISO/IEC 17025 accreditation RvA L465)

4.4 Stability study

ALS Scandinavia AB, Luleå, SE
(measurements in the scope of ISO/IEC 17025 accreditation SWEDAC 1087

GreenGas, Paskov, CZ
(measurements in the scope of ISO/IEC 17025 accreditation Czech Accreditation Institute 1091)

Nuon Power Generation NV, Utrecht, NL
(measurements in the scope of ISO/IEC 17025 accreditation RvA L465)

4.5 Characterisation

ALS Scandinavia AB, Luleå, SE
(measurements in the scope of ISO/IEC 17025 accreditation SWEDAC 1087)

ArcelorMittal Ostrava a.s., Hutní a chemické laboratore, Ostrava-Kuncice, CZ
(measurements under the scope of ISO/IEC 17025 accreditation Czech Accreditation Institute 464/2008)

ASCAL ENVIRONNEMENT, Forbach, FR
(measurements under the scope of ISO/IEC 17025 accreditation COFRAC 1-1589)

Australian Nuclear Science and Technology Organisation (ANSTO), Kirrawee DC , AU

Czech Coal Services a.s., Most, CZ
(measurements under the scope of ISO/IEC 17025 accreditation Czech Accreditation Institute 624/2009)

Energie AG Oberösterreich Kraftwerke GmbH, St. Pantaleon, AT

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Institut Jožef Stefan (IJS), Department of Environmental Sciences, Ljubljana, SI
(measurements under the scope of ISO/IEC 17025 accreditation Slovenska Akreditacija LP-090)

Intertek Testing Services Switzerland, Schlieren, CH

Mitteldeutsche Braunkohlengesellschaft mbH (MIBRAG), Zentrallabor, Zeitz, DE
(measurements under the scope of ISO/IEC 17025 accreditation DGA-PL1161.00)

Nuon Power Generation NV, Utrecht, NL
measurements in the scope of ISO/IEC 17025 accreditation RvA L465

PEGOP - Energia Eléctrica, S.A., Laboratório Químico, Pego, PT
(measurements under the scope of ISO/IEC 17025 accreditation IPAC L0223)

SGS Nederland B.V., Vlissingen, NL
(measurements under the scope of ISO/IEC 17025 accreditation BELAC 005-TEST)

SGS Latvija Ltd, Riga, LV
(measurements under the scope of ISO/IEC 17025 accreditation LATAK T-320-04-2006-A)

Solvias AG, Kaiseragust, CH

Studiecentrum voor Kernenergie (SCK-CEN), Mol, BE
(measurements in the scope of ISO/IEC 17025 accreditation BELAC 015-TEST)

Technische Universiteit Delft, Reactor Institute Delft, Delft, NL
(measurements under the scope of ISO/IEC 17025 accreditation RvA L049)

Verbund Umwelttechnik GmbH, Standort FHKW Mellach, Wildon, AT

Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, BE

Voestalpine Stahl GmbH, B4P4 - Umwelt- und Betriebsanalytik, Linz, AT
(measurements under the scope of ISO/IEC 17025 accreditation BMFWJ 20)

5 Material processing and process control

5.1 ERM-EF411, hard coal

Hard coal (120 kg) from the LaLoma open pit mine, Colombia, was provided by RWE Power AG, Cologne, DE. The material consisted of coarse particles of up to 1 cm (see Figure 1). Based on the content of volatile matter (42 %), the coal is classified as gas coal/flame coal. As-delivered moisture content was 12 % (determined by oven drying at 105 °C).

Figure 1: Raw material for ERM-EF411

The material was sieved with a 2.5 mm sieve and the fraction < 2.5 mm (81 kg) was processed further. As the lid of the original containers showed condensation, it was decided to dry the material before the first milling step. The material was therefore dried at 50 °C for 48 h, bringing the total moisture content down to approximately 2 %. The dried material was milled to a particle size of < 3 mm to break up agglomerates, dried again to a moisture

content of about 2.7 % and moved into a cone mixer. The mixer was flushed with nitrogen (5 L/min) for two days before the material was filled into aluminium-laminated sachets, each containing 50 g dried coal.

Because of the drying at 50 °C, the material will not lose or even may take up moisture in the first drying step at 37 °C, applied for the determination of hygroscopic moisture.

5.2 ERM-EF412, brown coal

Fluidized-bed lignite powder (120 kg) were provided by RWE Power AG, Cologne, DE. The brown coal originates from the Hambach open pit mine in the Rhineland area. The material was delivered as powder (see Figure 2). As-delivered moisture content was 11.5 % (determined by oven drying at 105 °C).

Figure 2: Raw material for ERM-EF412

At IRMM, the material was dried for 7 h at 50 °C. Subsequently, the material was transferred into a cone mixer and was mixed for 17 days under a stream of dry nitrogen (flow 10 L/min) at a temperature of 37 °C. After 17 days, the water content stabilised at 69 g/kg and filling started. 2000 aluminium-laminated sachets containing 50 g each were filled while maintaining the nitrogen flow. The sachets were put into a second plastic pouch to further decrease potential oxygen uptake.

Because of the drying at 50 °C, the material will not lose or even may take up moisture in the first drying step at 37 °C, applied for the determination of hygroscopic moisture.

5.3 ERM-EF413, furnace coke

Furnace coke (200 kg) were provided by the Voestalpine Stahl GmbH, Linz (AT) as lumps of about 10 cm size ready for use in steel production (see Figure 3). After manual crushing of the biggest pieces, smaller particles were produced using a jaw crusher. The crushed material was further milled using a heavy duty mill with a 4 mm sieve insert. The ground material was placed into a cone mixture and filled into aluminium laminated plastic sachets. Mixing heated the material up to 30 °C, leading to condensation of water in the mixer.

Figure 3: Raw material for ERM-EF413

6 Assessment of homogeneity

A key requirement for any reference material is the equivalence between the various units. In this respect, it is not relevant whether the variation between units is significant compared to the analytical variation, but whether this variation is significant to the certified uncertainty. Consequently, ISO Guide 34 requires RM producers to quantify the between-unit variation. This aspect is covered in between-unit homogeneity studies.

The within-unit homogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an aliquot that is representative for the whole unit. Quantification of within-unit homogeneity is therefore necessary to determine the minimum sample intake.

6.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that - within the stated uncertainty- the certified values of the CRM are valid for all units of the material. The number of selected units should correspond to approximately the cubic root of the total number of the produced units. Homogeneity of the three materials was assessed from two series of experiments: the initial homogeneity study and the long-term study.

15 units were selected for the initial between-unit homogeneity test using a random stratified sampling scheme covering the whole batch. For this, each batch was divided into 15 groups (with similar number of units) and one unit was randomly selected from each group. From each unit, three independent samples were taken and analysed.

As the repeatabilities of results for trace metals of this initial homogeneity study for ERM-EF411 and ERM-EF413 were very poor, data from the long-term stability study were used, as well. This was possible as no trend over time was observed, hence the samples over all storage times are equivalent. This study comprised 20 samples from each material, also taken using a random stratified sampling scheme. In this case, two replicate analyses were performed on each unit. As the stability study was limited to those elements that had shown sufficient homogeneity in the initial homogeneity study, this second assessment could not be performed for all elements.

The following methods were used:

- Trace metals: Samples were digested using a mixture of HNO_3 and HF. Element concentrations in the digests were determined by ICP-SFMS or ICP-AES as described in the literature [21]
- Proximates: ISO methods were used for GCV (ISO 1928), volatile matter (ISO 562), ash (ISO 562), C/H/N (ISO/TS 12902) and S (ISO 351). National standard methods were used for moisture and hygroscopic moisture (CSN 443177) and Cl (DIN 38414-S17)

The measurements were performed under repeatability conditions and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The results were corrected for the water content determined in each unit (see Section 6.2). The results are shown as graphs in Annex A.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. Trends in the analytical sequence that were significant on a 99 % confidence level were visible for some analytes, pointing at an instability of the analytical system. As the analytical sequence and the unit numbers were not correlated, correction for these trends can improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities. Therefore, trends in the analytical sequence were corrected if the trend was significant on at least a 99 % confidence level as shown below.

$$corrected\ result = measured\ result - b \cdot i$$

b = slope of the linear regression

i = position of the result in the analytical sequence

The trend-corrected dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. Some outlying individual results and outlying unit means were detected. Since no technical reason for the outliers could be found, all outlier data were retained for statistical analysis.

Quantification of between-unit homogeneity was performed by an analysis of variance (ANOVA), which separates the between-unit variation (s_{bb}) from the within-unit variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative for the whole unit.

Evaluation by ANOVA requires unit means which follow at least an unimodal distribution and results for each unit that follow unimodal distributions with approximately the same standard deviations. Distribution of the unit means was tested using histograms and normal probability plots. Too few data are available for each unit to make a clear statement of the distribution of individual results. Therefore, it was checked whether or not the individual data follow a unimodal distribution using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not grossly affect the estimate of between-unit standard deviations. The results of all statistical evaluations are given in Tables 1 through Table 3.

Table 1: Results of the statistical evaluation of the homogeneity study for ERM-EF411 (hard coal). Percentage figures in the columns "trend" give the significance level of the slope. Trends in the filling sequence, outliers and distributions were evaluated after correcting for trends in the analytical sequence significant on a 99 % confidence level

Method/Analyte	Trends		Outliers		Distribution	
	Anal. seq.	Filling sequence	Indiv. results	Unit means	Individual results	Unit means
GCV	no	95 %	no	no	unimodal	unimodal
Vol. matter (ISO 562/5071)	no	no	no	no	normal	normal
Ash (ISO 1171/ASTM D3174)	no	99 %	no	no	normal	normal
C	no	no	no	no	unimodal	unimodal
H	no	no	no	no	normal	normal
N	no	no	no	yes	normal	normal
S (ISO 19579/ASTM D4239)	99 %	no	no	no	normal	normal
Cl	no	no	no	no	normal	normal
Ca	no	no	yes	yes	not normal	skewed
Mg	no	no	yes	yes	not normal	skewed
Na	no	no	yes	yes	not normal	skewed
K	95 %	no	no	no	normal	normal
As	no	no	yes	yes	not normal	skewed
Cd	no	no	yes	yes	skewed	skewed
Co	no	no	yes	no	skewed	skewed
Cr	no	no	no	no	unimodal	normal
Cu	no	no	no	no	unimodal	normal
Hg	no	no	yes	no	unimodal	normal
Hg (stability)	no	no	no	yes	normal	unimodal
Mn	no	no	yes	yes	not normal	not normal
Ni	no	no	no	no	normal	normal
Pb	no	no	yes	no	unimodal	normal
Pb (stability)	no	no	yes	yes	unimodal	normal
Sb	no	no	no	no	unimodal	normal
Sb (stability)	no	no	yes	yes	unimodal	skewed
Se	no	no	no	no	unimodal	normal
Sn	no	no	no	no	normal	normal
Sn (stability)	no	no	no	no	normal	normal
Tl	no	no	yes	no	unimodal	normal
V	no	no	no	no	normal	normal
Zn	no	no	no	no	normal	normal

Table 2: Results of the statistical evaluation of the homogeneity study for ERM-EF412 (brown coal). Percentage figures in the columns "trend" give the significance level of the slope. Trends in the filling sequence, outliers and distributions were evaluated after correcting for trends in the analytical sequence significant on a 99 % confidence level

Method/Analyte	Trends		Outliers		Distribution	
	Anal. seq.	Filling sequence	Indiv. results	Unit means	Individual results	Unit means
GCV	no	no	no	no	normal	normal
Vol. matter (ISO 562/5071)	no	no	no	no	normal	normal
Ash (ISO 1171/ASTM D3174)	99 %	no	no	no	normal	normal
C	no	no	no	no	unimodal	normal
H	no	no	no	no	normal	normal
N	no	no	no	no	normal	normal
S (ISO 19579/ASTM D4239)	no	no	yes	no	normal	normal
Cl	no	no	no	no	normal	normal
Ca	no	no	no	no	normal	normal
Mg	99 %	no	no	no	normal	normal
Na	99 %	no	no	no	normal	normal
K	99 %	no	no	no	normal	unimodal
As	95 %	no	no	no	normal	normal
Cd	no	no	yes	no	unimodal	normal
Co	no	no	no	no	normal	normal
Cr	no	95 %	no	no	normal	normal
Cu	no	no	yes	no	unimodal	normal
Hg	95 %	no	no	no	unimodal	unimodal
Mn	no	no	no	no	normal	normal
Ni	no	no	no	no	unimodal	normal
Pb	no	no	yes	no	unimodal	unimodal
Sb	99 %	no	yes	no	normal	normal
Se	no	no	no	no	normal	normal
Sn	no	no	yes	no	normal	normal
Tl	no	no	yes	yes	not normal	not normal
V	95 %	no	no	no	normal	normal
Zn	no	no	no	no	normal	normal

Table 3: Results of the statistical evaluation of the homogeneity study for ERM-EF413 (furnace coke). Percentage figures in the columns "trend" give the significance level of the slope. *Trends in the filling sequence, outliers and distributions were evaluated after correcting for trends in the analytical sequence significant on a 99 % confidence level*

Method/Analyte	Trends		Outliers		Distribution	
	Anal. seq.	Filling sequence	Indiv. results	Unit means	Individual results	Unit means
GCV	no	no	no	no	normal	normal
Vol. matter (ISO 562/5071)	no	no	no	no	normal	unimodal
Ash (ISO 1171/ASTM D3174)	no	no	no	no	normal	normal
C	95%	no	no	no	normal	normal
H	no	no	no	no	normal	normal
N	no	no	no	no	normal	normal
S (ISO 19579/ASTM D4239)	no	no	no	no	normal	normal
Cl	no	no	no	no	normal	normal
Ca	no	no	no	no	normal	normal
Ca (stability)	no	no	no	no	normal	normal
Mg	no	no	yes	no	normal	normal
Mg (stability)	no	no	no	no	bimodal	bimodal
Na	no	no	no	no	normal	normal
Na (stability)	99 %	no	no	no	normal	normal
K	no	no	yes	no	unimodal	unimodal
K (stability)	no	no	no	no	normal	normal
As	no	no	yes	yes	unimodal	unimodal
As (stability)	no	no	no	no	normal	normal
Cd	no	no	no	no	normal	normal
Cd (stability)	no	no	no	no	normal	normal
Co	95 %	no	no	no	unimodal	normal
Co (stability)	no	no	yes	no	normal	normal
Cr	no	no	yes	yes	not normal	not normal
Cu	no	no	no	no	normal	normal
Cu (stability)	no	no	no	no	normal	normal
Hg	95 %	no	no	no	normal	normal
Hg (stability)	no	no	no	no	unimodal	normal
Mn	no	no	no	no	normal	normal
Mn (stability)	no	no	no	no	normal	bimodal
Ni	no	no	yes	yes	not normal	not normal
Pb	95 %	no	no	no	normal	normal
Pb (stability)	no	no	no	no	normal	normal
Sb	95 %	no	yes	yes	unimodal	unimodal
Se	no	no	yes	no	unimodal	unimodal
Se (stability)	no	no	no	no	normal	normal
Sn	no	no	no	no	normal	normal
Sn (stability)	no	no	yes	yes	unimodal	unimodal
Tl	95 %	no	no	no	normal	bimodal
Tl (stability)	99 %	no	yes	no	unimodal	normal
V	no	no	no	no	unimodal	normal
V (stability)	no	no	no	no	normal	normal
Zn	no	no	no	no	normal	normal
Zn (stability)	no	no	no	no	normal	normal

An in-depth analysis of the data of the initial homogeneity study showed that the mass fractions of Cr, Co and Ni in ERM-EF411 and ERM-EF413 are positively correlated. The

reason for this correlation is most likely contamination from the stainless steel equipment used for crushing and milling of ERM-EF411 and ERM-EF413 processing. A second correlation is visible for silicate particles. This correlation is absent for ERM-EF412, which was delivered to IRMM as powder.

For ERM-EF411, units number 381, 521 and 1378 were outliers for Ca, Mg and Na. All three replicate analyses of these units were consistent, demonstrating real inhomogeneity. Units number 258 and 1310 were outliers for As. These outlying means were caused by one outlying replicate analysis. Removal of this replicate would have brought the unit mean in line with the other units. However, the results were retained as there was no technical reason for exclusion.
The results of unit 787 was an outlier for Cd, as were the results for units number 1918, 521 and 381 for Mn.
Results for unit 1883 from the stability study revealed outliers for Hg, Pb and Sb, as were the results of unit number 2 for Sb and Pb and number 593 for Sb. The consistency of the results across the different replicates and elements indicates real inhomogeneity, most likely due to small "nuggets" of element-rich particles.
Unit number 1995 was flagged as outlier on a 99 % confidence level for N., but the difference of the outlier and the population mean was much smaller (5 % above the average)than it was the case for the elements. Also here the data from the stability study were checked and no outlier was found, demonstrating that the material is rather homogeneous for N.

ERM-EF412 was homogeneous, with only Tl having three outlying unit averages (units number 306, 772 and 1257). All of these three outliers were caused by one replicate that was about a factor 5 above the other results. Based on these results, the material was deemed to heterogeneous for Tl.

For ERM-EF413, all results of unit 743 were outliers for Cr and Ni. The third replicate of unit 606 was flagged as outlier for As and Sb, causing the whole unit average to become an outlier. The data from the stability study flagged both replicates of unit 95 as outlier for Sn and two individual replicates of the stability study were flagged as 99 % outliers for Tl (results about 10 % above the other results). These studies therefore show that the material is not sufficiently homogeneous for Cr, Ni, As, Sb and Sn.

Between-unit inhomogeneity was quantified using one-way analysis of variance (ANOVA). Relative method repeatability ($s_{wb,rel}$), relative between–unit standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{\bar{y}}}$$

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{\bar{y}}}$$

MS_{within} mean square within a unit from an ANOVA

$MS_{between}$: mean squares between-unit from an ANOVA

$\bar{\bar{y}}$ average of all results of the homogeneity study

n: average number of replicates per unit

$v_{MSwithin}$: degrees of freedom of MS_{within}

One has to bear in mind that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups (MS_{within}), resulting in negative arguments under the square root used for the estimation of the between-unit

variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum heterogeneity that could be hidden by method repeatability, was calculated as described in the literature. [22]. u^*_{bb} is comparable to the limit of detection of an analytical method, yielding the maximum heterogeneity that might be undetected by the given study setup.

$$u^*_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{v_{MSwithin}}}}{\bar{y}}$$

When a trend in the filling sequence was significant at least at 99 % confidence level or in case of the bimodal distributions for Mg and Mn for ERM-EF413, the uncertainty was assessed in a different way. Here, an uncertainty using a rectangular distribution between the highest and lowest unit mean was estimated ($u_{rec,rel}$). The uncertainty in those cases where there was a significant trend in the filling sequence is calculated as

$$u_{rec,rel} = \frac{\left|highest\ result - lowest\ result\right|}{2 \cdot \sqrt{3} \cdot median_y}$$

The same approach was used for estimation of uncertainties for those parameters that showed outlying mean values. The results of the evaluation of the between-unit variation are summarised in Table 4 to Table 6.

Table 4: Results of the homogeneity study of ERM-EF411; n.c.: cannot be calculated as $MS_{between} < MS_{within}$.

Analyte	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rec,\ rel}$ [%]
GCV	0.16	0.47	0.05	
Vol. matter (ISO 562/5071)	0.38	1.20	0.11	
Ash (ISO 1171/ASTM D3174)	0.51	filling trend		3.34
C	0.177	0.366	0.052	
H	0.402	0.693	0.118	
N	1.54	1.37	0.45	1.86
S(ISO 19579/ASTM D4239)	1.096	0.962	0.322	
Cl	20.8	6.53	6.23	
Ca	33.3	not applicable - outliers		34.8
Mg	48.2	not applicable - outliers		51.9
Na	17.0	not applicable - outliers		19.5
K	24.0	16.1	7.0	
As	112	not applicable - outliers		108.1
Cd	26.3	not applicable - outliers		27.6
Co	23.5	9.6	6.9	
Cr	22.1	22.6	6.5	
Cu	20.5	9.6	6.0	
Hg	40.6	n.c.	11.9	
Hg (stability)	6.55	not applicable - outliers		6.2
Mn	45.2	not applicable - outliers		42.5
Ni	18.4	15.3	5.4	
Pb	20.6	10.7	6.1	
Pb (stability)	3.31	not applicable - outliers		26.4
Sb	23.3	4.3	6.8	
Sb (stability)	2.60	not applicable - outliers		9.4
Se	10.7	n.c.	3.1	
Sn	15.5	10.2	4.5	
Sn (stability)	7.3	3.2	2.9	
Tl	43.2	n.c.	12.7	
V	18.3	11.6	5.4	
Zn	13.9	12.4	4.1	

The results of the statistical evaluations clearly show the improved repeatability of the element analyses coming from the stability study. One potential reason for this improvement could be that the need to grind the complete sample before taking analytical subsamples was emphasised stronger than in the homogeneity study.

The data show allowed reliable assessment of homogeneity of ERM-EF411 for GCV, volatile matter, ash, C, H, N, S, Cl, Co, Cu, Hg, Sb, Se, Sn, Tl, V and Zn. Uncertainties, including those that would include the outliers detected in the studies were deemed too large for value assignment for Ca, Mg, K, Na, As, Cd, Mn and Pb. Hg and Sb showed only one outlier in all of the studies which, in addition did not differ too much from the main population, so certification was envisaged.

Table 5: Results of the homogeneity study of ERM-EF412; n.c.: cannot be calculated as $MS_{between} < MS_{within}$

Analyte	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rec,\ rel}$ [%]
GCV	0.137	0.357	0.040	
Vol. matter (ISO 562/5071)	0.577	0.473	0.169	
Ash (ISO 1171/ASTM D3174)	1.630	n.c.	0.478	
C	0.194	0.132	0.057	
H	0.643	0.436	0.189	
N	1.96	1.21	0.57	
S (ISO 19579/ASTM D4239)	4.83	n.c.	1.42	
Cl	20.0	10.4	5.9	
Ca	2.26	n.c.	0.66	
Mg	2.45	n.c.	0.72	
Na	2.37	n.c.	0.70	
K	3.51	0.98	1.03	
As	11.0	n.c.	3.2	
Cd	21.8	3.8	6.4	
Co	3.70	n.c.	1.10	
Cr	4.31	filling trend		2.29
Cu	4.53	n.c.	1.33	
Hg	13.3	2.7	3.9	
Mn	3.27	n.c.	0.96	
Ni	3.94	2.50	1.16	
Pb	17.6	n.c.	5.2	
Sb	7.46	2.05	2.19	
Se	8.54	n.c.	2.51	
Sn	4.58	1.17	1.34	
Tl	77.8	not applicable - outliers		45.3
V	4.54	n.c.	1.33	
Zn	17.3	2.2	5.1	

The data show sufficient homogeneity of ERM-EF412 for all parameters except Tl.

Table 6: Results of the homogeneity study of ERM-EF413; n.c.: cannot be calculated as $MS_{between} < MS_{within}$

Analyte	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{rec,\ rel}$ [%]
GCV	0.106	0.389	0.031	
Vol. matter (ISO 562/5071)	6.5	8.4	1.9	
Ash (ISO 1171/ASTM D3174)	0.43	0.47	0.13	
C	0.196	0.075	0.058	
H	4.25	2.36	1.25	
N	1.614	n.c.	0.473	
S (ISO 19579/ASTM D4239)	1.565	n.c.	0.459	
Cl	17.1	14.3	5.0	
Ca	12.5	4.9	3.7	
Ca (stability)	2.7	2.3	1.1	
Mg	16.6	7.0	4.9	
Mg (stability)	5.5	bimodal		6.0
Na	14.5	6.4	4.3	
Na (stability)	4.6	n.c.	1.8	
K	20.1	n.c.	5.9	
K (stability)	6.7	n.c.	2.7	
As	43.3	not applicable - outliers		33.8
As (stability)	6.2	6.7	2.8	
Cd	27.4	n.c.	8.0	
Cd (stability)	13.7	13.4	5.5	
Co	21.5	6.7	6.3	
Co (stability)	3.9	2.0	1.5	
Cr	24.7	not applicable - outliers		36.7
Cu	15.6	7.8	4.6	
Cu (stability)	5.4	9.7	2.1	
Hg	22.1	n.c.	6.5	
Hg (stability)	45.0	n.c.	17.9	
Mn	19.8	7.3	5.8	
Mn (stability)	4.7	bimodal		6.7
Ni	26.7	not applicable - outliers		42
Pb	29.1	n.c.	8.7	
Pb (stability)	7.7	4.2	3.1	
Sb	44.6	not applicable - outliers		31.4
Se	12.3	10.1	3.6	
Se (stability)	4.9	3.9	1.8	
Sn	18.3	5.5	5.4	
Sn (stability)	11.6	not applicable - outliers		15.1
Tl	16.7	3.5	4.9	
Tl (stability)	3.5	1.9	1.4	
V	16.9	9.8	5.0	
V (stability)	6.6	n.c.	2.6	
Zn	27.4	5.1	8.1	
Zn (stability)	4.7	5.5	1.9	

As is the case for EF411, repeatabilities from the stability study are much better than those from the homogeneity study for ERM-EF413.

The homogeneity assessment demonstrated that ERM-EF413 is sufficiently homogeneous for GCV, ash, volatile matter ash C, H, N, S, Cl, Ca, Mg, Na, K, Cd, Co, Cu, Hg, Mn, Pn, Se,

Tl, V and Zn. Uncertainties that would include the detected outliers were deemed too large for value assignment for As, Cr, Ni, Sb and Sn

. As for setting the uncertainties, the following approach was chosen:

- As $u^*_{bb,rel}$ sets the limits for the detection power of the study, the larger value of $s_{bb,rel}$ and $u^*_{bb,rel}$ is adopted as uncertainty contribution to account for potential heterogeneity hidden by the intrinsic variation of the method.
- $u_{rec,\ rel}$ is used for analytes with a filling trend, outliers or bimodal distributions.
- Where results from both the initial homogeneity study and the data from the homogeneity assessment from the long-term study are available, the data from the study with the better repeatability are used.

The uncertainties of homogeneity ($u_{bb,rel}$) assigned are listed in Table 7.

Table 7: Uncertainties of inhomogeneity assigned to the analytes of the three materials.

Analyte	ERM-EF411 $u_{bb,\ rel}$ [%]	ERM-EF412 $u_{bb,\ rel}$ [%]	ERM-EF413 $u_{bb,\ rel}$ [%]
GCV	0.47	0.36	0.39
Vol. matter (ISO 562/ISO 5071)	1.20	0.47	8.4
Ash (ISO 1171/ASTM D3174)	3.3	0.48	0.47
C	0.37	0.13	0.075
H	0.69	0.44	2.4
N	1.86	1.21	0.47
S ISO 19579/ASTM D4239)	0.96	1.42	0.46
Cl	6.53	10.4	14.3
Ca	34.8	0.66	2.3
Mg	51.9	0.72	6.0
Na	19.5	0.70	1.84
K	16.1	1.03	2.7
As	108.1	3.22	33.8
Cd	27.6	6.40	13.4
Co	9.6	1.10	2.0
Cr	22.6	2.3	36.7
Cu	9.6	1.33	9.7
Hg	6.2	3.9	6.5
Mn	42.5	0.96	6.7
Ni	15.3	2.5	42
Pb	26.4	5.2	4.2
Sb	9.4	2.2	31.4
Se	3.1	2.5	3.9
Sn	3.2	1.34	15.1
Tl	12.7	45.3	1.87
V	11.6	1.33	2.6
Zn	12.4	5.1	5.5

The high uncertainties or presence of outliers made it clear that not all parameters tested for homogeneity could be certified. The subsequent studies (stability and characterisation) were therefore limited to those parameters that showed sufficient homogeneity in order to minimise cost.

6.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. Due to the intrinsic heterogeneity, individual aliquots of a material will not contain the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus can be used in an analysis. Sample sizes equal to or above the minimum sample intake guarantee the certified value within its stated uncertainty.

The minimum sample intake for elements was determined from the results of the characterisation study, using the method information supplied by the participants. The smallest sample intake that still yielded results with acceptable accuracy to be included in the respective studies was taken as minimum sample intake. It must be borne in mind that these amounts are only valid after the complete contents of a unit have been ground. Using the data from Annex D, the following minimum sample intakes after grinding of a complete unit are derived:

Hg: 30 mg

All other minor and trace elements: 200 mg

The minimum sample intake for operationally defined analytes is specified in the respective standards as:

GCV according to ISO 1928 and ASTM D5865: 1 g

Volatile matter according to ISO 562 or ISO 5071-1: 1 g

Ash according to ISO 1171/ASTM D3174: 1 g

S according to ISO 19579/ASTM D4239: 0.2 g

C, H, N: 70 mg

7 Stability

Time, temperature and radiation were regarded as the most relevant influences on stability of the materials. The influence of ultraviolet or visible radiation was minimised by the choice of the containment, which eliminates most of the incoming light. In addition, materials are stored and dispatched in the dark, thus practically eliminating the possibility of radiative degradation. Therefore, only the influences of time and temperature needed to be investigated.

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C could be reached and stability against these conditions must be demonstrated if transport at ambient temperature will be applied.

The stability studies were carried out using an isochronous design [23]. In that approach, samples are stored for a certain time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible ("reference conditions"), effectively "freezing" the degradation status of the materials. At the end of the isochronous storage, the samples are analysed simultaneously under repeatability conditions. Analysis of the material (after various exposure times and temperatures) under repeatability conditions greatly improves the sensitivity of the stability tests.

Stability studies were limited to those analytes that had shown sufficient homogeneity in the homogeneity study.

7.1 Short-term stability study

Samples were stored at 60 °C for 0, 1, 2 and 4 weeks for the short-term stability study. The reference temperature was set to +18 °C. Two samples per storage time were selected using a random stratified sampling scheme. From each unit, two subsamples were measured fpr proximates and four subsamples for elements using the same methods as described for the homogeneity study. The measurements were performed under repeatability conditions and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time.

The results were screened for outliers using the single and double Grubbs test on 99 % confidence levels. Some outlying individual results were found (see Table 8 to Table 10). Tentative removal of the outliers confirmed that their presence or absence did not change the statistical significance of the regression line. As no technical reason for the outliers could be found, all data were retained for statistical analysis.

Furthermore, the data were plotted against storage time and regression lines were calculated. The slope of the regression lines was tested for statistical significance (loss/increase due to shipping conditions).

The results of the measurements are shown in Annex B. The results of the statistical evaluation of the short-term stability are summarised in Table 8 to Table 10.

The material can be dispatched without further precautions under ambient conditions.

7.2 Long-term stability study

Samples were stored at 18 °C for 0, 4, 8, 12 and 20 months for the long-term stability study. The reference temperature was set to -20 °C. Two units per storage time were selected using a random stratified sampling scheme. From each unit, two subsamples were measured by digestion/ICP-AES or digestion/ ICP-SFMS as described for the homogeneity study for trace metals and by ISO 589 (moisture), ISO 1171 (ash), ISO 562 (volatile matter), ISO 1928 (calorific value), GC-TCD (C, H, N) and XRF (S, Cl). The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time.

The obtained data were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test.

Furthermore, the data were plotted against storage time and regression lines calculated. The slope of the regression lines was then tested for statistical significance (loss/increase due to storage conditions

The results of the measurements are shown in Annex C. The results of the statistical evaluation of the long-term stability study are summarised in Table 8 to Table 10.

Some elements not included in the original test were tested after the characterisation study: Two samples from reference stock and two samples from normal stock were tested in 4 replicates each and the results were compared using a t-test.

Table 8: Results of the statistical evaluation of the stability tests of ERM-EF411. For the short-term study of Cu and Sn only two subsamples per unit were analysed. Data marked with an asterisk come from the additional test after characterisation (t=44 months)

Analyte	Short-term study (60 °C)		Long-term study (18 °C)	
	Individual outlying results	Significance of the trend on a 99% confidence level	Individual outlying results	Significance of the trend on a 99% confidence level
GCV	no	no	no	no
Vol. matter (ISO 562)	no	no	no	no
Ash (ISO 1171)	no	no	no	no
C	no	no	no	no
H	no	no	2 (retained)	no
N	no	no	no	no
S	no	no	no	no
Cl	result at LOD		no	no
Co	no	no	no*	no*
Cu	yes	no	no data	
Hg	no	yes	no*	no*
Ni	no	no	no data	
Sb	no	no	no*	no*
Se	no	no	2 (retained)	no
Sn	no	no	no data	
Tl	no	yes	no*	no*
V	no	no	no*	no*
Zn	no	yes	no*	no*

Hg, Tl and Zn showed statistically significant trends in the short-term study. However, the extent of the trend was small enough to ensure negligible degradation during transport to the customer. It was therefore decided to include any potential trend from degradation in the assessment of uncertainties.

Table 9: Results of the statistical evaluation of the stability tests of ERM-EF412

Analyte	Short-term study (60 °C)		Long-term study (18 °C)	
	Individual outlying results	Significance of the trend on a 99% confidence level	Individual outlying results	Significance of the trend on a 99% confidence level
GCV	no	no	no	no
Vol. matter (ISO 562)	no	no	no	no
Ash (ISO 1171)	no	no	no	no
C	no	no	no	no
H	no	no	no	no
N	no	no	no	no
S	no	no	no	no
Cl	no	no	no	no
Ca	no	no	no	no
Mg	no	no	no	no
Na	1 (retained)	no	1 (retained)	no
K	no	no	no	no
As	no	no	no	no
Cd	no	no	2 (retained)	no
Co	1 (retained)	no	no	no
Cr	1 (retained)	no	no	no
Cu	no	no	1 (retained)	no
Hg	no	no	no	no
Mn	no	no	no	no
Ni	1 (retained)	no	no	no
Pb	no	no	no	no
Sb	2	no	2 (retained)	no
Se	2 (retained)	no	1 (retained)	no
Sn	no	no	no	no
V	1 (retained)	no	no	no
Zn	1 (retained)	no	no	no

Several outliers were observed. For ERM-EF412, one subsample digest gave an outlier for Na, Co, Cr, Co, Ni, Sb, V and Zn, indicating either contamination or a "nugget" of higher metal concentration. In any case, all outliers were retained, as no technical reason for exclusion was found. None of the regression lines was significant for ERM-412.

Table 10: Results of the statistical evaluation of the stability tests of ERM-EF413. For the short-term study for Ni, only two subsamples per unit were analysed. Data marked with an asterisk dome from the stest after the characterisation study

Analyte	Short-term study (60 °C)		Long-term study (18 °C)	
	Individual outlying results	Significance of the trend on a 99% confidence level	Individual outlying results	Significance of the trend on a 99% confidence level
GCV	no	no	no	no
Vol. matter (ISO 562)	no	no	no	no
Ash (ISO 1171)	no	yes	no	no
C	no	no	no	no
H	no	no	no	no
N	no	no	no	no
S	no	no	no	no
Cl	no	no	no	no
Ca	no	no	no	no
Mg	no	no	no	no
Na	no	no	2 (retained)	no
K	no	yes	no	no
As	no	no	no	no
Co	no	no	no	no
Cu	no	no	no	no
Hg	no	no	2 (retained)	no
Mn	no	no	no	no
Pb	no	no	no	no
Se	no	no	no	no
Sn	no	no	1 (retained)	yes
Tl	no	no	2 (retained)	no
V	no	no	no	no
Zn	no	no	no	no

For ERM-413, statistically significant trends were observed for the ash content (short-term study), K (short-term study) and for Sn (long-term study). The trend for ash does not make technical sense, as furnace coke is produced by calcination at temperatures much higher than 60 °C and the ashing itself also occurs at higher temperatures. The trend is therefore most likely a statistical artefact, which was also confirmed by the second test after characterisation, where the same result was found for samples stored at normal conditions and those stored at reference conditions.

It was decided to include the apparent degradation for K in the uncertainty of stability but base the uncertainty of stability for Sn on the second test after characterisation.

7.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results no study can rule out degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is 0 ± x % per time".

Uncertainties of stability during dispatch and storage were estimated as described in the literature [24] for each analyte. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contribution is then calculated as the product of the chosen shelf life and the uncertainty of the regression lines as

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{sl}$$

$u_{lts,rel}$	relative uncertainty due to potential degradation during storage
RSD	relative standard deviation of all results of the stability study
x_i:	time point for each replicate
$\bar{x}$:	mean results for all time points
t_{sl}:	proposed shelf life (24 months at 18 ºC in this case)

The uncertainty contribution for potential degradation during transport ($u_{sts,\ rel}$) is calculated using the same equation, using a t_{sl} of 1 week.

In case of the uncertainty of the short term stability for ash for ERM-EF412 as well as the uncertainty of the long term stability for Sn for ERM-EF413, the apparent degradation using the slope *b* was combined with the uncertainty due to the lack of fit around the regression line as

$$u_{lts,rel,\deg} = \sqrt{(b \cdot t_{sl})^2 + u_{lts,rel}^2}$$

The following uncertainties were estimated:

- $u_{sts,rel}$, the uncertainty of degradation during dispatch. This was estimated from the 60 °C studies for a time of 0.25 months (1 week). The uncertainty therefore describes the possible change during a dispatch at 60 °C lasting for one week.
- $u_{lts,rel}$, the stability during storage. This uncertainty contribution was estimated from the 18 °C studies. The uncertainty contribution therefore describes the possible degradation for 24 months at 18 °C.

The results of these evaluations are summarised in Table 11.

Table 11: Uncertainties of stability during storage and dispatch. $u_{sts,rel}$ was calculated for a temperature of 60 °C and 1 week; $u_{lts,rel}$ was calculated for a storage temperature of 18 °C and 2 years. u_{lts} for H cannot be quantified, as the results submitted by the laboratory were below the LOQ. Data marked with an asterisk come from the second test after the characterisation (44 months) .

Analyte	ERM-EF411		ERM-EF412		ERM-EF413	
	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]
GCV	0.054	0.18	0.073	0.16	0.051	0.092
Vol. matter (ISO 562)	0.32	0.293	0.131	0.202	0.72	6.80
Ash (ISO 1171)	0.42	1.13	0.17	0.50	0.36	0.46
C	0.062	0.49	0.061	0.40	0.051	1.046
H	0.080	1.03	0.087	0.85	1.03	n.a.
N	0.17	2.62	0.26	3.36	0.35	2.94
S	0.52	0.62	0.46	0.46	0.24	9.85
Cl	< LOD	1.92	2.50	0.57	2.18	10.5
Ca	not tested		0.35	0.71	0.31	1.96
Mg	not tested		0.22	1.02	0.60	4.01
Na	not tested		0.42	1.77	0.41	3.58
K	not tested		0.53	3.21	0.84	3.25
As	not tested		1.13	2.73	not tested	
Cd	not tested		2.55	10.6	0.86	10.5
Co	0.41	1.88*	0.44	1.96	1.11	2.40
Cr	not tested		1.18	1.81	not tested	
Cu	3.20		0.77	1.29	1.07	5.84
Hg	1.23	3.65	2.11	3.49	2.37	23.2
Mn	not tested		0.27	1.26	0.60	4.23
Ni	not tested		1.61	2.51	not tested	
Pb	not tested		1.98	3.82	1.81	4.82
Sb	0.64	4.05	1.58	2.79	not tested	
Se	0.53	8.3*	5.1	2.68	0.56	3.27
Sn	2.54	4.4	1.11	2.67	2.04	3.63*
Tl	1.84	6.7*	not tested		1.37	2.65
V	0.65	6.0*	1.37	1.41	0.39	3.36
Zn	2.85	5.8*	1.68	3.73	0.98	3.96

All uncertainties will be included in the overall uncertainty budget. Therefore the material can be transported at ambient conditions without special precautions.

After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to control its further stability.

8 Characterisation

The material characterisation was based on an intercomparison of expert laboratories, i.e. the properties of the material were determined in different laboratories. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty. Naturally, for method-defined analytes (ash, volatile matter, S, C, H, N) all laboratories applied the same method. For elemental analysis, different measurement procedures were applied to demonstrate the absence of a measurement bias. GCV and NCV is an intermediate case: while the principle is indeed method defined, the result should be independent of the particular standard used.

8.1 Selection of participants

22 laboratories were selected based on criteria that comprised both technical competence and quality management aspects. Each participant was required to operate a quality management system and to deliver documented evidence of its laboratory proficiency in the field by submitting results for intercomparison exercises or method validation reports. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 was obligatory. In fact, all laboratories for the proximate analysis were accredited for the measurements in question. Where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (Section 4).

8.2 Study setup

Characterisation of proximates and trace element content were organised in two separate studies, as few laboratories determine both trace elements and proximates. In addition, sample intakes for proximates are higher than for trace elements. Therefore, laboratories received more samples for proximate than for the trace element determination.

8.2.1 Proximates

All laboratories, with the exception of laboratory 4, which did not analyse brown coal (ERM-EF412), submitted offers for all three materials. Samples were sent in September 2011 and results were received within 4 months after sample dispatch.

Each laboratory received three units of the candidate CRMs for which it had submitted an offer and was requested to provide six independent results, two per unit. The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations and measurements had to be spread over at least three days to ensure intermediate precision conditions. This means on each day the complete content of one unit was ground and the ground sample was left to equilibrate with the laboratory atmosphere to make it less hygroscopic. Dry mass in the analytical sample was determined from this equilibrated sample and this equilibrated sample was also used for all other proximate analysis. The moisture content in the analysis sample had to be determined in each unit two times and results are reported on dry mass basis. Free moisture was determined on the unground sample.

Blinded certified reference materials were sent as quality control samples together with the candidate CRMs to allow independent assessment of method trueness and appropriateness of the calibration. The latter was especially important, as many methods for proximate analysis are not calibrated on a daily basis. The following certified reference materials were used:

- BCR-180 (gas coal) for the determination of GCV, C, H, N, ash; labelled as QCM A
- BCR-331 (steam coal) for the determination of S; labelled as QCM B
- NIST SRM 39j and Fluka 33045 (benzoic acid) for checking the calibration of the calorimeters; labelled as QCM C
- BCR-460, coal, for the determination of F; labelled as QCM D

The use of measurement uncertainties is not well-established for standardised methods. To obtain information on the accuracy obtained in the laboratory, laboratories were asked to indicate the standard deviation of the quality control chart for the respective analyte.

Laboratories reported deviations from the standard methods and the date of the last calibration or operation qualification together with the results.

8.2.2 Trace elements

Each laboratory received two units of the candidate CRMs for which it had submitted an offer and was requested to provide six independent results, three per unit. The units for material characterisation were selected using a random stratified sampling scheme and covered the

whole batch. The sample preparations and measurements had to be spread over at least three days to ensure intermediate precision conditions. This means, on each day the complete content of one unit was ground and the ground sample was left to equilibrate with the laboratory atmosphere to make it less hygroscopic. Dry mass in the analytical sample was determined from this equilibrated sample and this equilibrated sample was also used for trace metal analysis. The moisture content in the analysis sample had to be determined in each unit two times and results are reported on dry mass basis.

NIST SRM 1632d (bitumous coal) for the determination of trace elements, labelled as QCM E, was used as a blind quality control samples together with the candidate CRMs to allow independent assessment of method trueness and appropriateness of the calibration. Each laboratory received only a approximately 5 g of the material, precluding moisture determination. All results submitted by the laboratories were corrected by the 2 % moisture content given on the certificate. According to information from laboratory 20, actual moisture content can vary between 2 and 9 %, depending on the conditions in the laboratory, leading to a potential residual moisture induced bias of 7 %. This potential bias is sufficiently low to detect serious flaws in analytical methodology.

In addition to the measurement results, laboratories were also requested to give estimations of the expanded uncertainties of the mean value of the six results. No approach for the estimation was prescribed, i.e. top-down and bottom-up were regarded as equally valid procedures.

Elements for which the homogeneity studies had shown unacceptable inhomogeneity were excluded from the general characterisation. Only neutron activation analysis (NAA) laboratories were asked to provide data for all elements, as for these methods the additional results come with negligible additional costs. The intention was not to certify these elements, but to provide these results as information values.

8.3 Methods used

8.3.1 Proximates

Various methods exist for the determination of proximates (see section 3.3). To make the material as widely applicable as possible, both ASTM and ISO methods were applied. Information was sought from the chairman of the respective ASTM technical committee which ASTM methods were equivalent to the respective ISO methods, so the results could be pooled. According to this information (backed up by results from intercomparisons provided as well), the following methods were applied:

Moisture in the analytical sample: Moisture in the analytical sample was determined by ISO 5068-2 (brown coal); ISO 11722 (hard coal); ISO 687 (coke) or ASTM D3173. The results of this analysis was used to correct the results to dry mass.

Ash: ISO 1171 and ASTM D3174 with the intention of pooling results of both methods.

Volatile matter: ISO 562 and ASTM 3175 with no intention of pooling results of both methods.

GCV at constant volume: ISO 1928 and ASTM D5865 with the intention of pooling results of both methods.

C, H, N: ISO 29541 and ASTM D5373 both describe the instrumental determination of CHN and are equivalent. In addition, separate ISO methods for C, H (ISO 609) and N (ISO 333) exist. Each of these methods could be used, with the intention of pooling the results of these methods. As it turned out, no laboratory used ISO 609.

S: ISO 19579 and ASTM D4239 deliver equivalent results, so both methods could be sued with the intention of pooling results of both methods. Measurements by XRF were asked to demonstrate the suitability of the materials for measurements using this method.

Cl: Laboratories were free to choose either ISO 587 or ASTM D4208, with the intention of pooling the results of these methods. In addition, data from neutron activation analysis were sought to potentially confirm the results. Measurements by XRF were asked to demonstrate the suitability of the materials for measurements using this method.

F: Laboratories were free to choose ISO 11724, ASTM D3761, ASTM D5987, with the intention of pooling the results of these methods.

Laboratories could also use other methods, e.g. national standard methods. In this case, evidence of the equivalence of these methods with the respective ISO or ASTM methods had to be provided with the results. The information on the methods used is given in Annex D.

8.3.2 Trace elements

A variety of digestion methods (open ashing, closed microwave, high pressure digestion using different instruments) with different quantification steps (AAS, ICP-MS, ICP-AES) as well as methods without sample preparation (INAA, k_0NAA) were used to characterise the material. The combination of results from methods based on completely different principles virtually should rule out undetected method bias.

All methods used during the characterisation study are summarised in Annex D. The laboratory code (e.g. L01) is a random number and does not correspond to the order of laboratories in Section 4.

8.4 Dry mass determination

For all measurements carried out during certification (homogeneity, stability and characterisation studies) the protocol specified in ISO 5068 (brown coal) 11722 (hard coal); ISO 687 (coke) or ASTM D3173 was applied:

A sample of 1 g of coal powder is dried in air or a stream of nitrogen at 105-110 °C until dry mass is obtained. For hard coal and coke, the drying can be done in air.

8.5 Evaluation of results

The characterisation campaign resulted in up to 14 datasets per analyte. All individual results of the participants, grouped per analyte are displayed in tabular and graphical form in Annex E.

8.5.1 Technical evaluation

The obtained data were first checked for compliance with the requested analysis protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- compliance with the analysis protocol: sample preparations and measurements performed on two days, and the analysis order and water content determination.
- absence of values given as below limit of detection or below limit of quantification
- method performance, i.e. agreement of the measurement results with the assigned value of the QCM

A preliminary compilation of results was sent to the laboratories on 12 August (proximates) and 28 August (elements) 2012 with the request for checking individual results. Deviation of results obtained for the QCMs from their certified value were highlighted especially. The answer and the technical investigations performed at IRMM, led to the following decisions (a summary of all issues is given in Table 12).

Proximates

No reliable uncertainty estimates are available for many of the results from procximate analysis. Data for the QMs were therefore deemed acceptable if they would have been in the population of data in the characterisation studies of these QCMs. The term "values submitted

during characterisation" in connection with a QCM therefore refers to the characterisation studies of BCR-180, BCR-331 and BCR-460 and not to the dataset of the current study.

Laboratory 1 reported results for Cl for QCM A significantly above the certified values. The results were therefore not used.

Laboratory 2 failed to report results for the quality control material for most analytes, so the results were not used for the evaluation.

Laboratory 3 reported high values for C for QCM A. It re-analysed the sample and found a value that was in agreement with the certified value for this material. However, as this involved a re-analysis of the material, the values were nevertheless excluded from the evaluation.

Laboratory 4 submitted results for GCV for QCM A above all values submitted during the characterisation, hinting at biased results. The laboratory repeated the analysis of QCM A and obtained results in agreement with the certified value, demonstrating its general method proficiency. Nevertheless, as there is a possibility that the results on the day of the characterisation measurements were biased, the results were excluded.

Laboratory 5 recognised that the value for volatile matter had not been corrected for the moisture content and that the net calorific value had been calculated on constant pressure, not on constant volume. Corrected values were accepted, as the corrections are based on a pure calculation without additional measurements.
The laboratory reported results for QCM A for Cl and N below all values submitted during characterisation, hinting at biased results. The results were therefore not used.

Laboratory 6 reported results for QCM A for H above all values submitted during characterisation, hinting at biased results. The results were therefore not used.

Laboratory 7 submitted results for GCV and Cl for QCM A above all values submitted during characterisation, hinting at biased results. The results were therefore not used.

Laboratory 8 did not provide results for the QCM for volatile matter and ash. The results were therefore not used.
The laboratory reported results for QCM A for N below all values submitted during characterisation, hinting at biased results. The results were therefore not used.

Laboratory 9 reported high values for H and low values for N for QCM A. In addition, the variation of the results for hydrogen was unusually high for the candidate CRM. Based on the results on the QCM A and the high variation for the candidate CRMs for hydrogen, these values were rejected.

Laboratory 10 submitted results for for GCV for QCM A below, for S for QCM B above and for F in QCM D below the values submitted during characterisation, hinting at biased results. The results were therefore not used.

Laboratory 11 reported results for H above all values submitted during characterisation, hinting at biased results. The results for F for QCM D were below the certified value. The results were therefore not used.

Laboratory 12 stated that they discovered soot after the combustion of QCM C for determination of GCV. This incomplete combustion explains the low finding for this QCM. The laboratory argued that this low finding was caused by the nature of the sample: the benzoic acid of QCM C was in powder form, whereas the laboratory usually uses pellets for calibration. The absence of influence on the other samples is shown by the correct value for QCM A. The values for GCV were retained. The laboratory did not find any explanation for the high findings for H and C for QCM A and the values were therefore rejected.

Laboratory 13 reported that it used thermogravimmetric analysis (TGA) for determination of ash and volatile matter in one run. This is fast, but analysis in two runs gives more reliable results for ash. The laboratory delivered a second set of results for ash where the ash values

were obtained in a separate run, which are in better agreement. As these results were received after information about the values, they are not included in the evaluation. The results for F for QCM D were below the certified value and were therefore not used. Triggerd by receiving the first draft of the certification report, L13 conducted made additional investigations on the source of the deviating result. They reported that originally they had determined volatile matter in a TGA without closing the crucible with a lid. Repeating the analyses with a closed crucible gave significantly lower results that were in better agreement with the certified values. However, as these tests were performed after disclosure of results and because they were not performed by the manual method, the new results were not included in the evaluation.

Laboratory 14 reported low results for C and high results for N and ash in QCM A as well as high results for QCM B. One explanation for the findings could be the calibration of the CHN analyser: the laboratory uses real samples, which might pick up moisture. However, z-scores over the last 5 years (about 18 per analyte) are very good, which speaks against this explanation. Based on the results on QCM A, the values for ash, C and nitrogen were excluded from the evaluation. For S, the result is explained by a difference in the methods used: the results from XRF differs from the ISO methods, if the samples contain FeS. Because of this method-dependence, the values were not included in the evaluation. Also Cl was determined by XRF. The laboratory was invited to participate with this method in the characterisation study to demonstrate the wide applicability of the assigned value. Because XRF requires matrix materials for calibration, traceability of the results is difficult to ensure. Therefore the results were used as confirmatory results rather than used for value assignment, although the results agreed with the other results submitted for Cl and although the results for the QCM agreed with the certified value.

Ash and volatile matter: Some results obtained by TGA for ash and volatile matter differed significantly from the results of the other methods, especially for brown coal and furnace coke. Discussion with the laboratories using this method clarified that determination of volatile matter by TGA is not straightforward. For each type of fuel, a correlation factor against the manual oven measurements must be obtained. If the fuel in question behaves differently from those with which the correlation was obtained, results will be biased. The lower familiarity with brown coal and furnace coke may explain why TGA results were biased especially for these two materials. TGA offers the possibility of determining volatile matter and ash in one analytical run, correlating these two results: if results for volatile matter are biased towards higher values, this automatically means that the results for ash are biased towards lower values and vice versa. Therefore, it was decided to exclude all results for volatile matter obtained by TGA, regardless of their agreement with the other oven techniques. Ash values by TGA were included in the analysis, unless the volatile matter was also determined by TGA in the same run. Therefore, results of laboratories 6, 10, 11 and 13 were not included in the characterisation for these parameters.

Elements

Laboratory 3: Results for Se for QCM E were significantly below the certified value. According to the laboratory, the indication of a method bias was confirmed by another interlaboratory comparison and the laboratory started investigation on how to improve the method. Because of this indication of method bias, the results for Se from Laboratory 3 were not used for value assignment.
The laboratory also checked its results V for QCM E. The laboratory re-analysed the samples and found results approximately 20 % higher, demonstrating general method proficiency. The results and variation is within the uncertainties reported by the laboratory and the results were therefore retained.
Results for QCM C for Ca, Mg, Na, K do not agree with the certified values within the respective uncertainties and were therefore not used.
Results for Tl for ERM-EF413 were partly below the LOQ and were therefore no used for

value assignment.
Uncertainties were taken from the reproducibility limits of the ASTM methods. These are very high and, looking at the variation of the lab's results, most likely overestimations of the true uncertainty.

Laboratory 7: In the case of ERM-EF412, the Tl mass fraction was significantly below the usual limit of detection of the laboratory. While the results are useful for comparison with the other values, they were excluded from value assignment.
The result of the laboratory also deviated significantly from the information value for Ni for QCM E. However, as this value is for information only, the result was retained.
The result for Mg for QCM C differs from the certified value. Therefore, the data were not used.
The measurement uncertainty reported for Zn for ERM-EF412 is significantly above those of the other laboratories. As the data are not comparable, the Zn results of Lab 7 for ERM-EF412 were not used for values assignment.

Laboratory 13 casted doubts on the accuracy of the values for Pb, as the mass fractions are at the low end of the working range. The data were not used for value assignment.
For As, the laboratory reported a low result for QCM E, which was still covered by the reported uncertainty. A second analysis gave results in agreement with the certified values. The laboratory stated that in its experience, hydride generation AAS frequently gives deviating results from ICP measurements. As the result was within the uncertainty stated by the laboratory, the results were retained.
The laboratory determined Cd with GFAAS as well as with ICP-AES. Results by GFAAS were consistently below the results by ICP-AES for mass fractions < 0.10 mg/kg. As the laboratory deemed the results by GFAAS more reliable, the GFAAS were used for ERM-EF411 and ERM-EF412. Two of the 6 results of ERM-EF413 were below the LOQ and one at the LOQ, indicating insufficient accuracy at that concentration. The values for ERM-413 were therefore not used.
The laboratory performed analyses on four days. The results of all four days (12 in total) were used.
Results for Tl for EF413 were on one day below the limit of quantification. Using only the results of day two would have led to biased results. The results were therefore not used for value assignment.

Laboratory 15 reported high uncertainties for Hg, Se and Mg: Se and Hg interfere spectrally. In these three materials, Se mass fraction is between 13 and 127 times the Hg mass fraction, so negatively affecting the Hg determination. In line with this expectation, the laboratory submitted results above the certified value of Hg for the QCM, which had a Se/Hg ratio of 13. The result submitted for Se for the QCM was low, but the difference was still covered by the respective uncertainties. Therefore, the results for Se were retained for ERM-EF411 and ERM-EF412, but not for ERM-EF413, where only three of the six results were above the LOQ.
At the given neutron fluxes, Al interferes with the determination of Mg, especially at high Al mass fractions, resulting in very high uncertainties for Mg for ERM-EF411, which has an approximate Al mass fraction of 8600 mg/kg. The same effect explains the low finding for Mg for QCM, which has an Al mass fraction of 9100 mg/kg. Therefore, the results of L15 were included for ERM-EF412 (low Al/Mg ratio), but were not included for ERM-EF411 and ERM-EF413 (higher Al/Mg ratio).
The standard deviation of the results for K for ERM-EF412 and ERM-EF413 were significantly higher than the ones of other laboratories, indicating worse method performance for this element. Therefore, results for K from Lab 15 were not used for value assignment.
The results for V for QCM E were below the certified value, but this is a result of the very low uncertainty reported by the laboratory and the very low uncertainty assigned to the certified value. The value was among ll other results for this QCM.. The values were therefore retained.

Laboratory 16 reported a very high Zn value for one sample preparation for ERM-EF412. The other subsamples for this sample gave much lower results. This high result was explained by the laboratory as being most likely caused by contamination. This individual result was excluded, retaining the other Zn values for the material.
The laboratory determined Cd by ID-TIMS, using both the $^{113}Cd/^{112}Cd$ and the $^{114}Cd/^{111}Cd$ ratio. These 12 results were pooled into one dataset.
Results for Ca and Sb for QCM E were below the certified values. The Ca results were therefore not used.

Laboratory 17 reported values for Ca, Na, K, Cr, Pb and Zn that disagreed with the certified values based on the stated uncertainties. The data were therefore not used. Also the results for QCM E for Ni were above the information value for Ni. As this value is for information only, the result was retained.

Laboratory 18 performed in total 12 determinations , of which two results for Mn for ERM-EF411 were very high. The laboratory performed in total 12 determinations, two of where so high. This was deemed to be due to sample inhomogeneity rather than due to technical reasons and the data were therefore retained.
The laboratory stated that results for Cr in ERM-EF412 were below the effective limit of determination. The results were therefore not used for value assignment.
The standard deviation of the results for K for ERM-EF413 were significantly higher than the ones of other laboratories, indicating worse method performance for this element. Therefore, results for K from Lab 18 were not used for value assignment.
The standard deviation of Zn for ERM-EF413 is unacceptably high (60 %), so the results were not used for value assignment.

Laboratory 20 also submitted results for NIST SRM 1365, sub-bituminous coal, which was digested and analysed together with the IRMM coals. Results for Pb and V were about 15 % below the certified values, which is below the accepted range of ± 10 % as set by the laboratory. Although this deviation is just covered by the uncertainty stated by the laboratory, the fact that the results are beyond the laboratory-internal limits led to exclusion of the results.
The laboratory also stated that the results for Hg in ERM-EF413, Cd (ERM-EF412 and ERM-EF413), Sb, Se, Sn and Tl (ERM-EF412) are close to the limit of quantification. This was reflected in their uncertainties and the values were therefore retained.
Results for Ca for QCM E were below the certified values. The Ca results were therefore not used.

Laboratory 21 had measurements performed by two different analysts. Results for Cu and Zn for ERM-EF412 and for Cr for ERM-EF413 between the two analysts differed by a factor 3 (Cu) and 2 (Zn, Cr), respectively. Because of the lack of intra-laboratory consistency, the values were not used for value assignment.
Uncertainty for Cd for ERM-EF413 was L21 for ERM-EF413 are confirmatory only. Results for Hg were at the LOQ and Tl were below the LOQ as stated by the laboratory. The results were therefore rejected.
The result for QCM E for As does not agree with the certified value. However, the low uncertainty reported by the laboratory indicates underestimation of the measurement uncertainty. The result was therefore retained.
The results for Sb for QCM E is below the certified value. The values were therefore not used for value assignment.

Laboratory 23 reported uncertainties for Mg that were significantly above those of the other laboratories. As the data are not comparable, the Mg results of Lab 23 were not used for values assignment.

Table 12: Datasets that showed deviations from the analysis protocol, technical specifications or deviating values for the QCM samples, and action taken

Analyte	Lab-method code	Description of problem	Action taken
GCV (ISO 1928/ASTM D5865)	L2	No results for the QCM A provided	data not used
	L12	Results for QCM C 4 % below the certified value: the lab discovered incomplete combustion, presumably caused by the fact that QCM C was a powder rather than a pellet; results for QCM A were also below the certified value.	data not used
	L4, L7, L10	Result for QCM A beyond all values reported during certification	data not used
NCV (ISO 1928/ASTM D5865)	L2	no results for the QCM A provided	data not used
	L4, L7, L10	results for QCM A for GCV deviated (see GCV)	data not used
Volatile matter (ISO 562, ISO 5071)	L2, L8	No results for the QCM A provided	data not used
	L6, L11, L13	TGA used for ash and Volatile matter	data not used
Ash (ISO 1171/ASTM D3174)	L2	No results for the QCM A provided	data not used
	L8	Results of the QCM A above all values reported during certification	data not used
	L6, L11, L13	TGA for ash and Volatile matter; results for QCM A above the certified value	data not used
C	L2	No results for the QCM A provide	data not used
	L3, L12, L14	Results of the QCM A 2 % above the certified values	data not used
H	L2	No results for the QCM A provided	data not used
	L6, L9, L11, L12	Results of the QCM A above all values reported during certification	data not used
N	L2	No results for the QCM A provided	data not used
	L5, L8, L9	Results of the QCM A below all values reported during certification	data not used
	L14	Results of the QCM A above all values reported during certification	data not used
S (ISO 19579/ASTM D4239)	L10, L14	Results for QCM B are 10 and 40 % above the certified values	data not used
Cl	L1	Result for QCM A above certified value	data not used
	L5, L7	Result for QCM A below certified value	data not used
	L14	Measurements by XRF: Despite agreement with the certified value for QCM A, the values were used as confirmation only.	values used for confirmation
F	L10, L11, L13	Results for QCM D below certified value	data not used
Ca	L3, L17	Results for QCM E above the certified value	data not used

Analyte	Lab-method code	Description of problem	Action taken
Mg	L3, L7, L16, L20	Results for QCM E below the certified value	data not used
	L15 (EF411,EF413)	Interference by Al resulting in high uncertainties	data not used
	L16b	Uncertainty is very large (34-56 %) for results from microwave digestion	data not used
Na	L3, L17	Results for QCM E above the certified value	data not used
K	L3, L17	Results for QCM E above the certified value	data not used
	L15 (EF412, EF413)	Standard deviation significantly higher than of other laboratories	data not used
	L18 (EF413)	Standard deviation significantly higher than of other laboratories	data not used
As	L21	Result for QCM E below the certified value, but estimated uncertainty presumably underestimated	result retained
	L13	Result for QCM E low, but within uncertainty, second result gave higher values	data retained
Cd	L13 (EF411, EF412)	Results from by GFAAS and ICP-AES provided. The results differ for mass fractions < 0.10 mg/kg	if < 0.010 mg/kg, GFAAS results used
	L13 (EF413)	Results partly below LOQ	data not used
	L20 (EF412, EF413)	Results close to LOQ	data retained
	L21 (EF413)	Uncertainty larger than average	data not used
Cr	L15	Significant Cr blank in the vials; resulted were blank corrected	data retained
	L17	Result for QCM E above the certified value	data not used
	L18 (EF412)	Result below LOD	data not used
	L21 (EF413)	Results differ between two analysts	data not used
Cu	L21 (EF411, EF412)	Results between two analysts differ by a factor of 3	data not used
Hg	L15	interference by Se	data not used
	L20 (EF413)	Results close to LOQ	data retained
	L21	Results partly below LOQ	data not used
Mn	L18	several very high results; most likely due to inhomogeneity	data retained
Ni	L7, L17	Results significantly above the information value of QCM E	data retained

Analyte	Lab-method code	Description of problem	Action taken
Pb	L13	Result on the lower end of the measurement procedure	data not used
	L17	Results for QCM E above the certified value	data not used
	L20	Results for SRM 1635 15 % below the certified value and below the range accepted by the laboratory.	data not used
Sb	L16, L21	Results for QCM E below the certified value	data not used
	L20 (EF412)	Results close to LOQ	data retained
Se	L3	Apparent method bias; result for QCM E below the certified value	data not used
	L20 (EF412)	Results close to LOQ	data retained
Sn	L20 (EF412)	Results close to LOQ	data retained
Tl	L7 (EF412)	Results below LOQ	data not used
	L13 (EF413)	Results partly below LOQ	data not used
	L20 (EF412)	Results close to LOQ	data retained
	L21	Results below the LOQ	data not used
V	L15	Result for QCM E below the certified value, but uncertainty presumably underestimated	data retained
	L20	Results for SRM 1635 15 % below the certified value, and below the range accepted by the laboratory	data not used
	L21	Result for QCM E below the certified value	data not used
Zn	L7 (EF412)	Stated uncertainty (57 %) is significantly higher than for other labs	data not used
	L16 (EF412)	One replicate for Zn very high, most mlikely caused by contamination	datum deleted, other data retained
	L17	Result for QCM E below the certified value	data not used
	L18 (EF413)	Large RSD (60 %)	data not used
	L21 (EF411, EF412)	Results from 2 analysts differ by a factor of 2	data not used

8.5.2 Statistical evaluation

The datasets accepted on technical grounds were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots and were tested for outlying means using the Grubbs test and using the Cochran test for outlying standard deviations, (both at a 99 % confidence level). Standard deviation within (s_{within}) and between ($s_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 13 - Table 15.

*Table 13: Statistical evaluation of the technically accepted datasets for ERM-EF411. p: number of technically valid datasets. n.a.: not applicable; ret: retained. n.c.: cannot be calculated as MSB < MSW * For results with outlying mean, the range of means rather than the average is given.*

	p	Outliers		Dist.	Statistical parameters				
		Means	Var.		Average*	*s*	$s_{between}$	s_{within}	Unit
GCV	9	no	no	normal	29.005	0.170	0.167	0.088	MJ/kg
NCV	8	no	no	normal	28.003	0.240	0.238	0.068	MJ/kg
Vol. matter (ISO 562/5071)	8	no	no	normal	38.083	0.288	0.270	0.247	g/100 g
Ash (ISO 1171 / ASTM D3174)	10	no	no	normal	8.288	0.258	0.245	0.194	g/100 g
C	10	no	no	normal	71.369	0.428	0.407	0.327	g/100 g
H	9	no	no	normal	4.798	0.111	0.108	0.059	g/100 g
N	9	no	no	normal	1.431	0.045	0.043	0.026	g/100 g
S (ISO 19579/ASTM D4239)	10	no	no	normal	0.598	0.011	0.0099	0.0130	g/100 g
Cl	10	no	L3, L4, L15, L19	normal	0.0099	0.0021	0.0020	0.0012	g/100 g
F	4	no	no	n.a.	0.00393	0.00035	0.0003	0.00055	g/100 g
Ca	5	no	no	normal	1643	92	70	192	mg/kg
Mg	4	no	n.a.	n.a.	950	169	n.c.	682	mg/kg
Na	5	no	no	normal	1219	82	63	86	mg/kg
K	5	no	L18	normal	1093	61	23	135	mg/kg
As	6	no	no	normal	4.485	0.663	0.670	0.637	mg/kg
Cd	3	n.a.			0.232	0.0028	0.028	0.037	mg/kg
Co	6	no	no	skewed	3.471	0.306	0.257	0.333	mg/kg
Cr	6	21		n.a.	15-28*	n.a.			mg/kg
Cu	2	n.a.			6.9	n.a.			mg/kg
Hg	7	no	L13, L16	normal	0.079	0.012	0.0114	0.0105	mg/kg
Mn	6	no	L18	normal	32.8	6.9	2.96	19.1	mg/kg
Ni	2	n.a.			14.8				mg/kg
Pb	4	no	no	normal	2.42	0.54	0.53	0.17	mg/kg
Sb	7	no	L15. L18. L19	normal	1.494	0.082	0.041	0.192	mg/kg
Se	9	no	no	normal	5.111	0.646	0.750	0.302	mg/kg
Sn	1	n.a.			0.19	n.a.		0.033	mg/kg
Tl	5	no	no	normal	0.236	0.019	0.0180	0.0118	mg/kg
V	5	no	L18	normal	22.496	1.855	1.445	3.907	mg/kg
Zn	5	no	L18	normal	13.2	1.3	1.1	2.3	mg/kg

*Table 14: Statistical evaluation of the technically accepted datasets for ERM-EF412. . p: number of technically valid datasets. n.a.: not applicable; ret: retained. n.c.: cannot be calculated as MSB < MSW * For results with outlying mean, the range of means rather than the average is given.*

Analyte	p	Outliers		Dist.	Statistical parameters				
		Means	Var.		Average	*s*	$s_{between}$	s_{within}	Unit
GCV	8	no	no	normal	26.022	0.061	0.058	0.046	MJ/kg
NCV	7	no	no	normal	24.984	0.189	0.188	0.045	MJ/kg
Vol. matter. (ISO 562/5071)	6	no	no	normal	50.089	0.368	0.362	0.160	g/100 g
Ash (ISO 1171/ ASTM D3174)	7	no	L1	normal	4.112	0.285	0.283	0.092	g/100 g
C	8	no	L10	normal	66.229	0.407	0.392	0.270	g/100 g
H	7	no	L1, L8	normal	4.875	0.152	0.150	0.064	g/100 g
N	8	no	L6	normal	0.737	0.034	0.032	0.025	g/100 g
S (ISO 19579/ASTM D4239)	10	no	L13	normal	0.360	0.032	0.032	0.014	g/100 g
Cl	9	L8	L11	n.a.	0.030-0.044	n.a.		0.0012	g/100 g
F	2	n.a.			0.0040	n.a.		0.0003	g/100 g
Ca	8	no	no	normal	9793	374	363	230	mg/kg
Mg	5	no	no	normal	3732	139	140	79	mg/kg
Na	8	no	no	normal	2195	103	101	53	mg/kg
K	7	no	L19	normal	229	11	12	10	mg/kg
As	10	L17	L19	n.a.	0.28-0.42*	n.a.		0.024	mg/kg
Cd	5	no	no	normal	0.0122	0.0009	0.0006	0.0016	mg/kg
Co	10	L17	L15	n.a.	0.09-0.19	n.a.		0.007	mg/kg
Cr	7	no	L15	skewed	0.46-0.64	n.a.		0.075	mg/kg
Cu	5	no	L7	normal	0.683	0.235	0.233	0.076	mg/kg
Hg	6	no	no	normal	0.0697	0.0082	0.0081	0.0036	mg/kg
Mn	11	no	L3, L21	normal	48.583	1.764	1.718	0.995	mg/kg
Ni	4	L17	L17, L21	n.a.	0.3-0.8*	n.a.		0.051	mg/kg
Pb	4	no	no	normal	0.252	0.034	0.032	0.023	mg/kg
Sb	5	no	L18, L19, L20	normal	0.0239	0.0028	0.0022	0.0041	mg/kg
Se	8	no	no	normal	0.962	0.083	0.081	0.047	mg/kg
Sn	5	no	L7	skewed	0.099	0.073	0.073	0.023	mg/kg
Tl	4	no	L7, L17	normal	1.29	0.64	0.48	1.0	µg/kg
V	7	no	L15	normal	0.567	0.028	0.024	0.040	mg/kg
Zn	7	no	L19	normal	0.988	0.153	0.135	0.208	mg/kg

*Table 15: Statistical evaluation of the technically accepted datasets for ERM-EF413. p: number of technically valid datasets. n.a.: not applicable; ret: retained. n.c.: cannot be calculated as MSB < MSW * For results with outlying mean, the range of means rather than the average is given.*

	p	Outliers		Distr.	Statistical parameters				
		Means	Var.		Average*	*s*	$s_{between}$	s_{within}	Unit
GCV	8	no	L6, L8	normal	29.52	0.45	0.45	0.13	MJ/kg
NCV	6	no	L6, L8	normal	29.43	0.49	0.52	0.11	MJ/kg
Vol. matter. (ISO 562/5071)	7	no	L3	bimodal	0.944	0.190	0.180	0.143	g/100 g
Vol. matter. (ASTM D3175)	1	n.a.			0.63	0.05	not applicable		g/100 g
Ash (ISO 1171/ ASTM D3174)	8	no	L1	bimodal	9.5-10.1*	not applicable		0.206	g/100 g
C	9	no	L1, L11	normal	87.83	0.65	0.63	0.35	g/100 g
H	7	L8	no	n.a.	0.1-0.7*	not applicable		0.019	g/100 g
N	9	no	no	normal	1.095	0.043	0.041	0.030	g/100 g
S (ISO 19579/ASTM D4239)	10	no	L9	normal	0.578	0.025	0.024	0.018	g/100 g
Cl	10	no	no	normal	0.0347	0.0032	0.0032	0.0021	g/100 g
F	3	n.a.			0.0064	0.0007	0.0007	0.0004	g/100 g
Ca	9	no	L18	normal	2920	196	168	191	mg/kg
Mg	5	n.a.			1228	57	46	95	mg/ kg
Na	9	no	L15, L18, L22	normal	642	50	50	36	mg/kg
K	7	no	no	normal	1451	90	88	41	mg/kg
As	10	L13	L13, L18	n.a.	1.8-6.7*	not applicable		0.56	mg/kg
Cd	3	n.a.			0.033	n.a.		0.002	mg/kg
Co	10	L3	L3	na.	5.7-17*	not applicable		0.64	mg/kg
Cr	5	no	no	normal	92	13	9	11	mg/kg
Cu	8	L3	L3, L22	n.a.	19-36*	not applicable		2.6	mg/kg
Hg	4	n.a.			0.0105	0.0094	0.0101	0.0078	mg/ kg
Mn	11	L20	L3, L18	n.a.	78-140*	not applicable		9.3	mg/kg
Ni	3	n.a.			48	8	7	4	mg/ kg
Pb	5	no	no	normal	8.41	1.28	1.25	0.60	mg/kg
Sb	4	n.a.			1.289	0.069	0.047	0.123	mg/ kg
Se	8	no	no	normal	1.334	0.309	0.232	0.103	mg/kg
Sn	5	no	L3	normal	0.79	0.45	0.45	0.10	mg/kg
Tl	3	n.a.			0.145	0.026	0.026	0.004	mg/ kg
V	8	L16, L20	L18	n.a.	23-42*	not applicable		1.5	mg/kg
Zn	9	no	L3, L19	normal	15.97	1.63	1.33	2.06	mg/kg

Most datasets showed some outlying variances. This merely reflects the fact that different methods have different intrinsic variability. As all measurement methods were found technically sound, all results were retained.

For ERM-EF411, the data for Cl from L13 did not agree with the tentatively assigned value within the respective uncertainties. This was attributed to the low uncertainty and the value

was therefore retained.
The results submitted by Laboratory 21 for Cr were an outlier on a 99 % confidence interval (laboratory average 28 mg/kg; other averages around 18 mg/kg). The results of the laboratory for QCM E were in line with the certified value. The high result was therefore deemed to reflect the inhomogeneity detected earlier, precluding assignment of any values.
The distribution of laboratory data for Co was skewed, with four results between 3.2 and 3.35 mg/kg and two results of 3.6 and 4.0 mg/kg, precluding assignment of a certified value.
Laboratory 18 submitted values between 700 and 4700 mg/kg for Mg. This resulted in a very high within-laboratory standard deviation, which was not flagged as a Cochran outlier, as the number of laboratories was too low. The situation was similar for K, where the laboratory submitted results ranging from 850 to 1600 mg/kg. The results were retained, as it is believed that this variation reflects material inhomogeneity rather than method problems.
Several more outliers of variance were found, which merely reflects the fact that different methods have different intrinsic variability. As all measurement methods were found technically sound, all results were retained.

For ERM-EF412, data for Cr were skewed, with three values of 0.46 and two values of 0.56 mg/kg, precluding certification.
For Sn, L7 was flagged only as 95 % but not as 99 % outlier. However, the result was a factor 2.5 above the next highest value. Most likely the low number of datasets for Sn (5) is responsible for this curious finding. In this case, the statistical test was overruled and the data were treated as if L7 were an outlier.
Data from L1 and L11 for ash did not overlap with the tentatively assigned value within the respective uncertainties. This is due to the low uncertainties rather than due to technical inconsistency. The values were therefore retained and assignment of a value is possible.

For ERM-EF413, the result for L7 for H was about a factor 7 above the other results, constituting a clear outlier. No reason for this deviating result was found.
Results for ash according to ISO methods followed a bimodal distribution, with one cluster of results around 9.6 g/100 g and one around 10 g/100 g. This bimodality precluded any value assignment.
Results for As, Co, Cu and Mn showed one outlying mean value each. No reasons for these deviation could be identified, precluding value assignment.
Results for Hg ranged from 0.002 to 0.02, making any value assignment impossible.
For Se, skewness/kurtosis test indicated normality. This, however, might be caused by one very low (1.0 mg/kg) and one very high (1.9 mg/kg) result each. The other five results ranged from 1.3 to 1.5 mg/kg.
Results for Sn followed a normal distribution. However, results ranged from 0.2 to 1.5 mg/kg, making value assignment not meaningful.
Results of L16 and L20 for V agreed very well, but were about half of the results submitted by the other laboratories. No reason for this difference could be found.
Results for GCV from L10 and for Se (L7) did not overlap with the tentatively assigned value within the respective uncertainties. This is due to the low uncertainties rather than due to technical inconsistency. The values were therefore retained and assignment of a value is possible.

9 Value Assignment

For these materials, certified, indicative and informative values have been assigned. No value is assigned to any analyte where the characterisation study contained unexplained outliers.

Certified values are values that fulfil the highest standards of accuracy. Procedures at IRMM require generally pooling of not less than 6 datasets to assign certified values. Full uncertainty budgets in accordance with the Guide to the expression of uncertainty in measurement [3] must be established.

Indicative values are values where either the uncertainty is deemed too large or where too few independent datasets were available to allow certification. Uncertainties are evaluated according to the same rules as for certified values.

Additional material information refers to values that have been obtained in the course of the study. For example, results reported from only one or two laboratories in cases where individual measurement uncertainty is high, would fall under this category.

9.1 Certified values and their uncertainties

Certified values for all analytes are based on the unweighted mean of the means of the accepted datasets as shown in Table 13 to Table 15.

The assigned uncertainty consists of uncertainties related to characterisation, u_{char} (see Section 8), potential between-unit homogeneity, u_{bb} (see Section 6) and potential degradation during transport (u_{sts}) and long-term storage, u_{lts} (see Section 7). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value ($U_{CRM,\ rel}$) with a coverage factor k as

$$U_{CRM,rel} = k \cdot \sqrt{u_{char,rel}^2 + u_{bb,rel}^2 + u_{sts,rel}^2 + u_{lts,rel}^2}\ .$$

- $u_{char,rel}$ was estimated as described in Section 8.5.2
- $u_{bb,rel}$ was estimated as described in Section 6.1. The uncertainties estimated for GCV were also assigned to NCV.
- $u_{sts,rel}$ was estimated as described in section 7.3. The uncertainties estimated for GCV were also assigned to NCV.
- $u_{lts,rel}$ was estimated as described in Section 7.3. The uncertainties estimated for GCV were also assigned to NCV.

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor *k* of 2 was applied, to obtain the expanded uncertainties.

The certified values and their uncertainties are summarised in Table 10 to Table 18.

Table 16: Certified values and their uncertainties for ERM-EF411

Property	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM,rel}$ [%]	Certified value[a]	U_{CRM}	Unit
GCV (ISO 1928/ASTM D5865)	0.19	0.47	0.054	0.176	1.08	29.0	0.4	MJ/kg
NCV (ISO 1928/ASTM D5865)	0.30	0.47	0.054	0.176	1.18	28.0	0.4	MJ/kg
Volatile matter (ISO 562/ ISO 5071)	0.27	1.20	0.32	0.29	2.61	38.1	1.0	g/100 g
Ash (ISO 1171/ASTM D3174)	0.98	3.37	0.421	1.125	7.42	8.3	0.7	g/100 g
C (ISO 29548/ASTM D5373)	0.19	0.37	0.062	0.489	1.29	71.4	1.0	g/100 g
H (ISO 609/TS12902/ASTM D5373)	0.77	0.69	0.080	1.032	2.93	4.80	0.14	g/100 g
N (ISO 333/TS12902/ASTM D5373)	1.05	1.86	0.17	2.62	6.77	1.43	0.10	g/100 g
S (ISO 19579/ASTM D4239)	0.58	0.96	0.524	0.620	2.77	0.598	0.017	g/100 g
Cl	6.71	6.53	0.000	1.924	19.12	99	19	mg/kg
Se	4.21	3.10	0.53	8.30	20.16	5.1	1.0	mg/kg

[a] on dry mass basis (see Section 8.4)

Table 17: Certified values and their uncertainties for ERM-EF412

Property	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM,rel}$ [%]	Certified value[a]	U_{CRM}	Unit
GCV (ISO 1928/ASTM D5865)	0.083	0.36	0.07	0.16	0.81	26.02	0.22	MJ/kg
NCV (ISO 1928/ASTM D5865)	0.29	0.36	0.07	0.16	0.98	24.98	0.25	MJ/kg
Volatile matter (ISO 562 and ISO 5071)	0.30	0.47	0.131	0.202	1.22	50.1	0.7	g/100 g
Ash (ISO 1171/ ASTM D3174)	2.62	0.48	0.167	0.496	5.43	4.11	0.23	g/100 g
C (ISO 29548/ASTM D5373)	0.22	0.13	0.061	0.399	0.95	66.2	0.7	g/100 g
H (ISO 609/TS12902/ ASTM D5373)	1.18	0.44	0.087	0.851	3.04	4.88	0.15	g/100 g
N (ISO 333/TS12902/ ASTM D5373)	1.63	1.21	0.259	3.360	7.87	0.74	0.06	g/100 g
S (ISO 19579/ASTM D4239)	2.81	1.42	0.463	0.463	6.43	0.360	0.023	g/100 g
Ca	1.49	0.66	0.350	0.710	3.62	9.8	0.4	g/kg
Na	1.66	0.70	0.420	1.770	5.12	2.20	0.12	g/kg
K	1.80	1.03	0.530	3.210	7.72	229	18	mg/kg
Hg	4.80	3.89	2.110	3.490	14.90	0.070	0.011	mg/kg
Mn	1.09	0.96	0.27	1.26	3.89	48.6	1.9	mg/kg
Se	3.01	2.51	5.100	2.680	14.37	0.96	0.14	mg/kg
V	1.87	1.33	1.370	1.410	5.75	0.57	0.04	mg/kg

[a] on dry mass basis (see Section 8.4)

Table 18: Certified values and their uncertainties for ERM-EF413

Property	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM,rel}$ [%]	Certified value[a]	U_{CRM}	Unit
GCV (ISO 1928/ASTM D5865)	0.54	0.39	0.051	0.092	1.35	29.5	0.4	MJ/kg
NCV (ISO 1928/ASTM D5865)	0.68	0.39	0.051	0.092	1.58	29.4	0.5	MJ/kg
C (ISO 29548/ASTM D5373)	0.25	0.08	0.051	1.046	2.16	87.8	1.9	g/100 g
N (ISO 333/TS12902/ ASTM D5373)	1.31	0.47	0.352	2.939	6.54	1.10	0.07	g/100 g
S (ISO 19579/ASTM D4239)	1.37	0.46	0.241	9.854	19.92	0.58	0.12	g/100 g
Ca	2.24	2.28	3.900	1.960	10.82	2.92	0.22	g/kg
Na	2.57	1.84	0.41	3.58	9.59	0.64	0.07	g/kg
Se	8.19	3.92	1.600	3.270	19.56	1.33	0.26	mg/kg
Zn	3.40	5.50	0.980	3.960	15.29	16.0	2.5	mg/kg

[a] on dry mass basis (see Section 8.4)

9.2 Indicative values and their uncertainties

Indicative values were assigned for a number or trace elements, because either fewer than six technically accepted datasets were received or because the uncertainties were deemed too large for certified values. As all laboratories had regularly successfully participate in proficiency tests, the results were regarded as sufficiently trustworthy to assign indicative values. The uncertainty budgets were set up as for the certified values.

For ERM-EF411, uncertainties of stability are not available for all elements. The uncertainties estimated for Hg were used in this case. Because of the large uncertainties, slight underestimation should not influence the assigned uncertainty.

All values are listed together with the assigned values and the reason why an indicative rather than a certified value was assigned in Table 19 to Table 21.

Table 19: Indicative values and their uncertainties for ERM-EF411. Codes in the column property: u: uncertainty too high for certified values. d: too few datasets for certification.

Property	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM,rel}$ [%]	Indicative value[a]	U_{CRM}	Unit
Co (u)	3.60	9.60	0.41	1.88	20.86	3.5	0.8	mg/kg
Hg (u)	5.63	6.20	1.23	3.65	18.44	0.079	0.015	mg/kg
Sb (u)	2.07	9.40	0.64	4.05	20.93	1.5	0.4	mg/kg
Tl (u, d)	3.54	12.70	1.84	6.70	29.93	0.24	0.07	mg/kg
V (u. d)	3.69	11.60	0.65	6.00	27.17	22	7	mg/kg
Zn (u, d)	4.40	12.40	2.85	5.84	29.35	13	4	mg/kg

[a]: reported on dry mass basis (see Section 8.4)

Table 20: Indicative values and their uncertainties for ERM-EF412. Codes in the column property: u: uncertainty too high for certified values. d: too few datasets for certification

Property	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM,rel}$ [%]	Indicative value[a]	U_{CRM}	Unit
Mg (d)	1.67	0.72	0.22	1.02	4.33	3.73	0.16	g/kg
Cd (u, d)	3.30	6.40	2.55	10.60	26.13	0.012	0.004	mg/kg
Cu (u, d)	15.39	1.33	0.77	1.29	31.04	0.68	0.22	mg/kg
Pb (u, d)	6.75	5.20	1.98	3.82	19.09	0.25	0.05	mg/kg
Sb (d)	5.24	2.20	1.58	2.79	13.04	0.024	0.004	mg/kg
Zn (u)	5.85	5.10	1.68	3.73	17.55	0.99	0.18	mg/kg

[a]: reported on dry mass basis (see Section 8.4)

Table 21: Indicative values and their uncertainties for ERM-EF413. Codes in the column property: u: uncertainty too high for certified values. d: too few datasets for certification

Property	$u_{char, rel}$ [%]	$u_{bb, rel}$ [%]	$u_{sts, rel}$ [%]	$u_{lts, rel}$ [%]	$U_{CRM,rel}$ [%]	Indicative value[a]	U_{CRM}	Unit
Cl (u)	2.96	14.30	2.18	10.50	35.75	0.35	0.13	g/kg
Mg (d, u)	2.32	6.00	0.60	4.01	15.21	1.23	0.19	g/kg
Pb (u)	6.79	4.20	1.81	4.82	19.00	8.41	1.6	mg/kg

[a]: reported on dry mass basis (see Section 8.4)

9.3 Additional material information

The mean of laboratory means for parameters for which at least two results were obtained in the characterisation study and where no outlying unit averages were detected in the homogeneity studies were assigned as additional material information. As these values only give a rough idea about the value of the, no uncertainty is estimated. The additional information values are listed in Table 22 to Table 24

Table 22: Information values for ERM-EF411. The information values are based on the average of p laboratory averages obtained in the characterisation study.

Property	*p*	Information value[a]	Unit
S (ASTM D3177)	3	0.59	g/100 g
F	4	39	mg/kg
Cu	2	7	mg/kg
Ni	2	15	mg/kg

[a]: reported on dry mass basis (see Section 8.4)

Table 23: Information values for ERM-EF412. The information values are based on the average of p laboratory averages obtained in the characterisation study.

Property	*p*	Information value[a]	Unit
S (ASTM D3177)	3	0.37	g/100 g
F	2	40	mg/kg
Sn	5	0.1	mg/kg

[a]: reported on dry mass basis (see Section 8.4)

Table 24: Information values for ERM-EF413. The information values are based on the average of p laboratory averages obtained in the characterisation study.

Property	*p*	Information value[a]	Unit
Ash (ISO 1171, ASTM D3174)	8	10	g/100 g
S (ASTM D3177)	3	0.55	g/100 g
F	3	64	mg/kg
K	7	1.5	g/kg
Tl	3	0.15	mg/kg

[a]: reported on dry mass basis (see Section 8.4)

9.4 Additional data from k0NAA

Laboratories 18, 19 and 22 also provided data for elements not requested in the characterisation study. These data are summarised in Table 25. These data list only those data where at least two laboratories submitted data and where the range of the averages was smaller than 30 %ofthe average.

Table 25: k0NAA results for ERM-EF411, ERM-EF412 and ERM-EF413.Only data where at least two laboratories submitted data and where the range of the averages was smaller than 30 % are shown.All data are in mg/kg.

	ERM-EF411		ERM-EF412		ERM-EF413	
	average [mg/kg]	range [mg/kg]	average [mg/kg]	range [mg/kg]	average [mg/kg]	range [mg/kg]
Al	8842	999	695	66	13987	658
Ba	205	16	109	6	171	10
Br	0.77	0.02	15.5	0.5	8.5	0.6
Ce	6.6	1.7	0.74	0.07	18	2
Cs	0.54	0.06	0.025	0.001	1.4	0.1
Dy	0.58	0.05			1.5	0.2
Eu	0.14	0.03	0.009	0.001		
Fe	4428	884	3264	240	6882	461
Ga	2.9	0.3			4.9	0.1
Hf	0.53	0.11	0.09	0.04	0.76	0.05
I			4.9	0.1	6.4	0.5
La	3.1	0.6	0.38	0.03	8.2	0.5
Mo	4.3	1.3			5.78	0.04
Nd	3.1	0.5	0.31	0.01	8.5	0.7
Rb	6.9	1.1	0.94	0.15	11	2
Sc	2.9	0.3	0.13	0.01	4.1	0.3
Sm	0.61	0.13	0.052	0.007	1.7	0.1
Sr	73	6	116	7	105	8
Ta			0.020	0.001		
Tb	0.10	0.01	0.009	0.001	0.25	0.02
Th	1.05	0.13	0.159	0.001	3.1	0.2
Ti	456	65			755	30
U	0.58	0.05			1.5	0.2
W	0.51	0.13			14	2
Yb			0.035	0.001		
Zr	25	6			29	6

10 Metrological traceability and commutability

10.1 Metrological traceability

Identity

Ca, Mg, Na, K, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V and Cl are chemically clearly defined substances. The participants used different methods for the sample preparation as well as for the final determination, demonstrating absence of measurement bias. The analyte is therefore structurally defined and independent of the measurement method.

GCV and the amount of volatile matter, ash, S, C, H and N in this case are method-defined analytes and can only be obtained by following the following procedure specified in ISO 1928 or ASTM D5865 (GCV, NCV), ISO 562 and ISO 5071 (volatile matter), ISO 1171 or ASTM D3174 (ash), ISO 609 ISO TC12902 or ASTM D5373 (C), ISO 25941 or ASTM D5373 (H) and ISO 333, ISO 29541 or ASTM D5373 (N). Adherence to these procedures was confirmed by agreement of the laboratories' results with the assigned value for the CRM that was used as quality control sample. The assigned value is therefore operationally defined by method.

Quantity value

Only validated methods were used for the determination of the assigned values of trace elements. Different calibrants/calibrants of known purity and specified traceability of their assigned values were used and all relevant input parameters were calibrated. The individual results are therefore traceable to the SI, as it is confirmed by the agreement among the technically accepted datasets, as well. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI, as well.

Traceability of the obtained results of the operationally-defined measurands is based on the traceability of all relevant input factors. Instruments in individual laboratories were verified and calibrated with tools ensuring traceability to the SI. Consistency in the interlaboratory comparison demonstrates that all relevant input factors were covered. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI as well.

10.2 Commutability

Many measurement procedures include one or more steps, which are selecting specific (or specific groups) of analytes from the sample for the subsequent steps of the whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all the analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is nowadays summarised in a concept called 'commutability of a reference material'. There are various definitions expressing this concept. For instance, the CSLI Guideline C-53A [25] recommends the use of the following definition for the term *commutability*:

> "The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and, thus, is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established in such cases, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrator.

ERM-EF411, EF412 and EF413 were produced from actual coals and, like other coal samples in a laboratory, still need to be processed further for analysis. The materials are commutable, as they are virtually identical to actual samples.

11 Instructions for use

11.1 Storage conditions

The materials shall be stored at 18 °C ± 5 ° in the dark. Care shall be taken to avoid change of the moisture content once the units are open.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

11.2 Safety and protection for the environment

The usual laboratory safety measures apply.

11.3 Preparation and handling of the material

Before using ERM-EF411 or ERM-EF413, the complete contents of each sachet shall be ground to < 250 μm. All analytical samples shall be taken from this ground material, sampling of the coarse material is not recommended and will lead to higher variation of results due to intrinsic inhomogeneity. ERM-EF412 can be used "as is".

The ground samples shall be left to equilibrate with the laboratory atmosphere before taking analytical subsamples.
Note: Due to the drying process, samples of ERM-EF411 and ERM-EF412 may take up water during this equilibration process.

11.3.1 Minimum sample intake

The minimum sample intake representative is:

Hg: 30 mg

All other minor and trace elements: 200 mg

GCV according to ISO 1928 and ASTM D5865: 1 g

Volatile matter according to ISO 562 or ISO 5071-1: 1 g

Ash according to ISO 1171/ASTM D3174: 1 g

S according to ISO 19579/ASTM D4239: 0.2 g

C, H, N: 70 mg

11.3.2 Dry mass correction

Dry mass determination shall be carried out according to ISO 5068-2 (brown coal); ISO 11722 (hard coal); ISO 687 (coke) or ASTM D3173:

A separate portion of at least 1 g of the ground and equilibrated material shall be dried in an oven at 105 – 110 °C until constant mass (separate weighing should not differ by more than 5 mg) is attained. For ERM-EF412, this drying shall be done in an oxygen-free atmosphere.

11.4 Use of the certified value

The main purpose of these materials is to assess method performance, i.e. for checking accuracy of analytical results/calibration. As any reference material, they can also be used for control charts or validation studies.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [26].

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_m).
- Combine measurement uncertainty (u_m) with the uncertainty of the certified value (u_{CRM}): $u_\Delta = \sqrt{u_m^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_Δ) from the combined uncertainty (u_Δ) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %
- If $\Delta_m \leq U_\Delta$ then there is no significant difference between the measurement result and the certified value, at a confidence level of about 95 %.

Use as a calibrant

It is not recommended to use this matrix material as calibrant. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

Use in quality control charts

The materials can be used for quality control charts. Different CRM-units will give the same results as heterogeneity was included in the uncertainties of the certified values.

12 Acknowledgments

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13 References

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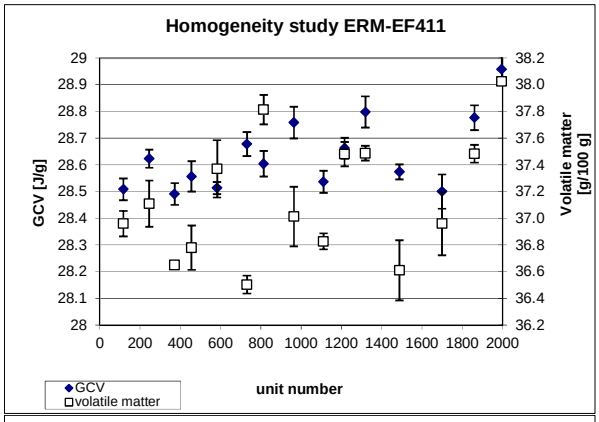
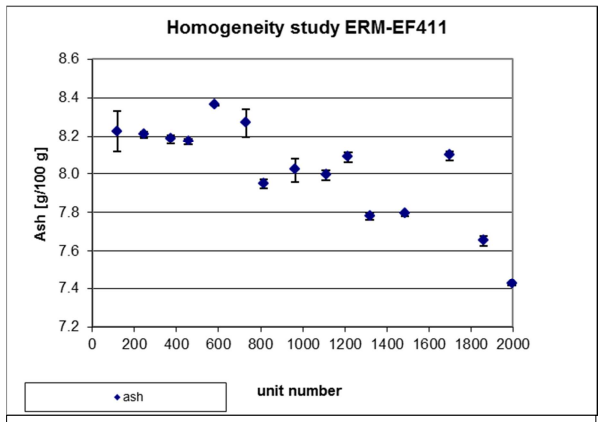
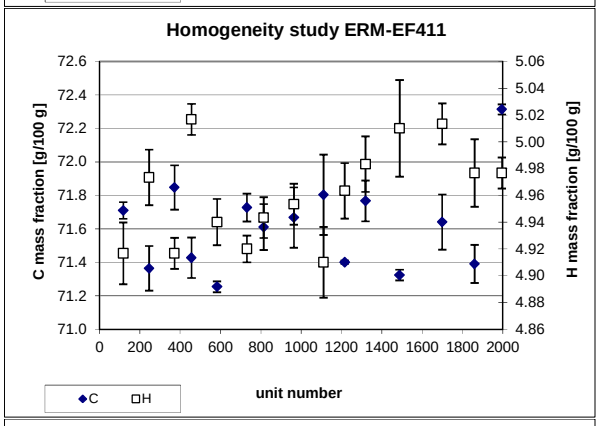
Annexes

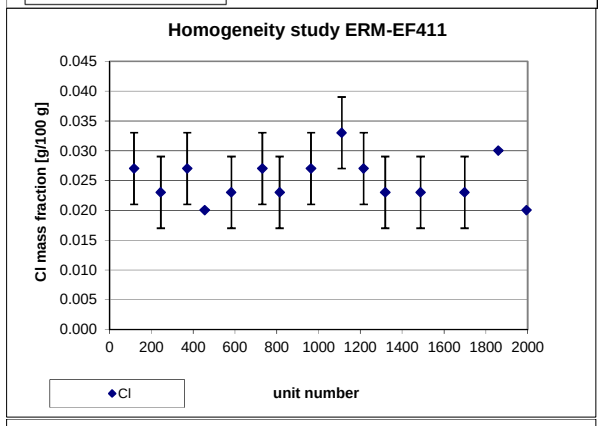
Annex A.1: Homogeneity data ERM-EF411

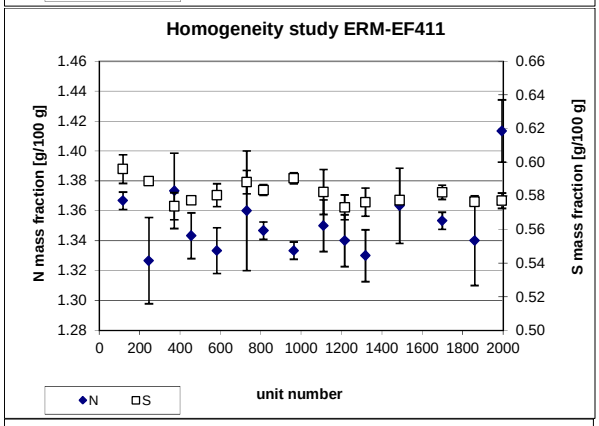
Shown are the average results and standard deviations of the three (initial homogeneity study) or two (long-term stability study) replicates of each unit. Where applicable, the results corrected for analytical trend are shown.

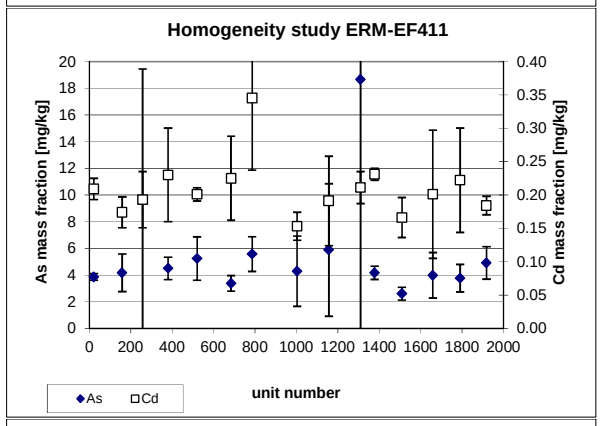


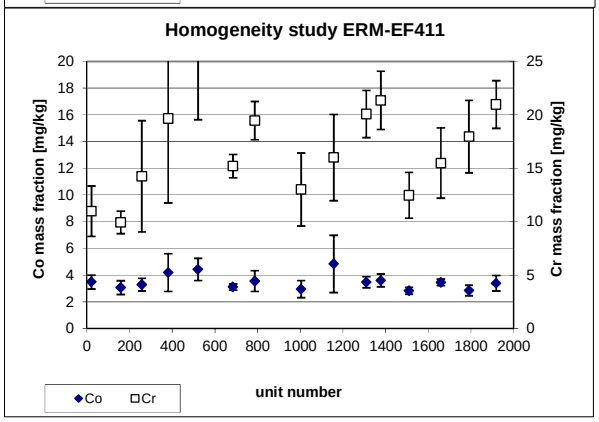


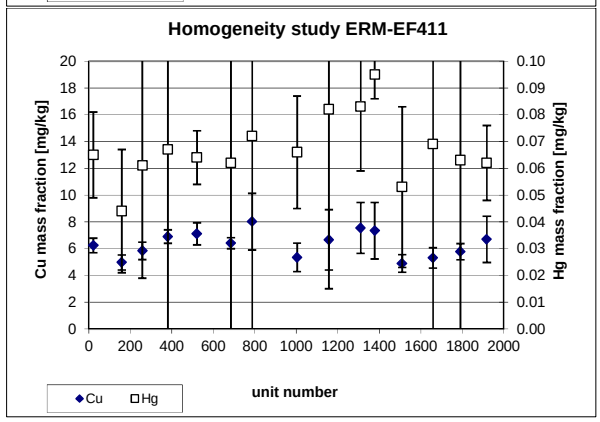


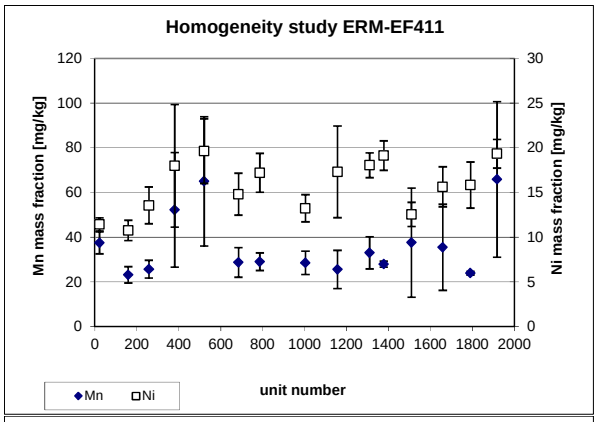


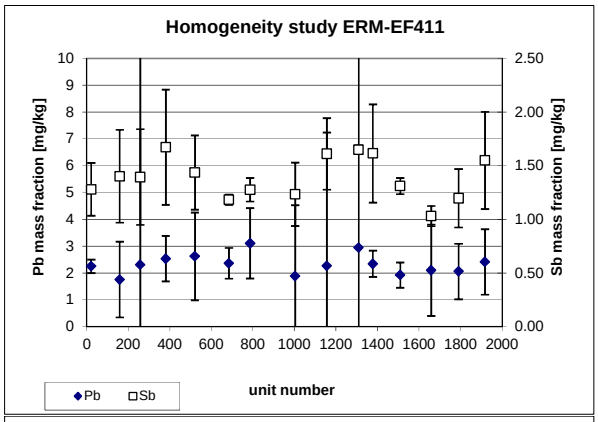


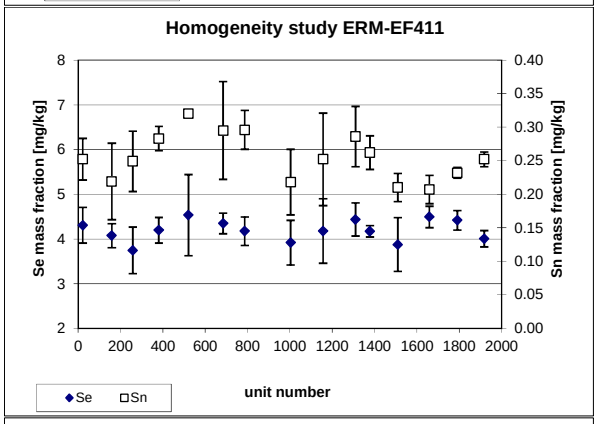


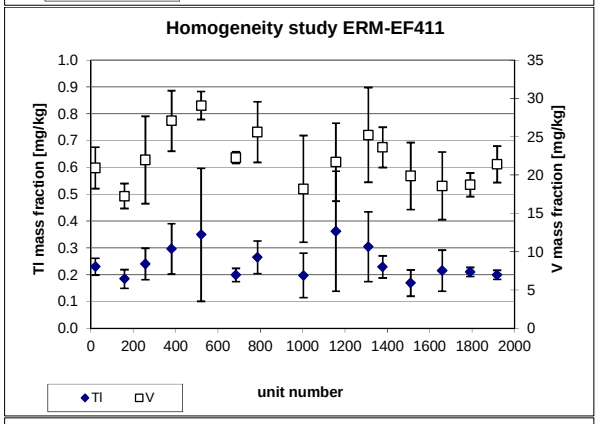


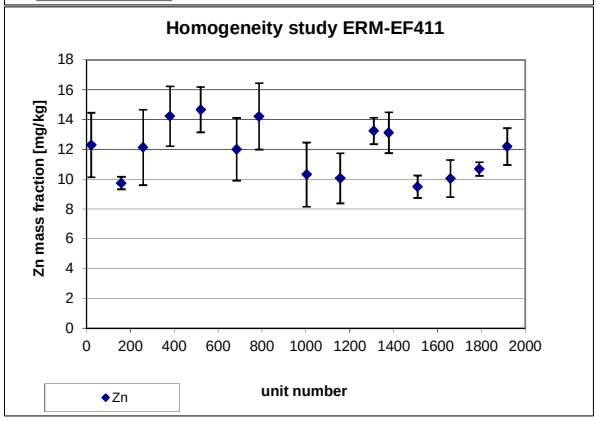


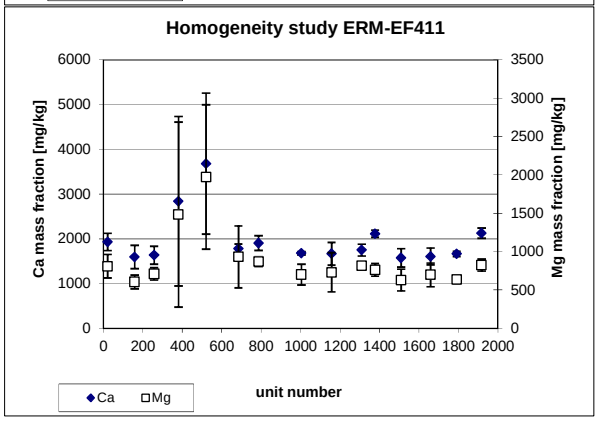

Homogeneity study ERM-EF411
Mn mass fraction [mg/kg]
Ni mass fraction [mg/kg]
Mn
Ni
unit number

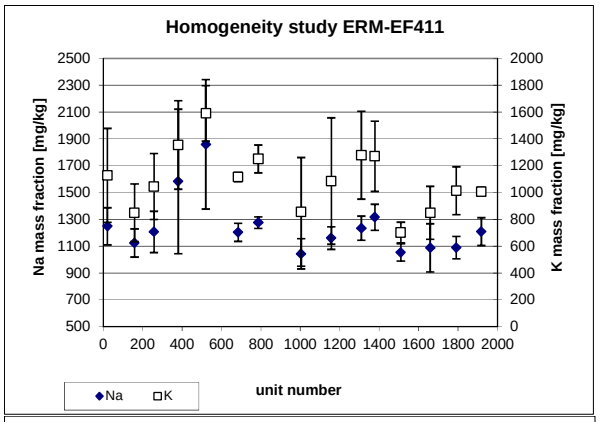

Homogeneity study ERM-EF411
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
Pb
Sb
unit number

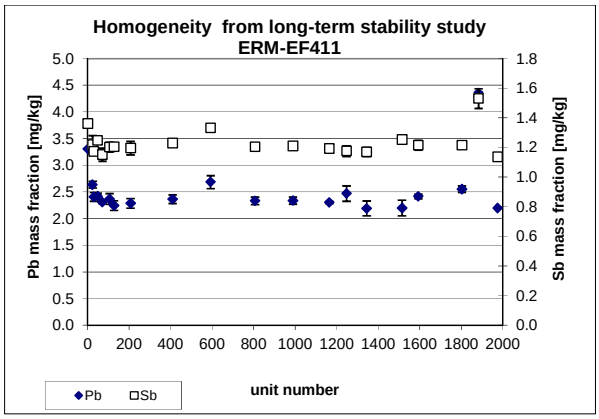

Homogeneity study ERM-EF411
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
Se
Sn
unit number

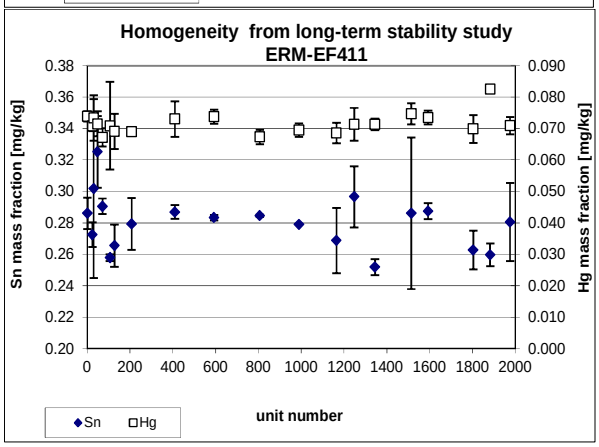

Homogeneity study ERM-EF411
Tl mass fraction [mg/kg]
V mass fraction [mg/kg]
Tl
V
unit number


Homogeneity study ERM-EF411
Zn mass fraction [mg/kg]
Zn
unit number


Homogeneity study ERM-EF411
Ca mass fraction [mg/kg]
Mg mass fraction [mg/kg]
Ca
Mg
unit number

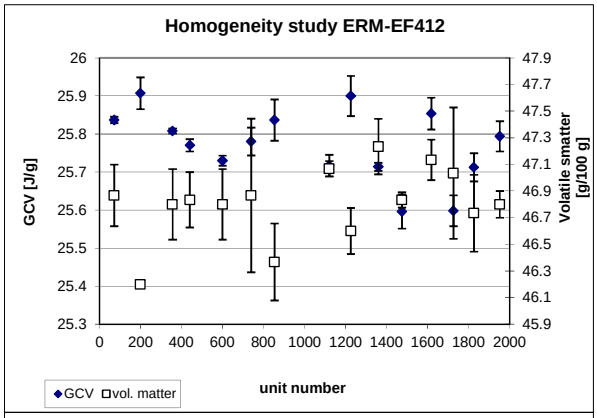

Homogeneity study ERM-EF411
Na mass fraction [mg/kg]
K mass fraction [mg/kg]
unit number
Na
K

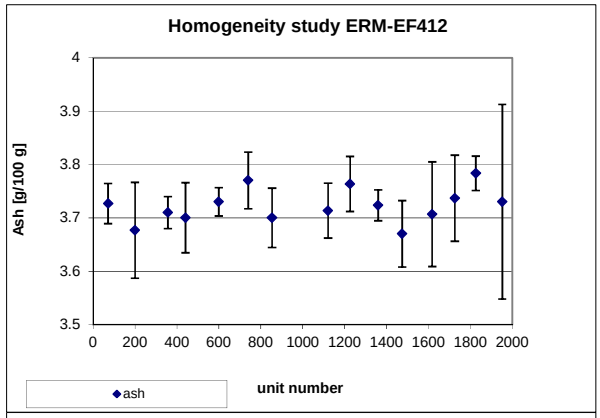

Homogeneity from long-term stability study
ERM-EF411
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
unit number
Pb
Sb

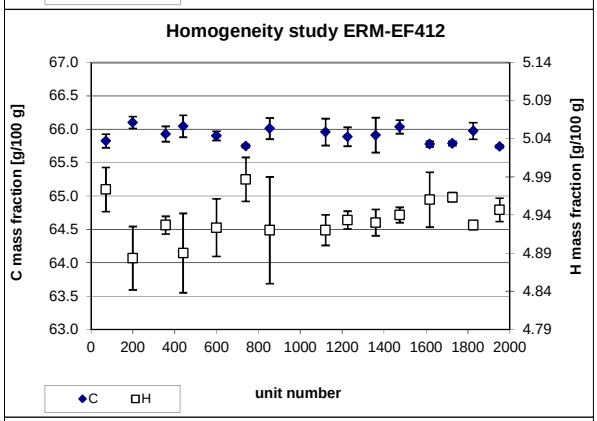

Homogeneity from long-term stability study
ERM-EF411
Sn mass fraction [mg/kg]
Hg mass fraction [mg/kg]
unit number
Sn
Hg

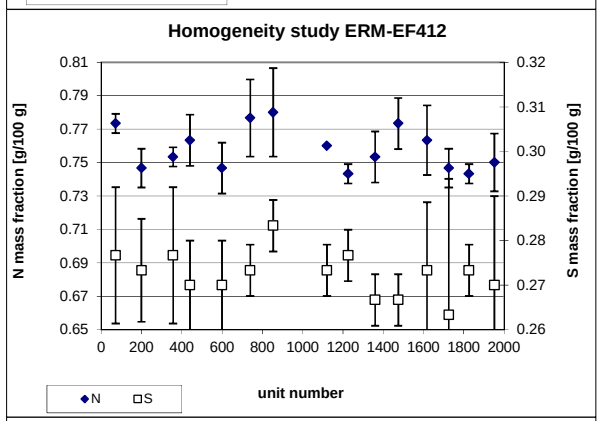
Annex A.2: Homogeneity data ERM-EF412

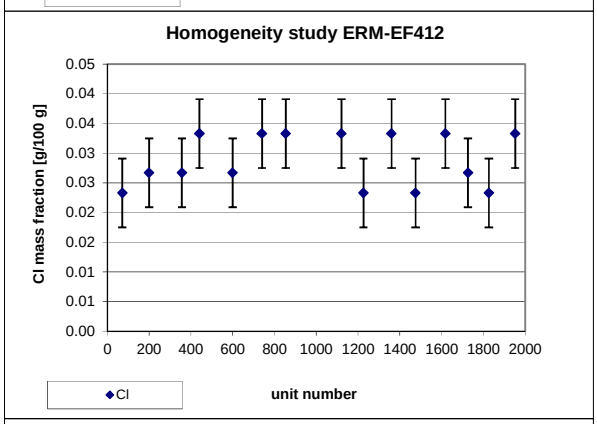
Shown are the average results after correction for potential analytical trends and standard deviations of the three replicates of each unit.

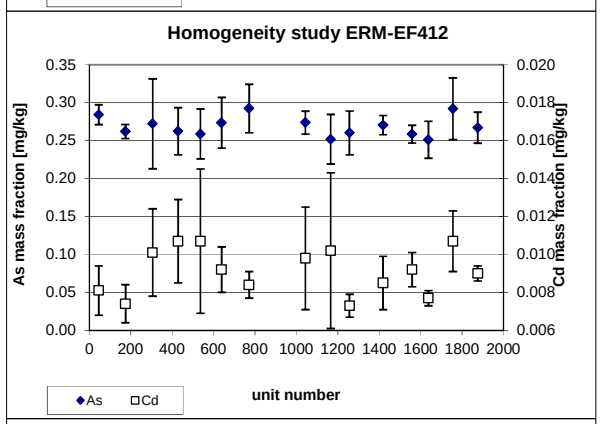


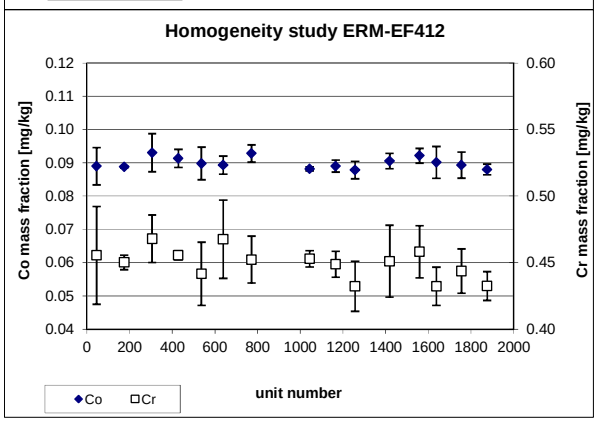


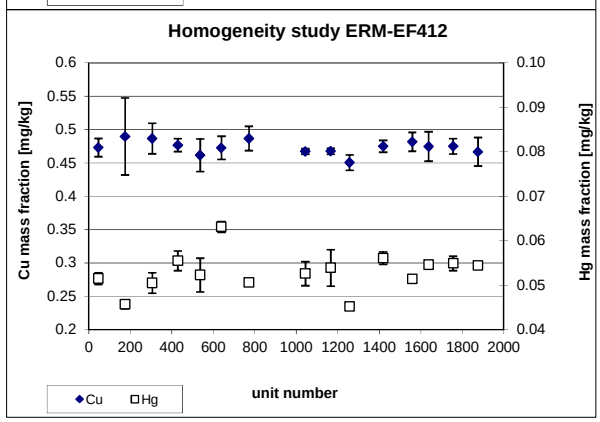


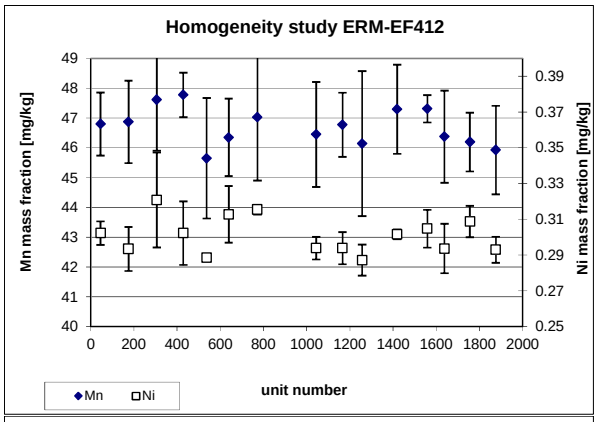


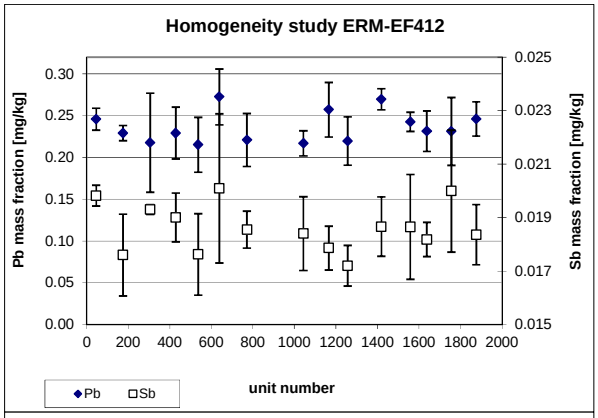


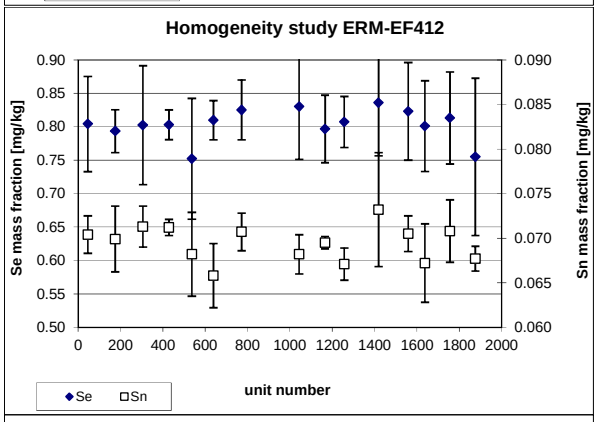


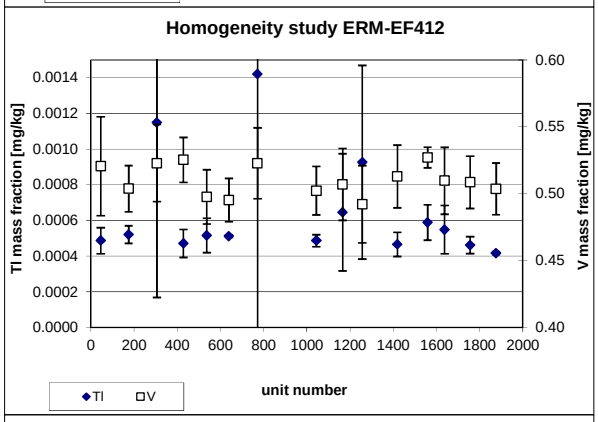


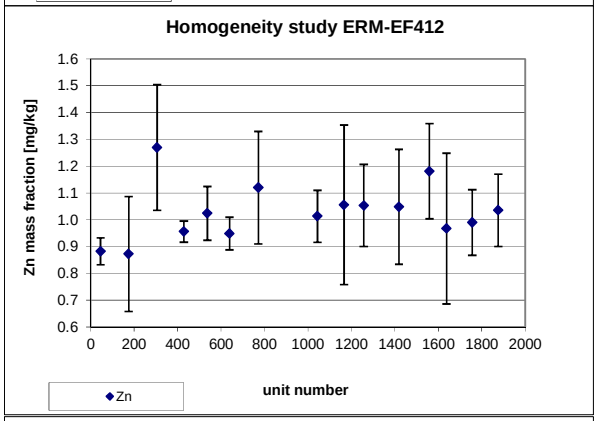


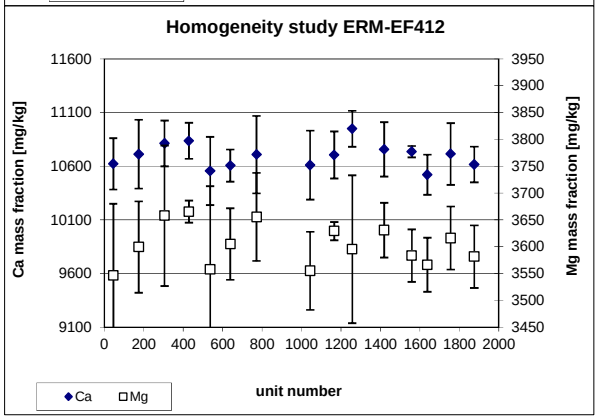

Homogeneity study ERM-EF412
Mn mass fraction [mg/kg]
Ni mass fraction [mg/kg]
unit number
Mn
Ni

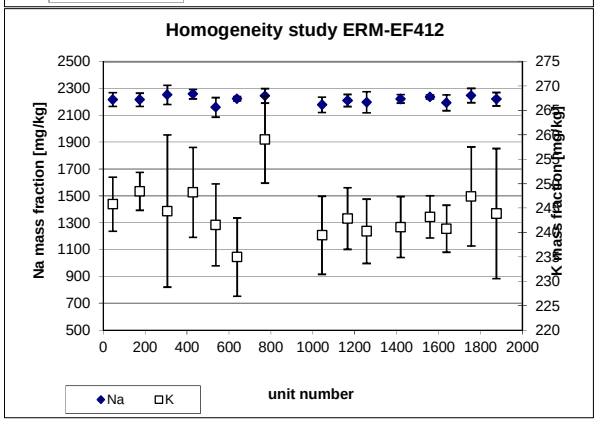

Homogeneity study ERM-EF412
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
unit number
Pb
Sb


Homogeneity study ERM-EF412
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
unit number
Se
Sn


Homogeneity study ERM-EF412
Tl mass fraction [mg/kg]
V mass fraction [mg/kg]
unit number
Tl
V

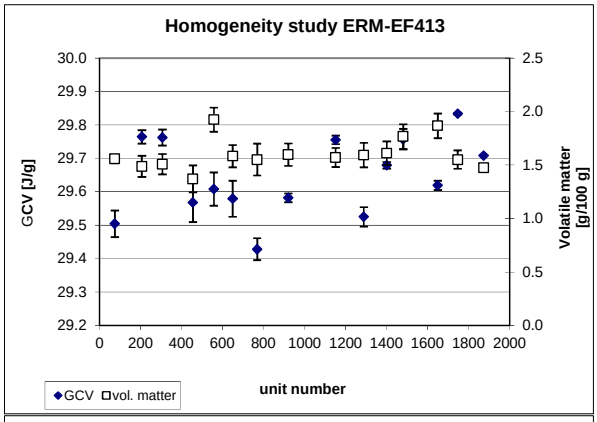

Homogeneity study ERM-EF412
Zn mass fraction [mg/kg]
unit number
Zn

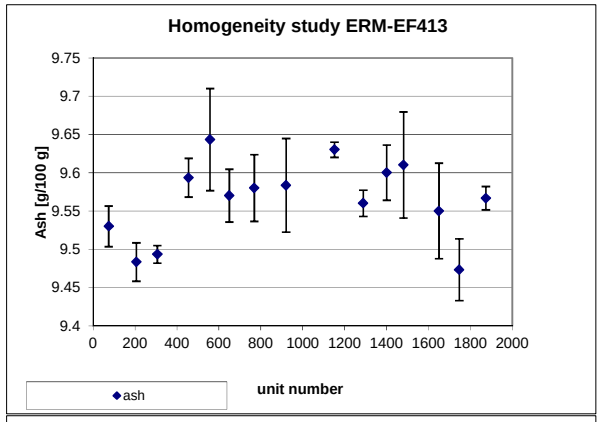

Homogeneity study ERM-EF412
Ca mass fraction [mg/kg]
Mg mass fraction [mg/kg]
unit number
Ca
Mg

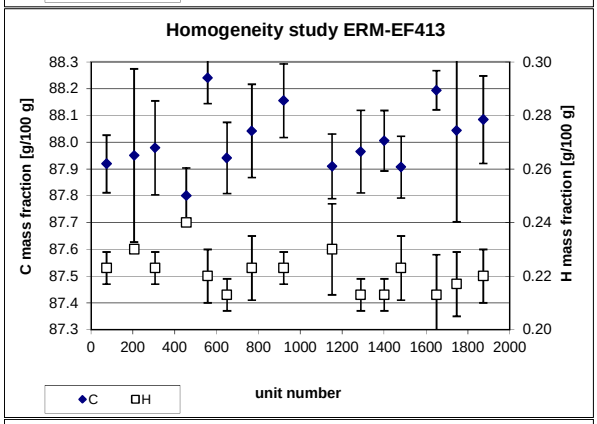

Homogeneity study ERM-EF412
Na mass fraction [mg/kg]
K mass fraction [mg/kg]
unit number
Na
K

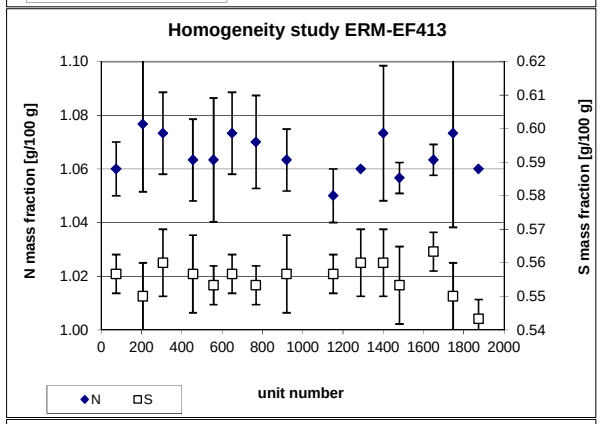
Annex A.3: Homogeneity data ERM-EF413

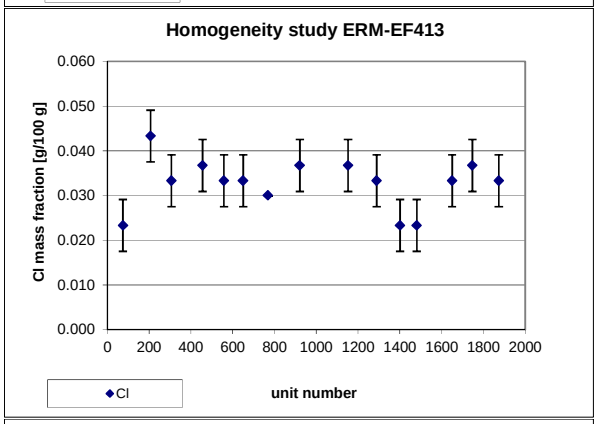
Shown are the average results after correction for potential analytical trends and standard deviations of the three replicates of each unit.

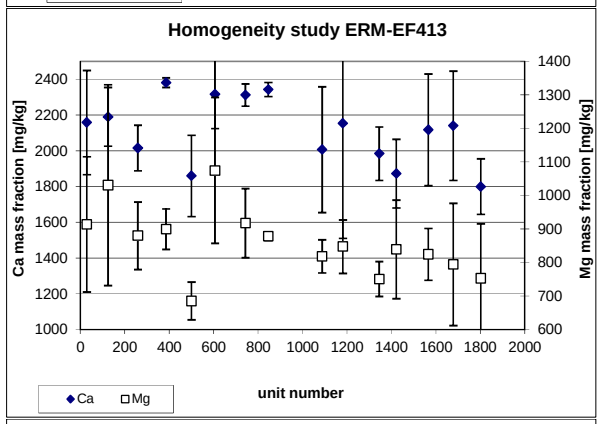


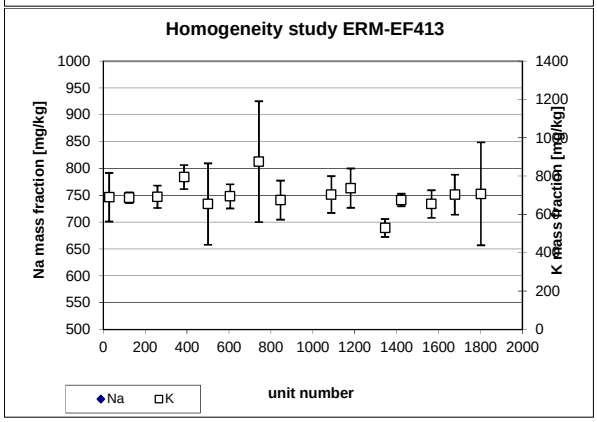


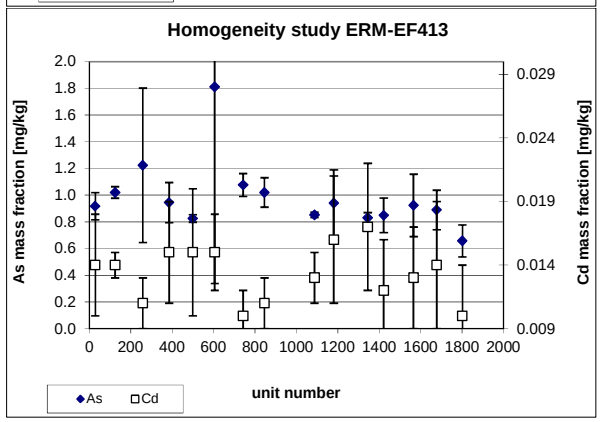


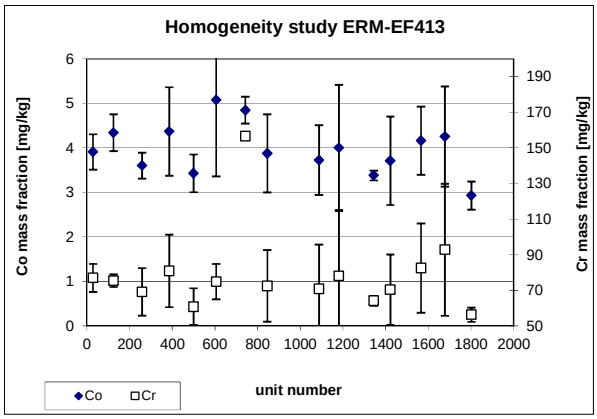


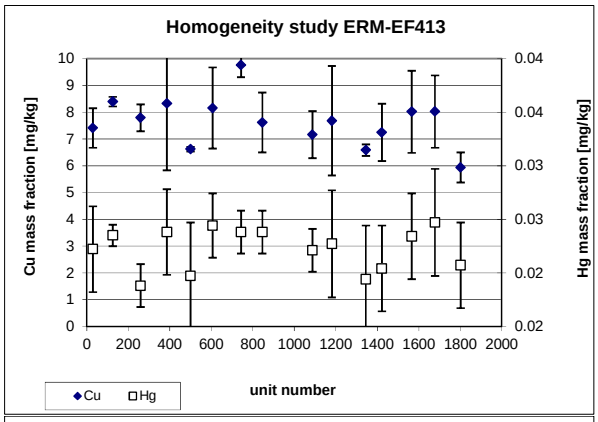


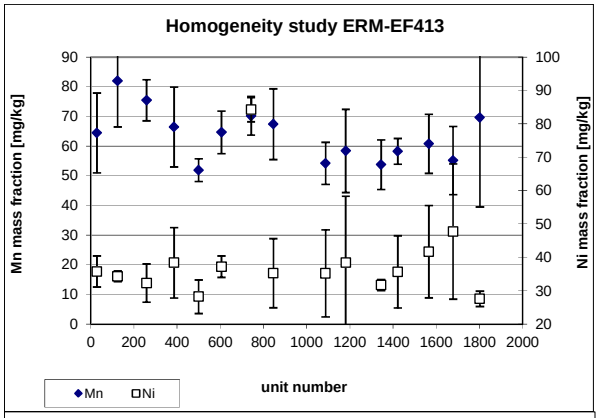


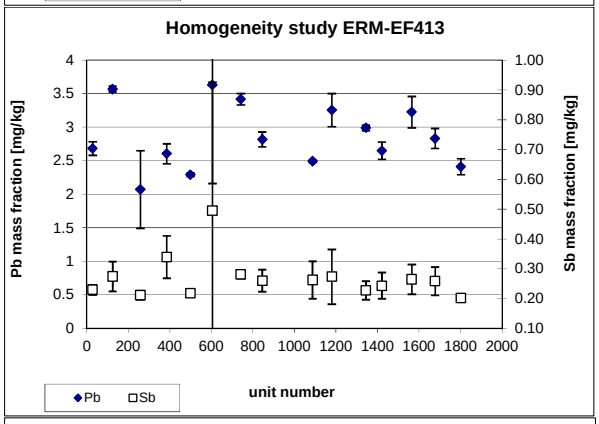


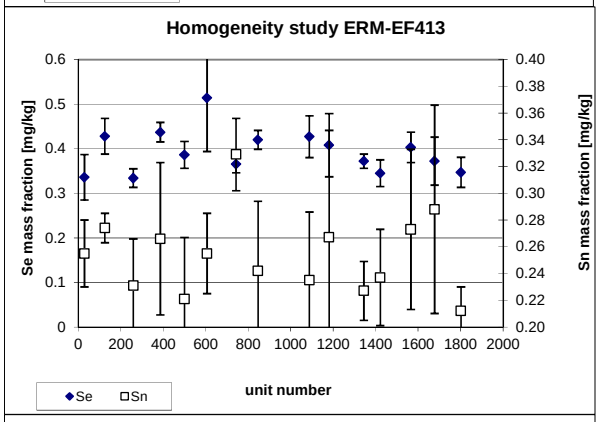


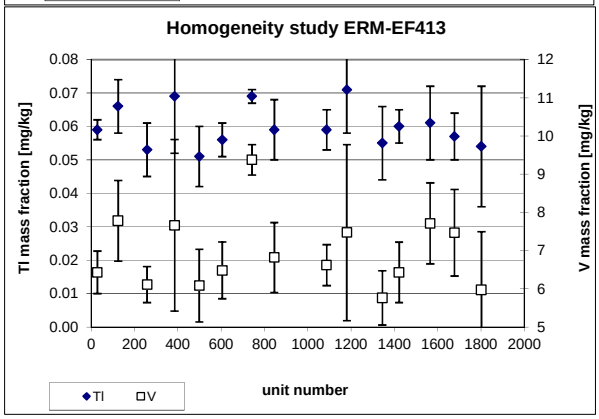

Homogeneity study ERM-EF413
Co mass fraction [mg/kg]
Cr mass fraction [mg/kg]
unit number
Co
Cr

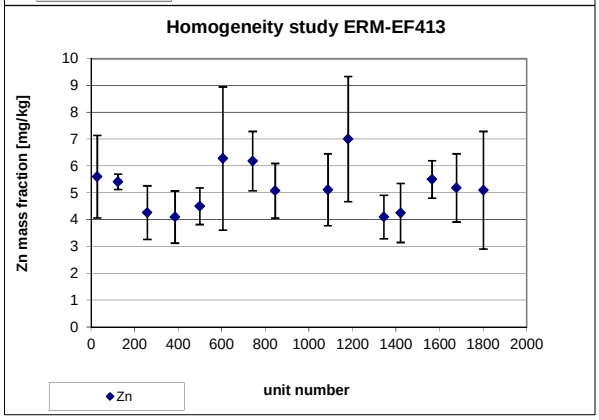

Homogeneity study ERM-EF413
Cu mass fraction [mg/kg]
Hg mass fraction [mg/kg]
unit number
Cu
Hg

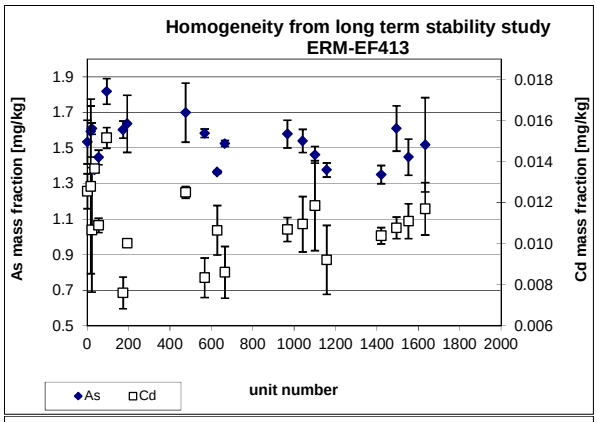

Homogeneity study ERM-EF413
Mn mass fraction [mg/kg]
Ni mass fraction [mg/kg]
unit number
Mn
Ni

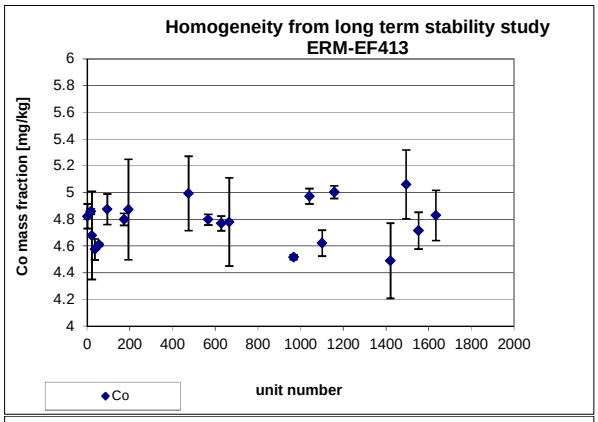

Homogeneity study ERM-EF413
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
unit number
Pb
Sb

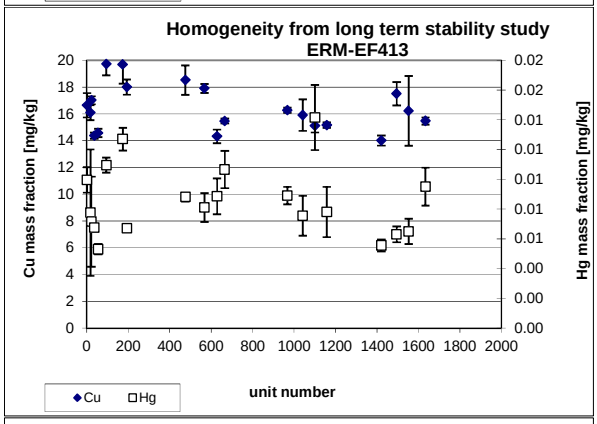

Homogeneity study ERM-EF413
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
unit number
Se
Sn

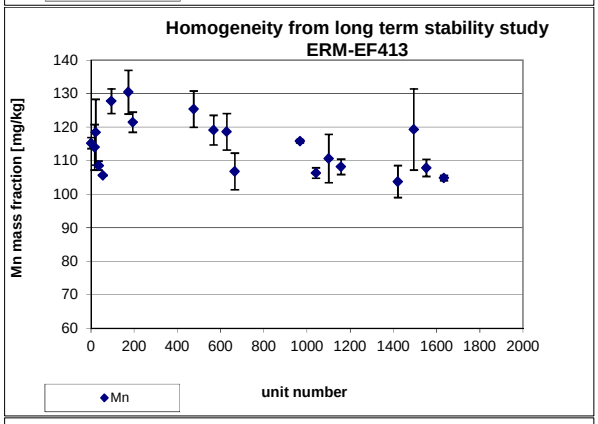

Homogeneity study ERM-EF413
Tl mass fraction [mg/kg]
V mass fraction [mg/kg]
unit number
Tl
V

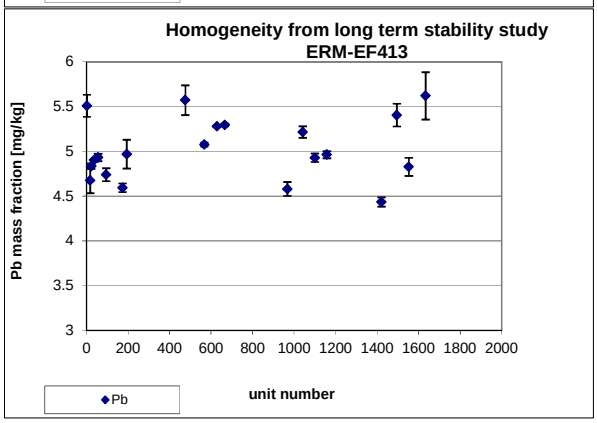

Homogeneity study ERM-EF413
Zn mass fraction [mg/kg]
unit number
Zn

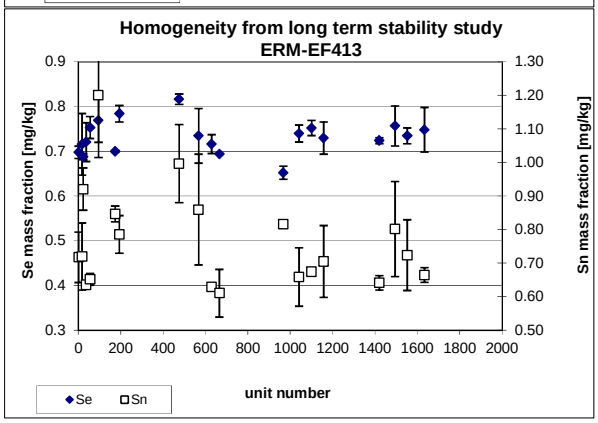

Homogeneity from long term stability study
ERM-EF413
As mass fraction [mg/kg]
Cd mass fraction [mg/kg]
unit number
As
Cd

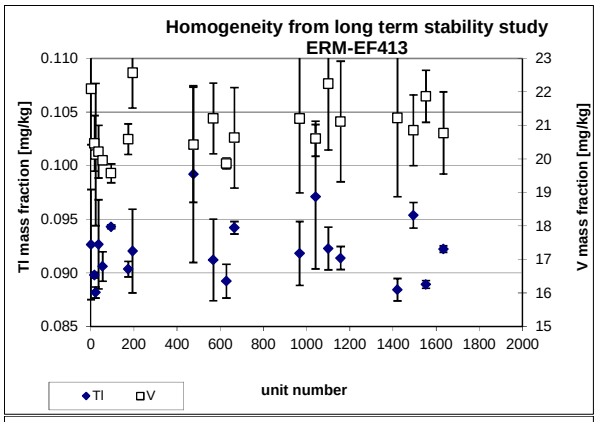

Homogeneity from long term stability study
ERM-EF413
Co mass fraction [mg/kg]
unit number
Co

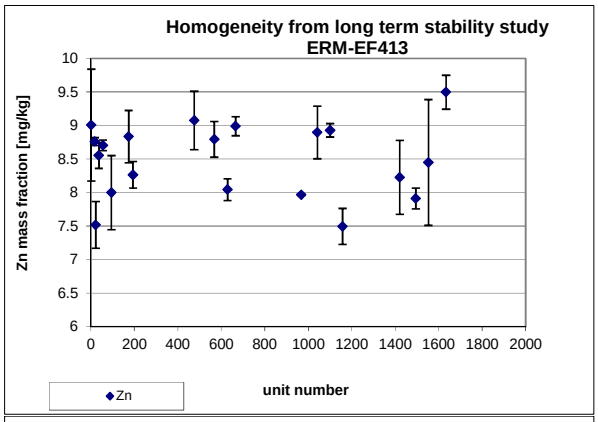

Homogeneity from long term stability study
ERM-EF413
Cu mass fraction [mg/kg]
Hg mass fraction [mg/kg]
unit number
Cu
Hg

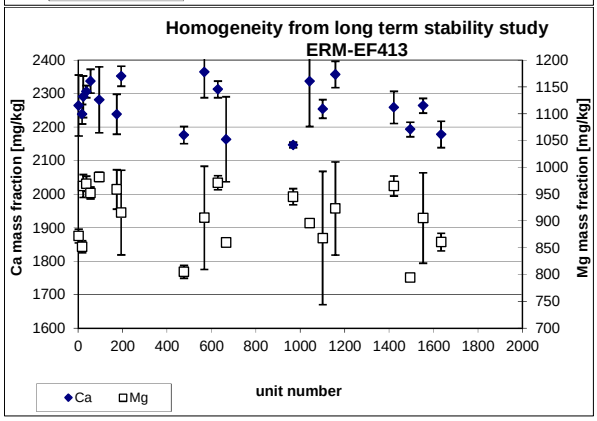

Homogeneity from long term stability study
ERM-EF413
Mn mass fraction [mg/kg]
unit number
Mn

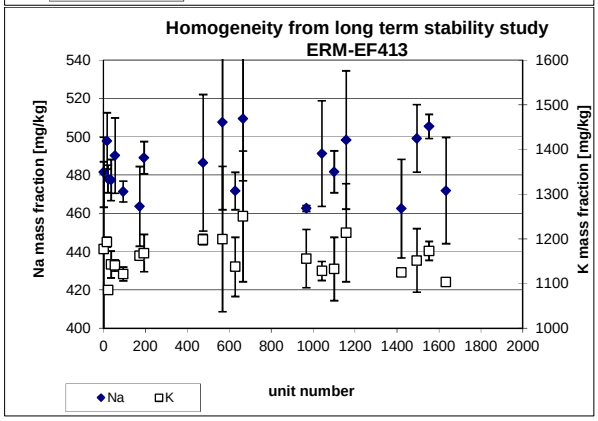

Homogeneity from long term stability study
ERM-EF413
Pb mass fraction [mg/kg]
unit number
Pb


Homogeneity from long term stability study
ERM-EF413
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
unit number
Se
Sn


Homogeneity from long term stability study
ERM-EF413
Tl mass fraction [mg/kg]
V mass fraction [mg/kg]
unit number
Tl
V

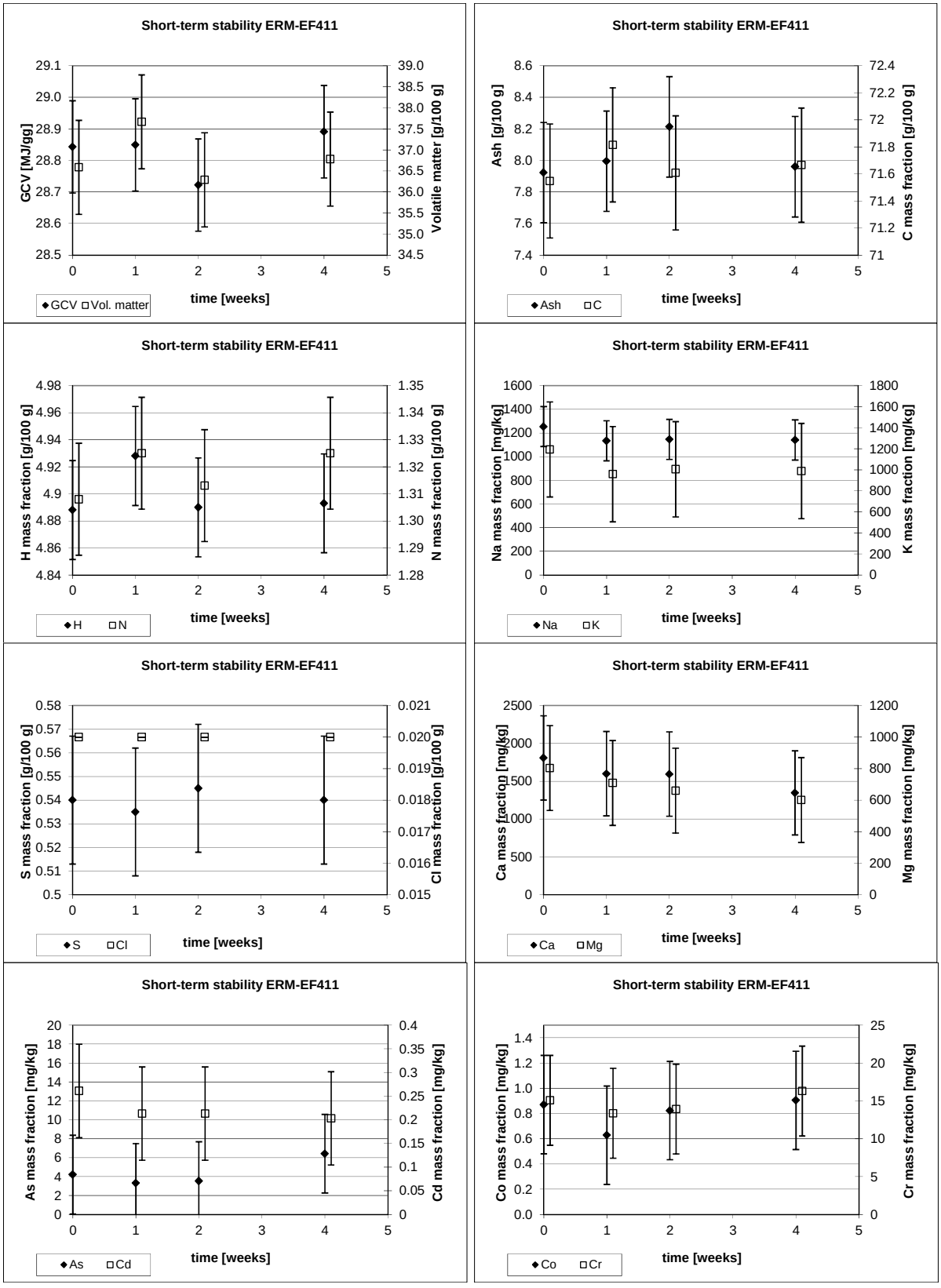

Homogeneity from long term stability study
ERM-EF413
Zn mass fraction [mg/kg]
unit number
Zn

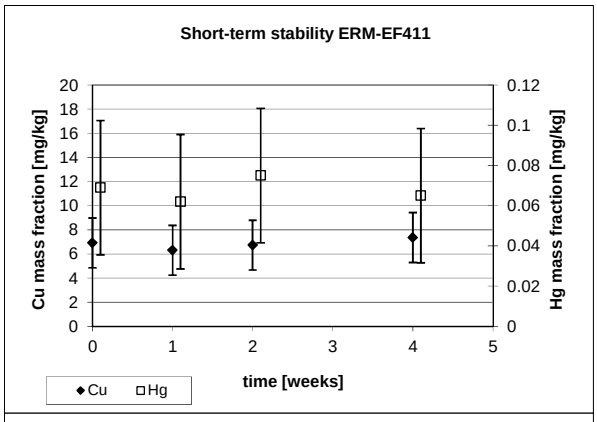

Homogeneity from long term stability study
ERM-EF413
Ca mass fraction [mg/kg]
Mg mass fraction [mg/kg]
unit number
Ca
Mg

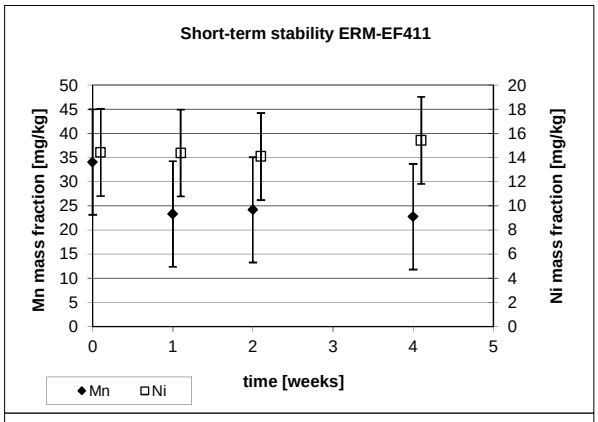

Homogeneity from long term stability study
ERM-EF413
Na mass fraction [mg/kg]
K mass fraction [mg/kg]
unit number
Na
K

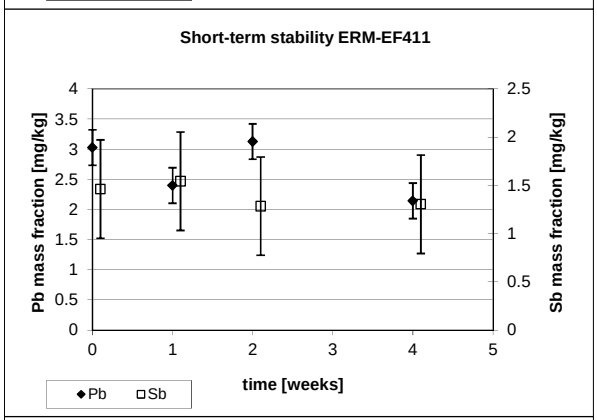
Annex B.1: Short-term stability data ERM-EF411

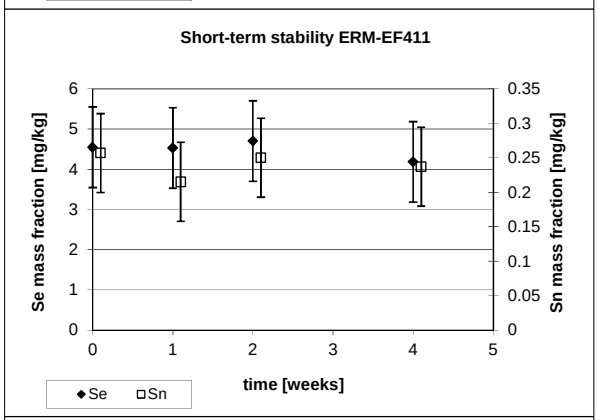
The averages and their 95 % confidence intervals of the four replicates are shown. Confidence intervals are based on the pooled repeatability standard deviation as obtained by ANOVA. The data points for the different elements were separated graphically to facilitate reading. No error bars can be given for Cl, as all results were identical.

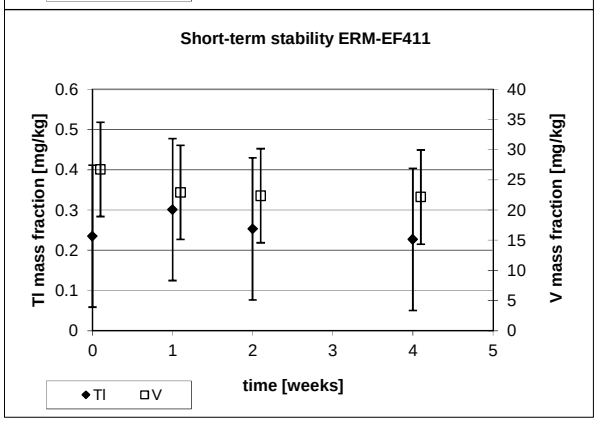


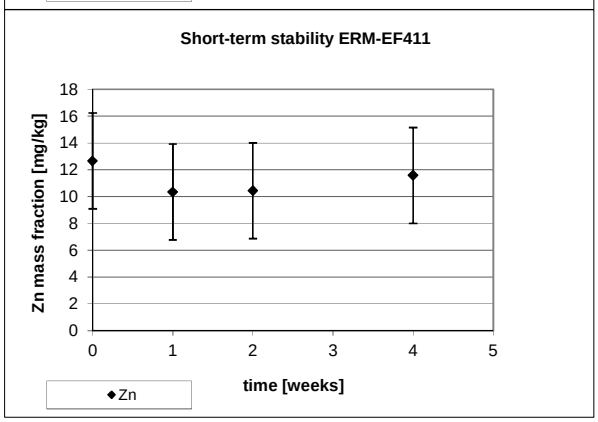

Short-term stability ERM-EF411
Cu mass fraction [mg/kg]
Hg mass fraction [mg/kg]
time [weeks]
Cu
Hg


Short-term stability ERM-EF411
Mn mass fraction [mg/kg]
Ni mass fraction [mg/kg]
time [weeks]
Mn
Ni


Short-term stability ERM-EF411
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
time [weeks]
Pb
Sb

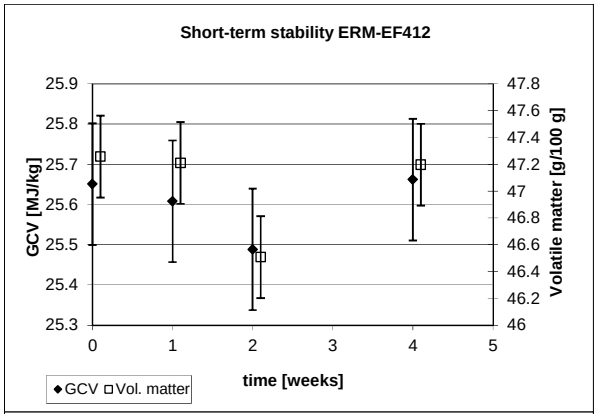

Short-term stability ERM-EF411
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
time [weeks]
Se
Sn

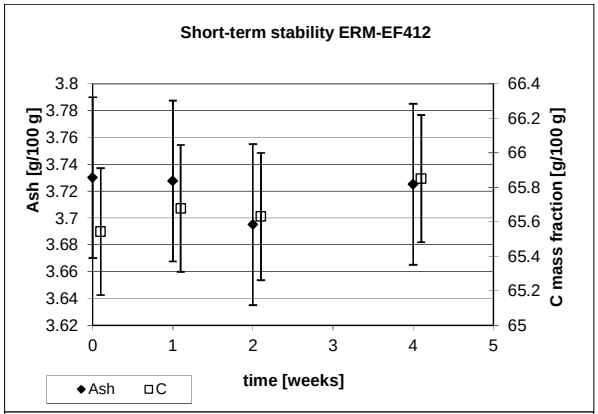

Short-term stability ERM-EF411
Tl mass fraction [mg/kg]
V mass fraction [mg/kg]
time [weeks]
Tl
V

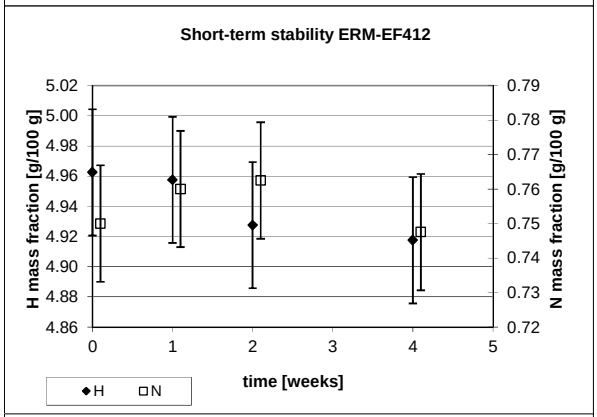

Short-term stability ERM-EF411
Zn mass fraction [mg/kg]
time [weeks]
Zn

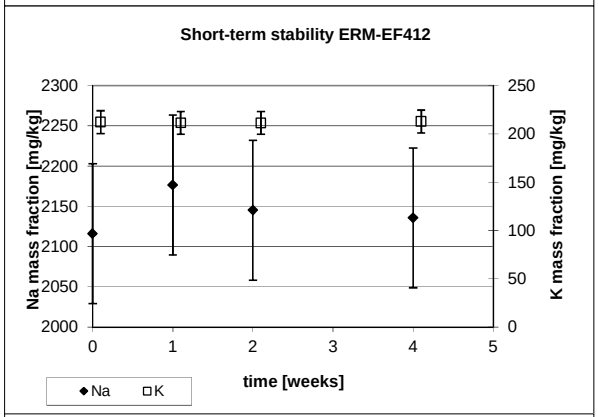
Annex B.2: Short-term stability data ERM-EF412

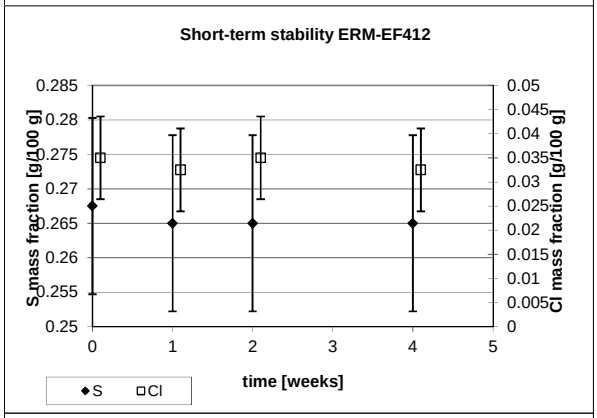
The averages and their 95 % confidence intervals of the four replicates are shown. Confidence intervals are based on the pooled repeatability standard deviation as obtained by ANOVA. The data points for the different elements were separated graphically to facilitate reading.

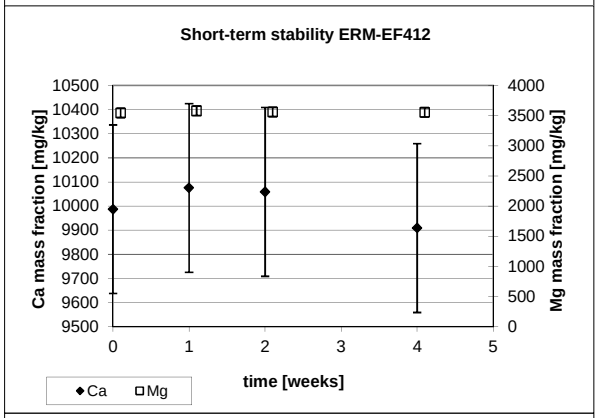


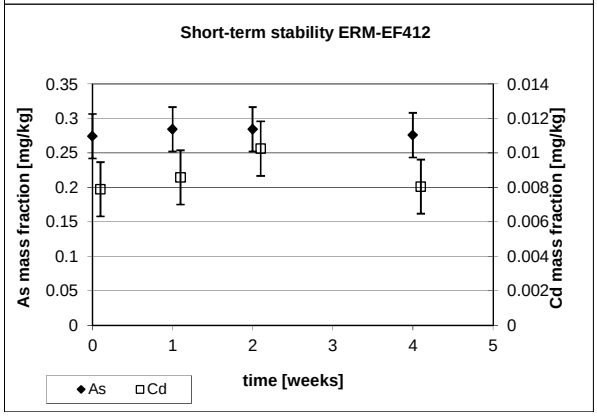


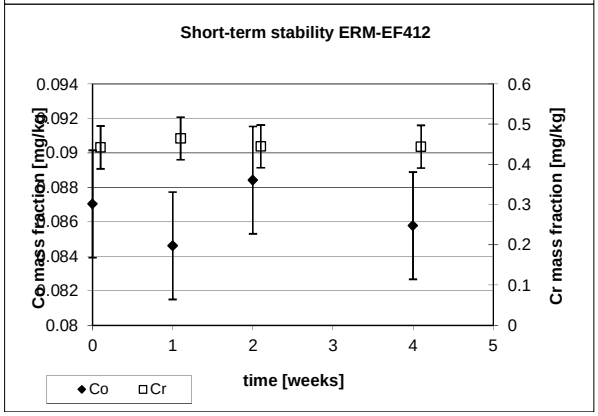


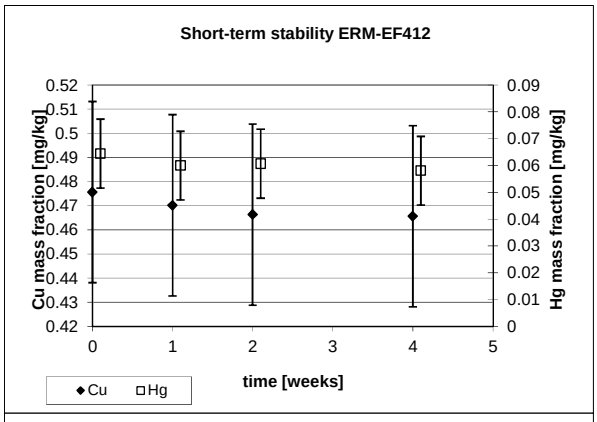


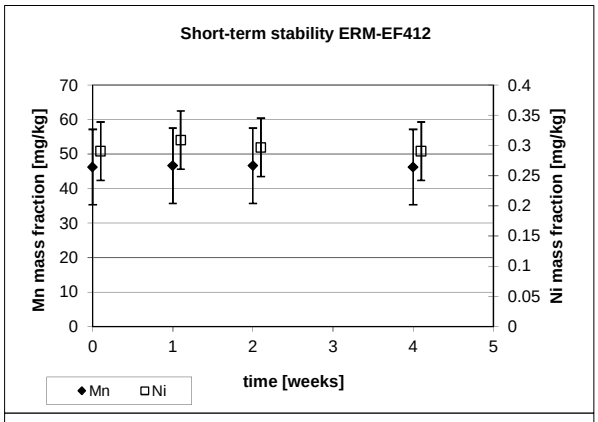


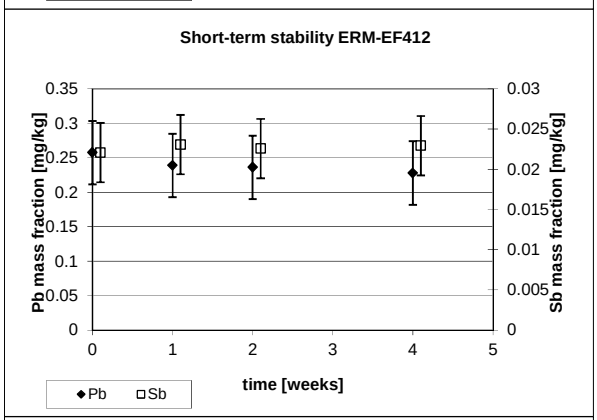


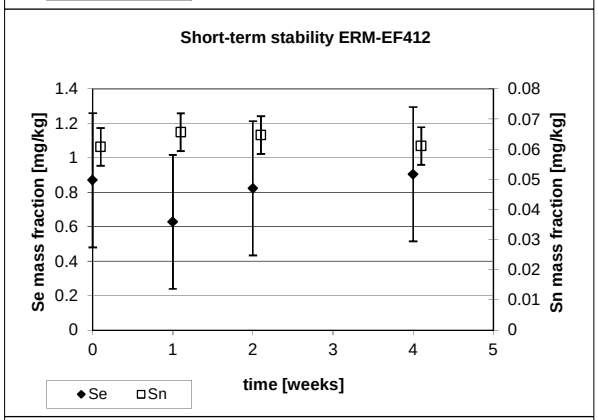


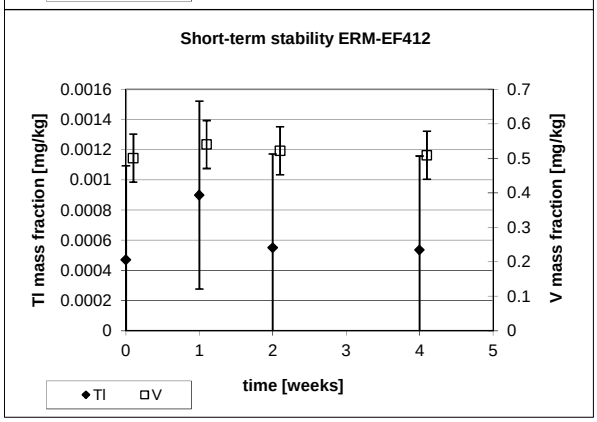


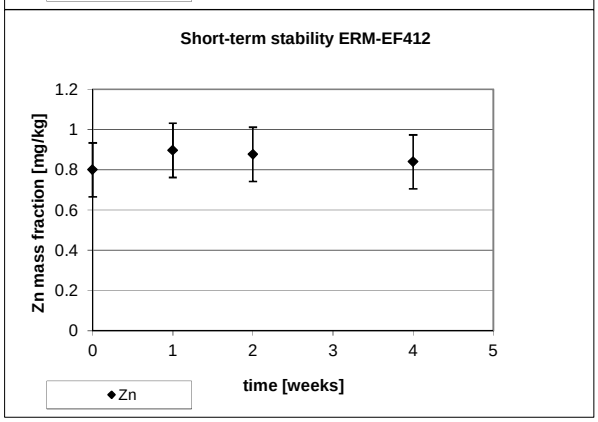

Short-term stability ERM-EF412
Cu mass fraction [mg/kg]
Hg mass fraction [mg/kg]
time [weeks]
Cu
Hg


Short-term stability ERM-EF412
Mn mass fraction [mg/kg]
Ni mass fraction [mg/kg]
time [weeks]
Mn
Ni


Short-term stability ERM-EF412
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
time [weeks]
Pb
Sb

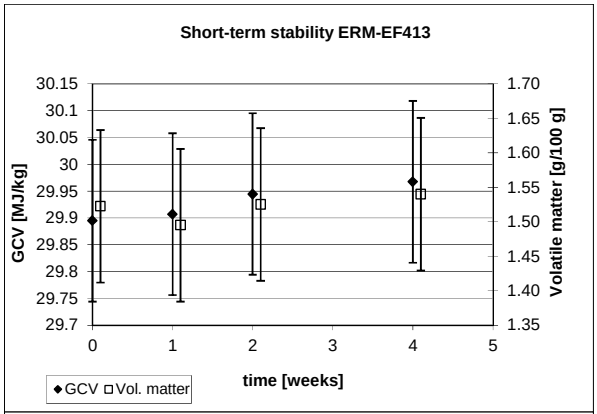

Short-term stability ERM-EF412
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
time [weeks]
Se
Sn

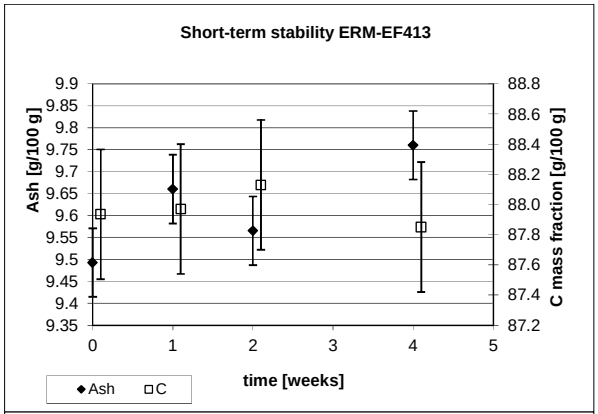

Short-term stability ERM-EF412
Tl mass fraction [mg/kg]
V mass fraction [mg/kg]
time [weeks]
Tl
V

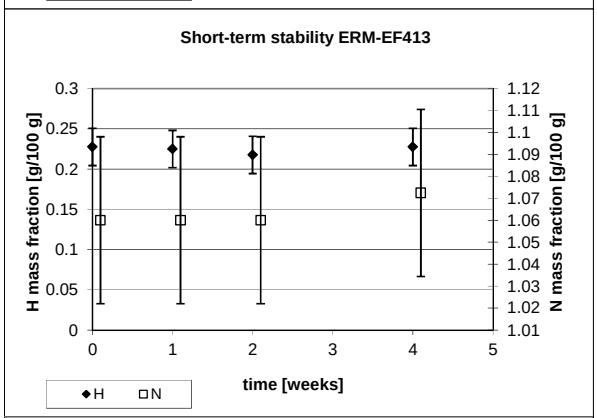

Short-term stability ERM-EF412
Zn mass fraction [mg/kg]
time [weeks]
Zn

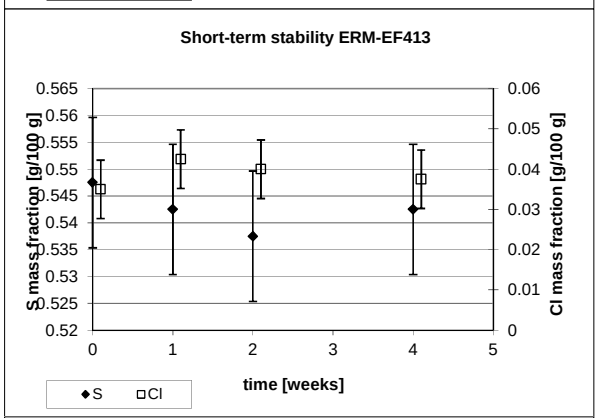
Annex B.3: Short-term stability data ERM-EF413

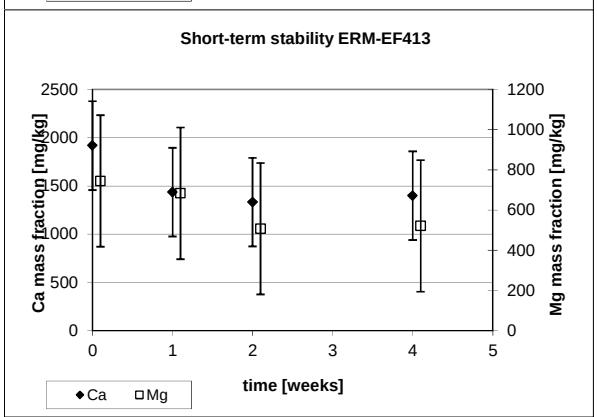
The averages and their 95 % confidence intervals of the four replicates are shown. Confidence intervals are based on the pooled repeatability standard deviation as obtained by ANOVA. The data points for the different elements were separated graphically to facilitate reading.

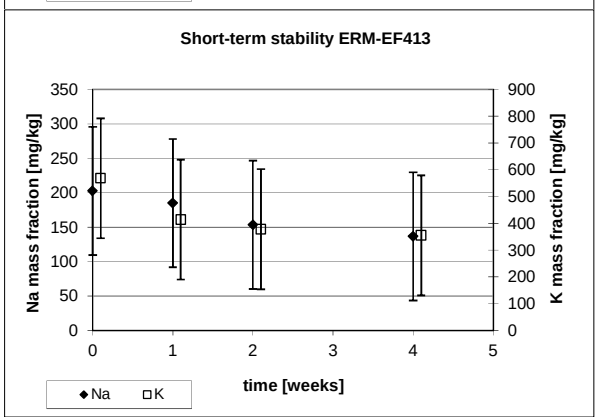


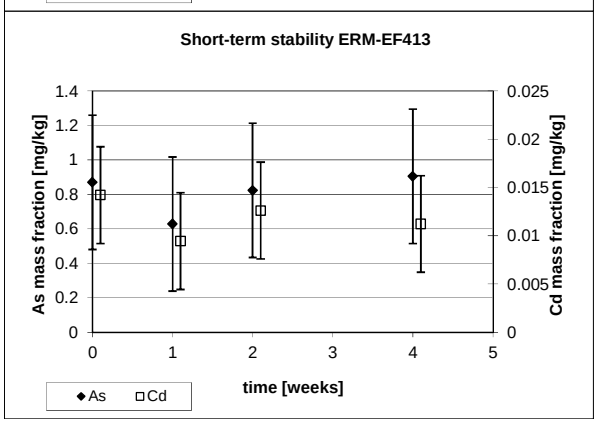


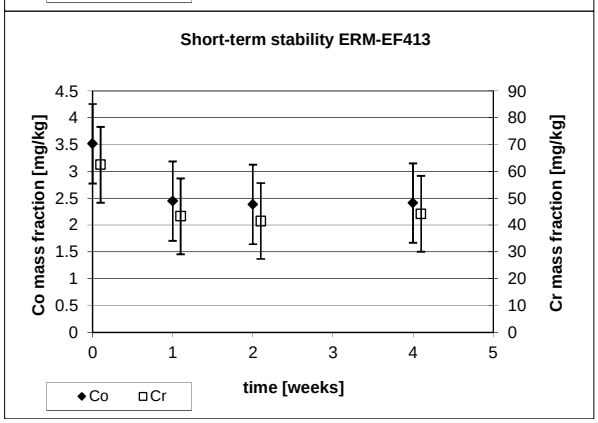


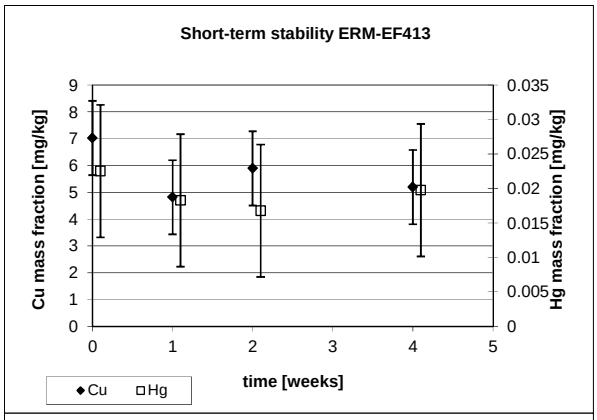


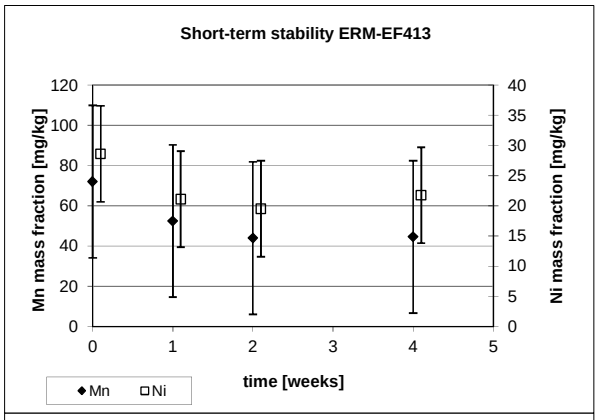


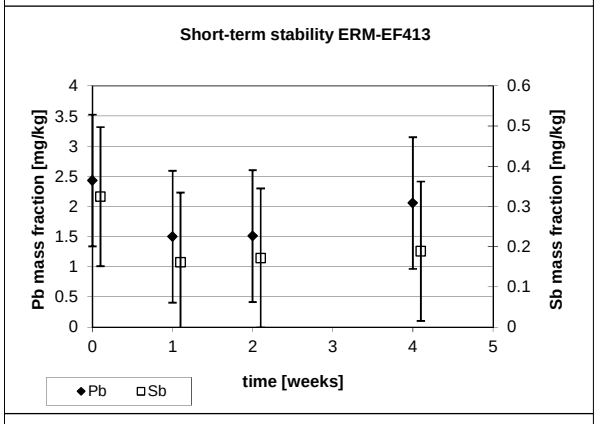


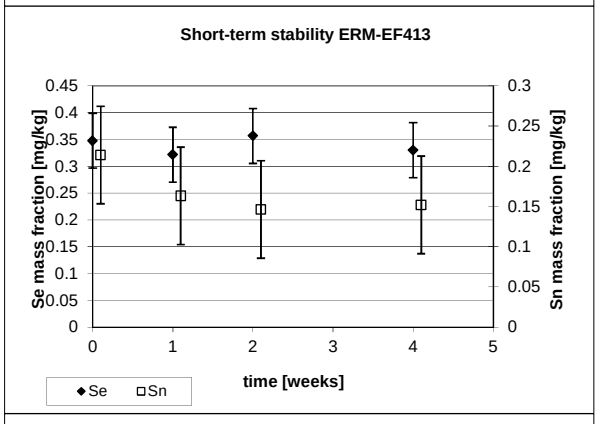


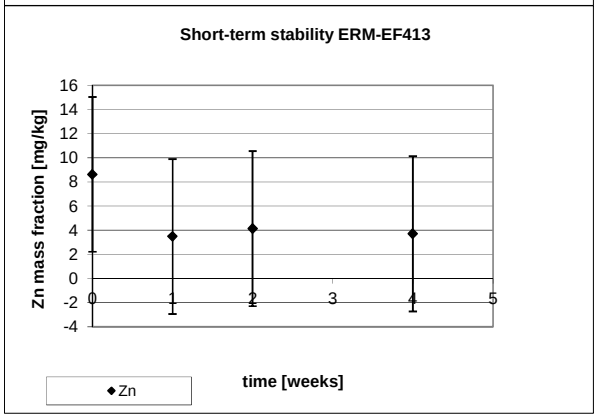


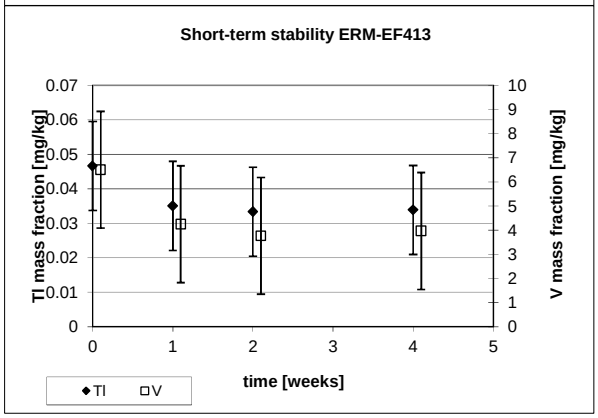

Short-term stability ERM-EF413
Cu mass fraction [mg/kg]
Hg mass fraction [mg/kg]
time [weeks]
Cu
Hg


Short-term stability ERM-EF413
Mn mass fraction [mg/kg]
Ni mass fraction [mg/kg]
time [weeks]
Mn
Ni


Short-term stability ERM-EF413
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
time [weeks]
Pb
Sb

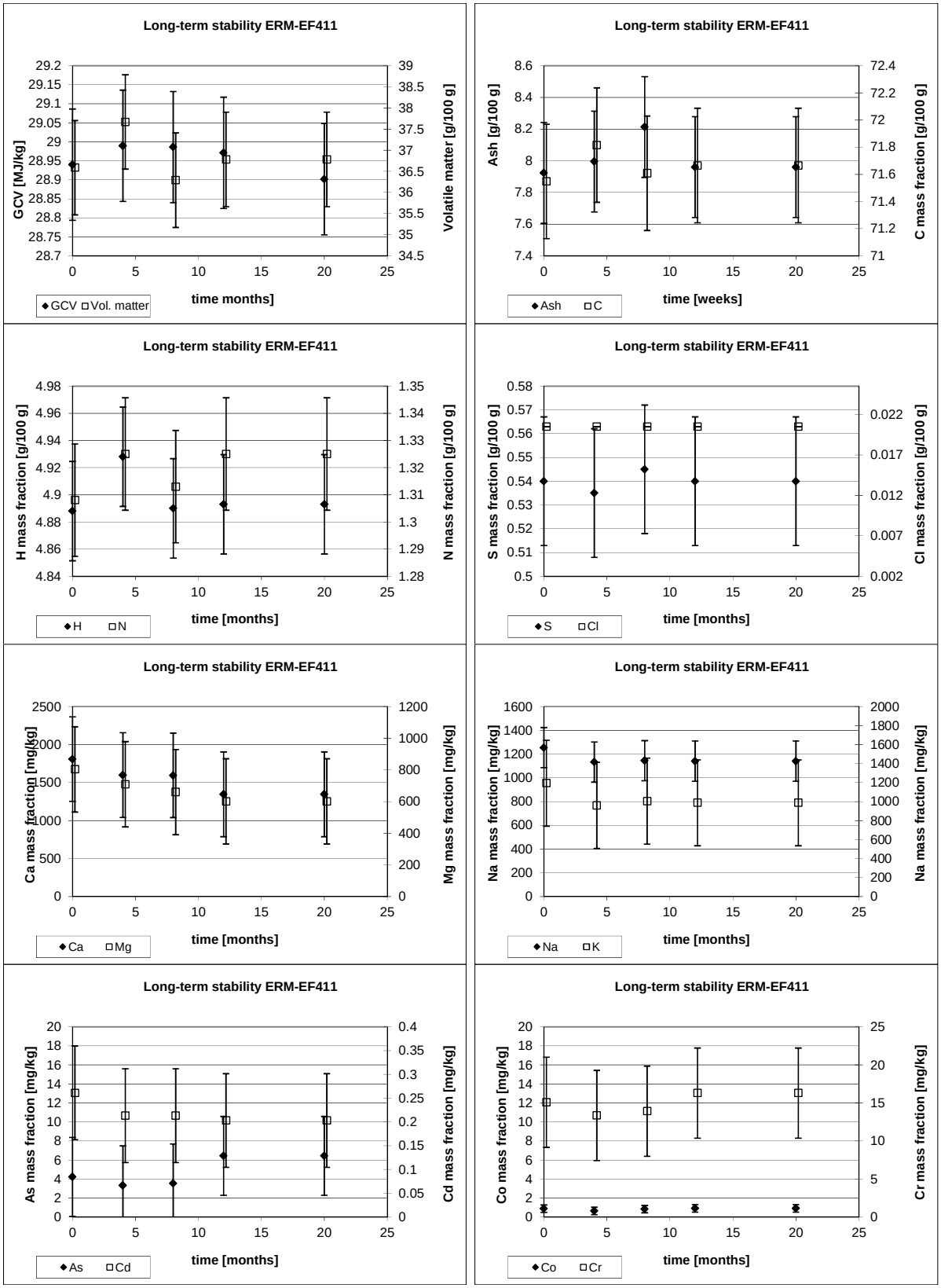

Short-term stability ERM-EF413
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
time [weeks]
Se
Sn

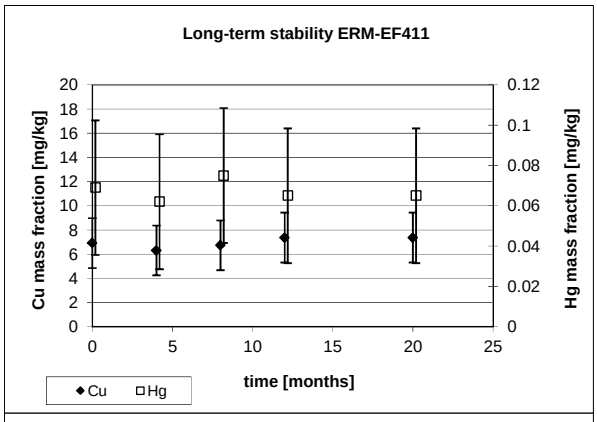

Short-term stability ERM-EF413
Zn mass fraction [mg/kg]
time [weeks]
Zn

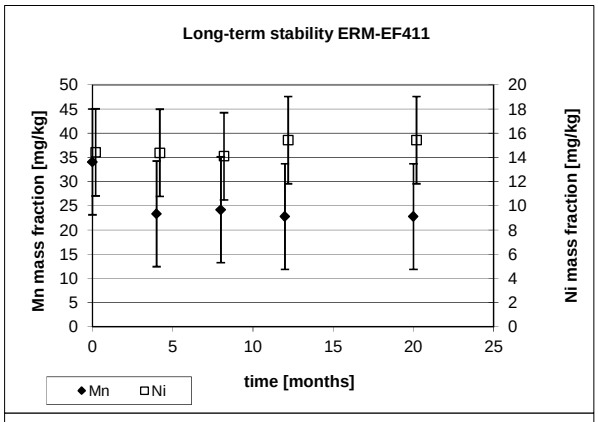

Short-term stability ERM-EF413
Tl mass fraction [mg/kg]
V mass fraction [mg/kg]
time [weeks]
Tl
V

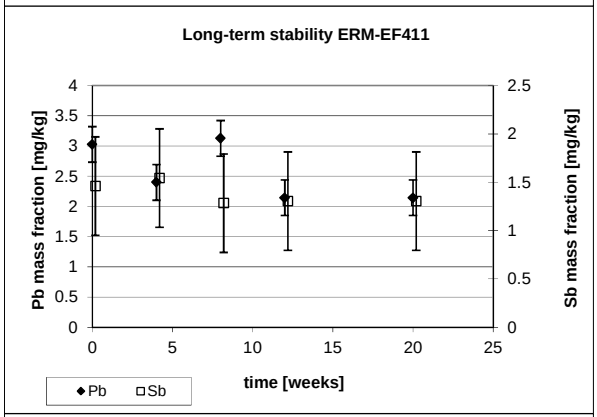
Annex C.1 Long-term stability data ERM-EF411

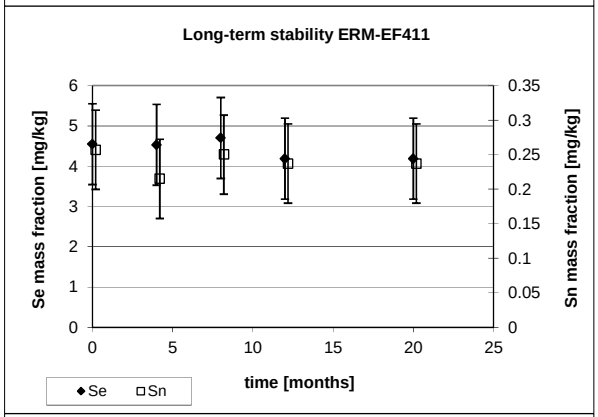
Shown are the averages their 95 % confidence intervals of the eight replicates for each time point. Confidence intervals are based on the pooled repeatability standard deviation as obtained by ANOVA. The points for the different elements were separated graphically to facilitate reading. No error bars are given for Cl as all results were identical.

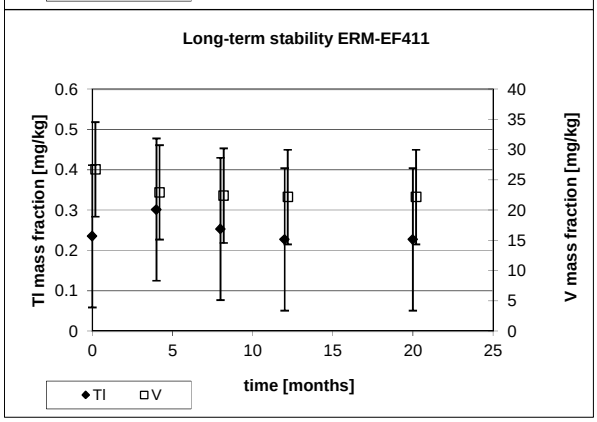


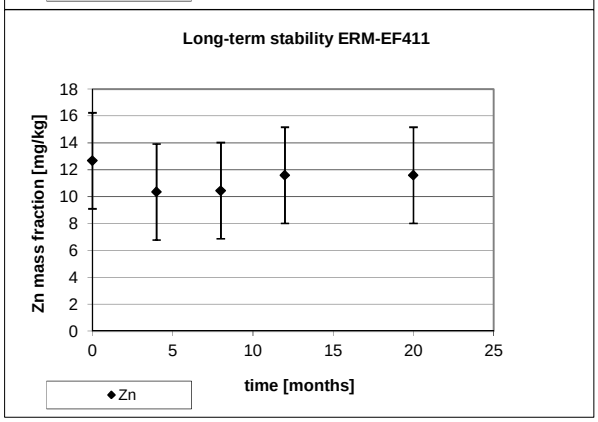

Long-term stability ERM-EF411
Cu mass fraction [mg/kg]
Hg mass fraction [mg/kg]
time [months]
Cu
Hg


Long-term stability ERM-EF411
Mn mass fraction [mg/kg]
Ni mass fraction [mg/kg]
time [months]
Mn
Ni


Long-term stability ERM-EF411
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
time [weeks]
Pb
Sb

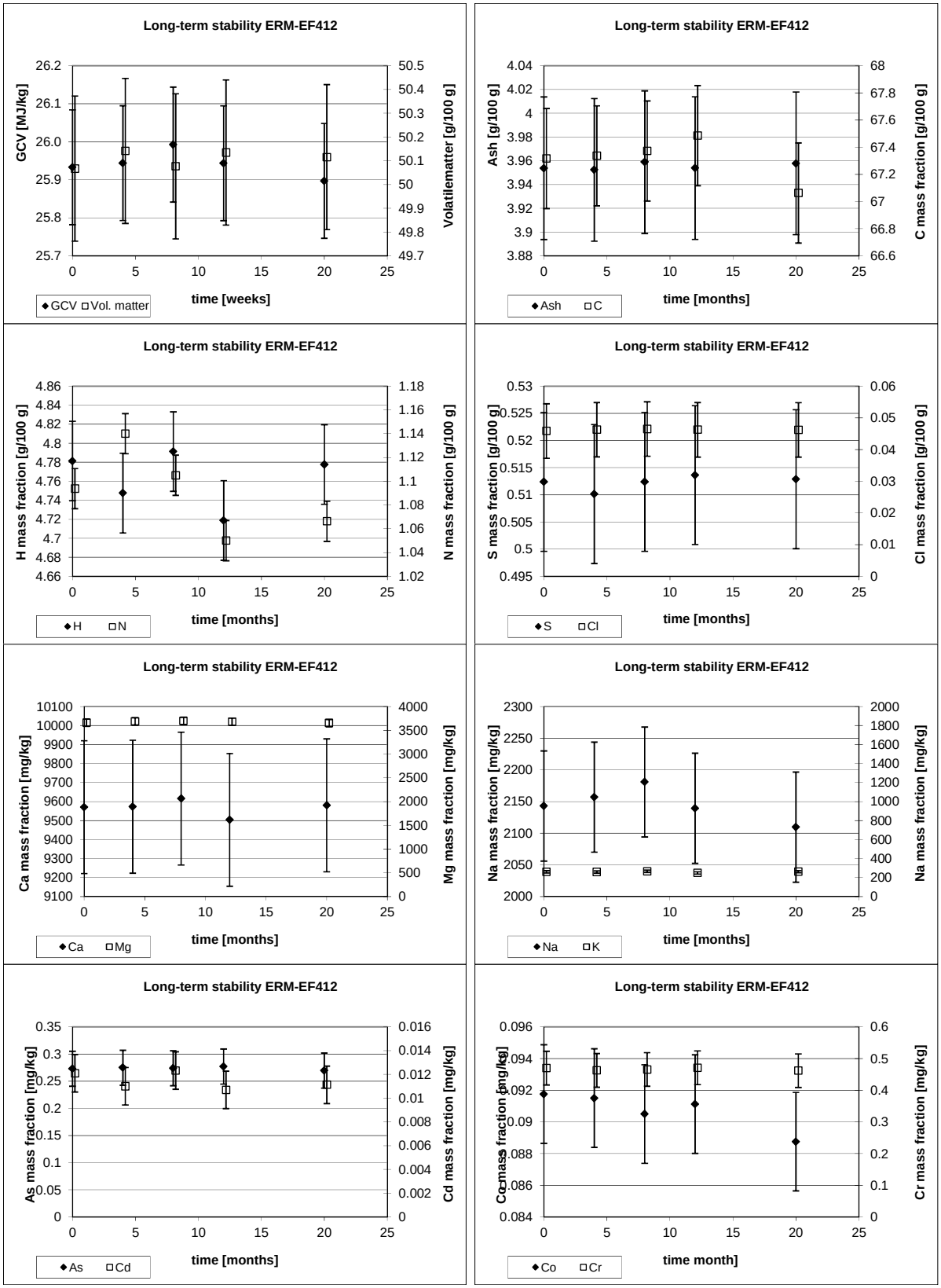

Long-term stability ERM-EF411
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
time [months]
Se
Sn

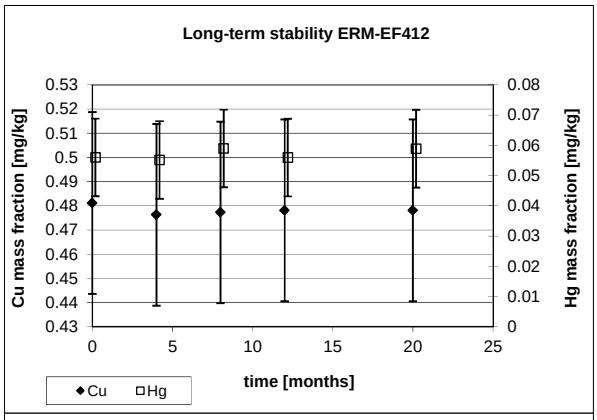

Long-term stability ERM-EF411
Tl mass fraction [mg/kg]
V mass fraction [mg/kg]
time [months]
Tl
V

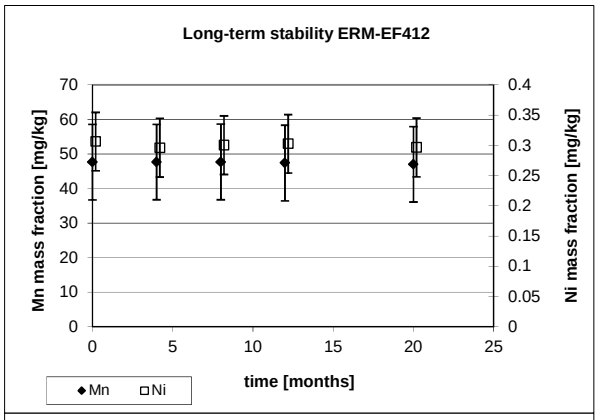

Long-term stability ERM-EF411
Zn mass fraction [mg/kg]
time [months]
Zn

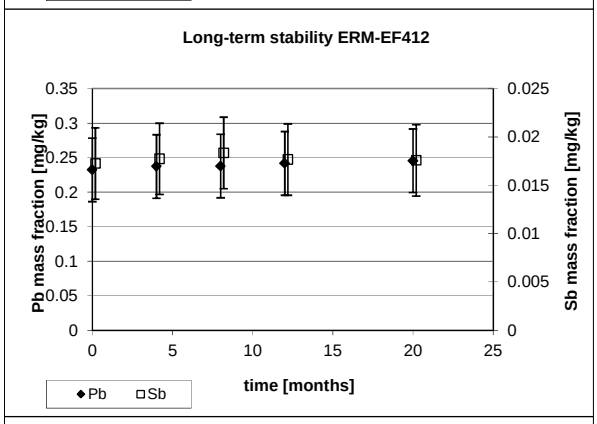
Annex C.2 Long-term stability data ERM-EF412

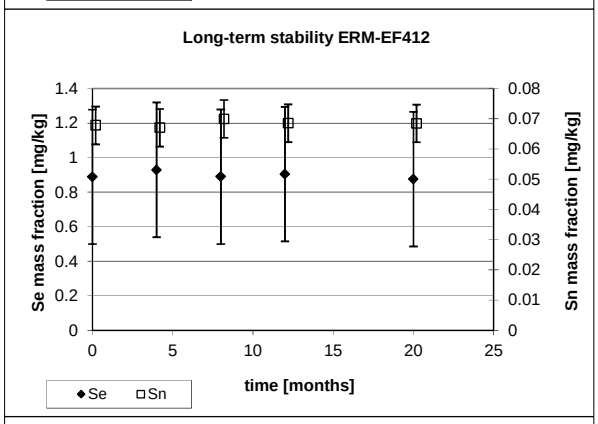
Shown are the averages their 95 % confidence intervals of the eight replicates for each time point. Confidence intervals are based on the pooled repeatability standard deviation as obtained by ANOVA. The points for the different elements were separated graphically to facilitate reading.

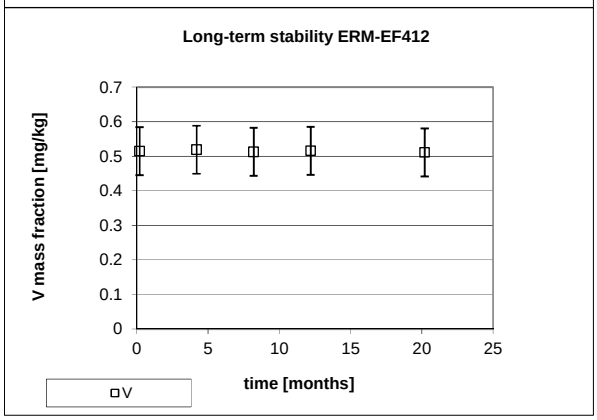


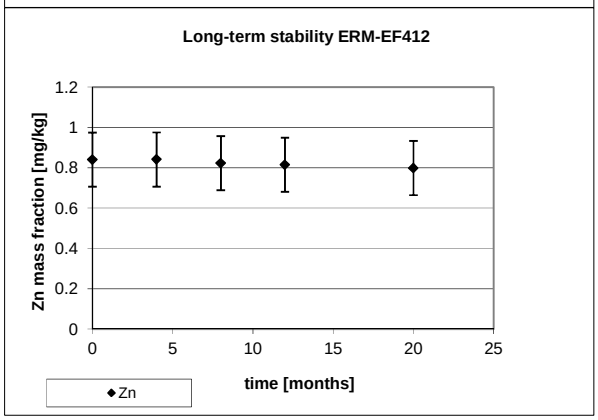

Long-term stability ERM-EF412
Cu mass fraction [mg/kg]
Hg mass fraction [mg/kg]
time [months]
Cu
Hg


Long-term stability ERM-EF412
Mn mass fraction [mg/kg]
Ni mass fraction [mg/kg]
time [months]
Mn
Ni


Long-term stability ERM-EF412
Pb mass fraction [mg/kg]
Sb mass fraction [mg/kg]
time [months]
Pb
Sb

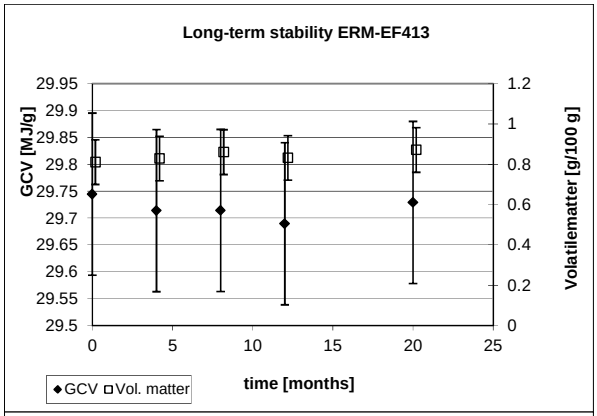

Long-term stability ERM-EF412
Se mass fraction [mg/kg]
Sn mass fraction [mg/kg]
time [months]
Se
Sn

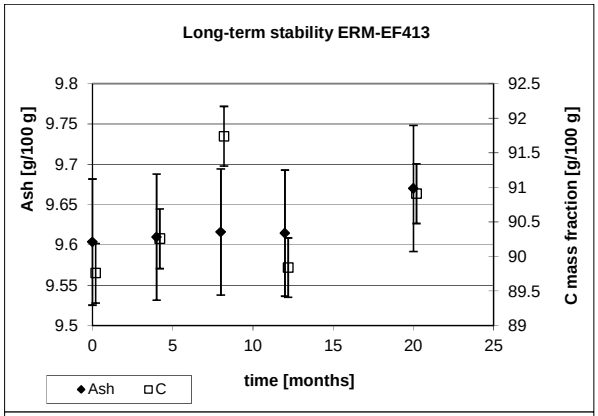

Long-term stability ERM-EF412
V mass fraction [mg/kg]
time [months]
V

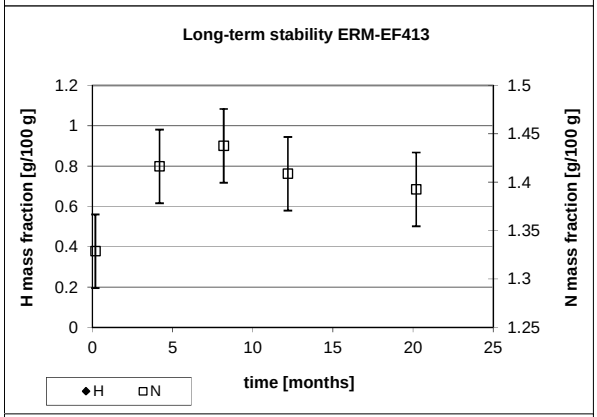

Long-term stability ERM-EF412
Zn mass fraction [mg/kg]
time [months]
Zn

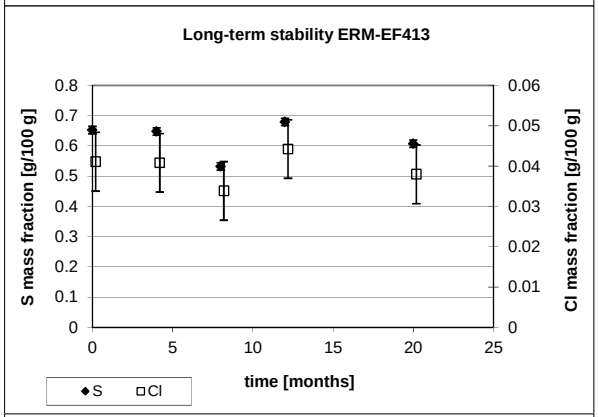
Annex C.3 Long-term stability data ERM-EF413

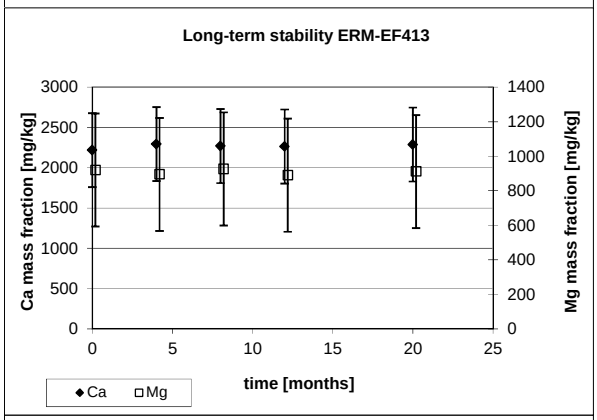
Shown are the averages their 95 % confidence intervals of the eight replicates for each time point. Confidence intervals are based on the pooled repeatability standard deviation as obtained by ANOVA. The points for the different elements were separated graphically to facilitate reading.

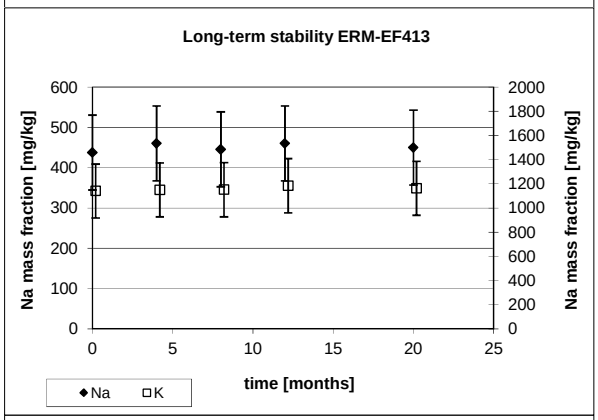


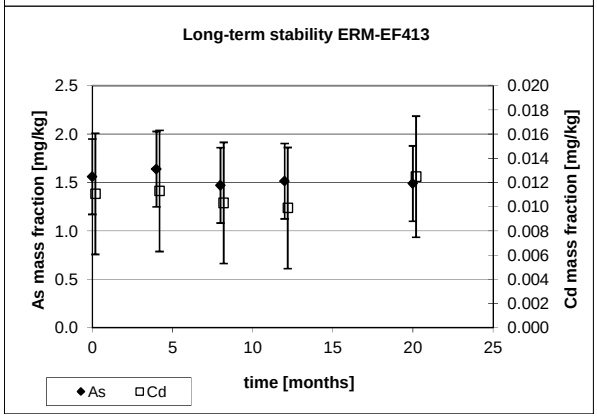


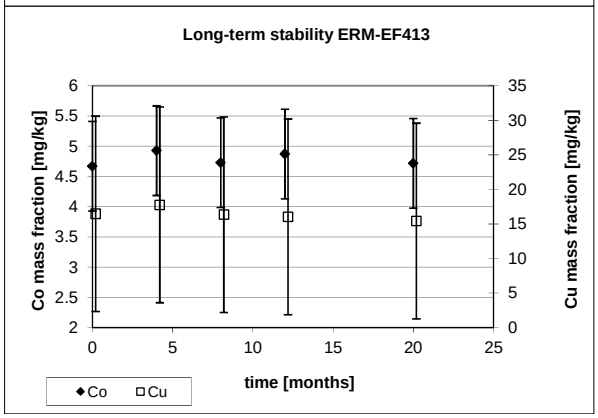


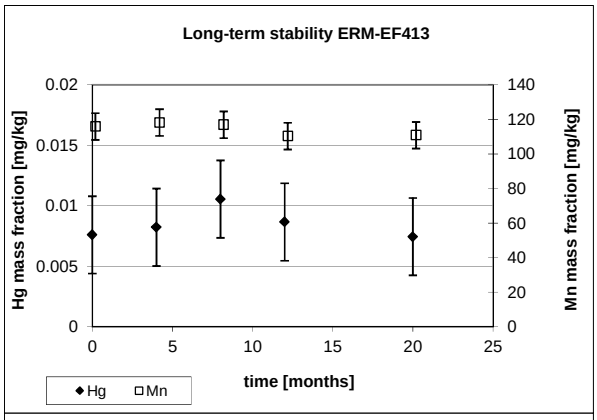


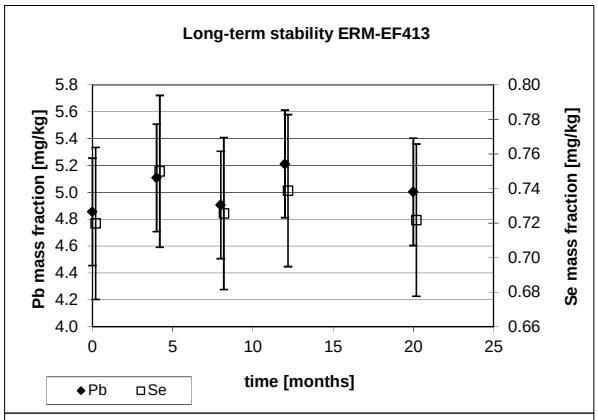


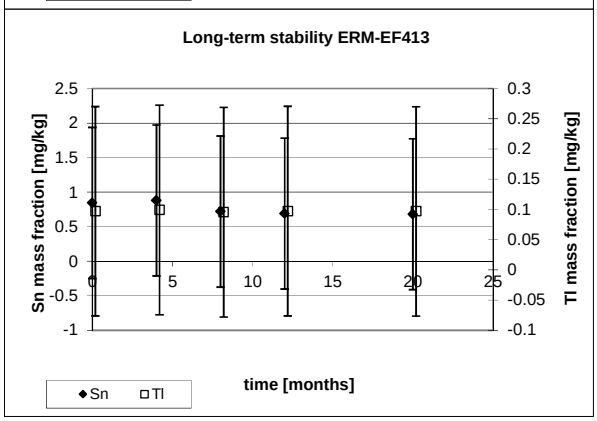


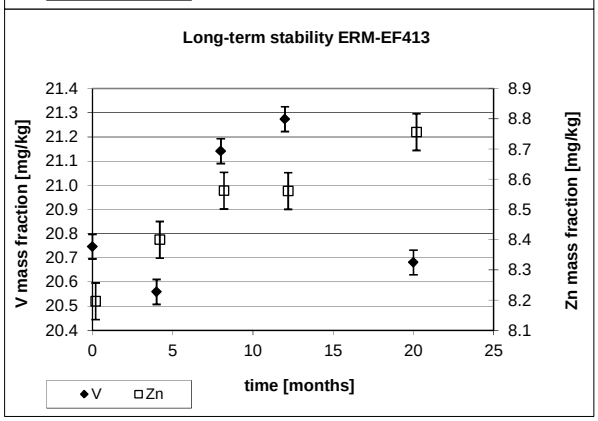





Long-term stability ERM-EF413
Hg mass fraction [mg/kg]
Mn mass fraction [mg/kg]
time [months]
Hg
Mn


Long-term stability ERM-EF413
Pb mass fraction [mg/kg]
Se mass fraction [mg/kg]
time [months]
Pb
Se


Long-term stability ERM-EF413
Sn mass fraction [mg/kg]
Tl mass fraction [mg/kg]
time [months]
Sn
Tl


Long-term stability ERM-EF413
V mass fraction [mg/kg]
Zn mass fraction [mg/kg]
time [months]
V
Zn

Annex D.1: Methods used for determination of proximates: Grinding and free moisture

Information given is the text as provided by the laboratories.

Lab	Grinding		Free moisture
	Method/equipment	Checked by	Method/equipment
L01	vibratory mill VM4, 0.2 mm		Air 105°C (EF411, EF412) 150°C (EF413)
L02	no information given		
L03	HOLMES Pulverizer 500 DG, 212 µm	screen test	Nitrogen/air 37 °C
L04	no information given		
L05	Fritsch Pulverisette rotor mill, 210 □m	Laser diffraction	Air, 22 °C
L06	Laboratory ball mill, 250 µm		Nitrogen 35 °C
L07	Planetary ball mill, < 212 µm	air jet sieving	
L08	HOLMES Pulverizer- 350, 250 µm		Nitrogen 40 °C
L09	Ball mill, < 200 µm	sieving	Nitrogen 30 °C
L10	Ball mill, < 212 µm	sieving	Oxygen 40 °C
L11	Vibratory disc mill, 99,5 % < 200 µm	air jet sieving	Air, 40 °C
L12	laboratory mill RETSCH ZM100, 212 µm	sieving apparatus "FRITSCH analysette 3 PRO", screen - mesh diameter 0,212 µm	Air, 105 °C (EF411), 200 °C (EF413)
L13	Vibratory disc mill, 99,5 % < 200 µm	air jet sieving	Air; 4 h 38 °C
L14	Herzog HSM 100-P grinding mill, < 200 µm		Air, 35 °C

Annex D.1: Methods used for determination of proximates: moisture in the analytical sample and ash

Information given is the text as provided by the laboratories. latest QC date of the latest quality control chart test before the measurements of this study

Lab	Moisture in the analytical sample		Ash	
	Method/equipment	Latest QC.	Method/equipment	Latest QC.
L01	ČSN 44 1377 drying FED 53	19.1.2011	ISO 1171, one oven muffle furnace MP 05	12.5.2010
L02	no information given			
L03	ISO 11722/5068-2 /687 Carbolite MSF/ WTW Binder	26.6.2011/ 26.4.2011	ISO 1171, two ovens Carbolite OAF and AAF	OAF 1.12.2011 AAF 1.5.2011
L04	ÖNORM G 1074/D/06-04 Leco TGA 601	11/2011	ÖNORM G 1074 (eq. ISO 1171), one oven Leco TGA 701	11/2011
L05	ASTM D5142 Las Navas Instruments, TGA-2000	28/6/2011	ASTM D5142, ISO 1171, one oven Las Navas Insruments TGA-2000 (ASTM D5142), Lenton (ISO 1171)	28.6.2011
L06	TGA eq. to ASTM D7582-10 LECO-TGA701	9/2011	ASTM D7582-10, one oven LECO-TGA701	9/2011
L07	ISO 11722/5068-2 /687 Sartorius Balance / Heraeus Drying oven		ISO 1171, two ovens Sartorius Balance / Heraeus Muffle Furnance	
L08	BS 1016-104.1 (eq. ISO 11722) "Carbolite" MFS/1	14.12.2011	ISO 1171, 2 ovens "Carbolite" AAF 11/18	20.12.2011
L09	ISO 5068-2 / ISO 11722 / ISO 687 Carbolite Oven	Thermocouple before measurement	ISO 1171, one oven Heraeus Oven M110	Thermo couple before measurement
L10	Standard M03-037 Method C Mettler LP16	daily	NF 03-003 Carbolite CWF 1200	daily
L11	TGA eq. to ISO 5068-2 Leco TGA 501	23.11.2011	ISO 1171, one oven Leco TGA 501	23.11.2011
L12	ČSN 44 1377, 105 °C (EF411), ČSN ISO 687, 135 (EF413) BMT oven	26.9.2011; monthly internal check	ISO 1171, one oven Carbolite	27.9.2011
L13	TGA eqw. to ÖNORM G 1074 Verfahren D Leco TGA 701	18.8.2011	ÖNORM G 1074 (eq. ISO 1171), one oven Leco TGA 701	18.8.2011
L14	ISO 11772, one oven Carbolite NFS1	17-11-2010; latest internal check 8.11.2011	ISO 1171, one oven Carbolite OAF 10/1	17.11.2010; latest internal check 8.11.2011

Annex D.1: Methods used for determination of proximates: Volatile matter and GCV
Information given is the text as provided by the laboratories. latest QC: date of the latest quality control chart test before the measurements of this study

Lab	Volatile matter		GCV	
	Method/equipment	Latest QC	Method/equipment	Latest QC
L01	ISO 5071-1, 2 ovens (EF412) ISO 562, 1 oven (EF411, EF413) muffle furnace MP 05	12.5.2010	ISO 1928, automated LECO AC 500	16.9.2010
L01	ISO 562; no method information given			
L03	ISO 562 (EF411, EF413), 2 ovens ISO 5071 (EF412), two ovens Carbolite VMF	1.5.2011	ISO 1928, automated IKA C5000	17/18.10. 2011
L04	DIN 51720 (eq, ISO 562), 1 oven Muffelofen Hereus M110	10/2011	DIN 51900-3 (2005-01) (eq. ISO 1928), semi-automatic IKA C5003	10/2011
L05	ISO 562, one oven Nabertherm	28.6.2011	ISO 1928, automated IKA C5000 duo No nitrogen correction	1.11. 2011
L06	TGA equivalent to ASTM D7582-10, one oven LECO-TGA701	9/2011	ASTM D5865-10, automated LECO-AC500	9/2011
L07	ISO 562 (EF411, EF413), two ovens ISO 5071 (EF412), two ovens Sartorius Balance / Carbolite Muffle Oven		ISO 1928, automated IKA Calorimeter System	
L08	ISO 562, 2 ovens "Carbolite" VMF 10/6	14.12. 2011	ISO 1928, automated Parr 6300	Benzoic acid, every 7 working days
L09	ISO 562 / ISO 5071, one oven Heraeus Oven M110	before measurement	ISO 1928, automated IKA C 5003	2/12/2011
L10	ASTM D3175_07 Carbolite CWF 1200		ISO 1928, automated IKA C5003 (EF413) / Parr 6300 (EF411, EF412)	daily
L11	TGA eq. to ISO 5071 (EF412); ISO 562 (EF411, EF413) Leco TGA 501	23.11.2011	ISO 1928, automated IKA Kalorimeter C 5000	12.12.2011
L12	ISO 562,one oven laboratory oven Martínek	27.9.2011; monthly check	ISO 1928, automated IKA C5000	27.9.2011
L13	TGA eq. to ÖNORM G 1074 Verfahren I (eq. ISO562/ISO 5071), one oven Leco TGA 701	18.8.2011	DIN 51900 Teil 3 (eq. ISO 1928) IKA Kalorimeter C 5000	13.12.2011
L14	ISO 562, one oven Carbolite VMF 10/15	17.11.2010; latest internal check 8.11.2011	ISO 1928, partially automated IKA C5000	SRM 39i (benzoic acid) on 23.11.2011

Annex D.1: Methods used for determination of proximates: C and H

Information given is the text as provided by the laboratories. latest QC: date of the latest quality control chart test before the measurements of this study

Lab	**Carbon**		**Hydrogen**	
	Method/equipment	Latest QC	Method/equipment	Latest QC
L01	ISO/TS 12902 LECO TruSpec	12.5.2010	ISO/TS 12902 LECO TruSpec	12.5.2010
L02	no information given			
L03	ISO 29541 LECO Truspec CHN-S	22.11.2011	ISO 29541 LECO Truspec CHN-S	22.11.2011
L04	DIN 51732 (eq. ISO 29541) Flash EA 1112	17.11. 2011	DIN 51732 (eq. ISO 29541) Flash EA 1112	17.11. 2011
L05	ASTM D5373 Elementar Variomax CHN	daily with phenylalanine	ASTM D5373 Elementar Variomax CHN	daily with phenylalanine
L06	ASTM D5373-08 LECO-Truspec CHN	9/2011	ASTM D5373-08 LECO-Truspec CHN	9/2011
L07	ISO 29541 LECO TrueSpec	daily drift calibration	ISO 29541 LECO TrueSpec	Daily Drift Calibration
L08	ASTM D 5373 ELTRA CHS-500 ; ELTRA CHS-580	daily	ASTM D5373 ELTRA CHS-500 ; ELTRA CHS-580	daily
L09	ISO 29541 CE Instruments EA 1108 (now Thermo Scientific)	daily	ISO 29541 CE Instruments EA 1108 (now Thermo Scientific)	daily
L10	ISO/TS 12902 Elementar Vario EL III	daily	ISO TS 12902 Elementar Vario EL III	daily
L11	ISO 29541 Leco Truespec CHN	23.11. 2011	ISO 29541 Leco Truespec CHN	23.11. 2011
L12	ASTM D 5373 – 08 LECO TruSpec CHN	26.9.2011	ASTM D5373 – 08 LECO TruSpec CHN	26.9. 2011
L13	DIN 51732 (eq. ISO 29541) Leco Truspec CHN-Analysator	14.12. 2011	DIN 51732 (eq. ISO 29541) Leco Truspec CHN-Analysator	14.12. 2011
L14	In house method: Combustion oven in combination with GC and TCD detector Costech ECS 4010	21.02.2011. Correction with a CRM (ASCRM-013-8) in every run	In house method: Combustion oven in combination with GC and TCD detector Costech ECS 4010	21.02. 2011. Correction with a CRM (ASCRM-013-8) in every run

Annex D.1: Methods used for determination of proximates: N and S
Information given is the text as provided by the laboratories. latest QC: date of the latest quality control chart test before the measurements of this study

Lab code	**Nitrogen**		**Sulfur**	
	Method/equipment	Latest QC	Method/equipment	Latest QC
L01	ISO/TS 12902 LECO TruSpec	12.5.2010	CSN 441395 (eq. ISO 19579) LECO SC 144DR	12.5.2.10
L02	no information given			
L03	ISO 29541 LECO Truspec CHN-S	22.11.2011	ISO 19579 LECO Truspec CHN-S	28.9.2011/30.11.2011
L04	DIN 51732 (eq. ISO 29541) Flash EA 1112	17/11/2011	DIN 51724-3 (eq. ISO 19579) Leco SC144 DR	14.12.2011
L05	ASTM D5373 Elementar Variomax CHN	with phenylalanine each day of operation	ASTM D4239 (IR-detection, method B) Eltra CS 2000	25.10.11 adjustment
L06	ASTM D5373-08 LECO-Truspec CHN	9/2011	ASTM D4239 LECO-Truspec S	9/2011
L07	ISO 29541 LECO TrueSpec	Daily Drift Calibration	ISO 19579 LECO SC632	Daily Drift Calibration
L08	ISO 333 InKjel P digestion apparatus - "behrotest InKjel P" ; behr S 4 fully automatic steam distillation apparatus	Checked twice a month - samples of "Round Robin" LQSI test program	ASTM D4239 ELTRA CHS-500 ; ELTRA CHS-580	daily
L09	ISO 29541 CE Instruments EA 1108 (now Thermo Scientific)	daily	ISO 351 Titration against $BaClO_4$	daily
L10	ISO TS 12902 Elementar Vario EL III	daily	M03-038 Method B Sylab IRS 2000 (infrared sulfur)	
L11	ISO 29541 Leco Truespec CHN	23.11.2011	ISO 19579 Leco SC 144	23.11.2011
L12	ASTM D 5373 – 08 LECO TruSpec CHN	26.9.2011	ASTM D 4239 LECO TruSpec S	26.9.2011
L13	DIN 51732 (eq. ISO 29541) Leco Truspec CHN-Analysator	14.12.2011	ÖNORM G 1071 (eq. ISO 19579) Leco Truspec Sulfur Add-On Module	14.12.2011
L14	In house method: Combustion oven in combination with GC and TCD detector Costech ECS 4010	21.02.2011. Correction with a CRM (ASCRM-013-8) in every run	XRF in-house method Axios Panalytical in combination with Uniquant 5 callibration software	18.11.2011 (half-yearly)

Annex D.1: Methods used for determination of proximates: Cl and F

Lab	**Chlorine**		**Fluorine**	
	Method/equipment	Latest q.c.	Method/equipment	Latest q.c.
L01	Turbo Quant – pellets Spectro Xepos – XRF 8/2011 calibration by Spectro	8/2011	not tested	
L02	No information given		No information given	
L03	Ion - Chromatography In-house method TOX-100 Metrohm IC	24.10.2011	Eq. ISO 11724 TOX-100 Metrohm IC	24.10.2011
L04	DIN 51727 (ion chromatography) Pyrrohydrolysis with Automatic Quick Furnace AQF-100 , IC with Dionex ICS 3000	30/11/2011	QI B4P-4 402: porrohydrolysis – IC Pyrrohydrolysis with Automatic Quick Furnace AQF-100 , IC with Dionex ICS 3000	30/11/2011
L05	Ion chromatography from bomb calorimeter water, ISO 10304 Dionex DX-120	25/06/2011	Ion chromatography from bomb calorimeter water, ISO 10304 Dionex DX-120	25/06/2011
L07	ASTM 4208 (eq. ISO 11724) IKA Calorimeter System / DIONEX DX 600 / DIONEX ICS 2000		ISO 11724 Prüfer - Tube combustion furnance / DIONEX DX 600 / DIONEX ICS 2000	
L08	ASTM D 4208 For range: 220 - 2100 ppm - 48.4 + 0.13 x X, where X - average result Parr 6300 ; Chloride Ion Selective Electrode - "pHoenix Co" - "Consort".	Checked twice a month - samples of "Round Robin" LQSI test program	not tested	
L10	M03-009 Mettler Titrator DL21	daily	not tested	
L11	ASTM D4208 IKA Kalorimeter C 5000, IC system Dionex ICS-90;	12.12.2011	ASTM D4208 IKA Kalorimeter C 5000, IC system Dionex ICS-90;	12.12.2011
L13	Analog ÖNORM G1075 (eq. ISO 10304-1) DIONEX ICS-2000	15.12.2011	Analog ÖNORM G 1075 (eq. ISO 10304-1) DIONEX ICS-2000	15.12.2011
L14	XRF in-house method Axios Panalytical in combination with Uniquant 5 callibration software	18.11.2011 (half-yearly)	not tested	
L15, L18, L19, L20 L22	k0NAA and INAA: See Annex D2		not tested	

Annex D2: Methods used for the determination of trace elements

Information given is the text as provided by the laboratories.

Lab	Sample preparation	Analytical technique	Calibration
L03	Sample intake: 200 mg Minor elements except Hg: Open destruction of the ash with 20 ml HF / 5 ml HNO3 / 15 ml HCl. The result is dissolved in 50 ml water with HNO_3. Sample diluted 20x and internal standard added. Na, Mg, Na, K: ashing with subsequent fusion with $Li_2B_4O_7$ Hg: none	ICP-MS according ASTM D6357 Hg: LECO AMA-254 mercury analyser (ASTM D6722	Multilelement standard from Inorganic Ventures; 3 point line Internal standard: Rh Calibration confirmed with NIST SRM 1633b Select ICRM Coal 2008-2 // Nist SRM 1568a
L07	Sample intake: 400 mg Closed Microwave (Anton Paar Multiwave 3000) 10 mL HNO_3/ 2 mL HF 90 min/60 bar/200-240 °C Subsequent addition of H_3BO_3	ICP-MS (trace elements): ICP-MS Thermo Xseries 2; dilution 1:10 Ca, Mg, Na, K: ICP-OES Perkin Elmer Optima 3000XL; dilution 1:5	Multilelement standard from High Purity Standards; 4 point line Internal standard: Rh Calibration confirmed with NIST SRM 1633b
L13	Sample intake: 200 mg Closed Microwave (Anton Paar GmbH; Multiwave 3000) 8 mL HNO3 /1 mL HCl/1 mL 30 min/60 bar/200-240 °C Subsequent addition of 10 mL saturated H_3BO_3; 10 min/50 bar/240 °C	As, Se: HGAAS; FIAS400+AAS5100 Perlin Elmer Hg: CVAAS; FIMS , Perkin Elmer others: ICO-OES, Varian VISTA MPX CCD, axial	External calibration prepared in an acid mixture of the same concentration Multielement standards Merck; 3 points calibration curve; traceability via NIST STM 3149

Lab	Sample preparation	Analytical technique	Calibration
L15	Sample intake: 200 mg	INAA Irradiation: 10 s irradiation at $1.82*10^{13}$ neutrons/cm^3/s followed by 2 h at $4.95*10^{12}$ neutrons/cm^3/s Decay time: 10 min, 5 d and 21 d Detector 10 min and 5 d: HPGe 2 x planar Detector 21 d: HPGe well-type Quantification via all γ-lines; blank from empty HDPE capsule	Calibration: holistic single comparator method with many calibration samples used in the past (mostly NIST certified solutions and reference materials)
L16a	Sample intake: 500 mg High Pressure Asher (Anton Paar) 90 min /100 bar/240 °C (twice) Step1 : 3 mL HNO_3 +1 mL HCl Step 2 : 1 mL HNO_3	Na, K, Ca, Mg: ICP-AES Perkin-elmer 3000 DV Others: SF-ICP-MS (high resolution)	As, Cr, Cu, Ni, Pb, Se, V, Zn: multielement standard Spex; traceability via NIST SRM 3149a; Mn,
L16b	Sample intake: 250 mg Closed Microwave (Milstone mls 1200 Mega) Step 1: 2 mL HF + 3 mL HNO3 + 1 ml HCL; left overnight; then 19 min in the microwave Step 2: addition of 1 mL HNO_3; 19 min in the microwave Step 3: addition of 22 mL HBO_3 and 3 min in the microwave Dilution gravimetrically to 50 mL	Ca, Mg, Na, K, Mn: ICP-AES ICP-AES Perkin-Elmer Optima 3000 DV; Ca; Mg; Na and K measured radial, Mn axial Hg: cold vapor-atomic fluorescence spectrometry (CVAFS)	Spex Certiprep monoelement standards verified against NIST SRMs 3109a (Ca), 3131a (Mg), 3152a (Na), 3141a (K) Multielement standard CPI verified against NIST SRM3100 series (Mn)

Lab	Sample preparation	Analytical technique	Calibration
L17	Sample intake 200 mg Digestion : Closed microwave (Anton Paar Multiwave 300) 8 mL HNO_3/2 mL HF/1 mL H_2O_2 200 °C/60 bar/70 min dilution to 50 mL	As, Cd, Cr, Co, Cu, Hg, Mn, Ni, Pb, Tl, V, Zn, Ca, Mg, Na, K: ICP-MS Hg: CV-AAS with $NaBH_4$/HCl	As, Cd, Cr, Cu., Mn, Ni, Pb, Tl, V, Zn, Multielement standards from Teknolab AB verified against NIST SRMs Hg, Ca, Mg, Na, K: Multielement standards from Teknolab AB verified against NIST SRMs
L18	Sample intake: 100-150 mg	k_0NAA Mn, V, Mg, Cl: irradiation for 1.5 min with about 2 *10^{13} neutrons/cm^3/s As, Co, Cr, Sb, Se, Zn, Ca, Na, K: irradiation for 720 min at about 6*10^{12} neutrons/cm^3/s Detector: Ortec GEM 25% P-type high purity germanium Quantification using single γ-lines	Mn, V, Mg, Cl: Flux monitor: NIST 3121 As, Co, Cr, Sb, Se, Zn, Ca, Na, K: Flux monitor: IRMM 530-RC Blank via empty capsule
L19	Sample intake: 30 mg (Hg); 250 mg (NAA)	Hg: DMA (Milestone Sr): controlled combustion at 650-750 °C; quantification by AAS As, Co, Cr, Sb, Se, V, Zn, Ca, Na, K: k_0NAA Irradiation for 1080 min at 1.1*10^{12} neutrons/cm^3/s HPGe coaxial detector (40 and 45%) Mn, V, Mg, Cl: k_0NAA Irradiation for 5 min at 1.1*10^{12} neutrons/cm^3/s HPGe coaxial detector (40 and 45%)	Hg: Single element standard HACH LANGE GmbH verified against NIST SRM Flux monitor: Al-Au0.1% alloy (IRMM-530R) Blank: SPRONK system (pure polyethylene ampoule)

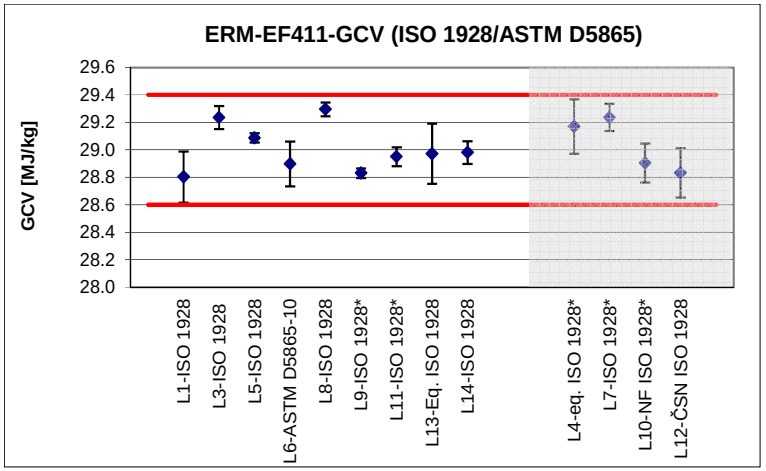
Lab	Sample preparation	Analytical technique	Calibration
L20	Sample intake: 200 mg Digestion: closed microwave (CEM MARS 5) 5ml HNO_{3+}0.5 ml H_2O_2+0.1 ml HF > 140 bar Dilution with 1.4 M HNO_3	ICP-SFMS with mass resolutions of 300 (Cd, Hg, Pb, Sb, Sn, Tl), 3400 (Cr, Cu, Ni, V, Zn, Ca, Mg, Na) and 12000 (As, Se, K)	Multielement standards Ultra Scientific traceable via NIST SRM 31xx series Internal standard: In
L21	Sample intake: 200 mg Digestion: Closed microwave (Milestone ultraClave IV) 4 mL HNO_3 + 0.1 mL HCl 250 °C/160 bar/60 min Dilution to 10 mL	ICP-MS Mass resolution for all elements: 300 1 isotope per element	Multielement standards Perkin Elmer traceable via NIST 31xx series Internal standards: Li, Sc, Y, In, Tb, Lu, Bi
L22	Sample intake: 200-500 mg	k_0NAA Mn, V, Mg, Cl: irradiation for 10 min with about 2 *10^{11} neutrons/cm^3/s – decay of 5 and 30 min. As, Co, Cr, Sb, Se, Zn, Ca, Na, K: irradiation for 7 h at about 3*10^{11} neutrons/cm^3/s - decay of 1-2 days and 21 days	Flux monitor: IRMM 530-R Blank via empty capsule QC via several IRMM CRM's

Annex E.1: Results obtained in the characterisation study for ERM-EF411.

The graphs give the average results and the expanded uncertainties estimated as two times the standard deviation from the control chart (proximates) or as stated by the laboratories (elements). An asterisk after the method means that two times the standard deviation of the results from the characterisation exercise was used as measurement uncertainty. The solid red lines give the certified range, the dashed red lines the indicative range. Shaded results are results not accepted on technical grounds.

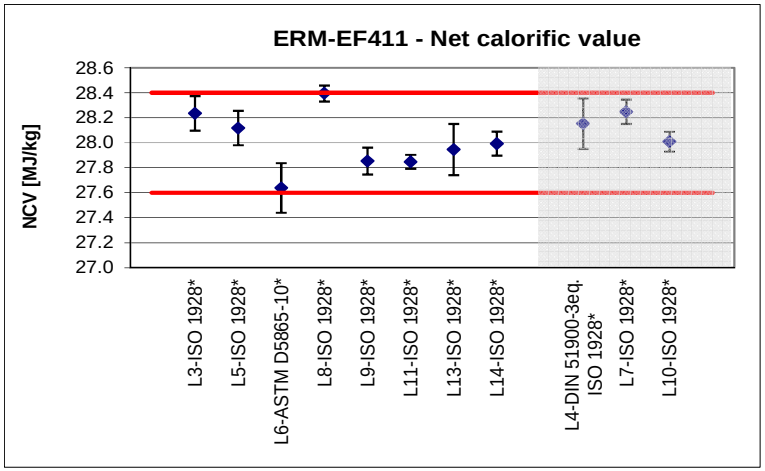
ERM-EF411-GCV (ISO 1928/ASTM D5865) in MJ/kg (certified value)

Lab	Results					
L1	28.599	28.635	28.855	28.789	28.959	28.972
L3	29.145	29.142	29.327	29.256	29.316	29.226
L5	29.018	28.979	29.082	29.132	29.158	29.146
L6	29.01	29	28.809	28.952	28.776	28.834
L8	29.34	29.32	29.26	29.3	29.25	29.3
L9	28.83	28.72	28.78	28.87	28.84	28.94
L11	28.98	28.95	28.92	28.9	28.96	28.99
L13	28.84	28.84	29.01	28.98	29.07	29.09
L14	28.911	28.93	28.99	28.991	29.036	29.023
Results not accepted on technical grounds						
L4	29.17	29.139	29.063	29.075	29.278	29.297
L7	29.24	29.23	29.259	29.147	29.298	29.239
L10	28.809	28.849	28.927	28.941	28.891	29.009
L12	28.88	28.88	28.88	28.81	28.8	28.74



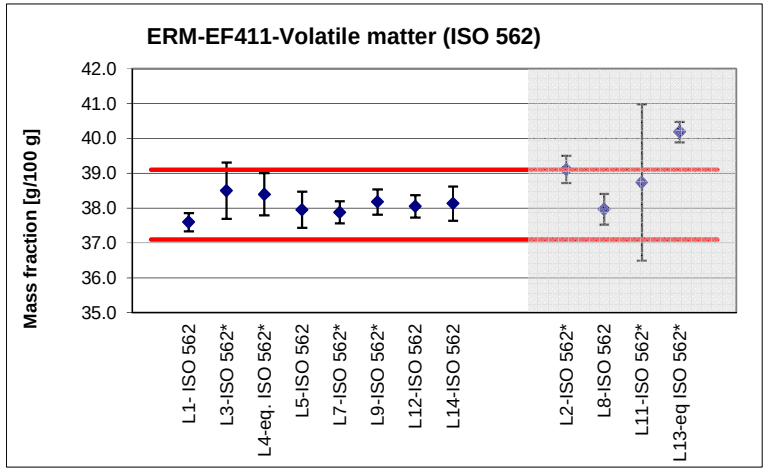
ERM-EF411- NCV (ISO 1928/ASTM D5865) in MJ/kg (certified value)

Lab	Results					
L3	28.161	28.157	28.319	28.248	28.304	28.213
L5	28.056	28.017	28.11	28.16	28.185	28.173
L6	27.761	27.72	27.56	27.693	27.522	27.572
L8	28.436	28.424	28.366	28.398	28.353	28.39
L9	27.83	27.82	27.88	27.93	27.78	27.88
L11	27.87	27.84	27.82	27.81	27.86	27.88
L13	27.82	27.83	27.98	27.94	28.04	28.06
L14	27.927	27.944	28.01	27.996	28.052	28.026
Results not accepted on technical grounds						
L4	28.155	28.147	28.034	28.044	28.258	28.272
L7	28.248	28.238	28.275	28.162	28.308	28.249
L10	27.974	27.955	28.03	28.044	27.995	28.052



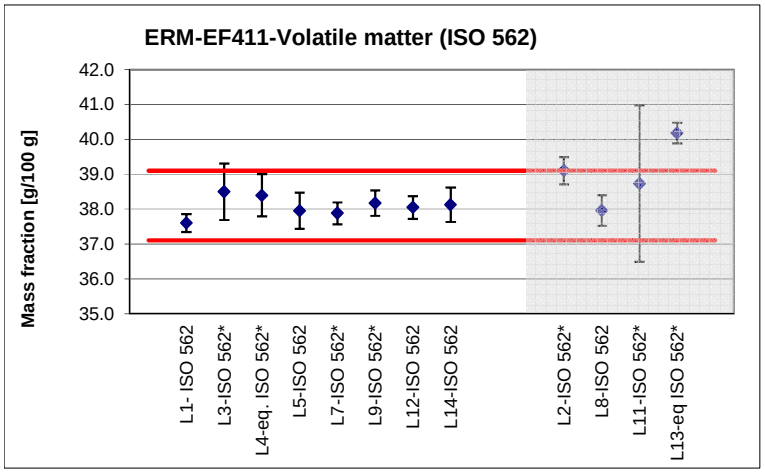
ERM-EF411-Volatile matter (ISO 562) in g/100 g (certified value)

Lab	Results					
L1	37.47	37.62	37.52	37.47	37.75	37.74
L3	38.649	38.076	38.126	38.261	39.069	38.809
L4	38.72	38.55	38.46	38.6	38.07	37.97
L5	37.636	37.604	38.084	38.047	38.153	38.17
L7	38.08	38.04	37.66	37.77	37.85	37.86
L9	37.95	37.972	38.311	38.168	38.402	38.254
L12	38.01	38.15	38.33	37.96	37.9	37.94
L14	38.102	37.848	37.918	38.241	38.103	38.538
Results not accepted on technical grounds						
L2	38.84	39.08	39.23	39.27		
L8	38.316	38.11	37.983	37.804	37.752	37.811
L11	38.9	39	39.1	39.3	36.5	39.6
L13	40.3	40.2	40.3	40.2	39.9	40.2



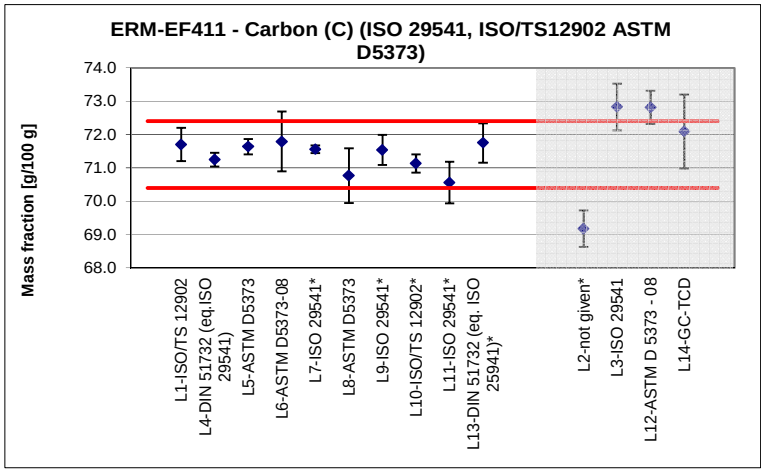
ERM-EF411 - Ash (ISO 1171/ASTM D3174/ASTM D5142) in g/100 g (certified value)

Lab	Results					
L1	9.15	9.17	8.55	8.58	8.43	8.44
L3	8.005	8.036	7.541	7.564	7.711	7.753
L4	8.284	8.318	8.378	8.376	8.029	8.06
L5-ISO	8.693	8.539	8.32	8.313	8.176	8.164
L5-ASTM	8.505	8.622	8.297	8.332	8.163	8.163
L7	8.39	8.34	8.38	8.38	8.24	8.27
L9	8.8	8.756	8.354	8.398	8.419	8.056
L10	8.3	8.4	8.4	8.4	8.4	8.4
L12	7.96	7.9	7.95	7.87	8.13	8.15
L14	8.4	8.392	8.243	8.261	8.144	8.141
Results not accepted on technical grounds						
L2	8.11	8.19	8.3	7.95	8.03	8.12
L6	8.19	8.31	8.53	8.57	8.47	8.58
L8	8.766	8.682	8.697	8.716	8.653	8.701
L11	8.22	8.15	8.35	8.25	8.21	8.16
L13	8.57	8.6	8.27	8.26	8	8.07



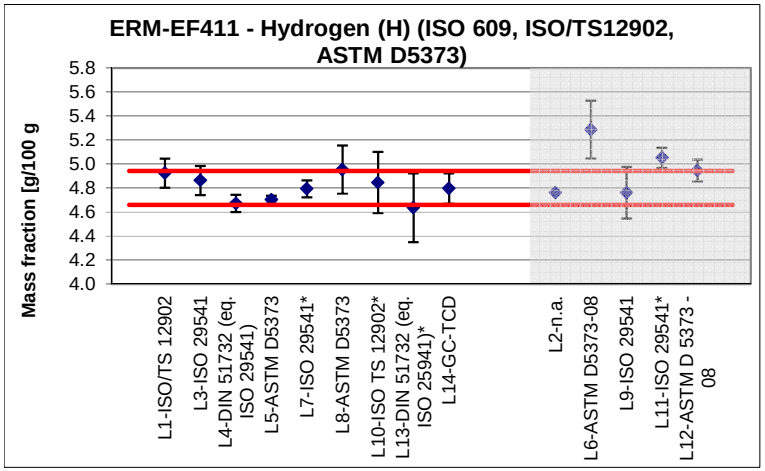
ERM-EF411 - Carbon (C) (ISO 29541, ISO/TS12902 ASTM D5373) in g/100 g (certified value)

Lab	Results					
L1	71.23	70.79	72.08	71.82	72.11	72.17
L4	71.43	71.39	70.84	70.81	71.56	71.47
L5	71.573	71.407	71.683	71.621	71.781	71.75
L6	71.72	71.6	71.87	71.83	71.75	71.98
L7	71.5	71.53	71.55	71.67	71.57	71.55
L8	71.182	71.177	70.709	70.962	70.372	70.207
L9	71.201	71.206	71.576	71.033	72.089	72.136
L10	71.2	70.9	71.1	71.3	71.1	71.2
L11	70.72	71.01	70.41	70.12	70.71	70.41
L13	71.3	71.5	71.8	71.9	71.9	72.1
Results not accepted on technical grounds						
L2	69.28	69.52	68.77	69.19	69.13	
L3	73.014	72.784	72.841	72.988	72.651	72.672
L12	72.67	72.95	72.94	73.04	72.54	72.74
L14	71.96	71.82	71.64	72.19	72.67	72.3



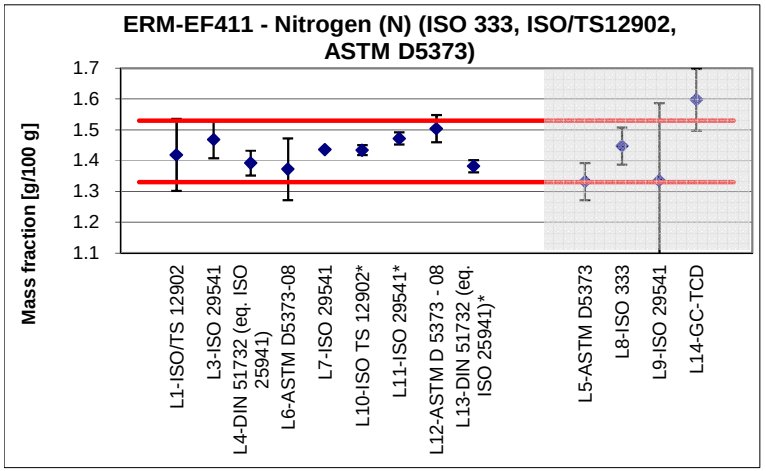
Hydrogen (H) (ISO 609, ISO/TS12902, ASTM D5373) in g/100 g (certified value)

Lab	Results					
L1	4.92	4.98	4.88	4.84	4.97	4.95
L3	4.789	4.768	4.872	4.914	4.913	4.913
L4	4.65	4.55	4.71	4.73	4.68	4.7
L5	4.654	4.681	4.736	4.701	4.738	4.708
L7	4.81	4.82	4.78	4.76	4.78	4.81
L8	4.988	4.953	4.93	4.911	4.963	4.973
L10	4.76	4.78	5	4.86	4.83	4.84
L13	4.66	4.63	4.75	4.72	4.52	4.53
L14	4.78	4.79	4.76	4.83	4.77	4.84
Results not accepted on technical grounds						
L2	4.76	4.77	4.75	4.75		
L6	5.24	5.24	5.29	5.33	5.29	5.32
L9	4.673	4.672	4.375	4.586	5.142	5.116
L11	5.03	5.09	5.04	5.02	5.08	5.05
L12	4.96	4.94	4.92	4.95	4.96	4.94



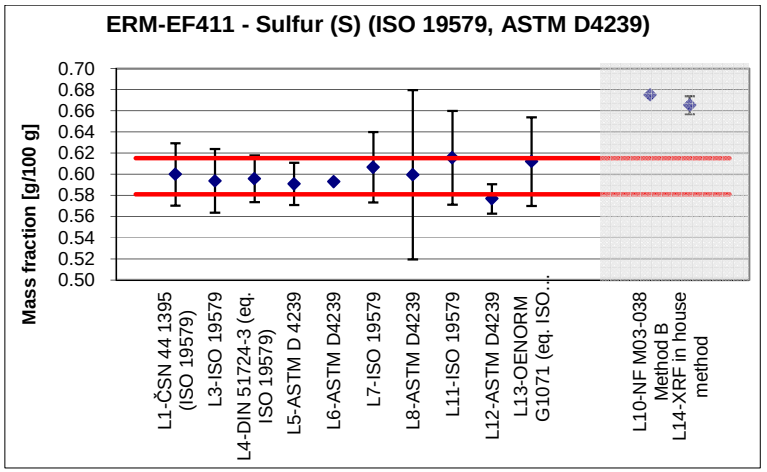
Nitrogen (N) (ISO 333, ISO/TS12902, ASTM D5373) in g/100 g (certified value)

Lab	Results					
L1	1.41	1.42	1.44	1.4	1.41	1.43
L3	1.464	1.475	1.456	1.477	1.494	1.441
L4	1.36	1.36	1.36	1.38	1.44	1.45
L6	1.35	1.36	1.42	1.41	1.34	1.35
L7	1.45	1.42	1.38	1.4	1.46	1.5
L10	1.43	1.44	1.44	1.44	1.42	1.43
L11	1.48	1.46	1.48	1.46	1.47	1.48
L12	1.52	1.5	1.53	1.49	1.5	1.48
L13	1.4	1.37	1.38	1.38	1.38	1.38
Results not accepted on technical grounds						
L5	1.317	1.329	1.324	1.325	1.374	1.324
L8	1.442	1.444	1.448	1.435	1.449	1.463
L9	1.335	1.335	1.335	1.335	1.335	1.335
L14	1.65	1.61	1.57	1.61	1.55	1.59



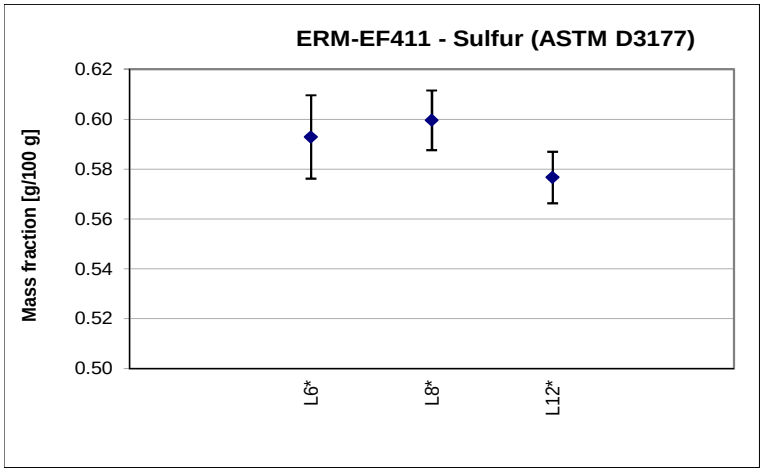
ERM-EF411 - Sulfur (S) (ISO 19579, ASTM D4239) in g/100 g (certified value)

Lab	Results					
L1	0.602	0.602	0.605	0.597	0.593	0.6
L3	0.595	0.589	0.611	0.585	0.589	0.593
L4	0.602	0.606	0.608	0.602	0.581	0.576
L5	0.601	0.6	0.587	0.585	0.59	0.582
L6	0.606	0.598	0.593	0.582	0.59	0.588
L7	0.595	0.613	0.616	0.632	0.588	0.595
L8	0.606	0.607	0.598	0.599	0.592	0.595
L11	0.63	0.647	0.623	0.608	0.599	0.586
L12	0.58	0.57	0.58	0.58	0.57	0.58
L13	0.611	0.594	0.641	0.634	0.6	0.592
Results not accepted on technical grounds						
L10	0.67	0.68	0.67	0.68	0.67	0.68
L14	0.67	0.669	0.668	0.664	0.661	0.66



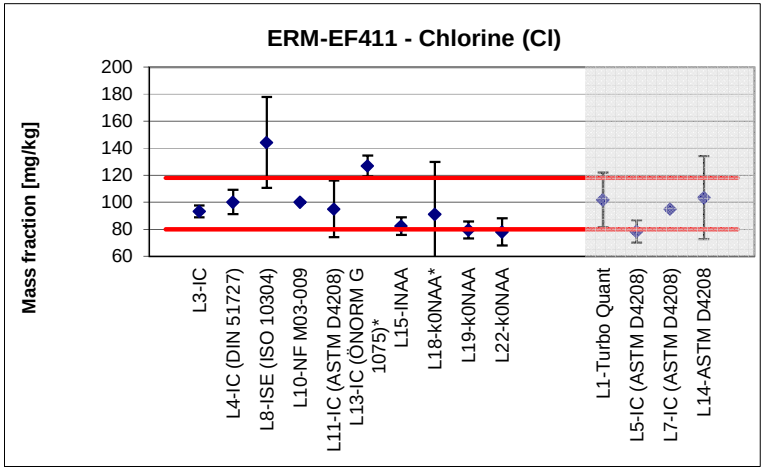
Sulphur (S) (ASTM D3177) in g/100 g (additional material information value)

Lab	Results					
L6	0.606	0.598	0.593	0.582	0.59	0.588
L8	0.606	0.607	0.598	0.599	0.592	0.595
L12	0.58	0.57	0.58	0.58	0.57	0.58



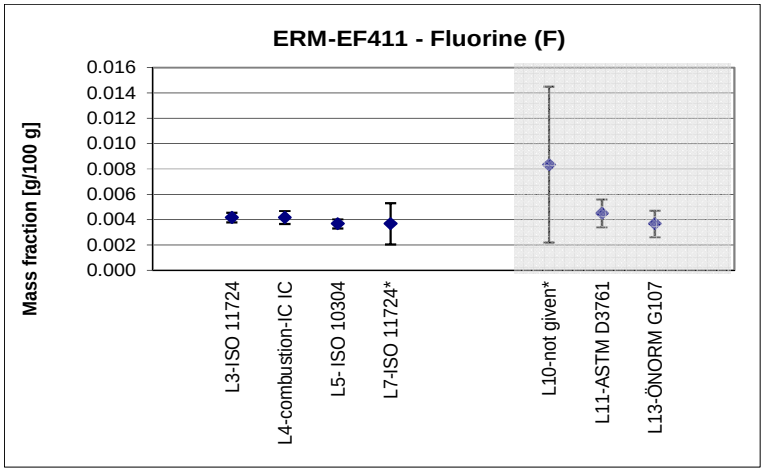
Chlorine (Cl) in mg/kg (certified value)

Lab	Results					
L3	89	88	90	105	87	100
L4	130	90	90	90	100	100
L8	161	160	149	148	123	124
L10	100	100	100	100	100	100
L11	100	80	100	90	90	110
L13	119	119	127	135	140	121
L15	78	83	79	79	88	87
L18	89	82	84	87	148	72
	84	95	91	93	92	75
L19	82	83	81	77	76	78
L22	70	80	76	86		
Results not accepted on technical grounds						
L1	90	100	110	100	100	110
L5	80	70	80	80	80	80
L7	100	80	90	110	90	100
L14	100	110	100	100	100	110



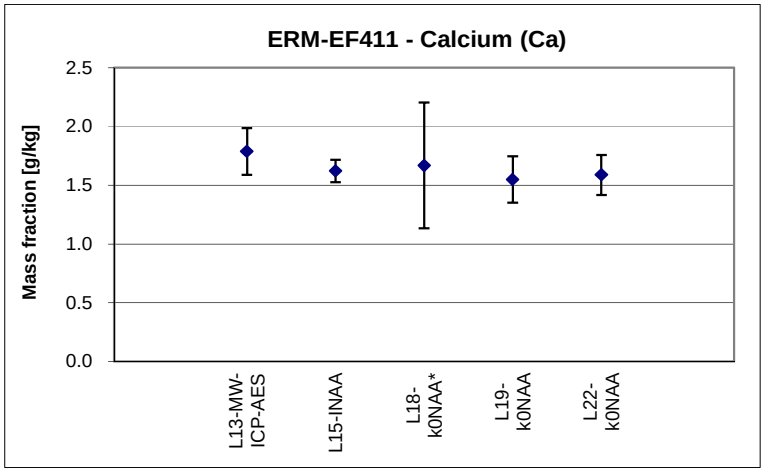
Fluorine (F) in g/100 g (additional material information value)

Lab	Results					
L3	0.004	0.004	0.005	0.004	0.004	0.004
L4	0.005	0.004	0.004	0.004	0.004	0.004
L5	0.003	0.003	0.004	0.004	0.004	0.004
L7	0.004	0.005	0.003	0.003	0.003	0.004
Results not accepted on technical grounds						
L10	0.005	0.009	0.007	0.008	0.007	0.014
L11	0.005	0.004	0.005	0.004	0.005	0.004
L13	0.004	0.004	0.004	0.003	0.004	0.003



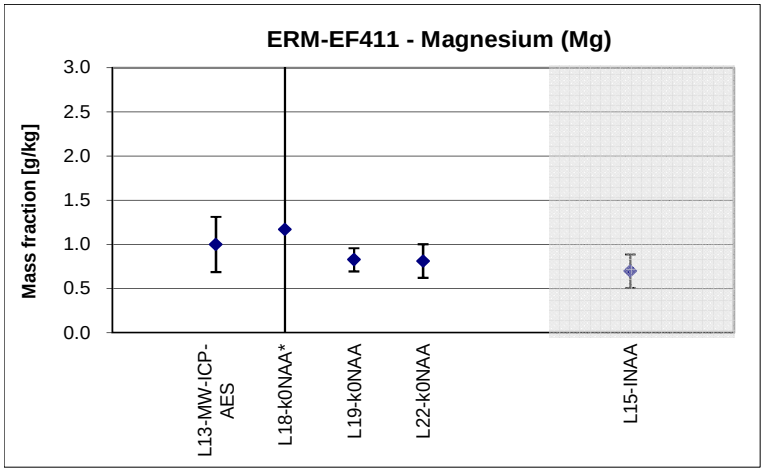
ERM-EF411 – Calcium (Ca) in g/kg (no value assigned)

Lab	Results					
L13	1.729	1.686	1.643	1.892	1.724	1.68
	1.912	1.947	1.881	1.749	1.773	1.827
L15	1.639	1.936	1.163	1.783	1.581	1.657
L18	1.28	1.45	1.49	2.07	1.33	1.71
	2.15	1.54	1.74	1.71	1.78	1.77
L19	1.577	1.655	1.522	1.617	1.471	1.449
L22	1.62	1.64	1.37	1.71	1.7	1.49



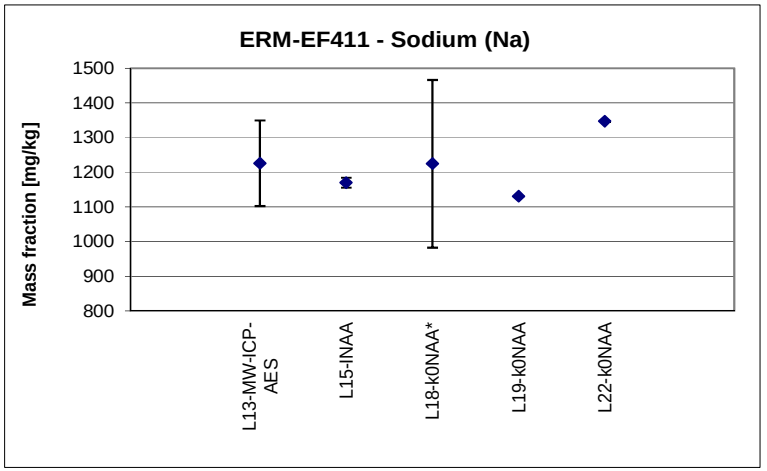
ERM-EF411 – Magnesium (Mg) in g/kg (no value assigned)

Lab	Results					
L13	0.954	0.995	0.874	1.084	0.975	0.917
	1.095	1.087	1.069	0.942	0.937	1.052
L18	1.264	0.748	0.654	0.623	4.718	0.606
	0.761	0.766	1.535	1.148	0.572	0.631
L19	0.875	0.753	0.854	0.867	0.743	0.854
L22	0.835	0.76	0.72	0.88	0.8	0.86
Results not accepted on technical grounds						
L15	0.622	0.811	0.697	0.639	0.683	0.732



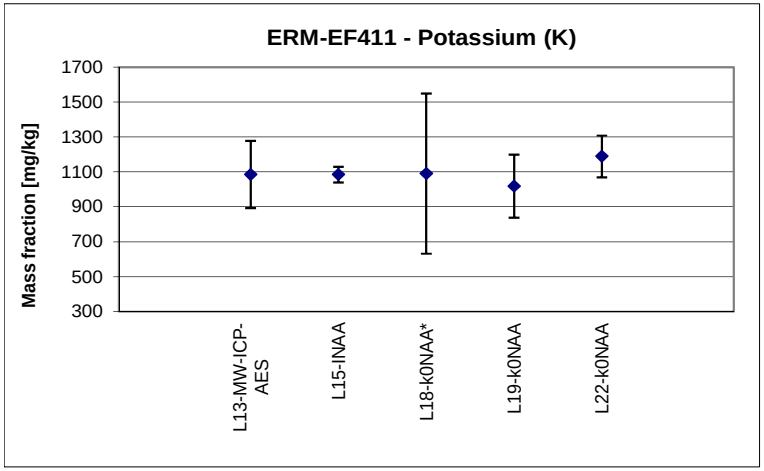
ERM-EF411 – Sodium (Na) in mg/kg (no value assigned)

Lab	Results					
L13	1221	1226	1192	1286	1216	1240
	1249	1255	1248	1185	1188	1202
L15	1195	1219	1225	1149	1100	1134
L18	1080	1230	1160	1230	1170	1170
	1540	1190	1210	1100	1310	1300
L19	1170	1171	1091	1197	1074	1079
L22	1280	1560	1400	1210	1280	1350



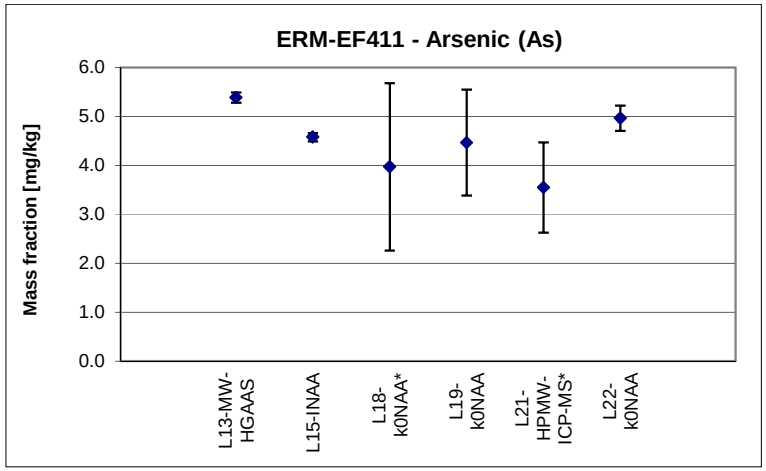
ERM-EF411 - Potassium (K) in mg/kg (no value assigned)

Lab	Results					
L13	1036	1042	1007	1115	1094	1102
	1100	1127	1115	1085	1111	1082
L15	1101	1250	1023	1015	1078	1042
L18	850	1140	910	990	940	848
	1580	1090	990	1100	1460	1180
L19	1092	1102	955	1085	929	945
L22	1190	1140	1180	1150	1240	1230



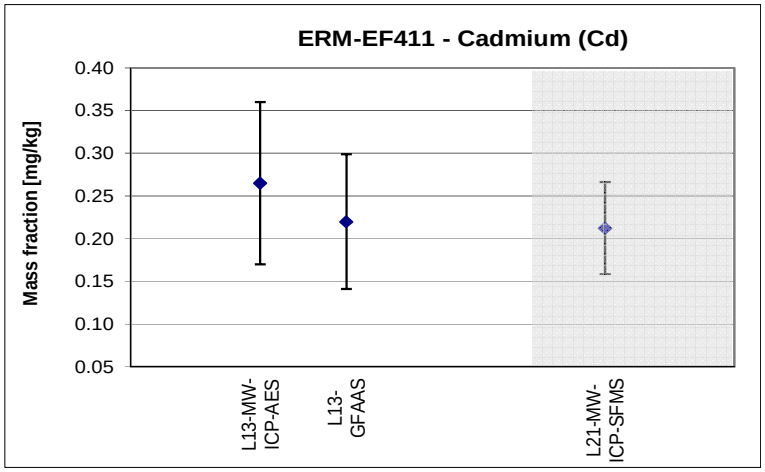
ERM-EF411 – Arsenic (As) in mg/kg (no value assigned)

Lab	Results					
L13	5.16	5.28	5.1	5.27	5.41	5.34
	6.04	5.44	5.46	5.28	5.64	5.21
L15	4.353	4.142	4.812	6.153	3.787	4.21
L18	3.58	3.46	3.23	4.53	3.28	3.00
	4.67	2.86	5.43	4.05	5.12	4.41
L19	4.81	4.99	4.1	4.99	3.85	4.06
L21	3.13	3.13	3.13	3.97	3.86	4.07
L22	4.53	5.56	4.9	4.66	4.16	5.98



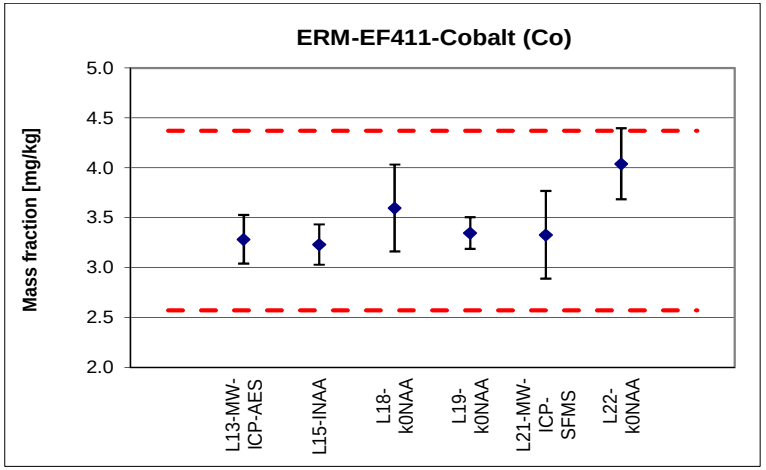
ERM-EF411 – Cadmium (Cd) in mg/kg (no value assigned)

Lab	Results					
L13 – ICP-AES	0.26	0.28	0.27	0.27	0.29	0.21
	0.22	0.37	0.25	0.24	0.27	0.25
L13 - GFAAS	0.16	0.23	0.24	0.23	0.19	0.27
Results excluded on technical grounds						
L21	0.188	0.188	0.188	0.23	0.24	0.24



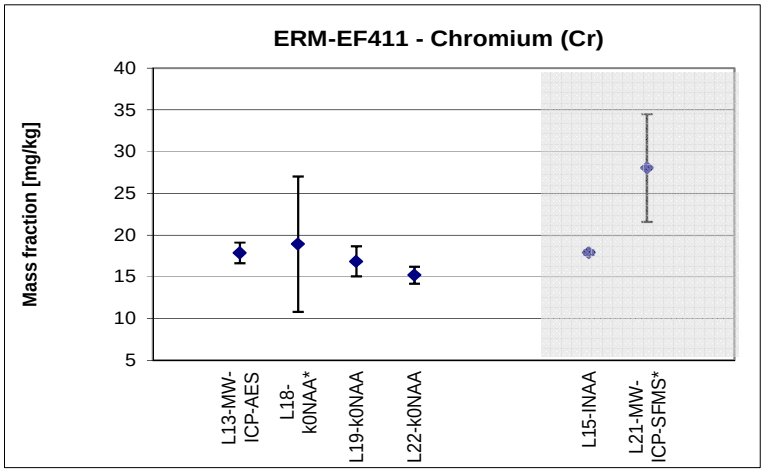
ERM-EF411-Cobalt (Co) in mg/kg (indicative value)

Lab	Results					
L13	3.49	3.53	3.56	3	3.24	3.26
	3.26	3.54	3.2	3.27	2.72	3.32
L15	3.153	3.015	3.533	3.027	3.345	3.307
L18	3.81	3.08	3.15	4.22	3.52	3.01
	3.74	3.47	3.34	4.36	3.5	3.97
L19	3.47	3.52	3.21	3.48	3.18	3.22
L21	2.93	2.93	2.93	3.76	3.66	3.76
L22	3.71	4.38	4.27	3.49	4.25	4.14
L13	3.47	3.52	3.21	3.48	3.18	3.22



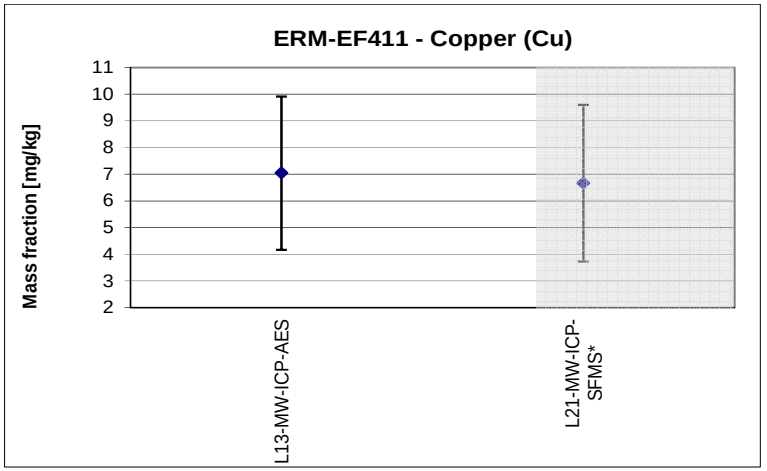
ERM-EF411 – Chromium (Cr) in mg/kg (no value assigned)

Lab	Results					
L13	16.2	16.9	19	15.5	19	18.8
	16.9	18	16.1	19.3	19.1	19.3
L18	12.6	18.1	14.2	20.5	19.7	19
	24.8	19.8	20.9	13.3	18.5	25.5
L19	16.9	18.1	16.4	17.1	16.3	16.2
L22	13	17.4	17.8	12.4	14.1	16.4
Results not accepted on technical grounds						
L15	15.41	18.43	20.48	14.53	18.46	19.97
L21	25.1	25.1	25.1	31.3	30.3	31.3



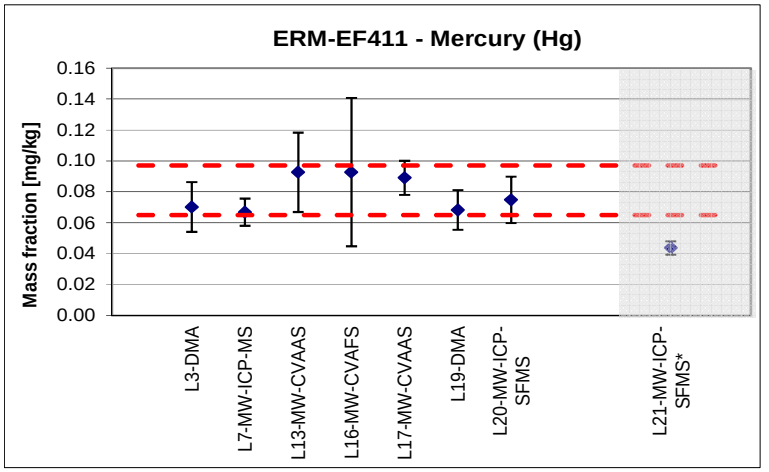
ERM-EF411 – Copper (Cu) in mg/kg (no value assigned)

Lab	Results					
L13	5.8	5.6	6.3	9.4	7.8	9.6
	6.8	6.7	6.7	6.6	6.6	6.6
Results not accepted on technical grounds						
L21	5.33	5.33	5.33	8.04	7.94	8.04



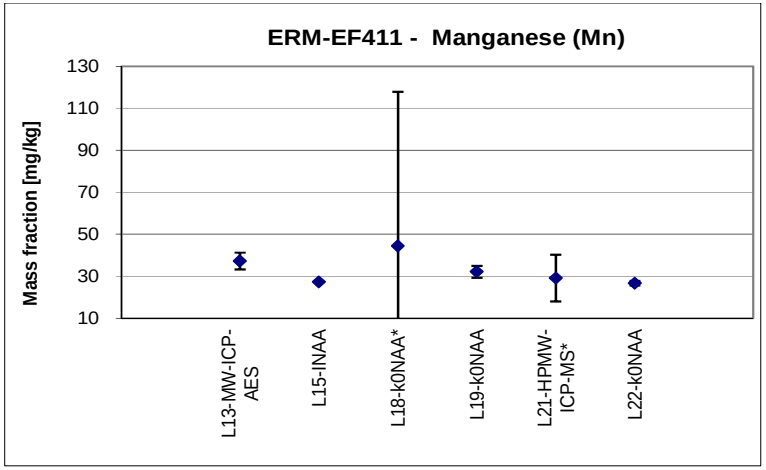
ERM-EF411 – Mercury (Hg) in mg/kg (indicative value)

Lab	Results					
L3	0.073	0.074	0.066	0.07	0.068	0.07
L7	0.0618	0.0652	0.0621	0.07	0.0705	0.0713
L13	0.099	0.088	0.087	0.117	0.085	0.107
	0.09	0.094	0.091	0.079	0.094	0.08
L16	0.094	0.066	0.078	0.076	0.126	0.116
L17	0.091	0.088	0.087	0.091	0.092	0.085
L19	0.0624	0.0644	0.0747	0.0639	0.0675	0.0764
L20	0.076	0.075	0.076	0.075	0.073	0.074
Results not accepted on technical grounds						
L21	0.053	0.051	0.052	0.037	0.035	0.034



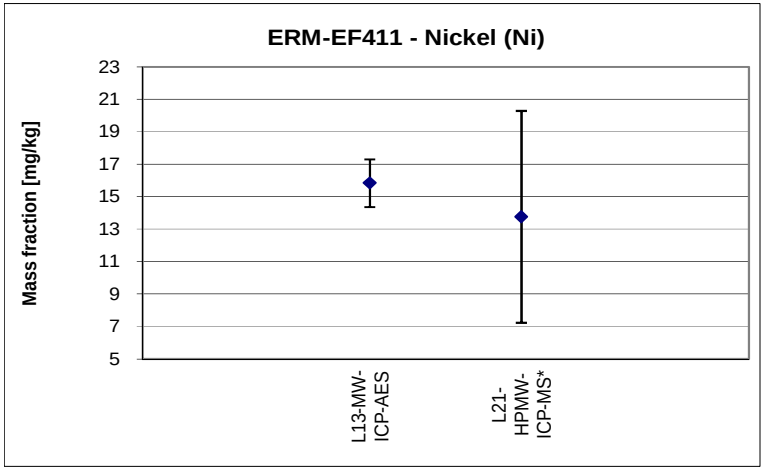
ERM-EF411 - Manganese (Mn) in mg/kg (no value assigned)

Lab	Results					
L13	36.9	35.3	33.1	38.8	39.2	36.1
	38.1	38.8	37.4	40.5	35.4	37
L15	25.14	36.35	27.79	21.91	26.08	26.22
	30.8	23.1	22.2	20.3	117.9	22.1
L18	27.3	47.4	121.9	52.5	21.1	26.3
L19	31.6	32.1	33.1	30.7	32.4	32.5
L21	24	24	24	34.5	33.4	34.5
L22	26.3	22.2	20.9	26.6	31.5	32.3



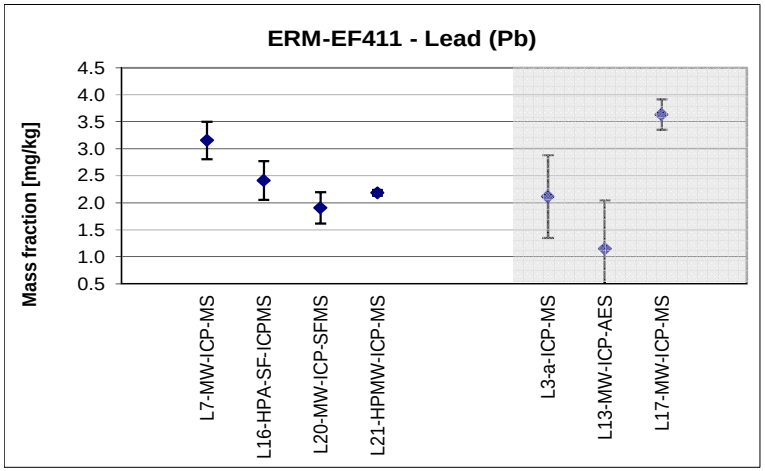
ERM-EF411 Nickel (Ni) in mg/kg (no value assigned)

Lab	Results					
L13	14.5	14.4	16.8	14.1	16.2	16.4
	14.7	16.4	14.9	17.1	17	17.5
L21	10.44	11.49	10.44	16.71	16.71	16.71



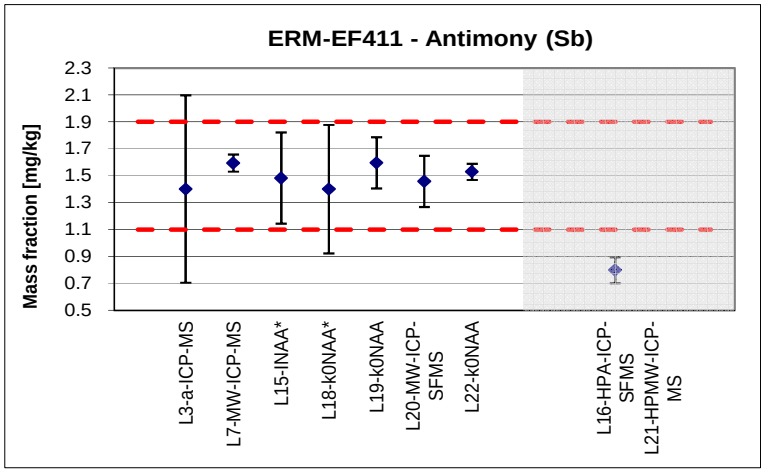
ERM-EF411 Lead (Pb) in mg/kg (no value assigned)

Lab	Results					
L7	3.003	3.023	2.968	3.366	3.306	3.264
L16	2.565	2.406	2.397	2.34	2.339	2.425
L20	1.92	1.88	1.89	1.98	1.9	1.87
L21	1.95	1.96	1.93	2.49	2.35	2.43
Results not accepted on technical grounds						
L3	2.2	2.1	2.2	2.1	2	2.1
L13	< 1	< 1	< 1	< 1	1	1.3
L17	3.512	3.561	3.448	3.537	3.875	3.863



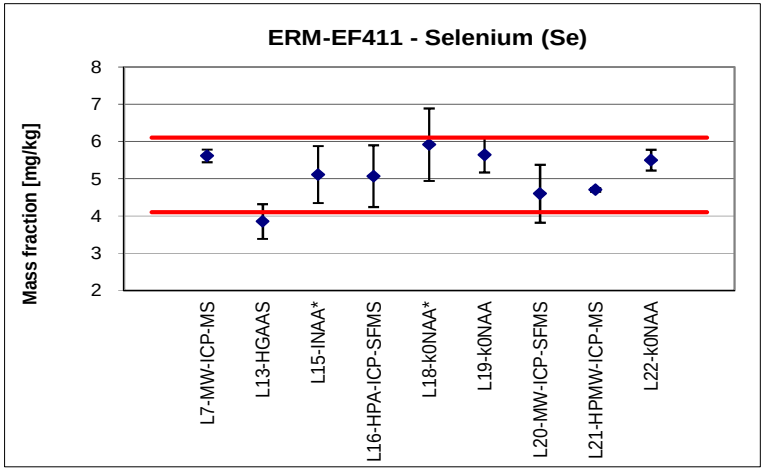
ERM-EF411 – Antimony (Sb) in mg/kg (indicative value)

Lab	Results					
L3a	1.4	1.4	1.4	1.4	1.4	1.4
L7	1.611	1.612	1.637	1.578	1.548	1.575
L15	1.587	1.306	1.713	1.537	1.477	1.271
L18	1.016	1.55	1.38	1.8	1.22	0.996
	1.32	1.38	1.48	1.52	1.47	1.66
L19	1.67	1.67	1.54	1.65	1.53	1.51
L20	1.47	1.48	1.48	1.47	1.45	1.39
L22	2.17	1.32	1.33	1.37	1.79	1.19
Results not accepted on technical grounds						
L16	0.804	0.778	0.857	0.844	0.727	0.773
L21	0.057	0.058	0.065	0.018	0.021	0.024



ERM-EF411 - Selenium (Se) in mg/kg (certified value)

Lab	Results					
L7	5.517	5.634	5.609	5.652	5.512	5.75
L13	4.47	4.06	3.75	3.91	3.89	3.87
	3.72	3.85	3.63	3.58	3.73	3.79
L15	4.648	4.859	5.584	5.561	5.013	5.001
L16	5.456	5.352	4.907	4.682	5.29	4.725
L18	6	7.09	5.22	5.73	5.86	6.19
	5.57	5.3	6.22	5.79	5.97	6.01
L19	5.72	5.65	5.47	5.74	5.5	5.77
L20	4.66	4.69	4.65	4.49	4.54	4.55
L21	4.31	4.48	4.5	4.93	4.91	5.08
L22	5.46	5.4	5.46	5.58	5.4	5.7

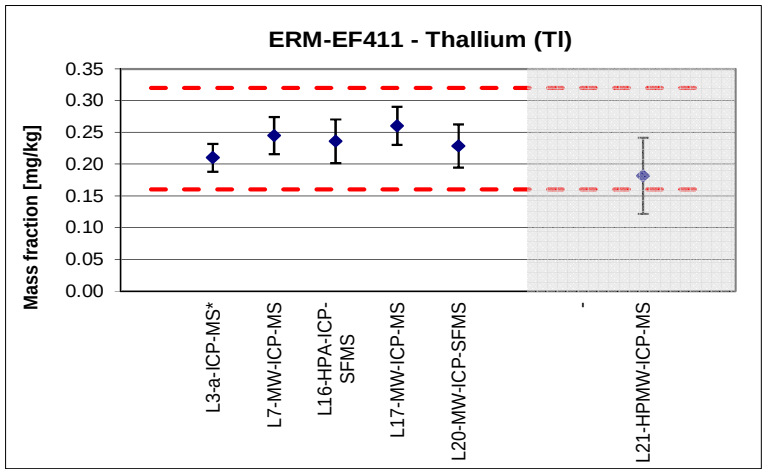


ERM-EF411 Tin (Sn) in mg/kg (no value assigned)

Lab	Results					
L21	0.178	0.157	0.157	0.23	0.219	0.219

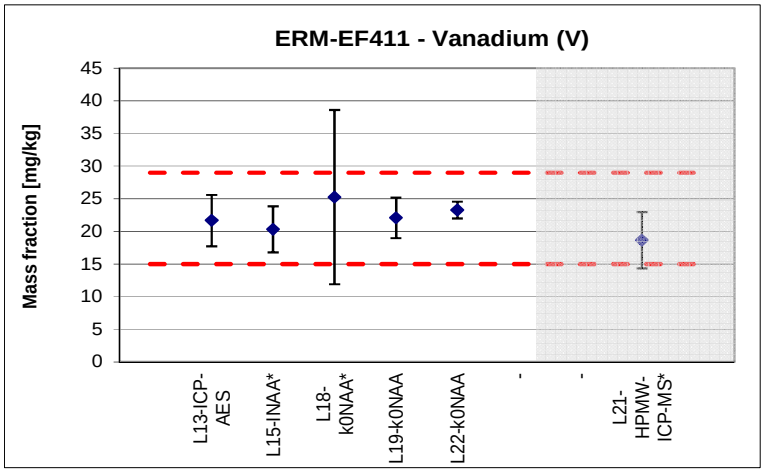
ERM-EF411 - Thallium (Tl) in mg/kg (indicative value)

Lab	Results					
L3	0.2	0.2	0.2	0.22	0.22	0.22
L7	0.234	0.232	0.231	0.264	0.259	0.248
L16	0.229	0.259	0.252	0.219	0.218	0.238
L17	0.265	0.267	0.26	0.261	0.25	0.258
L20	0.223	0.221	0.23	0.235	0.232	0.228
Results not accepted on technical grounds						
L21	0.193	0.266	0.26	0.105	0.13	0.135



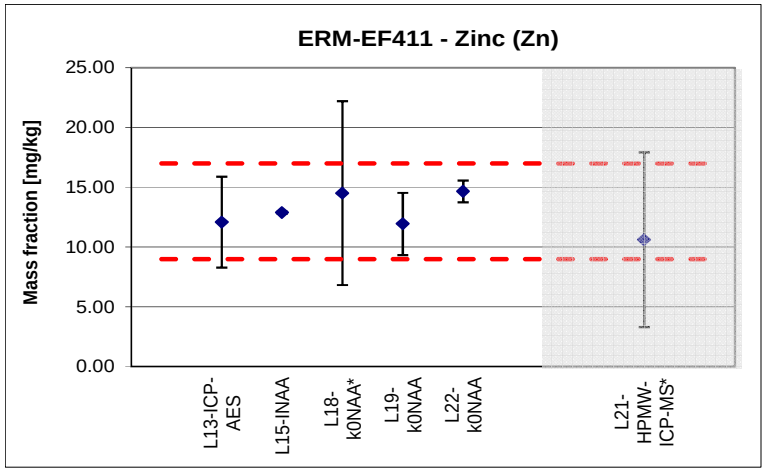
ERM-EF411 - Vanadium (V) in mg/kg (indicative value)

Lab						
L13	22.1	21.6	20.3	22.8	21.2	20.9
	22.5	22.5	21.1	21	21	22.5
L15	21.17	22.94	18.11	21.22	19.16	19.28
L18	28.6	24.4	21.1	18.8	36.7	26.8
	18.4	20.6	26.6	38.3	23.8	18.7
L19	23.8	23.4	21.4	22.2	20.5	21
L22	18.3	25.2	21.5	26.4	24.3	23.8
Results not accepted on technical grounds						
L21	16.7	16.7	16.7	20.9	19.9	20.9



ERM-EF411 - Zinc (Zn) in mg/kg (indicative value)

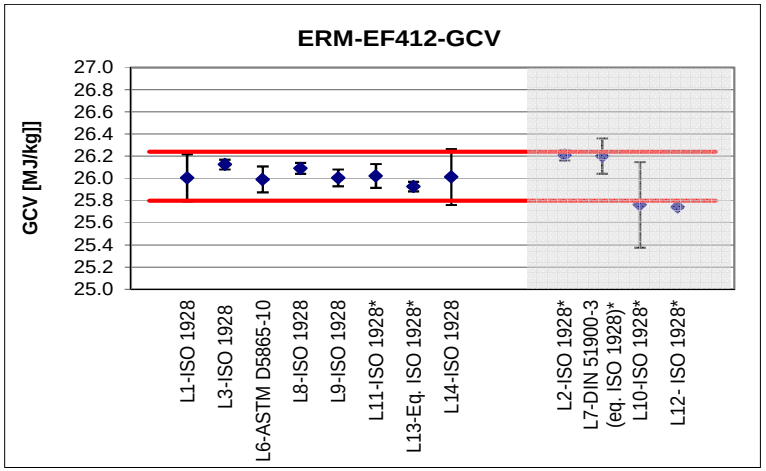
Lab						
L13	10.6	11.4	14.7	11.1	14.2	10.6
	11.8	12.2	11.5	11.2	12.5	11.4
L15	13.67	12.84	12.39	11.65	12.91	13.67
L18	11.1	15.5	11.5	11.2	10.8	11.1
	17	22.6	12.5	10.8	14.8	17.4
L19	13.4	13.1	11.3	12.6	10.7	10.5
L22	14.7	14.6	13.7	15.6	15.8	14.7
Results not accepted on technical grounds						
L21	7.83	7.94	8.04	14.6		7.83



Annex E.2: Results obtained in the characterisation study for ERM-EF412. The graphs give the average results and the expanded uncertainties estimated as two times the standard deviation from the control chart (proximates) or as stated by the laboratories (elements). An asterisk after the method means that two times the standard deviation of the results from the characterisation exercise was used as measurement uncertainty. The solid red lines give the certified range, the dashed red lines the indicative range. Shaded results are results not accepted on technical grounds.

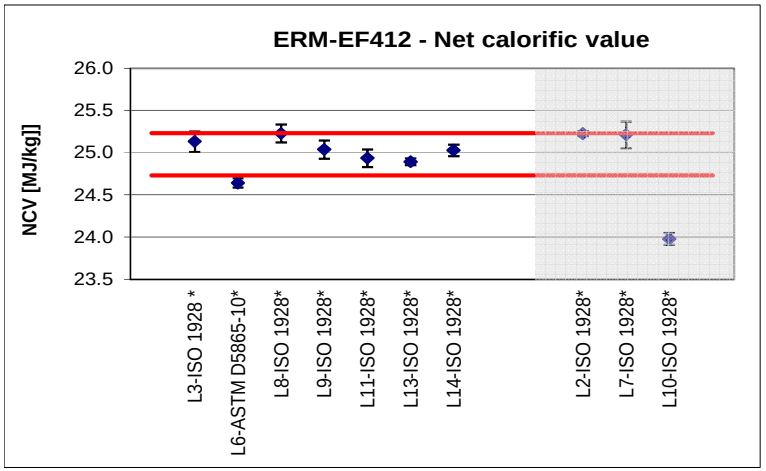
ERM-E F412-Gross calorific value (GCV) (ISO 1928/ASTM D5865) in MJ/kg (certified value)

Lab						
L1	25.908	25.998	26.044	26.127	26.018	25.931
L3	26.103	26.171	26.178	26.175	26.038	26.084
L6	25.987	25.971	25.962	25.987	26.046	25.992
L8	26.04	26.074	26.14	26.087	26.089	26.108
L9	25.99	25.96	26.03	26.01	26.04	26
L11	25.97	25.96	26.07	26.09	26	26.04
L13	25.92	25.89	25.92	25.94	25.95	25.94
L14	26.009	26.007	26.061	26.043	25.969	25.978
Results not accepted on technical grounds						
L2	26.19	26.23				
L7	26.118	26.09	26.275	26.213	26.284	26.215
L10	25.792	25.398	25.922	25.917	25.723	25.812
L12	25.76	25.7	25.77	25.67	25.81	25.73



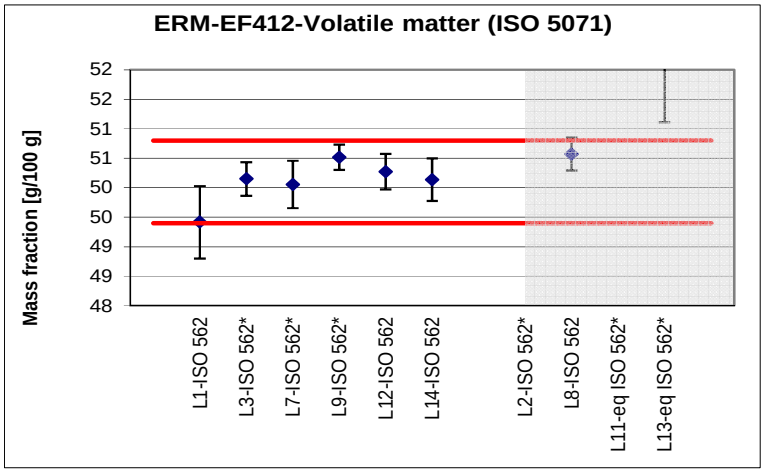
ERM-EF411 – Net calorific value (NVV) in MJ/kg (certified value)

Lab	Results					
L3	25.116	25.184	25.181	25.177	25.04	25.086
L6	24.65	24.644	24.603	24.629	24.685	24.634
L8	25.185	25.226	25.167	25.203	25.285	25.298
L9	25.05	24.99	25.09	25.08	25.05	24.95
L11	24.89	24.88	24.99	25	24.9	24.94
L13	24.89	24.86	24.88	24.9	24.92	24.9
L14	25.022	25.018	25.078	25.051	24.983	25.002
Results not accepted on technical grounds						
L2	25.21	25.24				
L7	25.129	25.102	25.285	25.222	25.295	25.225
L10	24.012	23.976	23.952	23.921	24	24



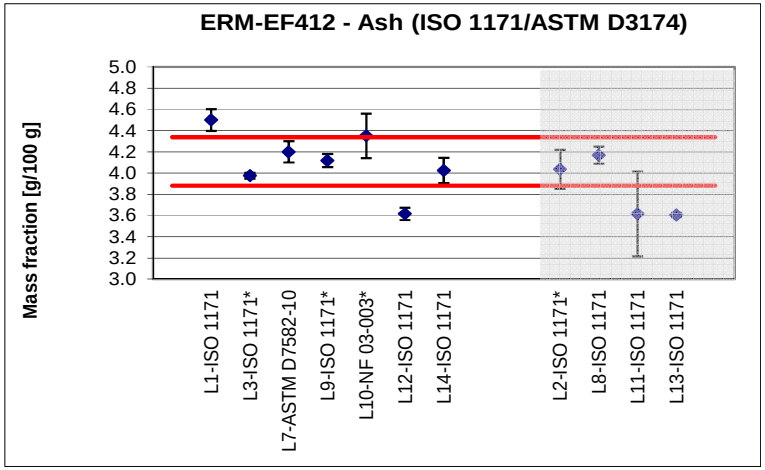
ERM-EF412-Volatile matter (ISO 562, ISO 5071) in g/100 g (certified value)

Lab	Results					
L1	49.36	49.51	49.3	49.33	49.51	49.47
L3	49.99	49.978	50.301	50.13	50.297	50.199
L7	50.27	50.33	49.98	49.85	50.01	49.88
L9	50.593	50.601	50.432	50.338	50.598	50.521
L12	50.36	50.46	50.26	50.19	50.06	50.29
L14	50.235	50.035	50.156	49.736	50.244	50.404
Results not accepted on technical grounds						
L2	46.33	46.24				
L8	50.289	50.574	50.53	50.925	50.613	50.477
L11	55.3	55.6	55.8	55.0	54.7	54.7
L13	55.1	55.1	55.4	54.6	54.7	51.1



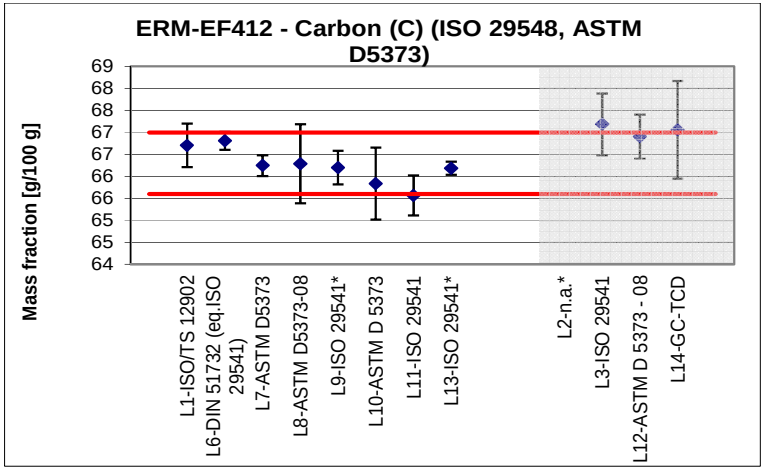
ERM-EF412 - Ash (ISO 1171/ASTM D3174) in g/100 g (certified value)

Lab	Results					
L1	4.33	4.34	4.42	4.47	4.73	4.71
L3	3.99	3.975	3.955	3.989	3.973	3.964
L7	4.22	4.26	4.15	4.21	4.14	4.22
L9	4.134	4.091	4.118	4.11	4.169	4.085
L10	4.3	4.3	4.5	4.4	4.4	4.2
L12	3.67	3.55	3.6	3.64	3.58	3.65
L14	4.079	4.126	4.128	4.017	3.895	3.899
Results not accepted on technical grounds						
L2	3.97	4.10				
L8	4.139	4.109	4.131	4.304	4.087	4.242
L11	3.63	3.61	3.62	3.6	3.61	3.62
L13	3.61	3.59	3.61	3.62	3.6	3.6



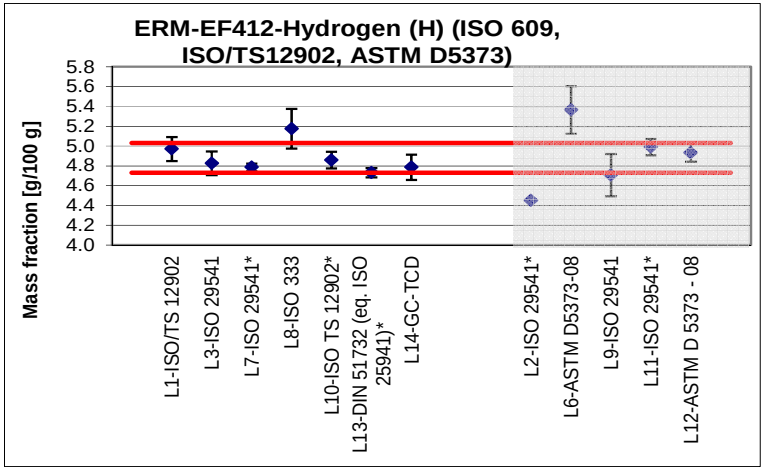
ERM-EF412 - Carbon (C) (ISO 29548, ASTM D5373) in g/100 g (certified value)

Lab	Results					
L1	66.41	66.48	66.69	67.03	66.65	66.97
L6	66.43	66.55	67.09	66.88	66.98	66.92
L7	66.29	66.15	66.27	66.25	66.13	66.39
L8	66.135	66.42	66.089	66.197	66.626	66.244
L9	66.266	66.21	66.012	65.933	66.435	66.331
L10	66	65	66.6	66.1	65.4	65.9
L11	65.5	65.31	65.5	65.44	65.77	65.89
L13	66.1	66.1	66.2	66.3	66.2	66.2
Results not accepted on technical grounds						
L2	61.15	61.06				
L3	67.526	67.526	67.05	67.05	66.989	66.967
L12	66.9	66.78	67.15	66.79	66.89	66.9



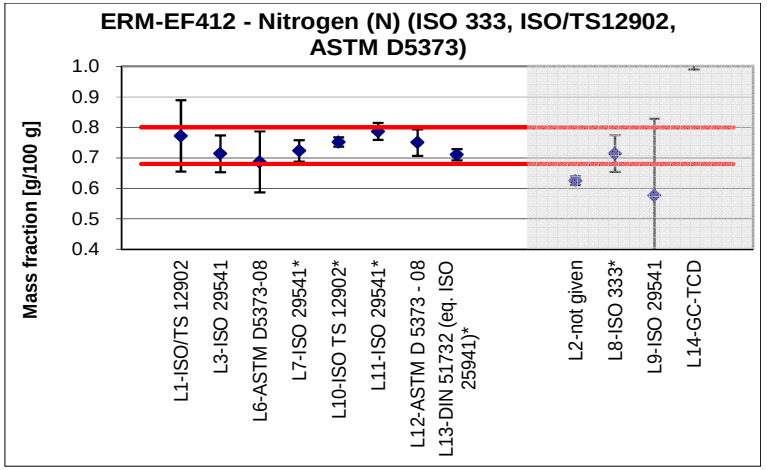
Hydrogen (H) (ISO 609, ISO/TS12902, ASTM D5373) in g/100 g (certified value)

Lab	Results					
L1	5.01	5.09	4.88	4.93	4.95	4.96
L3	4.761	4.815	4.837	4.848	4.856	4.834
L7	4.79	4.81	4.8	4.77	4.76	4.78
L8	5.229	5.201	5.303	5.301	4.992	5.02
L10	4.83	4.93	4.82	4.83	4.88	4.86
L13	4.71	4.72	4.74	4.76	4.75	4.7
L14	4.79	4.8	4.77	4.82	4.79	4.74
Results not accepted on technical grounds						
L2	4.43	4.47				
L6	5.3	5.25	5.43	5.41	5.41	5.39
L9	4.599	4.687	4.547	4.512	4.798	5.098
L11	4.95	4.96	4.96	4.99	5.03	5.05
L12	4.91	4.92	4.92	4.94	4.95	4.96



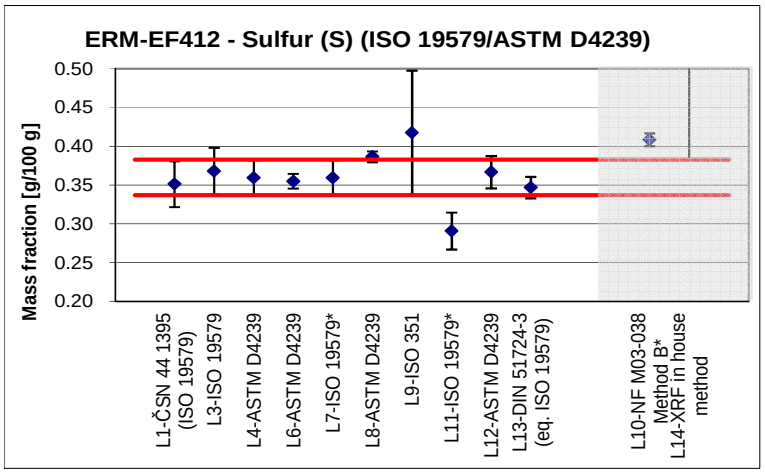
Nitrogen (N) (ISO 333, ISO/TS12902, ASTM D5373) in g/100 g (certified value)

Lab	Results					
L1	0.775	0.769	0.758	0.825	0.742	0.761
L3	0.714	0.729	0.709	0.7	0.716	0.712
L6	0.65	0.64	0.78	0.72	0.66	0.67
L7	0.699	0.728	0.732	0.75	0.717	0.714
L10	0.76	0.74	0.76	0.75	0.75	0.75
L11	0.801	0.797	0.789	0.764	0.792	0.776
L12	0.77	0.79	0.73	0.72	0.73	0.76
L13	0.696	0.719	0.709	0.704	0.712	0.72
Results not accepted on technical grounds						
L2	0.62	63				
L8	0.657	0.716	0.719	0.708	0.748	0.736
L9	0.566	0.586	0.566	0.587	0.566	0.587
L14	1.15	1.21	1	1.05	1.07	1.06



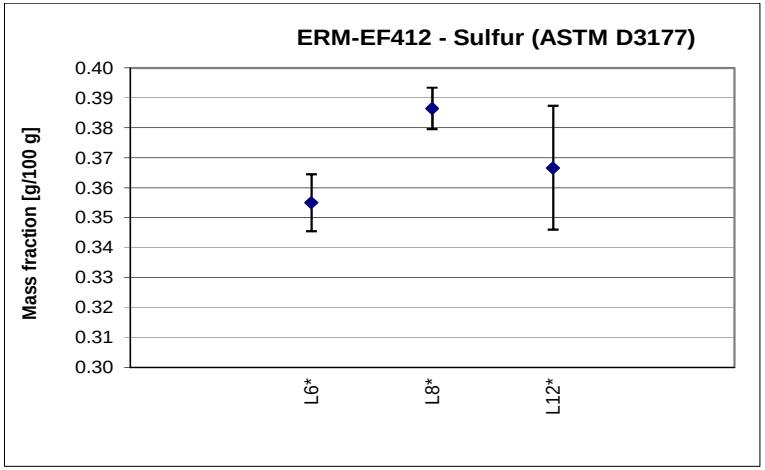
ERM-EF412 - Sulfur (S) (ISO 19579/ASTM D4239) g/100 g (certified value)

Lab	Results					
L1	0.367	0.37	0.343	0.366	0.329	0.332
L3	0.394	0.384	0.358	0.351	0.358	0.362
L4	0.365	0.345	0.374	0.356	0.368	0.349
L6	0.361	0.353	0.358	0.347	0.356	0.355
L7	0.365	0.345	0.374	0.356	0.368	0.349
L8	0.393	0.385	0.383	0.387	0.386	0.385
L9	0.42	0.392	0.424	0.426	0.422	0.422
L11	0.285	0.275	0.301	0.288	0.287	0.308
L12	0.36	0.36	0.38	0.38	0.36	0.36
L13	0.322	0.336	0.376	0.384	0.326	0.337
Results not accepted on technical grounds						
L10	0.41	0.4	0.41	0.41	0.41	0.41
L14	0.511	0.505	0.502	0.504	0.499	0.499



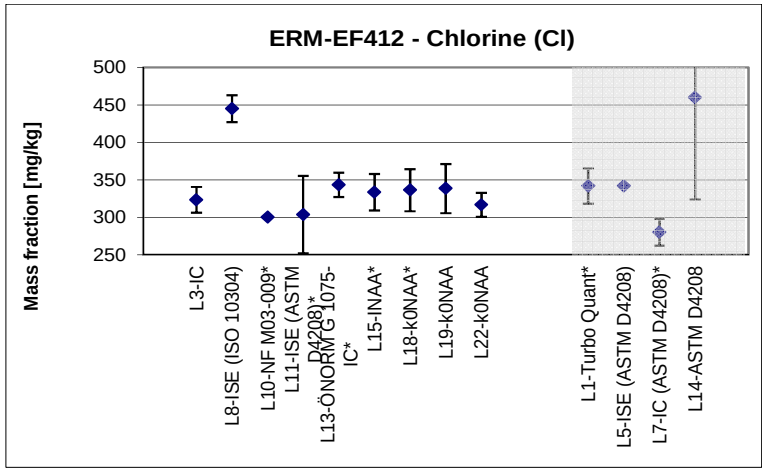
ERM-EF412 - Sulfur (S) (ASTM D3177) g/100 g (no value assigned)

Lab	Results					
L6*	0.361	0.353	0.358	0.347	0.356	L6*
L8*	0.393	0.385	0.383	0.387	0.386	L8*
L12*	0.36	0.36	0.38	0.38	0.36	L12*



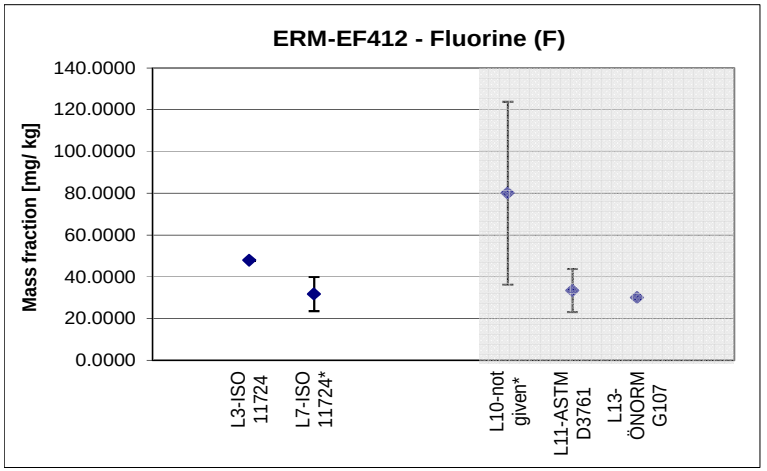
ERM-EF412 – Chlorine (Cl) in mg/kg (no value assigned)

Lab	Results					
L3	320	310	340	330	320	320
L8	450	450	440	450	430	450
L10	300	300	300	300	300	300
L11	300	280	320	340	310	270
L13	340	330	350	350	340	350
L15	320	320	340	330	340	350
L18	340	320	320	340	330	350
	330	360				
L19	330	340	340	360	330	330
L22	310	320	320	320	320	310
Results not accepted on technical grounds						
L1	350	340	330	340	330	360
L5	350	340	330	340	330	360
L7	290	290	280	280	270	270
L14	470	460	460	460	460	450



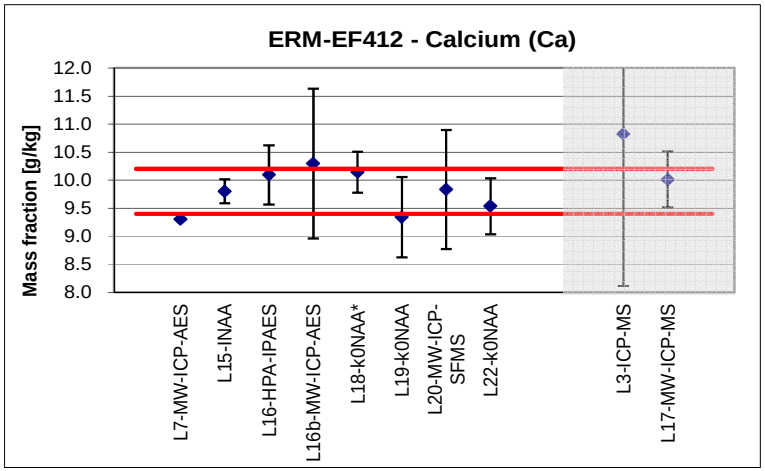
ERM-EF412 – Fluorine (F) in mg/kg (additional material information value)

Lab	Results					
L3	50	47	51	49	46	44
L7	40	30	30	30	30	30
Results not accepted on technical grounds						
L10	50	70	100	110	80	70
L11	40	30	30	40	30	30
L13	30	30	30	30	30	30



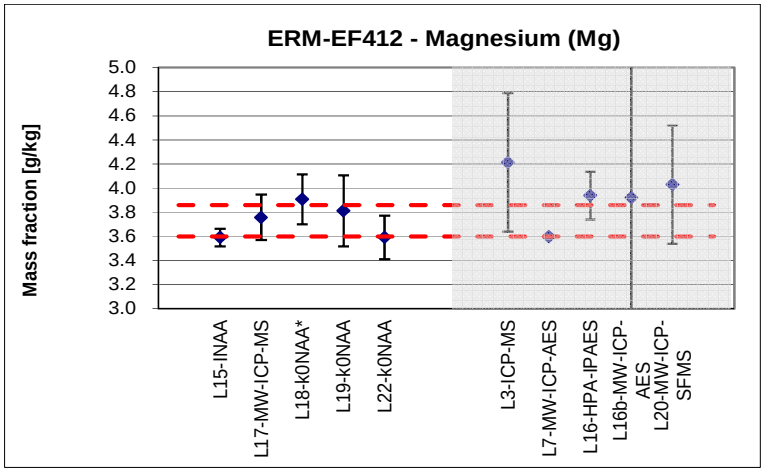
ERM-EF412 - Calcium (Ca) in g/kg (certified value)

Lab	Results					
L7	9.311	9.305	9.283	9.364	9.229	9.317
L15	10.28	9.658	9.543	9.698	9.89	9.728
L16	10.09847	10.2619	10.327	9.8407	9.7113	10.32089
L16b-MW	10.49426	9.93516	10.688	9.9269	10.629	10.10659
L18	9.99	10.28	10.17	10.28	10.34	10.13
	9.78	10.2				
L19	9.262	9.329	9.114	9.458	9.517	9.369
L20	9.9	9.9	9.7	10	9.8	9.7
L22	9	9.3	9.8	9.8	9.7	9.6
Results not accepted on technical grounds						
L3	10.45	10.32	10.33	11.32	11.19	11.31
L17	10.199	10.01	10.03	9.93	9.96	9.94



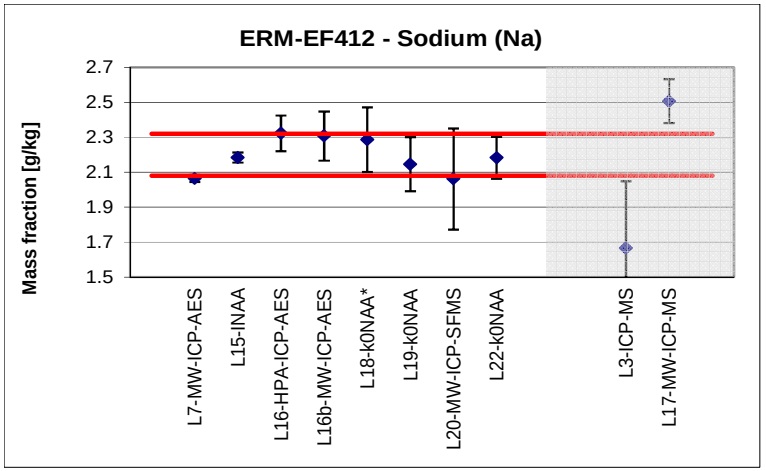
ERM-EF412 - Magnesium (Mg) in g/kg (indicative value)

Lab	Results					
L15	3.536	3.633	3.709	3.493	3.502	3.671
L17	3.730	3.829	3.736	3.725	3.737	3.789
L18	3.925	3.81	3.789	3.834	3.893	3.988
	3.917	4.1				
L19	3.842	3.748	3.722	3.884	3.834	3.84
L22	3.45	3.64	3.61	3.63	3.61	3.61
Results not accepted on technical grounds						
L3	4.01	4.06	3.95	4.39	4.46	4.41
L7	3.602	3.583	3.608	3.622	3.566	3.606
L16	3.960	3.987	4.045	3.833	3.799	4.006
L16b	4.054	3.825	4.056	3.841	4.083	3.659
L20	3.94	3.96	3.95	4.15	4.08	4.09



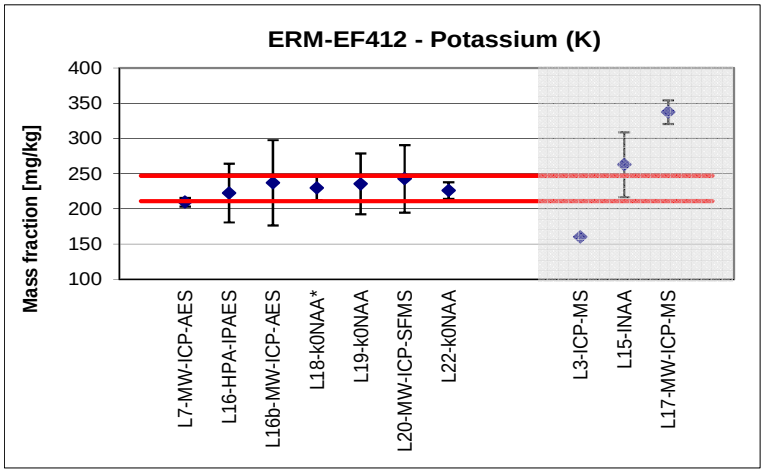
ERM-EF412 - Sodium (Na) in g/kg (certified value)

Lab	Results					
L7	2.084	2.055	2.071	2.054	2.07	2.054
L15	2.174	2.17	2.207	2.168	2.185	2.202
L16	2.36	2.33	2.36	2.29	2.24	2.367
L16b-MW	2.35	2.24	2.37	2.28	2.37	2.22
L18	2.34	2.19	2.43	2.21	2.22	2.38
	2.32	2.2				
L19	2.157	2.13	2.116	2.156	2.151	2.166
L20	2.11	2.02	2.13	2.01	2	2.1
L22	2.19	2.18	2.15	2.22	2.18	2.18
Results not accepted on technical grounds						
L3	1.62	1.61	1.58	1.71	1.71	1.76
L17	2.418	2.555	2.516	2.422	2.588	2.544



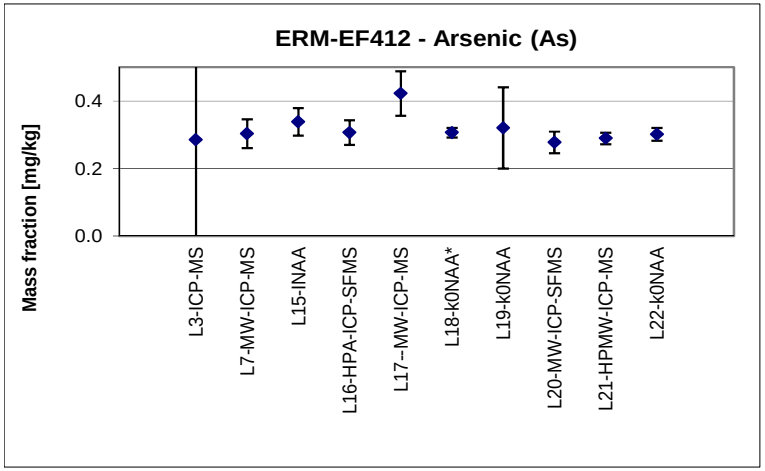
ERM-EF412 - Potassium (K) in mg/kg (certified value)

Lab	Results					
L7	209.5	211.7	212.9	211.4	207.4	203.5
L16	253.099	240.139	222.55	202.525	200.86	214.511
L16b	231.238	253.239	222.33	232.703	250.007	232.085
L18	228	233	220	237	219	239
L19	230	239	272	220	217	234
L20	237	249	241	246	239	243
L22	226	222	225	232	227	223
Results not accepted on technical grounds						
L3	150	140	150	180	170	170
L15	246	394	255	237	149	295
L17	327	346	357	348	327	320



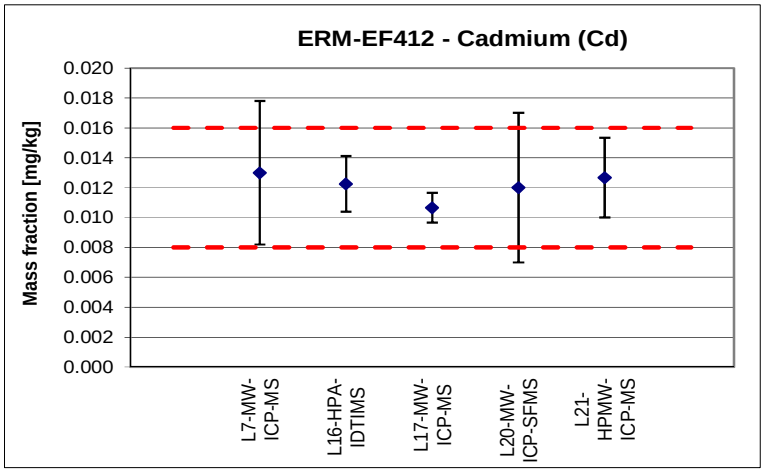
ERM-EF412 – Arsenic (As) in mg/kg (no value assigned)

Lab	Results					
L3	0.26	0.3	0.29	0.29	0.3	0.27
L7	0.314	0.322	0.318	0.313	0.282	0.271
L15	0.318	0.343	0.351	0.313	0.329	0.373
L16	0.317	0.309	0.317	0.29	0.291	0.313
L17	0.418	0.387	0.425	0.426	0.405	0.472
L18	0.297	0.3	0.309	0.302	0.314	0.313
L19	0.27	0.33	0.24	0.36	0.4	0.32
L20	0.287	0.277	0.264	0.278	0.279	0.276
L21	0.289	0.29	0.289	0.286	0.296	0.283
L22	0.311	0.3	0.305	0.31	0.28	0.3



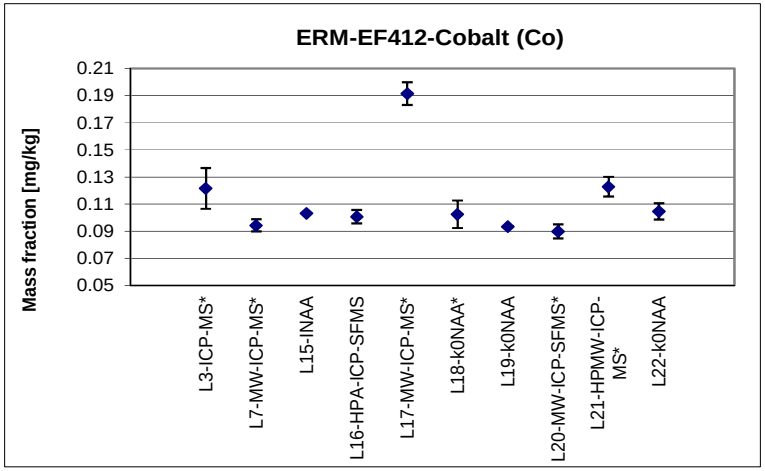
ERM-EF412 - Cadmium (Cd) in mg/kg (indicative value)

Lab						
L7	0.014	0.014	0.017	0.011	0.01	0.012
L16	0.013	0.012	0.015	0.01	0.015	0.015
	0.012	0.011	0.013	0.01	0.012	0.012
L17	0.011	0.012	0.01	0.011	0.01	0.01
L20	0.011	0.011	0.013	0.011	0.014	0.012
L21	0.013	0.013	0.013	0.013	0.011	0.013



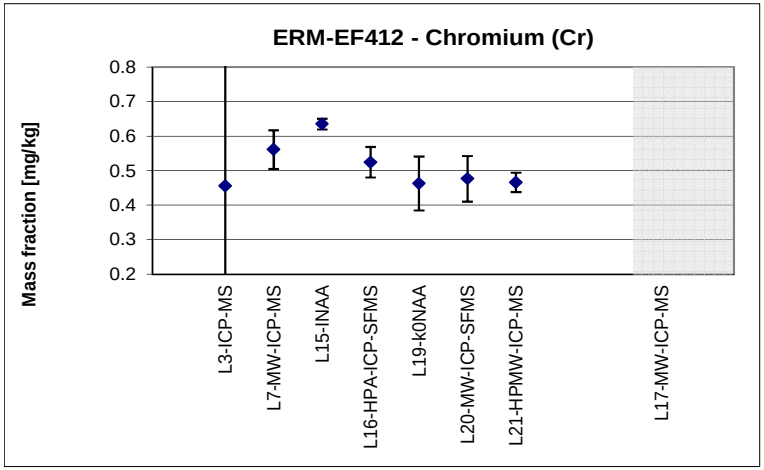
ERM-EF412 – Cobalt (Co) in mg/kg (no value assigned)

Lab	Results					
L3	0.12	0.13	0.13	0.12	0.11	0.12
L7	0.095	0.094	0.094	0.094	0.098	0.091
L15	0.119	0.11	0.079	0.088	0.102	0.122
L16	0.101	0.1	0.103	0.096	0.102	0.102
L17	0.189	0.189	0.189	0.189	0.199	0.194
L18	0.103	0.106	0.106	0.099	0.094	0.107
L19	0.094	0.093	0.092	0.096	0.09	0.096
L20	0.091	0.09	0.09	0.094	0.089	0.086
L21	0.122	0.127	0.127	0.123	0.12	0.118
L22	0.103	0.098	0.102	0.115	0.105	0.105



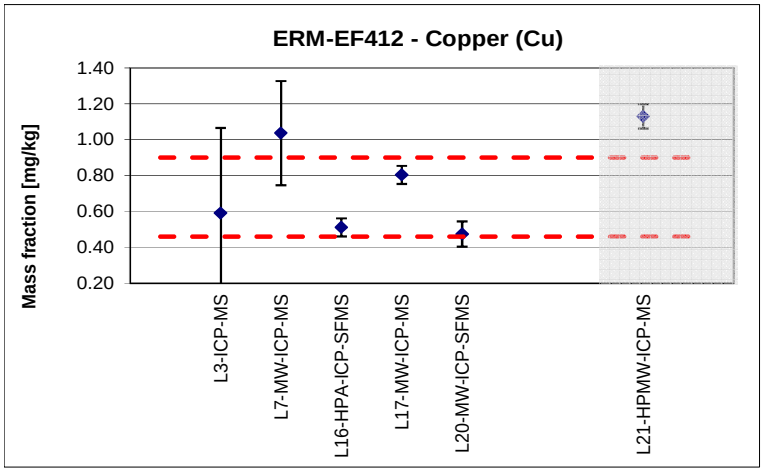
ERM-EF412 - Chromium (Cr) in mg/kg (no value assigned)

Lab	Results					
L3	<0.42	0.46	0.45	0.48	0.45	0.44
L7	0.545	0.594	0.595	0.55	0.526	0.555
L15	0.76	0.3	0.593	0.8	0.767	0.589
L16	0.538	0.502	0.526	0.506	0.513	0.561
L19	0.435	0.423	0.439	0.512	0.492	0.475
L20	0.473	0.477	0.474	0.467	0.488	0.479
L21	0.466	0.487	0.482	0.454	0.468	0.439
Results not accepted on technical grounds						
L17	1.16	1.31	1.1	1.27	1.16	1.21



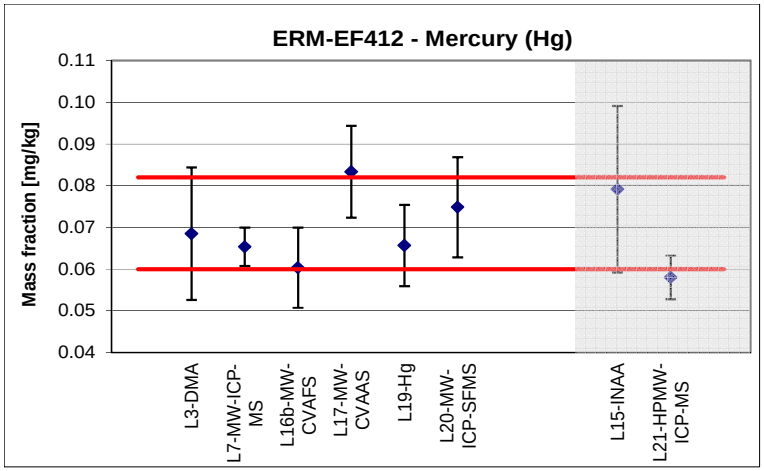
ERM-EF412 - Copper (Cu) in mg/kg (indicative value)

Lab	Results					
L3	0.59	0.64	0.62	0.51	0.53	0.65
L7	0.933	0.941	0.985	1.199	0.917	1.247
L16	0.529	0.482	0.526	0.481	0.542	0.508
L17	0.802	0.762	0.855	0.889	0.763	0.751
L20	0.469	0.472	0.473	0.475	0.486	0.471
Results not accepted on technical grounds						
L21	0.51	0.519	0.515	1.65	1.75	1.83



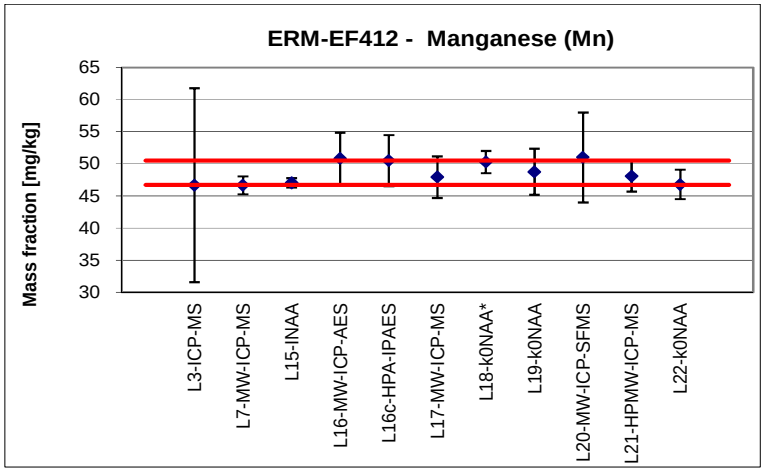
ERM-EF412 - Mercury (Hg) in mg/kg (certified value)

Lab	Results					
L3	0.065	0.066	0.068	0.064	0.075	0.073
L7	0.067	0.068	0.064	0.063	0.067	0.063
L16b	0.064	0.067	0.056	0.062	0.056	0.057
L17	0.08	0.082	0.085	0.085	0.08	0.088
L19	0.068	0.062	0.064	0.07	0.06	0.07
L20	0.076	0.075	0.076	0.075	0.073	0.074
Results not accepted on technical grounds						
L15	0.044	0.078	0.088	0.099	0.072	0.094
L21	0.062	0.059	0.093	0.051	0.039	0.044



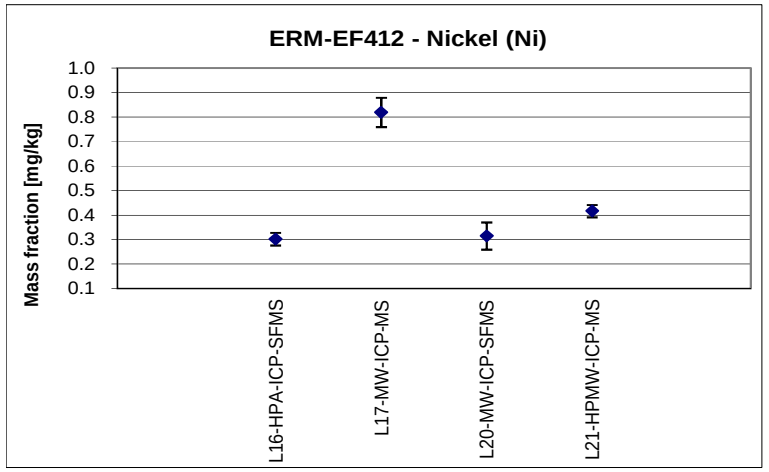
ERM-EF412 - Manganese (Mn) in mg/kg (certified value)

Lab	Results					
L3	44	49	49	46	46	46
L7	46.99	45.9	46.2	46.18	47.13	47.44
L15	47.57	47.13	46.99	46.71	47.03	46.62
L16	50.353	49.966	52.025	50.753	51.176	50.538
L16c	51.221	49.124	51.722	50.649	50.048	50.119
L17	47.94	48.33	47.75	47.43	48.14	47.98
L18	50.3	48.8	49.4	50.6	50.3	50.9
	50.3	51.6				
L19	49	49	48.6	49.1	49.2	47.6
L20	50.5	51.9	51.6	50.4	51.8	49.8
L21	48	49.5	50.6	46.9	47	46.5
L22	47.4	46.6	47.9	46.5	45.7	46.6



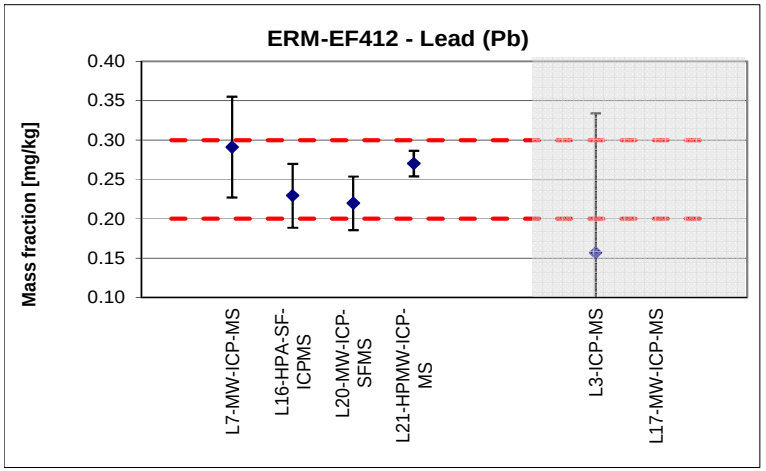
ERM-EF412 – Nickel (Ni) in mg/kg ((no value assigned)

Lab	Results					
L16	0.299	0.324	0.304	0.287	0.292	0.306
L17	0.702	0.793	0.889	0.856	0.738	0.935
L20	0.315	0.308	0.311	0.316	0.328	0.309
L21	0.437	0.404	0.419	0.487	0.386	0.363



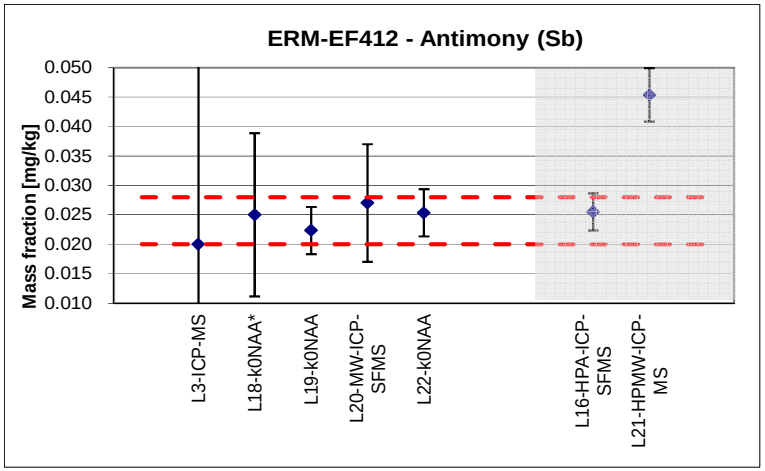
ERM-EF412 - Lead (Pb) in mg/kg (indicative value)

Lab	Results					
L7	0.3134	0.3361	0.3097	0.2538	0.2631	0.2695
L16	0.235518	0.24567	0.232	0.22668	0.21417	0.22106
L20	0.226	0.22	0.212	0.218	0.219	0.223
L21	0.25	0.241	0.243	0.292	0.296	0.299
Results not accepted on technical grounds						
L3	0.14	0.21	0.16	0.11	0.17	0.15
L17	1.146	1.088	1.233	1.033	1.1	1.44



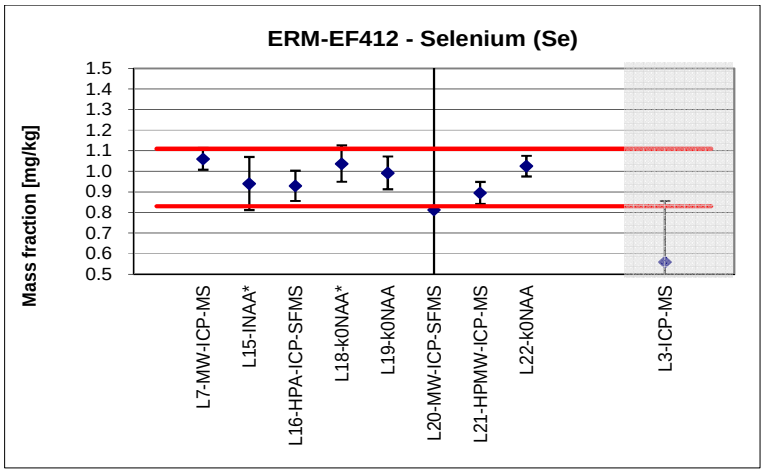
ERM-EF412 - Antimony (Sb) in mg/kg (indicative value)

Lab	Results					
L3	0.02	0.02	0.02	0.02	0.02	0.02
L18	0.026	0.026	0.03	0.025	0.025	0.027
	0.032	0.009				
L19	0.024	0.023	0.022	0.02	0.025	0.02
L20	0.028	0.026	0.028	0.028	0.027	0.025
L22	0.032	0.027	0.02	0.024	0.022	0.027
Results not accepted on technical grounds						
L16	0.028	0.026	0.026	0.024	0.024	0.025
L21	0.027	0.143	0.037	0.013	0.038	0.014



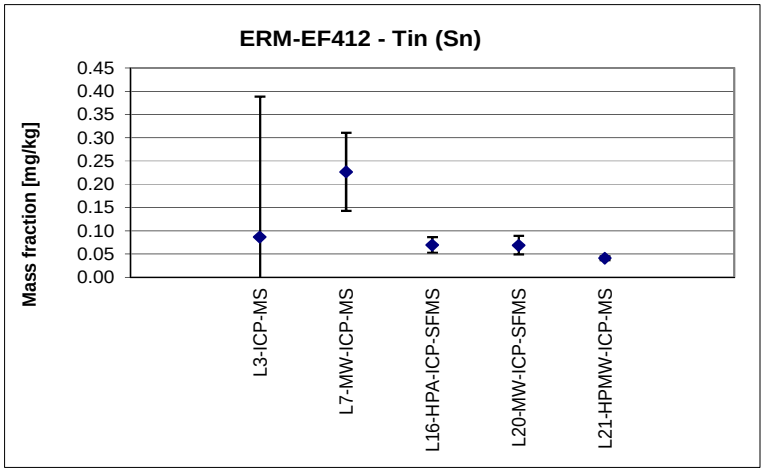
ERM-EF412 - Selenium (Se) in mg/kg (certified value)

Lab	Results					
L7	1.064	1.071	1.07	1.006	1.061	1.09
L15	0.94	0.903	1.004	0.918	0.851	1.024
L16	0.964	0.94	0.925	0.936	0.896	0.916
L18	0.976	1.121	1.026	1.036	1.049	0.994
	1.066	1.033				
L19	1.03	1	0.97	0.97	0.97	1.01
L20	0.803	0.809	0.795	0.845	0.811	0.815
L21	0.822	0.822	0.858	0.941	0.926	1
L22	1.01	0.96	0.97	1.13	1	1.08
Results not accepted on technical grounds						
L3	0.49	0.48	0.59	0.59	0.62	0.59



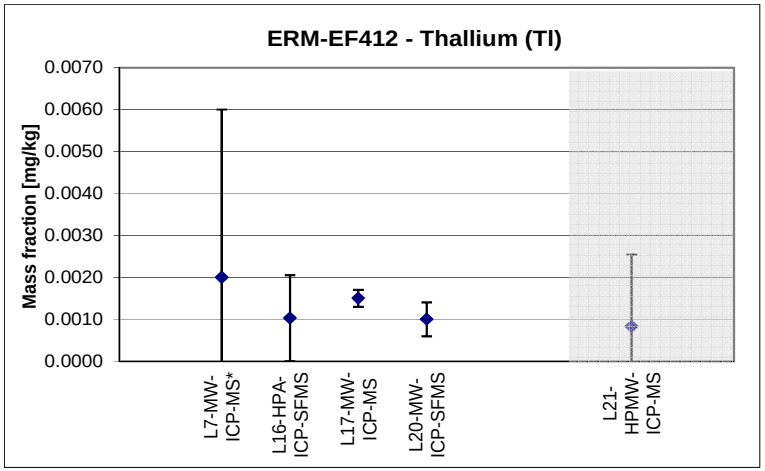
ERM-EF412 – Tin (Sn) in mg/kg(additional material information va lue)

Lab	Results					
L3	0.07	0.08	0.07	0.08	0.1	0.12
L7	0.27	0.248	0.273	0.196	0.172	0.202
L16	0.072	0.068	0.066	0.085	0.067	0.06
L21	0.006	0.055	0.029	0.058	0.055	0.044
Results not accepted on technical grounds						
L20	0.068	0.068	0.067	0.07	0.071	0.071



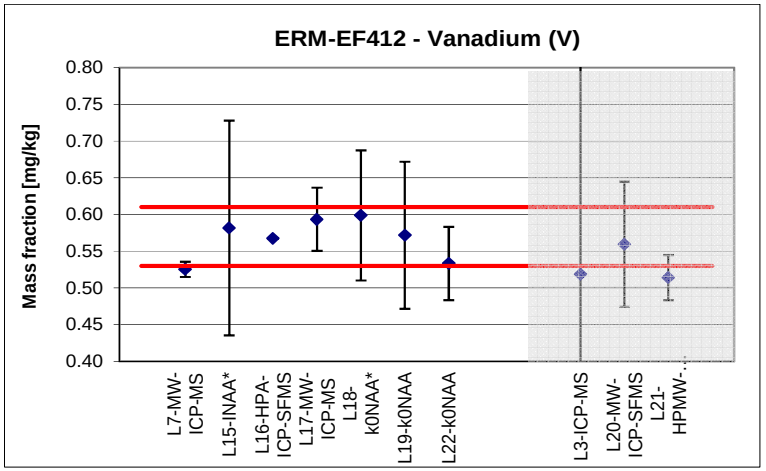
ERM-EF412 – Thallium (Tl) in mg/kg (no value assigned)

Lab	Results					
L7	0.001	0.002	-0.001	0.005	0.003	0.002
L16	0.001	0.001	0.001	0.001	0.001	0.001
L17	0.001	0.001	0.002	0.002	0.002	0.001
L20	0.001	0.001	0.001	0.001	0.001	0.001
Results not accepted on technical grounds						
L21	0	0	0.005	0	0	0



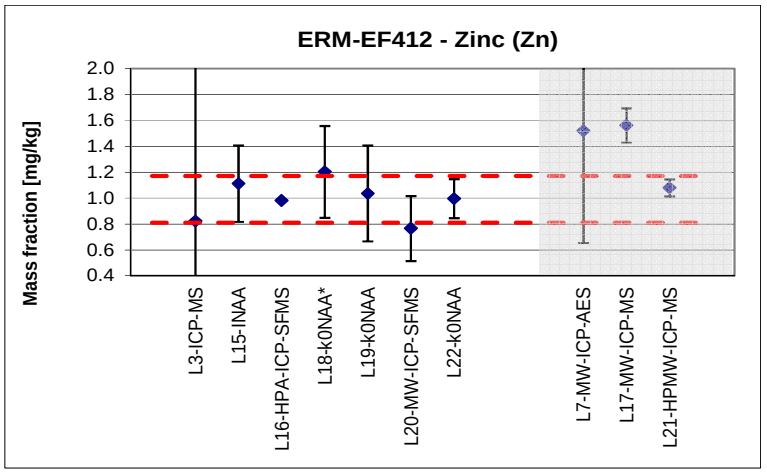
ERM-EF412 - Vanadium (V) in mg/kg (certified value)

Lab	Results					
L7	0.522	0.529	0.523	0.524	0.536	0.518
L15	0.455	0.579	0.58	0.567	0.655	0.653
L16	0.586	0.566	0.581	0.552	0.52	0.599
L17	0.582	0.586	0.597	0.606	0.605	0.584
L18	0.61	0.543	0.618	0.676	0.631	0.553
	0.591	0.568				
L19	0.6	0.53	0.59	0.53	0.64	0.54
L20	0.548	0.553	0.555	0.563	0.578	0.559
L22	0.51	0.53	0.52	0.54	0.58	0.52
Results not accepted on technical grounds						
L3	0.5	0.56	0.56	0.51	0.5	0.48
L21	0.51	0.525	0.523	0.514	0.506	0.506



ERM-EF412 - Zinc (Zn) in mg/kg (indicative value)

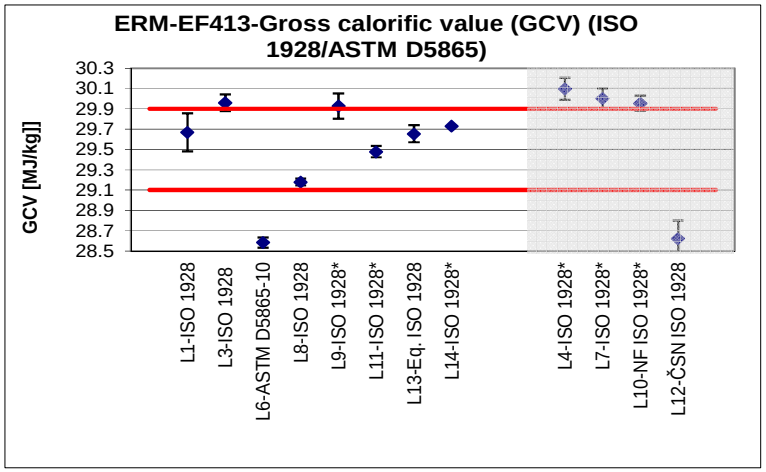
Lab	Results					
L3	0.86	1	0.92	0.71	0.73	0.71
L15	1.17	1.41	1.11	1.12	1.21	0.65
L16	1.031	1.045	0.992	0.906		0.933
L19	1.19	1.83	0.86	0.73	0.76	0.84
L20	0.759	0.781	0.788	0.767	0.749	0.749
L22	0.87	0.97	1.02	1	0.97	1.14
Results not accepted on technical grounds						
L7	2.135	1.667	1.834	1.357	1.106	1.018
L17	1.411	1.554	1.482	1.553	1.662	1.695
L18	1.21	1.27	1.58	1.1	1.21	1.07
	1.19	0.99				
L21	0.8	0.789	0.759	1.318	1.516	1.285



Annex E.3: Results obtained in the characterisation study for ERM-EF413. The graphs give the average results and the expanded uncertainties estimated as two times the standard deviation from the control chart (proximates) or as stated by the laboratories (elements). An asterisk after the method means that two times the standard deviation of the results from the characterisation exercise was used as measurement uncertainty. The solid red lines give the certified range, the dashed red lines the indicative range. Shaded results are results not accepted on technical grounds.

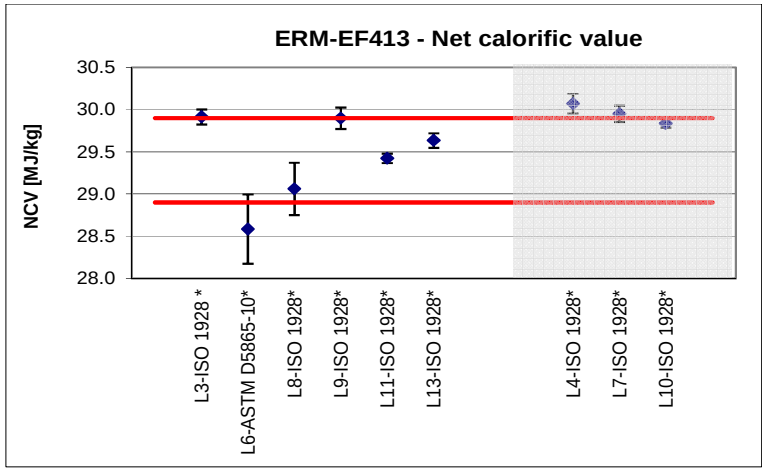
ERM-EF413-Gross calorific value (GCV) (ISO 1928/ASTM D5865) in MJ/kg (certified value)

Lab	Results					
L1	29.77	29.846	29.328	29.432	29.807	29.831
L3	29.911	29.972	30.013	29.92	30.014	29.932
L6	28.512	28.298	28.42	28.759	28.7	28.818
L8	29.37	29.34	29.2	29.114	29.005	29.049
L9	29.87	29.9	29.94	29.86	30	30
L11	29.53	29.46	29.45	29.48	29.47	29.48
L13	29.73	29.67	29.61	29.61	29.64	29.67
L14	29.638	29.623	29.751	29.744	29.826	29.798
Results not accepted on technical grounds						
L4	30.095	30.08	30.02	30.072	30.166	30.155
L7	29.993	29.963	30.023	29.935	30.064	30.042
L10	29.942	29.915	29.966	30.009	29.981	29.917
L12	28.91	28.93	28.21	28.11	28.77	28.8



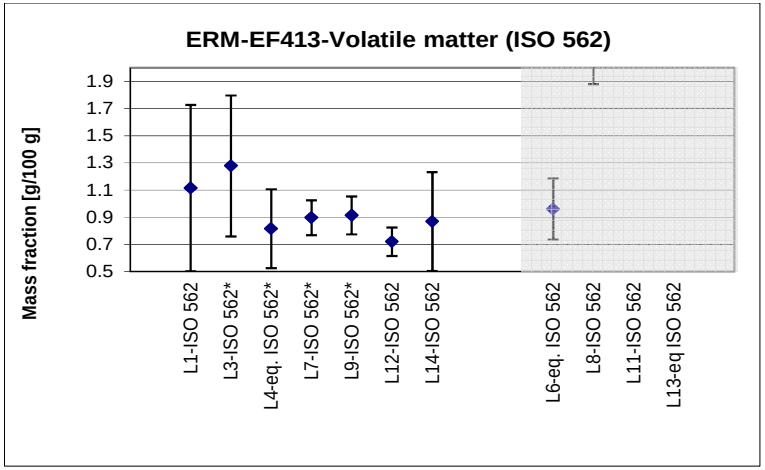
ERM-EF413 – Net calorific value (NCV) in MJ/kg (certified value)

Lab	Results					
L3	29.87	29.93	29.963	29.871	29.962	29.879
L6	28.512	28.299	28.421	28.76	28.702	28.816
L8	29.257	29.227	29.079	28.992	28.885	28.928
L9	29.83	29.88	29.9	29.83	29.97	29.97
L11	29.47	29.4	29.39	29.42	29.42	29.43
L13	29.7	29.65	29.59	29.59	29.62	29.65
Results not accepted on technical grounds						
L4	30.066	30.052	29.987	30.039	30.142	30.128
L7	29.941	29.911	29.969	29.88	30.009	29.987
L10	29.822	29.795	29.846	29.859	29.861	29.827



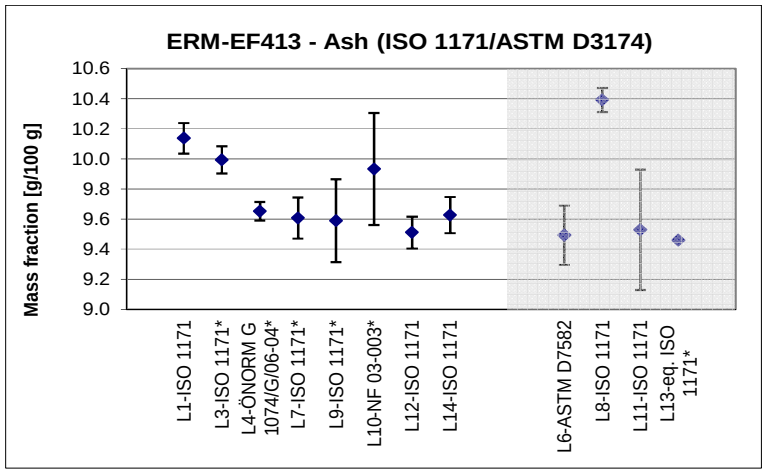
ERM-EF413 – Volatile matter (ISO 562) in g/100 g (no value assigned)

Lab	Results					
L1	1.04	1.02	1.22	1.25	0.99	1.17
L3	1.093	0.865	1.282	1.374	1.512	1.538
L4	0.78	0.86	0.92	1.02	0.64	0.68
L7	0.866	0.947	0.968	0.807	0.943	0.853
L9	0.932	0.822	0.922	0.953	0.845	1.01
L12	0.67	0.65	0.55	0.66	0.9	0.89
L14	0.887	0.91	1.06	0.831	0.794	0.731
Results not accepted on technical grounds						
L6	0.8	0.84	1.02	1.08	1	1.02
L8	2.002	2.074	2.222	2.201	2.258	2.208
L11	5.01	5.08	5.06	5.09	4.74	4.34
L13	4.22	4.54	4.12	4.2	3.66	3.89



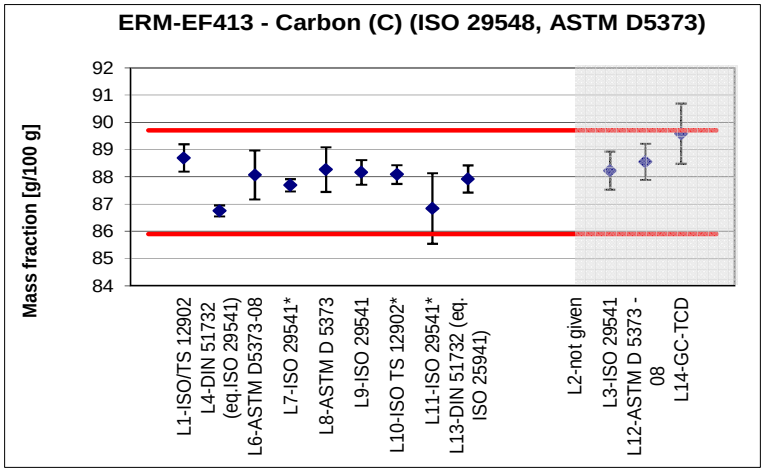
ERM-EF413 - Ash (ISO 1171/ASTM D3174) in g/100 g (no value assigned)

Lab	Results					
L1	9.7	9.7	10.78	10.79	9.92	9.93
L3	10.007	10.022	10.045	10.003	9.924	9.956
L4	9.674	9.699	9.656	9.64	9.62	9.621
L7	9.55	9.52	9.68	9.69	9.59	9.61
L9	9.634	9.665	9.743	9.656	9.415	9.419
L10	9.9	9.8	10.2	10.1	9.9	9.7
L12	9.49	9.44	9.5	9.59	9.51	9.53
L14	9.746	9.743	9.604	9.652	9.492	9.517
Results not accepted on technical grounds						
L6	9.39	9.35	9.59	9.57	9.52	9.53
L8	10.437	10.434	10.385	10.34	10.351	10.402
L11	9.59	9.65	9.53	9.56	9.41	9.43
L13	9.54	9.56	9.47	9.48	9.35	9.35



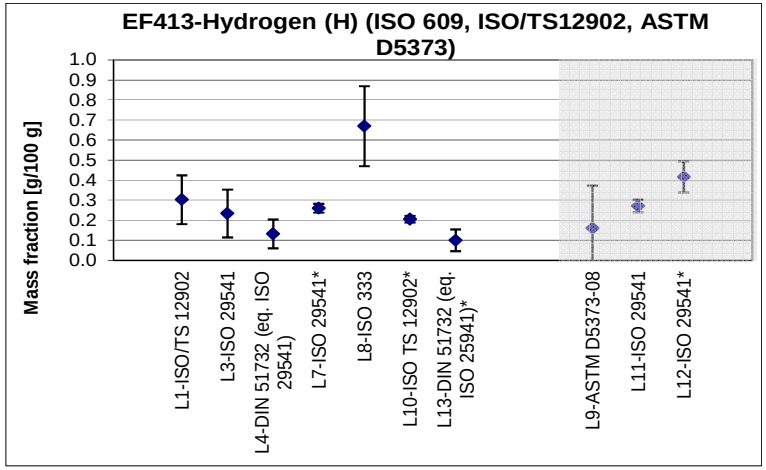
ERM-EF413 - Carbon (C) in g/100 g (certified value)

Lab	Results					
L1	89.53	89.4	87.95	88.14	88.74	88.38
L4	86.72	86.93	86.53	86.55	86.76	87.01
L6	88.07	87.98	87.91	88.03	88.25	88.16
L7	87.76	87.74	87.85	87.57	87.56	87.66
L8	88.077	88.337	88.427	88.341	88.233	88.158
L9	88.29	87.975	88.296	88.455	87.816	88.136
L10	88.1	88.4	88	88.1	88	87.9
L11	86.78	86.5	86.31	86.17	87.57	87.68
L13	88.2	88.1	87.7	87.6	88.1	87.8
Results not accepted on technical grounds						
L2	69.28	69.52	68.77	69.19	69.13	
L3	88.56	88.58	87.998	88.099	88.051	88.082
L12	88.55	88.34	88.59	88.72	88.63	88.46
L14	89.29	91.6	89.08	88.64	89.75	89.14



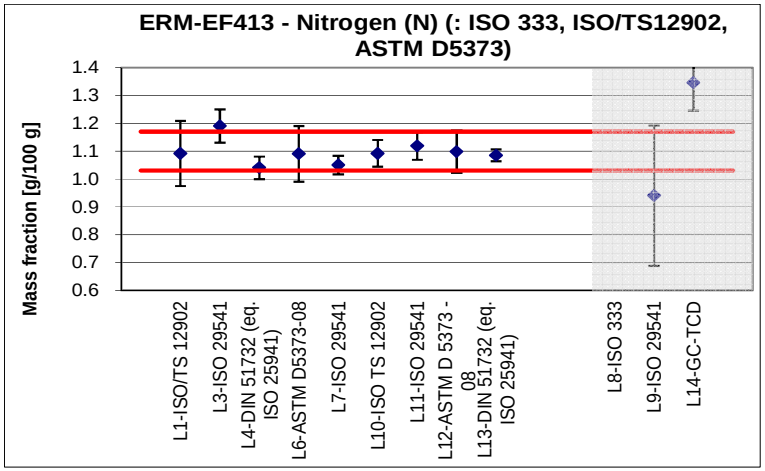
ERM-EF413 - Hydrogen (H) in g/100 g (no value assigned)

Lab	Results					
L1	0.283	0.279	0.317	0.293	0.314	0.327
L3	0.198	0.209	0.211	0.27	0.256	0.255
L4	0.13	0.13	0.15	0.15	0.11	0.12
L7	0.241	0.261	0.252	0.268	0.264	0.27
L8	0.66	0.658	0.673	0.674	0.673	0.676
L10	0.2	0.2	0.2	0.2	0.21	0.22
L13	0.107	0.124	0.066	0.112	0.065	0.122
Results not accepted on technical grounds						
L9	0.202	0.13	0.201	0.161	0.13	0.13
L11	0.267	0.277	0.283	0.289	0.265	0.245
L12	0.42	0.42	0.4	0.42	0.41	0.43



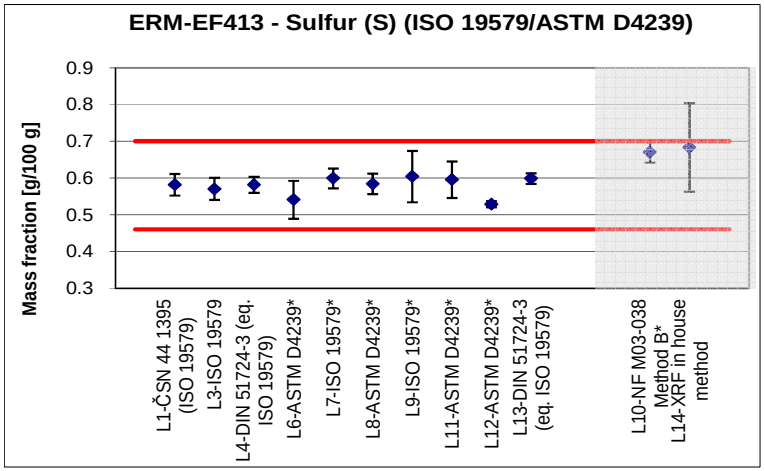
ERM-EF413 - Nitrogen (N) in g/100 g (certified value)

Lab	Results					
L1	1.15	1.12	1.03	1.09	1.06	1.1
L3	1.225	1.205	1.187	1.146	1.174	1.204
L4	0.98	0.99	1.03	1.05	1.09	1.1
L6	1.09	1.09	1.08	1.15	1.06	1.07
L7	1.04	1.07	1.03	1.05	1.04	1.07
L10	1.11	1.13	1.08	1.09	1.07	1.07
L11	1.16	1.13	1.09	1.11	1.12	1.1
L12	1.12	1.11	1.07	1.08	1.1	1.11
L13	1.08	1.08	1.09	1.1	1.09	1.07
Results not accepted on technical grounds						
L8	0.458	0.463	0.462	0.455	0.509	0.561
L9	0.945	0.9	1.026	0.872	1.026	0.872
L14	1.43	1.32	1.44	1.31	1.29	1.28



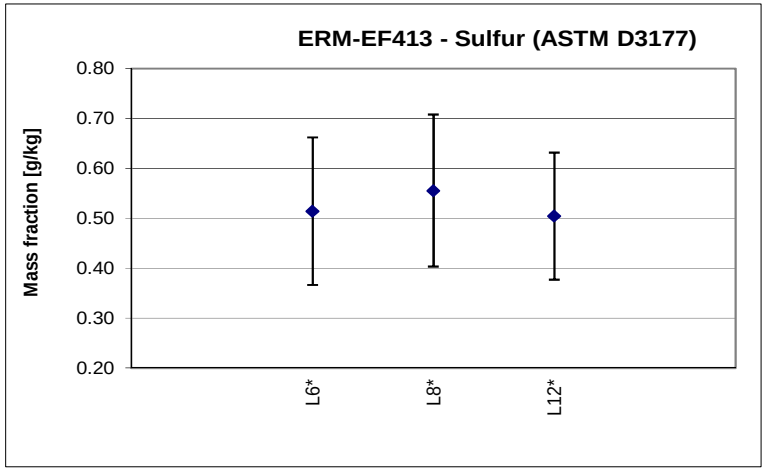
ERM-EF413 - Sulfur (S) (ISO 19579/ASTM D4239) in g/100 g (certified value)

Lab	Results					
L1	0.585	0.585	0.556	0.583	0.594	0.588
L3	0.576	0.587	0.56	0.563	0.566	0.569
L4	0.587	0.586	0.587	0.584	0.572	0.572
L6	0.493	0.53	0.548	0.561	0.552	0.559
L7	0.615	0.595	0.596	0.615	0.583	0.589
L8	0.606	0.597	0.577	0.574	0.577	0.572
L9	0.564	0.593	0.639	0.655	0.585	0.589
L11	0.572	0.626	0.618	0.585	0.605	0.566
L12	0.52	0.53	0.53	0.53	0.53	0.53
L13	0.614	0.587	0.606	0.59	0.601	0.592
Results not accepted on technical grounds						
L10	0.69	0.65	0.67	0.68	0.66	0.67
L14	0.699	0.695	0.679	0.684	0.67	0.673



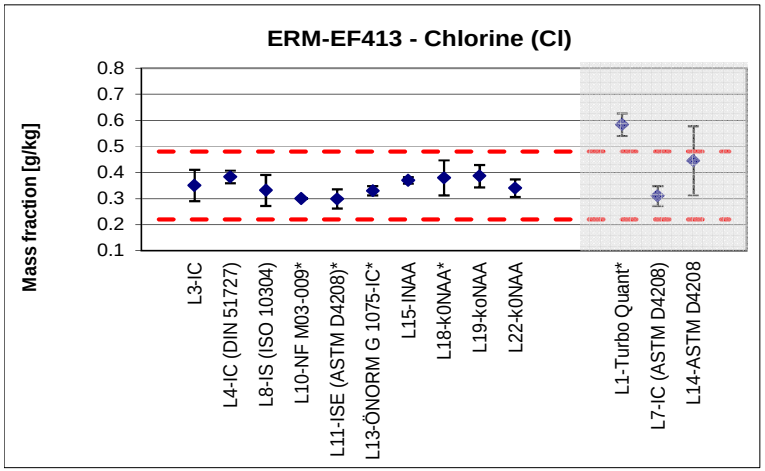
ERM-EF413 - Sulfur (S) (ASTM D3177) in g/100 g (no value assigned)

Lab	Results					
L6*	0.493	0.53	0.548	0.561	0.552	0.559
L8*	0.606	0.597	0.577	0.574	0.577	0.572
L12*	0.52	0.53	0.53	0.53	0.53	0.53



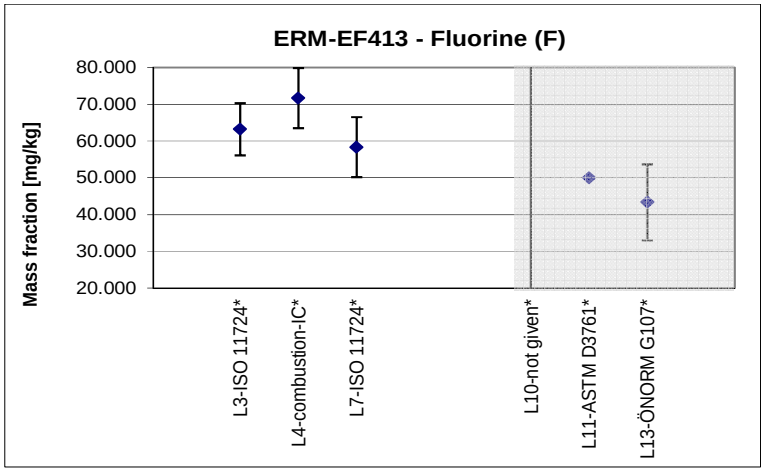
ERM-EF413 - Chlorine (Cl) in g/kg (indicative value)

Lab	Results					
L3	0.32	0.33	0.35	0.37	0.35	0.38
L4	0.37	0.39	0.4	0.39	0.37	0.38
L8	0.32	0.32	0.34	0.34	0.35	0.32
L10	0.3	0.3	0.3	0.3	0.3	0.3
L11	0.32	0.29	0.32	0.28	0.28	0.3
L13	0.32	0.33	0.32	0.34	0.33	0.34
L15	0.39	0.37	0.34	0.35	0.4	0.37
L18	0.4	0.36	0.43	0.35	0.36	0.36
	0.36	0.44	0.34	0.4	0.4	0.35
L19	0.383	0.372	0.391	0.37	0.386	0.415
L22	0.33	0.33	0.31	0.34	0.34	0.39
Results not accepted on technical grounds						
L1	0.57	0.6	0.57	0.57	0.57	0.62
L7	0.33	0.33	0.3	0.32	0.29	0.29
L14	0.46	0.44	0.44	0.45	0.44	0.44



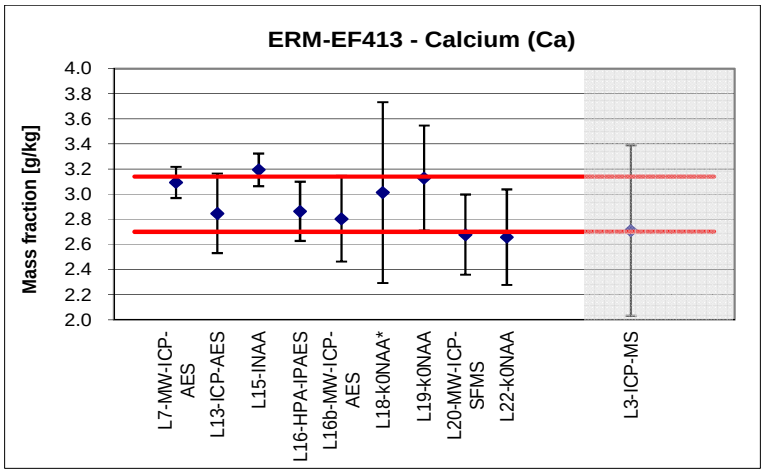
ERM-EF413 – Fluorine (F) in mg/kg (additional material information value)

Lab	Results					
L3	61	65	66	66	57	64
L4	70	70	70	70	70	80
L7	60	60	60	60	50	60
Results not accepted on technical grounds						
L10	80	90	90	60	50	260
L11	50	50	50	50	50	50
L13	40	50	40	40	40	50



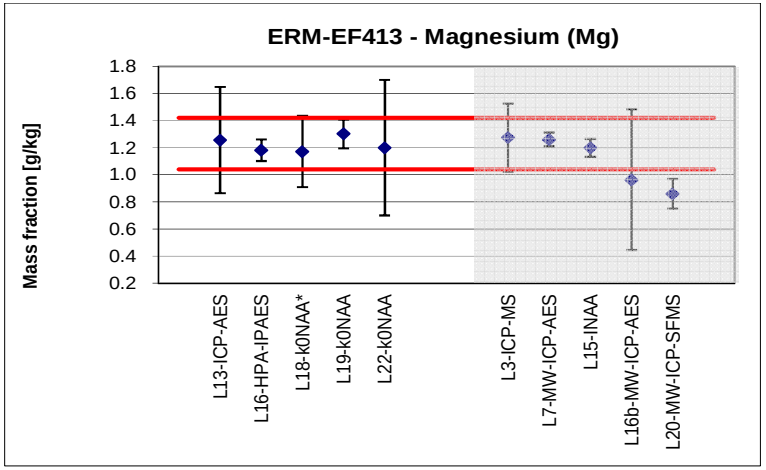
ERM-EF413 - Calcium (Ca) in g/kg (certified value)

Lab	Results					
L7	3.074	3.172	3.149	3.127	3.014	3.026
L13	2.786	2.793	2.749	2.837	2.78	2.739
	2.943	2.917	2.889	2.877	2.953	2.9
L15	3.251	3.071	3.325	3.322	3.136	3.062
L16	2.892	2.693	3.039	2.830	2.801	2.928
L16b	2.935	2.767	2.766	2.836	2.689	2.834
L18	2.78	2.66	2.76	3.25	3.42	3.77
	3.33	2.98	2.58	2.93	2.72	2.97
L19	3.005	3.012	3.267	2.934	3.399	3.151
L20	2.65	2.68	2.72	2.65	2.73	2.64
L22	2.7	2.33	2.89	2.8	2.49	2.74
Results not accepted on technical grounds						
L3	2.9	2.9	2.89	2.54	2.5	2.53



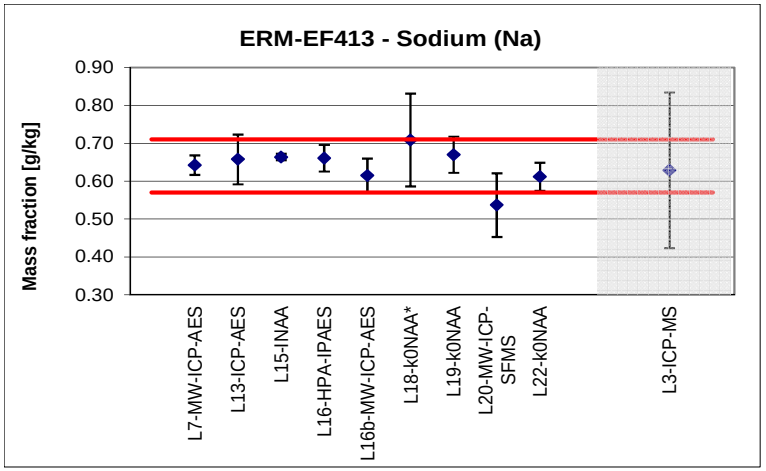
ERM-EF413 - Magnesium (Mg) in g/kg (indicative value)

Lab	Results					
L13	1.23	1.236	1.232	1.264	1.248	1.222
	1.284	1.271	1.278	1.261	1.274	1.276
L16	1.164	1.137	1.247	1.190	1.153	1.200
L18	1.206	1.076	1.027	1.063	1.151	1.032
	1.331	1.344	1.06	1.406	1.222	1.134
L19	1.282	1.341	1.297	1.264	1.3	1.328
L22	1.3	1.2	1.1	1.2	1.1	1.3
Results not accepted on technical grounds						
L3	1.36	1.34	1.33	1.22	1.18	1.22
L7	1.264	1.271	1.309	1.227	1.246	1.249
L15	1.422	1.174	1.21	0.873	1.193	1.324
L16b	0.814	1.088	1.146	0.943	0.960	0.826
L20	0.844	0.835	0.865	0.888	0.859	0.871



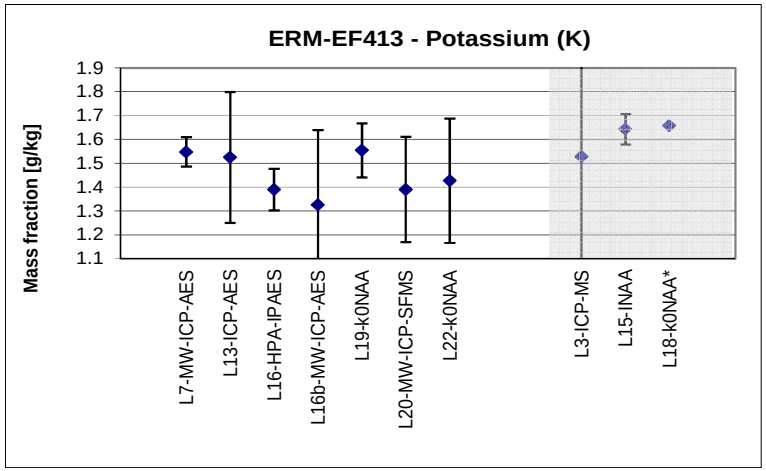
ERM-EF413 - Sodium (Na) in g/kg (certified value)

Lab	Results					
L7	0.6299	0.6285	0.6602	0.641	0.6467	0.6465
L13	0.664	0.67	0.649	0.678	0.683	0.661
	0.656	0.648	0.643	0.641	0.649	0.645
L15	0.66	0.613	0.629	0.652	0.693	0.745
	0.651					
L16	0.666	0.6366	0.686	0.670	0.647	0.658
L16b	0.650	0.604	0.600	0.625	0.589	0.617
L18	0.672	0.778	0.601	0.719	0.716	0.779
	0.635	0.805	0.702	0.727	0.72	0.651
L19	0.671	0.66	0.667	0.673	0.674	0.672
L20	0.543	0.534	0.55	0.517	0.543	0.532
L22	0.654	0.604	0.553	0.626	0.612	0.62
Results not accepted on technical grounds						
L3	0.62	0.61	0.61	0.64	0.66	0.63



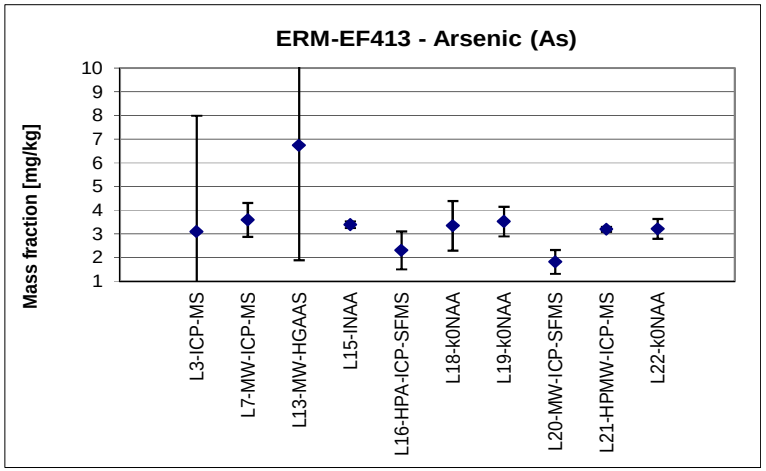
ERM-EF413 – Potassium (K) in g/kg (additional material information value)

Lab	Results					
L7	1.517	1.579	1.583	1.574	1.518	1.514
L13	1.509	1.512	1.492	1.546	1.532	1.504
	1.549	1.539	1.531	1.523	1.525	1.525
L16	1.400	1.357	1.473	1.362	1.366	1.383
L16b	1.564	1.536	1.552	1.539	1.578	1.553
L19	1.360	1.400	1.350	1.400	1.410	1.420
L20	1.510	1.390	1.310	1.510	1.430	1.410
L22	1.283	1.396	1.392	1.309	1.297	1.277
Results not accepted on technical grounds						
L3	1.53	1.51	1.53	1.52	1.57	1.51
L15	1.767	1.356	1.512	1.593	1.523	2.105
L18	1.46	2.54	1.35	1.63	1.63	1.57
	1.49	1.38	1.52	2.74	1.38	1.2



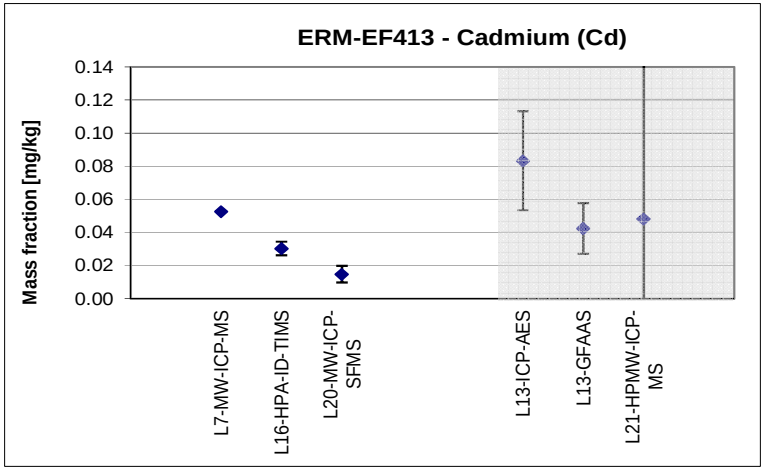
ERM-EF413 – Arsenic (As) in mg/kg (no value assigned)

Lab	Results					
L3	2.7	3.3	3.2	3.1	3.2	3.1
L7	3.44	3.505	3.383	3.827	3.632	3.747
L13	5.42	5.26	5.16	6.48	6.42	5.44
	7.64	7.66	7.93	7.64	8.16	7.68
L15	3.317	3.34	3.37	3.465	3.293	3.545
L16	2.344	2.061	2.478	2.193	2.34	2.416
L18	3.75	3.06	3.75	3.04	4.55	3.38
	3.69	2.91	2.68	3.38	2.95	3
L19	3.48	3.46	3.5	3.71	3.48	3.51
L20	1.78	1.79	1.79	1.87	1.83	1.85
L21	3.17	3.1	3.16	3.21	3.57	2.95
L22	3.31	3.09	2.86	3.47	3.36	3.2



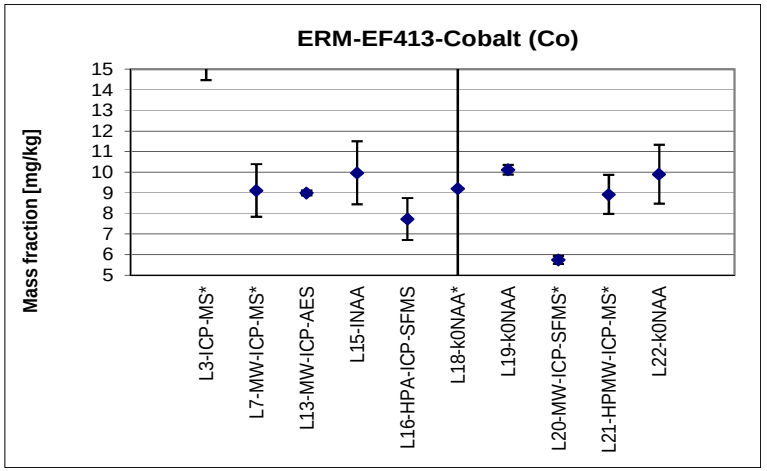
ERM-EF413 Cadmium (Cd) in mg/kg (no value assigned)

Lab	Results					
L7	0.056	0.057	0.051	0.053	0.048	0.051
L16	0.029	0.027	0.029	0.031	0.031	0.031
	0.031	0.027	0.029	0.033	0.033	0.034
L20	3.17	3.1	3.16	3.21	3.57	2.95
Results not accepted on technical grounds						
L13 (ICP-AES)	0.13	0.15	0.12	0.11	0.08	0.06
	0.07	0.08	0.05	0.02	0.08	0.05
L13 (GFAAS)	0.02	0.11	0.03	<0.01	<0.01	0.01
L21	0.045	0.044	0.042	0.053	0.059	0.046



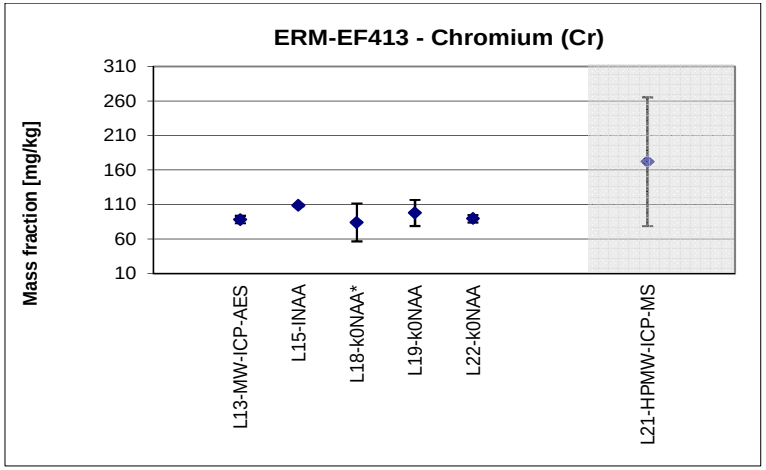
ERM-EF413-Cobalt (Co) in mg/kg (no value assigned)

Lab	Results					
L3	17	18	19	16	16	16
L7	9.14	9.067	8.961	9.351	9.095	9.062
L13	9	10.1	9.6	8.1	8.6	9
	9.4	8.7	8.7	9.2	9	8.6
L15	9.197	9.79	9.871	9.64	9.893	9.197
L16	7.682	6.922	8.314	7.667	8.241	7.682
L18	9.56	9.42	9.22	10	8.8	9.56
	10	9.32	8.15	9.46	9.3	7.9
L19	10.2	10	10.1	10	10.3	10.1
L20	5.65	5.71	5.62	5.87	5.77	5.83
L21	9.01	9.11	9.01	9.51	8.08	9.01
L22	9.9	10.1	8.5	10.5	10.1	9.9



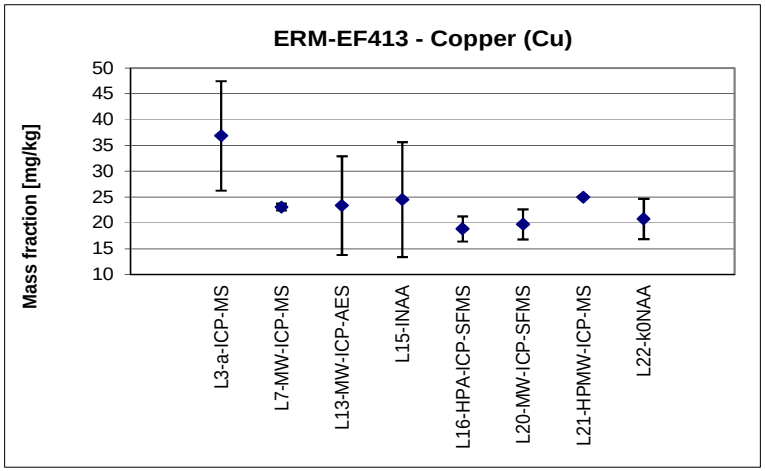
ERM-EF413 - Chromium (Cr) in mg/kg (no value assigned)

Lab	Results					
L13	84	94	86	90	81	89
	82	85	86	96	91	95
L15	94.94	103.5	110.2	132.9	99.4	111.4
L18	84.2	71.7	76.6	81.8	81.8	88.3
	115.6	81.3	67.3	100	92	67.9
L19	99.9	87.9	104	85.5	106	104
L22	90	80.3	75.2	100	103	89
Results not accepted on technical grounds						
L21	131.7	128.6	131.7	212.4	232	195



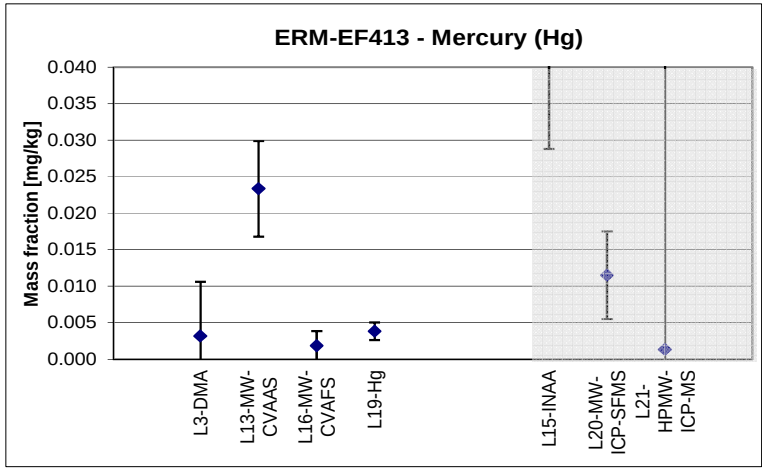
ERM-EF413 - Copper (Cu) in mg/kg (no value assigned)

Lab	Results					
L3	35	42	47	32	31	34
L7	22.35	23.06	23.16	23.04	23.43	23.34
L13	22.9	25.8	23.2	24.2	24.7	23.1
	21.3	23.2	22.6	24.8	21.8	22.5
L15			23.2	26.7	23.6	
L16	18.236	16.661	20.027	19.162	19.597	19.24
L20	19.4	19.5	19.3	20.1	19.7	20.2
L21	24.6	24.7	24.4	25.5	27.4	23.3
L22	26	23.4	20	19.2	17	19



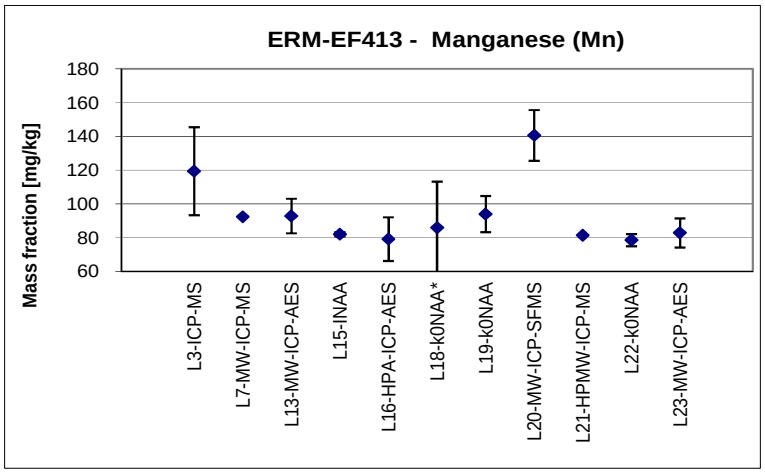
ERM-EF413 - Mercury (Hg) in mg/kg (no value assigned)

Lab	Results					
L3	0.004	0.003	0.004	0.002	0.003	0.003
L13	0.024	0.016	0.018	0.053	0.02	0.015
	0.026	0.031	0.017	0.034	0.02	0.006
L16	0.0011	0.0013	0.0027	0.003	0.0006	0.0023
L19	0.004	0.003	0.005	0.003	0.004	0.004
Results not accepted on technical grounds						
L15	0.12					
L20	0.014	0.012	0.013	0.009	0.011	0.01
L21	0.003	0.004	0.001	0	0	0



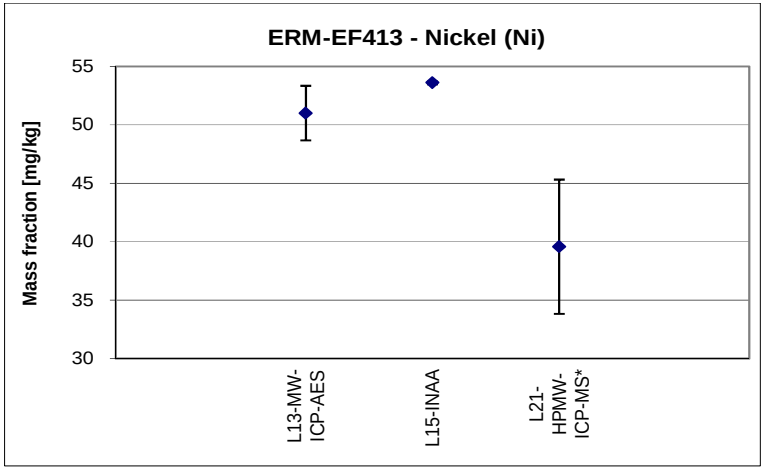
ERM-EF413 - Manganese (Mn) in mg/kg (no value assigned)

Lab	Results					
L3	120	132	132	110	109	113
L7	88.12	92.41	90.89	93.69	94.79	94.09
L13	93.6	87.1	89	97.2	98.9	86.6
	97.6	97.3	97.6	88.9	90.1	89.9
L15	77.37	89.41	74.75	82.42	77.72	90.51
L16	76.323	71.862	82.653	83.966	81.323	79.088
L18	85.2	79.4	88.4	75.4	65.7	77.1
	83.4	117.7	83.6	105.4	85.1	82.6
L19	91.7	90.6	93.3	101	90.2	96.5
L20	138	139	133	147	143	143
L21	85.8	86.2	85.4	77.8	83.4	69.8
L22	74.1	80.6	81.9	75	73.4	86
L23	84.839	81.371	79.612	84.202	81.062	86.04



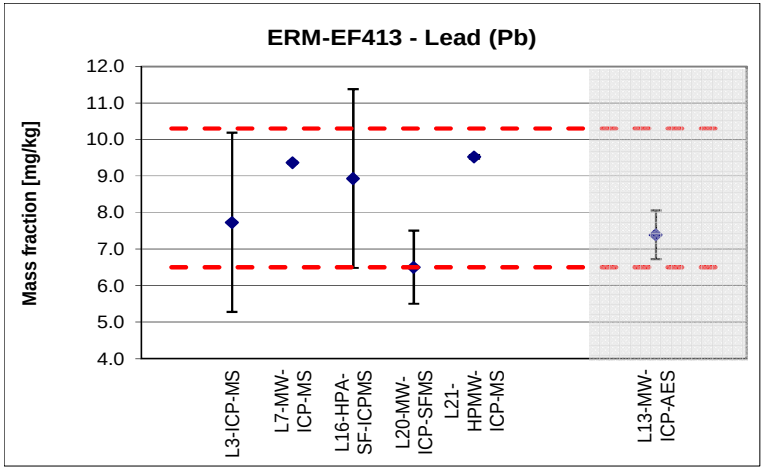
ERM-EF413 - Nickel (Ni) in mg/kg (no value assigned)

Lab	Results					
L13	48.5	54.6	51.6	48.9	44.9	51.2
	48	49.7	48	56.5	54.3	55.8
L15	53.81	46.85	54.45	60.02	59.25	47.21
L21	41.2	41.2	41.2	38.3	41.3	34.2



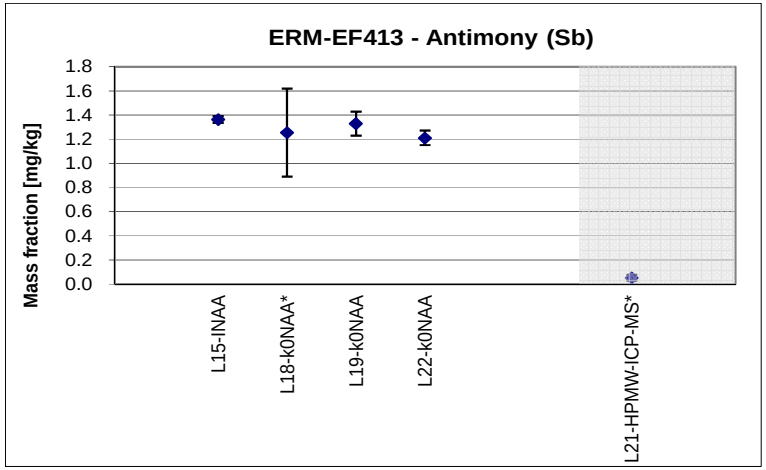
ERM-EF413 - Lead (Pb) in mg/kg (indicative value)

Lab	Results					
L3	7	8.5	9.1	7.3	7.3	7.2
L7	9.295	9.232	9.292	9.475	9.49	9.436
L16	8.682	7.758	10.277	8.863	9.502	8.682
L20	6.45	6.39	6.51	6.65	6.54	6.45
L21	9.55	9.32	9.23	10.4	8.86	9.55
Results not accepted on technical grounds						
L13	6.6	7	7.4	6.9	6.9	6.6
	7.5	8	7.7	7.9	8.5	8.4



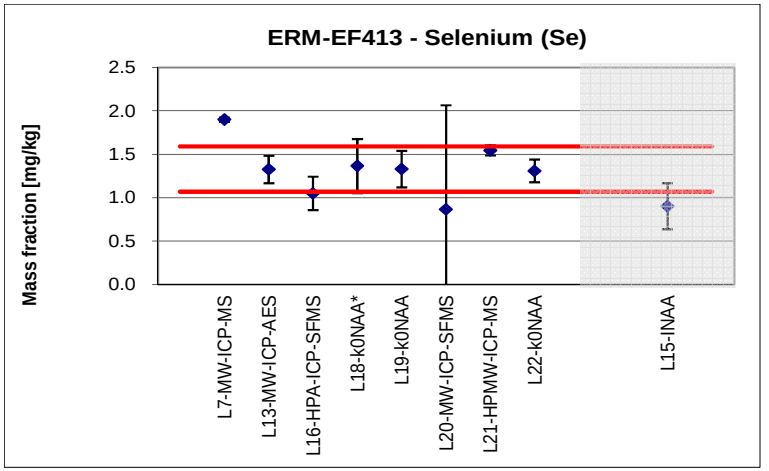
ERM-EF413 - Antimony (Sb) in mg/kg (no value assigned)

Lab	Results					
L15	1.38	1.381	1.401	1.369	1.324	1.325
L18	1.28	1.41	1.73	1.22	1.28	1.1
	1.26	1.16	1.028	1.3	1.13	1.16
L19	1.33	1.33	1.36	1.31	1.31	1.33
L22	1.31	1.22	1.11	1.18	1.24	1.2
Results not accepted on technical grounds						
L21	0.07	0.06	0.06	0.04	0.05	0.04



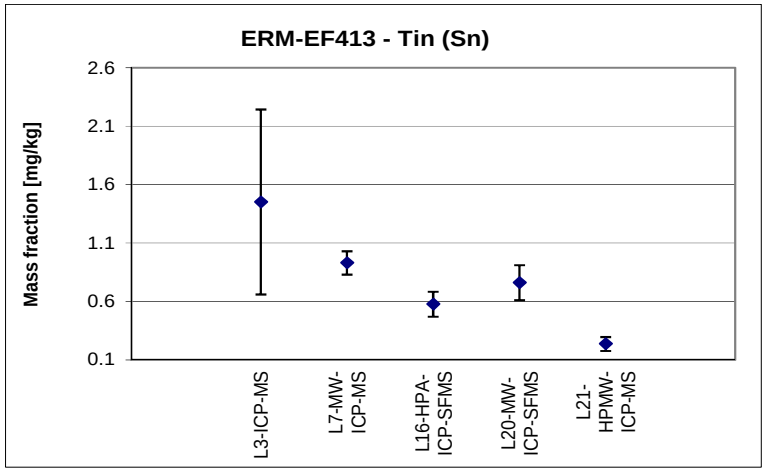
ERM-EF413 - Selenium (Se) in mg/kg (certified value)

Lab	Results					
L7	1.895	1.858	1.955	1.995	1.877	1.895
L13	1.32	1.34	1.26	1.3	1.24	1.32
	1.27	1.39	1.29	1.39	1.42	1.34
L16	1.096	0.924	1.067	1.095	1.131	1.096
L18	1.46	1.15	1.54	1.43	1.19	1.46
	1.23	1.49	1.33	1.65	1.23	1.41
L19	1.15	1.42	1.32	1.37	1.34	1.15
L20	0.875	0.86	0.866	0.848	0.878	0.875
L21	1.49	1.48	1.44	1.75	1.45	1.49
L22	1.24	1.3	1.29	1.32	1.53	1.24
Results not accepted on technical grounds						
L15	< LOQ	< LOQ	1.13	0.76	0.81	< LOQ



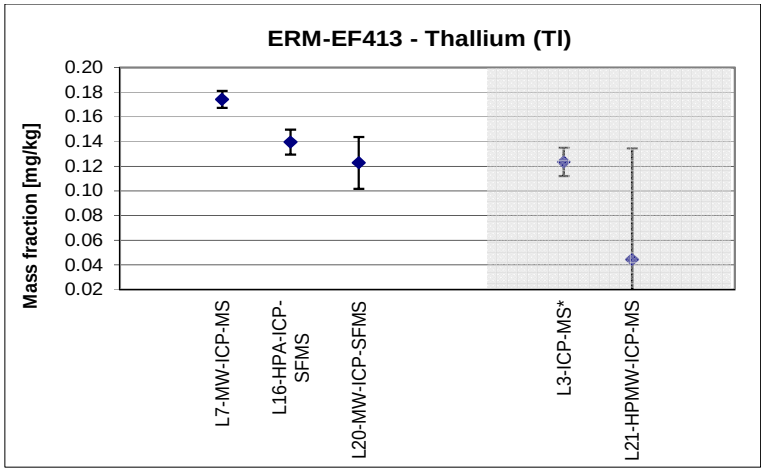
ERM-EF413 - Tin (Sn) in mg/kg (no value assigned)

Lab	Results					
L3	1.2	1.3	1.6	1.3	1.7	1.6
L7	0.934	0.97	0.991	0.914	0.873	0.884
L16	0.59	0.476	0.623	0.613	0.586	0.564
L21	0.165	0.205	0.227	0.248	0.269	0.295
Results not accepted on technical grounds						
L20	0.776	0.753	0.747	0.752	0.767	0.756



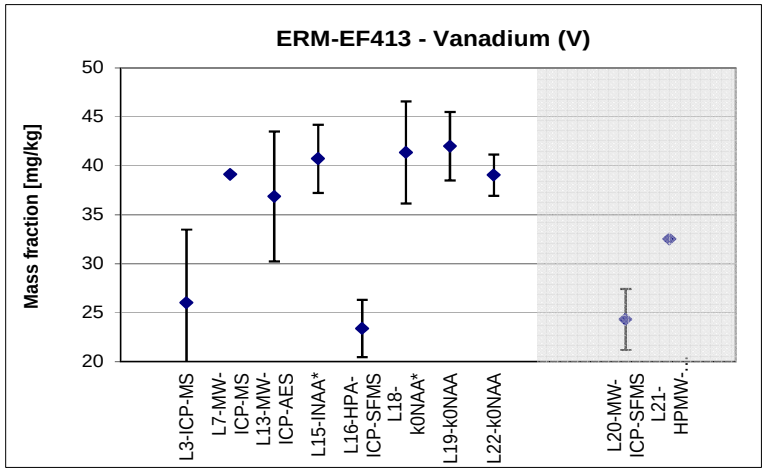
ERM-EF413 - Thallium (Tl) in mg/kg (additional material information value)

Lab	Results					
L7	0.169	0.172	0.173	0.176	0.177	0.177
L16	0.142	0.13	0.144	0.139	0.142	0.139
L20	0.119	0.121	0.123	0.128	0.123	0.122
Results not accepted on technical grounds						
L3	< LOQ	< LOQ	< LOQ	0.12	0.12	0.13
L21	0.068	0.079	0.075	0.007	0.036	0



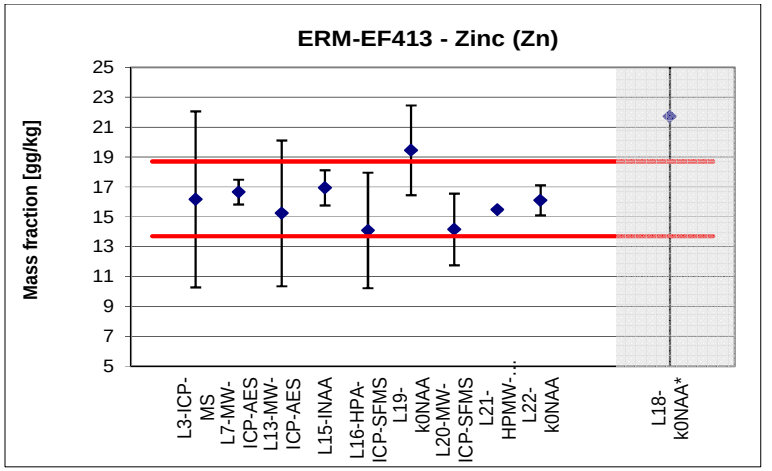
ERM-EF413 - Vanadium (V) in mg/kg (no value assigned)

Lab	Results					
L3	25	29	31	25	23	23
L7	38.26	39.32	38.62	39.51	39.73	39.23
L13	36.8	36.2	36.1	36.3	35.5	36
	38.1	37.9	36.7	37.4	37.9	37.6
L15	39.46	39.46	44.1	40.49	40.1	40.71
L16	23.508	23.187	23.959	22.2	24.391	23.06
L18	41.9	41.8	45.1	40.5	42.2	44.2
	43.3	42.2	36	42.1	37.9	39.1
L19	42.2	41	41.9	41.5	41.6	43.8
L22	40.1	38.6	41.6	38.4	37	38.6
Results not accepted on technical grounds						
L20	24.3	24.1	23.5	24.9	23.8	25.3
L21	32.2	32	32.8	32.5	35.3	30.3



ERM-EF413 - Zinc (Zn) in mg/kg (certified value)

Lab	Results					
L3	16	18	23	13	14	13
L7	17.14	16.83	16.54	16.72	15.8	16.82
L13	13.4	15.8	14.7	15.2	16.1	16.2
	14.7	15.6	14.4	15.9	16.1	14.6
L15	17.82	14.22	18.29	15.95	19.51	15.82
L16	13.762	12.059	14.466	13.912	15.001	15.317
L19	16.6	16.5	19.6	17.3	28	18.7
L20	13.9	13.7	13.7	14.5	14.3	14.8
L21	14.7	15.1	15.9	15.7	17.2	14.2
L22	15.9	16.1	14.7	16.5	16.8	16.6
Results not accepted on technical grounds						
L18	19.6	14.1	19	14.8	26.1	14.4
	16.2	19.5	31.3	14.1	59.5	11.8



European Commission

EUR 26197 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: The certification of the gross calorific value and mass fractions of ash, C, H, N, S, Cl, major elements and trace elements in three coal materials: ERM®-EF411 (hard coal), ERM®-EF412 (brown coal) and ERM®-EF413 (furnace coke)
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European Commission, Joint Research Centre,Institute for Reference Materials and Measurements (IRMM), Geel, Belgium

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Abstract
This report describes the production of ERM-EF411, ERM-EF412 and ERM-EF413, three coal materials certified for proximates and trace elements. The materials have been produced following ISO Guide 34:2009.
Industrial hard coal, brown coal and furnace coke were obtained, dried, milled (ERM-EF411 and ERM-EF413) and filled into aluminium laminated sachets.
Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006. Within-unit heterogeneity was quantified to determine the minimum sample intake.
The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no outlier was eliminated on statistical grounds only.
Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible heterogeneity and instability and to characterisation.
The materials are intended for quality control and assessment of method performance. As any reference material, they can be used for control charts or validation studies, as well. The CRMs are available in sachets containing 50 g of dried material. The minimum amount of sample to be used, depending on the analyse, varies from 30 mg to 1 g.
The CRM was accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.
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