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ERM European Reference Materials

CERTIFICATION REPORT

The certification of the mass fractions of C, H, N and O in the certified reference materials ERM®-EB090a and ERM®-EB090b

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Directorate F – Health, Consumers and Reference Materials

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Abstract

This report describes the certification of the C, N, H and O mass fraction in the CRMs ERM-EB090a and ERM-EB090b, which are titanium materials that were certified for their trace element mass fractions in 2018. Also the new values for C, H, N and O were certified in accordance with ISO 17034 and ISO Guide 35:2017.
Between unit-homogeneity was quantified in accordance with ISO Guide 35:2017. The minimum sample intake was derived from the sample intakes of laboratories participating in the characterisation study. Based on the nature of the material, potential uncertainty for degradation during transport and storage is negligible.
The material was characterised by an interlaboratory comparison of laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no statistical outlier was eliminated unless a technical reason for the deviation was found.
Uncertainties of the certified values were calculated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible inhomogeneity, instability and characterisation.
The materials are primarily intended for the quality control and assessment of method performance. As with any reference material, they can be used for establishing control charts or validation studies. The CRMs are available in discs (ERM-EB090a: diameter 40 mm; height 20 mm; approximately 115 g) and 7 g of metal chips contained in glass vials (ERM-EB090b). The minimum sample intake representative for C is 150 mg and for H, N and O 50 mg.

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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 certification of the C, N, H and O mass fraction in the CRMs ERM-EB090a and ERM-EB090b, which are titanium materials that were certified for their trace element mass fractions in 2018. Also the new values for C, H, N and O were certified in accordance with ISO 17034 [1] and ISO Guide 35:2017 [2].

Between unit-homogeneity was quantified in accordance with ISO Guide 35:2017 [2]. The minimum sample intake was derived from the sample intakes of laboratories participating in the characterisation study. Based on the nature of the material, potential uncertainty for degradation during transport and storage is negligible.

The material was characterised by an interlaboratory comparison of laboratories of demonstrated competence and adhering to ISO/IEC 17025. Technically invalid results were removed but no statistical outlier was eliminated unless a technical reason for the deviation was found.

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The materials are primarily intended for the quality control and assessment of method performance. As with any reference material, they can be used for establishing control charts or validation studies. The CRMs are available in discs (ERM-EB090a: diameter 40 mm; height 20 mm; approximately 115 g) and 7 g of metal chips contained in glass vials (ERM-EB090b). The minimum sample intake representative for C is 150 mg and for H, N and O 50 mg.

The following values were assigned:

Element	ERM-EB090a		ERM-EB090b	
	Certified value 3) [g/kg]	Uncertainty 4) [g/kg]	Certified value 3) [g/kg]	Uncertainty 4) [g/kg]
C 1)	0.325	0.022	0.325	0.022
H	0.043	0.007	0.043	0.005
N 2)	0.155	0.030	0.155	0.026
O	3.57	0.19	3.57	0.19

1) As obtained using combustion analysis with infrared detection.

2) As obtained using inert gas fusion with thermal conductivity detection

3) Certified values are values that fulfil the highest standards of accuracy. The given values represent the 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).

4) The uncertainty of the certified value 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.

Table of contents

Glossary

ANOVA	Analysis of variance
ASTM	ASTM International, a standardisation organisation
BCR®	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
COMB	Combustion
CRM	Certified reference material
ERM®	Trademark of European Reference Materials
GUM	Guide to the Expression of Uncertainty in Measurements, also released as ISO/IEC Guide 98-3
IGF	Inert gas fusion
IR	Infrared spectrometry
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
$MS_{between}$	Mean of squares between-unit from an ANOVA
MS_{within}	Mean of squares within-unit from an ANOVA
n	Number of replicates per unit
n.a.	Not applicable
PAA	Photon activation analysis
PGAA	Promt gamma activation analysis
rel	Index denoting relative figures (uncertainties etc.)
RM Unit	Reference Materials Unit of JRC, Directorate F
s	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added when 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
TCD	Thermal conductivity detection
u	standard uncertainty
U	expanded uncertainty
$u^{\cdot}_{bb}$	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability/intermediate precision; an additional index "rel" is added as appropriate
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added as appropriate
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_{Δ}	Combined standard uncertainty of measurement result and certified value
Δ_{meas}	Absolute difference between mean measured value and the certified value
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}
ν_{eff}	Effective degrees of freedom as calculated from the Welch-Satterthwaithe equation

1 Introduction

1.1 Background

The two certified reference material (CRMs) ERM-EB090a and ERM-EB090b, trace elements in titanium, were released with certified values for trace metals in 2018 [4]. Because of the limited number or datasets for C, H, N and O and the poor agreement of some datasets, no certified values could be assigned for these elements. However, the mass fractions of these elements are important for the mechanical characteristics of titanium. Therefore, a new study was organised with the goal to gather data of sufficient quality to certify the mass fractions of these elements, so that the materials ERM-EB090a and ERM-EB090b can also replace titanium CRMs that were certified only for these elements.

1.2 Choice of the material

The existing and certified materials ERM-EB090a (discs of a diameter of 40 mm and a height of 20 mm) and ERM-EB090b (chips of a diameter of approximately 6 mm and a height of 1-2 mm) were used.

The rationale of choosing this format is given in [4].

1.3 Design of the CRM project

The project consisted of a new assessment of the homogeneity of the two materials followed by characterisation in an interlaboratory comparison among laboratories of demonstrated competence in the determination of C, H, N and O mass fractions in titanium. Existing CRMs were analysed alongside the two materials ERM-EB090a and ERM-EB090b to detect potential technical errors.

The project was subjected to peer-review both from JRC staff as well as from external experts before the updated certificate was released.

2 Participants

2.1 Project management and data evaluation

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, Geel, BE
(accredited to ISO 17034 for production of certified reference materials, BELAC No. 268-RM)

2.2 Homogeneity study

Revierlabor, Essen, DE
(measurements under the scope of ISO/IEC 17025 accreditation DAkkS D-PL-18336-01-00)

2.3 Characterisation

Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, DE
(measurements under the scope of ISO/IEC 17025 accreditation DAkkS D-PL-18336-01-00)

ChemiLytics GmbH & Co. KG, Goslar, DE
(measurements performed under the scope of ISO/IEC 17025 accreditation DAkkS D-PL-21316-01-00)

Evans Analytical Group SAS, Tournefeuille, FR
(measurements performed under the scope of ISO/IEC 17025 accreditation COFRAC 1-1993)

FRAMATOME - UGINE, Ugine, FR
(measurements performed under the scope of ISO/IEC 17025 accreditation COFRAC 1-6548)

OCAS nv, Zelzate, BE
(measurements under the scope of ISO/IEC 17025 accreditation BELAC 604-TEST)

Revierlabor, Essen, DE
(measurements under the scope of ISO/IEC 17025 accreditation DAkkS D-PL-18336-01-00)

University of Texas, Nuclear Engineering Teaching Lab, Austin, USA

Ústav jaderné fyziky AV ČR (Nuclear Physics Institute of the Czech Academy of Sciences), Rez, CZ

3 Material processing and process control

The processing of the two CRMs, started with conventional alloying of titanium, followed by vacuum arc re-melting, a plasma rotating electrode powder process and was concluded by

hot isostatic pressing to obtain bars. Water-jet cutting was used to cut the bars into the discs of ERM-EB090a. Water-jet cutting was also used to cut the bars into approximately 2 mm thick discs, out of which the chips of ERM-EB090b were punched. The processing of the material is described in detail in [4]. Each of the bars was used to produce some discs and some chips, so the mass fraction of the elements should be the same. This assumption was also confirmed for the trace metals [4].

4 Homogeneity

A key requirement for any reference material aliquoted into units is equivalence between those units. In this respect, it is relevant whether the variation between units is significant compared to the uncertainty of the certified value, but it is not relevant if this variation between units is significant compared to the method repeatability. Consequently, ISO 17034 requires reference material producers to assess the between unit variation. This aspect is covered in between-unit homogeneity studies. The degrees of freedom for the between-unit variation of C, H, N, O during the original homogeneity assessment [4] were too low for assigning certified values, therefore a new study was organised.

The within-unit inhomogeneity 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 inhomogeneity is therefore necessary to determine the minimum sample intake.

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values of the CRMs are valid for all units of the material, within the stated uncertainties.

ISO Guide 35:2017 [2] recommends at least 9 degrees of freedom for the between-unit variation. Therefore, 10 units of each material were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. For this, the batch was divided into 10 groups (with a similar number of units) and one unit was selected randomly from each group. Three independent samples were taken from each selected unit, and analysed by combustion (ASTM E1941) for C and inert gas fusion (ASTM E1409, ASTM E1447) for H, N and O. The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential measurement drift from a trend in the filling sequence. The results are shown as graphs in Annex A.

Regression analyses were performed to evaluate potential trends in the measurement sequence. None of the datasets showed a trend in the measurement sequence that was significant on a 95 % confidence level. Regression analyses were performed to evaluate potential trends in the

production sequence. None of the datasets showed a trend in the processing sequence that was significant on a 99 % confidence level.

All datasets were assessed for consistency using Grubbs outlier tests at a confidence level of 99 % on the individual results and on the unit means. No outlying unit means or individual values were detected.

Quantification of between-unit inhomogeneity was undertaken by 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 were representative for the whole unit.

Evaluation by ANOVA requires mean values per unit, which follow a unimodal distribution and results for each unit that follow unimodal distributions with approximately the same standard deviations. The distribution of the mean values and of all individual values was visually tested using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations. The normal probability plots support the hypothesis of normal or at least unimodal distributions for all datasets.

It should be noted that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and are 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 inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [5]. u^*_{bb} is comparable to the limit of detection of an measurement procedure, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,rel}$) (equivalent to the within-unit standard deviation), between–unit standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}} \qquad \textbf{Equation 1}$$

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}} \qquad \textbf{Equation 2}$$

$$u^*_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{\nu_{MSwithin}}}}{\bar{y}} \qquad \textbf{Equation 3}$$

MS_{within}	mean of squares within-unit from an ANOVA
$MS_{between}$	mean of squares between-unit from an ANOVA
$\bar{y}$	mean of all results of the homogeneity study
n	mean number of replicates per unit
$\nu_{MSwithin}$	degrees of freedom of MS_{within}

Table 1: Results of the homogeneity study

CRM	Element	$s_{wb,rel}$ [%]	$s_{bb,rel}$ [%]	$u^*_{bb,rel}$ [%]	$u_{bb,rel}$ [%]
ERM-EB090a	C	5.04	2.09	1.64	2.09
	H	8.16	5.32	2.65	5.32
	N	6.86	6.11	2.23	6.11
	O	1.05	0.61	0.34	0.61
ERM-EB090b	C	6.48	n.c.[1]	2.10	2.10
	H	5.29	n.c.[1]	1.72	1.72
	N	10.28	n.c.[1]	3.34	3.34
	O	1.30	n.c.[1]	0.42	0.42

[1)] n.c.: cannot be calculated as $MS_{between} < MS_{within}$

The homogeneity study showed no outlying unit means or trends in the filling sequence. Therefore the between-unit standard deviation can be used as estimate of u_{bb}. As u^*_{bb} sets the limits of the study to detect inhomogeneity, the larger value of s_{bb} and u^*_{bb} is adopted as uncertainty contribution to account for potential inhomogeneity.

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus should be used in an analysis. Using sample sizes equal or above the minimum sample intake guarantees the certified value within its stated uncertainty.

The minimum sample intake 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 repeatability in the respective studies was taken as minimum sample intake. From the data from Annex B it can be derived that the following sample intakes are representative for a whole unit:

C: 150 mg

H, N, O: 50 mg

It should be noted that the characterisation study also showed a high risk of a positive bias for the H mass fraction when combining sample intakes below 150 mg with an etching step and that negative bias can occur for the N and O mass fractions in case of sample intakes significantly larger than 150 mg (see instructions for use).

5 Stability

Titanium is very resistant to many chemicals. In fact, this resistance is the basis for its use in chemical industry. As the elements in the material are homogeneously distributed in the metal titanium matrix, no change of the element mass fraction can occur. Based on knowledge of the nature of the material, it is concluded that the risk of changes during storage at room temperature or transport at ambient conditions are negligible. Although change of the material during long-term storage is virtually impossible, the validity of the certificate is limited to 5 years because of product liability. Users may opt to prolong the validity on their own responsibility, as long as they have evidence of stability of the material [6].

6 Characterisation

The material characterisation is the process of determining the property values of a reference material.

This was based on an interlaboratory comparison of expert laboratories, i.e. the mass fractions of C, H, N and O of the material were determined in different laboratories to demonstrate the absence of a measurement bias. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty. Most laboratories applied combustion for C and inert gas fusion (IGF) for N, O and H, which are the methods usually applied for these elements. Measurements by photon activation analysis (PAA) for the oxygen mass fraction and prompt gamma irradiation analysis (PGAA) for the H mass fraction were performed to identify potential method biases.

6.1 Influence of the sample preparation step

Ti a corrosion resistant metal because of the formation of a passivation (thin oxide) layer or passive oxide coating. Ti also forms nitrides, hence removal of the surface layer may be necessary for correct O and N measurement results. A study of the generation of TiO_2 in an oxygen plasma showed that the maximum oxide thickness at a plasma power of 240 W was 7.6 nm [7]. Such a film would increase the oxygen mass fraction by 0.1 %.

Different protocols exist for sample preparation. An investigation on the most suitable sample pre-treatment conducted in the scope of the development of CRMs for C, H, N and O concluded that samples should be etched [8]. This is also standard practice by some laboratories. On the other hand, the ASTM standards for the determination of the mass fractions of C, H, N and O in Ti prescribes etching for N and O, but not for H and C. To decide on the proper way forward, the influence of an etching step for removal of surface contamination was investigated. For the etching, samples were immersed in a mixture of 1 part concentrated HF and 4 parts concentrated HNO_3 until a reaction was visible (5-10 seconds), then rinsed three times with water, rinsed with acetone and dried.

Two samples of ERM-EB090b were analysed in quadruplicate both "as is" as well as after the etching procedure described below. All quantification steps were performed under repeatability conditions. One result for N for the “as is” chips gave a 50 % higher result than all other results. As this clearly is an measurement error or a fluke contamination, this result was excluded from the following analysis. The ratios of the means of the etched samples/as is samples are shown in Figure 1.

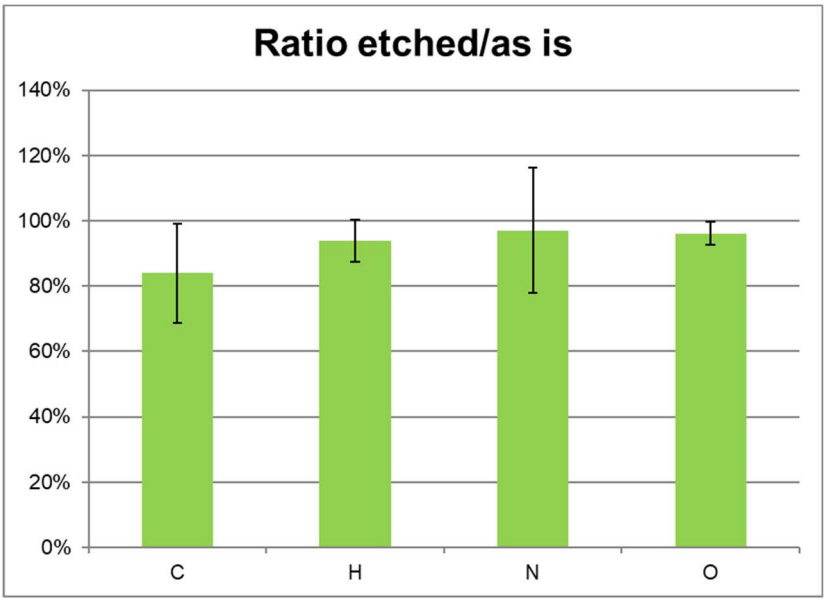

Figure 1: Ratios of the element mass fraction etched/as is. The error bars are the 95 % confidence intervals of the ratios.

The differences between the means were tested using double-sided *t*-tests. The differences were found significant on an 95 % confidence level for C and O (the results were significant on a 97 % confidence level). Discussion with the laboratory confirmed this finding: according to the laboratory, short etching leads to a slight reduction of C, H, N, O due to the removal of surface contamination. However, care must be taken to keep the etching period short to avoid H accumulation in the sample. Therefore, an etching step was prescribed in the characterisation study. One laboratory did not apply the etching, but applied a degreasing step with acetone. The results agree with the other laboratories, confirming that a degreasing alone is sufficient.

6.2 Selection of participants

Eight laboratories were selected based on criteria that comprised both technical competence and quality management aspects. Each participating laboratory was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the determination of C, H, N and O in non-iron metals. This evidence was demonstrated by providing results of results of proficiency tests or by results in previous characterisation exercises organised by the JRC or by scientific publications. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 was obligatory. Where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (Section 2).

Six laboratories delivered results for ERM-EB090a and ERM-EB090b and additional two laboratories delivered results for ERM-EB090b.

6.3 Study setup

Participants were instructed to etch samples by immersion in a mixture of 1 part concentrated HF and 4 parts concentrated HNO_3 until a reaction was visible (5-10 seconds), then rinsing three times with water, rinsing with acetone and drying.

Combustion/inert-gas fusion

Each laboratory received two units of ERM-EB090a and/or ERM-EB090b and was requested to provide six independent measurement results, three per unit. The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The measurements had to be spread over at least two days to ensure intermediate precision conditions.

In addition to ERM-EB090a and/or ERM-EB090b, laboratories applying combustion and inert gas fusion also performed two measurements on the following CRMs as quality control (QC) samples:

BCR-276, zircaloy 4 (98.3 % Zr, 1.4 % Sn, 0.2 % Fe, 0.09 % Cr):
certified C mass fraction 108 ± 11 mg/kg;
certified O mass fraction: 1.54 ± 0.08 g/kg

BCR-318, titanium: certified H mass fraction 12.2 ± 0.6 mg/kg

BCR-24C, titanium: certified N mass fraction 117 ± 13 mg/kg

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.

All laboratories were instructed to use a cooled, slow-rotating disc for cutting the samples if cutting was necessary (especially for ERM-EB090b).

Photon activation analysis/Prompt gamma activation analysis

Due to measurement constraints, the measurement setup was different for measurements by PAA and PGAA.

For PGAA, the laboratory measured 8 chips from 2 bottles (each measurement came from one chip). In addition, two discs were measured. The discs were measured without cutting and were irradiated as a whole. Two measurements on each disc were performed, one on each side. It should be noted that the neutrons and gamma rays transcend the whole disc, but shielding somewhat limits the signal from greater depths.

For PAA, three sets of 1.5 g of chips were measured. The results were corrected for interferences by Mo, Fe and for Ti as described in [9]. In principle, also C and N can be determined by PAA, but for these samples, the levels were too low compared to the interfering elements.

6.4 Methods used

For C, all laboratories used combustion with quantification by IR spectrometry. For N, all laboratories used IGF followed by thermal conductivity detection (TCD). For O and H, most laboratories used IGF - IR, but for O, one dataset using PAA and for H, one dataset using PGAA was obtained.

All methods used during the characterisation study are summarised in Annex B. The laboratory codes (e.g. L1) are randomised and do not correspond to the order of laboratories in Section 2. The lab-method code consists of a number assigned to each laboratory (e.g. L1) and abbreviation of the measurement method used, (e.g. L1-IGF).

6.5 Evaluation of results

The characterisation study resulted in 5-6 datasets per element and material. All individual results of the participants, grouped by element are displayed in tabular and graphical form in Annex C.

6.5.1 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
- 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 QC sample. This was based on the uncertainties stated by the laboratories following the approach described in ERM Application Note 1 [11].
- internal consistency of results, i.e. agreement between the results for ERM-EB090a and ERM-EB090b.

All results on the CRMs used as quality control materials agreed with the certified values. A telephone conference with the laboratories was held to discuss the preliminary evaluation and to identify potential causes of unexpected results. Deviations from the technical protocol, and internal inconsistencies are listed together with the outcome of the technical evaluation below and in Table 2.

L4: The laboratory had performed all measurements only on one unit of ERM-EB090a/ERM-EB090b rather than spreading the results over two units. As homogeneity of the material had been confirmed on beforehand, this should not influence the results.
The results of L4 showed much higher results for discs than for the chips for H and N. Interestingly, the results for the discs for H were higher than the results of the other laboratories (with the chips being in line with the other labs), whereas for N the results for the discs were in line with the other laboratories and the results for the chips were lower than the other laboratories. According to the laboratory, it usually does not etch for H and N. It also applied its standard procedure, which gave different results. A discussion with the other participants identified the sample intake as the most likely source of deviation: For H, L4 had used a sample intake of 40-90 mg for the discs but 200-290 mg for the chips. With the small sample intake used for the discs, already a slight release of H during the etching can result in a positive bias. The laboratory re-tested the chips with sample intakes of 110-180 mg and obtained an mean of 39.1 mg/kg, in line with the results for the chips and the other laboratories. This finding is also in line with the assumed cause. As this re-testing was done after disclosure of the result, neither the original nor the new data L4 for the ERM-EB090a was used for characterisation.
The situation for N is the opposite: The laboratory used 110-150 mg for the discs but 240-300 mg for the chips. This sample intake was regarded as too high for N, as not all N might be extracted. Re-testing by the laboratory confirmed this assumption, as sample intakes of 140-200 mg yielded an mean of 131.5 mg/kg, in line with the results of the other laboratories. As this re-testing was done after disclosure of the result, neither the original nor the new data L4 for the ERM-EB090b was used for characterisation.

L5: Due to a misunderstanding, L5 delivered 6 results on each of the two units of ERM-EB090a and ERM-EB090b. As the evaluation is based on the mean of laboratory means, this does not increase the impact of the result of L5 and all results were used for characterisation.

L6: The laboratory had performed a degreasing step with acetone, but had not etched the sample with acid. Its sample pre-treatment was therefore somewhere between the “as is” and the “etched”, although the acetone should remove fat or organic substances adsorbed on the surface. Therefore, the results were retained.

L7: The laboratory had performed all measurements only on one unit of ERM-EB090a/ERM-EB090b rather than spreading the results over two units. As homogeneity of the material had been confirmed on beforehand, this should not influence the results.
The laboratory degreased the samples for the determination of H and N, but did not apply the etching procedure. Its sample pre-treatment was therefore somewhere between the “as is” and the “etched”. As the acetone should remove most surface fat, the results were retained. The 6th result for both discs and chips was higher for N and O. The difference was 22 % for N and 7 % for O. The laboratory performed another three measurements, which were in line with results 1-5. As no technical reason for the deviation of result 6 was found, all 9 values for O and N were used.

Table 2: Outcome of the technical evaluation.

Element	Lab.	Material	Observation	Action
C	L4, L7	both	All measurements performed on one unit	Results retained
	L5	both	6 measurements performed per unit	Results retained
	L6, L7	both	Samples degreased with acetone, but not etched	Results retained
H	L4	ERM-EB090a	Release of H from the etching led to a positive bias because of the low sample intake.	Results not used for characterisation
		ERM-EB090b	All measurements performed on one unit	Results retained
	L5	both	6 measurements performed per unit	Results retained
	L6, L7	both	Samples degreased with acetone, but not etched	Results retained
N	L4	ERM-EB090a	All measurements performed on one unit	Results retained
		ERM-EB090b	Not all N could was extracted because of the high sample intake.	Results not used for characterisation
	L5	both	6 measurements performed per unit	Results retained
	L6	both	Samples degreased with acetone, but not etched	Results retained
	L7	both	Result # 6 deviated from other results, so additional three measurements were performed.	Results retained
O	L4, L7	both	All measurements performed on one unit	Results retained
	L5	both	6 measurements performed per unit	Results retained
	L6	both	Samples degreased with acetone, but not etched	Results retained
	L7	both	Result # 6 deviated from other results, so additional three measurements were performed.	Results retained

Statistical evaluation

Data for ERM-EB090a and ERM-EB090b were evaluated separately as described below.

The statistical evaluation was performed in three steps: First, data for ERM-EB090a and b were evaluated separately for consistency. Second, the values for ERM-EB090a and b were compared to confirm/refute the assumption of equivalence. Finally, consistent datasets were pooled and again evaluated for consistency.

The datasets for ERM-EB090a and ERM-EB090b that were accepted based on technical reasons were tested for outlying means using the Grubbs test and using the Cochran test for outlying standard deviations (both at a 99 % confidence level). Where more than 5 datasets were available, the distributions of dataset means were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots and standard deviations within (s_{within}) and between ($s_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 3 and Table 4.

ERM-EB090a

Table 3: Statistical evaluation of the technically accepted datasets for ERM-EB090a, titanium discs. *p*: number of technically valid datasets.

Element	*p*	Outliers		Statistical parameters			
		Means	Variances	Mean [mg/kg]	*s* [mg/kg]	$s_{between}$ [mg/kg]	s_{within} [mg/kg]
C	5	no	no	329.95	18.06	16.26	10.83
H	5	no	no	43.05	5.69	5.41	4.01
N	5	no	no	162.47	17.67	15.61	9.90
O	5	no	1 (L6)	3480.4	116.0	99.21	101.07

No outlying laboratory mean was detected. L6 showed an outlying variance for O, but this simply reflects different levels of method performance. All datasets were therefore consistent.

ERM-EB090b

Table 4: Statistical evaluation of the technically accepted datasets for ERM-EB090b, titanium chips. *p*: number of technically valid datasets. n.a.: Not applicable because of too few datasets

Element	*p*	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean [mg/kg]	*s* [mg/kg]	$s_{between}$ [mg/kg]	s_{within} [mg/kg]
C	6	no	1 (L6)	yes	326.26	25.02	23.81	12.38
H	6	no	no	no	44.34	5.41	5.13	4.06
N	5	no	no	n.a.	157.34	35.93	31.84	15.06
O	7	no	3 (L4, L2, L7)	yes	3584.57	234.43	176.03	107.01

For H, the data seem to cluster in two groups, with L1, L4 and L5 obtaining results between 38.8 and 40.3 mg/kg and L6, L7 and L8 forming a second cluster with means between 48.5 and 49.8. As all laboratories agree with the mean of means within the reported expanded uncertainties, the apparent clustering is therefore maybe a statistical artefact.
The results for C show one and for O show several outlying variances. This simply reflects different levels of method performance. The uncertainties stated by the laboratories were sufficiently small to allow meaningful evaluation of results.
It was therefore concluded that also the datasets for ERM-EB090b were consistent.

As ERM-EB090a and ERM-EB090b are derived from the same titanium bars, the values should be indistinguishable from each other. This was tested in two ways. In a first step, the mean values shown in Table 3 and Table 4 were tested for significant differences on a 95 % confidence level. This was done using *t*-tests assuming equal variances and unequal numbers of observations. The difference was not significant for all elements.

As seen in Table 3 and Table 4, differences between laboratories are in several cases larger than within laboratories. The between-laboratory differences could therefore mask a between-material effect. Therefore, a more sensitive test aimed at eliminating the between-laboratory effects was applied. The technically accepted datasets of the laboratories that had tested both ERM-EB090a and ERM-EB090b (L1, L2, L3, L4 and L6) were normalised to the respective laboratory mean of ERM-EB090a. For each element, a double-sided *t*-test for differences between the two means was performed. The tests were based on the individual results for each material (12 – 36) which resulted in much higher degrees of freedom. The results of these tests are shown in Table 5.

Table 5: Differences and the error probability when rejecting the hypothesis of a difference of zero.

Element	Difference [%]	Error probability [%]
C	0.39	78
H	5.82	16
N	1.93	70
O	0.93	14

Also, this test did not indicate any statistically significant differences between the element mass fractions of ERM-EB090a and ERM-EB090b, confirming the assumption, based on the material processing, of the equivalence between discs and chips.

As there were no outlying laboratory means when taking the uncertainties into account, accepted datasets for the two materials were pooled. Laboratory 8 had performed 4 measurements on the discs and 8 measurements on the chips. Pooling the individual values would therefore give more weight to the chips than the discs. Therefore, the pooling was based on the laboratory means for each element and material. This means, the pooled dataset consisted for each laboratory of the mean values obtained for ERM-EB090a and ERM-EB090b, i.e. one or two data per element and material. This means that no meaningful result for the within-laboratory standard deviation is obtained, but a more realistic estimate of each laboratory mean can be calculated.
As described below, the uncertainty of characterisation is based on the standard error of the mean of laboratory means. Therefore, a more reliable estimate of laboratory means is more important than an estimate of the within-laboratory standard deviation.

The pooled results were evaluated as described above, i.e. testing for outlying means and variances, checking the agreement of the distribution with an assumed normal distribution, performing an ANOVA to calculate the between laboratory standard deviation and calculating for each element the mean and standard deviations of laboratory means. Due to the setup of the pooling, testing for outlying variances and calculation of a within-unit standard deviation is not meaningful. The results are shown in Table 6.

Table 6: Statistical evaluation of the combined technically accepted datasets for ERM-EB090a and ERM-EB090b. *p*: number of technically valid datasets.

Element	*p*	Outliers	Normally distributed	Statistical parameters		
		Means		Mean [mg/kg]	*s* [mg/kg]	$s_{between}$ [mg/kg]
C	6	no	yes	325.18	20.96	15.89
H	6	no	yes	43.35	4.83	3.95
N	6	no	yes	154.84	28.31	26.24
O	7	no	yes	3571.9	239.8	201.3

The laboratory means agree with the assumption of normal distributions. None of the data contains outlying means. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value.

Measurements on C, H, N and O have also been performed during the original characterisation of ERM-EB090a and ERM-EB090b [4], although without sample preparation. The information values for C and H assigned then agree with the mean values in the new characterisation exercise (see graphs in Annex C). In the original characterisation, no value could be assigned for O and N due to one widely deviating value. The results in this characterisation exercise are in agreement with the 2 (N) and 3 (O) other values in the original characterisation study. Because of the stricter quality control criteria in the new study, the inclusion of certified quality control materials and the higher

number of datasets, the results in this study are more reliable than the values for C, H, N, O in the previous study.

The uncertainty related to the characterisation is estimated as the standard error of the mean of laboratory means (Table 7).

Table 7: Uncertainty of characterisation for ERM-EB090a and ERM-EB090b

Element	*p*	Mean [mg/kg]	*s* [mg/kg]	u_{char} [mg/kg]	$u_{char,rel}$ [%]
C	6	325.18	20.96	8.56	2.63%
H	6	43.35	4.83	1.97	4.55%
N	6	154.84	28.31	11.56	7.46%
O	7	3571.9	239.8	90.64	2.54%

7 Value Assignment

Based on the results of this study, certified values for C, H, N and O were assigned.

Certified values are values that fulfil the highest standards of accuracy. Procedures at the JRC, Directorate F 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] were established.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table **6** was assigned as certified value for each parameter.

The assigned uncertainty consists of uncertainties relating to characterisation, u_{char} (Section 6 and potential between-unit inhomogeneity, u_{bb} (Section 3), while uncertainties of potential degradation during transport, u_{sts}, and long-term storage, u_{lts} (Section 5) are negligible. These different contributions were combined to estimate the relative expanded uncertainty of the certified value ($U_{CRM,\ rel}$) with a coverage factor *k* given as:

$$U_{CRM,rel} = k \cdot \sqrt{u_{bb,rel}^2 + u_{char,rel}^2} \qquad \textbf{Equation 4}$$

- u_{char} was estimated as described in Section 6
- u_{bb} was estimated as described in Section 3.

The effective number of degrees of freedom (ν_{eff}) for the value of each element was calculated using the Welch-Sattertwaithe equation [3] and ranged from 6 to 13. This number of degrees of freedom is sufficient to justify a *k*-value of 2 for all certified values to obtain expanded uncertainties. The certified values and their uncertainties are summarised in Table 8. For the sake of consistency with the certified values for trace elements in the two materials, the certified values are expressed in g/kg.

Table 8: Certified values and their uncertainties for ERM-EBB090a and ERM-EB090b with ν_{eff}: effective degrees of freedom of the uncertainty of the certified values

Material	Element	u_{char} [%]	u_{bb} [%]	u_{crm} [%]	ν_{eff}	Certified value [g/kg]	U_{CRM} [g/kg]
ERM-EB090a	C	2.63	2.09	3.36	10	0.325	0.022
	H	4.55	5.32	7.00	13	0.043	0.007
	N	7.46	6.11	9.65	11	0.155	0.030
	O	2.54	0.61	2.61	6	3.57	0.19
ERM-EB090b	C	2.63	2.10	3.37	12	0.325	0.022
	H	4.55	1.72	4.86	6	0.043	0.005
	N	7.46	3.34	8.18	7	0.155	0.026
	O	2.54	0.42	2.57	6	3.57	0.19

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

O and H are chemically clearly defined elements. The participants used two completely different measurement principles for the final determination, demonstrating absence of measurement bias. The measurand is therefore structurally defined and independent of the measurement method as long as appropriate sample preparation protocols are followed.

While also C and N are clearly defined elements, all laboratories used combustion-IR (C) and IGF-TCD (N) and it can therefore not be demonstrated that other methods would give the same results. The measurands for C and N are therefore defined as “as obtained by combustion-IR” (C) and “as obtained by IGF-TCD” (N).

Quantity value

Only validated methods were used for the determination of the assigned values. Different calibrants/calibrants of known purity and specified traceability of their assigned values were used and all relevant input parameters were calibrated, as was demonstrated by the agreement of the results on the CRMs used as quality control. The individual results are therefore traceable to the SI, as it is also confirmed by the agreement among the technically accepted datasets. As the assigned values are combinations of agreeing results individually traceable to the International System of units (SI), the assigned quantity values themselves are traceable to the SI as well.

8.2 Commutability

Many measurement procedures include one or more steps which select specific (or specific groups of) analytes from the sample for the subsequent 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 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 summarised in a concept called 'commutability of a

reference material'. There are various definitions that define this concept. For instance, the CLSI Guideline C53-A [10] 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 is therefore a crucial characteristic when applying different measurement methods. When the commutability of a CRM is not established, 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 calibrant.

ERM-EB090a and ERM-EB090b were produced using standard processes for titanium production. The analytical behaviour will be the same as for a routine sample of titanium.

9 Instructions for use

9.1 Safety information

The usual laboratory safety measures apply.

9.2 Storage conditions

The materials should be stored at ambient temperatures the dark.

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

9.3 Preparation and use of the material

Too big samples (especially the discs) can be cut with a cooled, slow-going cutting disc, to avoid heating the sample.

Samples need to be degreased before use. This can be done by immersion in a mixture of 1 part concentrated HF + 4 parts concentrated HNO_3 for 5-10 sec (until a reaction is visible). Then rinse three times with water, then with acetone and drying. Care must be taken to keep the immersion short enough to avoid an increase of the H-mass fraction.
Alternatively, samples can be degreased with acetone. Rinse the samples with acetone and air-dry.

Samples should be handled with tweezers after cleaning to avoid contamination.

9.4 Minimum sample intake

The minimum sample intake representative for C is 150 mg and for H, N and O 50 mg.

However, very small sample intakes of H (< 100 mg), especially when combined with HNO_3/HF etching may lead to too high values for H, so for H, sample intakes of 150 mg and above are recommended. Samples intakes larger than 150 mg may lead to too low values for N and O.

9.5 Use of the certified value

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

<u>Use as a calibrant</u>

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.

Comparing an measurement 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, https://crm.jrc.ec.europa.eu/e/132/User-support-Application-Notes [11].

When assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is summarised here:

- Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).
- Combine the measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2}$
- 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 $\Delta_{meas} \leq U_{\Delta}$ then no significant difference exists between the measurement result and the certified value, at a confidence level of approximately 95 %.

Use in quality control charts

The materials can be used for quality control charts. Using CRMs for quality control charts has the added value that a trueness assessment is built into the chart.

10 Acknowledgments

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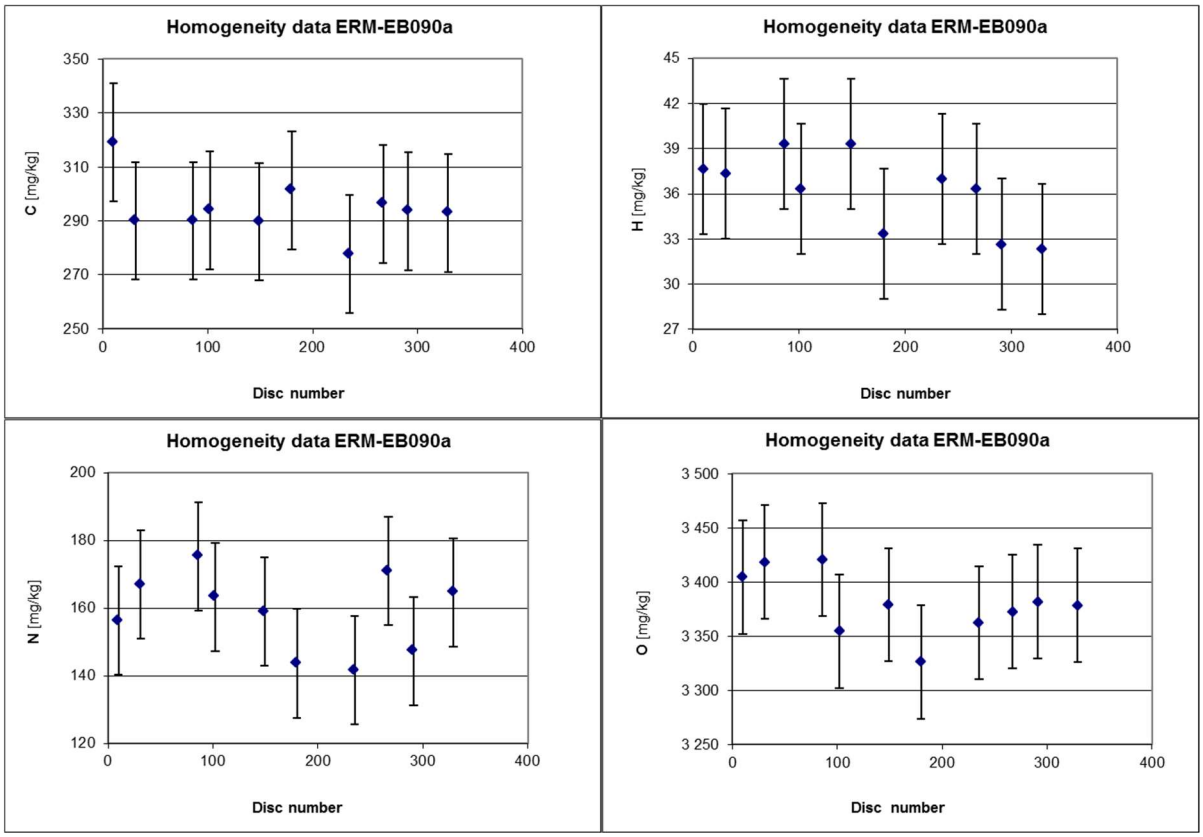
12 Annexes

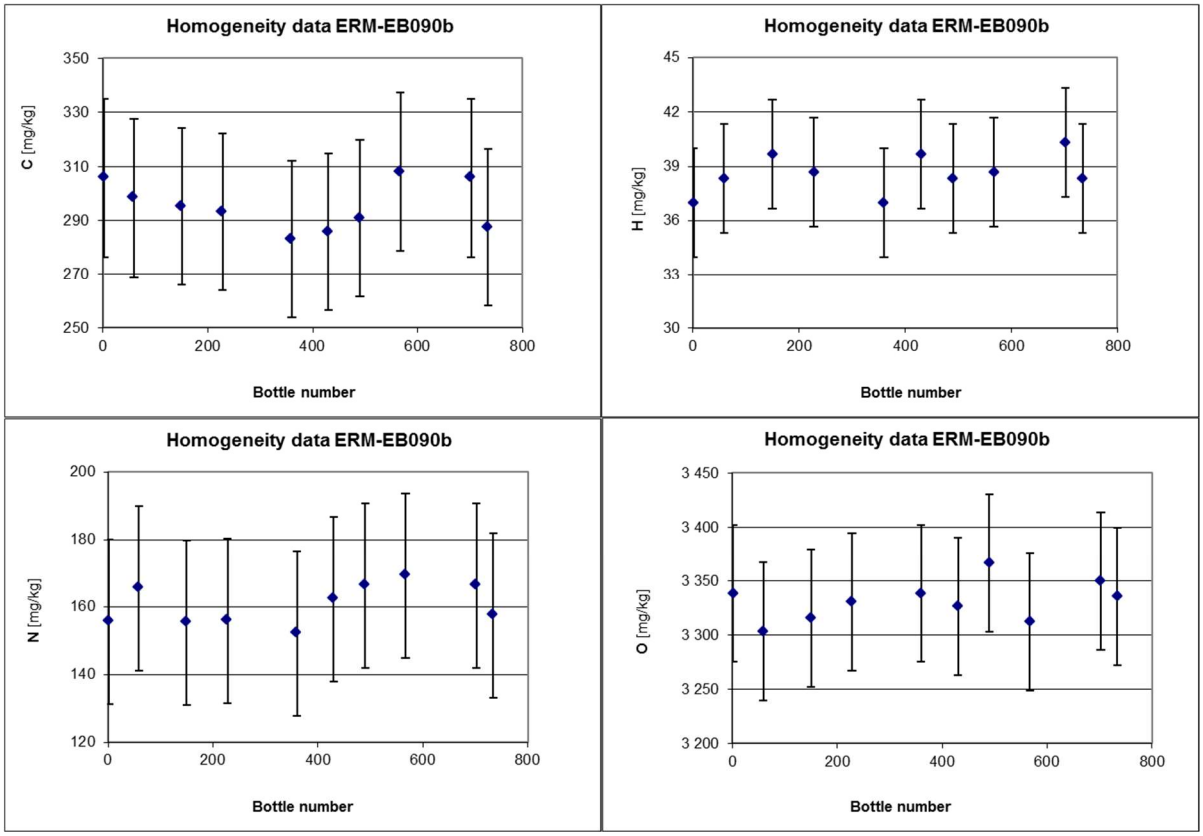
Annex A: Results of the homogeneity measurements

Annex B: Summary of methods used in the characterisation study

Annex C: Results of the characterisation measurements

Annex A: Data used for the assessment of the homogeneity. The error bars are the 95 % confidence interval of the means of each unit based on the within-group standard deviation as obtained by one-way ANOVA.





Annex B: Summary of methods used in the characterisation study: The column Laboratory code-/method consists of a combination of the laboratory (e.g. L1) and the method employed. If one laboratory used several methods, they are listed separately but all under the same laboratory code.

Laboratory code/method	Sample preparation	Elem ents	Sample intake	Quantification	Calibration
L1-COMB	ERM-EB090a: Cutting with a cooled, slow going cutting disc, Etching: mixture of 1 part HF+ 4 parts of HNO_3, rinsing in water and acetone, drying	C	≈ 500 mg	Bruker G4 Icarus IR detection	One-point calibration using Alpha Resources AR 891 (steel pins)
L1-COMB		H	≈ 200 mg	Eltra OH900 TCD	One-point calibration using Alpha AR 650 (titanium pins)
L1-IGF		O, N	≈ 100 mg	Leco TCH 600 O: IR detection N: TCD	Three point calibration Leco 502-201, Leco 502-879 , Leco 502-881 (titanium pins)
L3--COMB	Etching: 1 x ca. 30 ml (4 parts HNO_3, 65 % / 1 part HF, 40 %) for 60 s Rinsing 3 x ca. 30 ml Milli-Q-Wasser, 3 x ca. 30 ml methanol; drying	C	450 -550 mg	Eltra CS 800 IR detection	8 point calibration with Na2C03
L3-IGF		O, N	190-270 mg	Leco TCH 600 O: IR detection N: TCD	3 (N) or 4(O) point calibration using KNO_3 (N) or Fe_2O_3 (ECRM-686-1)
L4-COMB	ERM-EB090a: a slice was cut very slowly with a precision cutting machine with cooling. Afterwards, the slice was nibbled into small chips. Etching:Mixture of 1 part HF+ 4 parts of HNO_3 for 5-10 s, rinsing in water and aceton, drying	C	ERM-EB090a: 160-350 mg ERM-EB090b: 340-370 mg	LECO CS600 IR detection	CRMs from Elemental Microanalysis (B1510, B2501)) and BAS (EURO 284-2, BCS 237-1)
L4-IGF		H	ERM-EB090a: 40 - 90 mg ERM-EB090b: 205 - 290 mg	G8 Galileo H TCD	One-point calibration Alpha Resources AR 642 (titanium pins)
L4-IGF		O, N	ERM-EB090a: 110-150 mg ERM-EB090b: 240-300 mg	G8 Galileo ONH O: IR detection N: TCD	One (O) and two (N) point calibration using Alpha Resources AR 649, AR 635 and AR 642 (Ti pins)
L5-COMB	ERM-EB090a: cut with precision cut-off wheels tool under water cooling in order to avoid any heating. Pieces of 0.10 / 0.15g were abraded to remove surface impurities Etching: acid mixture HF / HNO_3 (1:4) until to see chemical yellow reaction. Samples were rinsed in	C	ERM-EB090a: 140-170 mg ERM-EB090b: 210 - 300 mg	LECO CS844 IR detection	2 point calibration using Leco 502-867 / IARM 314B
L5-IGF		H	ERM-EB090a: 100-210 mg ERM-EB090b: 110-300 mg	LECO ONH836 IR detection	3 point calibration using Leco 502-891 / Leco 502-881 / AR556

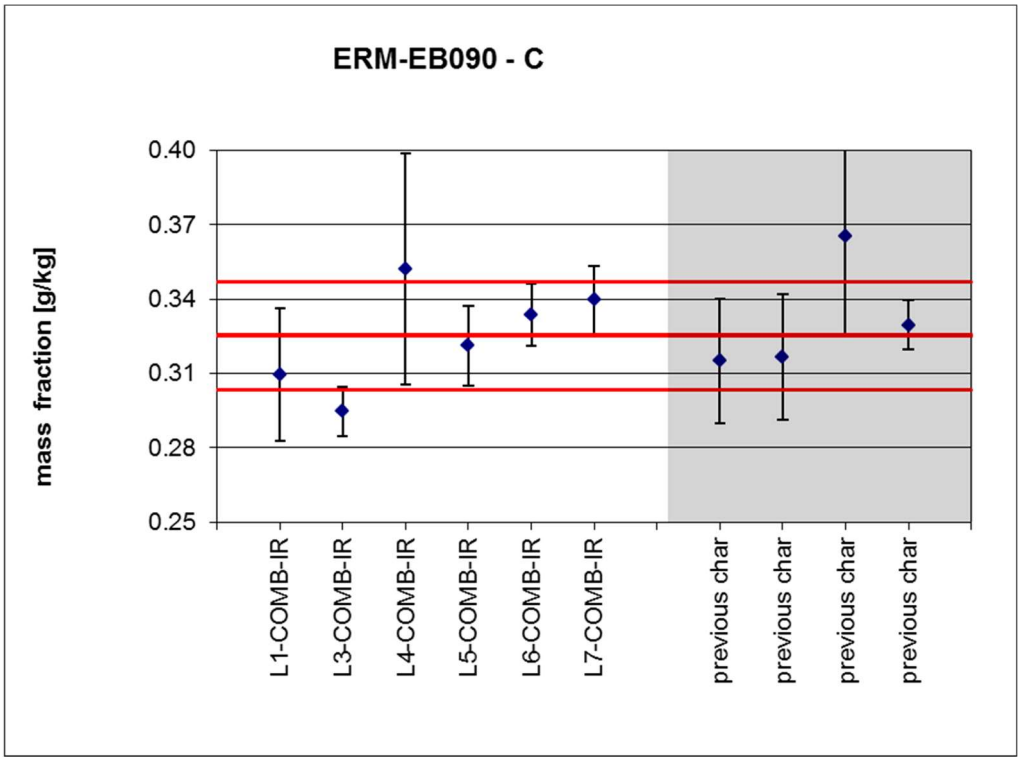
Laboratory code/method	Sample preparation	Elem ents	Sample intake	Quantification	Calibration
L5-IGF	DI water several times then immersed in solvent (acetone) for degreased. Pieces were finally warmed just prior analysis.	O, N	ERM-EB090a: 85-150 mg ERM-EB090b: 100-240 mg	LECO ONH836 O: IR detection N: TCD	3 point calibration using Leco 502-876 / Leco 502-891 / AR 649 (O), Leco 502-928 / Leco 502-891 / AR649 (N)
L6-COMB	ERM-EB090a: The disc was sawn, polished and shredded using a lever shearing machine. The pieces were then cleaned in acetone. ERM-EB090b: The chips were shredded using a lever shearing machine. The pieces were then cleaned in acetone.	C	ERM-EB090a: 500-1000 mg ERM-EB090b: 490-560 mg	Leco C744 IR detection	One point calibration using BAM ZRM 83-1
L6-IGF		O, N, H	ERM-EB090a: 46-54 mg ERM-EB090b: 50-120mg	LECO ONH836 O, H: IR detection N: TCD	One point calibration using CRMs from Alpha Resources
L7-COMB	ERM-EB090a: cut in slices, slice then cut in small pieces for different analyses Specimens for C & H were degreased, acid etching was applied for N/O analysis.	C	210-330 mg	LECO CS844 IR detection	One point calibration using Euronorm ZRM-83-1
L7-IGF		H	ERM-EB090a: 170-270 mg ERM-EB090b: 210-290 mg	LECO RH 404 TCD	Ti internal standard ; Correctness of the calibration checked with AR651, BCR-318 and LECO502-881
L7-COMB		O, N	110-140 mg	LECO TCH 600 O: IR detection N: TCD	Ti internal standard ; Correctness of the calibration checked with BCR-059 and BCR-024

Laboratory code/method	Sample preparation	Elements	Sample intake	Quantification	Calibration
L2-PAA	Etching: HF:HNO_3 1:4 for 5-10 s, then rinsed 3 times with deionized water, then with aceton, and dried. 5-6 chips were packed in aluminium foil in "5 on a playing cube" or "pentagon flower" layouts. Additional measurement and calculation of an mean sample thickness was done to make necessary corrections.	O	≈ 1400 mg	3 min irradiation at 4×10^{11} cm^{-2} s^{-1} photons (16-23 MeV) produced as bremsstrahlung at MT-25 microtron; samples were positioned directly behind the converter and beam stopper. Each sample was irradiated independently and counted 11 times for 60 s repacked from Al foil to a clean PE bag. Detector: HPGe detector Canberra-Packard GR3020 (CP, 30%, reverse, Be window, FWHM 2.3 keV at 1332 keV), connected to a Lynx® Digital Signal Analyzer Canberra GENIE 2000 Acquisition and Analysis software Evaluation of the 511 keV line of ^{15}O (decay curve analysis). Results corrected for interferences from Ti, Mo and Fe (negligible from other elements).	Cellulose (Fluka 22182) assuming a a stoichiometry of $(C_6H_{10}O_5)_n$. ^{11}C subtraction by decay curve analysis Fe and Mo standards for interference corrections prepared from pure metal powders
L8-PGAA	Etching: HNO_3 and HF with a 4:1 (by mass) ratio diluted with 85% deionized water. Samples were placed in the solution until a reaction was observed (less than 10 seconds). Samples were then rinsed three times with deionized water, then once with acetone, and finally dried. Samples were kept in sealed containers at approximately 20 °C in the dark when not being measured and handling was minimized.	H	ERM-EB090a: 1 disc ERM-EB090b: ≈ 250 mg	6-8 h irradiation; estimated thermal-equivalent neutron flux of 5.6E5 n/cm2-sec. Detector: Ortec GEM65P4 Poptop High Purity Germanium (HPGe) detector with a FWHM resolution of 1.81 keV at 1.33 MeV. ERM-EB090a: Ti: 1381 keV, 2205 keV, 2240 keV, and 3027 keV peaks; H 2223 keV peak ERM-EB090b: Ti 1381 keV peak; H:2223 keV peak Canberra GENIE 2000 Acquisition and Analysis software with the Interactive Peak Fit Module	Energy efficiency: Eu-152 calibration standard (Analytics SRS 73338-598); extrapolated to higher energies using an iron foil sample (Goodfellow FE000405/17) H/Ti ratio: NIST SRM 2454: H in Ti

Annex C: Tabular and graphical representation of the characterisation data: The column labcode consists of a combination of the laboratory (e.g. L1) and the method employed. Data are given as reported by the participants, with the expanded uncertainty depicted being the mean uncertainty reported for the mean values of 6 results on ERM-EB090a and ERM-EB090b.
The central red line shows the certified value; the outside lines the uncertainty. in red:expanded uncertainties for ERM-EB090a; in orange: uncertainty for ERM-EB090b. previous char: data from first characterisation attempt with too few participants.

Carbon

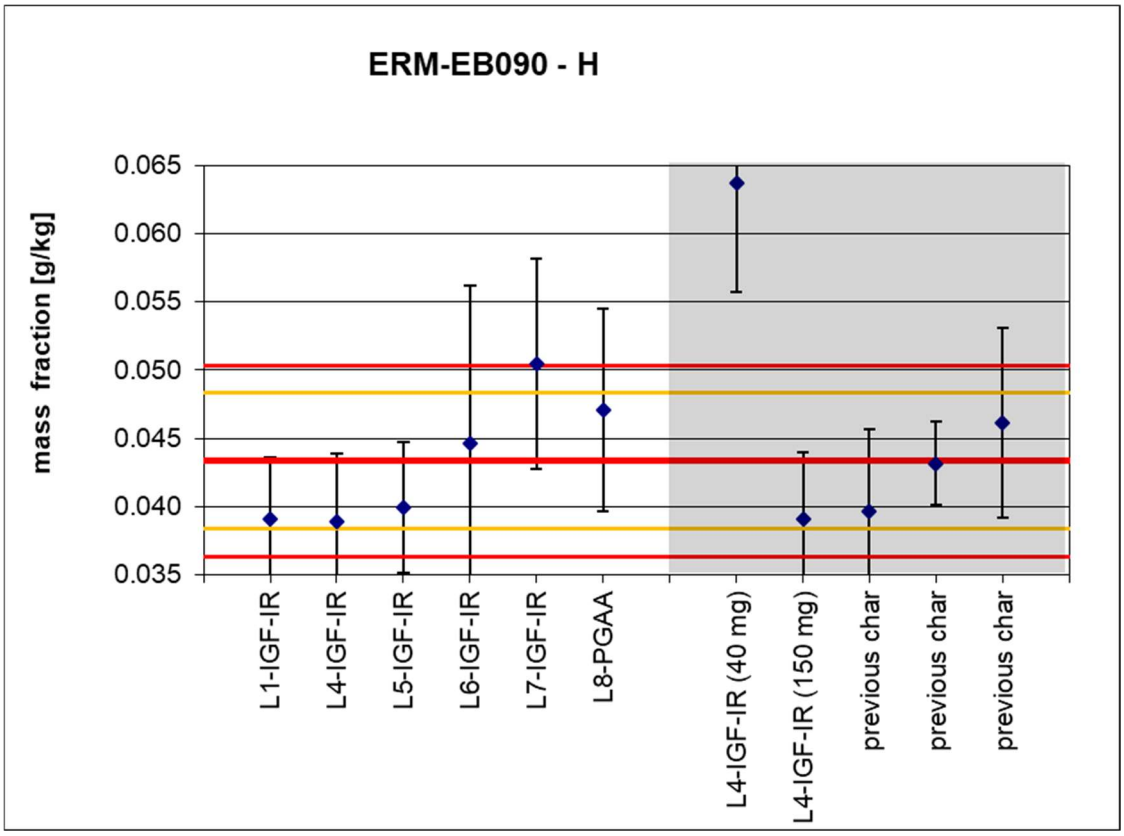
Labcode	Sample	Individual results						Mean [mg/kg]	*U* [%]
L1-COMB-IR	ERM-EB090a	295	305	294	309	325	327	309.5	8.6
	ERM-EB090b	315	306	320	316	287	315		
L3-COMB-IR	ERM-EB090b	295	302.2	295.4	287	296.5	292.6	294.8	3.4
L4-COMB-IR	ERM-EB090a	344	356	368	316	353	367	352.2	13.2
	ERM-EB090b	334	368	329	369	384	338		
L5-COMB-IR	ERM-EB090a	338	340	342	333	341	324	321.3	5.0
		335	335	325	324	330	331		
	ERM-EB090b	326	311	323	295	304	310		
		312	299	317	314	299	305		
L6-COMB-IR	ERM-EB090a	315	309	311	311	312	325	333.7	3.7
	ERM-EB090b	377	345	348	347	351	353		
L7-COMB-IR	ERM-EB090a	345	344	351	335	343	341	339.7	4.0
	ERM-EB090b	336	327	332	330	344	348		



Certified ranges are the same for ERM-EB090a and ERM-EB090b

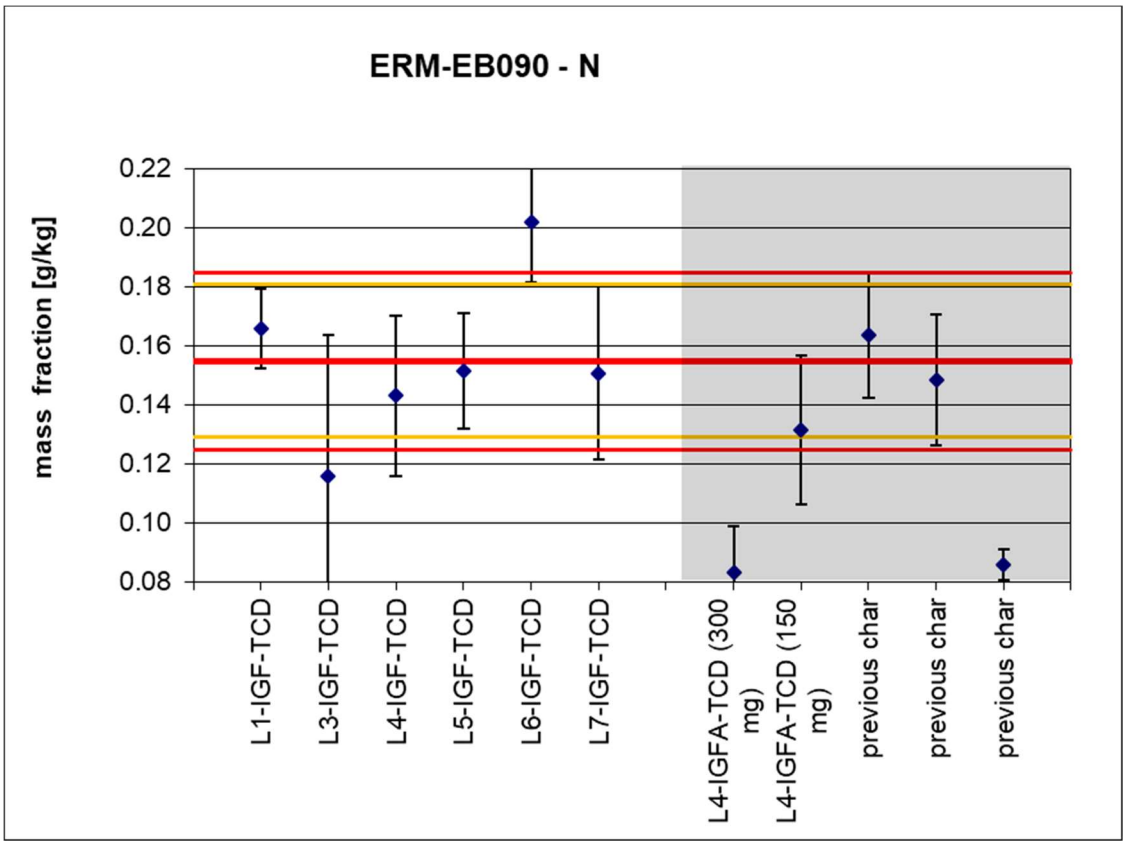
Hydrogen

Labcode	Sample	Individual results						Mean [mg/kg]	*U* [%]
L1-IGF-IR	ERM-EB090a	38	37	38	42	40	39	39.1	11.5
	ERM-EB090b	42	37	40	35	41	40		
L4-IGF-IR	ERM-EB090b	34.56	43.87	31.65	39.09	46.34	37.61	38.9	12.9
L5-IGF-IR	ERM-EB090a	40.5	39	41.8	36.5	39.8	42.9	39.9	12.0
		40.3	40.2	38.4	43.8	35.3	36.4		
	ERM-EB090b	43.3	39.5	40	41.4	43.5	36.9		
		41.3	40.3	42.4	36.7	39.1	39.1		
L6-IGF-IR	ERM-EB090a	50	48	34	34	37	36	44.7	25.7
	ERM-EB090b	56	42	51	49	52	47		
L7-IGF-IR	ERM-EB090a	53.22	54.48	45.18	53.49	50.96	57.53	50.5	15.3
	ERM-EB090b	46.81	44.46	48.11	54.35	46.67	50.51		
L8-PGAA	ERM-EB090a	46	47.5	43.5	40.5			47.1	15.7
	ERM-EB090b	56.3	44.4	55.9	42.8	44.2	51.7		
		53.8	48.9						
Not used for characterisation									
L4-IGF-IR (40 mg)	ERM-EB090a	63.43	67.08	55.06	81.95	49.05	65.65	63.7	13
L4-IGF-IR (150 mg	ERM-EB090a	38.4	38.4	40.6	39.8	33.8	43.7	39.1	13



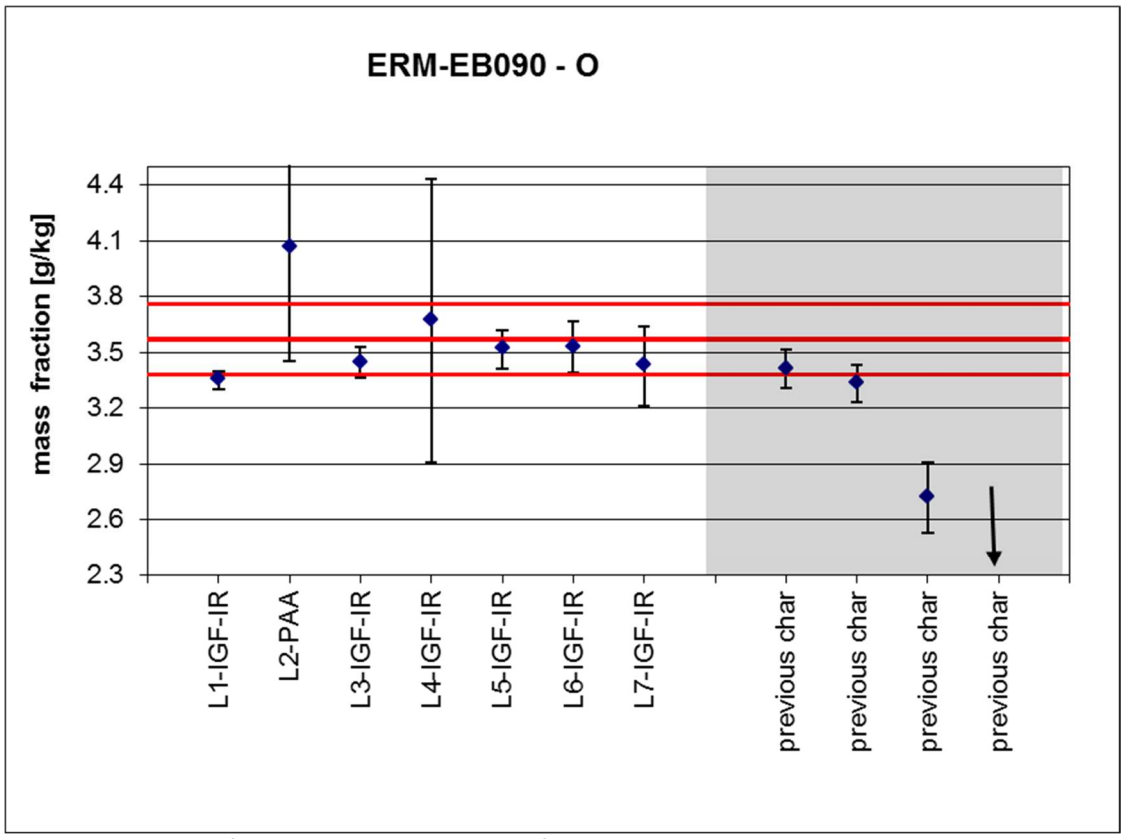
Nitrogen

Labcode	Sample	Individual results						Mean [mg/kg]	*U* [%]
L1-IGF-TCD	ERM-EB090a	172	163	172	168	167	161	165.9	8.1
	ERM-EB090b	170	163	162	178	151	164		
L3-IGF-TCD	ERM-EB090b	154	132	93	119	101	97	116.0	41.0
L4-IGF-TCD	ERM-EB090a	151	134	144	141	160	128	143.0	18.9
L5-IGF-TCD	ERM-EB090a	145	146	158	158	162	164	151.5	12.9
		151	151	147	161	162	163		
	ERM-EB090b	137	142	141	160	162	162		
		138	154	127	157	133	156		
L6-IGF-TCD	ERM-EB090a	207	206	191	179	179	179	201.8	10.2
	ERM-EB090b	220	217	218	215	212	199		
L7-IGF-TCD	ERM-EB090a	162	144	162	146	141	179	150.7	19.5
					160	156	157		
	ERM-EB090b	155	148	148	138	125	180		
					131	125	156		
Not used for characterisation									
L4-IGF-TCD (300 mg)	ERM-EB090b	130	77	70	83	79	60	83.2	19.0
L4-IGF-TCD (150 mg)	ERM-EB090b	133.13	121.43	121.53	115.38	157.56	140.06	131.5	19.0



Oxygen

Labcode	Sample	Individual results						Mean [mg/kg]	*U* [%]
L1-IGF-IR	ERM-EB090a	3311	3347	3339	3344	3394	3340	3350	1.4
	ERM-EB090b	3382	3357	3359	3368	3317	3344		
L2-PAA	ERM-EB090b	4235	3951	4013				4066	15.0
L3-IGF-IR	ERM-EB090b	3452	3495	3394	3458	3477	3402	3446	2.4
L4-IGF-IR	ERM-EB090a	3568	3337	3616	3670	3907	3832	3670	20.7
	ERM-EB090b	4100	3647	3418	3699	3532	3712		
L5-IGF-IR	ERM-EB090a	3468	3495	3486	3489	3558	3549	3517	2.9
		3492	3516	3465	3601	3503	3461		
	ERM-EB090b	3505	3543	3427	3579	3585	3583		
		3437	3483	3492	3548	3597	3538		
L6-IGF-IR	ERM-EB090a	3572	3541	3554	3398	3434	3387	3527	3.9
	ERM-EB090b	3636	3590	3600	3565	3545	3499		
L7-IGF-IR	ERM-EB090a	3352	3344	3416	3466	3406	3654	3427	6.2
					3389	3299	3392		
	ERM-EB090b	3402	3395	3422	3500	3509	3685		
					3367	3317	3374		



Certified ranges are the same for ERM-EB090a and ERM-EB090b

European Commission

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