Certification Report

for the

Isotope Reference Materials

ERM®-AE101a and ERM®-AE125

Preparation and Certification of Two Boron Isotope Reference Materials Certified for its Boron Isotope Amount Ratio, ERM®-AE101a, or its δ^{11}B-value, ERM®-AE125

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Table of contents

1. Summary

Isotope reference materials are essential to enable reliable and comparable isotope data. Besides the correction of instrumental mass fractionation or mass discrimination isotope reference materials are indispensable for validation and quality control of analytical procedures. This report describes the production and certification of a set of two isotope reference materials ERM®-AE101a and ERM®-AE125, for boron isotope analysis. The isotopic composition of both materials has been adjusted by mixing a boron mother solution enriched in ^{10}B with a boron stock solution having natural-like isotopic composition under full gravimetric control. All mother solutions have been analysed for their boron mass fraction as well as their boron isotopic composition by multi-collector thermal ionization mass spectrometry (MC-TIMS). For both reference materials, the isotopic composition obtained based on the gravimetric data agrees with the isotopic composition obtained from MC-TIMS and multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) measurements.

The certified isotopic composition of ERM®-AE101a and the certified $\delta^{11}B_{NIST\ SRM951a}$ of ERM®-AE125 can be obtained from the table below. ERM®-AE101a and ERM®-AE125 are certified according to ISO 17034 and ISO Guide 35. The certified values are based on values obtained by different analytical techniques under highest metrological requirements, especially in terms of measurement uncertainty and traceability. The analytical procedure for the certification of boron iCRMs is also listed as *Calibration and Measurement Capability* (CMC) in the data base of the *Bureau de Poids et Mesure* (BIPM).

Together with the formerly certified materials ERM®-AE102a, ERM®-AE103, ERM®-AE104a, ERM®-AE120, ERM®-AE121, ERM®-AE122, ERM®-AE123 and ERM®-AE124 a unique set of ten certified reference materials (CRM) for boron isotope analysis is now available from BAM covering the whole natural range of boron isotope variations and the whole range of industrial applications.

Certified quantity	Unit	Certified value	Uncertainty *
ERM®-AE101a			
Isotope amount ratio $n(^{10}B)/n(^{11}B)$	mol/mol	0.282 12	0.000 38
Isotope amount ratio $n(^{11}B)/n(^{10}B)$	mol/mol	3.5446	0.0048
Isotope amount fraction $n(^{10}B)/n(B)$	mol/mol	0.220 04	0.000 23
Isotope amount fraction $n(^{11}B)/n(B)$	mol/mol	0.779 96	0.000 23
Molar mass $M(B)$	g/mol	10.790 07	0.000 23
ERM®-AE125			
$\delta^{11}B_{NIST\ SRM951a}$	‰	-124.00	0.48

*) Expanded uncertainty $U = k \cdot u_c$ with $k = 2$

2. Introduction

Based on its position between metals and non-metals in the periodic system of the elements boron features distinct physical properties. Due to its high hardness, its thermal and chemical resistance boron or its carbides are especially suited for components in chemical industry, brake and clutch facings, platings, body armours and many more. The oxidic compounds of boron mainly are used in ceramic and detergent industry or for production of fluxing agents, herbicides, fertilizers etc (Holleman and Wiberg 1995).

Because of its affinity for oxygen, boron never appears in its elemental form in nature, but always as oxidic compound. In aqueous solution two dominant boron species occur: $B(OH)_3$ and the $B(OH)_4^-$ anion. Thereby ^{11}B prefers the triangular planar structure of $B(OH)_3$, whereas ^{10}B prefers the tetrahedral structure of $B(OH)_4^-$ (Palmer et al. 1992). In rocks or minerals $B(OH)_4^-$ is preferably assembled so that $B(OH)_3$ stays in the aqueous phase (Palmer et al. 1987). The isotope fractionation of boron caused by this and by biochemical processes lead to isotopic variations of up to 90 ‰ in nature. Due to instrumental mass fractionation all measured isotope ratios always must be related to an Isotopic Certified Reference Material (iCRM), apart from “Calibrated Measurements” (Absolute Measurements).

Another important property of boron is the very high neutron cross section of ^{10}B, which amounts 3.84×10^3 barns and therefore exceeds 8×10^5 times that of ^{11}B (Lide 2001). This property makes boron well-suited as “neutron catcher” in nuclear technology as demonstrated in Eqn. 1:

$^{10}B\ (n,\alpha)\ ^{7}Li$ Eqn. 1

Applying this process, the thermal power in nuclear power plants working with pressurized water reactors is being controlled by the boric acid in the primary cooling circuit. The concentration of ^{10}B permanently must be monitored, as the overall amount of ^{10}B and consequently the neutron absorption in the primary coolant agent steadily is decreasing. This is accomplished by the determination of the boric acid concentration and the isotope amount ratio $n(^{10}B)/n(^{11}B)$, which requires suitable iCRMs.

The already existing set of boron iCRMs is extended by two more iCRMs, one of which is certified for its boron isotope amount ratios to support calibration and validation of any mass spectrometric technique applied to boron isotope ratio measurements, while the other iCRM is certified for its $\delta^{11}B_{\text{NIST SRM951a}}$ value and supports quality control and validation in boron delta-measurements.

Details on the characterization of these new iCRMs as well as the certification procedure used to make them certified reference materials under the ERM® label are described here in detail.

3. Experimental Section

3.1. Chemicals, Reagents and Lab-ware Used for all Preparations and the Processing of the Candidate iRMs

Boron as ubiquitous element is highly susceptible to any contamination. This affects the analysis and the results in a particularly negative way, especially when working with enriched isotopes. Therefore, all handling was carried out using specially cleaned plastic labware (PFA: bottles, beakers, micro container; PE: pipette tips). Details on the cleaning procedure can be obtained from the literature (Vogl and Rosner 2012). All dilutions

to produce these candidate iCRMs are carried out at BAM with ultrapure water from a Milli-Q Advantage A10 water purification system. Nitric acid and hydrochloric acids (p.a. grade) were further purified by a two-stage sub-boiling distillation process applying Teflon stills in a cleanroom environment.

Synthetic boron isotope mixtures can be prepared either from pure isotopes or as in this case from natural boron compounds and together with compounds enriched in ^{10}B. The employed base materials are described in detail in Vogl and Rosner (2012).

3.2. Principle Procedure

Aqueous solutions of boric acid with distinct isotopic compositions can be produced by mixing either a solution enriched in ^{10}B or in ^{11}B with a boric acid solution of natural isotopic composition under full gravimetric control. For the mixing components, the boron mass fraction and the isotopic composition should be known exactly. All requirements, obstacles and their solution are described in detail in Vogl and Rosner (2012).

3.3. Candidate Material Preparations, Processing and Bottling

ERM-AE101a shall replace the exhausted reference material ERM®-AE101, while ERM®-AE125 is diluted from the same stock solution and shall be certified for its delta-value. Thus, the target value for the isotopic composition is a ^{10}B isotope amount fraction of 0.22. This can be achieved by mixing suitable amounts of ^{10}B mother solution to the mother solution with natural boron isotopic composition.

Table 1: Boron isotopic composition and mass fraction of the starting materials used for the preparation of the candidate iCRM with their combined standard uncertainties given in brackets and applying to the last one or two digits

Quantity		Boric acid	
		enriched in ^{10}B	natural
Isotope amount ratio / (mol·mol^{-1})	$n(^{10}B)/n(^{11}B)$	48.019(34)	0.247 33(19)
	$n(^{11}B)/n(^{10}B)$	0.020 825(15)	4.0432(31)
Isotope amount fraction/ (mol·mol^{-1})	$n(^{10}B)/n(B)$	0.979 600(14)	0.198 29(24)
	$n(^{11}B)/n(B)$	0.020 400(14)	0.801 71(24)
Molar mass / (g·mol^{-1})	$M(B)$	10.033 263(14)	10.811 74(12)
Mass fraction / (mg·kg^{-1})	$w(B)$	1011.63(67)	5625.1(75)

The exact masses with their corresponding uncertainties are displayed in Table 2. The mixing process has been carried out under full gravimetric control. Subsequently ultrapure water has been added to reach a boron mass fraction of approximately 1000 mg/kg. ERM®-AE125 was diluted further to yield a final boron mass fraction of approximately 100 mg/kg. The exact masses and mass fractions are also displayed in Table 2. The resulting solutions have been filled in pre-cleaned 20 mL PFA-bottles. The bottles have been closed tightly, labelled, sealed in polyethylene-aluminium-composite foil bags and stored in a refrigerator at (5 ± 3) °C. The filling process has been controlled gravimetrically to guarantee a minimum filling quantity of 20 mL. Three bottles – one at the beginning, one in the middle and one at the end of each filling sequence – out of each material have been withdrawn for the characterization study and the homogeneity check.

Table 2: Masses of the mother solutions used for the preparation of the iCRM and the final boron mass fraction in the iCRM; combined standard uncertainties are given in brackets

Material	Mass of solution / g			Dilution	w(B) / (mg·kg^{-1})
	^{10}B-sol.	B nat.	Ultrapure water	Factor	
ERM®-AE101a	32.76791(34)	222.1170(23)	996.1961(97)	1	1026.2(13)
ERM®-AE125	32.76791(34)	222.1170(23)	996.1961(97)	0.098821	101.41(13)

Fig. 1: Photographs of the candidate reference materials ERM®-AE101a and ERM®-AE125

3.4. Homogeneity

ERM®-AE101a and -AE125 have been produced by dissolution of high-purity boron materials followed by subsequent dilutions. Such solutions of target elements are, in principle, homogenous for their mass fractions. More importantly though, these solutions are also homogeneous with respect to their isotopic composition regardless of any variations in their mass fractions. Therefore, the solutions of ERM®-AE101a and -AE125 are taken to be homogeneous for its intended use as an iCRM. Contamination issues are also not relevant because the laboratory blank levels at BAM for boron are in the low nano-gram range (Geilert at al. 2015). Moreover, after mixing and equilibration, the resulting solution will itself be homogeneous with respect to its boron isotopes, regardless of their source. The characterization study (value assignment) showed no indication of a potential inhomogeneity. Nevertheless, the results obtained on three individual units of ERM®-AE101a and ERM®-AE125 by MC-ICP-MS (Table 4 and 5) were used to verify homogeneity by F-test and assess the potential uncertainty contribution using ANOVA. MC-ICP-MS results were used, as this technique is more

precise by a factor of up to 12 compared to MC-ICP-MS. The results of the homogeneity check, which are listed in Table 3, demonstrate that there is no homogeneity issue and that potential uncertainty contributions are negligible.

Table 3: The overall means of the boron isotope amount ratios of ERM®-AE101a (Tables 4) and of the $\delta^{11}B$ values for ERM®-AE125 with their corresponding F-values.

Material	ERM®-AE101a	ERM®-AE125
Parameter	$n(^{10}B)/n(^{11}B)$ / mol/mol	$\delta^{11}B$ / ‰
Mean	0.282 084	-123.925
Std. dev.	0.000 033	0.037
Rel. Std. dev. in %	0.012	0.030
F-value tested	2.054 *	1.148 **
F-value tabulated	3.680 *	3.35 **
MS_{within}	9.863E-10	0.001 370
$MS_{between}$	2.026E-9	0.001 573
s_{bb}	0.000 013	0.0045
s_{bb} rel.	0.0047 %	0.0036 %
u^*_{bb}	0.000 0077	0.0061
u^*_{bb} rel.	0.0027 %	0.0049 %

* Significance level 5 %, ν_1=k-1=2, ν_2=N-k=15

** Significance level 5 %, ν_1=k-1=2, ν_2=N-k=27

3.5. Stability

Experience acquired over two decades of using various BAM isotope spikes and calibration solutions as well as work carried out at the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) and the National Institute of Standards and Technology (NIST, Gaithersburg, Maryland USA) demonstrate that aqueous solutions which contain one element without any specific difficulties with the stability at mass fractions in the mg/kg range can be stored under normal laboratory conditions for long periods with no measurable change in the isotopic composition of the solutions.

The factors which can affect the stability of both the mass fraction and the isotopic composition of such solutions are contamination, adsorption on container walls, evaporation of solvent and redox reactions. Contamination, until first use at the customer's lab, is excluded by the use of PFA bottles. The PFA material of these bottles also prevents adsorption on the container walls. Evaporation is reduced to a minimum by sealing the bottles in polyethylene-aluminium-composite foil bags. Redox reactions cannot take place as no suitable oxidizing and/or reducing agents are present. Therefore, ERM-AE101and -AE125 are assumed to be stable regarding their isotopic composition and no extra uncertainty was applied. Note that even if there was some evaporative solvent loss through the PFA material despite the additional foil bag seal that causes the mass fraction of boron to change slightly over 10 years, this loss of solvent cannot change the boron isotope amount ratios. The possible changes in the boron mass fraction are covered by the expanded uncertainty of 2 %. Note

that the mass fraction is reported as an indicative value and not a certified quantity. More details on this topic may be obtained from Vogl and Rosner (2012) and from certification reports of previous boron iCRMs.

The minimum shelf life of ERM®-AE101a and -AE125 is 10 years from the issue of the certificate.

3.6. Value Assignment

The individual isotope amount ratios of both materials obtained from the MC-TIMS boron isotope measurements using the $Na_2BO_2^+$ technique and obtained from the MC-ICP-MS measurements are displayed in Table 4 together with the isotope amount ratios calculated from the gravimetric data. As ERM®-AE125 is a dilution of ERM®-AE101a, the isotope amount ratios and the isotopic composition has been determined in ERM-AE101a only; but it is valid for both materials. A detailed description of the MC-TIMS $Na_2BO_2^+$ technique can be obtained from Vogl and Rosner (2012); those for the MC-ICP-MS measurements can be obtained from Geilert et al. 2015. Instrumental mass fractionation/discrimination during MC-TIMS and MC-ICP-MS measurements was corrected with a correction factor obtained from concurrently measured IRMM-011.

Table 4: Isotope amount ratios for the stock solution (unit 6.5 & 7.6) of ERM®-AE101a and ERM®-AE125 as obtained by TIMS and by gravimetric preparation and individual isotope amount ratios for several units of the bottled material ERM®-AE101a as obtained by MC-TIMS and MC-ICP-MS; standard uncertainties are given in brackets.

Unit / Measurement No.		**Isotope amount ratio $n(^{10}B)/n(^{11}B)$ in ERM®-AE101a / (mol/mol)**		
		TIMS	MC-ICP-MS	Gravimetry
(Unit 6.5)	1	0.282 16(18)	n.a.	n.a.
	2	0.282 16(18)	n.a.	n.a.
	3	0.282 15(18)	n.a.	n.a.
(Unit 7.6)	1	0.282 19(18)	n.a.	n.a.
	2	0.282 05(18)	n.a.	n.a.
	3	0.282 27(18)	n.a.	n.a.
(Unit 1)	1	0.281 94(18)	0.282 04(18)	
	2	0.282 03(18)	0.282 06(18)	
	3	0.282 01(18)	0.282 06(18)	
	4	0.282 03(18)	0.282 13(18)	
	5	n.a.	0.282 05(18)	
	6	n.a.	0.282 05(18)	
(Unit 3)	1	0.282 43(18)	n.a.	n.a.
	2	0.282 60(18)	n.a.	n.a.
	3	0.282 53(18)	n.a.	n.a.
	4	0.282 55(18)	n.a.	n.a.
	5	0.282 51(18)	n.a.	n.a.
	6	0.282 19(18)	n.a.	n.a.
	7	0.282 13(18)	n.a.	n.a.
	8	0.282 14(18)	n.a.	n.a.
	9	0.282 11(18)	n.a.	n.a.
	10	0.282 27(18)	n.a.	n.a.

Unit / Measurement No.	Isotope amount ratio $n(^{10}B)/n(^{11}B)$ in ERM-AE101a / (mol/mol)		
	TIMS	MC-ICP-MS	Gravimetry
(Unit 24) 1	0.282 05(18)	n.a.	n.a.
2	0.282 08(18)	n.a.	n.a.
3	0.281 97(18)	n.a.	n.a.
4	0.282 10(18)	n.a.	n.a.
5	0.281 98(18)	n.a.	n.a.
6	0.282 18(18)	n.a.	n.a.
7	0.282 05(18)	n.a.	n.a.
8	0.282 24(18)	n.a.	n.a.
9	0.282 29(18)	n.a.	n.a.
10	0.282 25(18)	n.a.	n.a.
(Unit 25) 1	0.282 29(18)	0.282 12(18)	n.a.
2	0.282 15(18)	0.282 07(18)	n.a.
3	0.282 20(18)	0.282 06(18)	n.a.
4	n.a.	0.282 05(18)	n.a.
5	n.a.	0.282 08(18)	n.a.
6	n.a.	0.282 12(18)	n.a.
(Unit 51) 1	0.282 01(18)	n.a.	n.a.
2	0.281 94(18)	n.a.	n.a.
3	0.281 94(18)	n.a.	n.a.
4	0.281 94(18)	n.a.	n.a.
5	0.281 84(18)	n.a.	n.a.
6	0.282 14(18)	n.a.	n.a.
7	0.282 11(18)	n.a.	n.a.
8	0.282 10(18)	n.a.	n.a.
9	0.282 10(18)	n.a.	n.a.
10	0.281 94(18)	n.a.	n.a.
(Unit 52) 1	0.281 87(18)	0.282 08(18)	n.a.
2	0.282 03(18)	0.282 05(18)	n.a.
3	0.282 01(18)	0.282 13(18)	n.a.
4	0.281 95(18)	0.282 12(18)	n.a.
5	n.a.	0.282 11(18)	n.a.
6	n.a.	0.282 13(18)	n.a.
Average	0.282 13(18)	0.282 08(18)	0.28213(20)
$s(n(^{10}B)/n(^{11}B))$/(mol/mol)	0.000 18	0.000 033	
$SE(n(^{10}B)/n(^{11}B))$/(mol/mol)	0.000 026	0.000 0078	

MC-ICP-MS and MC-TIMS results agree with one another for each individual reference material unit. The difference between the overall mean of both analytical procedures is significantly smaller than the combined standard uncertainty. Both results show an excellent agreement with the gravimetric value. The results clearly demonstrate that the production of boron isotope reference materials under gravimetric control yields results which are metrologically compatible with the results obtained by MC-TIMS measurements and both nearly identical measurement uncertainties are dominated by the contribution deriving from the iCRM applied for correction of instrumental mass fractionation. This result, however, can only be achieved, when the production is carried out under full gravimetric control, the contamination issue is fully under control and the corresponding uncertainty budgets have been set up properly. When combining the results obtained by MC-TIMS, MC-ICP-MS and gravimetric preparation an isotope amount ratio $n(^{10}B)/n(^{11}B)$ of 0.28212 mol/mol is being obtained with an associated combined uncertainty of 0.00019 mol/mol. It is obvious that a potential uncertainty contribution originating from the homogeneity study of 0.000013 mol/mol (s_{bb}) can be neglected.

Delta measurements for ERM-AE125 have been obtained with MC-ICP-MS and with MC-TIMS, the latter by applying the $Na_2BO_2^+$-technique. Following the international convention NIST SRM 951a has been used as

delta zero standard using the standard-sample bracketing technique (Brand et al. 2014). The δ^{11}B values were calculated according to Eqn. 2 and are listed in Table 5.

$$\delta^{11}\mathrm{B} = \delta^{11/10}\mathrm{B}_{\text{NIST SRM 951a}} = \left(\frac{R_{sample}^{measured}\left(\frac{^{11}\mathrm{B}}{^{10}\mathrm{B}}\right)}{R_{NIST\ SRM\ 951a}^{measured}\left(\frac{^{11}\mathrm{B}}{^{10}\mathrm{B}}\right)} \right) - 1 \qquad \text{Eqn. 2}$$

Table 5: Individual δ^{11}B values for ERM®-AE125 as obtained by MC-TIMS, MC-ICP-MS and by gravimetric preparation; standard uncertainties are given in brackets.

Unit / Measurement No.		**Delta value δ^{11}B in ERM®-AE125 / ‰**		
		TIMS	MC-ICP-MS	Gravimetry
(Unit 101a-3/Unit 125-4)*	1	-123.44(25)	-123.91(19)	n.a.
	2	-124.13(25)	-123.97(19)	n.a.
	3	-124.23(25)	-123.92(19)	n.a.
	4	-123.92(25)	-123.92(19)	n.a.
	5	-123.89(25)	-123.90(19)	n.a.
	6	n.a.	-123.95(19)	n.a.
	7	n.a.	-123.90(19)	n.a.
	8	n.a.	-123.87(19)	n.a.
	9	n.a.	-123.89(19)	n.a.
	10	n.a.	-123.88(19)	n.a.
(Unit 101a-24/Unit 125-27)*	1	-124.50(25)	-123.94(19)	n.a.
	2	-124.15(25)	-123.90(19)	n.a.
	3	-124.49(25)	-123.97(19)	n.a.
	4	-124.61(25)	-123.86(19)	n.a.
	5	-124.25(25)	-123.98(19)	n.a.
	6	n.a.	-123.91(19)	n.a.
	7	n.a.	-123.94(19)	n.a.
	8	n.a.	-123.95(19)	n.a.
	9	n.a.	-123.94(19)	n.a.
	10	n.a.	-123.92(19)	n.a.
(Unit 101a-51/Unit 125-58)*	1	-123.97(25)	-123.96(19)	n.a.
	2	-123.84(25)	-123.86(19)	n.a.
	3	-123.94(25)	-123.88(19)	n.a.
	4	-123.80(25)	-123.95(19)	n.a.
	5	-124.09(25)	-123.95(19)	n.a.
	6	n.a.	-123.89(19)	n.a.
	7	n.a.	-123.95(19)	n.a.
	8	n.a.	-123.98(19)	n.a.
	9	n.a.	-123.99(19)	n.a.
	10	n.a.	-123.91(19)	n.a.
Average		-124.08(26)	-123.92(19)	-123.46(71)
$s(\delta^{11}\mathrm{B})$ / ‰		0.31	0.037	
$SE(\delta^{11}\mathrm{B})$ / ‰		0.079	0.0066	

* TIMS measurements have been carried out in the same units as for the characterization of ERM®-AE101a (stock solution of ERM®-AE125), as $Na_2BO_2^+$-technique requires a higher boron amount per measurement; MC-ICP-MS measurements have been carried out in three different units of ERM®-AE125

As a quality control the previously certified reference materials ERM®-AE120, -AE121 and -AE122 have been analysed in the same MC-ICP-MS sequence as the candidate reference materials ERM®-AE101a and -AE125. The δ^{11}B values of -(20.32 ± 0.38) ‰, +(19.67 ± 0.38) ‰ and +(39.52 ± 0.38) ‰ as determined for of ERM®-AE120, -AE121 and -AE122 are metrologically compatible with the certified δ^{11}B-values of -(20.2 ± 0.6) ‰, +(19.9 ± 0.6) ‰ and +(39.7 ± 0.6) ‰, respectively and yield E_n-values of less than 1. Furthermore, NIST SRM

951a measured as a sample in the beginning of the sequence yielded a δ^{11}B-value of -(0.03 ± 0.38) ‰, which agrees well with the theoretical value of 0.

All results, whether obtained by the gravimetric preparation, MC-TIMS or MC-ICPMS agree well within the stated standard uncertainties, demonstrating again the high performance of preparation as well those of the mass spectrometric measurements. For the calculation of the final δ^{11}B value, however, the result of the gravimetric preparation will not be considered as the measurement uncertainty is limited by the absolute isotopic composition of the stock solution which in turn is dominated by the measurement uncertainty of NIST SRM 951a. In delta measurements, however, the measurement uncertainty of the scale defining material is not considered by its definition. When combining the results obtained by TIMS and MC-ICP-MS a δ^{11}B value of -124.00 ‰ is being obtained with an associated combined standard uncertainty of 0.24 ‰. It is obvious that a potential uncertainty contribution originating from the homogeneity study of 0.0061 ‰ (u^*_{bb}) can be neglected.

The isotopic composition of both materials has been calculated based on the arithmetic mean of MC-TIMS measurements, MC-ICP-MS measurements and gravimetric data and is displayed in Table 6. According to the currently valid definitions of “The International Systems of Units (SI)” the molar mass of a particle X is obtained from its relative atomic mass A_r(X) by the following equation (Mohr et al. 2012):

$$M(\mathrm{X}) = A_\mathrm{r}(\mathrm{X}) \cdot M_\mathrm{u} \qquad \text{Eqn. 3}$$

With M_u being the Molar Mass Constant with its exact value of $1 \cdot 10^{-3}$ kg/mol. Thus, the relative atomic masses can be directly converted into the molar masses without changing their values and uncertainties.

4. Certification

For the certification of a reference material in general all data altering or affecting the quantity value to be certified or its combined uncertainty must be collected and used for establishing the certified quantity value. Commonly, the results from homogeneity, stability and characterization are combined. The here described reference materials are certified according to ISO 17034 and ISO Guide 35 (ISO 2016 & 2017). The certified values are based on values obtained by different analytical techniques under highest metrological requirements, especially in terms of measurement uncertainty and traceability. The analytical procedure for the certification of boron iCRMs is also listed as *Calibration and Measurement Capability* (CMC) in the data base of the *Bureau de Poids et Mesure* (BIPM) (BIPM 2020).

As explained above possible inhomogeneity issues and instability issues do not apply to either of these new iCRMs. Consequently, the certified values and their associated uncertainties are calculated from Table 4 and 5 as described in the characterization section and are displayed in Table 6.

The relative expanded uncertainty for the isotope amount ratio $n(^{10}\mathrm{B})/n(^{11}\mathrm{B})$ in ERM®-AE101a is 0.13 %. For the isotope amount fractions $n(^{10}\mathrm{B})/n(\mathrm{B})$ and $n(^{11}\mathrm{B})/n(\mathrm{B})$ the relative expanded uncertainties are 0.10 %, and 0.029 %, respectively. For the case of the molar masses the relative expanded uncertainty is 0.0021 %. With almost 100 % the major contribution to the uncertainty associated with the isotope amount ratio $n(^{10}\mathrm{B})/n(^{11}\mathrm{B})$ determined in an individual measurement sequence derives from the uncertainty contributions of the iCRM IRMM-011, which was used to correct for instrumental mass fractionation/discrimination.

Table 6: Certified quantity values of ERM-AE101a and -AE125 with their associated combined uncertainties u_c, their associated expanded uncertainties $U = k \cdot u_c$ with $k = 2$ and their associated relative expanded uncertainties U_{rel}

Quantity	Unit	Value	u_c	U	U_{rel} in %
ERM-AE101a					
$n(^{10}B)/n(^{11}B)$	mol/mol	0.282 12	0.000 19	0.000 38	0.13
$n(^{11}B)/n(^{10}B)$	mol/mol	3.5446	0.0024	0.0048	0.14
$n(^{10}B)/n(B)$	mol/mol	0.220 04	0.000 12	0.000 23	0.10
$n(^{11}B)/n(B)$	mol/mol	0.779 96	0.000 12	0.000 23	0.029
$M(B)$	g/mol	10.790 07	0.000 12	0.000 23	0.0021
ERM-AE125					
$\delta^{11}B$	‰	- 124.00	0.24	0.48	0.39

By calibration of all mass spectrometers against iCRM IRMM-011 and all balances against SI-traceable weights, the boron isotopic composition and the boron mass fraction of the certified isotope reference materials ERM®-AE101a and ERM®-AE125 are traceable to “The International System of Units (SI)” in the most direct way possible.

As described above the $\delta^{11}B$ value of ERM®-AE125 is calculated as the mean of the measurement results obtained by MC-TIMS and by MC-ICP-MS, the associated expanded measurement uncertainty is 0.48 ‰. Thus, it is 20 % smaller than obtained in previous projects (Vogl and Rosner 2012). The $\delta^{11}B$ value of ERM®-AE125 is traceable to the international δ=0 standard NIST SRM 951a.

The B mass fractions in both ERM® materials are provided as indicative values (Table 7).

Table 7: Indicative quantity values of ERM®-AE101a and -AE125 with their associated expanded uncertainties $U = k \cdot u_c$ with $k = 2$

Material	Quantity	Unit	Indicative value	U	U_{rel} in %
ERM®-AE101a	B mass fraction	mg/kg	1026	21	2.0
ERM®-AE125	B mass fraction	mg/kg	101.4	2.0	2.0

5. Storage and Handling

ERM-AE101a and -AE125 should be stored under cool (5 ± 3) °C and dark conditions to reduce evaporation effects. Once opened, the bottle lid should be left open as little as possible. Its weight should be monitored to track any evaporative losses during storage. These losses however will only affect the nominal boron mass fraction in the solution and will not affect the certified boron isotope amount ratios or the certified $\delta^{11}B$ value. The introduction of any contaminant to this solution may change the boron isotope ratios and the $\delta^{11}B$ value.

6. References

BIPM (2020)
CIPM MRA Database, https://www.bipm.org/kcdb/ (last accessed 07/09/2020)

Brand WA, Coplen TB, Vogl J, Rosner M, and Prohaska T (2014)
Assessment of International Reference Materials for Isotope Ratio Analysis (IUPAC Technical Report), Pure and Applied Chemistry, 86, 425-467

Geilert S, Vogl J, Rosner M, Voerkelius S, and Eichert T (2015)
Boron isotope fractionation in bell pepper, Mass Spectrometry and Purification Techniques, 1 1, doi:10.4172/mso.1000101

Holleman AF and Wiberg E (1995)
Lehrbuch der Anorganischen Chemie, Walter de Gruyter Verlag, Berlin

ISO (2016)
General requirements for the competence of reference material producers (ISO 17034:2016), International Standards Organization, Geneva, https://www.iso.org/standard/29357.html (last accessed 07/09/2020)

ISO (2017)
Reference materials — Guidance for characterization and assessment of homogeneity and stability (ISO Guide 35:2017), International Standards Organization, Geneva, https://www.iso.org/standard/60281.html (last accessed 07/09/2020)

Lide DR (2001)
CRC Handbook of Chemistry and Physics, CRC Press LLC, Boca Raton

Mohr PJ, Taylor BN, and Newell DB (2012)
CODATA Recommended Values of the Fundamental Physical Constants: 2010. Journal of Physical and Chemical Reference Data 41(4): doi:10.1063/1.4724320

Palmer MR, London D, Morgan GB, and Babb HA (1992)
Experimental Determination of Fractionation of $^{10}B/^{11}B$ between Turmaline and Aqueous Vapour: A Temperature and Pressure Dependent Isotopic System, Chemical Geology, 101, 123-129

Palmer MR, Spivack AJ, and Edmond JM (1987)
Temperature and pH controls over Isotopic Fractionation during Adsorption of Boron on Marine Clay, Geochimica et Cosmochimica Acta, 51, 2319-2323

Vogl J and Rosner M (2012)
Production and Certification of a Unique Set of Isotope and Delta Reference Materials for Boron Isotope Determination in Geochemical, Environmental and Industrial Materials, Geostandards and Geoanalytical Research, 36, 161-175