Certification Report

for the

Reference Materials

ERM-AE102a, AE104a, AE120, AE121 & AE122

Certified for their boron isotope composition or δ^{11}B-values

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Table of contents

1. Abstract

Isotope reference materials are essential to enable reliable and comparable isotope data. Besides the correction of mass fractionation or mass discrimination isotope reference materials are indispensible for validation and quality control of analytical procedures. This article describes the production and certification of a set of five isotope reference materials ERM-AE102a, 104a, AE120, 121 and 122, for boron isotope analysis. The isotopic composition of all materials has been adjusted by mixing boron mother solutions enriched in ^{10}B or ^{11}B with a boron mother 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 TIMS using IDMS as calibration technique. For all five reference materials the isotopic composition obtained on the basis of the gravimetric data agrees very well with the isotopic composition obtained from different TIMS techniques. Performed stability and homogeneity studies show no significant influence on the isotopic composition as well as on the related uncertainties.

The certified isotope abundances for ^{10}B are 0.29995 (27) for ERM-AE102a and 0.31488 (28) for ERM-AE104a. The certified $\delta^{11}B$ values are -20.2 (6) ‰ for ERM-AE120, 19.9 (6) ‰ for ERM-AE121 and 39.7 (6) ‰ for ERM-AE122.

Together with the formerly certified ERM-AE101 and -AE103 a unique set of seven certified reference materials (CRM) for boron isotope analysis is now available from BAM.

2. Introduction

Based on its position between metals and nonmetals 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 various industrial applications (e.g. brake and clutch facings, plating, body armors). The oxidic compounds of boron are mainly used in ceramic and detergent industry or for production of fluxing agents, herbicides or fertilizers (Hollemann *et al.* 1995).

Because of its affinity for oxygen, boron never appears in its elemental form in nature, but always as oxidic compound. Depending on the pH value two dominant boron species occur in aqueous solution: $B(OH)_3$ and the $B(OH)_4^-$ anion. Thereby ^{11}B prefers the triangular planar structure of $B(OH)_3$, whereas ^{10}B prefers the tetrahedric structure of $B(OH)_4^-$ (Palmer *et al.* 1992). In rocks or minerals preferably $B(OH)_4^-$ is assembled so that $B(OH)_3$ stays in the aqueous phase (Palmer *et al.* 1987). The therewith combined isotope fractionation of boron leads to isotopic variations of up to 90 ‰ in nature. This large variation allows the investigation of geochemical processes (Leeman & Sisson, 1996) or anthropogenic influences in water reservoirs (Eisenhut *et al.* 1996, Vengosh *et al.* 1999).

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). Thus boron is used as neutron absorber as demonstrated in eqn. 1:

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

In nuclear power plants working with pressurized water reactors the thermal power is being controlled that way by keeping a certain concentration of boric acid in the primary cooling circuit. The concentration of ^{10}B permanently has to be monitored, as the overall amount of ^{10}B and consequently the neutron absorption in the primary cooling agent is steadily decreasing. Therefore the boric acid concentration and the $^{10}B/^{11}B$ isotope abundance ratio have to be determined on a regular basis to enable the adjustment of the ^{10}B concentration. Apart from industrial application boron isotopes are increasingly used in geochemical and environmental studies.

Because all mass spectrometric measurements are affected by mass discrimination or mass fractionation, the determined isotope ratios are biased relative to the “true value”. To enable comparable isotope data, the measurements have to be carried out in a way that the results are traceable either to the International System of Unit (SI) or to an internationally accepted standard. This means that the determination of isotope abundance ratios has to be corrected for mass discrimination or mass fractionation by applying a Reference Material (RM) being certified for its isotopic composition. The determination of relative differences or so-called δ-values can be related to RM being certified for their δ-values. More details on this topic can be obtained from Vogl and Pritzkow 2010a.

Until 2001 only IRMM and NIST offered boron isotope RM either with natural isotopic composition (NIST SRM 951, $\delta^{11}B = 0$; IRMM-011 & 611) or highly enriched in ^{10}B (NIST SRM 952, IRMM-610). The operators of nuclear power plants require boron isotope RM in form of aqueous boric acid solutions with ^{10}B isotopic abundances between those materials. To meet these needs BAM certified

in 2001/2002 a set of boron isotope RM, enriched in ^{10}B and labeled BAM-I001, I002, I003 and I004, which became ERM-AE101, AE102, AE103 and AE104 in 2004.

ERM-AE102 and 104 run short and therefore new batches have been produced and certified. As no RM for boron with $\delta\,^{11}B \neq 0$ is available yet and there is an increasing need for these materials due to an increased number of boron isotope measurements for geochemical and environmental applications, a set of boron RM certified for δ-values has been produced and certified in parallel.

This need for boron isotope reference materials is being demonstrated by two recent publications on laboratory intercomparisons for $\delta^{11}B$-determinations. Gonfiantini et al. (2003) conducted a laboratory intercomparison on $\delta^{11}B$ in water and mineral samples. This study showed good results for simple samples (high B mass fraction, simple matrix) but poor agreement for more difficult samples (low B mass fraction, more complex matrices). Significant differences in the applied analytical procedures (P-TIMS, N-TIMS, ICP-MS) have not been observed, although the ICP-MS results generally showed a larger spread of the results. The conclusion was that the analytical procedures require improvement, because the observed spread was larger in all cases than the stated precision. A second conclusion was that at least one additional reference materials is required offering a $\delta^{11}B$-value with an offset of some tens of per mill relative to NIST SRM 951.

Aggarwal et al. (2009) presented a paper on the production of 2 standards with 2 different gravimetrically established $\delta^{11}B$-values, which they have used to perform another laboratory intercomparison. The published uncertainties are unreproducible and seem to be heavily underestimated. For example the $\delta^{11}B$ of standard 1, calculated from the gravimetric data, is reported as (9.86 ± 0.07) ‰. Moreover, a weighted mean of all laboratory results is presented showing a value of (9.99 ± 0.08) ‰, while the real spread of results range from approximately -2.5 ‰ (minimum value) to approximately +20 ‰ (maximum value). It is somehow surprising how a mean value of 9.99 ‰ with an “uncertainty” of 0.08 ‰ could be achieved. Weighting the mean, presumably for the stated uncertainties of the laboratory result, is not sound, because these uncertainties are not reliable as stated in the paper. A more robust statistical tool would have been the Median giving a value of approximately 11 ‰ in this case, which would not agree that well with the gravimetric value.

Unfortunately there is still a poor understanding of reference materials, certified values, measurement uncertainties or metrology in general. In isotope analysis especially when determining isotope variations and δ-values we often can read that simple repeatability such as standard deviation is used to express a measurement uncertainty, without mentioning whether they are combined or expanded ones (Aggarwal et al. 2009).

A complete measurement uncertainty, however, gives the dispersion of the measurement results, in which the result is regarded to be precise and true. Reproducibility only accounts for the precision, trueness is not considered. This fundamental difference gets visible in laboratory intercomparisons, when small reproducibilities are stated as uncertainties, but there is no overlap between the stated range and the mean value of the intercomparison. Another critical point is the differentiation between certified values and references or between certified reference materials and any kind of stated reference sample.

Gonfiantini et al. (2003) stated the certified value of NIST SRM 951 as being 4.04362 ± 0.00137 ($^{11}B/^{10}B$) with reference to the literature (Catanzaro *et al.* 1970). The certificate of NIST SRM 951, however, gives the $^{10}B/^{11}B$ value as 0.2473 ± 0.0002. From this an $^{11}B/^{10}B$ value can be calculated as 4.0437 ± 0.0033, with an absolute maximum of 4 decimal places, but in no case 5. Thus the above stated value is no certified value; otherwise it would have been printed in the certificate.

These examples have been discussed to create awareness for the proper application of metrological principles (e.g. measurement uncertainty) and for the exact use of the right terminology. More details on these topics can be obtained from the "International Vocabulary of Metrology" and from Vogl and Pritzkow (2010a, 2010c).

3. Experimental Section

3.1. 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. Unfortunately boric acid cannot be used easily for preparing a primary standard, because it contains variable mass fractions of water. Strong drying procedures are not applicable, because boric acid will be dehydrated at around 100 °C and will be converted into metaboric acid HBO_2. Therefore, no drying course can be applied providing a distinct boron compound with an exact stoichiometry offering an uncertainty of less than 0.1 % for the elemental mass fraction.

Due to the problem of residual water in crystalline boric acid is a boron spike solution, enriched in ^{10}B, has been prepared and characterized by applying a primary assay for boron (for details see next chapter). This boron spike was used as ^{10}B mother solution and to determine the boron mass fraction in the mother solution of the boric acid with natural isotopic composition and in the ^{11}B mother solution by applying IDMS. Using these three mother solutions each of the target boron isotope ratio can be mixed.

3.2. Chemicals, Reagents and Labware

For all dilutions and manipulations ultrapure water has been used obtained from a Milli-Q Advantage A10 water purification system. Nitric acid has been purchased p.a. grade and has been purified by twofold subboiling distillation (1st stage quartz still, 2nd stage Teflon still). Only quartz, PTFE or PFA labware has been used in this project. All preparation steps have been carried out in a low boron laboratory environment (Rosner et al. 2005).

Boric acid with approximately natural isotopic composition has been purchased from Merck, Darmstadt, Germany in suprapure quality. Enriched ^{11}B has been obtained from MaTek GmbH, Jülich, Germany in metal form with a purity of 99.9995 %. This material was offered as boron metal without statement, that in fact it is enriched in ^{11}B. For the boron spike a pure (> 99.5 %) boric acid enriched in ^{10}B was used.

3.3. Gravimetric Determinations

The preparation of solutions has been carried out under full gravimetric control. To enable this, a few practical aspects have to be considered, as the weighing process is influenced by different effects such as buoyancy, electrostatic effects and evaporation. Moisture content of boron compounds has to be considered separately. Other stability issues do not apply here.

Buoyancy or more exactly air buoyancy expresses the difference in air buoyancy between the object to be weighed and the built-in reference of the balance, which causes a bias. The effect is well-known and corrections are applied according to eqn.2 whenever reference weighing is performed, e.g. for RM characterisation (Kehl *et al.* 2000, Reichmuth *et al.* 2004). In eqn. 2 m_{x_obs} is the reading of the balance, ρ_{Air}, ρ_{bal} and ρ_x are the densities of the air, the built-in weights of the balance and of the sample. For objects with a density of around 10^3 kg·m^{-3} (e.g. water) the resulting bias is in the order of 10^{-3} relative and should be corrected (Pozivil *et al.* 2006).

$$m_x = m_{x\_obs} \cdot \frac{\left(1 - \frac{\rho_{air}}{\rho_{bal}}\right)}{\left(1 - \frac{\rho_{air}}{\rho_x}\right)} \qquad \text{eqn. 2}$$

Electrostatic charging of plastic containers cannot be corrected, but reduced or even avoided by specific tools compensating the electrostatic charge. This can be accomplished best by blowing ionized nitrogen onto the containers surface with a ring ionizer combined with a blow-out gun (Type RI 65 P 7187 500, Haug GmbH, Leinf.-Echterdingen, Germany). This device cannot be used, when powders have to be weighed on open plastic trays. Logically, for any handling only cotton gloves should be used, because plastic gloves would produce new electrostatic charges. Gloves in general are required to avoid fingerprints on the container, which could easily make up a mass bias of a tenth of a mg.

The weighing of solutions into a container seems to be an easy task. However, performing it on a reference level some specific aspects have to be considered. It is advisable to fill a polyethylene syringe with the solution and place a pipette tip on the tip of the syringe to reduce the orifice and a sealed pipette tip to close the reduced orifice. Then the filled syringe is being weighed, the desired mass is being dosed into the container and the syringe is being weighed back. This gives the exact mass of the solution which has been released. When pouring the solution into the container and weighing the mass difference in the container, first the relation of container mass to solution mass is less advantageous (weighing a mouse on an elephants back) and second during the pouring solvent will evaporate, which will not be considered. The syringe approach considers this, because the released mass is being determined. Consequently, all prepared solutions have to be monitored for their mass during storage, because from each bottle the solvent (water or dilute acid) will evaporate in small amounts and will change the mass fraction of the solution. Monitoring the mass of the solution can be used to correct for this.

All solutions within this project have been prepared considering these facts and therefore an uncertainty budget can be set up. The full uncertainty budget for the ^{11}B enriched back-spike is listed in Table 10 (Appendix).

3.4. Mass Spectrometric Determinations

Boron isotope ratios of all samples have been determined by TIMS using the $Na_2BO_2^+$ and the $Cs_2BO_2^+$ technique on a Sector 54 instrument (Micromass, Manchester, UK).

The $Na_2BO_2^+$ technique has been applied for the characterization of all boron solutions and reference materials within this project, whereas the $Cs_2BO_2^+$ technique has been applied only for characterizing the final RM as well as for cross-checking and confirming the $Na_2BO_2^+$ data.

$Na_2BO_2^+$ TIMS technique

For the $Na_2BO_2^+$ technique the samples have been evaporated to dryness in a cold nitrogen stream and were subsequently dissolved in stoichiometric amounts of NaOH. The mass of 15 µg boron was loaded on Re single filaments (boat design), which were placed on a turret and introduced into the mass spectrometer. After evacuation of the ion source (< 10^{-8} mbar) the automatic measurements started with a high voltage of 8 kV. Each filament was heated up to 1.3 A filament current. Then a series of scanning for analyte signal, peak centering and autofocusing started, each followed by an additional rise of the filament current. This was carried out until an ion intensity of 1.6 V had been reached at the monitor mass (here: 89, $^{23}Na_2{}^{11}B^{16}O_2$). Then the measurements were started, whereby the filament current was automatically controlled to yield an intensity of 2 V at the monitor mass. Data were recorded in one block of 300 cycles. The achieved repeatability between individual filaments is better than 0.05 % for the ion current ratio.

The multi-collector design allows the simultaneous measurement of the masses 88 ($^{23}Na_2{}^{10}B^{16}O_2^+$) and 89 ($^{23}Na_2{}^{11}B^{16}O_2^+$), which enables more precise isotope ratio determinations than a single collector instrument. As the ion $^{23}Na_2{}^{10}B^{16}O^{17}O^+$ also occurs on mass 89 the observed isotope ratios have to be corrected using the so-called oxygen-correction (De Bièvre *et al.* 1969). For correcting the mass fractionation always IRMM-011 was used, because this isotope RM is metrologically more coherent than NIST SRM 951. $\delta^{11}B$ values have been calculated versus NIST SRM 951, because traditionally the origin of the boron δ-scale is being represented by NIST SRM 951.

$Cs_2BO_2^+$ graphite TIMS technique

The $Cs_2BO_2^+$ graphite TIMS technique has been applied as published by Rosner & Meixner 2004.

The dry sample was dissolved in 2 molar HCl (2-4µL) and mixed with Cs_2CO_3-solution (1 mol B : 2 mol Cs). A degassed tantalum filament was coated with a graphite/ethanol slurry and was heated at 0.7 A until it reached complete dryness. An aliquot of the sample solution containing 0.5 µg B was then loaded on top of the graphite. Once the sample was completely dry, the current was raised to 1.4 A at a rate of 0.02 A s^{-1} and left there for 20 s.

Boron isotope ratio measurements were carried out on a Micromass Sector 54 thermal ionization mass spectrometer by peak jumping on the axial faraday cup. The isotope ratio of B was measured on

masses 308 ($Cs_2{}^{10}BO_2{}^+$) and 309 ($Cs_2{}^{11}BO_2{}^+$) with filament currents between 1.35 A and 1.75 A and ion beam intensities between 5 * 10^{-13} A and 5 * 10^{-12} A on mass 309 using a high voltage of ~7.5 kV. Measurements start with two baselines (5 s) at mass 307.5 followed by 150 subsequent scans at masses 308 (4 s) and 309 (2 s). Magnet settling time was set to 1 s to reduce the time delay between the measurement of the ^{10}B and ^{11}B ion beam. Due to the used peak jumping routine a linear time interpolation between the measurement of the $Cs_2{}^{10}BO_2{}^+$ and $Cs_2{}^{11}BO_2{}^+$ ion beams was performed in order to correct for the usually observed systematic decrease of the ion beam. Typically the first un-fractionated 50 isotope ratios were averaged to calculate the mean B isotope ratio of a measurement. Oxygen isotope correction was carried out by subtraction of 0.00079 (De Bièvre *et al.* 1969) from the measured $Cs_2{}^{10}BO_2{}^+/Cs_2{}^{11}BO_2{}^+$ ratio to get the final observed $^{11}B/^{10}B$ isotope ratio. From these data $\delta^{11}B$ values have been calculated versus NIST SRM 951.

3.5. Spike Characterization

A ^{10}B spike has been prepared by dissolving enriched boric acid (^{10}B: 98 %) in water. The water content of the enriched boric acid has been determined by Karl-Fischer-titration. Before using this spike it has to be characterized for its boron mass fraction and its isotopic composition, which is usually carried out by reverse IDMS using a primary assay or so-called back-spike (Vogl 2007). A gravimetric value is usually not sufficiently accurate due to unknown impurities, unproven stoichiometry or water contents. In the case of boron the selection of a suitable material for the preparation of a primary assay is difficult, because each of the available materials (crystalline boric acid, boron oxide and boron metal) has specific drawbacks. Therefore we decided to use three different materials at first (Table 1).

Table 1: Boron materials of high purity, which are used as back-spikes

Material	**Formula**	**Purity**	**Isotopic composition**	**Producer/Provider**
Boric acid	H_3BO_3	99.9999 %	Natural	Merck KgAa Darmstadt, Germany
Boron oxide	B_2O_3	99.999 %	Natural	MaTeck Jülich, Germany
Boron metal	B	99.9995 %	Enriched in ^{11}B	MaTeck Jülich, Germany

All three materials offer sufficient purity above 99.999 %, which in principle makes all materials suitable. However, boric acid and boron oxide carry unknown amounts of water, which disturb accurate gravimetric preparation. Therefore the materials have been analysed for their water content by applying Karl-Fischer-Titration. Additionally there might be uncertainties with the stoichiometry. In the case of B metal, the material requires decomposition in a high pressure asher with nitric acid to achieve complete dissolution. From all materials solutions have been prepared, which have been used as back-spikes. From each back-spike solution 5 mixtures with the ^{10}B spike solution have been

prepared, so-called blends, and reverse IDMS has been carried out. The results of the mass fraction of ^{10}B in the spike solution obtained with the three different reverse IDMS series are listed in Table 2 together with the gravimetric result, which of course have been corrected for water content. The TIMS measurements have been carried out by applying the Na_2BO_2 technique and by correcting for mass fractionation using the IRMM-011 reference material.

Table 2: Mass fractions of ^{10}B in the spike solution obtained with the three different reverse IDMS and gravimetric result with their combined standard uncertainties

Procedure	Unit	Mass fraction of ^{10}B in the spike	Combined standard uncertainty (k=1)
Reverse IDMS using boric acid as back-spike	$mg \cdot kg^{-1}$	985.0	0.7
Reverse IDMS using boron oxide as back-spike	$mg \cdot kg^{-1}$	993.1	0.7
Reverse IDMS using boron metal as back-spike	$mg \cdot kg^{-1}$	987.3	0.7
Gravimetric data *	$mg \cdot kg^{-1}$	986.80	0.23

* Corrected for water content as determined by Karl-Fischer-Titration

The ^{10}B mass fraction of the spike solution obtained with boric acid and boron metal agree well with the gravimetric value within their expanded uncertainties. The mass fraction obtained with boron oxide does not agree within the uncertainty with the results obtained with boric acid and boron oxide. Reasons for this mismatch is presumably a bias in the stoichiometry and water content which partially was not accessible by Karl-Fischer-Titration, both leading to lower B mass fraction in the back-spike than assumed, which in turn leads to a higher result for the B mass fraction in the spike. The result obtained with the boron metal back-spike and the gravimetric value show the closest agreement. Therefore it was decided to use the value obtained with reverse IDMS and boron metal as back-spike, because this allows the double IDMS approach for future IDMS analysis. Double IDMS yields results with smaller uncertainties compared to single IDMS (Vogl & Pritzkow 2010b).

3.6. Characterization of the Mother Solutions

For the preparation of the CRM three boron mother solutions with different isotopic composition have been used: a boric acid solution with natural isotopic composition, a boric acid solution enriched in ^{10}B and a boron solution enriched in ^{11}B. The boric acid solution enriched in ^{10}B is identical with the ^{10}B spike, which has been characterized by reverse IDMS. The boric acid solution with natural isotopic composition and the one enriched in ^{11}B are not identical with the back-spike solutions described above. They have been prepared separately because larger volumes are required for the preparation of the CRM. The boric acid solution with natural isotopic composition has been prepared from the suprapure grade boric acid from Merck KgaA and the boric acid solution enriched in ^{11}B has been prepared from a second fraction of the enriched boron metal.

The ^{10}B solution has already been characterized by reverse IDMS, the natural and the second ^{11}B solution have been characterized by IDMS using the ^{10}B solution. Five blends have been prepared for each solution and have been measured using the above described Na_2BO_2 technique by correcting for mass fractionation using the IRMM-011 reference material. The resulting boron mass fractions and the isotopic compositions of the mother solutions are displayed in Table 3. These data have been used subsequently to calculate the gravimetric values for the isotope abundance ratios of the mixtures (see next paragraph).

Table 3: Boron mass fractions and isotopic composition of the mother solutions used for the preparation of the CRM with their combined standard uncertainties given in brackets and applying to the last one or two digits

Quantity		Boron mother solution		
		enriched in ^{10}B	natural	enriched in ^{11}B
Abbreviation		^{10}B-sol.	B nat.	^{11}B sol.
Mass fraction in mg·kg^{-1}	B	[a]	3619.4 (3.1)	1012.5 (1.0)
	^{10}B	987.3 (7) [b]	[a]	[a]
Isotope abundance ratio	$^{10}B/^{11}B$	48.019 (34)	0.24949 (16)	0.009239 (7)
	$^{11}B/^{10}B$	0.020825 (15)	4.0082 (26)	108.24 (9)
Isotope abundance	^{10}B	0.979600 (14)	0.19967 (11)	0.009154 (7)
	^{11}B	0.020400 (14)	0.80033 (11)	0.990846 (7)
Molar mass in g·mol^{-1}	M(B)	10.033263 (14)	10.81036 (11)	11.000184 (7)

[a] not used, but can be calculated from the data presented here
[b] corrected for evaporation through container wall and screw cap since characterization by reverse IDMS

3.7. Preparation of the Isotope Reference Materials

ERM-AE102a and AE104a shall replace the nearly exhausted reference materials ERM-AE102 and -AE104. Thus the target value for the isotopic composition is a ^{10}B isotope abundance of 30 % and 31.5 % respectively. This can be achieved by mixing suitable amounts of ^{10}B mother solution (^{10}B sol.) to the mother solution with natural boron isotopic composition (B nat.).

In the case of ERM-AE120, -AE121 and -AE122 the target values have been selected such that together with NIST SRM 951 most of the natural boron isotope variation is covered in equidistant intervals. The target $\delta^{11}B$-values have been selected as -20 ‰, +20 ‰ and +40 ‰. ERM-AE120 has been mixed from ^{10}B sol. and B nat.; ERM-AE121 and -AE122 have been mixed from B nat. and the second ^{11}B mother solution (^{11}B sol.). The exact masses with their corresponding uncertainties are displayed in Table 4. The mixing process has been carried out under full gravimetric control as described above in the section “gravimetric determination”. Subsequently ultrapure water has been added to reach a boron mass fraction of approximately 1000 mg/kg. ERM-AE120, -AE121 and -AE122 have been diluted further to give a final boron mass fraction of approximately 100 mg/kg. The exact masses and mass fractions are also displayed in Table 4. These stock solutions have been filled in

pre-cleaned PFA-bottles. The bottles have been closed tightly, labelled, sealed in plastic 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 overfilled by 2 mL to 3 mL. This volume has been removed later by pouring to enable the measurements for homogeneity and characterization study.

Table 4: Masses of the mother solutions used for the preparation of the isotope RM together with the isotope abundance ratios and the boron mass fractions calculated from gravimetric data and data from Table 3; combined standard uncertainties are given in brackets

Material	Mass of solution in g				Dilution
	^{10}B-sol.	B nat.	^{11}B sol.	Ultrapure water	Factor
ERM-AE102a	121.099 (10)	246.596 (10)	n.a.	647.688 (10)	
ERM-AE104a	138.712 (10)	240.316 (10)	n.a.	630.971 (10)	
ERM-AE120	2.172 (10)	278.405 (10)	n.a.	729.404 (10)	0.099999 (10)
ERM-AE121	n.a.	272.250 (10)	24.132 (10)	713.616 (10)	0.100007 (10)
ERM-AE122	n.a.	267.754 (10)	40.284 (10)	701.968 (10)	0.100000 (10)

Quantities calculated from gravimetric data			
	B mass fraction	Isotope abundance ratio	
	in mg·kg^{-1}	^{11}B/^{10}B	^{10}B/^{11}B
ERM-AE102a	999.5 (8)	2.3332 (15)	0.42860 (27)
ERM-AE104a	999.9 (8)	2.1745 (14)	0.45988 (30)
ERM-AE120	99.99 (9)	3.9628 (26)	0.25234 (17)
ERM-AE121	99.99 (9)	4.1245 (27)	0.24245 (16)
ERM-AE122	99.99 (9)	4.2055(28)	0.23778 (16)

3.8. Homogeneity Test

Dilute solutions of an element in principle are homogenous. However, when mixing different solutions of the same element, but with different isotopic compositions, it is necessary that only one species occurs or the occurring species are equilibrated. Then an equilibrium regarding the isotope distribution can be assumed and the solution is homogenous regarding the isotopic composition of the analyte element.

In all solutions used for the preparation of the boron isotope RM boron is present as boric acid in balance with $B(OH)_4^-$. Therefore all prepared solutions can be assumed homogenous. This has been demonstrated already for the ERM-AE101, -AE102, -AE103 and -AE104 (Vogl et al. 2002). Nevertheless, the homogeneity of the here described isotope RM has been checked. Three samples out of each material have been selected during the filling sequence: one sample at the beginning, one

in the middle and one at the end. Each sample has been measured at least 5 times. For homogeneity issues it is sufficient to look at the ion current ratios 89/88, because the following corrections are identical for all samples. In Fig. 1 the ion current ratios for the homogeneity check are displayed. The error bars represent the upper limit for the repeatability of 0.05 %, which has been established on a long term basis for the ion current ratios 89/88. These data clearly demonstrate that there is no visible drift in the filling sequence and no heterogeneity within or between bottles can be observed.

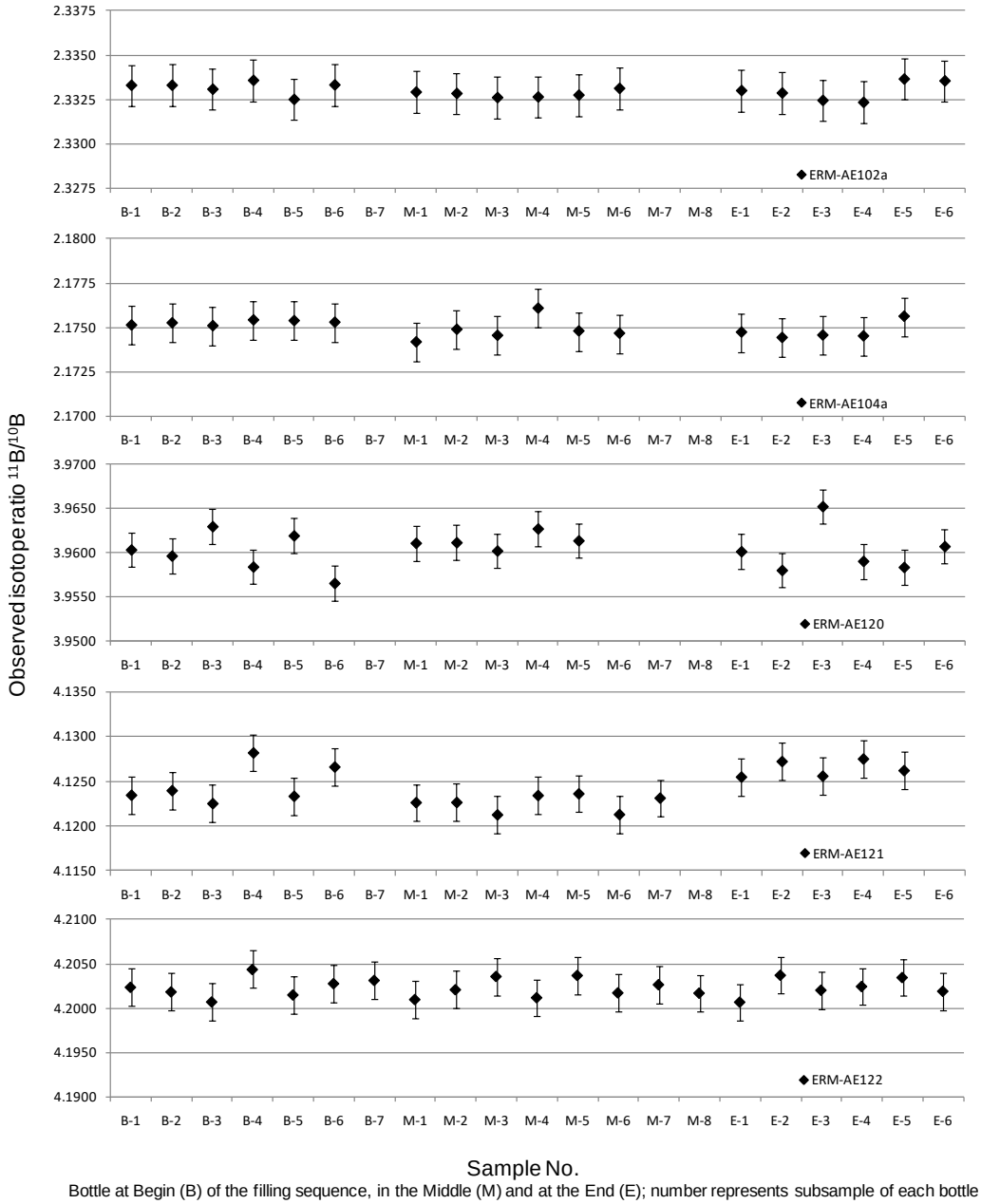

Figure 1: Ion current ratios 89/88 for the homogeneity check of the materials ERM-AE102a, -AE104a, -AE120, -AE121 and -AE122, with error bars representing the upper limit of the repeatability of 0.05%

For each data set a one way ANOVA has been carried out yielding the values displayed in the Table 5. Except for ERM-AE121 all obtained values are much smaller than the tabulated F-values indicating no difference between the groups, thus supporting homogeneity of the material. Only for

ERM-AE121 the obtained value is higher. All materials have been produced in the same way from the same mother solutions. Therefore, only degradation in the reproducibility of the measurement can be the reason. The data shown in Fig. 1 have been obtained with the $Na_2BO_2^+$ technique. Additional measurements which have been carried out using the $Cs_2BO_2^+$ technique do not reveal any indication for inhomogeneity.

Putting together the theoretic assumptions from above, the experience from former isotope RM production and the observed data from Fig. 1, it can be concluded that the materials are sufficiently homogenous and no extra uncertainty has to be added, especially as the reproducibility of the applied analytical procedure is already included in the characterization data.

Table 5: Calculated and tabulated F-values for the all data sets obtained within the homogeneity test

Material	F-value tested	F-value tabulated	Significance level	Degree of Freedom	
				1	2
ERM-AE102a	1.302	3.682	5 %	2	15
ERM-AE104a	1.729	3.739	5 %	2	14
ERM-AE120	0.564	3.739	5 %	2	14
ERM-AE121	9.832	3.682	5 %	2	15
ERM-AE122	0.065	3.555	5 %	2	18

3.9. Stability Test

Previous work and our own experience (Vogl et al. 2002) in the field of boron analysis show, that aqueous solutions of boric acid in the $mg \cdot kg^{-1}$ range are stable over years for their isotopic composition as well as for their mass fraction. To guarantee stability of the boron mass fraction contamination, adsorption to container walls and evaporation of water have to be avoided. For the reference materials discussed here this has been achieved by using pre-cleaned PFA bottles and storage under dark and cool, (5 ± 3) °C, conditions. The preceding material ERM-AE104 was monitored for the weight change due to evaporation. This revealed a mass loss of only 0.02 % over 6 years, which caused an increase in the boron mass fraction of 0.02 %, being much smaller than the uncertainty of 2 % for the boron mass fraction in ERM-AE104. To gain more information on this topic an extensive testing has been carried out to estimate evaporation of water through container walls and the screw cap.

Ten PFA-bottles have been weighed empty and have been filled subsequently with 20 mL water. Then these bottles have been weighed again and have been placed in plastic zipbags. Five bottles have been stored at room temperature (24 ± 3) °C and five have been store in a refrigerator at (5 ± 3) °C. After 1, 2, 4, 8 and 12 weeks the bottles have been weighed. The bottles in the refrigerator have been weighed additionally after 24 weeks. The weighing results showing the loss in weight due to evaporation are displayed in Fig. 2, where the loss is already expressed relative to filling mass. These data have been averaged for each dataset and two trendlines have been calculated, which are displayed together with their linear equation obtained from a linear fit. It is obvious that the slope of the

trendline representing increasing evaporation with time is five times higher for the bottles stored at room temperature than that for the bottles in the refrigerator. Therefore all reference materials have been sealed in plastic bags and have been stored at (5 ± 3) °C. This data can also be used to extrapolate the mass loss for the future, when storage conditions stay unchanged. For ten years (520 weeks) the evaporation will be less than 0.47 %, indicating a maximum increase of the boron mass fraction of less than 0.47%. This can be converted into an uncertainty contribution of 0.5 % for the mass fraction, when aiming at a shelf life of ten years. Considering higher temperatures during shipment another 0.5 % will be added. Thus the relative expanded uncertainty for the boron mass fraction is 2 % (Table 9).

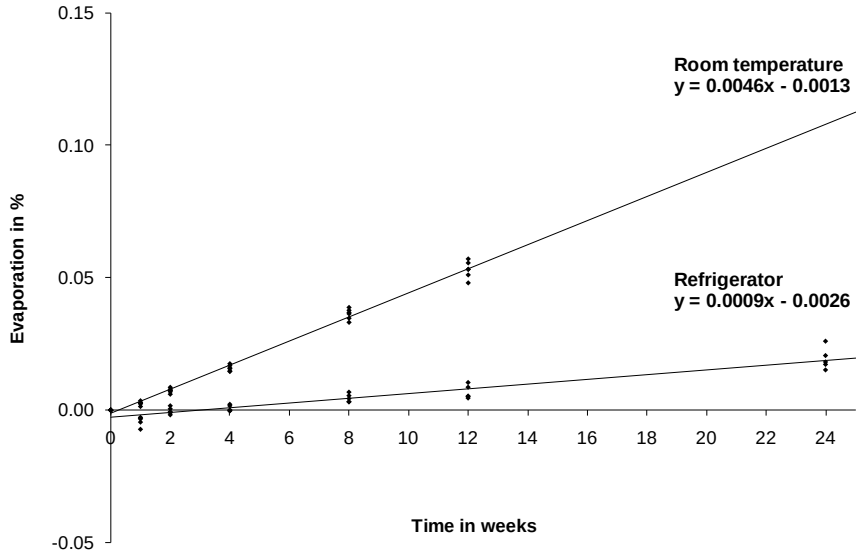

Figure 2: Evaporation of water (solvent) out of the PFA bottles used for the ERM materials under room temperature (24 ± 3) °C and under refrigerated temperature (5 ± 3) °C; evaporation is expressed as lost mass fraction referring to a filling of 20 mL

The stability of the isotopic composition is solely compromised by contamination with boron having a different isotopic composition. Pre-cleaned PFA bottles and the high boron mass fraction in the solution (1000 $mg \cdot kg^{-1}$ and 100 $mg \cdot kg^{-1}$) reduces the risk of contamination to a minimum. In the preceding series of boron isotope RM, ERM-AE101 to -AE104, a stability monitoring took place over nine years. The data for ERM-AE101 to -AE103, which are displayed in Fig. 3, demonstrate the stability of these materials over nearly 10 years. Boron isotope RM produced under the same conditions as ERM-AE101 to -AE104 are expected to be stable at least for ten years. Again the repeatability of the analytical technique is already included in the characterization and thus no extra contribution for the stability test has to be added to the uncertainty budget for the isotopic composition.

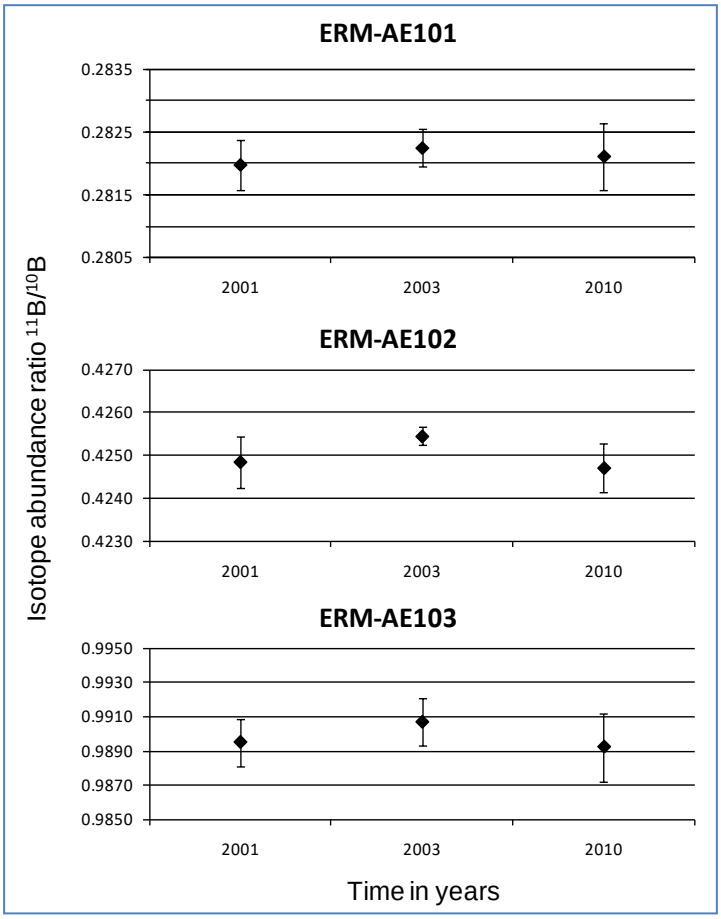

Figure 3: Stability monitoring of the boron isotope reference materials ERM-AE101, -AE102 and -AE103 over nearly 10 years; error bars for 2001 represent the expanded uncertainties (k=2) of the certificate, those from 2003 and 2010 represent the twofold standard deviation of repeated measurements

3.10. Characterization

The isotopic compositions of all materials have been calculated on basis of the gravimetric data as well as on the basis of the TIMS boron isotope measurement results obtained with the $Na_2BO_2^+$ technique (Table 6). Instrumental mass fractionation during TIMS measurements was corrected with a correction factor obtained from concurrently measured IRMM-011. Boron isotope data calculated from the gravimetric results and those obtained from TIMS measurements are displayed in Table 6. Gravimetric results and TIMS results agree perfectly with one another for each single reference material. The difference between both values is smaller than the combined standard uncertainty for all presented reference materials. This clearly states that the production of boron isotope reference materials under gravimetric control yields results which are comparable to results obtained by TIMS measurements. This, however, can only be achieved, when the production is carried out under full gravimetric control and the corresponding uncertainty budgets have been set up properly.

Table 6: Isotopic composition of ERM-AE102a, -AE104a, -AE120, -AE121 and -AE122 calculated from TIMS measurement results and from gravimetric data (Table 4); all quantity data are given with combined standard uncertainties in brackets and applying to the last two digits

ERM	Proc. [a]	Isotope abundance ratio		Isotope abundance		Molar mass
Nr.		$^{10}B/^{11}B$	$^{11}B/^{10}B$	^{10}B	^{11}B	in g·mol^{-1}
AE102a	TIMS	0.42848 (28)	2.3338 (15)	0.29995 (14)	0.70005 (14)	10.71044 (14)
	Gravim.	0.42860 (27)	2.3332 (15)	0.30001 (13)	0.69999 (13)	10.71038 (13)
AE104a	TIMS	0.45960 (30)	2.1758 (14)	0.31488 (14)	0.68512 (14)	10.69557 (14)
	Gravim.	0.45988 (30)	2.1745 (14)	0.31501 (14)	0.68499 (14)	10.69544 (14)
AE120	TIMS	0.25236 (17)	3.9627 (26)	0.20150 (11)	0.79850 (11)	10.80853 (11)
	Gravim.	0.25235 (17)	3.9628 (26)	0.20150 (11)	0.79850 (11)	10.80854 (11)
AE121	TIMS	0.24233 (16)	4.1266 (27)	0.19506 (10)	0.80494 (10)	10.81495 (10)
	Gravim.	0.24245 (16)	4.1245 (27)	0.19514 (10)	0.80486 (11)	10.81487 (10)
AE122	TIMS	0.23782 (16)	4.2048 (27)	0.19213 (10)	0.80787 (10)	10.81787 (10)
	Gravim.	0.23778 (16)	4.2055 (28)	0.19210 (10)	0.80790 (10)	10.81790 (10)

[a] analytical procedure: TIMS represents PTIMS with $Na_2BO_2^+$ technique and mass fractionation correction with IRMM-011; Gravim. means calculation on basis of gravimetric data;

$\delta^{11}B$-values for the reference materials ERM-AE120, -AE121 and -AE122 have been obtained from gravimetric values as well as from TIMS measurements ($Na_2BO_2^+$ technique). Additionally $\delta^{11}B$-values versus NIST SRM 951 have been produced with TIMs using the $Cs_2BO_2^+$-graphite technique to demonstrate the commutability for other analytical procedures as well as to assure the quality of the results by a second independent analytical procedure. All $\delta^{11}B$-data for the reference materials ERM-AE120, -AE121 and -AE122 are displayed in Table 7. The different $\delta^{11}B$-values agree well with each other with in the expanded uncertainties for each isotope RM, although the spread for ERM-AE120 is slightly larger than for ERM-AE121 and -AE122.

Table 7: $\delta^{11}B$-values vs. NIST SRM 951 for ERM-AE120, -AE121 and -AE122 with combined standard uncertainties calculated from TIMS measurement results and from gravimetric data (Table 4); all quantity data are given with combined standard uncertainties in brackets applying to the last one or two digits

Procedure	Reference	$\delta^{11}B$ in ‰		
		ERM-AE120	ERM-AE121	ERM-AE122
Gravimetric	NIST SRM 951	-20.0 (8)	20.0 (8)	40.0 (8)
TIMS, $Na_2BO_2^+$	NIST SRM 951	-20.57 (28)	19.97 (29)	39.26 (27)
TIMS, $Cs_2BO_2^+$	NIST SRM 951	-19.90 (25)	19.66 (29)	39.86 (30)
Mean	NIST SRM 951	-20.16 (28)	19.88 (30)	39.71 (30)

3.11. Observations on IRMM-011 and NIST SRM 951

During this certification campaign we obtained an interesting by-product, when comparing the measurements ($^{11}B/^{10}B$) on IRMM-011 (n = 14) and NIST SRM 951 (n = 22). When calculating the correction factors for mass fractionation, the so-called K-factors, we observed a difference in the *K*-factors of 0.536 ‰. When looking at the certificates of IRMM-011 and NIST SRM 951, a difference of 0.162 ‰ appears between the certified values, with IRMM-011 representing the higher value and NIST SRM 951 representing the lower value.

The observed and oxygen corrected but not mass fractionation corrected $^{11}B/^{10}B$ isotope ratios of both series, IRMM-011 and NIST SRM 951, reveal a difference of 0.375 ‰ for the mean values. IRMM-011 gives the lower value and NIST SRM 951 the higher one. This observed difference is only related to the real difference between both materials, because the same measurement procedure and the same cup configuration have been used. Both series have been measured over several turrets.

This is consistent, because for the calculation of K-factors the observed isotope ratio and the certified isotope ratio are used. When both, the observed isotope ratio and the certified isotope ratio, differ in opposite direction for IRMM-011 and NIST SRM 951, the difference of the *K*-factors is the sum of the difference of the observed isotope ratios and the difference of the certified isotope ratio. The difference of the observed isotope ratios is 0.375 ‰, the difference of the certified isotope ratios is 0.162 ‰ and the sum is 0.537 ‰. This corresponds perfectly to the difference in the *K*-factors of 0.536 ‰.

As we performed fewer measurements for NIST SRM 951 during the past years, we wanted to assure and cross-check the results we obtained on NIST SRM 951. Therefore we tested two different units of NIST SRM 951 for potential differences. The measurements (n = 5 each) revealed a difference of less than 0.08 ‰, which is insignificant. No heterogeneity has been observed. Thus the observed difference of -0.375 ‰ between IRMM-011 and NIST SRM 951 is consistent. It has to be noted, that this difference is very small and is fully covered by the stated uncertainties within the certificates. Nevertheless it explains the difference in the values and might be of interest to some readers.

4. Certification

For the certification of a reference material all data altering or affecting the quantity value to be certified or its combined uncertainty have to collected and used for establishing the certified quantity value. In most cases this means, that the results from the homogeneity, the stability and the characterization study are combined to establish the certified value. In the case of the here described boron isotope RM there is neither a bias introduced by homogeneity or stability issues nor an additional uncertainty contribution has to be added. Therefore the certified quantity values (Table 8) derive only from the characterization study. In the case of ERM-AE102a and 104a the $Na_2BO_2^+$ TIMS results are used to certify the isotope abundance ratios of these materials. The certified boron isotopic compositions as well as the atomic weights are being calculated therefrom.

ERM-AE120, -AE121 and -AE122 are certified for their respective $\delta^{11}B$-values (vs. NIST SRM 951) only. These certified $\delta^{11}B$-values are the arithmetic mean of the gravimetric value, the $Na_2BO_2^+$ TIMS value and the $Cs_2BO_2^+$ TIMS value with its corresponding uncertainties.

The boron mass fractions in all materials, as well as the boron isotopic composition of ERM-AE120, -AE121 and -AE122 are information values only (Table 9). The relative expanded uncertainties of the boron mass fractions have been set to 2 % based on the results of the stability study.

Table 8: Certified quantity values of ERM-AE102a, -AE104a, -AE120, -AE121 and -AE122 with their expanded uncertainties (k=2)

ERM	$\delta^{11}B$ [a]	Isotope abundance ratio		Isotope abundance		Molar mass
Nr.	in ‰	$^{10}B/^{11}B$	$^{11}B/^{10}B$	^{10}B	^{11}B	in g·mol^{-1}
AE102a	n/a	0.4285 (6)	2.3338 (30)	0.29995 (27)	0.70005 (27)	10.71044 (27)
AE104a	n/a	0.4596 (6)	2.1758 (28)	0.31488 (28)	0.68512 (28)	10.69557 (28)
AE120	-20.2 (6)	n/a	n/a	n/a	n/a	n/a
AE121	19.9 (6)	n/a	n/a	n/a	n/a	n/a
AE122	39.7 (6)	n/a	n/a	n/a	n/a	n/a

[a] vs. NIST SRM 951

The here presented boron isotope reference materials ERM-AE102a and -AE104a are primarily intended to be used as standard for correcting mass discrimination (mass bias) in single collector ICP-MS and as quality control sample. ERM-AE120, -AE121 and -AE122 are primarily intended to be used for quality control in all $\delta^{11}B$ determinations and for validation of chemical and mass spectrometric procedures for the determination of $\delta^{11}B$ values. These reference materials should be stored under dark and cool, (5 ± 3) °C, conditions.

Table 9: Informative quantity values of ERM-AE102a, -AE104a, -AE120, -AE121 and -AE122 with their expanded uncertainties (k=2)

ERM	B mass fraction	Isotope abundance ratio		Isotope abundance		Molar mass
Nr.	in mg·kg^{-1}	$^{10}B/^{11}B$	$^{11}B/^{10}B$	^{10}B	^{11}B	in g·mol^{-1}
AE102a	999 (20)	n/a	n/a	n/a	n/a	n/a
AE104a	1000 (20)	n/a	n/a	n/a	n/a	n/a
AE120	100.0 (2.0)	0.25236 (33)	3.963 (6)	0.20150 (21)	0.79850 (21)	10.80853 (21)
AE121	100.0 (2.0)	0.24233 (32)	4.127 (6)	0.19506 (21)	0.80494 (21)	10.81495 (21)
AE122	100.0 (2.0)	0.23782 (31)	4.205 (6)	0.19213 (20)	0.80787 (20)	10.81787 (20)

5. Appendix: Exemplary uncertainty budgets

Table 10: Uncertainty budget for the boron mass fraction in the back-spike (^{11}B solution)

Quantity	Value	Standard uncertainty	Unit	Type A/B	Description	Index
p_{air}	1023.000	0.577	mbar	B	air pressure	0.0 %
T_{air}	298.150	0.289	K	B	temperature of the air	0.0 %
H_{rel}	87.000	0.577	%	B	relative humidity	0.0 %
$p_{svp\text{-}water}$	26.4400	0.0500	mbar	B	saturation vapour pressure of water at T_{air}	0.0 %
ρ_{air}	1.18557	0.00133	kg/m^3	B	density of the air	*
ρ_{bw1}	8000.0	10.0	kg/m^3	B	density of the balance weights of the microbalance	0.0 %
ρ_{bw2}	7950.0	10.0	kg/m^3	B	density of the balance weights of the analytical balance	0.0 %
ρ_z	2350.00	5.00	kg/m^3	B	density of the boron metal	0.0 %
ρ_{Lsg}	1045.00	2.89	kg/m^3	B	density of the solution	0.1 %
k_{mz}	1.00035648	0.00000116		B	buoyancy correction factor for microbalance	*
k_{sol}	1.00098651	0.00000334		B	buoyancy correction factor for analytical balance	*
P_z	0.9999950	0.0000900		B	purity of boron metal	89.1 %
$m_{total\text{-}obs}$	326.94300	0.00275	g	B	observed mass of bottle with solution	2.1 %
$m_{bottle\text{-}obs}$	126.91720	0.00275	g	B	observed mass of bottle	2.1 %
$m_{z\text{-}obs}$	203616.00	5.00	µg	B	observed mass of boron metal	6.6 %
m_z	203687.6	19.0	µg	B	mass of boron metal	*
$m_{z\text{-}sol\text{-}obs}$	200.02580	0.00389	g	B	observed mass of the solution	*
$m_{z\text{-}sol}$	200.22313	0.00395	g	B	mass of solution	*
w_z	1017.3029	0.0970	µg/g	B	Mass fraction boron in the back-spike solution	
w_z	1017.30	0.19	µg/g	B	Mass fraction boron in the back-spike solution, expanded unc. (k=2)	

* Intermediate result

Equation system:

$\rho_{air} = (0.3485 * p_{air} / T_{air}) - 0.00132 * p_{svp\text{-}water} * (H_{rel}/T_{air});$
$k_{mz} = (1 - (\rho_{air} / \rho_{bw1})) / (1 - (\rho_{air} / \rho_z));$
$k_{sol} = (1 - (\rho_{air} / \rho_{bw2})) / (1 - (\rho_{air} / \rho_{Lsg}));$
$m_z = m_{z\text{-}obs} * k_{mz} * P_z;$
$m_{z\text{-}sol\text{-}obs} = (m_{total\text{-}obs} - m_{bottle\text{-}obs});$
$m_{z\text{-}sol} = m_{s\text{-}sol\text{-}obs} * k_{sol};$
$w_z = m_z / m_{sol};$

Table 11: Uncertainty budget for the isotope abundance ratio $^{10}B/^{11}B$ of ERM-AE102a as determined by TIMS

Quantity	Value	Standard uncertainty	Unit	Type A/B	Description	Index
$R_{co\text{-}10/11}$	0.24744696	0.00000890	-	A	Observed isotope abundance ratio in IRMM-011, oxygen corrected	0.3 %
$R_{102ao\text{-}10/11}$	0.4288030	0.0000275	-	A	Observed isotope abundance ratio in ERM-AE102a, oxygen corrected	1.0 %
$R_{c\text{-}10/11}$	0.247260	0.000160	-	B	Certified isotope abundance ratio $^{10}B/^{11}B$ in IRMM-011	98.7 %
$R_{c\text{-}11/10}$	4.04433	0.00262	-	B	Calculated isotope abundance ratio $^{11}B/^{10}B$ in IRMM-011	*
K_{11}	1.000756	0.000649	-	B	Factor for correcting mass fractionation	*
$R_{102a\text{-}11/10}$	2.33384	0.00152	-	B	Isotope abundance ratio $^{11}B/^{10}B$ in ERM-AE102a	
$R_{102a\text{-}11/10}$	2.3338	0.0030	-	B	Isotope abundance ratio $^{11}B/^{10}B$ in ERM-AE102a, with expanded uncertainty (k=2)	

* Intermediate result

Equation system:

$R_{c\text{-}11/10} = 1 / R_{c\text{-}10/11}$;

$K_{11/10} = R_{c\text{-}11/10} / (1 / R_{co\text{-}10/11})$;

$R_{102a\text{-}11/10} = K_{11/10} \cdot (1 / R_{102ao\text{-}10/11})$;

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7. Amendment: 2nd batch of ERM-AE120, -AE121 & and -AE122

A second batch of ERM-AE120, -AE121 & and -AE122 has been bottled after diluting the stock solutions under full gravimetric control. Dilution, weighing and bottling has been carried out as described in detail above. The exact weighing values and the resulting mass fractions are displayed in Table 12. The boron mass fractions of the final solutions of ERM-AE120, -AE121 and -AE122 resulting from the dilution of the corresponding stock solutions in all cases exactly provides the indicative values of 100 mg·kg^{-1} as printed on the certificates (within uncertainties).

Table 12: Weighing data and resulting mass fractions for the 2nd batch of ERM-AE120, -AE121 and -AE122 with their combined uncertainties given in brackets (k = 1)

Quantity	Unit	ERM-AE120	ERM-AE121	ERM-AE122
w(B) in stock solution	mg·kg^{-1}	999.90 (85)	999.80 (85)	999.90 (85)
f_{el} [a]	g	1.0012900 (50)	1.0007804 (50)	1.0004979 (50)
m stock solution	g	101.916 (14)	106.669 (14)	103.595 (14)
m diluted solution	g	1020.448 (14)	1067.403 (14)	1036.399 (14)
w(B) in diluted solution	mg·kg^{-1}	99.993 (86)	99.991 (86)	99.996 (86)
w(B), indicative value [b]	mg·kg^{-1}	100.0 (1.0)	100.0 (1.0)	100.0 (1.0)

[a] Factor for correcting evaporation loss in stock solution
[b] as shown on the certificate

The last bottled unit of each of the materials was withdrawn for verification measurements. The δ^{11}B values of the three ERM materials were determined according to the method described in Geilert *et al.* 2015.[1] The obtained results are listed in Table 13 and show a good agreement with the certified values within their expanded measurement uncertainties. The solutions diluted from the stock solutions thus agree with the certificate and there is no indication for any alteration. Thus, the 2nd batch is ready for dispatch.

Table 13: Determined δ^{11}B values in the 2nd batch of ERM-AE120, -AE121 and -AE122 and the certified δ^{11}B values, both with their associated expanded measurement uncertainty (k = 2)

Quantity	Unit	ERM-AE120	ERM-AE121	ERM-AE122
δ^{11}B, determined [a]	‰	-20.4 ± 0.5	+19.6 ± 0.5	+39.4 ± 0.5
δ^{11}B, certificate [b]	‰	-20.2 ± 0.6	+19.9 ± 0.6	+39.7 ± 0.6

[a] arithmetic mean of five measurements
[b] as shown on the certificate under

[1] Geilert S, Vogl J, Rosner M, Voerkelius S and Eichert T, Boron isotope fractionation in bell pepper, Mass Spectrom. Purif. Tech. 1 (2015) 1, doi:10.4172/ mso.1000101

8. Amendment: extension of the stability of ERM-AE102a and ERM-AE104a to 20 years

For the remaining units of ERM-AE102a (30 units) and ERM-AE104a (1 unit) the sale was stopped in October 2020, because the stated shelf-life was reached. Further sale is possible after the certified values and thus further stability of the materials is reconfirmed. The required measurements were carried out in August and September 2021.

Applied analytical procedure

The certified values and the indicative values were analysed in four different measurement sequences using the MC-ICP-MS Neptune. Measurements were performed on one unit each of ERM-AE102a and ERM-AE104a. The materials were diluted under full gravimetric control to a final mass fraction of 200 µg/kg. These diluted samples were used for isotope ratio analysis and quantification of the boron mass fraction. For isotope ratio analysis the isotopic reference material IRMM-011 was applied to correct for instrumental isotope fractionation. Measurements were performed according to SOP BAM-1.1-ISO-100. In total 8 analysis of ERM-AE102a and 9 analysis of ERM-AE104a were performed. The analytical procedure for obtaining the boron mass fractions was calibrated using the recently bottled certified reference material ERM-AE120 (full gravimetric control) and applying a four-point calibration. The 200 µg/kg-standard was regularly repeated after two sample measurements to enable a drift correction. The drift standards were evaluated for their boron mass fraction as well to check for a correct drift correction. These standards agreed well with the certified values as demonstrated by E_n values of < 0.32.

Results for the certified quantity values

In Table 14 the analytical results obtained in the stability check 09/2021 are displayed and compared to the certified quantity values from 10/2010 each with the associated expanded measurement uncertainty (k = 2).

Table 14: Determined isotope amount ratios and derived quantities of ERM-AE102a and ERM-AE104a as obtained during the stability test and the corresponding certified quantity values of ERM-AE102a and ERM-AE104a with their associated expanded measurement uncertainties (k = 2)

ERM-AE102a			
Quantity	Unit	Certified value	Determined value
Isotope amount ratio $n(^{10}B)/n(^{11}B)$	mol/mol	0.4285 ± 0.0006	0.4286 ± 0.0006
Isotope amount ratio $n(^{11}B)/n(^{10}B)$	mol/mol	2.3338 ± 0.0030	2.3332 ± 0.0031
Isotope amount fraction $n(^{10}B)/n(B)$	mol/mol	0.29995 ± 0.00027	0.30001 ± 0.00028
Isotope amount fraction $n(^{11}B)/n(B)$	mol/mol	0.70005 ± 0.00027	0.69999 ± 0.00028
Molar Mass $M(B)$	g/mol	10.71044 ± 0.00028	10.71038 ± 0.00027

ERM-AE104a			
Quantity	Unit	Certified value	Determined value
Isotope amount ratio $n(^{10}B)/n(^{11}B)$	mol/mol	0.4596 ± 0.0006	0.4596 ± 0.0006
Isotope amount ratio $n(^{11}B)/n(^{10}B)$	mol/mol	2.1758 ± 0.0028	2.1756 ± 0.0028
Isotope amount fraction $n(^{10}B)/n(B)$	mol/mol	0.31488 ± 0.00028	0.31490 ± 0.00028
Isotope amount fraction $n(^{11}B)/n(B)$	mol/mol	0.68512 ± 0.00028	0.68510 ± 0.00028
Molar Mass $M(B)$	g/mol	10.69557 ± 0.00028	10.69555 ± 0.00028

Results for the indicative quantity values

In Table 15 the analytical results obtained in the stability check 09/2021 are displayed and compared to the indicative quantity values from 10/2010 each with the associated expanded measurement uncertainty ($k = 2$). For simplifying the assessment of the date E_n values, which depict the metrological compatibility for values ≤ 1, are added.

Table 15: Determined boron mass fractions of ERM-AE102a and ERM-AE104a as obtained during the stability test and the corresponding indicative quantity values of ERM-AE102a and ERM-AE104a with their associated expanded measurement uncertainties ($k = 2$)

Material	Quantity	Indicative value	Determined value	E_n values
ERM-AE102a	B mass fraction / mg/kg	999 ± 20	949 ± 71	0.697
ERM-AE104a	B mass fraction / mg/kg	1000 ± 20	964 ± 47	0.695

Conclusion

The isotope amount ratios and the derived quantities obtained in the stability test for ERM-AE102a and ERM-AE104a fully agree with the certified quantity values from 10/2010. Thus, the material is stable, and the shelf-life can be extended to 20 years.

The boron mass fractions obtained in the stability test for ERM-AE102a and ERM-AE104a agree with the indicative quantity values from 10/2010 within the associated expanded uncertainties, as demonstrated by E_n values significantly below 1. Both data are thus metrologically compatible and the materials are also considered stable concerning the boron mass fractions. To ensure the validity of the boron mass fractions for an extension of the shelf-life to 20 years the relative expanded uncertainty for the indicative quantity value of the boron mass fraction is increased to 10 %.