Certification Report

for the

Isotope Reference Materials

ERM-AE143, ERM-AE144 and ERM-AE145

A set of three primary isotope reference materials certified for their magnesium isotope amount ratios, with ERM-AE143 additionally serving as the new δ=0 standard for magnesium

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1. Summary

Magnesium (Mg) isotope amount ratios are commonly used in applications ranging from biology and nutrition to terrestrial and extra-terrestrial geochemistry. Despite their increasing use, only one certified isotope amount ratio reference material is currently available for Mg: NIST SRM 980. Because SRM 980 was suspected to be heterogenous, two Mg solutions (DSM-3 and CAM1) have been provided by the geochemical community to anchor the Mg delta scale. This means that, at present, there is no suitable certified isotope reference material available for calibrating Mg isotope ratio measurements.

To fill this gap, a set of three primary Mg isotope reference materials, have been produced. All three materials have been certified for their Mg isotopic composition by an *ab initio* calibration without making any *a priori* assumptions. These new certified reference materials offer the most direct SI traceability and the possibility of calibrating any Mg isotope amount ratio measurements. ERM-AE143 additionally is designed to anchor the Mg delta scale and to serve as new "δ = 0 material".

Details on the certification of these isotope reference materials are provided in this report.

Certified quantity	Unit	Certified value	Uncertainty *
ERM-AE143			
Isotope amount ratio $n(^{25}Mg)/n(^{24}Mg)$	mol/mol	0.126 590	0.000 020
Isotope amount ratio $n(^{26}Mg)/n(^{24}Mg)$	mol/mol	0.139 362	0.000 043
Isotope amount fraction $n(^{24}Mg)/n(Mg)$	mol/mol	0.789 920	0.000 046
Isotope amount fraction $n(^{25}Mg)/n(Mg)$	mol/mol	0.099 996	0.000 014
Isotope amount fraction $n(^{26}Mg)/n(Mg)$	mol/mol	0.110 085	0.000 028
Molar mass $M(Mg)$	g/mol	24.305 017	0.000 073
ERM-AE144			
Isotope amount ratio $n(^{25}Mg)/n(^{24}Mg)$	mol/mol	0.126 486	0.000 022
Isotope amount ratio $n(^{26}Mg)/n(^{24}Mg)$	mol/mol	0.139 138	0.000 039
Isotope amount fraction $n(^{24}Mg)/n(Mg)$	mol/mol	0.790 124	0.000 039
Isotope amount fraction $n(^{25}Mg)/n(Mg)$	mol/mol	0.099 939	0.000 013
Isotope amount fraction $n(^{26}Mg)/n(Mg)$	mol/mol	0.109 936	0.000 025
Molar mass $M(Mg)$	g/mol	24.304 664	0.000 063
ERM-AE145			
Isotope amount ratio $n(^{25}Mg)/n(^{24}Mg)$	mol/mol	0.126 514	0.000 016
Isotope amount ratio $n(^{26}Mg)/n(^{24}Mg)$	mol/mol	0.139 185	0.000 029
Isotope amount fraction $n(^{24}Mg)/n(Mg)$	mol/mol	0.790 078	0.000 028
Isotope amount fraction $n(^{25}Mg)/n(Mg)$	mol/mol	0.099 956	0.000 010
Isotope amount fraction $n(^{26}Mg)/n(Mg)$	mol/mol	0.109 967	0.000 021
Molar mass $M(Mg)$	g/mol	24.304 741	0.000 046

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

2. Introduction

Magnesium isotope amount ratios (hereafter referred to as Mg isotope ratios) are increasingly used in biology, cosmochemistry, geochemistry and nutrition within the past fifteen years (Galy *et al.* 2000, Bohn *et al.* 2004, Black *et al.* 2006, Ra and Kitagawa 2007, Shen *et al.* 2013). Until today, the only certified isotope reference material (iRM) available for the calibration of absolute magnesium isotope ratio measurements is NIST SRM 980 (Catanzaro *et al.* 1966), which is still sold by NIST in the form of metal chips. Some years later a solution of a NIST SRM 980 aliquot was made available as IRMM-009.

Unfortunately, NIST SRM 980 turned out to show significant heterogeneity (Galy *et al.* 2003). Although this isotope heterogeneity is largely covered by the expanded uncertainty, it is too large for today's magnesium isotope research. Such a large inhomogeneity renders NIST SRM 980 unsuitable for delta measurements and consequently other artefacts are thus currently applied by the community (Galy *et al.* 2003).

Consequently, a replacement of this material is urgently needed (Vogl *et al.* 2004, Vogl *et al.* 2013). Such a new magnesium isotope reference material can only be characterized via the so-called synthetic isotope mixture approach. The main requirements are: adequate homogeneity of the isotope amount ratio (≤ 0.01 %), which can easily be achieved by providing the isotope reference material (iRM) in the form of a solution, and a relative expanded uncertainty < 0.02 % for the Mg isotope ratios, which would be small enough to serve the needs of current experimental magnesium isotope ratio analyses (relative precision of 0.01 % to 0.02 %) (Galy *et al.* 2003, Chang *et al.* 2003).

To prepare isotope mixtures with expanded uncertainties of ≤ 0.02 % for the mass fractions, however, two primary solutions of different isotopically enriched materials are required each with expanded uncertainties of ≤ 0.014 % for the mass fractions. The best commercially available mono-elemental solutions have much larger relative expanded uncertainties of approx. 0.4 %. Therefore, in the first stage of the project primary isotope solutions have been specifically prepared for this purpose. For the first time, relative expanded uncertainties for the Mg mass fraction of ≤ 0.005 % have been achieved, and relative expanded uncertainties for the Mg masses in the binary isotope mixtures were ≤ 0.007 % (Brandt *et al.* 2016). These solutions were used to calibrate the mass spectrometers (all MC-ICPMS) at three different laboratories and thus characterize the candidate reference materials ERM-AE143, -AE144 and -AE145 (Vogl *et al.* 2016).

Details on the characterization of these new iRMs 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

All dilutions carried out at BAM to produce these candidate iRMs used ultrapure water from a Milli-Q Advantage A10 water purification system. Nitric acid and hydrochloric acids (originally of p.a. grade) were further purified by a two-stage sub-boiling distillation process (1st stage: quartz still, 2nd stage: Teflon still). The purification was checked by analysing the corresponding Mg blanks by sector field ICP-MS, which were found negligible for Milli-Q water (10 pg/g), nitric acid (19 pg/g), and hydrochloric acid (48 pg/g). Only quartz,

fluorinated ethylene propylene (FEP) or perfluoralkoxy polymer (PFA) lab-ware were used for all preparations. More details on this topic can be obtained from (Brandt *et al.* 2016).

3.2. Candidate Material Characterizations, Processing and Bottling

ERM-AE143 was produced from a compact magnesium material purchased from Alfa Aesar with a nominal purity of 0.998 kg/kg (Table 1). The material (15 rods) was purchased and characterized for the primary pure substances program at BAM. An aliquot of approximately 3 g was cut off using water jet cutting and was then further purified by a standard magnesium etching process: An etching solution was prepared by mixing 50 mL ethanol (absolute, p.A., Merck KGaA), 6 mL hydrochloric acid (0.32 g/g, "S.G.", Thermo Fisher), and 4 mL nitric acid (0.65 g/g, "anal. Reag. Grade", Thermo Fisher). The sample was etched in this solution for 30 s, then cleaned with ultra-pure water (six times), finally soaked in pure ethanol, and then dried. This material was weighed in for preparation of the candidate stock solution.

ERM-AE144 was produced from magnesium turnings purchased from Alfa Aesar with a nominal purity of better than 0.99 kg/kg (Table 1). The material comes in the form of turnings with visible surface traces of the cutting tool. The material has a perceivably dull surface, indicating oxidation. This material was used beforehand as the test material to develop the sublimation protocol for the isotopically enriched Mg materials. During this course, the purity of this material was well established based on analytical results (ICPMS and GDMS). This material was not etched, instead it was used as-is.

ERM-AE145 was produced from an inhouse purified magnesium material (Table 1). Approximately 184 mg of the base material used for ERM-AE144 was purified by a two-fold high-vacuum sublimation at BAM, yielding approx. 178 mg of purified material. The whole material was used for preparing the parent solution without etching.

Table 1 Description of the base materials used for the preparation of the Mg iRM Candidates.

Parameter	ERM-AE143	ERM-AE144	ERM-AE145
Source	Alfa Aesar	Alfa Aesar	BAM
Description	Mg rod, Lot G27R008	Mg turnings, Lot 10146809	sublimation of ERM-AE144
Appearance	compact	turnings	compact, sublimate disk
Pre-treatment	etching	none	none
Mass of Material	2.14347825 g	2.535933 g	0.1780076 g
Purity / (kg/kg)	> 0.998 [a]	≥ 0.999 [b]	> 0.999 [c]

[a] Nominal purity provided by producer / supplier.

[b] Based on glow discharge mass spectrometric (GDMS) measurements.

[c] Based on GDMS measurements of parallel sublimated samples.

The base materials of ERM-AE143 and ERM-AE144 were weighed (approx. 2 g setup size) and transformed into 2 L (2 kg) of 1000 mg/kg parent solutions. The ultra-purified material of ERM-AE145 has a lower mass, due to the limitations of the sublimation technique. As this material was used for preceding density measurements and to test the dissolution procedure, a relatively high-concentrated solution of candidate ERM-AE145 was initially prepared (≈ 2000 mg/kg) with an HNO_3 mass fraction of 0.015 g/g, and then later transformed into a number of solutions with lower Mg mass fractions (1000 mg/kg, 10 mg/kg and 2 mg/kg), but at 0.02 g/g HNO_3.

The initial solutions of the three materials were created as shown in Table 2; ERM-AE143 and -AE144 were each prepared as 2 kg of solution at a mass fraction of 1000 mg/kg of Mg (0.02 g/g HNO_3), and candidate ERM-AE145 was prepared as a solution of 2000 mg/kg in 0.015 g/g HNO_3.

Later, these stock solutions were diluted to the final solutions with nominal magnesium mass fractions of 50 mg/kg (see Table 2), which were then bottled in 20 mL precleaned PFA bottles. The bottles have been closed tightly, labelled (see Fig. 1), sealed in plastic bags and stored in a refrigerator at (5 ± 3) °C.

Table 2: Dissolution of the base materials for preparing the stock solutions of ERM-AE143, -AE144 and -AE145

	Cand. ERM-AE143	Cand. ERM-AE144	Cand. ERM-AE145
	Dissolution, HNO_3 addition		
Mass of Mg metal / g, N = 10	2.14347825	2.019622	0.1780076
Mass of 0.06 g/g HNO_3 / g	900.0460	848.1654	37.698405
Mass fraction of HNO_3 / (g/g)	0.060001	0.060001	0.059979
Mass of HNO_3 added / g	54.0039	50.8910	2.261113
Mass HNO_3 after digestion / g [a]	899.5104	847.8193	37.673497
Obs. total mass loss / g	0.5356	0.3461	0.0249
Expected mass loss due to H_2 / g	0.1778	0.1675	0.0148
Obs. additional mass loss / g [b]	0.3578	0.1786	0.0101
	fill-up with water		
Mass of water added / g	1243.6238	1170.8520	51.30
Total mass of solution / g	2145.2723	2020.7119	89.8900
Mg mass fraction / (mg/kg)	999.16	999.46	1980.25
Remaining HNO_3 / g	42.8896	40.4189	1.3381
HNO_3 mass fraction / (g/g)	0.019993	0.020002	0.015003
	Dilution of stock solution		
Mass of stock solution / g	108.336(14)	102.6386(46)	52.1069(50)
Mg mass fraction stock / (mg/kg) [c]	999.5(10)	999.8(10)	1991.3(20)
Mass of diluted solution / g	2166.301(18)	2052.769(18)	2075.455(16)
Mass fraction of HNO_3 / (g/g)	0.020(2)	0.020(2)	0.020(2)
Mg mass fraction / (mg/kg)	49.985(50)	49.990(50)	49.994(50)

[a] Mass of solution after digestion, minus the mass of magnesium.

[b] Mass difference between acid filled in, and mass of acid determined later, minus the calculated stoichiometric mass loss due to H_2 formation.

[c] Mg mass fraction corrected for loss by evaporation, at the time of the dilution.

Fig. 1: Photographs of the candidate reference materials ERM-AE143, -AE144 and -AE145

3.3. Homogeneity

ERM-AE143, -AE144 and -AE145 have been produced by dissolution of high-purity Mg 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-AE143, -AE144 and -AE145 are taken to be homogeneous for its intended use as an iRM. Contamination issues are also not relevant because 1) the laboratory blank levels at BAM for Mg are in the pico-gram range (Brandt *et al.* 2016) and 2) any added contaminant would have a natural Mg isotopic composition which would have a minimal effect when mixed with the natural Mg isotopic composition already in solution. Moreover, after mixing and equilibration, the resulting solution will itself be homogeneous with respect to its Mg isotopes, regardless of their source. The characterization study, which was carried out on six individual units, supports this because there was no hint of variations due to inhomogeneity. Additionally, a blunder check was carried out on three individual units per each material spread over the filling sequence and with each unit measured five times. These units were measured for their $\delta^{26/24}$Mg and their $\delta^{25/24}$Mg (eqn.1) relative to a single reference solution of ERM-AE143.

$$\delta^{x/24}\mathrm{Mg} = \delta^{x/24}\mathrm{Mg}_{\text{ERM-AE143}} = \left(\frac{R_{sample}^{measured}\left(\frac{^{x}\mathrm{Mg}}{^{24}\mathrm{Mg}}\right)}{R_{ERM-AE143}^{measured}\left(\frac{^{x}\mathrm{Mg}}{^{24}\mathrm{Mg}}\right)} \right) - 1 \quad \text{with x = 25, 26} \qquad \text{eqn. 1}$$

Table 3: $\delta^{25/24}Mg_{ERM\text{-}AE143}$ *and* $\delta^{26/24}Mg_{ERM\text{-}AE143}$ *for verifying the isotopic homogeneity of ERM-AE143, -AE144 and -AE145; carried out for five (5) independent aliquots taken from each of three (3) units of ERM-AE143, -AE144 and -AE145*

ERM-AE143					ERM-AE144					ERM-AE145				
Bottle No.	$\delta^{25/24}Mg_{ERM\text{-}AE143}$ / ‰		$\delta^{26/24}Mg_{ERM\text{-}AE143}$ / ‰		Bottle No.	$\delta^{25/24}Mg_{ERM\text{-}AE143}$ / ‰		$\delta^{26/24}Mg_{ERM\text{-}AE143}$ / ‰		Bottle No.	$\delta^{25/24}Mg_{ERM\text{-}AE143}$ / ‰		$\delta^{26/24}Mg_{ERM\text{-}AE143}$ / ‰	
	value	2SD	value	2SD		value	2SD	value	2SD		value	2SD	value	2SD
03	0.005	0.068	0.001	0.067	02	-0.823	0.062	-1.600	0.061	03	-0.608	0.057	-1.277	0.087
03	-0.047	0.056	-0.071	0.089	02	-0.767	0.070	-1.538	0.078	03	-0.636	0.086	-1.285	0.102
03	-0.010	0.080	-0.017	0.080	02	-0.847	0.062	-1.646	0.079	03	-0.638	0.064	-1.325	0.069
03	-0.026	0.081	0.011	0.081	02	-0.865	0.086	-1.694	0.082	03	-0.635	0.078	-1.309	0.134
03	-0.037	0.089	-0.054	0.108	02	-0.827	0.077	-1.636	0.086	03	-0.648	0.071	-1.334	0.089
Mean	-0.023		-0.026			-0.826		-1.623			-0.633		-1.306	
SD	0.021		0.035			0.037		0.058			0.015		0.025	
51	-0.001	0.070	-0.016	0.077	46	-0.820	0.075	-1.608	0.078	46	-0.651	0.074	-1.361	0.094
51	-0.012	0.079	-0.008	0.067	46	-0.765	0.071	-1.522	0.056	46	-0.623	0.064	-1.292	0.105
51	-0.012	0.077	-0.007	0.079	46	-0.824	0.081	-1.628	0.099	46	-0.601	0.073	-1.297	0.084
51	-0.001	0.073	0.006	0.076	46	-0.855	0.077	-1.680	0.069	46	-0.639	0.082	-1.330	0.120
51	-0.011	0.088	-0.004	0.095	46	-0.841	0.065	-1.659	0.090	46	-0.663	0.075	-1.352	0.079
Mean	-0.007		-0.006			-0.821		-1.619			-0.635		-1.326	
SD	0.006		0.008			0.034		0.061			0.025		0.032	
93	-0.036	0.075	-0.036	0.078	91	-0.823	0.064	-1.621	0.072	89	-0.620	0.061	-1.287	0.073
93	0.032	0.064	0.038	0.078	91	-0.844	0.064	-1.643	0.089	89	-0.660	0.079	-1.364	0.075
93	0.007	0.064	0.027	0.078	91	-0.815	0.072	-1.635	0.097	89	-0.650	0.063	-1.329	0.068
93	0.015	0.074	0.023	0.103	91	-0.822	0.064	-1.629	0.075	89	-0.624	0.085	-1.295	0.086
93	-0.041	0.088	-0.052	0.098	91	-0.820	0.070	-1.625	0.100	89	-0.638	0.060	-1.320	0.063
Mean	-0.004		0.0002			-0.825		-1.630			-0.638		-1.319	
SD	0.032		0.0411			0.011		0.009			0.017		0.031	
Mean (all)	-0.01		-0.01			-0.82		-1.62			-0.64		-1.32	
SD (all)	0.02		0.03			0.03		0.05			0.02		0.03	

The delta values reflect the corresponding isotope ratio, but directly show the differences against the applied standard in ‰. The fifteen delta measurements obtained for each candidate reference material yielded standard deviations of ≤ 0.05 ‰ which are smaller than the combined uncertainties of the characterization study by a factor between 1.3 and 3. These results (Table 3) display in no way any indications for heterogeneity. An uncertainty contribution for inhomogeneity has therefore not been added to the overall uncertainty for this iRM.

3.4. 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 acidified aqueous solutions containing one element with 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 oxidation and/or reducing agents are present. Therefore, ERM-AE143, -AE144 and –AE145 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 Mg to change slightly over 10 years, this loss of solvent cannot change the Mg isotope amount ratios. The possible changes in the Mg 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. The minimum shelf life of ERM-AE143, -AE144 and -AE145 is 10 years from the issue of the certificate.

3.5. Value Assignment

As already mentioned in the introduction, isotope amount ratios or absolute isotope ratios at the required uncertainty level can only be obtained via the so-called synthetic isotope mixture approach. The preparation of isotope mixtures with expanded uncertainties of ≤ 0.007 % is a project in itself and is described in detail in Brandt *et al.* 2016. These solutions were used to calibrate the mass spectrometers (all MC-ICPMS) at BAM, PTB and LGC and thus characterize the candidate reference materials ERM-AE143, -AE144 and -AE145 (Table 4 - 6). The calibration and characterization is described in detail in Vogl *et al.* 2016 and will not be repeated within this report. It has to be noted here that within this work for the first time absolute isotope ratios have been obtained at an uncertainty level which is comparable to those of current delta measurements.

Table 4: All values (3 sequences) for absolute isotopic composition of the three iRM candidates measured at LGC, with expanded uncertainties (k = 2).

Parameter	ERM-AE143	ERM-AE144	ERM-AE145
Isotope amount fractions			
		$x(^{24}Mg)$ / (mol/mol)	
Solutions -1b	0.789931(18)	0.790132(19)	0.790065(19)
Solutions -2b	0.789972(19)	0.790167(19)	0.790079(24)
Solutions -3b	0.789967(20)	0.790165(26)	0.790066(27)
Mean	0.789957(19)	0.790155(22)	0.790070(24)
$s(x(^{24}Mg))$/(mol/mol)	0.000022	0.000020	0.0000078
		$x(^{25}Mg)$ / (mol/mol)	
Solutions -1b	0.099989(11)	0.099933(13)	0.099955(12)
Solutions -2b	0.099982(13)	0.099927(11)	0.099957(15)
Solutions -3b	0.099982(12)	0.099926(17)	0.099959(17)
Mean	0.099984(12)	0.099929(14)	0.099957(15)
$s(x(^{25}Mg))$/(mol/mol)	0.0000039	0.0000038	0.0000021
		$x(^{26}Mg)$ / (mol/mol)	
Solutions -1b	0.110080(16)	0.109935(16)	0.109980(17)
Solutions -2b	0.110045(17)	0.109906(18)	0.109963(22)
Solutions -3b	0.110052(18)	0.109909(23)	0.109975(25)
Mean	0.110059(17)	0.109917(19)	0.109973(22)
$s(x(^{26}Mg))$/(mol/mol)	0.000018	0.000016	0.0000084
Isotope amount ratios			
		$n(^{25}Mg)/n(^{24}Mg)$ / (mol/mol)	
Solutions -1b	0.126579(16)	0.126477(18)	0.126514(16)
Solutions -2b	0.126564(18)	0.126464(15)	0.126515(21)
Solutions -3b	0.126565(17)	0.126462(24)	0.126520(24)
Mean	0.126569(17)	0.126468(19)	0.126518(21)
$s(n(^{25}Mg)/n(^{24}Mg))$	0.0000084	0.0000079	0.0000028
		$n(^{26}Mg)/n(^{24}Mg)$ / (mol/mol)	
Solutions -1b	0.139354(23)	0.139135(23)	0.139203(24)
Solutions -2b	0.139303(25)	0.139092(25)	0.139180(31)
Solutions -3b	0.139312(26)	0.139096(32)	0.139197(36)
Mean	0.139323(25)	0.139108(27)	0.139193(31)
$s(n(^{26}Mg)/n(^{24}Mg))$	0.000027	0.000024	0.000012
Atomic weights		A_r(Mg)	
Solutions -1b	24.305001(32)	24.304655(32)	24.304766(34)
Solutions -2b	24.304925(35)	24.304591(35)	24.304736(43)
Solutions -3b	24.304937(37)	24.304597(45)	24.304760(49)
Mean	24.304954(35)	24.304614(38)	24.304754(42)
$s(A_r(Mg))$	0.000041	0.000035	0.000016

Table 5: All values (9 sequences) for absolute isotopic composition of the three iRM candidates measured at PTB, with expanded uncertainties (k = 2).

Parameter		ERM-AE143	ERM-AE144	ERM-AE145
Isotope amount fractions				
			$x(^{24}Mg)$ / (mol/mol)	
	(Solutions -1b) 1	0.789958(18)	0.790166(18)	0.790109(19)
	2	0.7899021(91)	0.7901089(91)	0.7900653(91)
	3	0.7899100(92)	0.7901136(91)	0.7900719(93)
	(Solutions -2b) 4	0.789900(10)	0.790102(10)	0.790066(10)
	5	0.789912(13)	0.790115(13)	0.790077(13)
	6	0.789907(10)	0.7901128(93)	0.7900714(92)
	(Solutions -3b) 7	0.789912(11)	0.790116(10)	0.790073(11)
	8	0.789941(26)	0.790138(41)	0.790114(25)
	9	0.789967(11)	0.790160(10)	0.790124(11)
	Mean	0.789923(14)	0.790126(17)	0.790086(14)
	$s(x(^{24}Mg))$/(mol/mol)	0.000025	0.000023	0.000023
			$x(^{25}Mg)$ / (mol/mol)	
	(Solutions -1b) 1	0.099980(12)	0.099924(12)	0.099941(13)
	2	0.1000030(55)	0.0999462(55)	0.0999622(56)
	3	0.0999920(55)	0.0999358(55)	0.0999518(56)
	(Solutions -2b) 4	0.1000080(67)	0.0999520(69)	0.0999660(66)
	5	0.1000025(63)	0.0999454(62)	0.0999610(63)
	6	0.1000037(55)	0.0999477(55)	0.0999624(54)
	(Solutions -3b) 7	0.0999903(75)	0.0999353(74)	0.0999498(76)
	8	0.099988(12)	0.099933(19)	0.099943(11)
	9	0.0999752(63)	0.0999187(62)	0.0999367(65)
	Mean	0.0999936(79)	0.0999375(93)	0.0999527(79)
	$s(x(^{25}Mg))$/(mol/mol)	0.000011	0.000011	0.000011
			$x(^{26}Mg)$ / (mol/mol)	
	(Solutions -1b) 1	0.110062(16)	0.109911(16)	0.109949(17)
	2	0.1100948(66)	0.1099449(66)	0.1099725(65)
	3	0.1100980(66)	0.1099506(65)	0.1099762(67)
	(Solutions -2b) 4	0.1100917(72)	0.1099460(72)	0.1099681(71)
	5	0.110085(11)	0.109939(11)	0.109962(11)
	6	0.1100891(72)	0.1099395(69)	0.1099662(68)
	(Solutions -3b) 7	0.1100979(71)	0.1099490(68)	0.1099768(72)
	8	0.110072(20)	0.109929(37)	0.109943(19)
	9	0.1100575(86)	0.1099209(76)	0.1099389(77)
	Mean	0.110083(11)	0.109937(15)	0.109961(11)
	$s(x(^{26}Mg))$/(mol/mol)	0.000016	0.000014	0.000014
Isotope amount ratios				
			$n(^{25}Mg)/n(^{24}Mg)$ / (mol/mol)	
	(Solutions -1b) 1	0.126564(17)	0.126459(17)	0.126490(18)
	2	0.1266018(80)	0.1264967(80)	0.1265240(82)
	3	0.1265865(81)	0.1264829(81)	0.1265098(82)
	(Solutions -2b) 4	0.126608(10)	0.126505(10)	0.126529(10)
	5	0.1265995(91)	0.1264947(89)	0.1265207(92)
	6	0.1266019(81)	0.1264980(80)	0.1265233(79)
	(Solutions -3b) 7	0.126584(11)	0.126482(11)	0.126507(11)
	8	0.126576(18)	0.126476(28)	0.126492(17)
	9	0.1265561(92)	0.1264537(90)	0.126482(10)
	Mean	0.126586(12)	0.126483(14)	0.126509(12)
	$s(n(^{25}Mg)/n(^{24}Mg))$	0.000018	0.000018	0.000017

Isotope amount ratios			
		$n(^{26}Mg)/n(^{24}Mg)$ / (mol/mol)	
(Solutions -1b)	1 0.139326(23)	0.139098(23)	0.139157(24)
	2 0.139378(10)	0.139152(10)	0.139194(10)
	3 0.139380(10)	0.139158(10)	0.139198(10)
(Solutions -2b)	4 0.139374(11)	0.139154(10)	0.139189/10)
	5 0.139364(16)	0.139143(16)	0.139179(16)
	6 0.139370(11)	0.139144(10)	0.139185(10)
(Solutions -3b)	7 0.139380(10)	0.139156(10)	0.139198(10)
	8 0.139342(30)	0.139127(54)	0.139148(28)
	9 0.139319(13)	0.139112(11)	0.139141(11)
	Mean 0.139359(16)	0.139138(22)	0.139177(16)
	$s(n(^{26}Mg)/n(^{24}Mg))$ 0.000024	0.000021	0.000022
Atomic weights		A_r(Mg)	
(Solutions -1b)	1 24.304955(32)	24.304597(32)	24.304692(34)
	2 24.305044(15)	24.304688(15)	24.304759(15)
	3 24.305040(15)	24.304689(15)	24.304756(15)
(Solutions -2b)	4 24.305043(16)	24.304696(16)	24.304754(16)
	5 24.305025(23)	24.304676(23)	24.304738(23)
	6 24.305034(16)	24.304679(15)	24.304747(15)
(Solutions -3b)	7 24.305038(16)	24.304685(16)	24.304755(16)
	8 24.304983(45)	24.304643(76)	24.304680(44)
	9 24.304942(19)	24.304612(17)	24.304666(17)
	Mean 24.305011(24)	24.304663(31)	24.304728(24)
	$s(A_r(Mg))$ 0.000040	0.000036	0.000037

Table 6: All values (10 sequences) for absolute isotopic composition of the three iRM candidates measured at BAM, with expanded uncertainties (k = 2).

Parameter		ERM-AE143	ERM-AE144	ERM-AE145
Isotope amount fractions				
			$x(^{24}Mg)$ / (mol/mol)	
(Solutions -1b)	1	0.789894(18)	0.790104(18)	0.790059(19)
	2	0.789889(10)	0.790102(10)	0.7900632(98)
	3	0.789880(11)	0.790087(10)	0.790051(10)
(Solutions -2b)	4	0.7899146(95)	0.7901237(96)	0.7900834(96)
	5	0.789913(12)	0.790124(12)	0.790081(12)
	6	0.789910(11)	0.790118(10)	0.7900787(98)
	7	0.789921(10)	0.790126(10)	0.790083(10)
(Solutions -3b)	8	0.789913(12)	0.790121(12)	0.790084(12)
	9	0.7899079(98)	0.790115(10)	0.7900698(98)
	10	0.7899113(99)	0.790118(10)	0.7900731(97)
	Mean	0.789905(12)	0.790114(11)	0.790073(12)
	$s(x(^{24}Mg))$/(mol/mol)	0.000013	0.000013	0.000012
			$x(^{25}Mg)$ / (mol/mol)	
(Solutions -1b)	1	0.099999(13)	0.099941(13)	0.099957(13)
	2	0.1000021(61)	0.0999450(58)	0.0999579(59)
	3	0.1000066(72)	0.0999500(67)	0.0999618(69)
(Solutions -2b)	4	0.1000035(58)	0.0999459(57)	0.0999595(58)
	5	0.1000004(71)	0.0999425(70)	0.0999570(70)
	6	0.1000101(60)	0.0999528(59)	0.0999655(58)
	7	0.1000009(57)	0.0999448(57)	0.0999582(57)
(Solutions -3b)	8	0.0999952(65)	0.0999378(61)	0.0999498(62)
	9	0.0999943(56)	0.0999387(61)	0.0999541(56)
	10	0.0999989(63)	0.0999435(64)	0.0999570(60)

Isotope amount fractions			
Mean	0.1000011(72)	0.0999442(72)	0.0999577(71)
$s(x(^{25}Mg))$/(mol/mol)	0.0000048	0.0000046	0.0000042
		$x(^{26}Mg)$ / (mol/mol)	
(Solutions -1b) 1	0.110107(15)	0.109955(15)	0.109985(15)
2	0.1101085(76)	0.1099534(79)	0.1099789(74)
3	0.1101129(83)	0.1099633(76)	0.1099875(76)
(Solutions -2b) 4	0.1100820(70)	0.1099305(72)	0.1099570(72)
5	0.1100866(88)	0.1099337(89)	0.1099615(89)
6	0.1100804(84)	0.1099292(78)	0.1099558(74)
7	0.1100783(82)	0.1099288(85)	0.1099585(82)
(Solutions -3b) 8	0.110092(10)	0.109941(10)	0.109966(10)
9	0.1100978(76)	0.1099465(77)	0.1099760(76)
10	0.1100897(73)	0.1099382(80)	0.1099699(71)
Mean	0.1100936(91)	0.1099419(91)	0.1099696(91)
$s(x(^{26}Mg))$/(mol/mol)	0.000012	0.000012	0.000012
Isotope amount ratios			
		$n(^{25}Mg)/n(^{24}Mg)$ / (mol/mol)	
(Solutions -1b) 1	0.126597(19)	0.126491(19)	0.126518(19)
2	0.1266027(89)	0.1264964(84)	0.1265189(86)
3	0.126610(10)	0.1265050(97)	0.1265258(99)
(Solutions -2b) 4	0.1266004(85)	0.1264939(83)	0.1265177(84)
5	0.126597(10)	0.126490(10)	0.126515(10)
6	0.1266095(87)	0.1265036(86)	0.1265260(84)
7	0.1265961(83)	0.1264922(83)	0.1265161(83)
(Solutions -3b) 8	0.1265902(93)	0.1264841(88)	0.1265053(88)
9	0.1265898(81)	0.1264863(88)	0.1265130(82)
10	0.1265951(91)	0.1264919(93)	0.1265161(88)
Mean	0.126599(10)	0.126493(10)	0.126517(10)
$s(n(^{25}Mg)/n(^{24}Mg))$	0.0000070	0.0000067	0.0000060
		$n(^{26}Mg)/n(^{24}Mg)$ / (mol/mol)	
(Solutions -1b) 1	0.139395(21)	0.139165(21)	0.139211(22)
2	0.139397(11)	0.139164(11)	0.139203(11)
3	0.139405(12)	0.139179(11)	0.139216(11)
(Solutions -2b) 4	0.139359(10)	0.139131(10)	0.139171(11)
5	0.139365(13)	0.139135(13)	0.139177(13)
6	0.139358(12)	0.139130(11)	0.139171(11)
7	0.139354(12)	0.139128(12)	0.139173(12)
(Solutions -3b) 8	0.139373(15)	0.139144(15)	0.139183(15)
9	0.139381(11)	0.139153(11)	0.139198(11)
10	0.139370(11)	0.139141(12)	0.139190(10)
Mean	0.139376(13)	0.139147(13)	0.139189(13)
$s(n(^{26}Mg)/n(^{24}Mg))$	0.000018	0.000017	0.000017
Atomic weights		A_r(Mg)	
(Solutions -1b) 1	24.305064(31)	24.304703(30)	24.304778(31)
2	24.305071(17)	24.304704(17)	24.304768(16)
3	24.305084(18)	24.304728(17)	24.304789(17)
(Solutions -2b) 4	24.305019(16)	24.304659(16)	24.304726(16)
5	24.305025(20)	24.304662(20)	24.304732(20)
6	24.305023(18)	24.304663(17)	24.304729(16)
7	24.305009(18)	24.304654(18)	24.304727(18)
(Solutions -3b) 8	24.305031(21)	24.304671(21)	24.304734(22)
9	24.305042(17)	24.304684(17)	24.304758(17)
10	24.305030(16)	24.304672(17)	24.304749(16)
Mean	24.305040(20)	24.304680(19)	24.304749(19)
$s(A_r(Mg))$	0.000025	0.000024	0.000023

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):

$$M(\mathrm{X}) = A_\mathrm{r}(\mathrm{X}) \cdot M_\mathrm{u} \qquad \text{eqn. 2}$$

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.

The final values for each quantity are obtained by calculating the arithmetic mean not from the laboratory means but from the individual results for each measured sequence (Table 4 - 6). The associated measurement uncertainties are calculated as the mean of the individual measurement uncertainties (eqn. 3) plus the standard deviation of the mean of all individual results (eqn. 4).

$$\bar{u} = \sqrt{\frac{\sum u_i^2}{n}} \qquad \text{eqn. 3}$$

$$u_\mathrm{c} = \sqrt{\left(\frac{s}{\sqrt{n}}\right)^2 + \bar{u}^2} \qquad \text{eqn. 4}$$

$$E_\mathrm{n} = \left|\frac{d_i}{U(d_i)}\right| \qquad \text{eqn. 5}$$

With $d_i = |x_i - \bar{x}|$

However, it turned out that between 1 and 7 of the 22 individual results are metrologically not compatible with the mean value, which means their normalized error, E_n (eqn. 5), is larger than 1. The conclusion is that either the uncertainties of the individual results or the uncertainty of the mean value, or both are underestimated. Reasons for that might be that the measured isotope ratios contain some assumptions based on separate measurements such as the blank correction or the absence of interferences. Although these measurement based assumptions nearly reflect the real conditions, there might be some cases where a tiny underestimation occurs, which gets visible when working with relative measurement uncertainties at the 0.005 % level. Based on the work by Kessel et al. we added an additional uncertainty contribution in order to establish the metrological compatibility of the results (Kessel *et al.* 2008). As the uncertainties of the individual results are carefully calculated and the agreement of the individual results is rather good (although not perfect), we added the additional uncertainty contribution to the mean value and not to the individual values. This additional uncertainty contribution was estimated such, that 95 % (21) of the 22 individual results show normalized errors equal to or less than 1. For the $n(^{25}\mathrm{Mg})/n(^{24}\mathrm{Mg})$ ratios the additional uncertainty contribution typically is equal to or less than the combined standard uncertainty of the mean value. In the case of the $n(^{26}\mathrm{Mg})/n(^{24}\mathrm{Mg})$ ratio the additional uncertainty contribution ranges between the one- and twofold of the combined standard uncertainty of the mean value. This is in agreement with the fact that the $n(^{26}\mathrm{Mg})/n(^{24}\mathrm{Mg})$ ratio measurement is more severely impeded by mass discrimination and by potential molecular interferences compared to the $n(^{25}\mathrm{Mg})/n(^{24}\mathrm{Mg})$ ratio measurement.

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 have to 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 on the basis of values obtained in a joint project between National Metrology Institutes and Designated Institutes, which fulfil the highest metrological requirements, especially in terms of measurement uncertainty and traceability.

As explained above possible homogeneity issues and instability issues do not apply to either of these new iRMs. Consequently, the certified values and their associated uncertainties are calculated from Table 4 - 6 as described in the characterization section and are displayed in Table 7.

Table 7: Certified quantity values of of ERM-AE143, -AE144 and -AE145 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-AE143					
$n(^{25}Mg)/n(^{24}Mg)$	mol/mol	0.126 590	0.000 010	0.000 020	0.016
$n(^{26}Mg)/n(^{24}Mg)$	mol/mol	0.139 362	0.000 021	0.000 043	0.031
$n(^{24}Mg)/n(Mg)$	mol/mol	0.789 920	0.000 023	0.000 046	0.0058
$n(^{25}Mg)/n(Mg)$	mol/mol	0.099 996	0.000 0068	0.000 014	0.014
$n(^{26}Mg)/n(Mg)$	mol/mol	0.110 085	0.000 014	0.000 028	0.025
$M(Mg)$	g/mol	24.305 017	0.000 036	0.000 073	0.000 30
ERM-AE144					
$n(^{25}Mg)/n(^{24}Mg)$	mol/mol	0.126 486	0.000 011	0.000 022	0.017
$n(^{26}Mg)/n(^{24}Mg)$	mol/mol	0.139 138	0.000 020	0.000 039	0.028
$n(^{24}Mg)/n(Mg)$	mol/mol	0.790 124	0.000 019	0.000 039	0.0049
$n(^{25}Mg)/n(Mg)$	mol/mol	0.099 939	0.000 0064	0.000 013	0.013
$n(^{26}Mg)/n(Mg)$	mol/mol	0.109 936	0.000 012	0.000 025	0.023
$M(Mg)$	g/mol	24.304 664	0.000 031	0.000 063	0.000 26
ERM-AE145					
$n(^{25}Mg)/n(^{24}Mg)$	mol/mol	0.126 514	0.000 008	0.000 016	0.013
$n(^{26}Mg)/n(^{24}Mg)$	mol/mol	0.139 185	0.000 015	0.000 029	0.021
$n(^{24}Mg)/n(Mg)$	mol/mol	0.790 078	0.000 014	0.000 028	0.0035
$n(^{25}Mg)/n(Mg)$	mol/mol	0.099 956	0.000 0048	0.000 010	0.010
$n(^{26}Mg)/n(Mg)$	mol/mol	0.109 967	0.000 010	0.000 021	0.019
$M(Mg)$	g/mol	24.304 741	0.000 023	0.000 046	0.000 19

The relative expanded uncertainties for the isotope amount ratios in the three iRM range from 0.013 % to 0.017 % for the $n(^{25}Mg)/n(^{24}Mg)$ ratio and from 0.021 % to 0.031 % for the $n(^{26}Mg)/n(^{24}Mg)$ ratio. For the isotope amount fractions $x(^{24}Mg)$, $x(^{25}Mg)$ and $x(^{26}Mg)$ the relative expanded uncertainties are 0.006 %, ≤ 0.015 % and ≤ 0.025 %, respectively. For the case of the molar masses the relative expanded uncertainties are ≤ 0.0003 %.

The most important contributions to the uncertainty associated with the isotope amount ratios $n(^{25}Mg)/n(^{24}Mg)$ and $n(^{26}Mg)/n(^{24}Mg)$ determined in an individual measurement sequence are the uncertainty contributions from the masses of the isotopically enriched Mg materials in the calibration mixtures, which

were introduced during the preparation of the calibration solutions in the first part of the project. These contributions themselves are dominated by the uncertainty contributions of the weighing and of the purity statement. The third largest contribution is the measured intensity ratio in the calibration mixture and only in fourth place comes the measured intensity ratio of the candidate material. This clearly shows, that a reduction of the final uncertainty is only possible, when the weighing procedure and the purity assessment is improved. An improvement of the ion intensity ratio measurement is only of secondary importance.

These certified isotope reference materials (iRM) are traceable to “The International System of Units (SI)” in the most direct way possible, by calibration of all mass spectrometers against the synthetic isotope mixtures, which are SI-traceable to the kg.

The Mg mass fractions in the three ERM materials are provided as indicative values (Table 8).

Table 8: Indicative quantity values of ERM-AE143, -AE144, and -AE145 with their associated expanded uncertainties $U = k \cdot u_c$ with $k = 2$

Material	Quantity	Unit	Indicative value	U	U_{rel} in %
ERM-AE143	Mg mass fraction	mg/kg	50.0	1.0	2.0
ERM-AE144	Mg mass fraction	mg/kg	50.0	1.0	2.0
ERM-AE145	Mg mass fraction	mg/kg	50.0	1.0	2.0

5. Storage and Handling

ERM-AE143, -AE144 and -AE145 should be stored under normal laboratory conditions (between 5 °C and 25 °C). 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 Mg mass fraction in the solution and not affect the certified Mg isotope amount ratios. The introduction of any contaminant to this solution may change the Mg isotope ratios, and will therefore render these certified values null and void.

6. References

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