

CrossMark  
click for updatesCite this: *J. Anal. At. Spectrom.*, 2016, **31**, 179

# Preparation and characterization of primary magnesium mixtures for the *ab initio* calibration of absolute magnesium isotope ratio measurements†

Björn Brandt,<sup>a</sup> Jochen Vogl,<sup>\*a</sup> Janine Noordmann,<sup>b</sup> Angela Kaltenbach<sup>b</sup> and Olaf Rienitz<sup>b</sup>

We report an appropriate preparation of binary isotope calibration mixtures of the three stable isotopes of magnesium to be used in the *ab initio* calibration of multicollector mass spectrometers (ICPMS and TIMS). For each of the three possible combinations of binary mixtures (<sup>24</sup>Mg + <sup>25</sup>Mg, <sup>24</sup>Mg + <sup>26</sup>Mg, and <sup>25</sup>Mg + <sup>26</sup>Mg), three individual setups have been prepared under gravimetric control, each of them with an isotope ratio close to unity, and a total magnesium mass fraction close to 20 mg kg<sup>-1</sup>. The preparation was designed to occur *via* an intermediate dilution of a parent solution of a highly purified specimen of the isotopically enriched magnesium materials. For the application as calibration mixtures, a complete uncertainty budget was set up, and is presented and discussed in detail, including the aspects that went into the design of the dilution and mixing approach to minimize uncertainty. The principle parameters for the purpose of the later calibration of the mass spectrometers are the absolute masses of isotopically enriched magnesium materials in the primary calibration mixtures. For the first time relative expanded uncertainties  $U$  ( $k = 2$ ) for these masses of  $\leq 0.005\%$  could be achieved for all mixtures.

Received 15th July 2015

Accepted 17th August 2015

DOI: 10.1039/c5ja00284b

www.rsc.org/jaas

## 1. Introduction

Since the first mass spectrometric detection of Ne isotopes by J. J. Thompson in 1910, it has been known that most chemical elements exist in the form of more than one stable isotope.<sup>1</sup> Mostly, the resulting isotopic composition is assumed to be invariant in nature and is taken as a quasi-constant value.<sup>2</sup> For most elements, however, small variations of their isotopic composition do exist.

Two approaches exist to denote isotopic composition:

The *absolute* isotopic composition of an element is expressed in either of two tautological representations: as isotope amount fractions (“isotope abundances”) for each isotope, or as isotope amount ratios. Although the expression in terms of isotope amount fractions is conceptually simpler, and directly yields the atomic weight and the molar mass of an element, the expression in terms of isotope amount ratios has found widespread use, since it is more directly connected to the experimental determination.

For many applications, however, the *absolute* isotopic composition is not required. In such cases, the isotopic

variation is reported as the *relative deviation* of the isotope ratio in the sample to the isotope ratio of an internationally accepted standard. Such relative deviations are expressed as so-called “delta-values” ( $\delta$  values).<sup>3</sup>

The main difference between both approaches is that for determining the *absolute* isotopic composition, all influencing quantities have to be considered, while for delta-measurements – where the isotope ratio measured in the sample is divided by the isotope ratio measured in the accepted standard – it is assumed that all corrections and/or calibrations are compensated for due to the assumed identical behaviour of the sample and the standard in the mass spectrometer. Consequently, measurement uncertainties for delta-values are much smaller than those for absolute measurements.

However, delta-values do not convey the full picture of the isotopic composition, and they lack absolute traceability on the basis of the international system of units (SI), and thus are burdened with a number of potential negative consequences. Additionally, difficulties may occur once the artefact used as an anchor point for the delta scale has been consumed, and thus needs to be replaced by a new material. It is for those reasons that absolute isotope ratio measurements are very desirable.

Until today, the sole universal method for high-accuracy isotope ratio determination is mass spectrometry. Practically no alternatives exist. The two most versatile methods for mass spectrometric isotope ratio determination are thermal ionization mass spectrometry (TIMS) and inductively coupled plasma-mass spectrometry (ICPMS), both exhibiting a number of

<sup>a</sup>BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany. E-mail: jochen.vogl@bam.de

<sup>b</sup>Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany. E-mail: olaf.rienitz@ptb.de

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5ja00284b



peculiarities that need to be taken into account for achieving accurate isotope ratios. The most important aspect, however, is that each ion current or ion intensity measured with a mass spectrometer such as TIMS or ICPMS is biased by mass fractionation or discrimination, detector efficiency, amplifier gain, and other effects. This in turn also applies to ion current ratios measured by using TIMS and ICPMS. The correction of such bias is accomplished by various approaches, such as external correction by using correction factors (“*K* factors”) or by  $\delta$ -measurements.<sup>4,5</sup> For both approaches, isotope reference materials (IRMs) are required.

Absolute IRMs can only be certified by mass spectrometric measurements, which, however, are subject to mass fractionation and/or mass discrimination, which in turn require a suitable calibration to correct the results. This dilemma has been solved by A. O. Nier, who pioneered the approach to calibrate mass spectrometers using synthetic isotope mixtures in 1950.<sup>6</sup> In this approach (see Fig. 1), isotopically enriched and chemically purified materials are used as the starting point to prepare isotope calibration mixtures in a number of steps under full gravimetric control, so that the theoretical isotope ratios in the calibration mixtures can be calculated using the weighing data and the isotope ratios of the isotopically enriched starting materials. To this point, however, the isotope ratios of the isotopically enriched materials are not yet known, and still need to be determined experimentally. Since, however, at this point the mass spectrometer is also not yet calibrated, the isotope ratios measured for the isotopically enriched materials are affected by mass fractionation and/or mass discrimination, as are the theoretically calculated isotope ratios in the isotope mixtures (which are based on those experimental determinations). This whole approach apparently gives rise to a catch-22 situation; however, although it thus may appear that the approach would not constitute an apt way to determine the calibration factors of the instrument, it turns out that, in reality, the system is overdefined, and all those unknowns can be determined from the same experiment: in the past, the corresponding equations were solved by an iterative approach, which was typically applied to mixtures of only two isotopes. The use of only two isotopes in a multi-isotope system, however, requires that the correction factors for the other isotope ratios need to be extra- or interpolated using empirical laws, which are not fully verified, and do not account for variations in detector efficiency and amplifier gain in multi-collector instruments. This changed when Pritzkow *et al.* used enriched materials for seven out of the eight naturally occurring cadmium isotopes to prepare isotope mixtures, yielding expanded uncertainties for the Cd isotope ratios down to 0.02%.<sup>7</sup> More recently, the equation system describing the synthetic isotope mixture approach was solved by exact analytical equations (verified for at least three isotopes), which yields the calibration factors without the need for iteration.<sup>8</sup> Both components together – the use of preferably all stable isotopes of an element for the mixtures, and the exact analytical equations – form the virtually ideal route for obtaining absolute isotope ratios. Moreover, it also fulfils the requirements for a primary method of measurement as defined by the CCQM.<sup>9</sup>

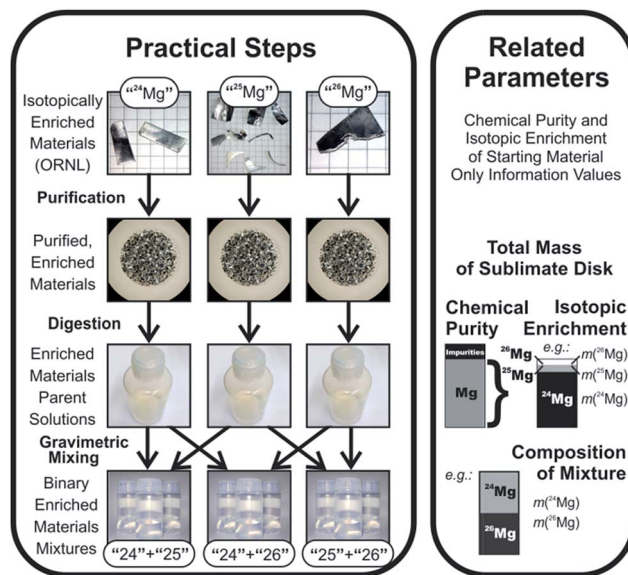


Fig. 1 Schematic approach of this work.

Magnesium has been selected as the target element of this demonstrative work since its isotope ratios are widely used in biology, cosmochemistry, geochemistry and nutrition.<sup>10–14</sup> Until today, the only certified isotope reference material available for the calibration of absolute magnesium isotope ratio measurements is NIST SRM 980;<sup>15</sup> this material is sold by NIST in the form of metal chips; additionally, a solution of an aliquot is available as IRMM-009.

Unfortunately, NIST SRM 980 turned out to show significant heterogeneity.<sup>16</sup> Although this isotope heterogeneity is largely covered by the expanded uncertainty, it is too large for today's magnesium isotope research. Also, this inhomogeneity renders SRM 980 unsuitable for delta measurements; other artefacts are thus currently applied by the community (CAM-1 and DSM-3).<sup>16</sup>

Consequently, a replacement of this material is urgently needed.<sup>5,17</sup> Such a new magnesium isotope reference material can only be characterized *via* the above described isotope mixture approach. The main requirements are: adequate homogeneity of the isotope amount ratio ( $\leq 0.01\%$ ), which can easily be achieved by providing the IRM in the form of a solution, and an expanded relative uncertainty  $< 0.02\%$  for the isotope amount 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%).<sup>16,18</sup>

To prepare isotope mixtures with expanded uncertainties of  $\leq 0.02\%$  for the mass fractions, however, two primary solutions of different isotopically enriched materials – each with expanded uncertainties of  $\leq 0.014\%$  for the mass fractions – are required as the starting materials to produce a blend. The best mono-elemental solutions available from commercial suppliers such as Merck, however, have much larger relative expanded uncertainties of approx. 0.4%.

The challenge of producing primary solutions of isotopes with relative expanded uncertainties of  $\leq 0.014\%$  was taken up in this project. This paper describes the preparation of those



calibration solutions, and their associated uncertainties, which are required as input parameters for the second step of the project – the calibration of the mass spectrometer, and the determination of the isotopic composition of the three IRM candidates.

## 2. Methods, instrumentation, and software

### 2.1 Uncertainty budgets

Estimations of uncertainties of all masses in the calibration mixtures are the central task in this project. All estimations of uncertainties are based strictly on the principles described in the Guide for the Expression of Uncertainty in Measurement (GUM).<sup>19</sup> In essence, those guidelines advise us to collect all information regarding the uncertainties of all experimental input values, and then propagate the respective probability distributions all the way to the final result through the applicable evaluation formulae. For this purpose, a number of mathematical approaches can be used. Practically, uncertainties in this work are calculated using software (GUM Workbench, version 2.4, Metrodata GmbH, Weil am Rhein, Germany<sup>20</sup>). GUM Workbench uses a simplified method for the propagation of variances, which is strictly valid only if the equation that propagates those variances is sufficiently linear.

This approach allows determination of the overall uncertainty of a resultant value based on the uncertainties of all input values, and to determine the largest contributors of uncertainty. If all input values are correctly represented, and the set of equations also represents all relevant “uncontrollable” systematic experimental influences (such as room temperature fluctuations), the resulting uncertainty can be assumed to adequately represent the uncertainty of the expectation value, and it can be expected that the two together span a range that contains the true value. Since the analysis allows determination of the largest contributors to the uncertainty of the final result, it can be used to reduce the uncertainty by improving the experiment and to get as close as practically possible to the true value. This work describes an improvement of experimental results based on such an analysis.

### 2.2 Isotopically enriched magnesium materials

Enriched specimens of the three isotopically enriched magnesium materials were obtained from Oak Ridge National Laboratory (ORNL) in March 2010. ORNL has an inventory of enriched magnesium materials that are stored in the oxidic form; for this work, those enriched magnesium oxides have been reduced by ORNL into the metallic form on our request.

All three isotopically enriched materials were delivered sealed into individual glass tubes, and are accompanied by assay analysis reports covering isotopic enrichment and basic assay of metallic purity based on spark source mass spectrometry. The details of the materials are listed in Table 1.

The analytical data provided by ORNL, however, have an insufficient degree of accuracy for our purposes. Additionally, the purity analyses by ORNL only consider metallic impurities,

Table 1 Data for the isotopically enriched magnesium materials (Oak Ridge National Labs)

Parameter		<sup>24</sup> Mg <sup>a</sup>	<sup>25</sup> Mg <sup>a</sup>	<sup>26</sup> Mg <sup>a</sup>
Appearance		2 pieces	10 pieces	1 chip
Mass of material	mg	200	200	201
<sup>24</sup> Mg amount	mol mol <sup>-1</sup>	0.9992	0.0180	0.0039
fraction <sup>a</sup>				
<sup>25</sup> Mg amount	mol mol <sup>-1</sup>	0.0005	0.9787	0.0017
fraction <sup>a</sup>				
<sup>26</sup> Mg amount	mol mol <sup>-1</sup>	0.0003	0.0033	0.9944
fraction <sup>a</sup>				

<sup>a</sup> According to the data supplied by manufacturer ORNL.

leaving non-metals such as oxygen aside, which are significant impurities for the case of Mg. To remove non-metals, and to reduce metallic impurities to sufficiently low levels, the isotopes were further purified in this project using high vacuum (HV) sublimation. Since the supplied reports regarding chemical purity are extremely spotty, new purity analyses were obtained experimentally.

### 2.3 Laboratory containers

For storage of isotopically enriched materials in their metallic form, and for all acids and solutions, containers manufactured from the synthetic organofluorine polymer resins FEP (fluorinated ethylene propylene) or PFA (polyfluoroalkoxy polymer) were used. Both FEP and PFA have a density of 2150 kg m<sup>-3</sup>.<sup>21,22</sup>

Solid isotopically enriched materials were stored in 15 mL jars with screw caps (Savillex Corp.). Solutions were stored in PFA (Sanplatec Corp., Japan) or FEP (Thermo Scientific™, Nalgene™) bottles. All PFA and FEP containers have been newly purchased, and have never been used for storage of any other solutions. They were cleaned following a six-step purification protocol:

- (1) Rinse inside and outside three to five times with ultrapure water (Milli-Q).
- (2) Fill to 1/3 with 0.10 g g<sup>-1</sup> HNO<sub>3</sub> (*p.a.*); close bottle.
- (3) Shake the filled bottle for at least 2 h.
- (4) Heat the filled bottle on the hot plate (<4 h, 120 °C).
- (5) After cooling: rinse five times with ultrapure water.
- (6) Dry at 40 °C inside a PE storage bag with cap unplugged.

All bottles are kept individually in polyethylene (PE) re-sealable zipper storage bags for protection against dust and lint. They were either labelled directly (using transfer print stickers) or the storage PE bags have been labelled. Bottles are handled exclusively using cotton laboratory gloves to preclude fingerprints.

### 2.4 Purification of metals by high vacuum-sublimation

For purification of metals, we use a high-vacuum (HV) sublimation apparatus at BAM that was built by and obtained from Empa.<sup>7</sup> In this apparatus, the feed magnesium metal is sublimated inside a small crucible system that consists of two parts – a crucible cylinder and a top lid, both machined from vitreous



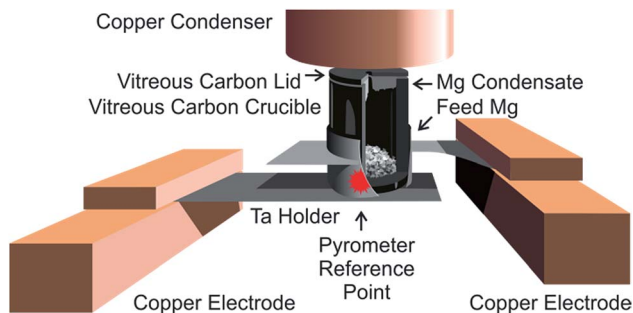


Fig. 2 HV-sublimation setup. Cutaway view of the crucible and holder.

(“glassy”) carbon (see Fig. 2). A thermal gradient over this crucible/lid system is established from the outside by resistance heating of the tantalum frame that holds it. The complete setup is housed in a high vacuum (base pressure approx.  $1 \times 10^{-8}$  hPa). The feed metal at the heated base of the crucible sublimates and condenses on the cooler lid, which acts as the primary condenser. Lower-boiling metallic impurities of the feed material also condense in a chilled copper cylinder (diameter: approx. 2.7 cm) mounted approx. 0.5 cm above the top lid, acting as the secondary condenser. Higher-boiling impurities ideally remain in the residue on the bottom of the crucible. Gaseous impurities are evacuated.

The vitreous carbon material used is Sigradur® G (HTW GmbH, Thierhaupten, Germany) with low impurity levels. According to communication from the manufacturer, the ash content of Sigradur® is  $0.000038 \text{ g g}^{-1}$ ; the main contents of the ash are silicon (25%) and calcium (20%); magnesium was found to be below 0.2%.

The tantalum holder systems are custom made using electrical erosion and laser beam welding by workshops at Empa, Technical University of Berlin (Germany), or DESY (Zeuthen, Germany); starting from semi-finished products: tantalum foils (0.3 mm) and tubes (O.D. 14 mm, wall 0.5 mm), obtained from Plansee SE, Reutte, Austria.

This tantalum holder is clamped onto chilled copper electrodes. Together with the chilled copper block secondary condenser, those chilled electrodes help to counter the resistance heating, and thereby establish the thermal gradient over the crucible system that is required for sublimation; the upper part of the tantalum holder is closer to the electrode, which results in the upper part of the tantalum holder getting less warm during heating than the lower base. The electrodes are mounted on chilled HV-high current feedthroughs (Trinos Vakuum-Systeme GmbH, Pfeiffer Vacuum, Göttingen, Germany).

This whole sublimation apparatus is housed in a cylindrical steel vacuum receiver ( $V = 53 \text{ L}$ ), topped with an O-ring-sealed flange. The base plate of the chamber is welded onto the vessel; the chilled vacuum high-current feedthroughs that carry the sublimation setup (Fig. 2) are mounted to this bottom flange. Various instruments are attached to this chamber *via* different flanges, typically using KF-seals. The vacuum receiver is evacuated *via* an air-cooled turbo-molecular drag pump (Pfeiffer

Vacuum, TMU260), using a membrane pump (Pfeiffer Vacuum, MD 4T) as the first pumping stage. The pressure inside the vessel is determined by two vacuum gauges (Balzers), one Pirani thermal conductivity gauge (TPR250) and a cold cathode gauge (IKR250) for the fine vacuum and the high vacuum ranges, respectively.

The temperature of the crucible system is controlled by an intensity ratio pyrometer (model IGA 120, impact GmbH) focused at a reference point at the front of the tantalum holder from the front side of the vacuum vessel through a quartz window. In order to reach a predefined temperature inside the crucible, the temperature at the reference point must be several ten degrees higher (as an example, for one holder/crucible combination, the difference was approx.  $50 \text{ }^\circ\text{C}$  for a sublimation temperature of  $520 \text{ }^\circ\text{C}$ ). Since the tantalum holder frame has a low resistance, a low voltage/high current galvanic power supply is used for resistance heating (power station pe2050, plating electronic GmbH, Denzlingen, Germany); a typical value for the heating is 1.0 V, 120 A to achieve a temperature approx.  $510 \text{ }^\circ\text{C}$  inside the vitreous carbon crucible; those values also are subject to larger variations between individual tantalum holders.

After sublimations, the chamber is backfilled with oxygen-free argon (purity 99.999%, Linde; residual oxygen filter “O<sub>2</sub>-free”, Air Liquide).

**2.4.1 Sublimation protocol.** During all sublimations, the empty, physically cleaned vitreous carbon crucible was first weighed, then filled with the sample (approx. 200 mg), and then topped with the vitreous carbon lid; the net weights of the metal and the clean crucible and lid were recorded. This crucible system was mounted on the tantalum holder, and the vacuum chamber was sealed, and then evacuated. Within 15 min, the system typically reached a pressure in the range of  $10^{-7}$  hPa, which was considered sufficient to begin purifications. The resistance heating power was increased slowly to intermediate temperatures (350 to  $400 \text{ }^\circ\text{C}$  at the reference point) to remove residual gases and humidity (approx. 15 min). Then, the system was heated to the predetermined sublimation temperature; for the case of magnesium, a temperature between 520 and  $615 \text{ }^\circ\text{C}$  at the reference point was used; the typical heating power was approx. 120 W (120 A, 1.0 V).

Two main factors determine the ideal sublimation temperature: (1) the physical and chemical properties of the metal to be sublimated, and (2) the slightly differing geometries of the individual tantalum holders due to the manual production, which result in slightly differing heat conductivity properties; two tantalum holders showed very similar properties (sublimation of 200 mg Mg within 6 h at  $560 \text{ }^\circ\text{C}$  at the reference point), while a third one that was used in the final sublimation rounds showed significantly different properties (sublimation of 200 mg Mg within 6 h at  $615 \text{ }^\circ\text{C}$  measured at the reference point).

For one tantalum holder, the following limiting practical conditions to sublimate 200 mg Mg quantitatively were found: at  $520 \text{ }^\circ\text{C}$ , quantitative sublimation required more than 24 h, while at  $560 \text{ }^\circ\text{C}$ , the sublimation completed within 6 h. The separation quality depends on the sublimation temperature and the number of sublimation cycles. Note that sublimation



may shift the isotopic enrichment due to mass fractionation effects.

## 2.5 Weighing procedures

Beside purity determination, the determination of absolute mass by means of weighing was the central practical exercise in this work, since all digestion, dilution and mixing steps have been controlled gravimetrically. The corresponding protocols were discussed in detail recently<sup>23</sup> and were applied here in essence. Four analytical balances have been used for different weighing procedures, three of them electronic force compensation comparator balances at BAM with various resolutions and allowed maximum loads (Mettler Toledo UMT2, AX205 and Sartorius LC5101S); the fourth balance was a mechanical beam balance at PTB (Mettler H315):

**2.5.1 Analytical balances.** All electronic comparator balances at BAM (UMT2, AX205 and LC5101S) are verified yearly using calibration weights of OIML class E2 according to EURAMET guide cg-18. The traceability to national standards is thereby certified. The mechanical balance Mettler H315 (at PTB) is conformity-checked once a year.

In all weighings, the electronic balances have been adjusted using the internal adjustment weights. The balances have stainless steel weights with a nominal density of 8000 kg m<sup>-3</sup> (electronic balances) or 7950 kg m<sup>-3</sup> (H315). Further details of the balances are listed in Table 2.

The analytical balance UMT2 was used for the determination of the magnesium masses. AX205 was used for weighing the empty PFA bottles, for weighing the filled bottles, and for difference weighing of solutions during the digestion, dilution and mixing process. LC-5101S was used for weighing the solutions, and the filled PFA bottles, particularly during the preparation of acids, and the parent solutions, while FCB12K0.1B was used only for one large setup of dilute HNO<sub>3</sub> (5 L of 0.02 g g<sup>-1</sup>, see below). The balance H315 was used at PTB for the preparation of the first series of calibration mixtures (not further described herein).

External certified weights of OIML class E2 of various masses ranging from 20 mg to 5 kg have been used in this project. Transfer weights with masses ≤ 1 g are made from Neusilber (German silver) with a nominal density of 8600 kg m<sup>-3</sup>; those with masses > 1 g are made from stainless, non-magnetic steel with a nominal density of 7950 kg m<sup>-3</sup>. All E2 weights are certified every four years by the Berlin-Brandenburg State Office

for Metrology, and had last been verified for this project on 07/11-2013.

**2.5.2 Weighing protocol.** All balances are equipped with circular levels to ensure that the balance movement occurs perpendicularly to the centre of gravity. The levelling of the balance is always verified before any weighing. Then, typically the balances are prepared by loading a mass close to the maximum load of the balance ten times. Immediately before each weighing process, the electronic comparator balances UMT2 and AX205 are adjusted with the internal adjustment weights using an automatic mechanism. After adjustment, the reading of balance AX205 is controlled using an external control weight (100 g, F2, no buoyancy correction) to ensure it complies with previous readings. The balance LC5101S is also always adjusted before weighings, but using an external weight (5 kg E2) that has to be loaded manually.

In case of important, non-repeatable weighings on the comparator balance UMT2, E2 weights (100 mg and 500 mg) are weighed additionally as a second means to allow calibration of the balance.

As the balances show different characteristics, the weighing protocols vary slightly, but follow a general procedure: the sample to be weighed was placed in the centre of the weighing platform, and it was waited until the mass reading had stabilized; in the case of balance UMT2, this typically took 30–40 s; the first stable value (as indicated by the balance's own electronics) was always used. In the case of AX205 and LC5101S, the value was followed for a certain time, and only if it had been stable for 30 s (at the AX205), or 10–15 s (LC5101S), the reading was accepted and recorded. Then, the sample was removed, and the balance was given time to return back to the tare value, which was also recorded, and the average between zero and tare was subtracted from the weighing result. In case of UMT2 no significant difference was observed.

Weighings were typically repeated for a number of times.

Solutions in bottles are stored under full weight-control, by recording the weight as well as the climate data before and after the bottle has been opened and solution has been withdrawn. This allows correcting the mass fractions for evaporation effects.

The electronic balances are so sensitive towards electrostatic charges on the PFA/FEP containers, particularly when they are empty, that practical measures have to be taken to obtain precise and true weighing values. At BAM, we apply a nitrogen ring ionizer/blow-out gun (RI65P7187500, Haug GmbH, Leinfelden-Echterdingen, Germany) to blow ionized nitrogen (N<sub>2</sub> 5.0, Linde) over the containers, and thereby remove electrostatic charge prior to any weighing procedure. Successful removal of charges is assumed when the balance reading is stable over a period of more than 30 seconds; if charges have not been removed successfully, the weighing value tends to creep during this time frame; in this case, repeated weighing results exhibit significant scatter.

The mechanical balance H315 is less sensitive towards electrostatic charging. For its case, a piezoelectric anti-static instrument (Sigma-Aldrich ZEROSTAT 3) was sufficient to

Table 2 List of the applied analytical balances

Balance type	Producer	Max. load	Readability	Calibration E2
UMT2	Mettler	2.1 g	0.1 µg	Yes
AX205	Mettler	220 g	0.01 mg	Yes
H315	Mettler	1.0 kg	0.1 mg	Yes
LC-5101S	Sartorius	5.1 kg	1 mg	Yes
FCB12K01.B	Kern	12.1 kg	0.1 g	No <sup>a</sup>

<sup>a</sup> The accuracy was verified by E2 transfer weights (5 kg, 100 g).



reduce electrostatic charges, and to remove dust and lint in parallel.

**2.5.3 Uncertainties.** For all calibrated balances, the measurement uncertainty is available from the calibration certificate. In the case of UMT2 balance, calibration was achieved using the certified conventional values of the E2 weights as brackets to correct the reading of the sample by a simple linear interpolation. In the case of balance H315, a standard uncertainty of 0.0005 g is used, which was estimated from the upper tolerance levels of repeatability and linearity.

**2.5.4 Buoyancy correction.** Due to the underlying physics, the displayed value  $W$  ("weighing value"), is not identical to the absolute mass of the sample,  $m$ . Buoyancy, the causative effect, makes a sample appear lighter than it should if its density is lower than the density of the calibration mass of the balance (typically made from steel). For example, native magnesium (density 1738 kg m<sup>-3</sup>) under standard ambient conditions (20 °C, 1013 hPa, 50% rel. humidity) would appear 0.54‰ lighter than its true mass on a balance calibrated with a steel weight of 8000 kg m<sup>-3</sup> density. By contrast, a sample of gold (density 19 300 kg m<sup>-3</sup>) would appear heavier on this balance by 0.088‰ under the same conditions. In order to obtain absolute masses, the weighing values need to be corrected for the influence of buoyancy of the surrounding medium, typically air. For transformation of a weighing value,  $W$ , into a true mass  $m$ , a buoyancy correction factor  $K$  has to be calculated, such that:<sup>23</sup>

$$m = KW \quad (1)$$

This correction factor can be readily calculated once the densities of sample ( $\rho_i$ ) and calibration weight ( $\rho_{\text{cal}}$ ) are known, together with the air densities during calibration ( $\rho_{\text{air1}}$ ) and weighing ( $\rho_{\text{air2}}$ ):

$$K = \frac{\left(1 - \frac{\rho_{\text{air1}}}{\rho_{\text{cal}}}\right)}{\left(1 - \frac{\rho_{\text{air2}}}{\rho_i}\right)} \quad (2)$$

For the calculation of air densities as a function of climate data, a number of fitting functions exist. The following function is based on one of the most comprehensive data analyses to date,<sup>24</sup> and has been applied in this work to calculate air densities from climate data:

$$\rho_{\text{air}} = \frac{0.348444 \text{ kg m}^{-3} \text{ hPa}^{-1} \times p - \varphi(0.252 \text{ kg m}^{-3} \text{ }^\circ\text{C}^{-1} \times \vartheta - 2.0582 \text{ kg m}^{-3})}{273.15 + \varphi \text{ }^\circ\text{C}^{-1}} \quad (3)$$

For determination of climate data at BAM, a calibrated device was used (Greisinger digital hydro-/thermo-/barometer GFTB200, GHM Messtechnik GmbH). At PTB, a calibrated reference measuring instrument (Testo 650 Testo AG, Lenzkirch, Germany) was used.

## 2.6 Determinations of solid and liquid densities

**2.6.1 Densities of solids.** Densities of solids were determined based on the hydrostatic method. According to this principle, a buoyant body loses as much of its apparent weight when immersed into a liquid as the weight of the liquid it replaces. In principle, two weighings of the sample body have to be conducted using this protocol: one weighing in air, and one weighing in a flotation liquid, which is chosen based on the expected density of the sample. The method is described in detail in ref. 25. Determinations for this work were conducted at PTB according to the SOP<sup>26</sup> on a Mettler AT1005 balance using E1 and E2 calibration weights.

**2.6.2 Densities of liquids.** Densities of liquids were determined at both PTB and BAM with quartz pycnometers, using the density of ultra-pure, air-saturated water as the reference value, which is known with high accuracy as a function of temperature.<sup>27–29</sup> Since the density of the sample solution is not yet known, a buoyancy correction of the weighing value cannot be conducted at first to determine the solution's mass. On the other hand, to determine the density from the solution's mass, the buoyancy correction of the weighing value would need to be conducted. A solution can be obtained mathematically, since enough information is already available in the combination of experimental data, and the set of coupled equations that describe the problem. The evaluation and formulae for this procedure are described elsewhere.<sup>30,31</sup> Using these formulae, a complete uncertainty budget can be setup using the GUM Workbench.

## 2.7 Liquid chemicals and reagents

**2.7.1 Ultrapure water.** Water used for the preparation of solutions and for cleaning the labware was obtained from a Milli-Q Advantage A10 unit (Merck Millipore). The unit is fed with de-ionized water. The electrical resistance of the ultrapure water was 18.2 MΩ cm (5.5 × 10<sup>-6</sup> S m<sup>-1</sup>) or better at 25 °C. The Mg blank level in this water is ≤12 pg g<sup>-1</sup>. Other impurities determined in the water are listed in Table S1 of the ESI.†

**2.7.2 Ultrapure acids.** Two mineral acids were used in this work: nitric acid (HNO<sub>3</sub>) as the solvent for digestion of magnesium metal, dilutions and mixing; and hydrochloric acid (HCl), which was used in chromatographic zinc separation during the analytical determination of purity using IDMS (see below). Pure specimens of both acids were obtained by two-

staged distillation under subboiling conditions of commercially available 0.65 g g<sup>-1</sup> HNO<sub>3</sub> and 0.32 g g<sup>-1</sup> HCl of analytical grade (Fisher Chemical).

The trace levels of the acids were later tested using ICPMS; for this purpose, the acids were concentrated by a factor of more than 10 using evaporation. The Mg blank level was determined



as 19 pg g<sup>-1</sup> for HNO<sub>3</sub> and 48 pg g<sup>-1</sup> for HCl. Other impurities are listed in Table S1 of the ESI.†

## 2.8 Analytical determination of impurities

**2.8.1 Impurity determination in solids.** During optimization of the sublimation parameters for magnesium, glow discharge mass spectrometry (GDMS) was used for rapid assays. GDMS allows determination of the trace levels – and their relative changes – directly in the solid samples, without the need for prior sample preparation. In this work, however, GDMS was only applied for rapid assays; since matrix-adapted calibration could only be conducted for a few impurities due to the lack of suitable reference materials, results should only be interpreted as guidance to deduce relative purification factors. Due to this fact, the absolute values for impurities obtained by GDMS shown in this work can easily be wrong by a factor of 2.

All GDMS results shown here were obtained using the instrument “Element GD” (Thermo Fisher Scientific). This instrument is equipped with a Grimm type high flow ion source, which was used in constant current mode at an Ar<sup>+</sup> ion current of 70 mA. Before the start of each measurement sequence, the sample was pre-sputtered to clean the sample surface from oxide layers and adsorbed impurities. A measurement sequence typically consisted of five to ten measurements in DC source mode. All mass fraction data are calculated from the ion beam ratios based on relative sensitivity factors.<sup>32</sup> For some elements, calibrations using internal reference materials (BAM AKP207 & 208) were conducted.

Magnesium shows a tendency to spark in the GD source, which leads to material overload in the mass spectrometer and unspecific, transient signal spikes of the material that can saturate the mass spectrometer and detector, and thereby severely influence the integrated detector signal, specifically of low-content impurities.<sup>32</sup> Such sparks, however, only show up in the signal of one isotope every tenth to hundredth sample, and can be easily spotted as outliers, since the intensity spikes are drastic.

Since the sublimated Mg samples are too small for the standard sample holder of the Element GD instrument, they were compressed into steel disk sample holders (BAM, I.D. 11 mm) using a hydraulic press (90 kN, 1 min). The steel piston of this press tool was carefully cleaned after each sample.

**2.8.2 Impurity determination in analytical solutions.** Unlike the natural magnesium, the expensive isotopically enriched materials could not be analysed using GDMS, since GDMS consumes prohibitive amounts of the material due to the high sputtering rates. Instead, analytical solutions were prepared in this case, which were analysed by ICPMS.

All ICPMS analyses were performed on sector field single collector instruments of type Element XR or Element 2 (Thermo Fisher Scientific). Instrument Element 2 is equipped with a jet interface, while the Element XR offers an additional Faraday cup detector (intensity range up to 10<sup>12</sup> s<sup>-1</sup>). Both instruments were used in standard configuration applying an ASX-520 autosampler (CETAC Technologies), a MicroMist nebulizer (200 μL min<sup>-1</sup>), and a cyclonic spray chamber (both

GlassExpansion). For external calibration, a commercial multi-element standard (ICP IV standard, Merck) and in-house prepared multi-element standards were used. Standard addition was conducted for selected elements using mono-elemental solutions of the same sources. Yttrium was used as an internal standard (Merck Certipur).

**2.8.2.1 Zinc quantification by IDMS.** In the case of the most abundant impurity in the isotopically enriched magnesium materials, zinc, standard calibration techniques provided insufficient degrees of uncertainty; in this case, isotope dilution mass spectrometry (IDMS) was applied as the reference method using the double IDMS calibration approach.<sup>33,34</sup>

For this purpose, an existing protocol for the quantification of zinc in aluminium was modified particularly for the separation of Zn from the metallic matrix. The analyte, Zn, is separated from the matrix, Mg, using anion exchange chromatography (mini-column AG 1-X8, chloride form, 200–400 mesh, Bio-Rad Laboratories Inc.), where Zn is retained as chloride complex in hydrochloric acid solution, while the Mg matrix runs through. The Zn was completely separated from Mg with near quantitative recovery (>90%). The IDMS analysis was conducted using a <sup>67</sup>Zn spike, which was calibrated against an in-house primary calibration solution prepared from a high-purity material (candidate BAM-Y014). The <sup>66</sup>Zn/<sup>67</sup>Zn isotope ratios were measured using instrument Element 2 in standard configuration and medium resolution mode. The isotope ratio reproducibility was 0.3%. Uncertainty calculations were carried out based on the double IDMS equation using GUM Workbench.

## 3. Design of the approach: minimize uncertainty

### 3.1 Uncertainty budget

The resultant values in this project are the masses (after purity-correction) of each isotopically enriched material in the binary mixtures. Those values and their uncertainties are to be calculated using GUM Workbench; they are based on the following input quantities:

- Weighing values measured by calibrated balances,
- Solid and liquid densities,
- Climate data (temperature, pressure, and relative humidity), and
- Total purity of the isotopically enriched materials.

Those mass ratios of the enriched materials in the binary mixtures together with the isotopic enrichments (which need to be determined in a second project based on mass spectrometry) result in the gravimetric isotope ratios, which are required for the calibration of the mass spectrometers in the second part. At this point, the isotopic enrichments of the commercial “<sup>24</sup>Mg”, “<sup>25</sup>Mg” and “<sup>26</sup>Mg” materials will be determined using the recent analytical solutions to the underlying equation system,<sup>8</sup> and in addition, using the established iterative approach.

This shows that the uncertainty of the mass ratios of the enriched materials in the binary mixtures predetermines the uncertainty of the gravimetric isotope ratios, and consequently the uncertainties of the *K*-factors obtained in the calibration



approach by synthetic isotope mixtures (binary mixtures). Therefore, the uncertainties of all quantities listed above have to be minimized. This requires an optimization of the dilution and blending procedures.

### 3.2 Constraints

In the minimization of the relative uncertainties of the binary mixtures used for calibration, two primary constraints had to be obeyed in this project:

- (1) The available amount of isotopically enriched materials, and
- (2) The available balances with their maximum loads, and their relative uncertainties.

The enriched magnesium materials, 200 mg each, had been purchased prior to this project. Thus, this value was considered as a fixed constraint to be used in the design of minimizing the overall uncertainty for the binary mixtures. This meant to minimize the uncertainty of the purity statement, as well as to achieve the best possible weighing results for determining the absolute mass of the isotopically enriched materials and the absolute masses of all dilutions and blending. For this purpose, we have applied the best available commercial balances whenever possible: e.g. Mettler-Toledo UMT-2 for weighing the sublimated isotopes, Mettler-Toledo AX-205 for dilutions and Sartorius LC-5101S for preparing diluted acids.

Additionally, the absolute amounts and mass fractions of parent solutions and intermediate dilutions were designed to make use of the maximum possible range of the best available balance; the approach was designed not to exceed the maximum load of this best possible balance, in order not to be forced to use a balance with larger maximum load, but lower relative accuracy.

## 4. Results

### 4.1 Preparatory work

A number of preparatory steps are named briefly in this section; extended descriptions have been moved to the ESI.† Preparations of dilute acids are described in section S2 in the ESI,† including tables about the exact mass fractions of the acids used and associated uncertainties. Determinations of densities of liquids and solids (for buoyancy correction) are described in section S3 in the ESI,† including tables of results and associated uncertainties.

### 4.2 Purification of magnesium isotopes; weighing

**4.2.1 Initial impurities of isotopically enriched Mg materials.** The impurity levels as stated by ORNL were either too inaccurate (17 mg kg<sup>-1</sup> zinc in the “<sup>26</sup>Mg” material, which turned out later to be too low by a factor of 100) or too imprecise for our purpose (zinc in the “<sup>24</sup>Mg” material denoted simply as “<500 mg kg<sup>-1</sup>”, which later turned out to be 52 mg kg<sup>-1</sup>). Therefore, a screening of all impurities, with a focus on zinc and cadmium, was carried out on the isotopically enriched materials (as delivered by ORNL) before purification. For this purpose, 5 mg aliquots of each material were analysed using

ICPMS standard addition and external calibration assays. Most impurities were found in the low mg kg<sup>-1</sup> range or below, while zinc and cadmium – together with the levels of other possible impurities – were significant. The zinc level in “<sup>24</sup>Mg” was 130 mg kg<sup>-1</sup>, in “<sup>25</sup>Mg”: 520 mg kg<sup>-1</sup>, and in “<sup>26</sup>Mg”: 1580 mg kg<sup>-1</sup> ( $U_{\text{rel}}(k=2) \approx 20\%$ ). Cadmium levels were: 9.3 mg kg<sup>-1</sup> (in “<sup>24</sup>Mg”), 44 mg kg<sup>-1</sup> (in “<sup>25</sup>Mg”), and 80 mg kg<sup>-1</sup> (in “<sup>26</sup>Mg”) ( $U_{\text{rel}}(k=2) \approx 10\%$ ).

**4.2.2 Optimization of sublimation conditions.** To find the optimal conditions for Mg purification by HV-sublimation, commercial native magnesium was selected as the test material, intentionally with a purity of  $\approx 0.99 \text{ g g}^{-1}$ . It was assumed that the impurities present in this test material would constitute something like the “worst case” scenario that could conceivably be faced later during the purification of the isotopically enriched materials, although the actual identity of the most abundant impurities might differ. This test magnesium also contained high amounts of zinc (approx. 45 mg kg<sup>-1</sup>), but only insignificant amounts of cadmium (1 mg kg<sup>-1</sup> or below). Other major impurities in this test material were typical impurities found in many technical magnesium samples (although not necessarily in the isotopically enriched materials): Si, Pb, Mn, Ca, and Fe – among others. To test the removal of those impurities, this sample was subjected to quantitative sublimation in the apparatus described above, and the removal of the impurities was characterized as a function of sublimation conditions (most importantly, sublimation temperature and number of sublimation cycles).

Approx. 200 mg of the test material was used for each round of test sublimation (the same amount as in the sublimation of the enriched materials). The test material was filled into the sublimation dish (vitreous carbon crucible with the top lid); the sublimation dish was transferred into the sublimation chamber, evacuated ( $<10^{-7}$  hPa), and then heated for 15 min to below 300 °C to remove adsorbed air and moisture; then, the temperature was increased to the sublimation condition, where it was held constant for a predetermined period. The purified material was collected as a condensate at the top lid of the vitreous carbon crucible, forming a disk of approx. 8 mm in diameter. Sublimation was always conducted quantitatively; the

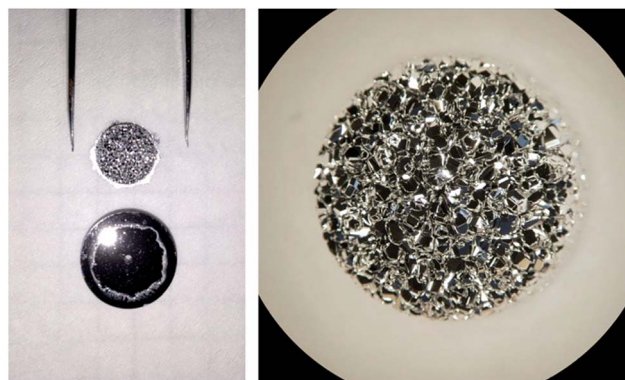


Fig. 3 Sublimate disk of magnesium (approx. 8 mm in diameter). Left: after removal from the lid. Right: microscopic image.





time to achieve quantitative sublimation was extrapolated from a number of incomplete sublimations in the first stage of those tests. A photo of the lid with the removed condensate disk and a microscopic image of a typical condensate disk are shown in Fig. 3.

GDMS was used to determine the purity of the test material and the condensates obtained during the test sublimations; details of the GDMS analysis of magnesium specimen can be found in Section 2.8 and in ref. 32.

All data considered here are from the initial fraction of the sublimation (the fraction that condensed first, in direct contact to the vitreous carbon lid), but agree with the data observed at the flipside of the condensate disk, except for Zn (where a slight fractionation over the course of sublimation is observed); approx. 60 s pre-sputter time was allowed for the GDMS to remove possible contaminants of the compression tool from the sample. The conversion from signal intensity to mass fraction was based on Mg reference materials where certified values for the impurity were available, and based on standard-RSF otherwise. This is completely sufficient for following the purification by individual sublimation cycles.

The test material was found to contain 15 impurities at levels above  $1 \text{ mg kg}^{-1}$ , which were focused on during the optimization. Parameters initially tested for their influence on the purification result were the sublimation temperature and the number of sublimation cycles.

#### 4.2.2.1 Influence of sublimation temperature on purification.

The practical sublimation temperature depends on the time it takes for quantitative sublimation, and on the purification result. Very high temperatures are expected to prevent the formation of a suitable temperature gradient and thus degrade the quantitative collection and the purification. On the other end of the scale, at the lowest practical sublimation temperature,  $510^\circ\text{C}$  at the reference point, it needed more than 30 h to quantitatively sublimate the 200 mg Mg. With the highest tested temperature, close to  $570^\circ\text{C}$ , sublimation was completed in 5 h. The recoveries of all tested conditions were typically  $>98\%$ .

Fig. 4 shows the purity of the condensed magnesium as a function of sublimation temperature and compared to the raw material (at the left side). The trace levels of most impurities were reduced to  $\leq 1 \text{ mg kg}^{-1}$  after just one cycle, at any viable temperature. Very obviously, the purification result depends only marginally on the temperature; and very clearly, temperatures towards the high end of our scale, where sublimation is fastest, do not result in deterioration of the separation result compared to the low temperatures, where sublimation is slow. Therefore, it was concluded to use  $560^\circ\text{C}$  at the reference point ( $\approx 510^\circ\text{C}$  inside the crucible) as a viable sublimation temperature.

4.2.2.2 Influence of number of cycles on purification. The effect of repeated sublimation on the purity of the condensed magnesium is shown in Fig. 5. While the results indicate that additional purification cycles can improve the purification result, the effect of later sublimation cycles compared to the first cycle is small. Since, however, the recovery per cycle is close to 100%, it was decided to use five sublimation cycles at  $560^\circ\text{C}$ .

4.2.3 Removal of metals with similar properties. The experiments plotted in Fig. 4 and 5 show that the mass fraction

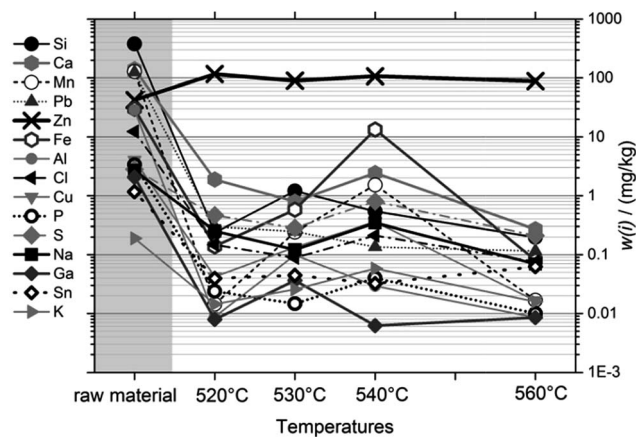


Fig. 4 Purification, presented as the mass fractions of 15 impurities, as a function of sublimation temperature. Temperatures given were measured at the reference point.

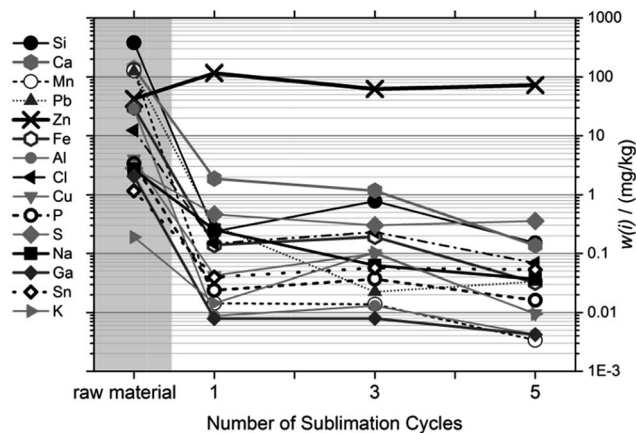


Fig. 5 Purification as a function of the number of sublimation cycles. All sublimations at  $520^\circ\text{C}$  at the reference point.

of one of the tested impurities, zinc, was not altered significantly; not shown is the level of cadmium (which was below  $1 \text{ mg kg}^{-1}$  in this test material, but is high in the isotopically enriched materials); this impurity also was found not to be removed during those sublimations. Those two impurities belong to a class of metals that are very similar to magnesium in their sublimation behaviour (metal vapour pressures as a function of temperature<sup>35</sup>).

The removal of zinc and cadmium in a sublimation process alone could not be improved significantly by a variation of the approaches (such as long-time tempering slightly below sublimation condition to allow the zinc and cadmium to transfer from the magnesium matrix to the surface, followed by fractional sublimation with discarding the initial 10% of material, or other such physicochemical approaches); it appears that gas phase thermodynamics of magnesium, zinc and cadmium are too similar. Also, the removal of the slightly lower-boiling zinc from the liquid phase magnesium (distillation) was not successful: magnesium was melted in the crucible in an inert (argon) atmosphere; however, the loss of magnesium was high,



while the purification concerning zinc was negligible. Alternative approaches to the physical methods were briefly tested, such as the approach to capture zinc (and cadmium) using possible alloying components, which melt below the sublimation temperature, but evaporate at much higher temperatures; the metal tested is tin. While the experiments indicate that this approach could scavenge up to approx. 25% of the zinc content in one cycle, the loss of material was high (20%), and not justifiable by the performance.

As none of the tested approaches yielded a significant separation efficiency for zinc and cadmium with a good recovery in parallel, it was decided to better quantify those two levels after the purification using sufficiently precise analytical techniques: IDMS was chosen as the method to determine the zinc content, while for cadmium and all other impurities, external calibration ICPMS was considered to be sufficiently accurate.

**4.2.4 Actual sublimation and determination of mass.** The three enriched magnesium materials were each purified by five sublimation cycles, with recoveries larger than 96% per cycle; the recovery over all five cycles (first-to-last) was above 88.5%. The corresponding data are compiled in Table S6 in the ESI.†

After the last sublimation cycle, the mass of the sublimate disk was determined by using the ultra-fine balance UMT2. This value is one of the most important resultant values in this project and was determined with utmost care. The enriched

magnesium materials are expected to be virtually free from oxygen and other reactive gases after the high-vacuum sublimation. In order to prevent oxygen from reacting with the magnesium, the following steps (after the sublimation) were all carried out using oxygen-free argon.

The timing of steps during sublimation, and until the finishing of weighing, was carried out using a precise time protocol; the steps following the completion of sublimation were carried out with time precision better than 1 min. After the heating had been switched off, the sample was left to cool for 60 min before the vacuum was broken. Switching off the pumps and venting the system with argon took another 14 min before the top lid of the sublimation apparatus was removed. The vitreous carbon crucible was then transferred to the operating desk in a stream of flowing argon; the top lid was lifted up and the condensate was removed from the lid using a steel forceps – all protected by a flowing argon atmosphere. The free sample was then visually inspected to be free from sublimation residue and other particles, and then transferred to a cleaned PFA jar, that was filled with argon, and closed. The whole process from opening the sublimation apparatus to the PFA jar being closed was engineered to take 2 min. The sample in the PFA jar was then transferred to the balance room, where it was put next to the balance for another 17 min to acclimatize.

Table 3 Determination of the final masses of the isotopically enriched materials

	<sup>24</sup> Mg <sup>a</sup>	<sup>25</sup> Mg <sup>a</sup>	<sup>26</sup> Mg <sup>a</sup>
Weighing date	28/01/2014	29/01/2014	27/01/2014
Weighing	Weighing values		
1	177.2927 mg	173.1579 mg	181.7187 mg
2	177.2928 mg	173.1582 mg	181.7188 mg
3	177.2929 mg	173.1583 mg	181.7186 mg
4	177.2929 mg	173.1584 mg	181.7181 mg
5	177.2932 mg	173.1587 mg	181.7182 mg
6	177.2934 mg	173.1586 mg	181.7181 mg
7	177.2930 mg	173.1592 mg	181.7180 mg
8	177.2930 mg	173.1587 mg	181.7179 mg
9	177.2927 mg	173.1586 mg	181.7177 mg
10	177.2925 mg	173.1588 mg	181.7181 mg
Average ( $N = 10$ )	177.29291 mg	173.15854 mg	181.71822 mg
$s$ ( $k = 1$ )	0.00026 mg	0.00036 mg	0.00036 mg
$W$ after interpolation	177.29363 mg	173.15923 mg	181.71931 mg
Air density	1.17625 kg m <sup>-3</sup>	1.18258 kg m <sup>-3</sup>	1.16970 kg m <sup>-3</sup>
Solid density	1707.3 kg m <sup>-3</sup>	1777.4 kg m <sup>-3</sup>	1848.7 kg m <sup>-3</sup>
Correction factor $K$	1.0005527 g g <sup>-1</sup>	1.0005282 g g <sup>-1</sup>	1.0004971 g g <sup>-1</sup>
$m$ after correction	177.39162 mg	173.25068 mg	181.80965 mg
$U$ ( $k = 2$ ) after corr.	0.0047 mg	0.0047 mg	0.0046 mg
Certificate (E2)		Transfer weights, masses determined ( $N = 10$ )	
$m_c = 20.004^a$ mg	20.00360 mg	20.00385 mg	20.00342 mg
$U$ ( $k = 2$ ) = 0.003 mg			
$m_c = 99.995^a$ mg	99.99381 mg	99.99370 mg	99.99341 mg
$U$ ( $k = 2$ ) = 0.005 mg			
$m_c = 500.004^a$ mg	499.99585 mg	499.99629 mg	499.99578 mg
$U$ ( $k = 2$ ) = 0.008 mg			

<sup>a</sup> Conventional mass.



Three calibration weights (20 mg, 100 mg, and 500 mg) of OIML class E2 were weighed ten times each during idle time less than one hour before the weighing of each magnesium sublimate disk. Thereafter, weighing of the sublimate disks started. Ten values were recorded in the first round, followed by a second round immediately thereafter. All twenty values exhibited no linear drift (which could be an indication either for balance instabilities or for reactions with air – e.g. oxidations). Table 3 lists the first ten values, which were used to determine the absolute mass of the three isotopically enriched materials. Those ten weighings were averaged, recalibrated using the bracketing and interpolation approach described in Section 2.5.3 (based on the E2 external weights), and finally corrected for the influence of buoyancy using the method described above to yield the physical mass. The ten individual weighing values, their average and standard deviations, the air densities calculated based on the recorded climate data, and the resultant buoyancy correction factors are compiled in Table 3; also compiled is the resultant mass of each isotope. The individual weighing values for each material do not exhibit a detectable trend, which could be due to effects such as temperature change, reactions with oxygen or moisture, possible uptake of dust, or the loss of substance due to the handling in between each weighing step. This fact is reflected in small standard

deviations between the individual weighings, which are much lower than the respective balance uncertainties.

Table 3 also compiles uncertainties  $U$  (for  $k = 2$ ) based on the UMT2 balance calibration using the E2 weights as discussed in Section 2.5.3. The weighing values, the certified conventional masses and the expanded uncertainties of the E2 weights are also listed in Table 3.

For the three masses of the enriched materials, the resulting expanded uncertainty  $U$  ( $k = 2$ ) was equal or less than 0.0047 mg in all cases based on the calibration.

### 4.3 Dissolution, and preparation of primary stock solutions

After weighing, the purified materials were immediately transferred into PFA containers using the same PE forceps applied during weighing (to move the materials onto and away from the ultra-fine balance tray). Prior to the transfer of the materials, the empty PFA bottles had been weighed ten times using balance AX-205; climate data have been recorded and buoyancy was corrected using the published value for PFA and FEP density ( $2.150 \text{ kg m}^{-3}$ , DuPont<sup>21,22</sup>).

The magnesium metal was dissolved under mild conditions using dilute nitric acid ( $0.06 \text{ g g}^{-1} \text{ HNO}_3$ ); the following aspects were considered: the reaction between  $\text{HNO}_3$  and magnesium

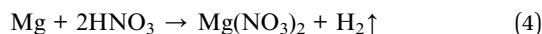
Table 4 Dissolution of the isotopically enriched magnesium materials

	<sup>24</sup> Mg <sup>a</sup>	<sup>25</sup> Mg <sup>a</sup>	<sup>26</sup> Mg <sup>a</sup>
Mass PFA bottle/g, $N = 10$	68.607305	68.141224	68.271606
Mass of Mg metal/g, $N = 10$	0.1773916	0.1732507	0.1818097
<b>Setup calculations</b>			
Target total mass/(g)	177.392	173.251	181.810
Mg target mass fraction/( $\mu\text{g g}^{-1}$ )	1000	1000	1000
$\text{HNO}_3$ target mass fraction/( $\text{g g}^{-1}$ )	0.020	0.020	0.020
Required $\text{HNO}_3$ (dissolution)/g	0.9321	0.8744	0.8822
Required $\text{HNO}_3$ (final sol.)/g	3.5479	3.4651	3.6363
Sum required mass of $\text{HNO}_3$ /g	4.4800	4.3395	4.5184
Required mass $0.06 \text{ g g}^{-1} \text{ HNO}_3$ <sup>a</sup> /g	74.692	72.349	75.333
<b>Actual setup, <math>\text{HNO}_3</math> addition</b>			
Mass of $0.06 \text{ g g}^{-1} \text{ HNO}_3$ /g	74.7452	72.3888	75.4209
Mass $\text{HNO}_3$ after digestion <sup>b</sup> /g	74.7138	72.3562	75.4028
Expected mass loss due to $\text{H}_2$ /g	0.0149	0.0140	0.0141
Obs. additional mass loss <sup>c</sup> /g	0.0165	0.0186	0.0039
<b>Actual setup, fill-up with water</b>			
Mass of water added/g	102.803	100.965	106.557
$W_{\text{total}}$ , bottle + solution/g	246.085	241.431	250.201
Total mass of solution/g	177.687	173.494	182.142
<b>Final solution before 1<sup>st</sup> use</b>			
$W_{\text{total}}$ , bottle + solution/g	246.0391	241.4227	250.1934
Total mass of solution/g	177.6399	173.4850	182.1342
Purity, enriched material/( $\text{g g}^{-1}$ )	0.999909	0.999740	0.998953
Mg mass fraction/( $\text{mg kg}^{-1}$ )	998.5113	998.3924	997.1760
$\text{HNO}_3$ mass fraction/( $\text{g g}^{-1}$ )	0.019995	0.019992	0.019996

<sup>a</sup> Based on the mass fraction of  $0.06 \text{ g g}^{-1} \text{ HNO}_3$ : ( $5.9979 \pm 0.0082$ )  $\text{g cm}^{-3}$ . <sup>b</sup> Weighing value of solution after digestion minus the mass of magnesium contained in the solution. <sup>c</sup> Mass difference between acid filled in and mass of acid determined later minus the calculated stoichiometric mass loss due to  $\text{H}_2$  loss.



follows eqn (4) under mild conditions, with virtually no alternative reactions – such as HNO<sub>3</sub> decomposition, as confirmed in prior test runs:



The magnesium is oxidized by the protons, which are reduced and are transformed into the gaseous hydrogen (H<sub>2</sub>), which leaves the reaction vessel. The other product is magnesium nitrate Mg(NO<sub>3</sub>)<sub>2</sub>. In essence, two molecules of HNO<sub>3</sub> are consumed per magnesium atom. Consequently, this reaction changes the pH value of the solution. This has to be accounted for when aiming at a final acid strength of 0.02 g g<sup>-1</sup> HNO<sub>3</sub>. For this purpose, the stoichiometric consumption of HNO<sub>3</sub> according to eqn (4) is calculated, and then the additional amount of HNO<sub>3</sub> required for achieving 0.02 g g<sup>-1</sup> HNO<sub>3</sub> in the

final solution is added. The total mass of HNO<sub>3</sub> is then converted into the required amount of 0.06 g g<sup>-1</sup> HNO<sub>3</sub> by using the exact mass fraction of the 0.06 g g<sup>-1</sup> acid (as determined in section S2.2 in the ESI†).

This calculated amount of 0.06 g g<sup>-1</sup> HNO<sub>3</sub> was added to the magnesium using PFA containers by difference weighing. The mixture was left standing overnight to complete the dissolution. Slightly brownish vapours above the liquid were observed, indicating a slight decomposition of the acid; also, some droplets of liquid condensed on the inner PFA walls due to the excess reaction heat.

After the completion of the dissolution, the weights of the solutions were determined using balance AX-205 as informational values. The resulting masses are only slightly below the expected values, which is mainly due to the loss of water and

**Table 5** Input raw data with associated uncertainties, resulting intermediate values and final mass fraction of parent solution of “<sup>24</sup>Mg” with expanded uncertainties ( $k = 2$ )

Parameter	“ <sup>24</sup> Mg”	$U^a$	Type <sup>b</sup>	Source
<b>Weighing, empty PFA bottle</b>				
$W$ (PFA bottle)/g	68.57936	0.00023	A	AX-205
Temperature $\vartheta$ /°C	21.1	2	B(n)	Upper bound
Rel. humidity $\varphi$ /%	29.6	6	B(n)	Upper bound
Abs. pressure $p$ /hPa	1014.1	10	B(n)	Upper bound
$\rho_{\text{PFA}}$ /(kg m <sup>-3</sup> )	2150	100	B(r)	Upper bound
$\rho_{\text{cal}}$ /(kg m <sup>-3</sup> )	8000	100	B(r)	Upper bound
$\rho_{\text{air}}$ /(kg m <sup>-3</sup> )	1.198	0.015	R	Eqn (3)
Buoyancy corr. $K$ /(g g <sup>-1</sup> )	1.000408	0.000030	R	Eqn (2)
$m$ (PFA bottle)/g	68.6073	0.0021	R	Eqn (1)
<b>Weighing, purified, enriched <sup>24</sup>Mg isotope</b>				
$W$ (“ <sup>24</sup> Mg” material)/g	0.17729363	0.00000468	A	UMT-2
Temperature $\vartheta$ /°C	22.4	2	B(n)	Upper bound
Rel. humidity $\varphi$ /%	18.8	6	B(n)	Upper bound
Abs. pressure $p$ /hPa	999.6	10	B(n)	Upper bound
$\rho$ (“ <sup>24</sup> Mg” material)/(kg m <sup>-3</sup> )	1707	17	B(n)	PTB meas.
$\rho_{\text{cal}}$ /(kg m <sup>-3</sup> )	8000	100	B(r)	Upper bound
Purity, $w$ (Mg)/(g g <sup>-1</sup> )	0.999906	0.000032	R	Table 6
$\rho_{\text{air}}$ /(kg m <sup>-3</sup> )	1.176	0.014	R	Eqn (3)
Buoyancy corr. $K$ /(g g <sup>-1</sup> )	1.0005423	0.0000098	R	Eqn (2)
$m$ (“ <sup>24</sup> Mg” material)/g	0.1773916	0.0000047	R	Eqn (1)
$m_{\text{net}}$ (“ <sup>24</sup> Mg” material)/g	0.1773755	0.0000062	R	Eqn (5)
<b>Total mass of solution before 1<sup>st</sup> use</b>				
$W_{\text{total}}$ (bottle + sol.)/g	246.0391	0.0010	A	H315
Temperature $\vartheta$ /°C	21.7	2	B(n)	Upper bound
Rel. humidity $\varphi$ /%	34	6	B(n)	Upper bound
Abs. pressure $p$ /hPa	1004	10	B(n)	Upper bound
$\rho_{\text{sol}}$ /(kg m <sup>-3</sup> )	1014.9	1.5	B(r)	Pycnometer
$\rho_{\text{cal}}$ /(kg m <sup>-3</sup> )	7950	50	B(r)	Upper bound
$\rho_{\text{air}}$ /(kg m <sup>-3</sup> )	1.182	0.015	R	Eqn (3)
Net $W$ (solution)/g	177.4593	0.0011	R	Difference
Buoyancy corr. $K$ /(g g <sup>-1</sup> )	1.001017	0.000013	R	Eqn (2)
$m$ (solution)/g	177.6399	0.0028	R	Eqn (1)
<b>Mass fraction of Mg before 1<sup>st</sup> use</b>				
Mg mass fraction/(mg kg <sup>-1</sup> )	998.511	0.039	R	Eqn (6)

<sup>a</sup> Uncertainties for values with normal (Gaussian) distribution are denoted for coverage factor  $k = 2$ ; values with rectangular distribution are denoted as the rectangle function's half widths. <sup>b</sup> Type A (observation), Type B: “n” denoting normal distribution, “r” denoting rectangular distribution. Type “R”: intermediate or final result.



eventually a minimal  $\text{HNO}_3$  decomposition. The solutions were filled up with ultra-pure water such that the target mass fraction of magnesium and of nitric acid was reached. Then, the total mass of solution was determined as an informational value using balance LC-5101S (which is not precise enough in this range of total mass to achieve results that are sufficiently accurate). Directly before the first use (1<sup>st</sup> dilution approach), the mass was determined again using balance H315 at PTB. Table 4 reflects all the steps and the associated data required to obtain those primary stock solutions of the enriched materials. Then, solution was withdrawn twice (once for analysis and once for dilutions).

Note that the mass fraction of magnesium in the obtained solution is purely a function of the original mass of magnesium in the bottle, its purity, and the total mass of solution. The latter is subject to change due to evaporation of the solvent, and therefore, masses before and after each withdrawal were recorded carefully to allow correction for evaporation.

Table 4 lists all calculated mass and mass fraction data directly before the first withdrawal. These data show that the mass fractions of magnesium were very close to the target of  $1000 \text{ mg kg}^{-1}$ . The nitric acid mass fraction is also very close to the target value ( $0.02 \text{ g g}^{-1}$ ); since this value mainly impacts the density (and thus buoyancy correction), it is, however, of minor significance here.

The corresponding uncertainty is calculated as described in Section 2.1 considering the following factors:

- The uncertainties of weighing values used as inputs, which are based on the balance calibration protocol for all values.
- Densities used as input for buoyancy corrections are either based on measurements (pycnometry, hydrostatic weighing) with full uncertainty budgets, or on tabulated data (PFA, balance weights, water,  $\text{HNO}_3$  other than  $0.02 \text{ g g}^{-1}$ ).
- The uncertainties of air densities are based on an uncertainty budget using eqn (3), and the uncertainties for the input values (as listed in Table 5).
- Purity of the solid magnesium, based on the analytical result (see below), including uncertainty.

The net mass of a metal is based on the weighed mass and purity:

$$m_{\text{net}} = m_{\text{gross}} \times w_{\text{pur}} \quad (5)$$

The mass fraction of magnesium in the solution is simply based on the net mass of magnesium metal, and the total mass of solution:

$$w_{\text{Mg}} = \frac{m_{\text{net}}}{m_{\text{total}}} \quad (6)$$

Table 5 lists the uncertainties used as the input to calculate the uncertainty for the parent solution of  $^{24}\text{Mg}$ .

The resulting uncertainty budget for the Mg mass fraction in the parent solution of  $^{24}\text{Mg}$  is exemplary displayed in Fig. 6 (left side); the uncertainty budgets for  $^{25}\text{Mg}$  and  $^{26}\text{Mg}$  are very similar. The Mg mass fraction in this solution has a value of  $998.511 \text{ mg kg}^{-1}$ , and an expanded uncertainty  $U$  ( $k = 2$ ) of

$0.039 \text{ mg kg}^{-1}$ , which corresponds to 0.0039% (Table 5). The single contributors are listed in Table 5. The visualization of the budget in Fig. 6 shows clearly that the major contributor to the overall uncertainty is the uncertainty associated with the weighing of the isotopically enriched materials, which accounts for 46.7% of the overall uncertainty, followed by the uncertainty of the purity of the isotopically enriched materials accounting for 29.6% of the overall uncertainty. Thus, the weighing and the purity determination of the purified, enriched materials are the limiting factor for preparing synthetic isotope mixtures in this case. All other parameters contribute no more than 25% to the total uncertainty. The overall total value of the uncertainty is excellent, as will be discussed later.

#### 4.4 Determination of purity

To this point, the masses of the enriched magnesium materials have not been corrected for the materials' actual purity, which is smaller than  $1 \text{ g g}^{-1}$ . Since not all the mass weighed out is, in fact, magnesium, the purity of the material needed to be determined to correct the data, and thereby establish the actual magnesium mass fractions in the primary solutions that have been created.

As described above, the purity of the enriched materials can only be determined in the primary solution, as no additional material can be spared for GDMS measurements, and the integrity of the sublimated materials should not be touched. Therefore, the mass fractions of 67 elements in the primary solutions were determined by ICPMS as described in Section 2.8.2. Zinc is the dominant metallic impurity in all three

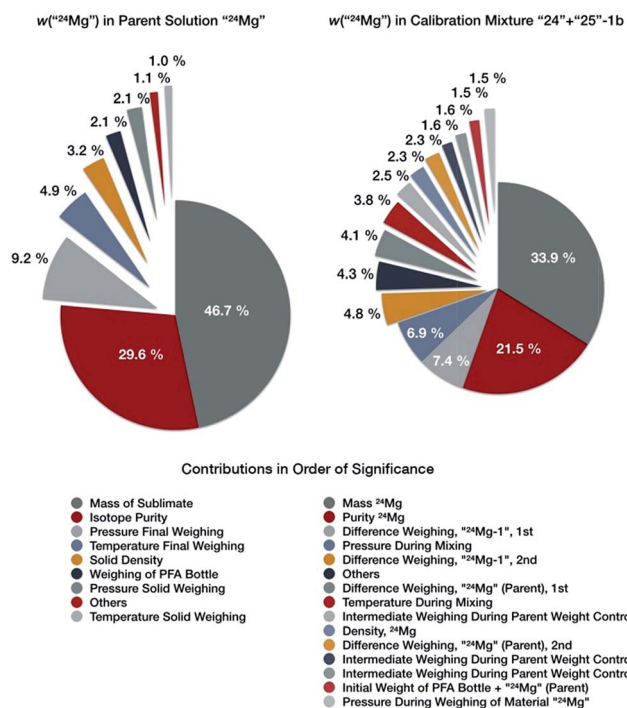


Fig. 6 Uncertainty budgets for the mass fraction of  $^{24}\text{Mg}$  in the parent solutions  $^{24}\text{Mg}$  (left), and in the binary calibration mixture  $^{24} + ^{25}\text{-1b}$  (right side).



isotopically enriched materials, and was determined by IDMS to achieve low enough uncertainties. The noble gases (He, Ne, Ar, Kr, and Xe) and hydrogen were not expected. For oxygen and nitrogen sound estimates were made, which are explained below. Carbon and halogens (F, Cl, Br, and I) were completely separated by the sublimation, which was verified by the GDMS measurements in the natural magnesium material; this applies also to yttrium, which was used as the internal standard in ICPMS. Radioactive elements (Tc, Pm, Po, At, Rn, Fr, Ra, Ac, and Pa) – besides U and Th (which have been measured) – were not expected.

The oxygen and nitrogen mass fractions cannot be quantified by ICPMS in the solutions; GDMS and other techniques such as carrier gas hot extraction are not allowed as the integrity of the purified materials should not be touched. Therefore, sound estimates were made. Generally, oxygen and nitrogen are expected to have been removed during HV sublimation (pressure around  $10^{-7}$  hPa); however, there was a risk of oxygen and nitrogen contamination by short contact to air during handling between the last sublimation and the weigh-out procedure. To preclude this, the isotopes were handled under the argon gas flow during all manipulations and were stored in argon-filled PFA jars during equilibration for weighing.

Additionally, a strictly timed protocol was adhered to, to admit all three enriched materials to the risk of coming into contact with air for the same amount of time, and thus results in similar oxygen and nitrogen uptake at trace levels, which would later cancel in their impact on the end results. The timing for all materials was as follows: backfilling the HV sublimation apparatus after cooling took 14 min; removal from the lid in flowing argon took 2 min until the sample was in the PFA jar under argon protective gas; then the jar was immediately transferred to the ultra-fine balance, and left there for 17 min for equilibration. The subsequent weighings do not indicate any systematic mass drift by a potential oxygen uptake due to the air contact during weighing (Table 3).

However, in order to account even for the small oxygen uptake during handling, data on typical oxide film thicknesses on pure magnesium in moist air were obtained from the literature, and transferred into a maximally conceivable upper limit. Nordlien and co-workers have studied the film thicknesses of magnesium oxide on freshly cleaved, pure magnesium using TEM for different conditions.<sup>36</sup> The relevant growth condition that was chosen as comparable to this work (25–30 °C, 35–55% rel. humidity, 15–60 min exposure) led to a film thickness of 25 nm, which was composed of magnesium hydroxide (0.5 kg kg<sup>-1</sup>) and magnesium oxide (0.5 kg kg<sup>-1</sup>) according to XPS measurements.

Using the dimensions of the Mg sublimate disk (diameter 8 mm, thickness 3 mm), a total surface area of 1.76 cm<sup>2</sup> could be estimated for it, which was increased to 3 cm<sup>2</sup> to account for the corrugation of the surface. With the film thickness of 25 nm, an oxide film volume of  $7.5 \times 10^{-6}$  cm<sup>3</sup>, and a film mass of 22.2 μg using the average density of MgO and Mg(OH)<sub>2</sub> (2.96 g cm<sup>-3</sup>) were obtained. The mass of oxygen in this film is 11 μg, which gives an oxygen mass fraction of 60 mg kg<sup>-1</sup> for a disk of 175 mg.

Since, however, the actual conditions in this case were less harsh, and the fresh magnesium surface has been in touch only for very short moments to dilute air, the actual amount of oxygen in the sublimate disk at the time of weighing will be much lower, and not such an extensive film. Thus, it was decided to assume a quarter of the amount (15 mg kg<sup>-1</sup>) of possible film thickness, with a relative uncertainty of 100% as maximally conceivable values. For the case of nitrogen, no literature could be found on atmospheric reactions; experience with other high purity metals lets us set a conceivable limit of ( $3 \pm 3$ ) mg kg<sup>-1</sup> for nitrogen.

Mass fractions of 68 elements were analysed; for 23 additional elements estimates were made, so that in total, mass fractions of 91 elements were used for calculation of purity. The complete list of results for all tested impurities is shown in Tables S7 and S8 in the ESI.†

The limit of detection (LOD) was calculated as three times the standard deviation of the blank, following the IUPAC definition; the limit of quantification (LOQ) was calculated as nine times the standard deviation of the blank. When a mass fraction below the LOD resulted from the measurements for a specific element, the value was set to the LOD value divided by two with a relative expanded uncertainty of 100%. Whenever a determined mass fraction of an element is above the LOD, but less than the LOQ, the value is taken as determined and an expanded uncertainty of LOQ/2 is added. The relative expanded uncertainties for mass fractions above LOQ are 30% for impurities determined by ICPMS; those for zinc, determined by IDMS, are calculated individually based on the double IDMS equation.

All individual impurities are summed up and are subtracted from ideal purity (1 g g<sup>-1</sup> = 1 kg kg<sup>-1</sup>); the individual uncertainties are propagated accordingly. The resulting purity of the purified enriched materials and the five major impurities are listed in Table 6, together with the associated expanded uncertainties.

#### 4.5 Dilution; blending to binary calibration mixtures

Dilution and blending was conducted in two campaigns. In the first campaign, the 2.5 g of the primary solutions of the enriched materials were diluted to 250 g yielding an

Table 6 Five major impurities (expanded uncertainties given in brackets) of the purified, enriched materials and resultant chemical purity with associated expanded uncertainty ( $k = 2$ )

Mass fraction/(mg kg <sup>-1</sup> )	<sup>24</sup> Mg <sup>n</sup>	<sup>25</sup> Mg <sup>n</sup>	<sup>26</sup> Mg <sup>n</sup>
Nitrogen	3(3)	3(3)	3(3)
Oxygen	15(15)	15(15)	15(15)
Sodium	3.6(1.1)	8.6(2.6)	0.38(38)
Zinc	52.20(40)	195.0(1.4)	957.4(6.1)
Cadmium	6.5(2.0)	22.5(6.7)	57(17)
Sum of all impurities	94	260	1047
$U(k = 2)$ for impurities	32	35	47
Purity $w_{\text{pur}}/(\text{kg kg}^{-1})$	0.999906	0.999740	0.998953
$U(k = 2)$ for purity/(kg kg <sup>-1</sup> )	0.000032	0.000035	0.000047



approximate mass fraction of  $10 \mu\text{g g}^{-1}$  each; those intermediate dilutions were then mixed 1 : 1, using 10 g of each stock solution, and filled up to 100 g yielding approximate magnesium mass fractions of  $2 \mu\text{g g}^{-1}$  in the three mixtures "24" + "25", "24" + "26" and "24" + "26". This was repeated three times, so that nine individual mixtures ( $3 \times$  "24" + "25",  $3 \times$  "24" + "26" and  $3 \times$  "24" + "26") resulted. The uncertainty analysis for this first campaign, however, showed that a relatively large uncertainty was introduced in the initial dilution step (where only 2.5 g of the parent solution were diluted to 250 g of intermediate dilution), which lead to an overall expanded uncertainty of 0.085% for the calibration mixtures. This uncertainty is significantly larger than the target expanded uncertainty of 0.02% aimed at in this project.

Also previously used densities of the solutions showed expanded uncertainties of 5% which were too large and contributed significantly to the overall uncertainty of the parent solution. Therefore, new densities of the solutions were determined, which are listed in Table S4 and described in section S3.1 (in the ESI†).

An improved dilution and mixing approach was created based on the experience obtained within the first campaign. The most important was that the first dilution step was not designed for optimum results. Instead, in the second approach, the dilution factor was set at 1 : 10, and this time, 10 g of parent solution were filled up to 100 g yielding magnesium mass

fractions of  $100 \text{ mg kg}^{-1}$ . Additionally, the weighings were carried out at the AX-205 balance, which offers significantly lower uncertainties in this range than the H315 balance. Difference weighing in a PFA bottle was used for this purpose. The binary mixtures were then created using the same approach as the first time (mixing 10 g of each of two intermediate solution, and fill up to 100 g), but this time starting from the ten times more concentrated intermediate solution, which resulted in ten times higher concentrations (mass fractions) in the binary mixtures than in the first round ( $20 \text{ mg kg}^{-1}$ , instead of  $2 \text{ mg kg}^{-1}$  total Mg mass fraction). The complete diluting and mixing scheme of the second improved campaign is shown in Fig. 7. Tables S9 and S10 (in the ESI†) compile representative values for the preparation of the intermediate dilutions and binary mixtures, respectively. Those tables also include relevant input uncertainties for the uncertainty budgets of one intermediate dilution (Table S9†), and one binary mixture (Table S10†) as examples; they also list the resulting values for the magnesium masses in the solutions.

The resulting masses and the associated uncertainties for all nine calibration solutions are compiled in Table 7. Those values are the final results of this project and form the only input quantities of the present work for the later calibration of the mass spectrometer, which will be described in a second publication.<sup>37</sup>

Using the optimized dilution and mixing approach, the relative expanded uncertainties for the masses in the mixtures could be reduced to values between 0.004% and 0.005%. Thus the relative expanded uncertainties for the total Mg masses in the mixtures and the mass ratios could be reduced to values between 0.0058% and 0.0069% compared to the 0.085% in the first campaign, demonstrating an improvement by a factor of more than 10. These relative expanded uncertainties meet the target uncertainty of 0.02% set for this project. This in turn means that the dilution and mixing scheme was successfully designed so that no additional significant uncertainty contributions were introduced; diluting and mixing thus did not contribute to the overall uncertainty.

## 5. Discussion

The three isotopically enriched Mg materials have been purified by high vacuum sublimation. A complete purity assessment has

### Magnesium, Isotopically Enriched Materials, Mixing Scheme

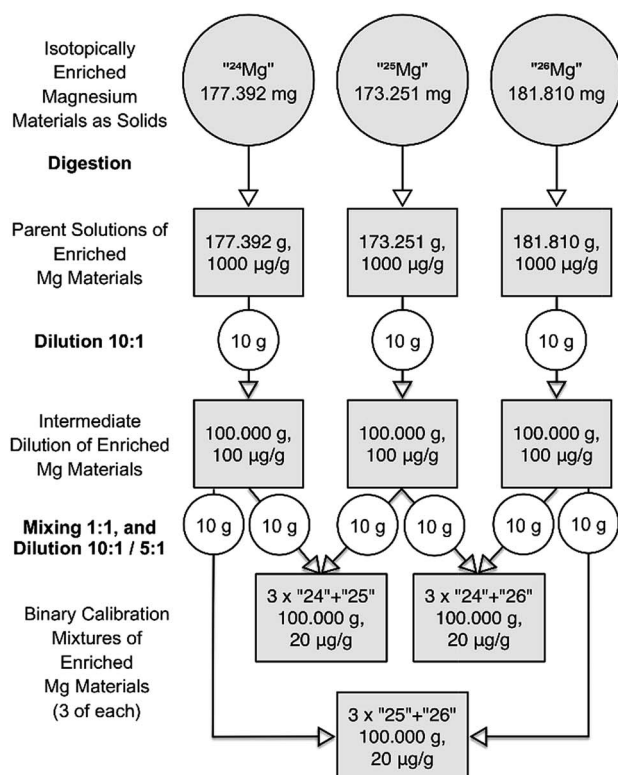


Fig. 7 Dilution and mixing scheme of the second campaign for producing the synthetic isotope mixtures.

Table 7 Masses and associated expanded uncertainties ( $k = 2$ ) of enriched magnesium materials in all binary calibration mixtures

Mixtures	<sup>24</sup> Mg	<sup>25</sup> Mg	<sup>26</sup> Mg
	<i>m</i> /mg	<i>m</i> /mg	<i>m</i> /mg
"24" + "25"-1b	1.014057(43)	1.033044(46)	
"24" + "25"-2b	1.027357(42)	1.029161(45)	
"24" + "25"-3b	1.029404(44)	1.116827(50)	
"24" + "26"-1b	1.032338(43)		1.006593(54)
"24" + "26"-2b	1.020895(43)		1.073835(57)
"24" + "26"-3b	0.998705(41)		1.028239(55)
"25" + "26"-1b		1.025770(45)	1.084446(57)
"25" + "26"-2b		0.997086(45)	0.995639(54)
"25" + "26"-3b		1.024665(45)	1.008705(53)



been applied for the first time to all three materials by using the indirect approach, where all possible impurities (91 elements) are assessed, mass fractions of the individual impurities are summed up and subtracted from ideal purity (1 kg kg<sup>-1</sup>). The determined purity was  $\geq 0.9989$  kg kg<sup>-1</sup> for all materials. The associated relative expanded uncertainties were between 0.0032% and 0.0047%, which is on par with the relative expanded uncertainties of the best primary pure substances worldwide ranging from 0.01% to 0.001%.<sup>38–40</sup> The weighing and dissolution of the enriched, purified materials were carried out such that relative expanded uncertainties for the Mg mass fraction between 0.0037% and 0.0050% could be achieved. As a comparison, primary solutions which were used for the CCQM key comparison K87 offer relative expanded uncertainties of  $\approx 0.1\%$  for elemental mass fractions of 1 g kg,<sup>41</sup> and primary standards used as back-spike in IDMS were commonly produced with relative expanded uncertainties down to 0.02%.<sup>33</sup> In the case of Mg the smallest relative expanded uncertainty being published is 0.018% and relates to the primary solution used for the CCQM key comparison K8.<sup>42</sup> Thus the primary solutions of the isotopically enriched Mg materials produced in this project are unsurpassed in their expanded uncertainty. From these primary solutions the synthetic isotope mixtures were prepared offering relative expanded uncertainties for the mass ratios between 0.0058% and 0.0069%, which has not been achieved before. Such synthetic isotope mixtures, being used as calibration solutions for MC-ICPMS, should enable the characterization and certification of Mg isotope reference materials with expanded uncertainties of  $\leq 0.02\%$  for isotope amount ratios.

Recently, an effort has been published, whose goal was to determine isotope amount ratios and the atomic weight of Mg representing bulk silicate earth *via* a double spike method using MC-ICPMS.<sup>43</sup> The preparation of a double spike, *i.e.* a mixture of two enriched isotopes, in principle is similar to the preparation of synthetic isotope mixtures. The large difference to our own project is that we have prepared calibration mixtures from *all* stable Mg isotopes, but the other authors have only used two isotopes in their double spike approach. Our approach has the advantage that all isotope ratios of magnesium can be directly calibrated *via* isotope mixtures, while Bizzarro *et al.* need to rely on auxiliary assumptions (such as the validity of mass fractionation laws, which are always simplifications, and not fully understood).

The work presented by Bizzarro *et al.* undoubtedly show Mg isotope measurements of high quality with a strong metrological emphasis. Nevertheless, there are also some deficiencies with the preparation of the double spike and the uncertainty considerations, leaving some doubts in the accuracy of the presented “absolute” isotopic composition. Our major criticism is the purity assessment of the enriched materials, which focuses on 12 elements only, selected on the basis of the ORNL assay and measured by an inadequate procedure (MC-ICPMS) in a very dilute Mg solution. Bulk oxygen impurities are not suitably addressed; the authors seem to have applied the ORNL materials without further purification. The authors make the central assumption that the impurities in both of the applied isotopically enriched materials are very similar. However, we

have worked with the exact same materials (identical batch from the same source, ORNL) in the present work – and the data presented here show clearly that those assumptions do not hold (see Tables 6, and S7 and S8†).

Also, the weighing of the enriched Mg isotopes in the cited work was denoted as “certified to the E2 level”, and resulted in uncertainties (not stated whether standard or expanded) of 0.0010 mg. These uncertainties are extremely low, considering that expanded uncertainties ( $k = 2$ ) can be as much as  $\approx 0.0053$  mg for a 100 mg weight of class E2; in fact, even the better OIML class E1 allows for an expanded uncertainty of  $\approx 0.0016$  mg for a 100 mg weight,<sup>44</sup> so that the question arises whether or not the authors actually wanted to qualify their weighing results for the magnesium isotopes as agreeing with E1 level (which would corroborate the uncertainties they state) – or more simply, whether a typing error occurred. In our work the weighing of the purified, isotopically enriched materials was carried out using the UMT2 balance, which we calibrated using E2 weights. The accordingly calculated expanded uncertainty was 0.0047 mg for masses between 170 mg and 180 mg, which is higher by a factor of nearly 5 than the uncertainties reported by Bizzarro *et al.* This also shows that the weighing uncertainty presented by those authors is not realistic for the E2 level.

Although Bizzarro *et al.* present no absolute value for the magnesium mass fraction in the double spike and its associated uncertainty, it can be assumed that the isotope mixtures presented in the present work are closer to the “true” value, because all influencing quantities have been considered and a full uncertainty budget has been calculated. Isotope amount ratios and molar mass will be compared in a follow-up publication.

We want to compare our work with a second recent work. Very recently, the determination of the atomic weight of Yb *via* synthetic isotope mixtures was published by Wang *et al.*<sup>45</sup> Three isotopically enriched Yb materials have been chemically purified, the purity has been determined, and isotope mixtures have been prepared. Based on the measurement results, complete uncertainty budgets have been provided by those authors. The only criticism is the measurement uncertainty of 0.1  $\mu\text{g}$  for the mass of the purified, isotopically enriched materials, which is far too low for a realistic uncertainty. However, this uncertainty is not important in the presented uncertainty budget, since in this case, the relatively large uncertainty of the purity determination of 0.01% dominates the overall uncertainty. This leads to a relative expanded uncertainty of  $\approx 0.026\%$  for the Yb mass fraction in the primary solutions of the enriched materials.

In our work, we achieved primary solutions of the enriched Mg materials with relative expanded uncertainties between 0.0032% and 0.0047%, which is better at least by a factor of 5. This is even more important, as our uncertainties are lower than the typical relative repeatability for Mg isotope ratio determination of 0.01%.

## 6. Conclusions

In the earliest studies only 2 isotopes were used for calibrating the mass spectrometers. In our atomic weight determination of





cadmium, we applied for the first time 7 of the 8 stable isotopes of this element for calibrating the mass spectrometer. Since then the situation has changed and studies for atomic weight determinations typically use more than 2 isotopes. Nevertheless, the work presented here is one of the rare cases where all isotopes of an element were calibrated, besides the recent work on Si.<sup>46</sup> Enriched materials for all Mg isotopes were purified, and subsequently characterized regarding their final purity. Primary solutions were prepared and blended to form binary mixtures (1 : 1 ratio) for each of the three possible binary combinations (“<sup>24</sup>Mg” + “<sup>25</sup>Mg”, “<sup>24</sup>Mg” + “<sup>26</sup>Mg”, and “<sup>25</sup>Mg” + “<sup>26</sup>Mg”). Three individual setups have been prepared under highest gravimetric control, each of them with an isotope ratio close to unity, and a target total magnesium mass fraction close to 20 mg kg<sup>-1</sup>, resulting in a total of nine calibration solutions. For this setup, relative expanded uncertainties for the Mg mass fraction in the primary isotope solutions of ≤0.005% have been achieved, and relative expanded uncertainties for the Mg masses in the binary isotope mixtures were ≤0.007%.

This work constitutes the first demonstrated case in which relative expanded uncertainties significantly below 0.01% have been achieved for the mass fractions in the binary isotope mixtures for all isotopes of an element. These solutions in turn lay the foundation for the first isotope reference material with measurement uncertainties for the “absolute” isotope ratios (isotope amount ratios), which lie in the same range as the typical reproducibility of Mg isotope ratio and delta measurements.<sup>5</sup>

This improvement also shows that the situation described previously by Vogl and Pritzkow<sup>4</sup> – broadly speaking, that only delta reference materials would serve the users’ needs – might be changed in the future for specific elements. To enable this, the measurement uncertainties still have to be lowered, which can be realised by following the setup approach described here, in combination with a more accurate weighing of the purified isotopes, e.g. by using E1 weights, and by improving the purity assessment of the isotopically enriched materials.

## Acknowledgements

Financial support by EMRP (the European Metrology Research Programme) is gratefully acknowledged (EMRP-SIB09 “Primary standards for challenging elements”).<sup>47</sup> The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union. The authors explicitly thank Heinrich Kipphardt and Wolfgang Pritzkow for helpful advice; Maren Koenig for assistance with the IDMS analyses; Dorit Becker, Ti Ha Le and Volker Görlitz for assistance with the preparative work; Andreas Schulz, Christian Meyer, Jens Pfeiffer, Alexei Plotnikov, Carola Pape and Christiane Niedergesäß for assistance with ICPMS, GDMS and density measurements. The authors also thank Joachim Hinrichs from Thermo Fisher Scientific for support with GDMS measurements.

## Notes and references

1 J. J. Thompson, *Philos. Mag.*, 1910, **10**, 752–767.

- 2 J. de Laeter, J. Böhlke, P. de Bièvre, H. Hidaka, H. Peiser, K. Rosman and P. Taylor, *Pure Appl. Chem.*, 2003, **75**, 683–800.
- 3 T. B. Coplen, *Rapid Commun. Mass Spectrom.*, 2011, **25**, 2538–2560.
- 4 J. Vogl and W. Pritzkow, *J. Anal. At. Spectrom.*, 2010, **25**, 923–932.
- 5 J. Vogl, M. Rosner and W. Pritzkow, *Anal. Bioanal. Chem.*, 2013, **405**, 2763–2770.
- 6 A. O. Nier, *Phys. Rev.*, 1950, **77**(2), 789–793.
- 7 W. Pritzkow, S. Wunderli, J. Vogl and G. Fortunato, *Int. J. Mass Spectrom.*, 2007, **261**, 74–85.
- 8 G. Mana and O. Rienitz, *Int. J. Mass Spectrom.*, 2010, **291**, 55–60.
- 9 *Report of the 5th meeting of the Consultative Committee for Amount of Substance (CCQM)*, Bureau International des Poids et Mesures (BIPM), 1999, Online available, <http://www.bipm.org/utis/en/pdf/CCQM5-EN.pdf>.
- 10 J. Black, Q.-Z. Yin and W. Casey, *Geochim. Cosmochim. Acta*, 2006, **70**, 4072–4079.
- 11 K. Ra and H. Kitagawa, *J. Anal. At. Spectrom.*, 2007, **22**, 817–821.
- 12 A. Galy, E. Young, R. Ash and R. O’Nions, *Science*, 2000, **290**, 1751–1753.
- 13 B. Shen, J. Wimpenny, C.-T. Lee, D. Tollstrup and Q.-Z. Yin, *Chem. Geol.*, 2013, **356**, 209–214.
- 14 T. Bohn, T. Walczyk, L. Davidsson, W. Pritzkow, P. Klingbeil, J. Vogl and R. Hurrell, *Br. J. Nutr.*, 2004, **91**, 113–120.
- 15 E. J. Catanzaro, T. J. Murphy, E. L. Garner and W. R. Shields, *J. Res. Natl. Bur. Stand., Sect. A*, 1966, **70**, 453–458.
- 16 A. Galy, O. Yoffe, P. Janney, R. Williams, C. Cloquet, O. Alard, L. Halicz, M. Wadhwa, I. Hutcheon, E. Ramon and J. Carignan, *J. Anal. At. Spectrom.*, 2003, **18**, 1352–1356.
- 17 J. Vogl, W. Pritzkow and P. Klingbeil, *Anal. Bioanal. Chem.*, 2004, **380**, 876–879.
- 18 V. Chang, A. Makishima, N. Belshaw and R. O’Nions, *J. Anal. At. Spectrom.*, 2003, **18**, 296–301.
- 19 Joint Committee for Guides in Metrology (JCGM/WG 1), *Evaluation of measurement data – Guide to the expression of uncertainty in measurement*, JCGM, 2008.
- 20 *Metrodata GmbH, GUM Workbench Pro 2.4.1.375*, Weil am Rhein, 2009.
- 21 *Teflon FEP Fluoroplastic Film Properties Bulletin*, DuPont, Wilmington, DE, USA, 2013.
- 22 *Teflon PFA Fluoroplastic Film Properties Bulletin*, DuPont, Wilmington, DE, USA, 2013.
- 23 A. Kaltenbach, J. Noordmann, V. Görlitz, C. Pape, S. Richter, H. Kipphardt, G. Kopp, R. Jährling, O. Rienitz and B. Güttler, *Anal. Bioanal. Chem.*, 2015, **407**, 3093–3102.
- 24 R. Nater, A. Reichmuth, R. Schwartz, M. Borys and P. Zervos, *Dictionary of Weighing Terms*, Springer, Berlin, 2009.
- 25 F. Spieweck and H. Bettin, *Methoden zur Bestimmung der Dichte von Festkörpern und Flüssigkeiten*, *Physikalisch-technische Bundesanstalt (PTB)*, Braunschweig, 1998.
- 26 C. Niedergesäß, *Hydrostatische Bestimmung der Dichte von Festkörpern (Arbeitsanweisung PTB 3.43-AA-02)*,



- Physikalisch-technische Bundesanstalt (PTB)*, Braunschweig, 2014.
- 27 F. Küster and A. Thiel, *Rechentafeln für die Chemische Analytik*, Walter de Gruyter, Berlin, New York, 104th edn, 1993.
- 28 H. Bettin and F. Spieweck, Die Dichte des Wassers als Funktion der Temperatur nach Einführung der Internationalen Temperaturskala von 1990, *PTB-Mitt.*, 1990, **100**, 195–196.
- 29 W. Gorski and H. Toth, Destilliertes Wasser als Dichtereferenzmaterial – Die elektrische Leitfähigkeit als Kriterium seiner Güte, *PTB-Mitt.*, 1988, **98**, 324–325.
- 30 O. Rienitz, A. Pramann and C. Pape, *Anal. Bioanal. Chem.*, 2013, **405**, 5627–5628.
- 31 O. Rienitz, A. Pramann and C. Pape, *Anal. Bioanal. Chem.*, 2013, **405**, 8691–8692.
- 32 A. Plotnikov, J. Pfeifer, S. Richter, H. Kipphardt and V. Hoffmann, *Anal. Bioanal. Chem.*, 2014, **406**, 7463–7471.
- 33 J. Vogl and W. Pritzkow, *MAPAN-Journal of Metrology Society of India*, 2010, **25**, 135–164.
- 34 J. Vogl, *Rapid Commun. Mass Spectrom.*, 2012, **26**, 275–281.
- 35 S. Dushman and L. Koller, Vapor pressures and rates of evaporation, in *Scientific Foundations of Vacuum Technique*, 2nd edn, 1949, pp. 691–703.
- 36 J. Nordlien, S. Ono, N. Masuko and K. Nisancioglu, *Corros. Sci.*, 1997, **39**, 1397–1414.
- 37 B. Brandt, J. Vogl, J. Noordmann, O. Rienitz and D. Malinovskiy, *J. Anal. At. Spectrom.*, 2015, in preparation.
- 38 BAM Primary Pure Substances, Online available at, [http://www.rm-certificates.bam.de/en/certificates/primary\\_pure\\_substances/index.htm](http://www.rm-certificates.bam.de/en/certificates/primary_pure_substances/index.htm).
- 39 H. Kipphardt, R. Matschat, J. Vogl, T. Gusarova, M. Czerwensky, H.-J. Heinrich, A. Hioki, L. Konopelko, B. Methven, T. Miura, O. Petersen, G. Riebe, R. Sturgeon, G. Turk and L. Yu, *Accredit. Qual. Assur.*, 2010, **15**, 29–37.
- 40 T. Zhou, S. Richter, R. Matschat and H. Kipphardt, *Accredit. Qual. Assur.*, 2013, **18**, 341–349.
- 41 O. Rienitz, D. Schiel, V. Görlitz, R. Jährling, J. Vogl, J. V. Lara-Manzano, A. Zon, W. Fung, M. Buzoianu, R. C. de Sena, L. A. dos Reis, L. Valiente, Y.-H. Yim, S. Hill, R. Champion, P. Fisicaro, W. Bing, G. C. Turk, M. R. Winchester, D. Saxby, J. Merrick, A. Hioki, T. Miura, T. Suzuki, M. Linsky, A. Barzev, M. Máriássy, O. Cankur, B. Ari, M. Tunc, L. Konopelko, Y. A. Kustikov and M. Bezruchko, Final report on CCQM-K87: mono-elemental calibration solutions, *Metrologia*, 2012, **49**, 08010.
- 42 H. Felber, M. Weber and C. Rivier, Final report on key comparison CCQM-K8 of mono-elemental calibration solution, *Metrologia*, 2002, **39**, 08002.
- 43 M. Bizzarro, C. Paton, K. Larsen, M. Schiller, A. Trinquier and D. Ulfbeck, *J. Anal. At. Spectrom.*, 2011, **26**, 565–577.
- 44 Weights of classes E1, E2, F1, F2, M1, M1-2, M2, M2-3 and M3, Part 1: Metrological and technical requirements, OIML R 111-1 International Recommendation, 2004.
- 45 J. Wang, T. Ren, H. Lu, T. Zhou and Y. Zhou, *J. Anal. At. Spectrom.*, 2015, **30**, 1377–1385.
- 46 A. Pramann, O. Rienitz, D. Schiel and B. Güttler, *Int. J. Mass Spectrom.*, 2011, **299**, 78–86.
- 47 Online available at, <http://www.ptb.de/emrp/sib09.html>.

