
CCQM-K182

Lithium isotope delta measurements

KEY COMPARISON

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CCQM-K182
Lithium isotope delta measurements

Key Comparison

September 2026

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SUMMARY

Five National Metrology Institutes and Designated Institutes participated in the Key Comparison CCQM-K182 “Lithium isotope delta measurements”. Participants were requested to evaluate the $\delta_{\text{LSVEC}}^7\text{Li}$, expressed in ‰, of two different Li_2CO_3 samples (BAM-1 & BAM-2) dissolved in dilute nitric acid. Due to the overall good agreement between the reported results for both measurands the arithmetic mean was selected as KCRV. Participants were encouraged to use MC-ICP-MS or the most accurate method available. Moreover, participants were required to apply appropriate measures to avoid the severe Li memory effect in their mass spectrometers. The following table summarizes the KCRVs:

Table 1: Summary of the KCRVs

Sample	$\delta_{\text{LSVEC}}^7\text{Li} / \text{‰}$	$U(\delta_{\text{LSVEC}}^7\text{Li}) / \text{‰}$ ($k = 2.78$)	$U_{\text{rel}}(\delta_{\text{LSVEC}}^7\text{Li}) / \%$
BAM-1	16.619	0.043	0.26
BAM-2	-2.630	0.070	2.7

Successful participation in CCQM-K182 demonstrates measurement capabilities in determining $\delta_{\text{LSVEC}}^7\text{Li}$, ranging from -17 ‰ to 17 ‰ in dilute nitric acid.

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ACRONYMS

BAM	Bundesanstalt für Materialforschung und -prüfung
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CMC	Calibration and measurement capability
DI	Designated institute
DoE	Degrees of equivalence
HFTLS	How far the light shines
IRWG	Isotope ratio working group
ISO	International Organization for Standardization
KCRV	Key comparison reference value
KRISS	Korea Research Institute of Standards and Science
LDPE	Low-density polyethylene
LSVEC	Isotope reference material for lithium
MC-ICP-MS	Multi collector inductively coupled plasma mass spectrometry
MetroPOEM	Metrology for the harmonisation of measurements of environmental pollutants in Europe
NIM	National Institute of Metrology (China)
NRC	National Research Council Canada
PFA	Perfluoroalkoxy alkanes
PTB	Physikalisch-Technische Bundesanstalt
SI	International System of Units
SSB	Standard-sample bracketing

INTRODUCTION

Lithium deltas describe the relative difference of the isotope ratio ${}^7\text{Li}/{}^6\text{Li}$ in a sample and the same ratio in a reference material (LSVEC (1,2)), see equation (0.1).

$$\delta_{\text{LSVEC}} {}^7\text{Li} = \frac{\frac{n_{\text{cmp}}({}^7\text{Li})}{n_{\text{cmp}}({}^6\text{Li})}}{\frac{n_{\text{LSVEC}}({}^7\text{Li})}{n_{\text{LSVEC}}({}^6\text{Li})}} - 1 \quad (0.1)$$

Isotope deltas are important quantities for reference material producers or providers of other measurement services, such as proficiency testing schemes. Evidence of successful participation in formal, relevant international comparisons is needed to document calibration and measurement capability claims (CMCs) made by national metrology institutes (NMIs) and designated institutes (DIs).

In July 2023, the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) approved the Key Comparison (KC) CCQM-K182 “Lithium isotope delta measurements”. CCQM-K182 was designed to assess participants’ capabilities to determine lithium isotope deltas in high purity materials. In the “Strategy for Rolling Programme Development (2021-2030)” of the CCQM Working Group on Isotope Ratios (IRWG) (3), the IRWG dedicates itself to foster the capabilities of its members to measure isotope deltas of metals, including experiment design, uncertainty evaluation etc. Hence, CCQM-K182 supports the aims of the IRWG and supports core capabilities of the participants. In parallel to CCQM-K182, PTB organized also CCQM-P233 “SI-traceable lithium isotope ratios”, therefore the reporting sheet, the technical protocol and the registration form contains both studies.

The following sections of this report document the timeline of CCQM-K182, the measurands, study material, participants, results, and the measurement capability claims that participation in CCQM-K182 can support. The appendices reproduce the official communication materials and summaries of information about the results provided by the participants.

TIMELINE

Table 2 lists the timeline for CCQM-K182.

Table 2: Timeline for CCQM-K182

Date	Action
04/2023	Proposed to CCQM
07/2023	IRWG authorized CCQM-K182
12/2023	Call for participation to IRWG members, circulation of draft protocol
06-09/2024	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
31 May 2025	Results due to coordinating laboratory
02/2026	Draft A report distributed to IRWG
08/2026	Draft B report distributed to IRWG
08/2026	Final report approved by IRWG

MEASURANDS

Participants were asked to determine the lithium isotope deltas ($\delta_{\text{LSVEC}}^7\text{Li}$) in two high purity Li_2CO_3 samples in dilute nitric acid ($w(\text{Li}) \approx 2 \mu\text{g/g}$, $w(\text{HNO}_3) \approx 0.01 \text{ g/g} = 1 \%$). To ensure traceability to the LSVEC scale, solutions of LSVEC in dilute nitric acid were additionally provided.

STUDY MATERIALS

Each participant received three samples: BAM-1, BAM-2, and LSVEC. BAM-1 and BAM-2 were the test materials with unknown $\delta_{\text{LSVEC}}^7\text{Li}$ values relative to LSVEC, while the LSVEC samples ensured traceability to the scale.

BAM-1 is a lithium carbonate (Li_2CO_3 , Honeywell Fluka, product L-5a). For its stock solution, about 1.5 g was dissolved in roughly 250 g nitric acid ($w(\text{HNO}_3) = 0.01 \text{ g/g}$), giving $w(\text{Li}) \approx 1140 \mu\text{g/g}$. This was diluted using roughly 3.5 g of stock solution and 1996.5 g nitric acid (same concentration), resulting in roughly 2000 g final solution with $w(\text{HNO}_3) = 0.01 \text{ g/g}$ and $w(\text{Li}) \approx 2 \mu\text{g/g}$. The solution was distributed into 50 mL PFA bottles, producing 40 units of roughly 40 g each.

BAM-2 is a lithium solution in nitric acid (Merck KGaA, lot HC17013029, $w(\text{Li}) \approx 985 \mu\text{g/g}$). A stock solution (roughly 500 g, $w(\text{HNO}_3) = 0.01 \text{ g/g}$, $w(\text{Li}) \approx 15 \mu\text{g/g}$) was prepared by diluting

roughly 7.5 g of BAM-2 with nitric acid. Further dilution yielded a final solution with $w(\text{Li}) \approx 2 \mu\text{g/g}$ and $w(\text{HNO}_3) \approx 0.01 \text{ g/g}$. This was also portioned into 50 mL PFA bottles, giving 40 units of roughly 40 g each.

For LSVEC, three units (0312, 0313, 0316; 0.5 g each) were combined and dissolved in nitric acid to form a stock solution, which was then diluted. The final solution (roughly 2000 g, $w(\text{HNO}_3) = 0.01 \text{ g/g}$, $w(\text{Li}) \approx 2 \mu\text{g/g}$) was likewise dispensed into 50 mL PFA bottles, yielding 40 units of roughly 40 g each. All solutions for the key comparison were filled into thoroughly cleaned, blank-checked, dried, labelled and weighed PFA bottles. Prior to sealing the bottles in film bags (12 μm polyester, 12 μm aluminium, 165 μm LDPE, type A 40 T, C. Waller, Eichstetten, Germany), each bottle was weighed again to keep track of losses during shipment and to be able to distinguish between unavoidable losses due to evaporation and losses due to leaking bottles. Participants were asked to weigh their samples immediately upon receipt and report the mass along with ambient conditions (temperature, humidity, and pressure). In case of one bottle a leak was detected so that a replacement was sent out.

Due to severe memory effects of Li in mass spectrometry systems, the coordinator proposed a way to minimize memory effects using an Si solution (4), and also provided a piece of high-purity silicon ($m \approx 250 \text{ mg}$, $w(\text{Si}) > 0.9999 \text{ g/g}$). Participants were free to use this piece of Si or to apply any other memory reducing strategy or none.

HOMOGENEITY ASSESSMENT OF STUDY MATERIAL

According to Vogl et al. (5,6) acidified aqueous mono-elemental solutions at the $\mu\text{g/g}$ level are stable and homogeneous over decades, so no explicit homogeneity tests were performed in this study.

STABILITY ASSESSMENT OF STUDY MATERIAL

Throughout the study, PTB analyzed three aliquots of each sample, confirming that the isotopic composition remained unchanged over one year. Although the lithium content may vary due to evaporation, this has a negligible impact on the study results.

The resulting $\delta_{\text{LSVEC}}^7\text{Li}$ values are plotted against time (in days) after sample preparation and shown in Figure 1 and Figure 2.

For each data set a linear regression curve was fitted and the results are summarized in Table 3. Since in all cases the uncertainty $u(a_1)$ of the slope is bigger than the slope a_1 itself, it can be judged that over the course of the study the isotopic composition of the samples did not change. The stability assessment was done in alignment with ISO 33405:2024 (7) .

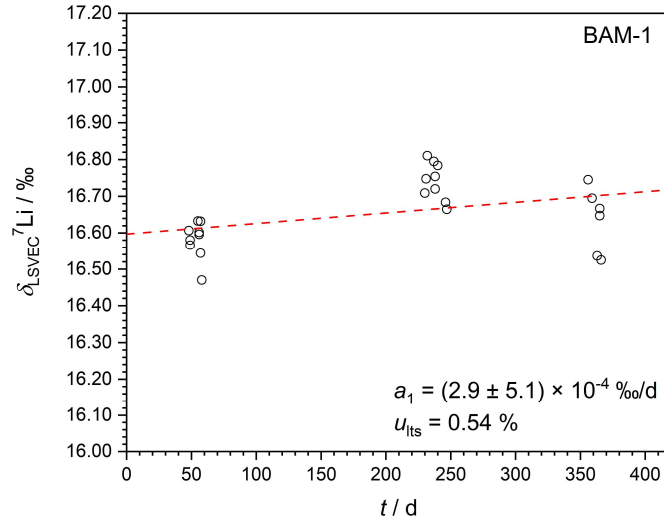


Figure 1: Stability assessment of $\delta_{\text{LSVEC}}^7\text{Li}$ in BAM-1 over the whole duration of the key comparison

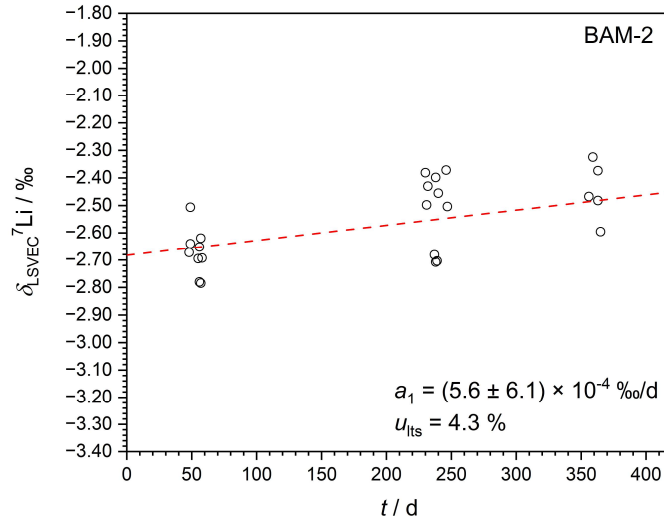


Figure 2: Stability assessment of $\delta_{\text{LSVEC}}^7\text{Li}$ in BAM-2 over the whole duration of the key comparison

Table 3: Summary of linear regression fits for the stability assessment. a_1 is the slope of the regression line. A coverage factor of $k = 2.069$ in case of BAM-1 and $k = 2.060$ in case of BAM-2 was applied.

sample	a_1	$k \times s(a_1)$	$[a_1]$	$u_{\text{ITS,rel}}$
BAM-1	2.9×10^{-4}	5.1×10^{-4}	‰/d	0.54 %
BAM-2	5.6×10^{-4}	6.1×10^{-4}	‰/d	4.3 %

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was distributed in December 2023 with the intent to distribute samples in April 2024, receive results in December 2024, and discuss results at the 2025 IRWG spring meeting in Paris, France, April 2025. See Table 2 for study timeline. APPENDIX A reproduces the Call for Participation and the registration form. APPENDIX B reproduces the Technical Protocol. Table 4 lists the institutions that registered for CCQM-K182

Table 4: Registered NMIs/DIs in alphabetic order

Participant	Acronym	Country
Bundesanstalt für Materialforschung und -prüfung	BAM	Germany
Korea Research Institute of Standards and Science	KRISS	Republic of Korea
National Institute of Metrology China	NIM	People's Republic of China
National Research Council Canada	NRC	Canada
Physikalisch-Technische Bundesanstalt	PTB	Germany

All samples were shipped by PTB in June 2024. Due to the late registration of KRISS, its samples were shipped in July 2024. Receipt at NIM was delayed until September 2024 due to unforeseen complications with the shipping company.

Participants were instructed to use the provided LSVEC aliquots and to measure the isotope delta (in ‰) of each sample at least five times using different subsamples. They were asked to report the individual results along with the mean, associated uncertainty, degrees of freedom, and coverage factor using the Excel form provided by PTB, see APPENDIX C: .

RESULTS

Participants were requested to report a single estimate of the isotope delta $\delta_{\text{LSVEC}}^{7\text{Li}}$ for each of the two carbonates – BAM-1 and BAM-2. In addition to the quantitative results, participants were instructed to describe their analytical methods and approach to uncertainty estimation. APPENDIX C: reproduces the report form. CCQM-K182 results were received from 5 of the 5 institutions that received samples.

METHODS USED BY PARTICIPANTS

Since all samples were high purity solutions in dilute nitric acid, no further sample treatment by the participants were required. PTB provided ready-to-use LSVEC solutions prepared from the same stock solution, therefore a common traceability to the LSVEC scale has been assured. Table 5 summarizes the measurement methods used by the participating NMIs/DIs for CCQM-K182

Table 5: Summary of measurement methods used

Participant	Analytical instrument	Memory reduction strategy	Source of traceability
BAM	Neptune Plus Thermo Fisher Scientific	Purging with NaCl	LSVEC, provided by PTB
KRISS	Neptune Plus Thermo Fisher Scientific	Si coating of cones	LSVEC, provided by PTB
NIM	Neptune Plus Thermo Fisher Scientific & Neoma MS/MS MC-ICP-MS Thermo Fisher Scientific	Purging with NaCl	LSVEC, provided by PTB
NRC	Neptune Plus Thermo Fisher Scientific	Purging with NaCl	LSVEC, provided by PTB
PTB	Neptune XT Thermo Fisher Scientific	Si coating of cones	LSVEC, provided by PTB

PARTICIPANTS' RESULTS FOR $\delta_{\text{LSVEC}}^7\text{Li}$ IN BAM-1 AND BAM-2

The results for CCQM-K182 for the determination of $\delta_{\text{LSVEC}}^7\text{Li}$ in BAM-1 and BAM-2 are detailed in Table 6 and

Table 7, and presented graphically in Figure 3 as well as in Figure 4, respectively.

Table 6: $\delta_{\text{LSVEC}}^7\text{Li}$ in BAM-1 as reported by the participants

Participant	$\delta_{\text{LSVEC}}^7\text{Li}$ in ‰	Standard uncertainty in ‰	Coverage factor, k	Expanded uncertainty in ‰
NIM	16.570	0.030	2.13	0.064
NRC	16.60	0.11	2	0.22
KRISS	16.635	0.020	2.78	0.056
BAM	16.64	0.20	2	0.40
PTB	16.655	0.083	2.07	0.17

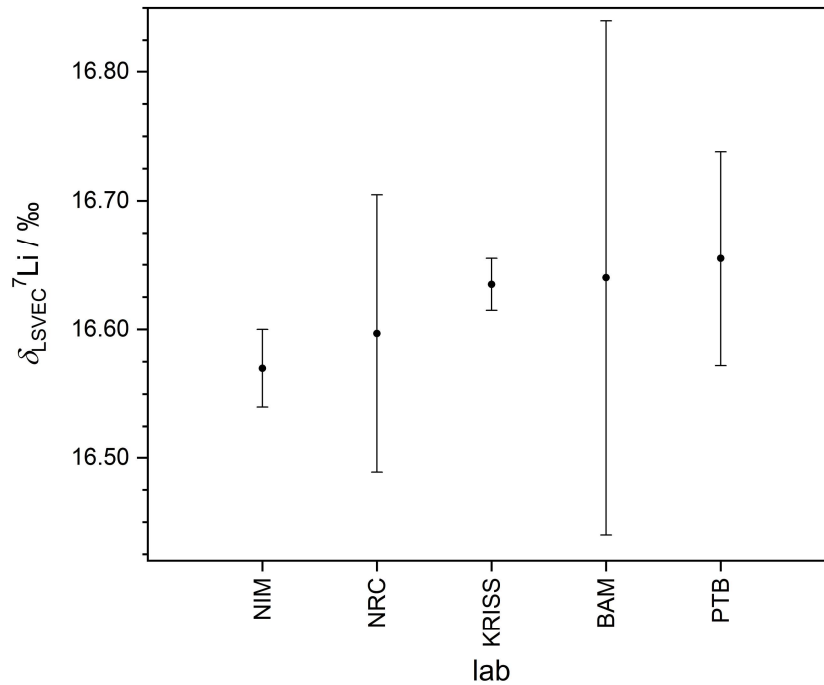


Figure 3: Results reported for $\delta_{\text{LSVC}}^7\text{Li}$ in BAM-1, error bars represent combined uncertainties u_c ($k = 1$)

Table 7: $\delta_{\text{LSVEC}}^7\text{Li}$ in BAM-2 as reported by the participants

Participant	$\delta_{\text{LSVEC}}^7\text{Li}$ in ‰	Standard uncertainty in ‰	Coverage factor, k	Expanded uncertainty in ‰
NRC	-2.69	0.13	2	0.25
BAM	-2.68	0.16	2	0.32
NIM	-2.630	0.030	2.13	0.064
KRISS	-2.579	0.015	2.78	0.04
PTB	-2.57	0.11	2.06	0.22

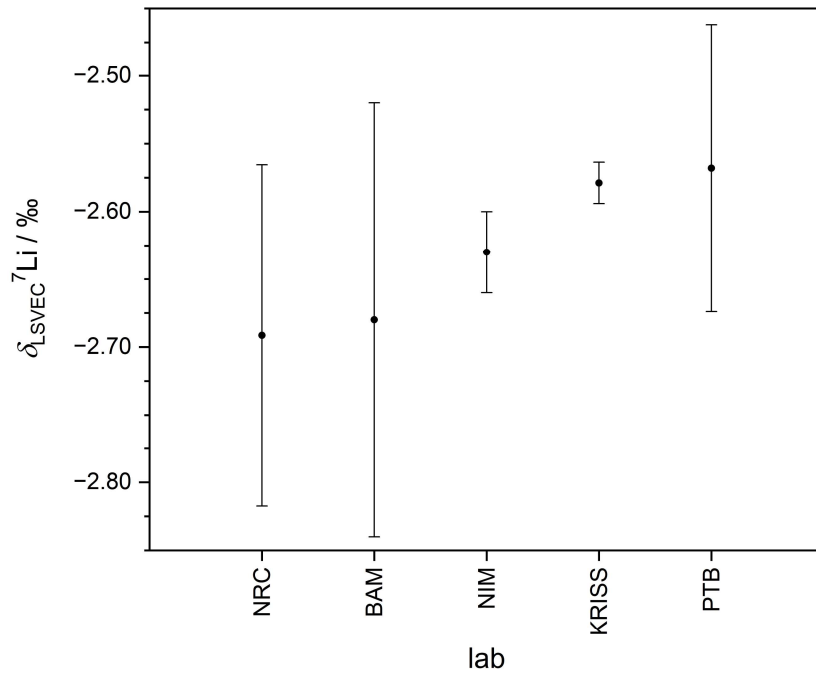


Figure 4: Results reported for $\delta_{\text{LSVC}}^7\text{Li}$ in BAM-2, error bars represent combined uncertainties u_c ($k = 1$)

DISCUSSION OF RESULTS

The results presented in Table 6 and

Table 7 show overall good agreement between all participants, therefore no further investigations were conducted.

KEY COMPARISON REFERENCE VALUE (KCRV)

Due to the good agreement among all reported results x_i , the participants agreed on using the arithmetic mean as estimator for the KCRV for both $\delta_{\text{LSVEC}}^{7\text{Li}}(\text{BAM-1})$ and $\delta_{\text{LSVEC}}^{7\text{Li}}(\text{BAM-2})$. The following equations were used to calculate the KCRV and its associated uncertainty.

$$x_{\text{KCRV}} = \frac{1}{N} \sum_{i=1}^N x_i \quad (0.2)$$

$$u(x_{\text{KCRV}}) = \frac{1}{\sqrt{N}} s(x) = \sqrt{\frac{1}{N(N-1)} \sum_{i=1}^N d_i^2} \quad (0.3)$$

$$d_i = x_i - x_{\text{KCRV}} \quad (0.4)$$

DEGREES OF EQUIVALENCE (DoE)

The absolute degrees of equivalence for the participants in CCQM-K182 are estimated as the difference between the combined value and the KCRV: $d_i = x_i - x_{\text{KCRV}}$. The associated uncertainties of each d_i were calculated using equation (0.5), which considers the correlation between x_i and x_{KCRV} (8). Moreover, it was tested if additional random effects increased the dispersion of the reported values or not, using the criterion in equation (0.5). While in case of BAM-2 an additional random effect could be detected in the data set, no such observation was made in case of BAM-1. Therefore, the uncertainties $U(d_i)$ associated with the DoEs had to be calculated in a different way, see equation (0.5).

$$u^2(d_i) = \left(1 - \frac{2}{N}\right) u^2(x_i) + u^2(x_{\text{KCRV}}) \quad \text{if} \quad s^2(x_{\text{KCRV}}) > \frac{1}{N^2} \sum_{i=1}^N u^2(x_i) \quad \wedge \quad u(x_i, x_{\text{KCRV}}) \neq 0 \quad (0.5)$$

$$u^2(d_i) = \left(1 - \frac{1}{N}\right) s^2(x_{\text{KCRV}}) \quad \text{if} \quad s^2(x_{\text{KCRV}}) \leq \frac{1}{N^2} \sum_{i=1}^N u^2(x_i) \quad \wedge \quad u(x_i, x_{\text{KCRV}}) \neq 0$$

Table 8 and Table 9 list the numeric values of d_i and $U(d_i)$ for all participants of CCQM-K182 for BAM-1 and BAM-2, respectively. A coverage factor of $k = 2.78$ was applied to reflect the number of participants $N = 5$.

Table 8: Degrees of Equivalence d_i for $\delta_{\text{LSVEC}}^7\text{Li}$ in the sample BAM-1

Participant	x_i in ‰	$u(x_i)$ in ‰	$u_{\text{rel}}(x_i)$ in %	d_i in ‰	$U(d_i)$ in ‰	$d_i / U(d_i)$
NIM	16.570	0.030	0.18	-0.049	0.087	-0.57
NRC	16.60	0.11	0.65	-0.023	0.087	-0.26
KRISS	16.635	0.020	0.12	0.016	0.087	0.18
BAM	16.64	0.20	1.2	0.021	0.087	0.24
PTB	16.655	0.083	0.50	0.036	0.087	0.41

Table 9: Degrees of Equivalence d_i for $\delta_{\text{LSVEC}}^7\text{Li}$ in the sample BAM-2

Participant	x_i in ‰	$u(x_i)$ in ‰	$u_{\text{rel}}(x_i)$ in %	d_i in ‰	$U(d_i)$ in ‰	$d_i / U(d_i)$
NRC	-2.69	0.13	4.7	-0.062	0.280	-0.22
BAM	-2.68	0.16	6.0	-0.050	0.351	-0.14
NIM	-2.630	0.030	1.1	0.000	0.095	0.00
KRISS	-2.579	0.015	0.59	0.051	0.077	0.66
PTB	-2.568	0.11	4.1	0.062	0.238	0.26

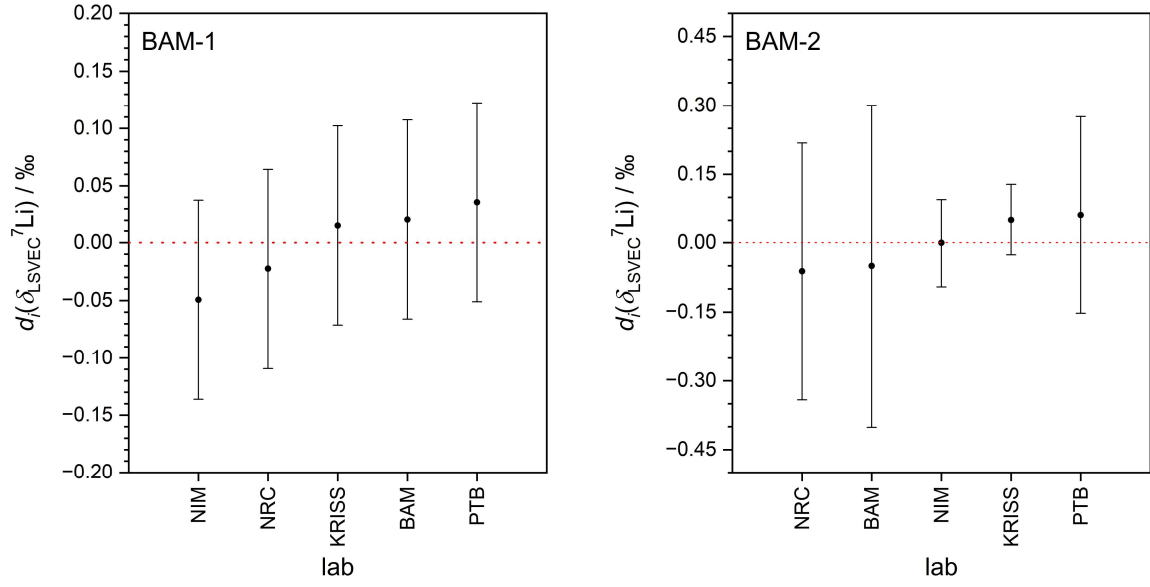


Figure 5: Plot of the degrees of equivalence d_i for $\delta_{\text{LSVEC}}^7\text{Li}$ in BAM-1 and in BAM-2. The black dots show the d_i , while the error bars denote the expanded uncertainty $U(d_i)$ (95 % confidence level) associated with the degree of equivalence. Results that encompass zero (red dashed line) within their uncertainty interval are considered to be consistent with the KCRV.

USE OF CCQM-K182 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

HOW FAR THE LIGHT SHINES, CORE CAPABILITY STATEMENTS AND CMC SUPPORT

Successful participation in CCQM-K182 demonstrates measurement capabilities in determining $\delta_{\text{LSVEC}}^{7\text{Li}}$ in mono-elemental Li solutions in dilute nitric acid within the interval of $-17\text{‰} \leq \delta_{\text{LSVEC}}^{7\text{Li}} \leq +17\text{‰}$, typically realized using a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) in low resolution mode and underpinned by using the internationally recognized reference material LSVEC. The reported measurement uncertainty represents the best demonstrated uncertainty achievable for the method employed.

To account for possible instrumental drift in isotopic fractionation (mass bias), the measurement sequence should be implemented using a standard-sample bracketing scheme.

The successful participation in this key comparison supports CMC claims for the determination of natural isotope delta values of elements measurable in low resolution mode, such as Li, Mg, Cl, Ni, Cu, Zn, Ga, Ge, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, In, Sb, Gd, Lu, Hf, W, Re, Os, Ir, Pt, Hg, Tl, Pb, U in high purity matrices like dilute nitric acid. For high purity metals, quantitative dissolution of metals should be demonstrated. For samples with more complex matrices, the ability to separate the analyte element from the matrix without altering the isotopic composition beyond the target uncertainty must be demonstrated. Alternatively, experience in matching the matrix of the delta standard to that of the sample matrix must be proven. In this case, additional uncertainty contributions may result in higher combined measurement uncertainties. The use of an internationally recognized delta standard is mandatory (2). In-house standards traceable to such a delta reference are acceptable, but its use typically results in larger associated uncertainties.

For both measurands all participants achieved normalized errors that fulfilled $|d_i/U(d_i)| < 1$, therefore all participants have supported their capabilities. CMCs aligning with the aforementioned HFTLS are supported.

CORE CAPABILITY TABLE

CCQM Study: CCQM-K182

Institute(s): BAM, KRISS, NIM, NRC, PTB

Method: Multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS)

Analyte(s): Lithium isotope delta $\delta(^7\text{Li})_{\text{LSVEC}}$ of high-purity materials in dilute nitric acid in a range of $\pm 17 \text{ ‰}$

Capabilities/Challenges	Not tested	Tested	Specific challenges encountered
Cross contamination control and correction: All techniques and procedures employed to reduce potential cross contamination of samples/reference materials as well as blank correction procedures. The level of difficulty is greatest for analytes that are environmentally ubiquitous and present at very low concentrations in the sample.	--	BAM, KRISS, NIM, NRC, PTB	Lithium shows massive memory effect in mass spectrometers
Signal detection: The detection and recording of the analyte signals. The degree of difficulty increases for samples with an isotope delta close to 0.	--	BAM, KRISS, NIM, NRC, PTB	--
Establishing traceability to the delta scale: Usage of internal agreed-on reference material(s) and proper sequence design for the determination of isotope deltas. Including normalization.	--	BAM, KRISS, NIM, NRC, PTB	--

CONCLUSIONS

In CCQM-K182 participants were asked to determine $\delta_{\text{LSVEC}}^7\text{Li}$ of high-purity materials in dilute nitric acid. The overall good agreement proves that participants successfully mastered this task and supports future claims of determining natural isotope deltas of various elements in simple matrices.

ACKNOWLEDGEMENTS

The study coordinators thank the participating laboratories for providing the requested information used in this study.

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APPENDIX A: Call for Participation and Registration Form

Invitation
to participate in the
Key comparison CCQM-K182
“Lithium δ -values”
and/or the
Pilot Study CCQM-P233
“SI-traceable lithium isotope ratios”

Announcement

PTB will organize a CCQM pilot study and a parallel key comparison. The key comparison is concerned with the determination of the isotope delta $\delta^7\text{Li}$ of two isotopically different samples A and B, while the subject of the pilot study is the determination of the SI-traceable isotope ratio $n(^7\text{Li})/n(^6\text{Li})$ of the widely used isotope reference material LSVEC.

The Isotope Ratio Working Group (IRWG) of the CCQM agreed to conduct the pilot study CCQM-P233 and key comparison CCQM-K182 during the meeting in Paris in April 2023.

Subject

Motivation of the comparison is to conduct the first key comparison about δ -values of a metallic element within the CCQM-IRWG. In case of the pilot study, the motivation arose within the EPM project MetroPOEM (Metrology for the harmonisation of measurements of environmental pollutants in Europe, 21GRD09). In this project, the idea of recharacterizing LSVEC (NIST RM 8545) came up, especially because the absolute Li isotope ratio is categorized as a non-certified value and originates from a publication by Qi et al. on the calibration of IRMM-016 [1]. Since lithium has only two stable isotopes, determining absolute isotope ratios applying the full gravimetric isotope mixture approach (FGIM) [2] should be less challenging. Though the recommended value has been determined by applying FGIM, it is still worth to recharacterize and potentially improve LSVEC in order to practise this primary method and further metrologically substantiate the LSVEC δ -scale.

Samples

Participants of the key comparison will be provided with three PFA bottles containing three different lithium solutions. The first bottle contains 40 g of a solution of LSVEC with $w(\text{Li}) \approx 2 \mu\text{g/g}$. The solvent is HNO_3 ($w(\text{HNO}_3) \approx 0.01 \text{ g/g} = 1 \%$). The two other bottles contain 40 g each of two isotopically different Li solutions with a similar matrix and Li mass fraction. Their delta values will differ from each other and from LSVEC by several ‰.

Participants of the pilot study will be provided with four PFA bottles four different Li solutions with a similar matrix and Li mass fraction like the samples in the key comparison. The first bottle contains 40 g of an LSVEC solution, the second bottle contains 40 g of a ^6Li spike solution, the third bottle contains 40 g of a ^7Li spike solution and the fourth contains 40 g of a blend of the ^6Li and ^7Li materials in approximately equal amounts ($n(^7\text{Li})/n(^6\text{Li}) \approx 1$).

mol/mol). Please note that institutes participating in the key comparison **and** in the pilot study will only receive one LSVEC solution. Participants having IRMM-016 in their lab are highly encouraged to measure this CRM in parallel and provide the data as additional values.

Measurands

For the key comparison the measurands are the two isotope deltas $\delta_{\text{LSVEC}}(^7\text{Li}/^6\text{Li})$ of sample solutions BAM-1 and BAM-2. Associated uncertainties must be determined according to the GUM.

In case of the pilot study, the mandatory measurand is the absolute isotope ratio $n(^7\text{Li})/n(^6\text{Li})$ of the LSVEC solution. An associated uncertainty must be determined according to the GUM. Moreover, the participants are encouraged to submit the absolute isotope ratios $n(^7\text{Li})/n(^6\text{Li})$ and associated uncertainties of the two spike solutions and the blend solution as well as the absolute isotope ratios $n(^7\text{Li})/n(^6\text{Li})$ of the two Li sample solutions A and B, which are distributed in the key comparison.

Measurement techniques and methods

For the determination of the absolute isotope ratio(s) in the pilot study, the use of an MC-ICP-MS (or at least a magnetic sector field ICP-MS) is highly recommended. However, we appreciate and encourage the participation of laboratories applying other suitable techniques and methods.

For the determination of the delta values in the key comparison, the use of any kind of ICP-MS seems to be reasonable, but participants are free to choose any suitable technique and method. Please note, that in case you plan to submit more than one result per measurand (e.g. determined using different techniques) you have to clearly state (at the latest when submitting your results) which one should be taken into account for the calculation of the KCRV.

Characteristic features of the analytical task

The particular challenge of the key comparison is to measure δ -values being traceable to the LSVEC-scale with an uncertainty reflecting the state of the art. In case of the pilot study the particular challenge is to determine the absolute (SI-traceable) lithium isotope ratio $n(^7\text{Li})/n(^6\text{Li})$ of LSVEC.

Publication

It is intended to publish the main result of the pilot study, the absolute lithium isotope ratio in LSVEC, in combination with the result from the study run in parallel within the EPM project MetroPOEM in a peer-reviewed scientific journal. Please note, that for the value assignment of the lithium isotope ratio in LSVEC, values can be excluded for technical/scientific reasons.

Time schedule

Registration deadline	29 February 2024
Dispatch of the samples	April 2024
Reporting deadline	31 December 2024

Registration

If you wish to participate in the pilot study and/or the key comparison, please return the completed form by e-mail until **29 February 2024** to

PTB
Olaf Rienitz
Bundesallee 100
38116 Braunschweig
Germany
Phone: +49 531 5923110
E-Mail: olaf.rienitz@ptb.de

and

PTB
Lukas Flierl
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38116 Braunschweig
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lukas.flierl@ptb.de

Please indicate below the measurands table whether you need a pro-forma invoice to help facilitate customs clearance processing.

Looking forward to your participation.

Sincerely yours,

Olaf Rienitz & Lukas Flierl

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Registration

CCQM-K182/CCQM-P233

“Lithium δ -values and SI-traceable lithium isotope ratios”

If you would like to participate, please complete this form

Contact person	
Institute	
Street City, postal code (no P.O. Box please)	
Country	
E-mail	
Phone	
Date	

Measurand	Participation in CCQM-K182	
	yes	no
$\delta^7\text{Li}$ in sample A		
$\delta^7\text{Li}$ in sample B		
Measurand	Participation in CCQM-P233	
	yes	no
$n(^7\text{Li})/n(^6\text{Li})$ in LSVEC		
$n(^7\text{Li})/n(^6\text{Li})$ in ^6Li spike A		
$n(^7\text{Li})/n(^6\text{Li})$ in ^7Li spike B		
$n(^7\text{Li})/n(^6\text{Li})$ in $^6\text{Li}+^7\text{Li}$ blend AB		
$n(^7\text{Li})/n(^6\text{Li})$ in sample BAM-1		
$n(^7\text{Li})/n(^6\text{Li})$ in sample BAM-2		

To help facilitate the customs clearance process (if any) I would like to receive a pro-forma invoice: yes/no.

Send it until **29 February 2024** by e-mail to

PTB
Olaf Rienitz
Bundesallee 100
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APPENDIX B: Technical Protocol

CCQM-K182 & CCQM-P233
“Lithium isotope delta measurements”
&
“Absolute lithium isotope ratio in LSVEC”

Technical Protocol

1. Introduction

Absolute isotope ratios, which are traceable to the International System of Units (SI), cannot be directly determined through mass spectrometry, as it is not an absolute method. This discrepancy is commonly known as *mass bias* and correction is needed. To address this limitation, certified isotope reference materials are required, or alternatively, isotope deltas traceable to a standard artifact can be utilized as a workaround. [1] The traceability of a reference material can be achieved through the application of the primary method for determining isotope ratios, known as Full Gravimetric Isotope Mixtures (FGIM). [2], [3] The lithium two-isotope system (^6Li and ^7Li) serves as an excellent example for members of the CCQM-IRWG to develop their proficiency in applying this method and to demonstrate their ability to measure isotope deltas ($\delta^7\text{Li}_{\text{LSVEC}}$) of a metallic element. The lithium two-isotope system simplifies the FGIM approach, and the availability of the certified reference material LSVEC [4–6] enables the cross-validation of results obtained by participants against the certified value of LSVEC. Therefore, both a key comparison (K182) aimed at determining the isotope deltas relative to LSVEC of two unknown solutions and a pilot study (P233) aimed at determining the absolute isotope ratio of LSVEC are organized.

2. Samples

For the key comparison, three samples were prepared: BAM-1, BAM-2, and LSVEC. BAM-1 is a lithium carbonate (Li_2CO_3 , Honeywell Fluka, Charlotte, North Carolina, USA, product name L-5a). For the stock solution of BAM-1 roughly 1.5 g were dissolved in nitric acid ($m \approx 250$ g, $w(\text{HNO}_3) = 0.01$ g/g, and $w(\text{Li}) \approx 1140$ $\mu\text{g/g}$). This stock solution was diluted, using approximately 3.5 g of the stock solution and 1996.5 g of nitric acid ($w(\text{HNO}_3) = 0.01$ g/g). The resulting final solution had a mass of approximately 2000 g, with a nitric acid concentration of 0.01 g/g and a lithium mass fraction of approximately 2 $\mu\text{g/g}$. This solution was portioned into 50 ml-PFA bottles, yielding 40 units, each containing approximately 40 g of the solution. BAM-2 is a solution of lithium in nitric acid (Merck KGaA, Darmstadt, Germany, lot number HC17013029, $w(\text{Li}) \approx 985$ $\mu\text{g/g}$). To prepare the stock solution of BAM-2 ($m_{\text{stock}} \approx 500$ g, $w(\text{HNO}_3) = 0.01$ g/g, and $w(\text{Li}) \approx 15$ $\mu\text{g/g}$) approximately 7.5 g of BAM-2 were diluted using nitric acid. The stock solution was further diluted, resulting in a final solution with a lithium mass fraction of approximately 2 $\mu\text{g/g}$ and a concentration of

nitric acid of approximately 0.01 g/g. Again, the final solution was portioned into 50 ml-PFA bottles, yielding 40 units, each containing approximately 40 g of the solution. For the preparation of the LSVEC stock solution, three units (0312, 0313, and 0316 each 0.5 g) of LSVEC were dissolved in nitric acid. Like the previous samples, the final LSVEC solution ($m \approx 2000$ g, $w(\text{HNO}_3) = 0.01$ g/g, and $w(\text{Li}) \approx 2$ $\mu\text{g/g}$) was divided into 50 ml-PFA bottles, yielding 40 units, each containing approximately 40 g of solution. The samples distributed within the key comparison are summarized in Table 1 and the sample preparation is depicted in Figure 1.

Table 1: Samples of key comparison CCQM-K182. Deltas of BAM-1 and BAM-2 are nominal values.

Bottle	Mass / g	Solution	$w(\text{Li})$ / ($\mu\text{g/g}$)	$\delta_{\text{LSVEC}} {}^7\text{Li}$ / ‰
50 mL	40	BAM-1	2	15
50 mL	40	BAM-2	2	-5
50 mL	40	LSVEC	2	0

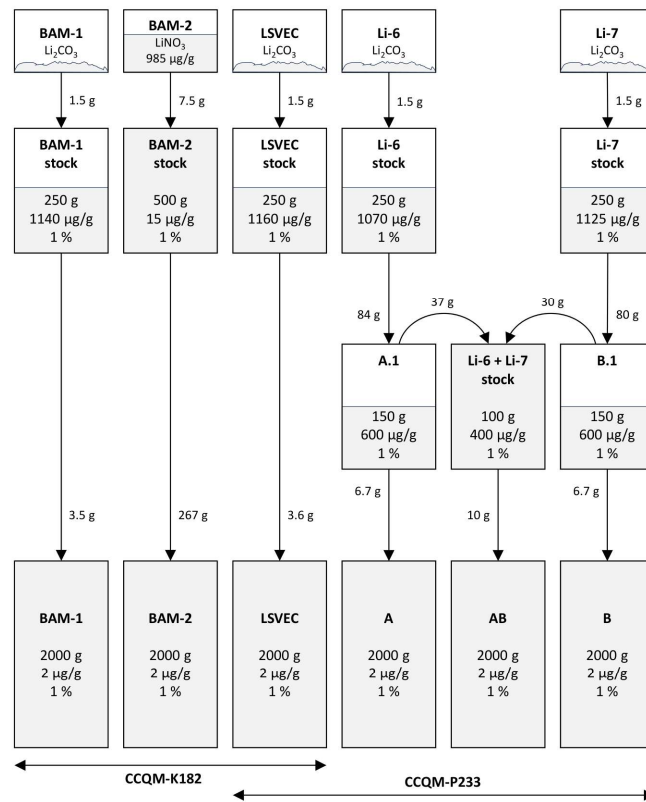


Figure 1: Preparation of the samples distributed in K182 and P233

For the pilot study, four samples were prepared: A, B, AB, and LSVEC. The LSVEC solution is identical to the one used in the key comparison. Please note, that participants registered for both the pilot study and the key comparison will receive only one bottle of LSVEC solution. Sample A is a combination of two lithium carbonates enriched in ^6Li . To prepare the stock solution of A, roughly 1 g of the first enriched carbonate (Sigma-Aldrich, Saint Louis, USA, batch number MBBB2987V, $x(^6\text{Li}) \approx 0.955$ mol/mol, $w(\text{Li}_2\text{CO}_3) > 0.99$ g/g) and roughly 0.6 g of the second spike (Sigma-Aldrich, Saint Louis, USA, batch number MBBC2913, $x(^6\text{Li}) \approx 0.954$ mol/mol, $w(\text{Li}_2\text{CO}_3) > 0.99$ g/g) were pooled and dissolved in nitric acid. The stock solution ($m \approx 250$ g) had a lithium mass fraction of approximately 1070 $\mu\text{g/g}$ and a nitric acid content of approximately 0.01 g/g. The stock solution was further diluted in two steps (see Figure 1) to achieve the final lithium concentration of roughly 2 $\mu\text{g/g}$ and nitric acid content of about 0.01 g/g. Sampling was conducted in a similar manner to the samples in the key comparison. Material B is a lithium carbonate depleted in ^6Li (Sigma-Aldrich, Saint Louis, USA, batch number MBBC7757, $x(^7\text{Li}) > 0.99$ mol/mol, $w(\text{Li}_2\text{CO}_3) > 0.99$ g/g). To prepare the stock solution of B, roughly 1.5 g of the carbonate were dissolved in nitric acid. The stock solution ($m \approx 250$ g) had a lithium mass fraction of about 1125 $\mu\text{g/g}$ and a nitric acid content of about 0.01 g/g. The stock solution was diluted in two steps (see Figure 1) to obtain the final lithium mass fraction of approximately 2 $\mu\text{g/g}$ and a nitric acid content of approximately 0.01 g/g. Sampling was conducted in a similar manner to the samples in the key comparison. Material AB is a blend of A and B. The preparation was done under gravimetric control to adjust an ion intensity ratio of roughly 1 V/V (assuming a K -factor of 1.29 (mol/mol)/(V/V)). Roughly 37 g of solution A.1 and 30 g of solution B.1 were mixed and diluted with roughly 34 g of nitric acid ($w(\text{HNO}_3) = 0.01$ g/g), please see Figure 1. This stock solution was thoroughly homogenized for 36 h using a mechanical shaker and subsequently further diluted to yield a final lithium concentration of roughly 2 $\mu\text{g/g}$ and a nitric acid content of about 0.01 g/g. Sampling was conducted in a similar manner to the samples in the key comparison.

Table 2: Samples of pilot study P233. Masses and mass fractions are nominal values.

Bottle	Mass / g	Solution	$w(\text{Li})$ / ($\mu\text{g/g}$)
50 mL	40	A	2
50 mL	40	B	2
50 mL	40	AB	2
50 mL	40	LSVEC	2

All solutions for the pilot study and the key comparison were filled into thoroughly cleaned, blank-checked, dried, labelled and weighed PFA bottles. Prior to sealing the bottles in film bags (12 μm polyester, 12 μm aluminium, 165 μm LDPE, type A 40 T, C. Waller, Eichstetten, Germany), each bottle was weighed again to keep track of losses during shipment and to be able to distinguish between unavoidable losses due to evaporation and losses due to leaking bottles.

Please weigh your sample bottles immediately after opening the film-bags. Please report this weight together with the relevant ambient conditions (air pressure, relative humidity, and air temperature) back to PTB. Please use a balance with a resolution of at least 1 mg. PTB will check whether the losses are in the usual range of evaporation or whether the bottle was leaking. Evaporation losses are not relevant for the evaluations of the results. Leaking bottles will be replaced.

3. Sample handling

In case of ICP-MS it is known that lithium causes a high and persistent memory effect. [6] This can be overcome by reducing the analyte concentration ($w(\text{Li}) \approx 10 \text{ ng/g}$) and using a desolvation system. An alternative way has been presented by Kipphardt *et al.* [7] In their work Kipphardt *et al.* used an Si solution ($w(\text{Si}) \approx 1000 \text{ } \mu\text{g/g}$, $w(\text{HF}) \approx 0.002 \text{ g/g}$ and $w(\text{HNO}_3) < 0.01 \text{ g/g}$) to coat their ICP-MS cones. This approach allows to reduce the memory effect and enables users to use higher analyte concentrations, which leads to an improved signal stability. First tests of the coating solution at PTB showed that measuring the Si solution prior to every single sample, blank or reference for 90 s reduced the sample signal to memory signal ratio (both on mass 7 g/mol) by a factor of 10. All participants will receive a piece of a suitable high-purity silicon ($m \approx 250 \text{ mg}$, $w(\text{Si}) > 0.9999 \text{ g/g}$) together with the samples.

4. Analysis

Please apply your most accurate methods of measurement, preferably MC-ICP-MS. Keep in mind the memory issue connected to measurements of Li isotope ratios/deltas and apply one of the two methods suggested in the previous section or any other suitable approach.

In case of the **key comparison**, you are asked to determine the following quantities:

- $\delta_{\text{LSVEC}}^{7\text{Li}}$ in solution BAM-1 and
- $\delta_{\text{LSVEC}}^{7\text{Li}}$ in solution BAM-2.

The deltas should be reported in ‰:

$$\delta_{\text{LSVEC}}^{7\text{Li}} = \left(\frac{r_{\text{smp}} \left(\frac{7\text{Li}}{6\text{Li}} \right)}{r_{\text{LSVEC}} \left(\frac{7\text{Li}}{6\text{Li}} \right)} - 1 \right) \times 1000 \text{ ‰} \quad (1)$$

Participants should use the provided LSVEC aliquots and are required to measure the isotope delta of each sample **at least 5 times** from different subsamples.

In case of the **pilot study**, you are asked to determine the following quantities:

- the absolute isotope ratio R of the provided LSVEC solution,
- the calculated K -factor, and
- the absolute isotope ratio R of the provided solutions A, B, **and** AB.

Participants are highly encouraged to also report the following quantities; however, this is **not** mandatory:

- the absolute isotope ratio $R(^6\text{Li}/^7\text{Li})$ of sample BAM-1,
- the absolute isotope ratio $R(^6\text{Li}/^7\text{Li})$ of sample BAM-2, and
- the absolute isotope ratio $R(^6\text{Li}/^7\text{Li})$ of LSVEC, using other (your own) LSVEC units.

Mass bias correction can be done by applying the following equation:

$$R = K \times r \quad (2)$$

The capital R is the absolute isotope ratio (unit: mol/mol), lower r is the measured ion intensity ratio (unit: V/V, A/A or s⁻¹/s⁻¹), and K is the so-called K -factor. According to [8], [9] the K -factor for a two-isotope system can be expressed as:

$$K = \frac{M(^7\text{Li})}{M(^6\text{Li})} \times \frac{m_A \times (r_A - r_{AB}) + m_B \times (r_B - r_{AB})}{m_A \times r_B \times (r_{AB} - r_A) + m_B \times r_A \times (r_{AB} - r_B)}. \quad (3)$$

The lower r s are the measured ion intensity ratios of the samples A, B and AB, respectively. The masses m_A and m_B are the masses of pure Li originating from the spike solutions A and B mixed to yield blend AB. Since several quantities (among them the mass fraction of Li in the carbonates used to prepare the solutions A and B) are unknown and inaccessible, the FGIM method [3] was combined with ion chromatography to get rid of this problem. In this context, a new equation was developed [10]:

$$K = \frac{m'_A \times (r_A - r_{AB}) + m'_B \times (r_B - r_{AB})}{m'_A \times r_B \times (r_{AB} - r_A) + m'_B \times r_A \times (r_{AB} - r_B)}. \quad (4)$$

Even though the “masses” m'_A and m'_B are in some way proportional to m_A and m_B , they have no longer an actual meaning and are calculated from several masses and ion chromatographic data. The ion chromatographic measurements will take place at PTB in parallel to the mass spectrometric measurements. As soon as the final values of m'_A and m'_B are available, they will be circulated among the participants together with the associated uncertainties and the correlation coefficient $r(m'_A, m'_B)$ in a timely manner to enable the participants to calculate the **K -factor according to equation (4)**.

Participants are required to measure the absolute isotope ratio of LSVEC **at least 5 times** from different subsamples.

5. Reporting

The new **deadline** for the submission of results is **31 January 2025**. Please send your report via E-mail and use the provided reporting sheets.

Please calculate uncertainties for all the results reported according to the GUM [11]. Please provide us with a detailed description of all experimental details. If you need further assistance or encounter any kind of problem, please contact Olaf Rienitz **and** Lukas Flierl.

Contact:

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	-3319
	lukas.flierl@ptb.de

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APPENDIX C: Reporting Form

AutoSave Off CCQM-... BAM-1

File Home New Ta Insert Draw Page La Formule Data Review View Automa Develop Help

A2 BAM-1

	A	B	C	D	E	F	G
1							
2	BAM-1			If you have done more than 5 repetitions and like to report them, just add extra rows. Please rename this file to include the acronym of your institute, like "CCQM-K182-reporting-sheet-PTB.xlsx".			
3	repetition	δ_{LSVEC} ^7Li in ‰	$u_c(\delta_{\text{LSVEC}}$ $^7\text{Li})$ in ‰				
4	1						
5	2						
6	3						
7	4						
8	5						
9	Mean						
10	STD of all repetitions						
11	combined uncertainty						
12	coverage factor k						
13	degrees of freedom						
14							
15							
16	BAM-2						
17	repetition	δ_{LSVEC} ^7Li in ‰	$u_c(\delta_{\text{LSVEC}}$ $^7\text{Li})$ in ‰				
18	1						
19	2						
20	3						
21	4						
22	5						
23	Mean						
24	STD of all repetitions						
25	combined uncertainty						
26	coverage factor k						
27	degrees of freedom						
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1	Please provide any additional information to aid in understanding your measurements, addressing the following questions:								
2									
3	1. Did you utilize a desolvator? If so, please specify which one and provide setting details.								
4	2. What were the concentrations of the solutions in your measurements?								
5	3. What was the sensitivity (signal-to-analyte content ratio) for the LSVEC sample?								
6	4. What were the typical tuning parameters?								
7	5. In what order were the samples measured?								
8	6. If you used a custom unit of LSVEC, which one was it?								
9	7. What type of instrument did you utilize (manufacturer and model)?								
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APPENDIX D: Summary of Participants' Analytical Information

Since ready-to-use high purity solutions were distributed, no further sample treatment (digestion, analyte separation by ion exchange chromatography, etc.) other than dilution was required. Table 5 summarizes all relevant information.

APPENDIX E: Summary of Participants' Uncertainty Estimation Approaches

Since all participants applied standard-sample bracketing (SSB), the sample matrix was pure nitric acid so that no sample treatment was necessary, the only uncertainty components were the reproducibility of the measured isotope ratios. All participants calculated the standard uncertainty according to the GUM. (9–12)