CIPM MRA
Comparison reports

CCQM-P233

Absolute lithium isotope ratio in LSVEC

PILOT STUDY

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CCQM-P233
Absolute lithium isotope ratio in LSVEC

Pilot Study

September 2026

Lukas Flierl, Olaf Rienitz, and Axel Pramann
Physikalisch-Technische Bundesanstalt
Braunschweig, Lower Saxony, Germany

With contributions from:

Anita Röthke
PTB
Braunschweig, Lower Saxony, Germany

Janine Eberhardt
PTB
Braunschweig, Lower Saxony, Germany

Dirk Arnold
PTB
Braunschweig, Lower Saxony, Germany

Lu Yang
NRC
Ottawa, Ontario, Canada

Jochen Vogl
BAM
Berlin, Berlin, Germany

Marcus Oelze
BAM
Berlin, Berlin, Germany

Pranav Seena Prem
BAM
Berlin, Berlin, Germany

Kyoung-Seok Lee
KRISS
Daejeon, Hoseo, Korea

Sung Woo Heo
KRISS
Daejeon, Hoseo, Korea

Young-Gwang Kim
KRISS
Daejeon, Hoseo, Korea

Tongxiang Ren
NIM
Beijing, People's Republic of China

Panshu Song
NIM
Beijing, People's Republic of China

SUMMARY

Five National Metrology Institutes and Designated Institutes participated in the Pilot Study CCQM-P233 “Absolute lithium isotope ratio in LSVEC”. Participants were requested to evaluate the isotope ratio $n(^6\mathrm{Li})/n(^7\mathrm{Li})$ in LSVEC dissolved in dilute nitric acid, expressed in mol/mol. An overall good agreement between all submitted results was obtained. 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 results will be the basis for a joint publication presenting a new absolute isotope ratio of LSVEC. Since this is a pilot study no reference value has been determined.

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ACRONYMS

BAM	Bundesanstalt für Materialforschung und -prüfung
CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CIPM	International Committee for Weights and Measures
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
FGIM	Full gravimetric isotope mixture model
IC	Ion Chromatography
ICeGIM	Ion Chromatography enhanced Gravimetric Isotope Mixtures

INTRODUCTION

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

$$\delta_{\mathrm{LSVEC}}{}^{7}\mathrm{Li}=\frac{\dfrac{n_{\mathrm{smp}}\left({}^{7}\mathrm{Li}\right)}{n_{\mathrm{smp}}\left({}^{6}\mathrm{Li}\right)}}{\dfrac{n_{\mathrm{LSVEC}}\left({}^{7}\mathrm{Li}\right)}{n_{\mathrm{LSVEC}}\left({}^{6}\mathrm{Li}\right)}}-1 \tag{0.1}$$

Isotope deltas are important quantities for reference material producers or providers of other measurement services, such as proficiency testing schemes. Though such relative scales eliminate instrument isotope fractionation, drifts (when standard-sample bracketing (SSB) is applied) and nearly all other systematic errors, only if the scale is traceable to the SI, comparability of isotope deltas is secured over space and time. The link to the SI can be achieved by determining the absolute isotope ratio (^{6}Li to ^{7}Li) of LSVEC. Since SI-traceability of a delta scale is rarely the case and determining absolute isotope ratios is non-trivial there is a traceability exception for isotope deltas. (3)

Currently the only general method to derive absolute isotope ratios by mass spectrometry is the full gravimetric isotope mixture model (FGIM). For this primary method isotopically enriched/depleted parent materials with known purities are gravimetrically blended. From the preparation data, the measured isotope ratios of the blends and the parent materials correction factors for each isotope ratio can be calculated. The following equation demonstrates how the correction factor for the two-isotope system lithium can be derived. The subscripts A, B, and AB indicate that the corresponding quantity belongs to A (enriched in ^{6}Li), B (enriched in ^{7}Li) or AB (a blend of A and B). *m* denotes a mass, *w* a mass fraction, and *M* the atomic mass of one of the two isotopes. The lowercase *r*'s denote the measured ion intensity ratios of the material indicated by the subscript.

$$K=\frac{M\left({}^{7}\mathrm{Li}\right)}{M\left({}^{6}\mathrm{Li}\right)}\frac{w_{\mathrm{A}}\left(\mathrm{Li}\right)m_{\mathrm{A}}(r_{\mathrm{A}}-r_{\mathrm{AB}})+w_{\mathrm{B}}\left(\mathrm{Li}\right)m_{\mathrm{B}}(r_{\mathrm{B}}-r_{\mathrm{AB}})}{w_{\mathrm{A}}\left(\mathrm{Li}\right)\times m_{\mathrm{A}}r_{\mathrm{B}}(r_{\mathrm{AB}}-r_{\mathrm{A}})+w_{\mathrm{B}}\left(\mathrm{Li}\right)\times m_{\mathrm{B}}r_{\mathrm{A}}\times(r_{\mathrm{AB}}-r_{\mathrm{B}})} \tag{0.2}$$

Since the original FGIM framework depends on the knowledge of the purities, which are not directly available without the knowledge of the absolute isotope ratios, PTB has developed a new primary method combining mass spectrometry and ion chromatography (IC) – called ion chromatography enhanced gravimetric isotope mixtures (ICeGIM). The impossible direct determination of the purity of the enriched/depleted parent materials is replaced by preparing

additional blends of the parent materials with an internal standard Y — in this study a rubidium solution was used — and performing additional IC measurements.

Applying this method equation (0.2) becomes (1.3). m_{YX} denotes the mass of the internal standard Y mixed with the parent material X ($X \in \{A;B\}$) and m_{XY} denotes the mass of one of the parent materials mixed with Y. f_X denotes the ratio of the rubidium peak area to the lithium peak area in the chromatogram.

$$K = \frac{\frac{m_{YA}}{m_{AY}} f_A m_A \left(r_A - r_{AB}\right) + \frac{m_{YB}}{m_{BY}} f_B m_B \left(r_B - r_{AB}\right)}{\frac{m_{YA}}{m_{AY}} f_A m_A \left(r_B r_{AB} - r_B r_A\right) + \frac{m_{YB}}{m_{BY}} f_B m_B \left(r_A r_{AB} - r_A r_B\right)} \tag{0.3}$$

Since the IC measurements were only performed by the organizer, PTB provided only the simplified version of equation (0.3), see equation (0.4). The numeric values and the associated uncertainties of the quantities m'_A and m'_B (see APPENDIX C) were distributed later in the course of the pilot study.

$$K = \frac{m'_A \times \left(r_A - r_{AB}\right) + m'_B \times \left(r_B - r_{AB}\right)}{m'_A \times r_B \times \left(r_{AB} - r_A\right) + m'_B \times r_A \times \left(r_{AB} - r_B\right)} \tag{0.4}$$

The absolute lithium isotope ratio was derived using:

$$\frac{n\left({}^{6}\mathrm{Li}\right)}{n\left({}^{7}\mathrm{Li}\right)} = r_{\mathrm{LSVEC}} \times \frac{m'_A \times \left(r_A - r_{AB}\right) + m'_B \times \left(r_B - r_{AB}\right)}{m'_A \times r_B \times \left(r_{AB} - r_A\right) + m'_B \times r_A \times \left(r_{AB} - r_B\right)} \tag{0.5}$$

This equation served as model for the uncertainty evaluation.

In July 2023, the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) approved the Pilot Study (PS) CCQM-P233 “Absolute lithium isotope ratio in LSVEC”. CCQM-P233 was designed to foster and assess participants’ capabilities to determine the absolute lithium isotope in LSVEC and test a novel primary method developed by PTB. (4) In the “Strategy for Rolling Programme Development (2021-2030)” of the CCQM Working Group on Isotope Ratios (IRWG) (5), the IRWG dedicates itself to foster the capabilities of its members to measure absolute isotope ratios by applying the FGIM approach and making the LSVEC scale SI-traceable. The respective capabilities include the experimental design, uncertainty evaluation etc. Hence, CCQM-P233 supports the aims of the IRWG and supports core capabilities of the participants. Furthermore CCQM-P233 follows a recommendation of the CIPM to link existing delta scales to the SI, like in case of LSVEC. (3)

In parallel to CCQM-P233, PTB organized CCQM-K182 “Lithium isotope delta measurements”. Therefore, the reporting sheet, the technical protocol and the registration form contain both studies.

The following sections of this report document the timeline of CCQM-P233, the measurands, study material, participants, results, and the measurement capability claims that participation in CCQM-P233 can support. The appendices reproduce the official communication materials and summarize the information about the results provided by the participants.

TIMELINE

Table 1 lists the timeline for CCQM-P233.

Table 1: Timeline for CCQM-P233

Date	Action
04/2023	Proposed to CCQM
07/2023	IRWG authorized CCQM-P233
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.
	Distribution of supplementary technical protocol
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 absolute lithium isotope ratio ($n(^6\mathrm{Li})/n(^7\mathrm{Li})$ in mol/mol) in a solution of LSVEC (Li_2CO_3) by applying the FGIM approach. LSVEC was dissolved in dilute nitric acid ($w(\mathrm{Li}) \approx 2$ µg/g, $w(HNO_3) \approx 0.01$ g/g = 1 %).

STUDY MATERIALS

Each participant received four samples: A (enriched in ^{6}Li), B (enriched in ^{7}Li), and LSVEC. The whole preparation is schematically presented in Figure 1.

Sample A was prepared by combining two lithium carbonates enriched in ^{6}Li. About 0.9 g of the first enriched carbonate (Sigma-Aldrich, Saint Louis, USA, batch MBBB2987V, $x(^6\mathrm{Li}) \approx 0.955$ mol/mol, $w(Li_2CO_3) > 0.99$ g/g) and 0.6 g of a second spike (batch MBBC2913, $x(^6\mathrm{Li}) \approx 0.954$ mol/mol, $w(Li_2CO_3) > 0.99$ g/g) were mixed and dissolved in nitric acid.

The resulting stock solution ($m \approx 250$ g) contained about 1070 µg/g lithium and 0.01 g/g nitric acid. It was then diluted in two steps to reach a final lithium concentration of roughly 2 µg/g while maintaining $w(HNO_3) \approx 0.01$ g/g. A total of 2 kg of solution was prepared.

Material B was a lithium carbonate depleted in ^{6}Li (Sigma-Aldrich, Saint Louis, USA, batch MBBC7757, $x(^7\mathrm{Li}) > 0.99$ mol/mol, $w(Li_2CO_3) > 0.99$ g/g). About 1.5 g of the carbonate was

dissolved in nitric acid to prepare the stock solution. The resulting solution ($m \approx 250$ g) contained roughly 1125 µg/g lithium and 0.01 g/g nitric acid. It was then diluted in two steps to achieve a final lithium mass fraction of roughly 2 µg/g while maintaining roughly 0.01 g/g nitric acid. A total of 2 kg of solution was prepared.

Material AB is a blend of A and B, prepared under gravimetric control to achieve an ion intensity ratio of about 1 V/V (assuming a *K*-factor of 1.29 (mol/mol)/(V/V)). About 37 g of solution A.1 and 30 g of solution B.1 were mixed and diluted with roughly 33 g of nitric acid (0.01 g/g), see Figure 1.

The mixture was homogenized for 36 h using a mechanical shaker and then further diluted to obtain a final lithium concentration of ≈ 2 µg/g and a nitric acid content of ≈ 0.01 g/g.

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 in one step to adjust the final solution of 2 kg to a lithium mass fraction of roughly 2 µg/g while maintaining roughly 0.01 g/g nitric acid.

The final solutions (roughly 2000 g, $w(HNO_3) = 0.01$ g/g, $w(Li) \approx 2$ µg/g) were likewise dispensed into 50 mL PFA bottles, yielding 4 × 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.

All weighing steps were performed at PTB using a mechanical balance (Mettler H315), which is checked annually and largely insensitive to electrostatic effects. Residual charges were minimized with a piezoelectric anti-static pistol (Sigma-Aldrich ZEROSTAT 3).

Participants were asked to weigh their samples immediately upon receipt and report the mass of each bottle along with the ambient conditions (temperature, humidity, and pressure). In case of two bottles, leaks were detected so that replacements were 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 (6), and also provided a piece of high-purity silicon ($m \approx 250$ mg, $w(Si) > 0.9999$ g/g). Participants were free to use this piece of Si or to apply any other memory reducing strategy or none.

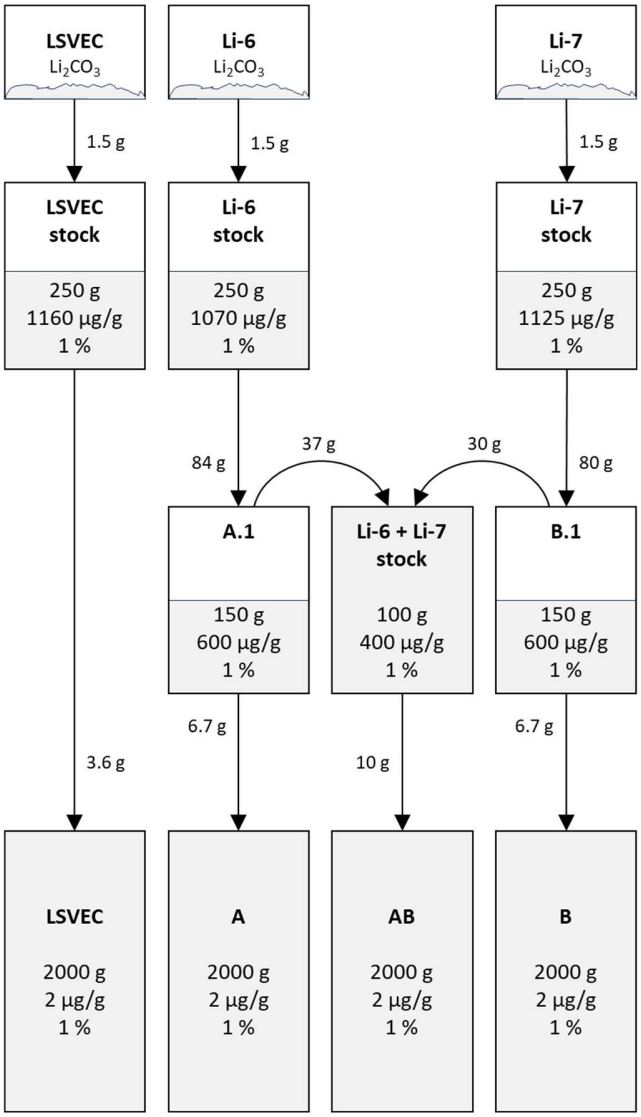

Figure 1: Schematic of sample preparation

Figure 2 illustrates the preparation of the additional blends AY and BY, which were required for the IC measurements to replace the conventional purity assessment. Each blend contained one parent material and an internal rubidium standard solution.

The Rb solution was prepared from high-purity RbCl (Sigma-Aldrich, lot MKCN5710, w(RbCl) ≈ 0.995 g/g) dissolved in nitric acid, resulting in w(Rb) ≈ 2000 µg/g and 0.0002 g/g = 0.02 % nitric acid. About 25 g of this solution, 8.3 g of one parent material, and 466.7 g ultrapure water were mixed to prepare AY and BY. The final blends contained w(Rb) ≈ 100 µg/g, w(Li) ≈ 10 µg/g, and $w(HNO_3)$ ≈ 0.2 mg/g = 0.02 %.

These concentrations were selected to achieve peak area ratios close to unity, minimizing the uncertainty. Previous IC experiments showed that the lithium sensitivity in the established setup is about ten times higher than that of Rb

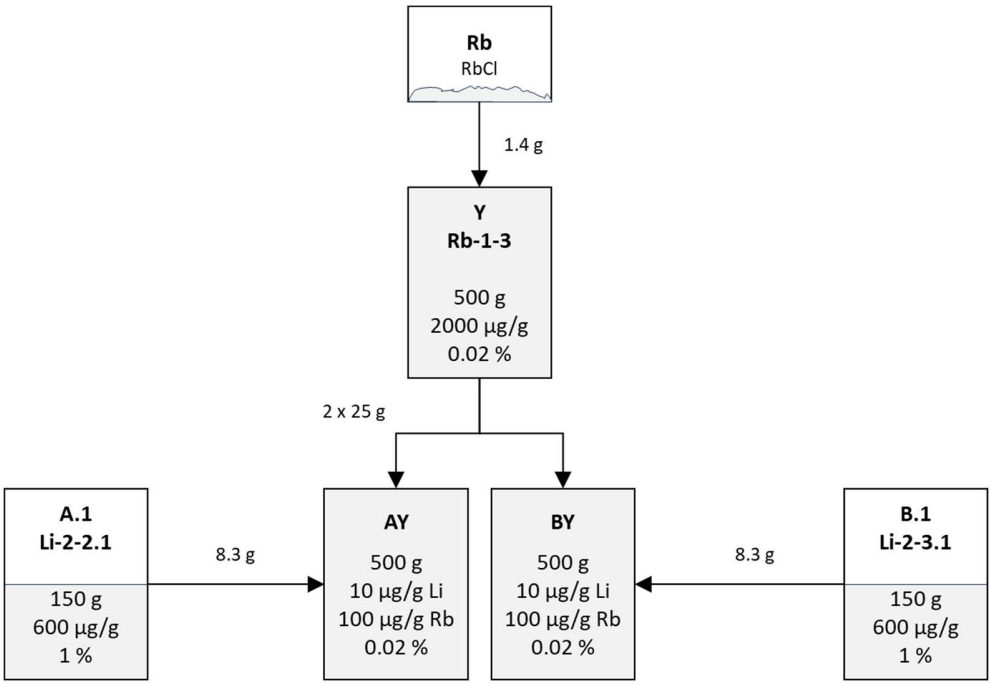

Figure 2: Schematic of the preparation of the additional solutions for the IC measurements

HOMOGENEITY ASSESSMENT OF STUDY MATERIAL

According to Vogl et al. (7,8) acidified aqueous mono-elemental solutions at the µg/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 absolute isotope ratios $n(^6\mathrm{Li})/n(^7\mathrm{Li})$ are plotted against time (in days) after sample preparation and shown in Figure 3 to Figure 6.

For each data set a linear regression curve was fitted. The results are summarized in Table 2. 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 (9).

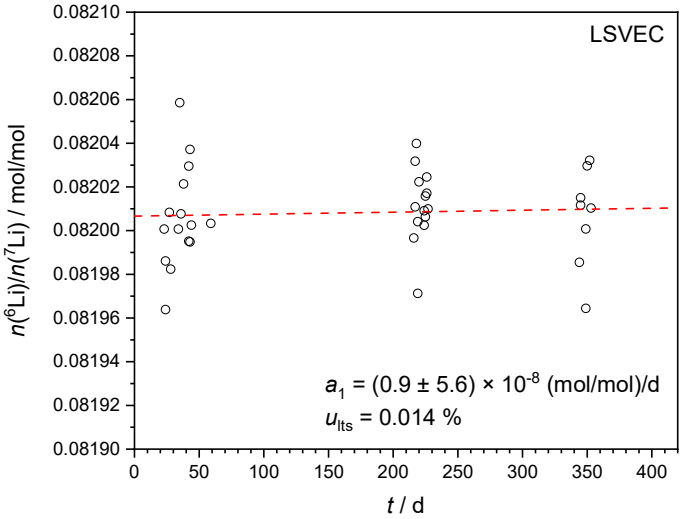

Figure 3: Stability assessment of $n(^6Li)/n(^7Li)$ in LSVEC, over the whole duration of the key comparison

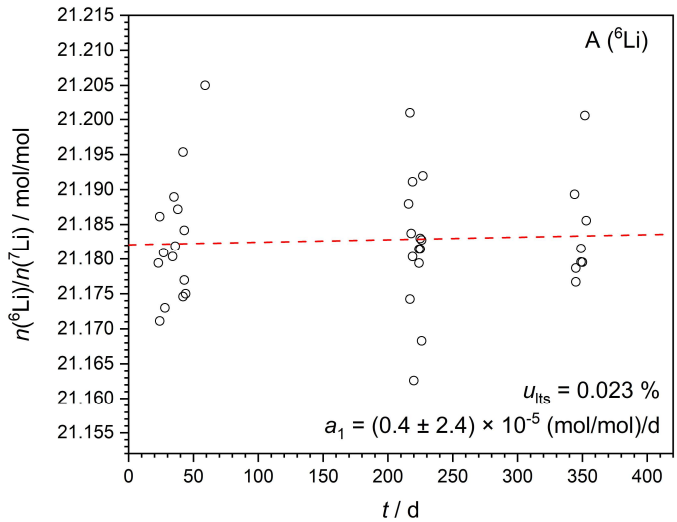

Figure 4: Stability assessment of $n(^6Li)/n(^7Li)$ in A, over the whole duration of the key comparison

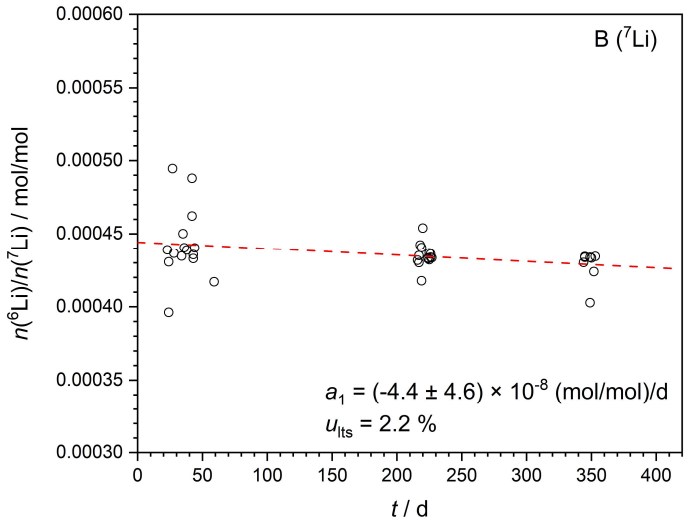

Figure 5: Stability assessment of $n(^6\text{Li})/n(^7\text{Li})$ in B, over the whole duration of the key comparison

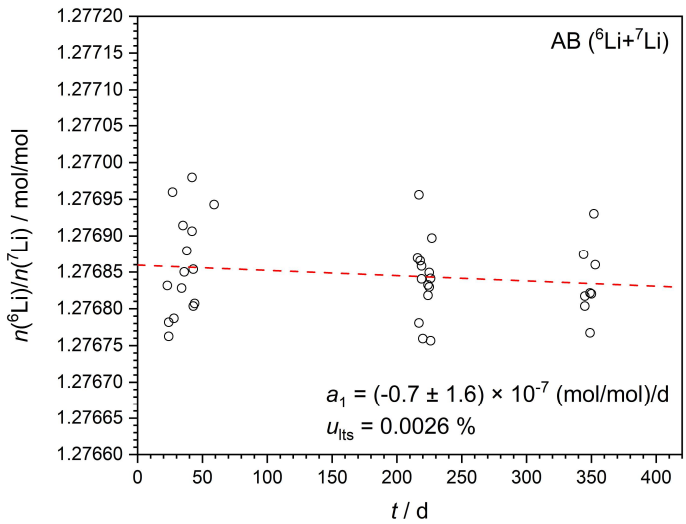

Figure 6: Stability assessment of $n(^6\text{Li})/n(^7\text{Li})$ in AB, over the whole duration of the key comparison

Table 2: Summary of linear regression fits for the stability assessment. a_1 is the slope of the regression line.

sample	a_1	$k \times s(a_1)$	$[a_1]$	$u_{\mathrm{lts,rel}}$
LSVEC	0.9×10^{-8}	5.6×10^{-8}	(mol/mol)/d	0.014 %
A	0.4×10^{-5}	2.4×10^{-5}	(mol/mol)/d	0.023 %
B	-4.4×10^{-8}	4.6×10^{-8}	(mol/mol)/d	2.2 %
AB	-0.7×10^{-7}	1.6×10^{-7}	(mol/mol)/d	0.0026%

RESULTS

Participants were asked to report a single estimate of the absolute isotope ratio $n(^6\mathrm{Li})/n(^7\mathrm{Li})$ in LSVEC. In addition to the quantitative results, participants were instructed to describe their analytical methods and approach to uncertainty estimation. APPENDIX D reproduces the report form. Results were received from 5 of the 5 registered institutes.

METHODS USED BY PARTICIPANTS

Since all samples were high purity solutions in dilute nitric acid, no further sample treatment by the participants was required. PTB provided ready-to-use LSVEC solutions prepared from the same stock solution. No reference material to establish SI-traceability was required because the FGIM is an ab-initio method that does not rely on a reference material. Table 3 summarizes the measurement methods used by the participating NMIs/DIs for CCQM-P233

Table 3: Summary of measurement methods used

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

PARTICIPANTS' RESULTS FOR $n(^6Li)/n(^7Li)$ IN LSVEC, A, B AND AB

The results for CCQM-P233 for the determination of $n(^6Li)/n(^7Li)$ in LSVEC are detailed in Table 4 and presented graphically in Figure 7. The results of $n(^6Li)/n(^7Li)$ in A are detailed in Table 5 and presented graphically in Figure 8. The results of $n(^6Li)/n(^7Li)$ in B are detailed in Table 6 and presented graphically in Figure 9. And finally, the results of $n(^6Li)/n(^7Li)$ in AB are detailed in Table 7 and presented graphically in Figure 10.

Table 4: $n(^6Li)/n(^7Li)$ in LSVEC as reported by the participants

Participant	$n(^6Li)/n(^7Li)$ in mol/mol	standard uncertainty in mol/mol	Coverage factor k	Expanded uncertainty in mol/mol
NIM	0.081944	0.000025	2.26	0.000057
NRC	0.081998	0.000051	2.00	0.00010
PTB	0.082006	0.000051	2.024	0.00010
KRISS	0.0820095	0.0000035	2.78	0.0000097
BAM	0.082022	0.000056	2.00	0.00011

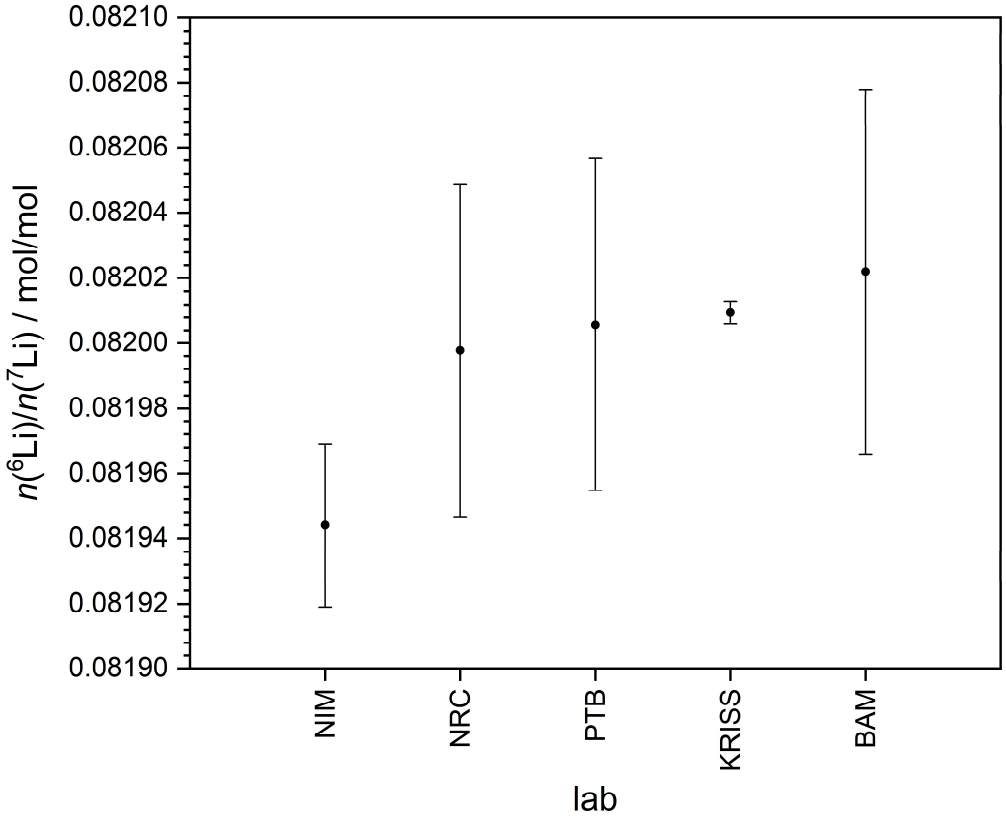

Figure 7: Results reported for $n(^6\mathrm{Li})/n(^7\mathrm{Li})$ in LSVEC, error bars represent combined uncertainties u_c (k = 1)

Table 5: $n(^6Li)/n(^7Li)$ in A (^6Li spike) as reported by the participants

Participant	$n(^6Li)/n(^7Li)$ in mol/mol	standard uncertainty in mol/mol	Coverage factor k	Expanded uncertainty in mol/mol
BAM	21.146	0.036	2.00	0.072
KRISS	21.1675	0.0024	2.78	0.0066
NIM	21.1750	0.0090	2.26	0.020
NRC	21.178	0.019	2.00	0.038
PTB	21.183	0.025	2.024	0.051

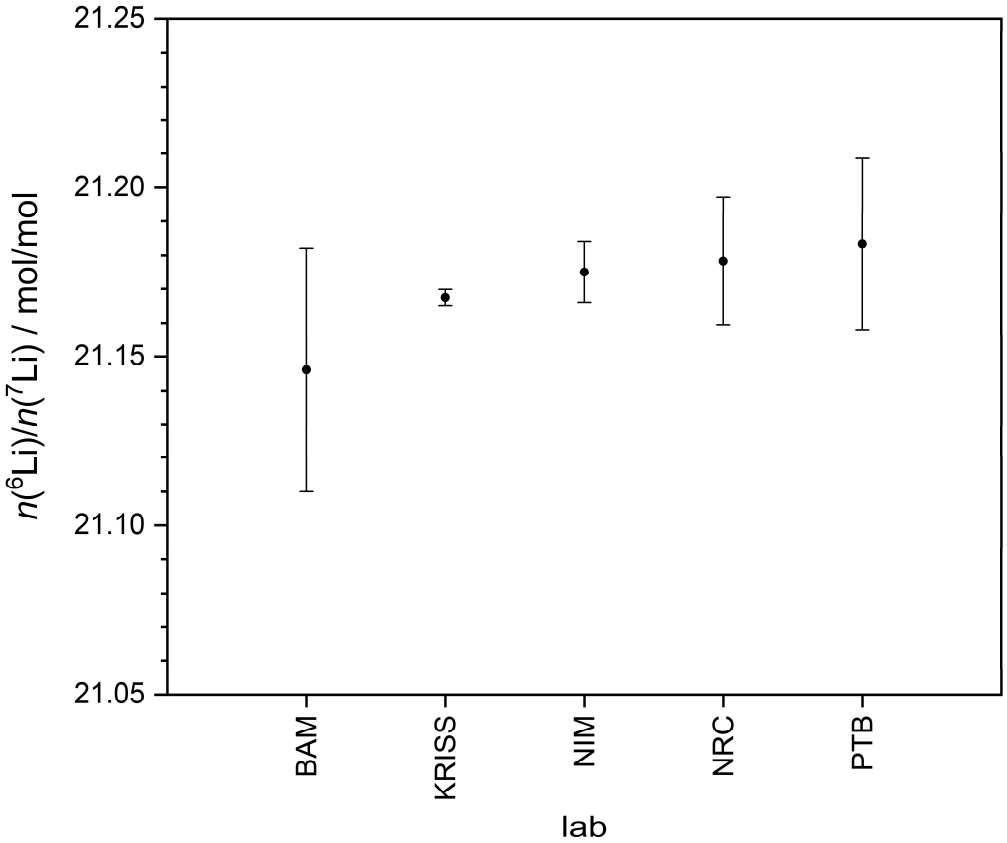

Figure 8: Results reported for $n(^6Li)/n(^7Li)$ in A, error bars represent combined uncertainties u_c ($k = 1$)

Table 6: $n(^6Li)/n(^7Li)$ in B (^7Li spike) as reported by the participants

Participant	$n(^6Li)/n(^7Li)$ in mol/mol	standard uncertainty in mol/mol	Coverage factor k	Expanded uncertainty in mol/mol
NIM	0.0004332	0.0000007	2.26	0.0000016
PTB	0.000435	0.000022	2.024	0.000045
NRC	0.0004355	0.0000072	2.00	0.000014
KRISS	0.0004427	0.0000010	2.78	0.0000028
BAM	0.0004522	0.0000088	2.00	0.000018

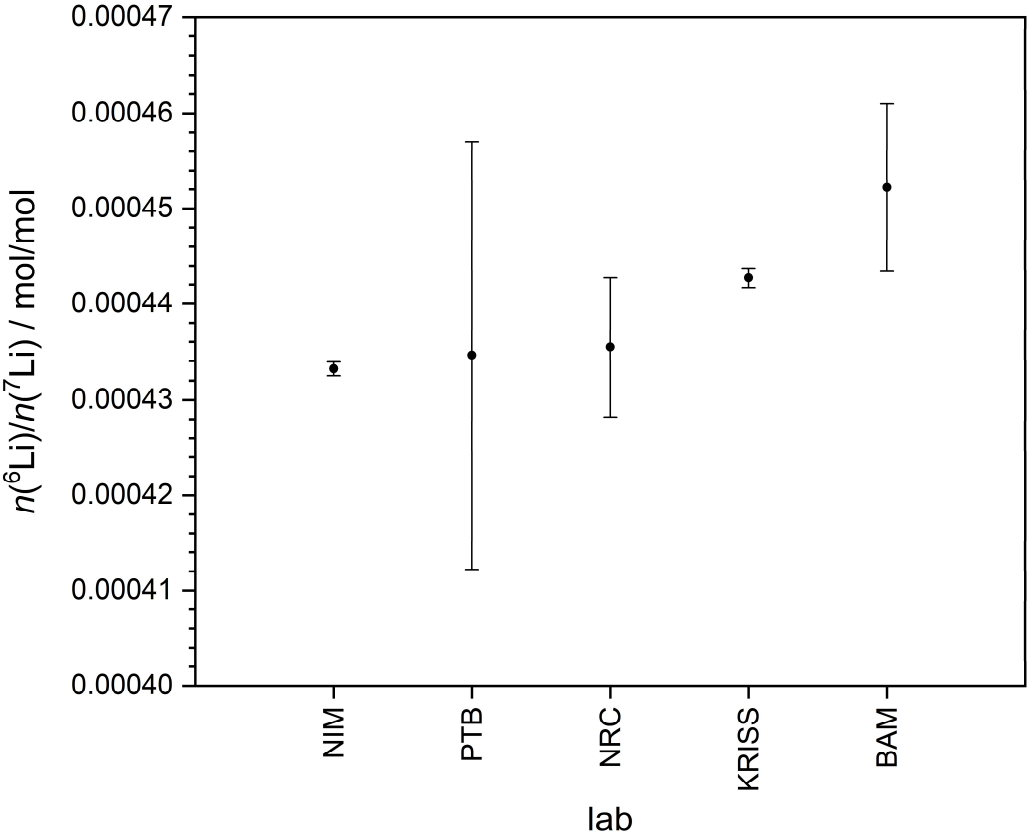

Figure 9: Results reported for $n(^6Li)/n(^7Li)$ in B, error bars represent combined uncertainties u_c (k = 1)

Table 7: $n(^6Li)/n(^7Li)$ in AB (blend of ^6Li and ^7Li spikes) as reported by the participants

Participant	$n(^6Li)/n(^7Li)$ in mol/mol	standard uncertainty in mol/mol	Coverage factor k	Expanded uncertainty in mol/mol
BAM	1.27665	0.00040	2.00	0.00080
KRISS	1.276766	0.000016	2.78	0.000043
NIM	1.27679	0.00038	2.26	0.00086
NRC	1.27682	0.00084	2.00	0.0017
PTB	1.27685	0.00037	2.024	0.00075

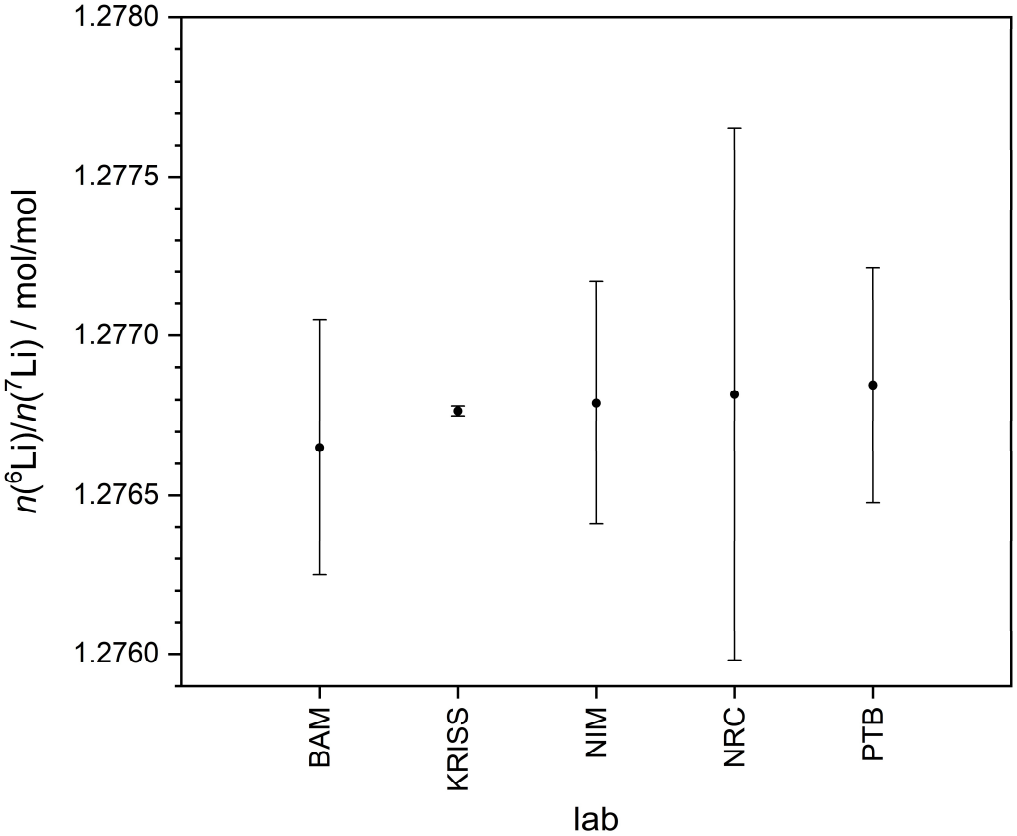

Figure 10: Results reported for $n(^6Li)/n(^7Li)$ in AB, error bars represent combined uncertainties u_c (k = 1)

DISCUSSION OF RESULTS

The results presented in Table 4 show overall good agreement between all participants, therefore no further investigations were conducted.

KEY COMPARISON REFERENCE VALUE (KCRV)

Since this is a pilot study, the calculation of a KCRV is not required. The data of this study will be the basis for a later joint publication presenting a new absolute Li isotope ratio of LSVEC.

DEGREES OF EQUIVALENCE (DoE)

Since this is a pilot study, the calculation of DoE is not required. The data of this study will be the basis for a later joint publication presenting a new absolute Li isotope ratio of LSVEC.

USE OF CCQM-P233 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

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

CCQM-P233 Absolute lithium isotope ratios in LSVEC

Successful participation in CCQM-P233 can be used as "additional evidence" when claiming measurement capabilities for the determination of $R(^6\mathrm{Li}/^7\mathrm{Li})$ in mono-elemental solutions of Li in dilute nitric acid within the interval of 4×10^{-4} mol/mol $\leq R(^6\mathrm{Li}/^7\mathrm{Li}) \leq 22$ mol/mol, typically realized using a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) in low resolution mode and applying an FGIM approach with enriched parent materials having known chemical purities (4). The reported measurement uncertainty is the best demonstrated uncertainty for the method employed.

For demonstrating the measurement capability, it is recommended that measures have to be taken to deal with the memory effect Li exhibits; e. g. employing an H_2SiF_6 (6), NaCl (10) solution or reducing the Li mass fraction during the measurements significantly by making use of a desolvator technique. To account for possible drifts of the instrumental isotopic fractionation (mass bias), the measurement sequence should be designed in a highly symmetric way or drift correction samples must be incorporated in the sequence to be able to apply a mathematical drift correction.

The successful participation in this pilot study can be used as supporting evidence for CMC claims for absolute isotope ratios of elements measurable in low resolution in high purity matrices like dilute nitric acid. For this, certain requirements are indispensable: Enriched parent materials for all isotopes of an element have to be available and their chemical purity is known or can be determined with a sufficiently low uncertainty. Another crucial requirement is the capability to do metrological weighings (calibrated balances, air buoyancy and evaporation correction). In case the sample has a more complex matrix, the capability to separate the analyte element from this matrix without changing the isotopic pattern outside the aimed at uncertainty needs to be demonstrated additionally. In any case, additional uncertainty contributions may result in higher associated uncertainties.

CONCLUSIONS

In CCQM-P233 participants were asked to determine $n(^6\text{Li})/n(^7\text{Li})$ in LSVEC in dilute nitric acid by applying the FGIM approach and having additional knowledge about the purity of the used enriched/depleted parent materials. The overall good agreement proves that participants successfully mastered this task and supports future claims of determining absolute isotope ratios 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

Physikalisch-Technische Bundesanstalt
National Metrology Institute

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 δ^7Li 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 $w(\text{Li}) \approx 2$ µg/g. The solvent is HNO_3 ($w(HNO_3) \approx 0.01$ 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 ^{6}Li spike solution, the third bottle contains 40 g of a ^{7}Li spike solution and the fourth contains 40 g of a blend of the ^{6}Li and ^{7}Li 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 $\delta_{LSVEC}(^7Li/^6Li)$ 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 $n(^7Li)/n(^6Li)$ 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 $n(^7Li)/n(^6Li)$ and associated uncertainties of the two spike solutions and the blend solution as well as the absolute isotope ratios $n(^7Li)/n(^6Li)$ 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 $n(^7Li)/n(^6Li)$ 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	and	PTB
Olaf Rienitz		Lukas Flierl
Bundesallee 100		Bundesallee 100
38116 Braunschweig		38116 Braunschweig
Germany		Germany
Phone: +49 531 5923110		+49 531 5923319
E-Mail: olaf.rienitz@ptb.de		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

Bibliography

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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**
δ^7Li in sample A		
δ^7Li 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 ^{6}Li spike A		
$n(^7\text{Li})/n(^6\text{Li})$ in ^{7}Li 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
38116 Braunschweig
Germany
Phone: +49 531 5923110
E-Mail: olaf.rienitz@ptb.de

and

PTB
Lukas Flierl
Bundesallee 100
38116 Braunschweig
Germany
+49 531 5923319
lukas.flierl@ptb.de

2023-10-23

APPENDIX B: Technical Protocol

Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin

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 (^{6}Li and ^{7}Li) 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 ($\delta\,^7\mathrm{Li}_{\mathrm{LSVEC}}$) 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, $w(HNO_3)$ = 0.01 g/g, and w(Li) ≈ 1140 µg/g). This stock solution was diluted, using approximately 3.5 g of the stock solution and 1996.5 g of nitric acid ($w(HNO_3)$ = 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 µg/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(Li) ≈ 985 µg/g). To prepare the stock solution of BAM-2 ($m_{\mathrm{stock}} \approx$ 500 g, $w(HNO_3)$ = 0.01 g/g, and w(Li) ≈ 15 µg/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 µg/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, $w(HNO_3) = 0.01$ g/g, and $w(\mathrm{Li}) \approx 2$ µg/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(Li) / (µg/g)	δ_{LSVEC} ^{7}Li / ‰
50 mL	40	BAM-1	2	15
50 mL	40	BAM-2	2	-5
50 mL	40	LSVEC	2	0

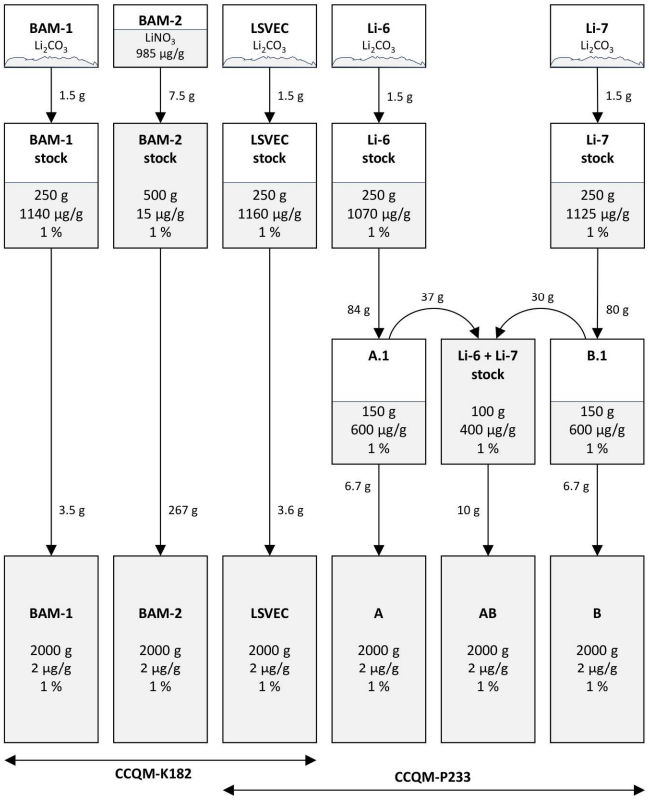

Figure 1: Preparation of the samples distributed in K182 and P233

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 ^{6}Li. To prepare the stock solution of A, roughly 1 g of the first enriched carbonate (Sigma-Aldrich, Saint Louis, USA, batch number MBBB2987V, $x(^{6}\mathrm{Li}) \approx 0.955$ mol/mol, $w(\mathrm{Li_2CO_3}) > 0.99$ g/g) and roughly 0.6 g of the second spike (Sigma-Aldrich, Saint Louis, USA, batch number MBBC2913, $x(^{6}\mathrm{Li}) \approx 0.954$ mol/mol, $w(\mathrm{Li_2CO_3}) > 0.99$ g/g) were pooled and dissolved in nitric acid. The stock solution ($m \approx 250$ g) had a lithium mass fraction of approximately 1070 µg/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 µg/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 ^{6}Li (Sigma-Aldrich, Saint Louis, USA, batch number MBBC7757, $x(^{7}\mathrm{Li}) > 0.99$ mol/mol, $w(\mathrm{Li_2CO_3}) > 0.99$ 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 µg/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 µg/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 ($w(\mathrm{HNO_3}) = 0.01$ 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 µg/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*(Li) / (µg/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(Li) ≈ 10 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(Si) ≈ 1000 µg/g, w(HF) ≈ 0.002 g/g and $w(HNO_3)$ < 0.01 g/g) to coat their ICP-MS cones. This approach allows to reduce the memory effect and enables users to use higher anlyte 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 ≈ 250 mg, w(Si) > 0.9999 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:

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

The deltas should be reported in ‰:

$$\delta_{\mathrm{LSVEC}}\,{}^{7}\mathrm{Li} = \left(\frac{r_{\mathrm{smp}}\left({}^{7}\mathrm{Li}/{}^{6}\mathrm{Li}\right)}{r_{\mathrm{LSVEC}}\left({}^{7}\mathrm{Li}/{}^{6}\mathrm{Li}\right)} - 1 \right) \times 1000\ ‰ \tag{1}$$

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

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

$$R = K \times r \tag{2}$$

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:

$$K = \frac{M\left({}^{7}\mathrm{Li}\right)}{M\left({}^{6}\mathrm{Li}\right)} \times \frac{m_{\mathrm{A}} \times (r_{\mathrm{A}} - r_{\mathrm{AB}}) + m_{\mathrm{B}} \times (r_{\mathrm{B}} - r_{\mathrm{AB}})}{m_{\mathrm{A}} \times r_{\mathrm{B}} \times (r_{\mathrm{AB}} - r_{\mathrm{A}}) + m_{\mathrm{B}} \times r_{\mathrm{A}} \times (r_{\mathrm{AB}} - r_{\mathrm{B}})}. \tag{3}$$

The lower rs 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]:

$$K = \frac{m'_{\mathrm{A}} \times \left(r_{\mathrm{A}} - r_{\mathrm{AB}}\right) + m'_{\mathrm{B}} \times \left(r_{\mathrm{B}} - r_{\mathrm{AB}}\right)}{m'_{\mathrm{A}} \times r_{\mathrm{B}} \times \left(r_{\mathrm{AB}} - r_{\mathrm{A}}\right) + m'_{\mathrm{B}} \times r_{\mathrm{A}} \times \left(r_{\mathrm{AB}} - r_{\mathrm{B}}\right)}. \tag{4}$$

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 $r\left(m'_{\mathrm{A}}, m'_{\mathrm{B}}\right)$ 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:

Dr. Olaf Rienitz		Dr. Lukas Flierl
Physikalisch-Technische Bundesanstalt		
Bundesallee 100		
38116 Braunschweig		
Germany		
Fax	+49-531-592-3015	
Phone	+49-531-592-3110	-3319
E-Mail	olaf.rienitz@ptb.de	lukas.flierl@ptb.de

6. References

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APPENDIX C: Supplementary Technical Protocol

Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin

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

Supplementary Technical Protocol

S1. "Masses" m'_A and m'_B

For the calculation of the mass bias correction factor K according to equation (4) in the Technical Protocol please use the values below:

X_i	x_i / g	$u_{rel}(x_i)$ / %	ν_{eff}
m'_A	107.774456	0.016	72
m'_B	75.802148	0.019	43
$u(m'_A, m'_B) \approx 0$			

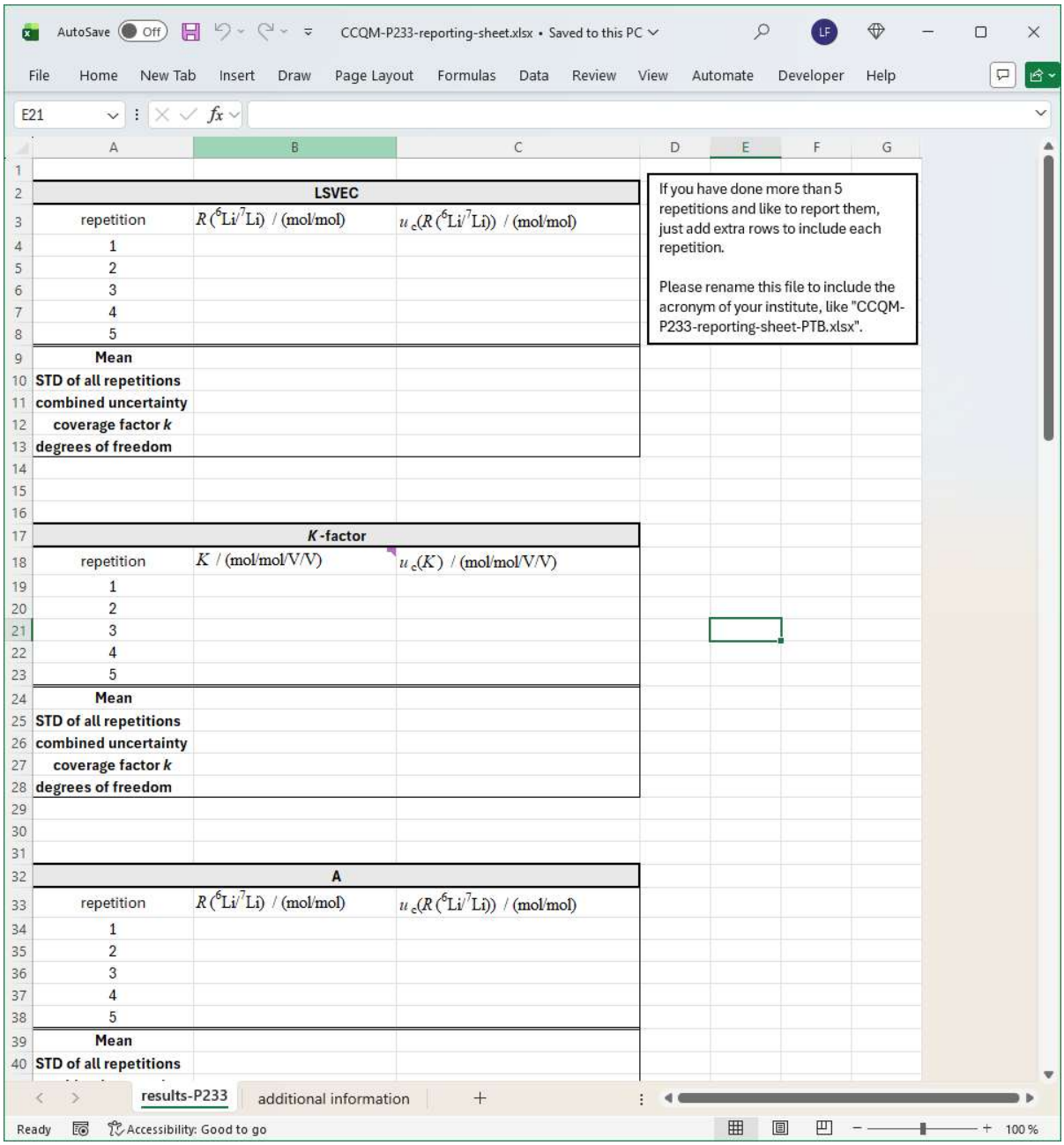
While rounding according to the uncertainty would result in three digits, three additional digits are given to achieve the highest accuracy in the final result (the absolute isotope ratio of LSVEC). Therefore, please use the values with all given digits in your calculations, only round the final result according to the GUM. The stated uncertainties are relative combined uncertainties with a coverage factor of $k = 1$. If any further assistance is needed, please contact us.

Contact:

Dr. Olaf Rienitz
Physikalisch-Technische Bundesanstalt
Bundesallee 100
38116 Braunschweig
Germany
Fax +49-531-592-3015
Phone +49-531-592-3110
E-Mail olaf.rienitz@ptb.de

Dr. Lukas Flierl
-3319
lukas.flierl@ptb.de

APPENDIX D: Reporting Form



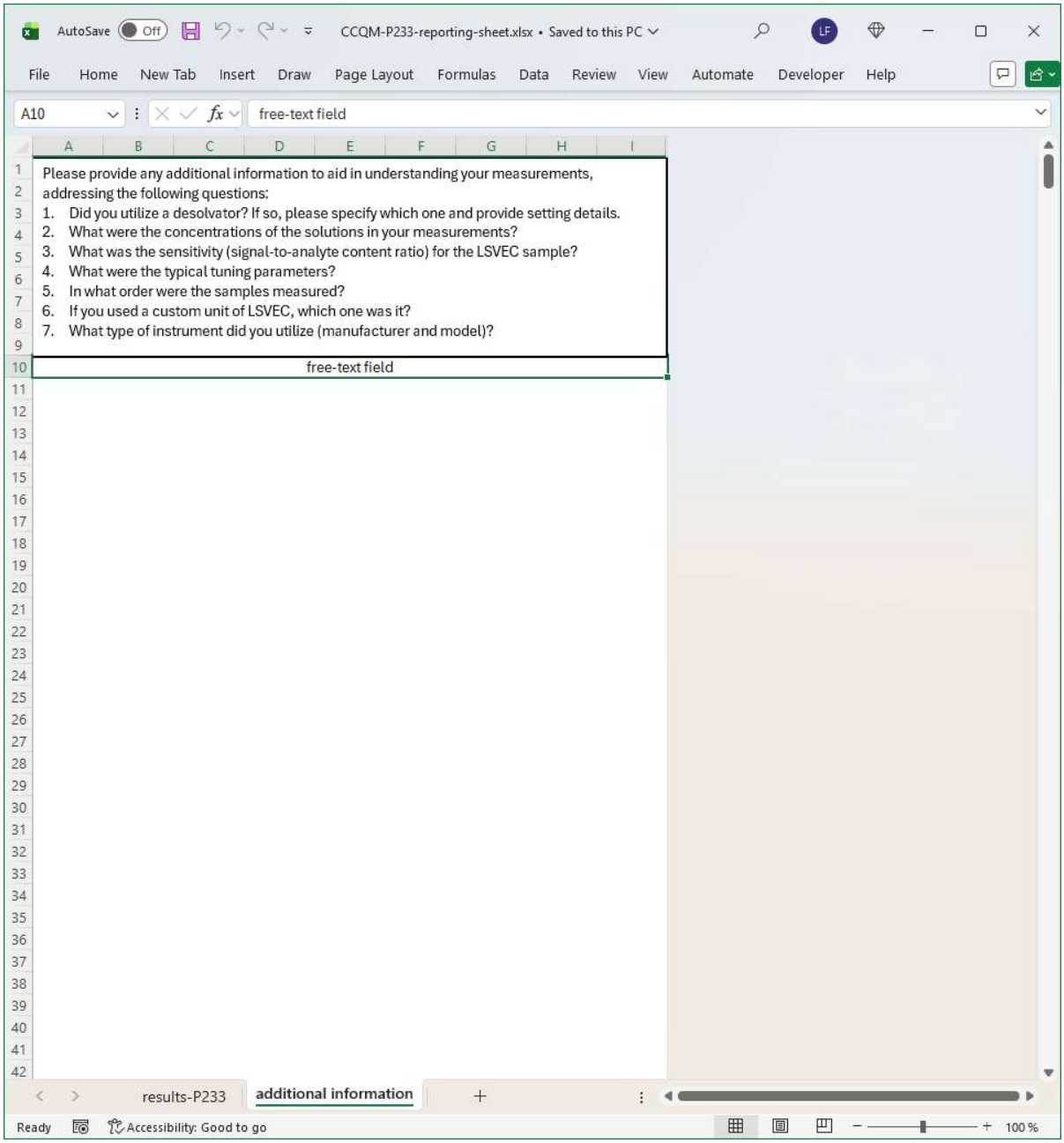
LSVEC		
repetition	$R(^6Li/^7Li)$ / (mol/mol)	$u_c(R(^6Li/^7Li))$ / (mol/mol)
1		
2		
3		
4		
5		
Mean		
STD of all repetitions		
combined uncertainty		
coverage factor *k*		
degrees of freedom		

If you have done more than 5 repetitions and like to report them, just add extra rows to include each repetition.

Please rename this file to include the acronym of your institute, like "CCQM-P233-reporting-sheet-PTB.xlsx".

***K*-factor**		
repetition	K / (mol/mol/V/V)	$u_c(K)$ / (mol/mol/V/V)
1		
2		
3		
4		
5		
Mean		
STD of all repetitions		
combined uncertainty		
coverage factor *k*		
degrees of freedom		

A		
repetition	$R(^6Li/^7Li)$ / (mol/mol)	$u_c(R(^6Li/^7Li))$ / (mol/mol)
1		
2		
3		
4		
5		
Mean		
STD of all repetitions		



Please provide any additional information to aid in understanding your measurements, addressing the following questions:

1. Did you utilize a desolvator? If so, please specify which one and provide setting details.
2. What were the concentrations of the solutions in your measurements?
3. What was the sensitivity (signal-to-analyte content ratio) for the LSVEC sample?
4. What were the typical tuning parameters?
5. In what order were the samples measured?
6. If you used a custom unit of LSVEC, which one was it?
7. What type of instrument did you utilize (manufacturer and model)?

free-text field

APPENDIX E: 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 3 summarizes all relevant information.

APPENDIX F: Summary of Participants' Uncertainty Estimation Approaches

All participants but KRISS used equation (0.5) as the model for the determination of the combined uncertainty according to the GUM (11–14). The uncertainty contributions were the reproducibility of the measured ion intensities (lowercase *r*) and the standard uncertainties associated with m'_A and m'_B provided by PTB.

KRISS reported the reproducibility of the absolute isotope ratio of LSVEC, which neglected the contributions of the aforementioned quantities according to the model equation.