National Institute of Standards and Technology
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Reference Material 8545
LSVEC
(Lithium Isotopes in Lithium Carbonate)
REFERENCE MATERIAL INFORMATION SHEET

Purpose: This Reference Material (RM) is an international measurement standard [1–2] that defines the δ-scale ($\delta^{7}Li_{LSVEC}$) for relative isotope ratio measurements of lithium (Li). The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) is LSVEC. The absolute lithium isotope ratio and its expanded uncertainty are also listed on this reference material information sheet. The International Union of Pure and Applied Chemistry (IUPAC) recommends all relative lithium isotopic measurements be reported as $\delta^{7}Li_{LSVEC}$ [2]; relative lithium isotopic values are given as $\delta^{7}Li_{LSVEC}$ in this document. Historically, absolute isotope ratios for lithium have been given as $^{6}Li/^{7}Li$ [3]; absolute values for lithium isotopes are given as $^{6}Li/^{7}Li$ in this document.

Description: A unit of RM 8545 consists of one bottle containing approximately 0.4 g of lithium-carbonate (Li_2CO_3).

Non-Certified Values: Although not certified, the assigned isotope-delta and absolute isotope-number ratio values for this RM, provided in Tables 1 and 2 below, are at present the best estimates of the true values.

Table 1. Non-Certified Value for $\delta^{7}Li_{LSVEC}$ in RM 8545

NIST RM Number	Name	Non-Certified Value $\delta^{7}Li_{LSVEC}$	Combined Uncertainty $\delta^{7}Li_{LSVEC}$ [(a)]	Expanded Uncertainty $\delta^{7}Li_{LSVEC}$ [(a)]
8545	LSVEC	0.0 ‰	0.0 ‰	0.0 ‰

[(a)] RM 8545 is given with a combined standard uncertainty in addition to an expanded uncertainty value, $k = 2$, for each assigned value. The expanded uncertainty is equal to $U = ku_c$, where u_c is the combined standard uncertainty and k is the coverage factor, as defined in the ISO/JCGM Guide [4]. Non-certified values and uncertainties are given in units of per mil (‰), which is equivalent to per thousand. The $\delta^{7}Li_{LSVEC}$ value is an exact value in units of per mil (‰) and is the anchor for the $\delta^{7}Li_{LSVEC}$ scale. Values for $\delta^{13}C$ are given in the text for historical purposes; this material is no longer recommended for $\delta^{13}C$ measurements. See important note below. This material, by definition, has no uncertainty; it has a value of zero for combined standard uncertainty and expanded uncertainty value, $k = 2$.

Period of Validity: The non-certified value is valid within the measurement uncertainty specified until **31 December 2032.** The value assignments are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Maintenance of Non-Certified Values: NIST will monitor this material to the end of its period of validity. If substantive technical changes occur that affect the non-certified values during this period, NIST will update this Reference Material Information Sheet and notify registered users. RM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the RM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (https://www.nist.gov/srm).

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Table 2. Non-Certified Value for the Absolute $^6Li/^7Li$ Isotope Ratio for RM 8545

NIST RM Number	Name	$^6Li/^7Li$[(a)]	Expanded Uncertainty $^6Li/^7Li$[(a)]
8545	LSVEC	0.08215	0.00023

[(a)] Expanded uncertainty ($k = 2$) [3]

IMPORTANT NOTE: The use of this reference material for $\delta^{13}C$ is no longer recommended. Recent $\delta^{13}C$ measurements at the IAEA [5] and USGS [6] have clearly established that LSVEC shows at least a 0.2 ‰ range in $\delta^{13}C$ values and therefore is no longer considered isotopically stable or homogeneous. **However, this does not affect the $\delta\,^7Li_{LSVEC}$ nor the absolute $^6Li/^7Li$ isotope-number ratio of this reference material**.

Metrological Traceability: LSVEC is the accepted "stated reference" zero point of the lithium isotope delta metrological traceability chains [2]. LSVEC is realized primarily and explicitly through the lithium carbonate RM 8545, where:

RM 8545 *Lithium carbonate*: $\delta^7Li_{LSVEC} \equiv 0$ ‰

Isotope-delta values for lithium are not traceable to the International System of Units (SI) or other higher-order reference system [4,7]. A *Traceability Exception* has been approved by the Bureau International des Poids et Mesures (BIPM) International Committee for Weights and Measures (CIPM), which states non-SI traceable isotope values "should be made traceable to materials recognized as International Standards" [7,8]. The absolute values of lithium isotope-number ratios made by Qi et al, 1997, were carried out on gravimetrically prepared solutions and therefore are SI traceable [3].

Safety: Consult the Safety Data Sheet (SDS) for hazard information.

Storage: RM 8545 (LSVEC) is stable at normal room temperatures and should be stored in the original container at ambient temperature (20 ºC to 30 ºC) to minimize the potential for contamination. See IMPORTANT NOTE above with regards to not using this RM for $\delta^{13}C$ measurements.

Additional Information: The distribution of RM 8545 is limited to one unit per customer per three-year period. Users are encouraged to prepare their own standards for daily use and calibrate those standards against international reference materials. Preparation, analysis, and reporting information can be found in Appendix A.

REFERENCES

[1] JCGM 200:2012; *International Vocabulary of Metrology – Basic and General Concepts and Associated Terms (VIM)*, 3rd ed.; Joint Committee for Guides in Metrology (JCGM) (2012); available at https://www.bipm.org/en/committees/jc/jcgm/publications (accessed Jan 2023).

[2] Brand, W.A.; Coplen, T.B.; Vogl, J.; Rosner, M.; Prohaska, T.; *Assessment of International Reference Materials for Isotope Ratio Analysis (IUPAC Technical Report)*; Pure and Appl. Chem., Vol. 86, pp. 425–467 (2014).

[3] Qi, H.P.; Taylor, P.D.P.; Berglund, M.; De Bièvre, P.; *Calibrated Measurements of the Isotopic Composition and Atomic Weight of the Natural Li Isotopic Reference Material IRMM-016*; International Journal of Mass Spectrometry and Ion Processes, Vol. 171, pp. 263–268 (1997).

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Technology, Gaithersburg, MD (2021); available at https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2021.pdf (accessed Jan 2023).
[8] BIPM Traceability Exception: Delta Value Isotope Ratio Measurements (2015); available at https://www.bipm.org/documents/20126/50116808/%5BQM%5D+Delta+value+isotope+ratio+measurements.pdf/4fe4f00a-7f3c-9683-59f2-e49a11db074a?version=1.4&download=true (accessed Jan 2023). Note that this document is a summary of Decision CIPM/104-26 from the International Committee for Weights and Measures (CIPM); *Proceedings of Session 1 of the 104th meeting: Executive Summary*; 9-10 March 2015, p. 34; available at https://www.bipm.org/utils/en/pdf/CIPM/CIPM2015-I-EN.pdf (accessed Jan 2023).
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Information Sheet Revision History: 24 January 2023 (Addition of uncertainty for absolute isotope-amount ratio of $^6Li/^7Li$; removal of $\delta^{13}C$ and $\delta^{18}O$ values; updated format; editorial changes); 01 November 2011 (Updated reference values; editorial changes); 22 June 1992 (Original certificate date).

Certain commercial equipment, instruments, or materials may be identified in this Reference Material Information Sheet to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Users of this RM should ensure that the Reference Material Information Sheet in their possession is current. This can be accomplished by contacting the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at https://www.nist.gov/srm.

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APPENDIX A

PREPARATION AND ANALYSIS

The technical aspects involved in the issuance of this RM were coordinated through the NIST Chemical Sciences Division by R.A. Kraft.

Support aspects involved in the issuance of this RM were coordinated through the NIST Office of Reference Materials.

Sample preparation: RM 8545 (LSVEC) was prepared by H.J. Svec, Iowa State University, Iowa, USA from high purity Li_2CO_3 from lithium ore primarily composed of spodumene (99.50 %), other components are reported by Flecsh et al, 1973 [9]. It was originally intended as an absolute Li isotopic reference material.

Analytical Methods: Absolute measurements of RM 8545 were made using a thermal ionization mass spectrometer (TIMS) with an NBS-type, 12-inch radius and 60° inflection, single focusing magnetic field mass spectrometer [3].

Homogeneity: According to previous analyses reporting Li isotope ratios of RM 8545, homogeneity of RM 8545 has not been assessed [3,10].

Absolute Li Isotope-Number Ratios in LSVEC: The absolute lithium isotope ratio along with its expanded uncertainty were determined for LSVEC by Qi et al., 1997 [3]. The measurements were made using calibrated lithium isotope mixtures and are absolute. Note that the isotopic composition of this material is statistically indistinguishable from IRMM-016, a certified lithium isotopic reference material prepared by the Institute for Reference Materials and Measurements (IRMM), Belgium [3,10]. In 2005 IRMM recalculated the absolute value and uncertainty of IRMM-016 based on updated guidelines given in the GUM [4,10]. The value given by Qi, and used in this certificate, is within the uncertainty of the new value IRMM calculated for IRMM-016 ($^6Li/^7Li = 0.082121 \pm 0.000087$).

Historical note: In 2006 LSVEC was proposed as a second ^{13}C anchor for a two-point normalization of the $\delta^{13}C$ scale with a value of –46.60 ‰ with no uncertainty, as a scale defining material [11]. As stated previously in the IMPORTANT NOTE, in 2016 measurements at the IAEA [6] and USGS [7] clearly established that LSVEC shows at least a 0.2 ‰ range in $\delta^{13}C$ values and therefore is no longer considered to be isotopically stable or homogeneous.

REPORTING:

Terminology: The terminology used here is based on the guidance given by IUPAC for isotope terminology, where stable isotope-number ratio refers to the number of atoms of one isotope relative to the number of atoms of a second isotope in the same system [2]. This is often abbreviated to stable isotope ratio. Isotope-delta value refers to the stable isotope-number ratio of a measured sample relative to the stable isotope-number ratio of a reference material (see example below). Isotope-amount ratio is numerically the same as isotope-number ratio but refers specifically to the amount (moles) of an isotope relative to the amount (moles) of another isotope in the same system [12].

Isotope-delta Values: The lithium stable isotope-delta value of a measured sample reported on the LSVEC scale is defined as the difference in measured isotope-number ratio of lithium in a sample relative to the stable isotope-number ratio of lithium in LSVEC:

$$\delta^7 Li_{LSVEC} = \frac{\left[\frac{N_{sample}(^7Li)}{N_{sample}(^6Li)}\right] - \left[\frac{N_{LSVEC}(^7Li)}{N_{LSVEC}(^6Li)}\right]}{\left[\frac{N_{LSVEC}(^7Li)}{N_{LSVEC}(^6Li)}\right]}$$

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