## Referenced Material

**LSVEC (Li-carbonate)**

Reference Material for Li-isotope ratio

Assigned values for the stable isotopic composition of LSVEC.

<table>
<thead>
<tr>
<th>Year</th>
<th>Assigned value</th>
<th>Combined uncertainty $(k=2)$</th>
<th>Note:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Lithium isotopes:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta^7\text{Li}, %$</td>
<td>0 $%$</td>
<td>n/a</td>
<td>Defined value</td>
</tr>
<tr>
<td>$^{7}\text{Li}/^{6}\text{Li}$</td>
<td>0.08215$^{(1)}$</td>
<td>$\pm0.00023^{(1)}$</td>
<td>Recommended value</td>
</tr>
</tbody>
</table>

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(1) the value and combined uncertainty $(k=2)$ are taken from [1].

(2) Former $\delta^{13}\text{C}$ values are provided in the text. This material is not anymore recommended as $\delta^{13}\text{C}$ reference material due to identified isotopic inhomogeneity for carbon this does not affect the lithium isotope composition.
**Intended use:**

*Lithium isotopes:*

The reference material LSVEC is intended for calibration of lithium stable isotope measurements, as performed by thermal ionisation mass-spectrometry and ICP-MS. No information on minimal sample size was provided in the characterisation study [1].

*Carbon and oxygen isotopes:*

The use of LSVEC as RM for δ\(^{13}\)C is strongly discouraged [2]. The use for δ\(^{18}\)O has never been foreseen at all for following reasons: (i) due to hydroscopic nature of material its δ\(^{18}\)O value is not stable; (ii) the carbonate-acid reaction with LSVEC is violent and temperature cannot be controlled.

**Preparation:**

Reference material (RM) LSVEC was prepared as 13 kg of highly purified chemical Li\(_2\)CO\(_3\) produced from Li-ores (mostly spodumene) thus preserving its natural Li-isotope composition (see Flesch et al. [3] and references therein). The material consists of Li\(_2\)CO\(_3\) (99.50%), 0.44% of total H\(_2\)O, and 0.004% of anions (Cl and SO\(_4\)) and 0.02% of cations (reported as Fe\(_2\)O\(_3\), CaO and Na\(_2\)O), see [3].

The LSVEC-bulk has been stored at NIST (in glass-jar containers) and is distributed by NIST as RM8545 (in the past as LSVEC) and by the IAEA as RM LSVEC.

*Note:* Glass vials with plastic cups are used for LSVEC distribution.

**Homogeneity of the material:**

According to Flesch et al. (1973) and Qi et al. (1997) who reported Li-isotope ratios, the homogeneity in Li isotope composition has not been assessed [1, 3].

No homogeneity in δ\(^{13}\)C was assessed when LSVEC was introduced as former RM for δ\(^{13}\)C [4]. When later LSVEC was introduced as the second anchor on the VPDB scale [5], its homogeneity in δ\(^{13}\)C was assessed. Recently Assonov et al. reported [6] on large scatter in δ\(^{13}\)C due to storage effects; inhomogeneity of the original LSVEC-bulk (stored in jar containers at NIST) cannot be excluded.

**Characterization and use as RM:**

*Lithium isotopes:*

No characterisation was required for LSVEC defining the scale for lithium relative stable isotope measurements, namely by its value δ\(^{7}\)Li = 0 ‰ [7]. Some laboratories may report data as δ\(^{6}\)Li values by using \(^{7}\)Li/\(^{6}\)Li ratio; respectively the LSVEC’ value is δ\(^{6}\)Li = 0 ‰. (Note: δ\(^{6}\)Li is not equal to δ\(^{7}\)Li. Conversion from δ\(^{6}\)Li to δ\(^{7}\)Li values should avoid approximations.)

The accepted value of \(^{7}\)Li/\(^{6}\)Li=0.08215±0.00023 (k=2) is based on calibration of thermal ionisation mass-spectrometry by gravimetric blending of \(^{6}\)Li and \(^{7}\)Li end-members [1]. The blends were used to determine the mass-bias correction and other systematic corrections. Previous characterization by thermal ionisation mass-spectrometry [3] was based on gravimetric mixtures of \(^{6}\)Li\(_2\)SO\(_4\) and \(^{7}\)Li\(_2\)SO\(_4\) and resulted in \(^{7}\)Li/\(^{6}\)Li =0.0832±0.0002 (based on 1 StDev); this value is currently not recommended.

*Carbon isotopes:*

See note below on the use of LSVEC as RM for δ\(^{13}\)C in the past.
Statement on the metrological traceability of assigned values and uncertainties:

**Lithium isotopes:**

The property value $\delta^{7}\text{Li} = 0$ ‰ was assigned as definition of the Li-isotope scale without uncertainty. The accepted value of $^{7}\text{Li}/^{6}\text{Li}=0.08215\pm0.00023$ (k=2) based on the work by Qi et al. (1997) includes the uncertainty of gravimetric blending of $^{6}\text{Li}$ and $^{7}\text{Li}$ entities and also their isotopic purity. As based on gravimetric mixing, this numeric value appears to be SI-traceable. No uncertainty component related to the homogeneity of material was considered.

**Instructions for use:**

The reference material LSVEC is supplied as 0.5 g units in glass vials with plastic cup. The material is found to be hydroscopic and storage in closed desiccators is recommended; chemisorption of air CO$_2$ is known. Notably, adsorbed water and CO$_2$ does not affect the long-term material integrity for lithium isotope ratio determinations.

**Issue and expiry date:**

The re-issue date of LSVEC is 27th June, 2018. Based on experience with similar materials, the expiry date for Li-calibration is set to 27th June, 2028.

**Limit of distribution:**

The material is available for limited distribution by allowing the purchase of up to three units of the material within a three year’s period per laboratory. This limit is set to keep this reference material available to as many laboratories as possible for an extended time period, and is therefore a measure to maximize the reference material usability.

**Absolute isotopic abundances:**

As the accepted value of $^{7}\text{Li}/^{6}\text{Li}=0.08215\pm0.00023$ (k=2) [1] is based on gravimetric mixing, this numeric value being SI-traceable.

**Historical note: Use of LSVEC as RM for $\delta^{13}\text{C}$ in the past.**

The IAEA consultants meeting (Vienna, December 1-3, 1993) provided the $\delta^{13}\text{C}$ value based on intercomparison data from 13 laboratories (with 2σ-outlier filtering) as $\delta^{13}\text{C}=-46.479\pm0.150$ ‰ (n=11, 1σ) [4, 8]. Note, without data filtering the average value was reported as $\delta^{13}\text{C}=-46.372\pm0.297$ ‰ (n=13, 1σ), no homogeneity in $\delta^{13}\text{C}$ was assessed [4].

In 2004, report on several NIST RMs including LSVEC demonstrated the value $\delta^{13}\text{C}=-46.56\pm0.11$ ‰ (n=5, 1σ; 2 data points filtered as outliers), the average without data filtering is $\delta^{13}\text{C}=-46.57\pm0.18$ ‰ (n=7, 1σ), see Table 10-D in [9]. The values are based on the $^{17}\text{O}$ isotopic correction with $\lambda=0.528$ and $^{17}\text{O}/^{16}\text{O}$ ratio determined in [10] and later recommended by IUPAC [11].

In 2006 LSVEC was proposed to be used as the second anchor on the VPDB scale, with the fixed value $\delta^{13}\text{C}=-46.60$ ‰ accepted with zero uncertainty [5]. Notably, this value has been based on the value $\delta^{13}\text{C}=-46.607$ ‰ obtained at MPI-BGC Jena, DE [12] and results obtained in [9] (see above) by using the $^{17}\text{O}$ isotopic correction with $\lambda=0.528$ and $^{17}\text{O}/^{16}\text{O}$ ratio determined in [10] and later recommended by IUPAC [11]. The homogeneity in $\delta^{13}\text{C}$ was not assessed.

In 2015, it was reported a large scatter in $\delta^{13}\text{C}$ values observed on numerous LSVEC samples from several vials not being in use as well as samples from four LSVEC-bulk containers stored at NIST [6]. The large scatter in $\delta^{13}\text{C}$ is thought to be due to storage effects, although inhomogeneity of original
LSVEC-bulk (stored in containers at NIST) cannot be excluded. Adsorption of atmospheric water followed by CO₂ chemisorption (presumably forming Li-bicarbonate) was proposed as the most likely explanation for data scatter and the δ^{13}C-drift towards less negative values. The asymmetric uncertainty for the value δ^{13}C= -46.60 ±0.30‰ -0.10‰ (conservative estimate, k=1) was derived on the VPDB scale (using the ^{17}O correction recommended by IUPAC [11]) as the best estimate based on numerous measurements done at the IAEA in 2015 (report in preparation), both on unused vials and bulk containers at NIST, thus reflecting inhomogeneity and storage effects due to CO₂ chemisorption from air. The value and uncertainty is aimed at ensuring re-calculations of previous data by users; this uncertainty may not address potential drifts due to storage at end-user laboratories. Several other laboratories confirm the findings.

In December 2015 LSVEC was removed from sales as RM for δ^{13}C at the IAEA. In 2017 IUPAC has recommended discontinuance of LSVEC as RM for δ^{13}C [2].

**Legal disclaimer:**
The IAEA makes no warranties, expressed or implied, with respect to the data contained in this reference sheet and shall not be liable for any damage that may result from the use of such data. Since the year of publication in 1997 [1], the accepted value of ^7Li/^6Li has not been re-confirmed. It is noted that LSVEC IS NOT RECOMMENDED AS REFERENCE MATERIAL FOR δ^{13}C. The stated value δ^{13}C= -46.60 ±0.30‰ -0.10‰ (conservative estimate, k=1) is given for historical reasons, to ensure re-calculations of previous data obtained by users.

**Compliance with ISO Guide 31:2015:**
The content of this IAEA Reference Sheet is in compliance with the ISO Guide 31:2015: Reference materials – Contents of certificates, labels and accompanying documentation [13].

**Citation of this reference sheet:**
It is suggested to cite this reference sheet according to the following example, as appropriate to the citation format used: INTERNATIONAL ATOMIC ENERGY AGENCY, Reference Sheet for LSVEC. IAEA, Vienna, 2018-06-27, 5 pp., available for download at https://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/13C18and7Li/LSVEC.htm (The latest version published applies, see “Note” below).

**Note:**
Certified values and associated uncertainties as stated in this reference sheet may be updated if more information and/or improvements of analytical techniques become available. Users of this material should ensure that the reference sheet in their possession is current. The current version may be found in the IAEA’s Reference Materials online catalogue: https://nucleus.iaea.org/rpst/referenceproducts/referencematerials/Stable_Isotopes/index.htm

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