REFERENCE SHEET

REFERENCE 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>Lithium isotopes:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta^7$Li, ‰</td>
<td>0 ‰</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>$^{6}$Li/$^{7}$Li</td>
<td>0.08215(^{(1)})</td>
<td>$\pm0.00023^{(1)}$</td>
</tr>
</tbody>
</table>

\(^{(1)}\) the value and combined uncertainty (k=2) are taken from [1].

\(^{(2)}\) Former $\delta^{13}$C values are provided in the text. This material is not anymore recommended as $\delta^{13}$C reference material due to identified isotopic inhomogeneity for carbon; this does not affect the homogeneity of the lithium isotopic 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 δ¹³C is discontinued and its further use is strongly discouraged due to observed variable and non-correctable changes in its carbon isotopic composition over time [2]. The use for δ¹⁸O has never been foreseen at all for following reasons: (i) due to hydroscopic nature of material its δ¹⁸O 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 Li₂CO₃ 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 Li₂CO₃ (99.50%), 0.44% of total H₂O, and 0.004% of anions (Cl and SO₄) and 0.02 % of cations (reported as Fe₂O₃, CaO and Na₂O), 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 δ¹³C was assessed when LSVEC was introduced as former RM for δ¹³C [4]. When later LSVEC was introduced as the second anchor on the VPDB scale [5], its homogeneity in δ¹³C was assessed. Recently Assonov et al. reported [6] on large scatter in δ¹³C 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 δ⁷Li = 0 ‰ [7]. Some laboratories may report data as δ⁶Li values; respectively the LSVEC’ value is δ⁶Li = 0 ‰. (Note: δ⁶Li is not equal to δ⁷Li. Conversion from δ⁶Li to δ⁷Li values should avoid approximations.)

The accepted value of δ⁶Li/⁷Li=0.08215±0.00023 (k=2) is based on calibration of thermal ionisation mass-spectrometry by gravimetric blending of δ⁶Li and δ⁷Li 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 δ⁶Li₂SO₄ and δ⁷Li₂SO₄ and resulted in δ⁶Li/⁷Li =0.0832±0.0002 (based on 1 StDev); this value is currently not recommended.

Carbon isotopes:

Not suitable for carbon isotopes; see note below on the use of LSVEC as RM for δ¹³C 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 $^6\text{Li}/^7\text{Li}=0.08215\pm 0.00023$ (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 $^6\text{Li}/^7\text{Li}=08215\pm 0.00023$ (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 inter-comparison data from 13 laboratories (with 2σ−outlier filtering) as $\delta^{13}\text{C}= -46.479\pm 0.150$ ‰ (n=11, 1σ) [4, 8]. Note, without data filtering the average value was reported as $\delta^{13}\text{C}= -46.372 \pm 0.297$ ‰ (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 $\delta^{13}\text{C}= -46.56\pm 0.11$ ‰ (n=5, 1σ; 2 data points filtered as outliers), the average without data filtering was $\delta^{13}\text{C}= -46.57\pm 0.18$ ‰ (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 had been based on the value $\delta^{13}\text{C}= -46.607$ ‰ obtained at MPI-BGC Jena, Germany [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, a large scatter was reported in δ¹³C values measured 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 and variable scatter in δ¹³C 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 δ¹³C-drift towards less negative values. An asymmetric uncertainty for the value δ¹³C= -46.60 +0.30‰ -0.10‰ (conservative estimate, k=1) was derived on the VPDB scale (using the ¹⁷O correction recommended by IUPAC [11]) as the best estimate based on numerous measurements done at the IAEA in 2015 [6], 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 possible re-calculations of previous data by users; this uncertainty may not fully address potential drifts due to storage at end-user laboratories. Several other laboratories confirm the findings. The material is unsuitable to be used as reference material for δ¹³C determinations, and especially unsuitable to use as former second anchor for the δ¹³C scale.

In December 2015 LSVEC was removed from sales as RM for δ¹³C at the IAEA.

In 2017 IUPAC has recommended discontinuance of LSVEC as RM for δ¹³C [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 ⁹Li/⁷Li has not been re-confirmed. It is noted that LSVEC IS NOT RECOMMENDED AS REFERENCE MATERIAL FOR δ¹³C. The stated value δ¹³C= -46.60 +0.30‰ -0.10‰ (conservative estimate, k=1) is given for historical reasons, to ensure the possibility of 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, Rev 02. IAEA, Vienna, 2020, 5 pp., available for download at https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/LSVEC.aspx (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/sites/ReferenceMaterials/SitePages/Home.aspx
Further information:
For further information regarding this material, please contact:
Terrestrial Environment Laboratory
International Atomic Energy Agency
Friedenstr. 1, 2444 Seibersdorf, Austria
Tel.: +43 1-2600-28237
E-mail: NAEI-Reference-Materials.Contact-Point@iaea.org

REFERENCES:
Revision Information:

-Rev 0: Original version (2018-06-27)
- Rev.01 (2020-12-16): correction of an error in the original version where the correct term ‘^{6}\text{Li}/^{7}\text{Li}’ for reported lithium isotope ratios had been wrongly printed reciprocal, the numerical values are not affected. Links to Websites have been updated.