

# Determination of Lithium Isotopic Composition by Thermal Ionization Mass Spectrometry

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**A mass spectrometric method has been proposed for the determination of the isotopic composition of lithium. It is based upon thermal ionization of LiOH loaded onto a single SiO<sub>2</sub>-coated Re filament. By this method, stable emissions of Li<sup>+</sup> ion have been achieved for an extended period of time. The proposed method is capable of analyzing trace quantities (~40 ng) of Li in the presence of sodium with an uncertainty of ±0.000 25 (two standard deviations of the mean).**

Precise isotopic analysis of Li is of great interest in geochemistry, nuclear chemistry, astrophysics, and biomedicines.<sup>1</sup> Li comprises two stable isotopes, <sup>6</sup>Li and <sup>7</sup>Li. The isotopic composition of Li in reagent chemicals and minerals from various locations has been determined in many laboratories. The listed natural abundance of <sup>6</sup>Li, e.g., 7.503%, in both the reagent chemicals and Li prepared from various minerals, is a weighted average value because the ratio is affected by geological cycles and isotopic fractionation during the chemical treatment.<sup>1</sup> Thermal ionization mass spectrometry (TIMS) has been the only means of such accurate analyses. Isotopic fractionation posed serious problems in isotopic ratio determination of Li due to the large mass difference between the two Li isotopes. To overcome this difficulty and minimize the isotopic fractionation effect, use of different heavier compounds of Li were considered.<sup>2–5</sup> Heavy molecular compounds of Li with single, double, and even triple filaments were tried for ionizing Li on the mass spectrometer (MS).<sup>6,7</sup> Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and LiF were used as loading materials, and their emissions in the form Li<sub>2</sub>BO<sub>2</sub><sup>+</sup> and Li<sub>2</sub>F<sup>+</sup> were measured at the respective magnetic fields. In all the cases, filament temperatures and heating pattern were precisely controlled for stable Li emissions.<sup>6</sup> A high-purity Li is essential to avoid unstable ion current. The presence of alkali metals such as Na and K needs a much higher ionization filament current to form a workable Li<sup>+</sup> ion beam intensity.

Table 1. Characteristics of Cation- and Anion-Exchange Resins Used during the Experiment

	resin type	
	cation exchange	anion exchange
porosity (mL/g)	0.63	0.97
capacity (mequiv/g)	4.30 (Na <sup>+</sup> )	4.20 (Cl <sup>-</sup> )
density (g/mL)	0.39	0.28
bead size (μm)	45–75	45–75
cross-linkage (%)	20	20
virgin form	H <sup>+</sup>	OH <sup>-</sup>

In the present work, new methods and means are suggested to minimize isotopic fractionation in low-Li-bearing samples in the presence of other elements, especially Na. Use of SiO<sub>2</sub> gel provides an excellent base to control variation in filament temperature; the depression in Li emissions due to the presence of Na in the sample and relatively lower filament current in the range from 1.4 to 1.65 A is required to obtain a stable, high-intensity Li<sup>+</sup> ion current for precise and reproducible measurement of lithium.

## EXPERIMENTAL SECTION

**Reagents and Materials.** All the chemicals used were of high grade purity and were obtained from E. Merck (Darmstadt, Germany).

The standard reference material for Li was L-SVEC in Li<sub>2</sub>CO<sub>3</sub> form.

The ion exchangers, both anion and cation types, were prepared at our laboratory as described elsewhere.<sup>8</sup> The specifications are given in Table 1.

Pure and Na-free SiO<sub>2</sub> gel was prepared at our laboratories by refinement of the procedure reported in the literature.<sup>9,10</sup>

**Instrumentation.** Isotopic measurements were carried out on a thermal ionization mass spectrometer VG-354 (VG isomass) equipped with Daly and two Faraday cups as detectors. Resistance (impedance) of the Collector measuring instrument was 10<sup>11</sup> Ω. Averaged Li emission strength maintained was of the order of 10<sup>-10</sup> A. Measured at mass numbers 235 and 238, the resolution of the instrument was better than 500 ppm. Abundance sensitivity was less than 5 ppm. The peak-to-peak noise electrometry was in the range of 10<sup>-14</sup> A, and the overall stability of the instrument was on the order of 50 ppm.

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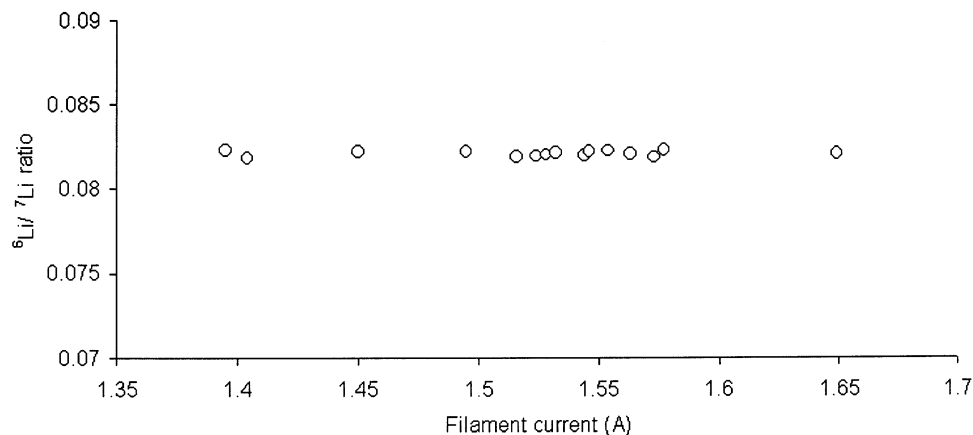


Figure 1. <sup>6</sup>Li/<sup>7</sup>Li ratios vs filament current.

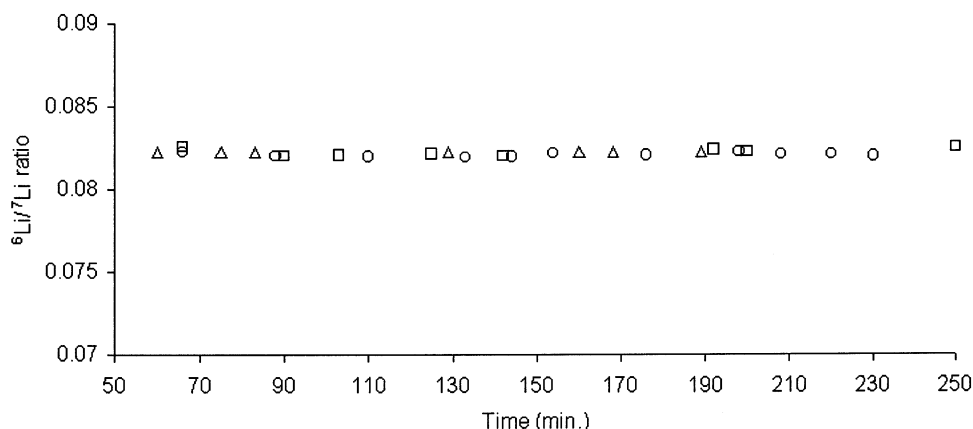


Figure 2. <sup>6</sup>Li/<sup>7</sup>Li ratio of standard sample L-SVEC determined at different times for three independent replicates.

**Column Preparation.** Cation- and anion-exchange resins, made at our laboratories,<sup>8</sup> were loaded onto the two separate columns (1 cm × 10 cm) to prepare 8-cm beds of each resin, respectively. Solutions of 1 mol/L HCl and 1 mol/L NaOH were passed through resins to convert them to H<sup>+</sup> and OH<sup>-</sup> forms, respectively. The resin beds were then washed with distilled water until the effluents were neutral.

A 1.0-g sample of Li standard obtained in the form of Li<sub>2</sub>CO<sub>3</sub>, was dissolved in 5 mL of 1 mol/L HCl to convert it to LiCl. The LiCl solution was loaded onto the cation-exchange resin and eluted with 0.5 mol/L HCl to separate Li from the aliquot. LiCl was converted to LiOH by using the anion-exchange resin, and to get 100% recovery of lithium, the procedure as adopted by Sahoo and Masuda<sup>1</sup> was employed. LiOH was used as loading material as the standard reference for Li.

**Mass Spectrometry.** Single rhenium filament assemblies, supplied by Cathedon (Cambridge, U.K.) were prebaked at 4.0 A for 2 h under vacuum (<10<sup>-6</sup> Torr) prior to use on the mass spectrometer. A 6.0-μL sample of a 4% suspension of silica gel in water was spread over the filament with a microsyringe (Hamilton) and heated to dryness at a current of 1.0 A to obtain a white visible SiO<sub>2</sub> deposition. A total of 40 ng of Li in the form of LiOH was applied and dried by resistance heating at a current of 1.0 A for 15 min. Mass spectrometric analyses were started when the pressure of the system reached 1.5 × 10<sup>-8</sup> Torr. An accelerating voltage of 8 kV was applied. All the measurements were made on an axial Faraday cup by using the general peak jumping

procedure against a baseline at *m/e* 5.5. The ion beam for each mass was measured with 5-s integration time. The sample produced an intensity of the order of 10<sup>-10</sup> A for several hours.

## RESULTS AND DISCUSSION

The isotopic composition of Li has been measured using 40 ng of LiOH on a single Re filament and the results are given in Table 2. Previously the isotopic fractionation effect was minimized by employing relatively heavier compounds of Li such as LiI, Li<sub>2</sub>B<sub>2</sub>O<sub>7</sub>, LiCl, and LiNO<sub>3</sub>. But the major disadvantage of these methods is the requirement of time for preparation of those compounds, their purification, washing, etc. Besides, at least milligrams of Li was required for some of those compounds to be prepared,<sup>1</sup> ultimately making these procedures unsuitable for the analysis of samples having low quantities of Li. Sahoo and Masuda<sup>1</sup> had reported strong and stable Li<sup>+</sup> emissions of a sample containing 100 ng of Li in the form of Li<sub>3</sub>PO<sub>4</sub> as loading material. They minimized the variation of <sup>6</sup>Li/<sup>7</sup>Li by heating the ionization filament without supplying current to the sample filament.<sup>1</sup> According to their observations, fractionation at the ionization filament due to sample deposition was decreased by employing a high ionization filament temperature; however, the presence of Na and K adversely affected the quality of the ion current. In the present work, by using a single Re filament and SiO<sub>2</sub> as base material, the effect on the Li emissions due to the presence of Na in the sample had reduced considerably. The sample relative in low quality (40 ng) produced strong and stable signals of the order

Table 2. Measurement of  $^6\text{Li}/^7\text{Li}$  Isotopic Ratio Using 40 ng of Li Deposited on the Filament

analysis	$^6\text{Li}/^7\text{Li}$ ratio
1	0.081 995
2	0.081 881
3	0.082 305
4	0.082 073
5	0.082 005
6	0.082 222
7	0.082 052
8	0.081 993
9	0.082 121
10	0.082 235
mean	0.082 087
SD ( $2\sigma$ )	0.000 250

Table 3. Comparison of Lithium Isotopic Composition of L-SVEC Standard

literature cited	measured ion	loaded as	$^6\text{Li}/^7\text{Li}$ ratio	ref
Flesch et al.	$\text{Li}^+$	LiI	$0.08321 \pm 0.0002$	11
Chan	$\text{LiBO}_2^+$	$\text{LiB}_4\text{O}_7$	$0.082821 \pm 0.0001$	5
Green et al.	$\text{Li}_2\text{F}^+$	LiF	$0.08201 \pm 0.0001$	2
Qi et al.	$\text{Li}^+$	$\text{Li}^+\text{H}_3\text{BO}_3$	$0.08215 \pm 0.0002$	12
Sahoo et al.	$\text{Li}^+$	$\text{LiPO}_4$	$0.082686 \pm 0.00009$	1
this study	$\text{Li}^+$	LiOH	$0.082605 \pm 0.000024$	

of  $1 \times 10^{-10}$  A of  $\text{Li}^+$  and permitted high precision measurement of Li isotopic ratios. Furthermore, we observed no isotopic fractionation effect due to high ionization filament current. Figure 1 shows the plot of the  $^6\text{Li}/^7\text{Li}$  ratio as a function of filament current. The enhanced stability of the plot over a range of filament currents from 1.4 to 1.65 A indicates negligible or no fractionation. A standard Li sample in the form of LiOH was run three times. Results for one of the runs, which comprises five analyses, are given in Table 4. The variations of the  $^6\text{Li}/^7\text{Li}$  ratio with time are

Table 4. Analytical Reproducibility for L-SVEC  $\text{Li}_2\text{CO}_3$  Using the Proposed Method

analysis	$^6\text{Li}/^7\text{Li}$ isotopic ratio
1	0.082 601
2	0.082 621
3	0.082 589
4	0.082 617
5	0.082 598
mean	0.082 605
SD ( $2\sigma$ )	0.000 024

plotted for each run and shown in Figure 2. It took about 230 min to complete each analysis. All the analyses comprised 12 blocks of measurements, where each block was a mean of 10 individual isotopic ratios. It clearly indicates that there is a negligible mass fractionation during the prolonged analysis time in each case.

To evaluate the reproducibility of the proposed method, a comparison of Li isotopic composition of the same reference material as reported in the literature is given in Table 3. It can be seen that the results obtained by this method are precise and comparable to those reported in the literature.

## CONCLUSION

The isotopic analysis of Li is quite tedious and difficult especially as regards formation and purification of different compounds, particularly for samples with very low contents of Li. This study revealed that the use of silica gel provides an excellent base for minimizing fractionation. This method is also capable of analyzing Li in the presence of Na and K, thus eliminating many tedious steps required for Li purification. The method is straightforward, less time-consuming, and accurate.

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