Challenge
Achieving high-precision lithium isotope ratios by ICP-MS, complicated by lithium–sodium separation challenges and column-induced lithium fractionation.

Solution
An improved Q-ICP-MS method that achieves high precision and separation of lithium from sodium and other matrix-based elements in a single-step chromatographic separation.

Intended audience
Key users include research labs, environmental agencies, geological surveys, pharmaceutical firms, and food and beverage manufacturers.

Advancing Lithium Isotope Ratios Analysis with Q-ICP-MS

Introduction

Accurate determination of lithium isotope ratios has traditionally relied on methods such as thermal ionization mass spectrometry (TIMS), quadrupole ICP-MS (Q-ICP-MS), and multi-collector ICP-MS (MC-ICP-MS). These techniques, while effective, present notable challenges, including susceptibility to instrumental mass bias, sensitivity to matrix elements, and complex separation procedures. Specifically, TIMS methods are known for substantial instrumental fractionation, large lithium mass requirements, and significant procedural blanks, all of which can impact precision and accuracy [1].

Although Q-ICP-MS is often grouped with traditional approaches, recent developments have positioned it as a promising alternative. It requires smaller lithium sample masses and can achieve precision comparable to TIMS and MC-ICP-MS. Nevertheless, challenges remain — particularly in the analysis of natural samples such as those from marine environments — where the presence of interfering elements necessitates effective quantitative separation of lithium.

In response to these challenges, we present an improved Q-ICP-MS method designed to overcome limitations associated with traditional techniques. This innovative method achieves high precision, offering superior matrix tolerance. Notably, with high precision (±0.3‰, 2RSD comparable to TIMS (±0.7‰ to ±2.5‰, 2σ), and MC-ICP-MS (±0.2‰ to ± 1.4‰, 2σ) [1]. The method's versatility is demonstrated through its successful application to lithium isotope measurements in diverse samples lithium ore samples and can be expanded to natural carbonate and fluid samples such as seawater or even brines.

Moreover, we introduce a single-step chromatographic separation that quantitatively separates lithium from interfering elements, such as sodium and other alkali elements. This chromatographic method ensures a low contamination blank, high lithium fraction recovery, and eliminates both chromatographic fractionation in eluent lithium and matrix-induced mass bias fluctuations. Importantly, this technique boasts a low procedural blank and the absence of column-induced fractionation effects.

Our developed method is characterized by its adaptability, making it suitable for various sample types, including seawater, geological samples, and more. By addressing the limitations of traditional approaches, this Q-ICP-MS method paves the way for precise lithium isotope ratio measurements across a broad spectrum of applications.

Materials and Methods

Samples and reagents

The following high-purity reagents were used for all solution preparations:

- Ultrapure water obtained from the Milli-Q system (resistivity of 18.2 MΩ cm, Millipore, Portugal)
- Nitric acid sub-boiled 69% (Analytik Jena GmbH+Co. KG)
- Hydrochloric acid Supra–quality 35% (ROTIPURAN® Supra)
- Hydrofluoric acid Supra quality 48% (ROTIPURAN® Supra)
- Reference Material 8545 L-SVEC (Li_2CO_3, powder, NIST, USA)

Instrumentation

The digestion of lithium ore samples was carried out by the closed-vessel microwave-assisted speedwave XPERT system.

Table 1 presents the operating conditions for the ICP-MS system, along with the column specifications used for the isolation of lithium from sodium and other matrix elements. To effectively analyze lithium isotopes, it is essential to separate lithium from interfering elements. We have developed a rapid single-column ion chromatography method (AG50W-X8, 200-400 mesh) that can isolate lithium from all interfering substances in lithium ores in under three hours. This new method significantly accelerates the separation process compared to previous techniques [2].

Sample preparation

For the sample digestion process, 100 mg of six powdered lithium ore, prepared in duplicate, were subjected to acid digestion using a mixture of 7 mL HF and HNO_3 (3:1 v/v) in the speedwave microwave. The samples were heated to a maximum temperature of 200 °C for 15 minutes. After digestion, the samples were dried down and refluxed with inverse aqua regia (1:3 M/M; conc. HNO_3: conc. HCl) on a hot plate at 95 °C overnight. This drying step was repeated, using the same amount of HCl, until the solution became clear. Following this process, the residues obtained were dissolved in 25 mL of 2% (v/v) HNO_3 solution. To separate the lithium from sodium, a column protocol (Table 1) was developed which involves a single-step procedure that effectively isolates lithium from the matrix in just 3 h 20 m (Figure 1). The total capacity of the wet resin used in this method is 24.4 meq, which is adequate for lithium separation from geological samples [3] with diverse matrix compositions, accommodating up to 25 meq.

Approximately, 134 mg of L-SVEC lithium carbonate (Li_2CO_3) was weighted and dissolved in 25 mL of 1%, (v/v) HNO_3 solution to prepare a 1000 ppm L-SVEC lithium stock solution. Subsequent lithium standards were prepared by gravimetric dilution of the stock solution.

Total concentrations of lithium and sodium were measured using a Q-ICP-MS system, for lithium isotope ratios determination, the standard-sample-bracketing (SSB) approach was used for enhanced accuracy. The L-SVEC lithium standard was utilized for mass bias correction, ensuring reliable and precise isotopic measurements throughout the analysis.

Table 1: PlasmaQuant MS Elite operating conditions and column protocol specs

Parameter	Specification	Column characteristics	Specification
Plasma gas flow	9.0 L/min	Column material	Polypropylene (Econo-Pac®, Bio Rad)
Auxiliary gas flow	1.50 L/min	Internal diameter	1.5 mm
Sheath gas flow	0.00 L/min	Resin type	AG 50W-X8 (200 – 400 mesh size)
Nebulizer gas flow	1.00 L/min (MicroMist TM)	Resin volume	14 mL (wet)
Sampling depth	5.0 mm	Resin capacity	24.4 meq (1.74 meq/mL wet capacity)

Parameter	Specification	Column characteristics	Specification
Plasma RF power	0.90 kW	Resin height	80 mm
Cones	Nickel	Flow rate	0.28 mL/min
Pump rate	10 rpm	Load sample	1 mL in 0.7 M HNO_3
Sample introduction	4 mL loop, ASXPressPlus (Tedelyne)	Load	14–23 meq/mL (0.1 g of Li Ores)
Stabilization delay	30 s	Pre-wash	6 M HCl (three column volume)
Dwell times	^{6}Li - 130000 µs ^{7}Li - 10000 µs	Conditioning	0.7 M HNO_3 (three column volume)
Scans per replicate	999 (peak hopping, 1 pt/peak)	Elution matrix	0.7 M HNO_3 (three column volume)
Number of replicates	6	Lithium fraction	32 to 57 g
Total acquisition time	15 min		

Results and Discussion

Chromatographic separation of lithium

Figure 2 represents the elution of lithium ore sample AMG 5.81 through the ion exchange column. Lithium elutes first, occurring between 32 and 57 g, while sodium elutes later. During lithium elution, the Na/Li ratio drops to nearly zero, indicating effective separation of both ions. For quality control, pre-cut (27 to 32 g) and post-cut (57 to 63 g) fractions were defined. The post-lithium fraction shows a lithium blank below 0.03 µg/L, confirming no lithium breakthrough or tailing, thus validating the efficiency of our separation method. Figure 3 illustrates lithium recoveries from six lithium ore samples (n = 12) across all four fractions, achieving a total recovery of 100.1 ± 5.6% in the 32 to 57 g fraction, with no sodium present.

Figure 1: Setup of ion exchange columns.

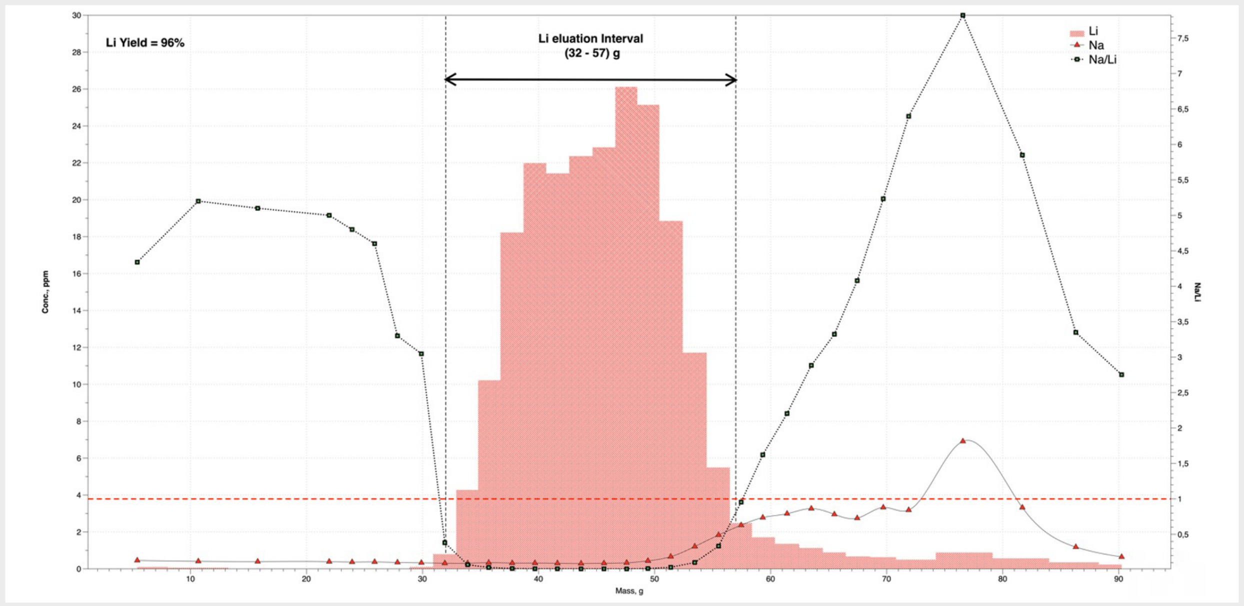

Figure 2: Elution profile of AMG 5.81, showing effective separation of lithium and sodium. Pre-cut and post-cut fractions are indicated.

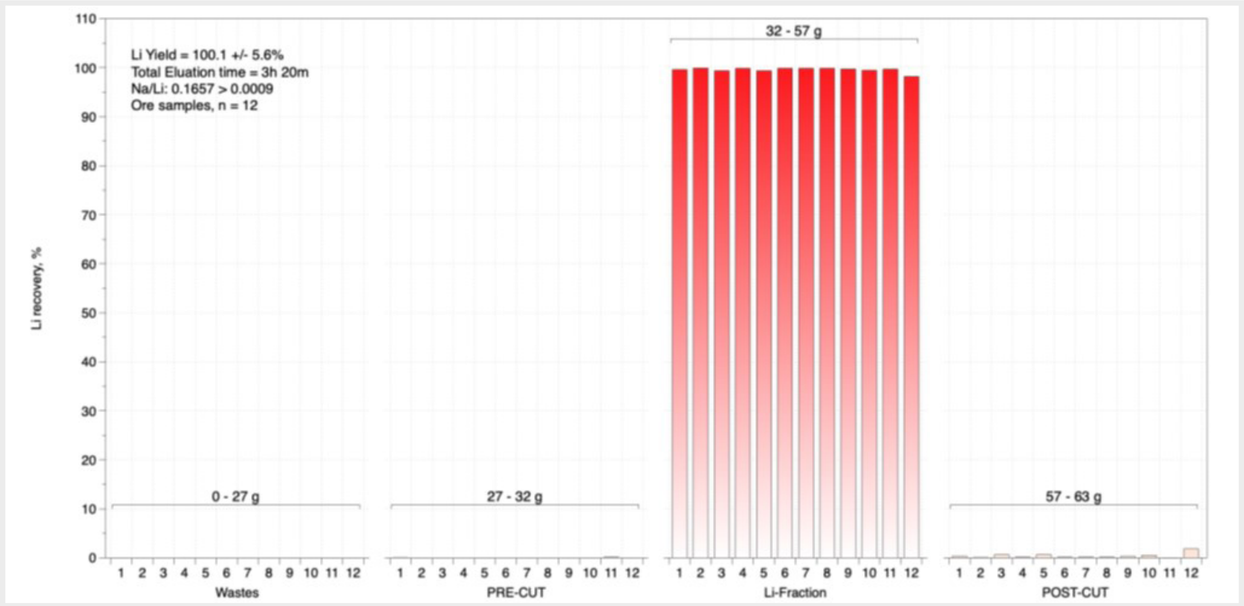

Figure 3: Lithium recoveries from 12 lithium ore samples across four fractions, with 100.1 ± 5.6% recovery in the 32-57 g fraction, free of sodium.

Lithium isotope ratio determination

Approximately 200 ppb of L-SVEC and each lithium ore solution were prepared in 1% (v/v) HNO_3 to determine the isotope ratios in accordance with the method parameters described in Table 1, following the SSB approach where two samples were bracketed by the L-SVEC isotopic standard. Table 2 shows the $^6Li/^7Li$ and δ^6Li (‰) obtained in accordance with the following calculation. This is because lithium isotopic variation can be expressed as the $^6Li/^7Li$ ratio, but smaller changes in the $^6Li/^7Li$ isotope ratio are better expressed in delta (δ) notation (per mil), which is defined as:

$$\delta(6Li)(‰) = \left\{\left[\frac{\left({}^{6Li}/_{7Li}\right)_{sample}}{\left({}^{6Li}/_{7Li}\right)_{standard}}\right] - 1\right\} \times 1000$$

where $({}^{6}Li/{}^{7}Li)_{sample}$ is the $^{6}Li/^{7}Li$ isotopic ratio of the sample and $({}^{6}Li/{}^{7}Li)$standard is the $^{6}Li/^{7}Li$ isotopic ratio of a standard, which is L-SVEC, NIST 8545 lithium carbonate.

According to the $\delta^{6}Li$ values obtained, it can be concluded that ^{6}Li enrichment is higher in Alijo Spodumene compared to the other lithium ores measured. In fact, Spodumene ores contain higher amounts of ^{6}Li when compared to other lithium ores such as Lepidolite and Petalite, with Petalite having the lowest amount of the light lithium isotope. This is consistent with studies showing that lithium isotopes separate during geological processes, leading to variations in their abundance across different mineral types [4].

The higher concentration of ^{6}Li in Spodumene is particularly significant because ^{6}Li has applications in nuclear reactors, where it can be used for tritium production and as a coolant in certain types of reactors [4]. This data indicates that the Spodumene from Alijo lithium ores have potential for further investigation, as the unique properties of ^{6}Li could be harnessed for various technological applications, including energy production and advanced materials [4].

Table 2: Lithium isotope ratios (6Li/7Li) and $\delta^{6}Li$ values obtained from different lithium ores. Mean values and standard deviations of n = 6 replicates.

Sample ID	6Li/7Li, n=6	$\delta^{6}Li$ (‰)
NIST 182_Petalite_1	0,08113 ± 0,00015	-12,40
NIST 182_Petalite_2	0,08126 ± 0,00026	-10,83
NIST 183_Lepidolite_1	0,08149 ± 0,00023	-7,97
NIST 183_Lepidolite_2	0,08167 ± 0,00025	-5,84
MCS 6.4 Spodumene_1	0,08173 ± 0,00008	-5,12
MCS 6.4 Spodumene_2	0,08173 ± 0,00019	-5,14
AMG 5.81_Conc._1	0,08149 ± 0,00013	-8,05
AMG 5.81_Conc._2	0,08163 ± 0,00010	-6,36
CBL 6.2.1_Spodumene_1	0,08222 ± 0,00008	0,85
CBL 6.2.1_Spodumene_1	0,08217 ± 0,00005	0,20
Alijo Spodumene Conc._1	0,08233 ± 0,00022	2,24

Figure 4 shows the overall stability of L-SVEC during sequence analysis, achieving only 0.03% (2RSD) and excellent accuracy, as all ratio values fall within the uncertainty interval. Additionally, lithium isotope ratios are presented as δ^6Li (‰) for the six different lithium ores analyzed.

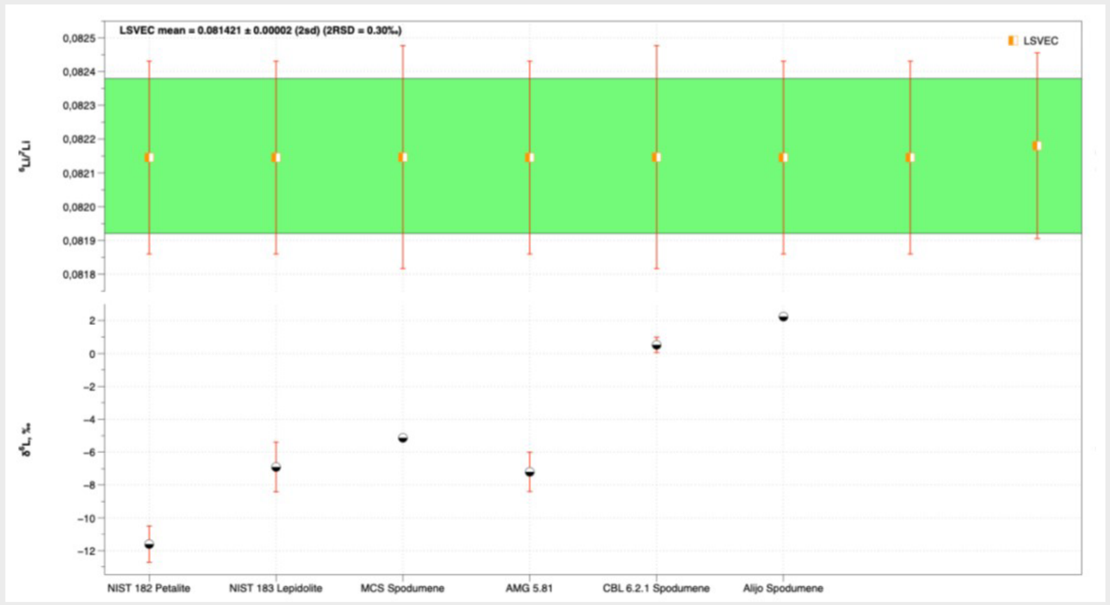

Figure 4: Lithium isotope ratios (δ^6Li, ‰) of different lithium ores are presented, including mean values and error bars for the duplicates. Additionally, the stability of L-SVEC over time (9 hours) is reported. The L-SVEC mean is 0.081421 ± 0.00002 (2 standard deviations), with a relative standard deviation (RSD) of 0.3‰ (2 RSD).

Summary

The innovative Q-ICP-MS protocol developed in this study significantly advances the measurement of lithium isotope ratios, offering a high level of precision and robustness suitable for a range of applications in earth and environmental science. Our approach not only achieves a remarkable long-term precision of 0.30‰ (2RSD) but also demonstrates exceptional tolerance to high-matrix samples, making it a valuable tool for geochemical investigations. The specialized column system designed for lithium separation effectively manages high sample loads, ensuring near-complete recovery and satisfactory purification. This capability is crucial for maintaining the integrity of isotopic measurements, particularly when analyzing chemically diverse materials such as Portuguese lithium ores and NIST lithium standards.

The successful application of this method to various geological samples underscores its versatility and commercial viability for future research. As the demand for lithium continues to rise, driven by the growth of renewable energy technologies and electric vehicles, our protocol provides a reliable framework for sustainable lithium resource management. By enhancing our understanding of lithium's isotopic composition, this work paves the way for further studies in mineral exploration and environmental monitoring, contributing to informed decision-making in resource utilization.

Figure 5: PlasmaQuant MS Elite

Recommended device configuration

Table 3: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant MS Elite	818-08021-2	The ICP-MS provides advanced research applications with exceptional sensitivity for the determination of low-abundance isotopes.
Teledyne-Cetac ASX-560 autosampler	810-88015-0	The Teledyne CETAC Technologies ASX-560, next generation autosampler with integrated rinse function is sleek and durable by design.
Cetac ASXPress Plus (or equivalent)	810-88017-0	The ASXPress Plus is a Rapid Sample Introduction Accessory which reduces autosampler movement, sample uptake, stabilization, and rinse times, significantly cutting down sample run times.

References

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