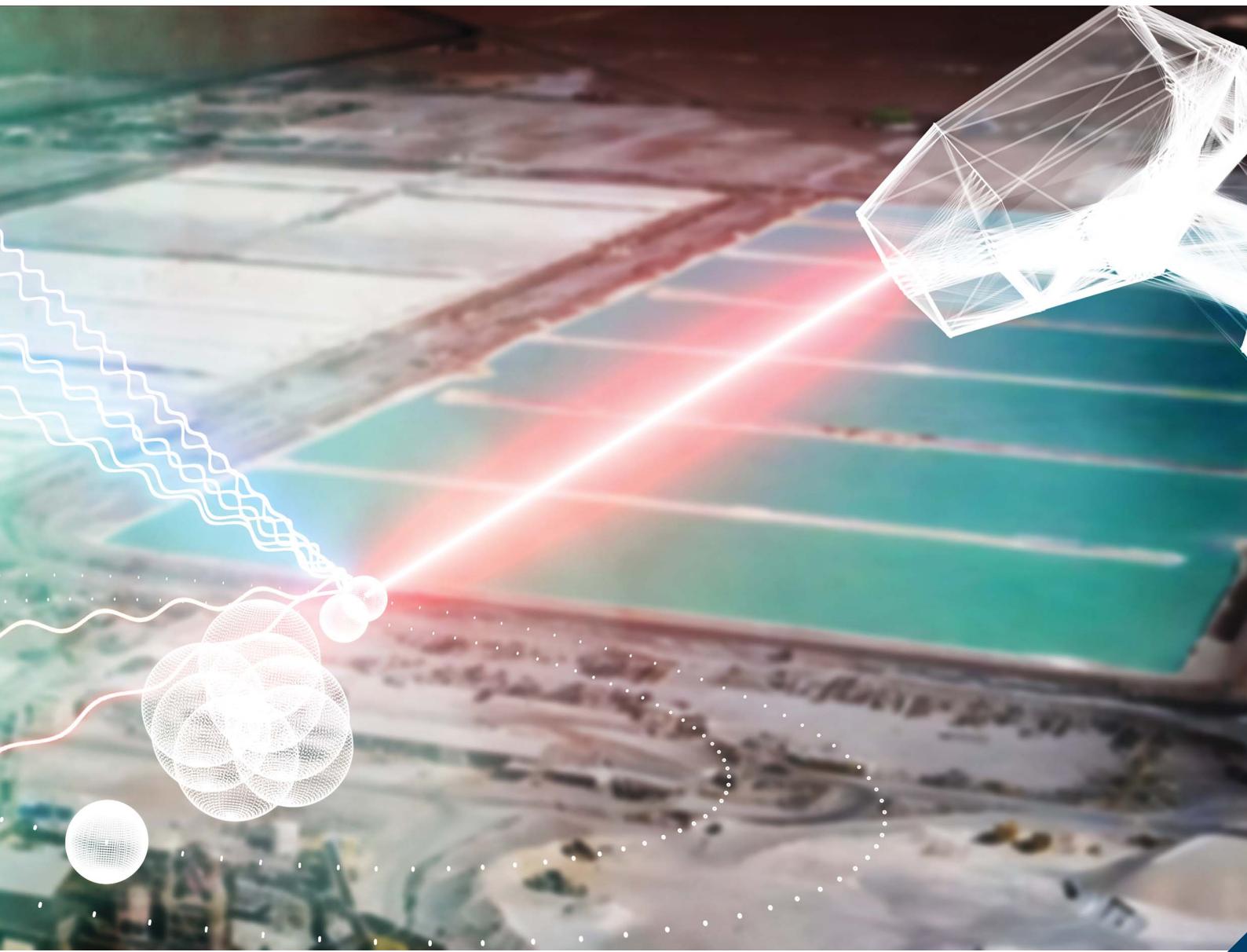


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Direct determination of lithium in brine samples using handheld LIBS without sample treatment: sample introduction by venturi system



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Splashing is the main problem for the direct analysis of aqueous samples using LIBS since it generates serious precision and accuracy issues. This study demonstrates the direct determination of Li content in brines for the control of industrial mining processes using a portable LIBS device based on the direct laser impact on the sample, without any sample treatment, through the design of a sample injection system based on the Venturi effect. Our results demonstrated that the utilization of the 653.3 nm hydrogen line as an internal standard reduces the model calibration fitting error from 0.440 root mean square error in a standard calibration curve to 0.123 on the internal standard curve. Conversely, the development of a Venturi effect-based injection device using compressed air converts the brine into a fine mist which decrease splashing, resulting in an up to 10-fold error reduction, all without the necessity of employing an internal standard. Our results, evaluated by comparing them to the ASTM D3561-11 standard method using flame atomic absorption spectrometry, indicate that it is feasible to determine the lithium content in brine samples with an error of under 20% and a detection limit of 13 mg kg⁻¹.

Direct determination of lithium in brine samples using handheld LIBS without sample treatment: sample introduction by venturi system

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Analytical techniques employed for the determination of lithium content in brines predominantly center around inductively coupled plasma optical emission spectroscopy (ICP-OES)² or flame atomic absorption spectroscopy (FAAS).³ Nevertheless, these technologies have limitations as they do not facilitate on-site analysis and involve extended response times, often exceeding hours, thus impeding timely decision-making in the production process. Additionally, the utilization of these technologies requires electrical installations and consumption of high-purity gases and water, resources that are challenging to acquire in remote desert environments.

Among portable analytical technologies that require minimal or no sample treatment for elemental analysis is X-ray fluorescence (XRF). However, most commercial portable X-ray fluorescence instruments only allow the determination of elements with Z greater than 11,⁴ and only a few models have achieved the determination of lighter elements, such as Be, up to heavier elements such as U. However, this detection capability is strongly hampered by long-wavelength and low sensitivity emission for direct determination.^{5,6} For lighter elements such as Li, it is not possible to directly determine their content using XRF, and this element is determined indirectly through XRF by precipitating it with iron compounds.⁷

Among portable alternatives for determining Li content in brines, the use of quantitative nuclear magnetic resonance spectroscopy (qNMR) was reported by Araneda *et al.*⁸ by following the ⁷Li signal. Excellent results were achieved in terms of limit of detection (LOD), precision and accuracy, with minimal sample treatment required. While it is true that this technology has allowed the construction of very simple and portable instruments, the possibility of using it with an independent battery is still not possible as it requires being plugged into standard power outlets.

New alternatives based on portable, self-contained instruments with independently built-in batteries, based on laser-induced breakdown spectroscopy (LIBS), are emerging in the market. This technique offers an additional advantage of being multi-elemental, including metals such as Li.

1 Introduction

Chile is one of the main producers of lithium compounds in the world.¹ Lithium reserves are located mainly in northern Chile in the Atacama Desert. The Li₂CO₃ production process in Chilean industries consists of extracting brine from the desert into solar evaporation pools where some salts are harvested, and others are eliminated. In this way, brines are concentrated at levels of around 5% Li by weight where Li₂CO₃ is obtained through a precipitation reaction adding a concentrated solution of Na₂CO₃ to the brine. Monitoring of Li content in brines throughout this production process is essential for good decision-making.

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In terms of a historical review of portable LIBS devices, one of the earliest reviews, where the performance of experimental portable LIBS devices designed for space exploration is discussed, was by Harmon in 2006.⁹ In space science, portability and low energy consumption are key considerations for real-time field measurements. The ChemCam team of the Curiosity rover designed the first instrument capable of remotely analyzing samples using the LIBS technique for elemental and quantitative analysis, including light elements such as H and Li.¹⁰

In 2020, Li *et al.*¹¹ published a review on LIBS applications for remote detection. The study reported precisions ranging from 5 to 25% RSD for major elements and 20 to 40% RSD for minor elements, primarily in samples such as soils and dust. The review also showcased noteworthy applications for underwater detection.

While portable LIBS systems have demonstrated success in analyzing solid samples, challenges arise when dealing with aqueous samples such as brines. The primary issue stems from the atomization process, which experiences significant energy interference due to the presence of water, particularly through the splashing effect. This phenomenon adversely affects precision and sensitivity. Most strategies to improve the precision of liquid sample analysis by LIBS have focused on using sorbent substrates or solid supports for surface-enhanced strategies. In a work by Keerthi *et al.*,¹² it was demonstrated that LIBS analysis on direct bulk liquid samples often suffered from splashing, thus hindering the detection of low concentrations, whereas solid residues on a substrate showed higher sensitivity detection in river water samples.

Among published works on the analysis of aqueous samples using LIBS and solid supports, we have the study by Wang *et al.*¹³ In this study, they addressed the splashing problem by combining an electrodeposition method on an Al metal plate with surface-enhanced discharge-assisted laser-induced breakdown spectroscopy for the determination of Pb in aqueous solution. This approach improved the limit of detection (LOD) from 0.05 mg L^{-1} in direct analysis mode to 0.008 mg L^{-1} in surface deposition mode.

To address the same issue, You *et al.*¹⁴ employed a system based on agarose films where water samples were converted into semi-solid hydrogels, increasing the sensitivity with a LOD below mg L^{-1} .

Eum *et al.*¹⁵ reported the determination of Mg, Ca, Na and K in raw bile juice by using Li as an internal standard. Sample were analyzed without pretreatment but were placed over a silicon wafer with crossed trenches to spread bile juice over the surface. A drying procedure was then conducted before analysis.

Wang *et al.*¹⁶ reported the determination of Hg in river and domestic wastewater samples, prepared as shear thickening fluids, using LIBS to increase the sensitivity to four times higher than that in a liquid drop sample.

Among studies opting to conduct LIBS analysis directly on untreated or dried aqueous samples, the research conducted by Zhang *et al.*¹⁷ is noteworthy. In their study, they demonstrated the determination of Na in a NaCl aqueous solution using

femtosecond LIBS within a continuous water film formed between two aluminum wires situated on either side of the water outlet. This approach resulted in a notable improvement in precision, achieving below 5% RSD and a LOD of 0.043 mg L^{-1} .

For Li determination in aqueous samples by LIBS, Wei *et al.*¹⁸ used an immersed Al metal substrate. They focused the laser beam on the surface of the substrate, resulting in a 24-fold increase in sensitivity of the Li signal, allowing for the determination of Li in seawater.

In the realm of Li determination in brine using LIBS, Xing *et al.*¹⁹ introduced a method in which sample introduction involved generating an aerosol with argon. Due to the high salt content and viscosity of the brine samples, issues such as splashing, quenching, and confinement effects greatly impact the sensitivity and quality of the analytical result. In this study, convolutional neural networks data analysis were used for data analysis to overcome these effects and improve the accuracy of Li determination. Through this approach, relative errors below 4% were achieved.

Our study aims to achieve the direct determination of Li in natural brines without the need for sample treatment, dilution, or pre-drying. The motivation behind this research arises from the significant economic value of lithium resources and growing demand for on-site elemental analysis techniques tailored for light elements such as Li. Our approach involves the direct application of laser energy onto the liquid sample using an injection system device based on an air-brine jet generated by the Venturi effect to mitigate splashing. With this strategy, sophisticated data processing methods are unnecessary and univariate calibration curves suffice.

2 Material and methods

2.1 Reagents and standards

Solutions were prepared using high-purity water (18 MU) from a Nanopure system (Barnstead, Dubuque, IA, USA), and chemical reagents were of high analytical grade. Glassware and plastic materials were cleaned with deionized water, soaked overnight in 10% (v/v) HNO_3 , and rinsed with deionized water before use. Calibration standards were prepared from LiCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ salts (Merck, 99% purity or higher) to simulate the average composition of a brine matrix in an industrial process.

2.2 Instrumental conditions

In this study, two methods were tested. Both methods utilized the SciAps handheld LIBS model Z903. The Z903 employs a laser wavelength of 1064 nm, producing laser pulse energy of 6 mJ with a 2 ns pulse duration (FWHM). The laser pulse rate is variable, ranging from 1 to 50 Hz. In this study, the Z903 was used in two different configurations.

In the first method, the Z903 is positioned above the surface of the brine liquid, which is contained in an open-topped canister, as shown in Fig. 1A. In this configuration, the sample is positioned carefully to ensure that the laser interacts



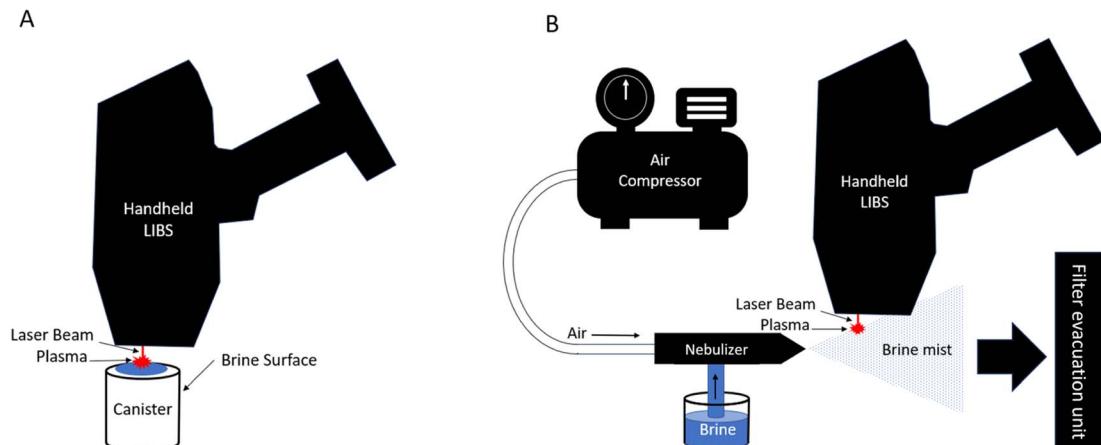


Fig. 1 Schematic showing Li content determination using handheld LIBS. (A): Method 1, laser beam plasma focused on the surface of brine in canister device where it creates plasma (not to scale). (B): Method 2, compressed airflow pulls brine from the sample cup via Venturi effect. Brine is sprayed out of nebulizer where laser creates plasma from brine mist (not to scale).

Table 1 Operational parameters for handheld LIBS method 1 and method 2 according to optical setups shown in Fig. 2

Parameter	Method 1 (canister)	Method 2 (venturi)
Data pulse averaging	1	64
Laser pulse rate (Hz)	1	50
Gas purge	Ar	Air
Li wavelength ^a (nm)	610.4	670.8
H Wavelength (nm)	656.3	656.3
Na wavelength (nm)	589.2	589.2
Mg wavelength (nm)	279.6	279.6
Laser pulse energy (mJ)	~6	~6
Reading time (s)	3	8
Sample flow (mL min ⁻¹)	—	5–10
Air flow (L min ⁻¹)	—	18

^a The chosen wavelength for Li was not the same and was selected based on the magnitude of the signal. In the case of method 1, the second most sensitive line at 610.4 nm was chosen, and in method 2, the most sensitive line at 670.8 nm was chosen to generate a Li peak emission intensity similar at the same concentration.

with the liquid surface, where the plasma is created, as previously demonstrated in our preliminary results.²⁰

In the second method, a new configuration has been further developed and commercially released as the SciAps Z9 LIBS system. The prototype used in this study is based on compressed air Venturi effect sample injection, where the brine sample is aspirated, forming an atomized brine spray perpendicular to the laser impact zone, as shown in Fig. 1B.

The operational conditions of both methods are shown in Table 1. Since the quantity of sample atomized by the laser impact is different, the signal sensitivity obtained varies between both methods. The Li signal for method 2 tends to be lower, as the atomized sample quantity is smaller than that of method 1. Therefore, to operate within similar linear ranges for both methods, allowing sample analysis without the need for dilution, in the case of method 2, a more sensitive wavelength (670.8 nm) was used instead of the second most sensitive line (610.4 nm), which was employed for method 1. The internal handheld LIBS optical setup is shown in Fig. 2.

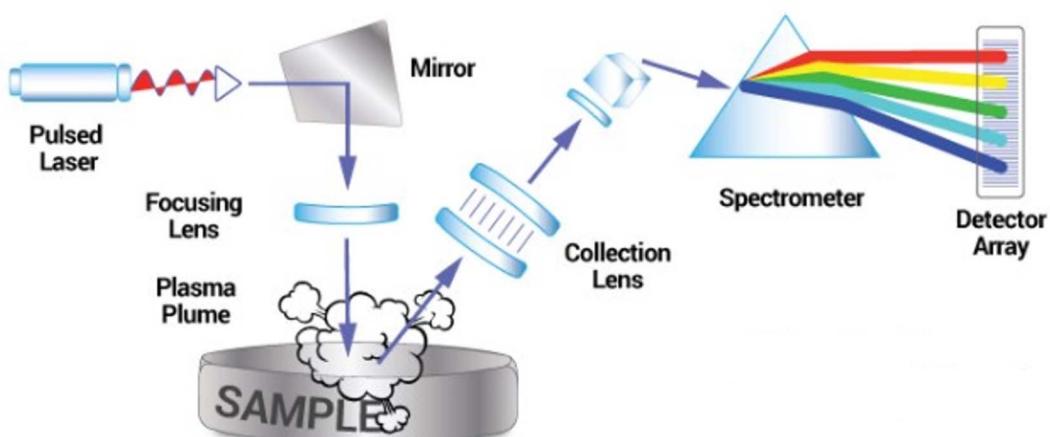


Fig. 2 Schematic diagram of handheld LIBS optical setup (SciAps).

2.3 Brine samples

The samples in this study correspond to process brines used for the synthesis of battery-grade Li_2CO_3 . These brines are obtained from natural brines extracted from the Atacama Desert in Chile. The natural brines are evaporated using solar energy, and crystallized salts are separated to increase Li concentrations. The typical composition of these process brines is provided in Table 2.

2.4 Sample treatment

No sample treatment is required in either of the two methods. In the case of method 1, brine is directly introduced into the canister. The canister should be filled completely up to the top to ensure a flat, level surface. To achieve best possible results, it is essential to avoid a convex or concave surface, as illustrated in Fig. 3.

In method 2, about 1 mL of brine is aspirated directly through suction *via* the Venturi effect, followed by the nebulization of the sample using an airbrush. No dilution or addition of any reagent is necessary. The only requirement for representativeness is that the brine sample must demonstrate homogeneity.

2.5 Calibration curves

The attempted Li linear range covered was 0.5–1.75% wt. Analyte salts were added based on a constant composition mother solution of 15% wt. NaCl, which is the major salt in the process

Table 2 Composition of major constituents in the process brines utilized for the synthesis of high-grade Li_2CO_3 for battery applications

Element	% wt min–max
Na	0.090–6.7
Mg	0.070–1.3
Ca	0.010–0.080
$\text{S}(\text{SO}_4^{2-})^a$	0.030–0.031
Li	1.2–5.8
Cl	0.36–34

^a Sulfur content is expressed as sulfate.

Table 3 Compositions of calibration solutions. All calibration solutions were prepared on a 15% NaCl wt matrix

Analyte	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6
LIBS method 1 (canister)						
Mg (% wt)	0.0050	0.010	0.019	0.074	0.10	0.19
Li (% wt)	0.43	0.76	0.98	1.1	1.6	1.7
$\text{S}(\text{SO}_4^{2-})^a$ (% wt)	0.0050	0.019	0.056	0.074	0.090	0.17
Ca (mg kg ⁻¹)	0.10	0.50	9.0	47	90	260
LIBS method 2 (venturi)						
Mg (% wt)	0.0040	0.0080	0.016	0.063	0.090	0.16
Li (% wt)	0.41	0.64	0.83	0.94	1.4	1.5
$\text{S}(\text{SO}_4^{2-})^a$ (% wt)	0.0041	0.016	0.047	0.062	0.077	0.15
Ca (mg kg ⁻¹)	0.10	0.50	9.0	39	75	220

^a Sulfur content is expressed as sulfate.

brines in Table 2, serves as a matrix match strategy to keep the Li sensitivity similar between samples and calibration solutions. The H line at 653.3 nm was always chosen as the best internal standard. The calibration curves used to test both LIBS methods were prepared on different days. Table 3 provides concentrations of the calibration curves for both methods, calculated based on the real mass of salts added to each flask.

The adjustment to the linear model of the calibration curves was estimated based on the root mean squared error (RMSE) parameter, which calculates the standard deviation of residual errors calculated from quadratic differences between the values of signals predicted by the model (\hat{y}) *versus* experimental signals (y_i), as shown in eqn (1).²¹

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N (y_i - \hat{y})^2} \quad (1)$$

It is important to note that this parameter is similar to the traditional coefficient of determination (R^2), except that the R^2 parameter calculates these residual errors in terms relative to the difference from the average response (\bar{y}), as shown in eqn (2).

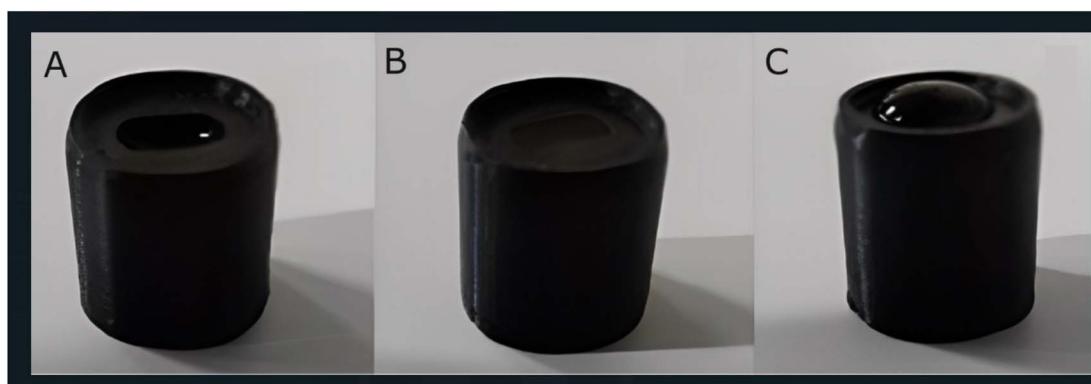


Fig. 3 Proper procedure for filling the canister with liquid samples. (A): Concave surface due to lack of sample. (B): Flat surface due to proper filling of the canister. (C): Convex surface due to excess sample.

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y})^2}{\sum_{i=1}^N (y_i - \bar{y})^2} \quad (2)$$

2.6 Trueness and precision determination

Trueness was determined by analyzing 13 samples of the process brines with the Li concentrations ranging from 1.26 to 4.56% wt. Reference values for Li were obtained by analyzing these brines using the ASTM D3561-11 reference method based on flame atomic absorption,²² a method applied by highly trained analysts, which represents one of the most reliable methods for this type of analysis to date. The trueness assessment criterion considered a relative bias of ± 20 relative to the reference value. The study was conducted only on method 2, which exhibited the best performance. The bias was calculated as the relative difference between the value determined by LIBS and value determined by the ASTM method (reference value) according to the IUPAC criteria.²³ Furthermore, to assess the accuracy of the entire dataset from the 13 brine samples, the paired samples *t*-test was applied with a 90% confidence level.

The precision at the repeatability level was carried out by measuring the lithium signal for 3 shots on the same sample by the same operator on the same day. For reproducibility, it was determined by analyzing 3 aliquots of the same sample, obtaining an average signal through 3 laser impacts in each analysis independently by different operators ($n = 9$), based on the criteria of IUPAC.²³ In both cases, precision was calculated as the relative standard deviation (% RSD).

3 Results and discussion

3.1 Calibration curves

To compare the quality of the linear regression between both methods, three types of calibration curves were evaluated: one external calibration curve and two internal standard curves with Na 589.2 nm and H 656.3 nm lines.

The selection of the H 653.3 nm line was based on two primary considerations. First, it addresses the impact of water on the atomization process and the associated splashing phenomenon, both of which significantly influence the quality of analytical results.¹² Second, the choice of the H 653.3 nm line is driven by its proximity to the analytical wavelengths of Li (610.4 nm for method 1 and 670.8 nm for method 2). In the case of the Na line, this internal standard was chosen because it is a metallic element from the same group as Li. In this study, the performance of calibration curves was evaluated within the same linear range of 0.4–1.7% Li wt.

Our calibration results for method 1 were unsatisfactory. They exhibited high residual errors, and it was not possible to fit a linear model. The external calibration curve presented an RMSE of 0.449. The use of Na as an internal standard following the 589.2 nm line reduced the RMSE to 0.295, which remains unsatisfactory for quantification purposes. Finally, employing H as an internal standard along the 656.3 nm line decreases the

RMSE error to 0.123, representing an improvement in curve fitting, but still insufficient. This could be explained by the splashing effect, which would be better compensated for by following the variation of the H atomic line associated with water, rather than a phenomenon of the atomization process, which may be compensated by normalizing with the Na atomic line.

In the case of LIBS method 2, regression parameters were improved substantially compared to those obtained for method 1. In terms of linear fitting, external calibration and those conducted with internal standards of Na 589.2 nm and H 656.3 nm yielded comparable regression parameters, with RMSE values ranging between 0.01 to 0.03. This represents an improvement in the RMSE of 10 to 20 times compared to those

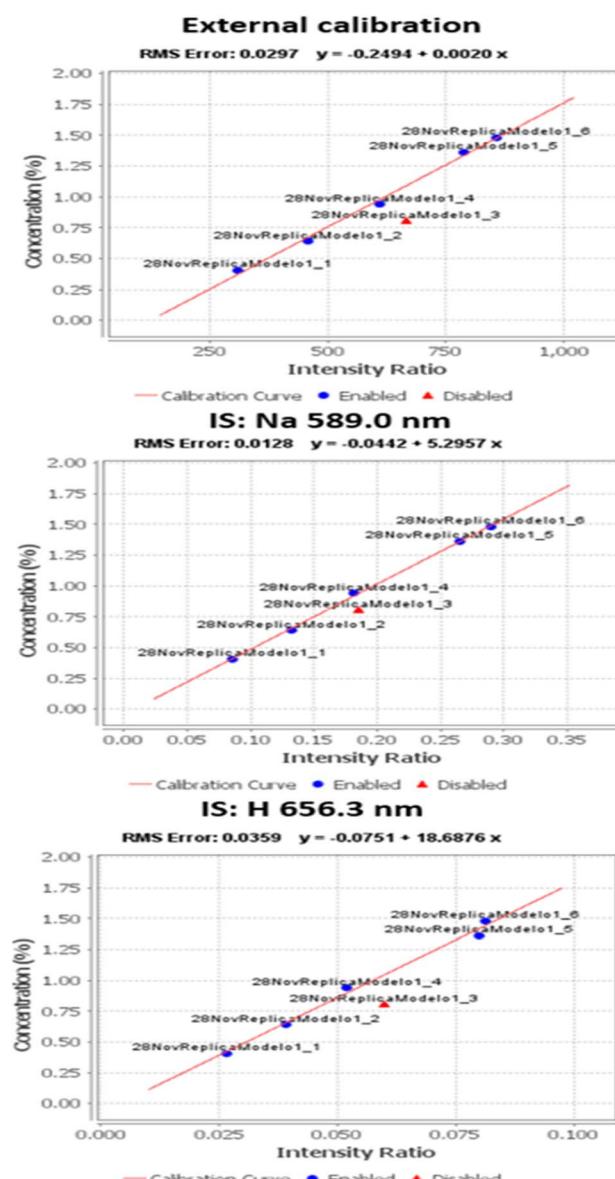


Fig. 4 Comparison of Li calibration curves for LIBS method 2 at 670.8 nm. Enabled: considers calibration points that were included in the linear regression model. Disabled: considers calibration points that were excluded from the linear regression model.

obtained in method 1, as illustrated in Fig. 4. When comparing the RMSE of the external calibration curve with the internal H standard curve, we can see that the values are very similar. This indicates that the splashing effect does not exert a significant

Table 4 Analytical figures of merit for the determination of Li in synthetic brine using LIBS method 2

Replicate	Li (mg kg ⁻¹)
1	56
2	64
3	61
4	66
5	66
Average Li	63
s.d.	4
LOD	13
LOQ	42
% RSD	7

Table 5 Evaluation of precision for the determination of Li in the brines by LIBS method 2 (Venturi)

Sample code	% Li wt	Precision method 2 (% RSD)	
		Repeatability	Reproducibility
L1	5.57	11	2.0
L4	1.32	3	0.4
L6	1.29	4	0.8
L8	1.34	2	1.1

impact on the quality of the regression model, and no internal H standard is needed for quantification purposes. Conversely, if we compare the RMSE values of the external calibration curve *versus* the internal Na standard curve, we can see that the internal Na standard curve has an RMSE that is 2 to 3 times lower, demonstrating a degree of compensation for the error associated with the atomization of a metallic element. However, both RMSE values are still sufficiently good for quantification purposes, which is why we chose to work with the external calibration curve. The limit of detection and quantification were determined using the standard deviation of Li determination of 0.005% wt. Li brine ($n = 5$) multiplied by 3 or 10 times the standard deviation of this analysis for the determination of the detection and quantification limits, respectively, in accordance with the IUPAC criteria.²³ Under best working conditions, the LOD obtained in this test was 13 mg kg⁻¹. The results are shown in Table 4.

3.2 Precision

The precision of Li determination in the brines was evaluated at the level of repeatability²⁴ and reproducibility²⁵ in agreement with the IUPAC definition of both terms. The results are shown in Table 5.

As can be seen in Table 5, the repeatability and reproducibility for method 2 are about 5% or less in most cases. It is important to mention that these values are 3 to 5 times better than method 1. It is clear that the splashing effect limits precise detection, as was described by Keerthi *et al.*¹² This repeatability is close to that reported by Bol'shakov *et al.*, which reported a %

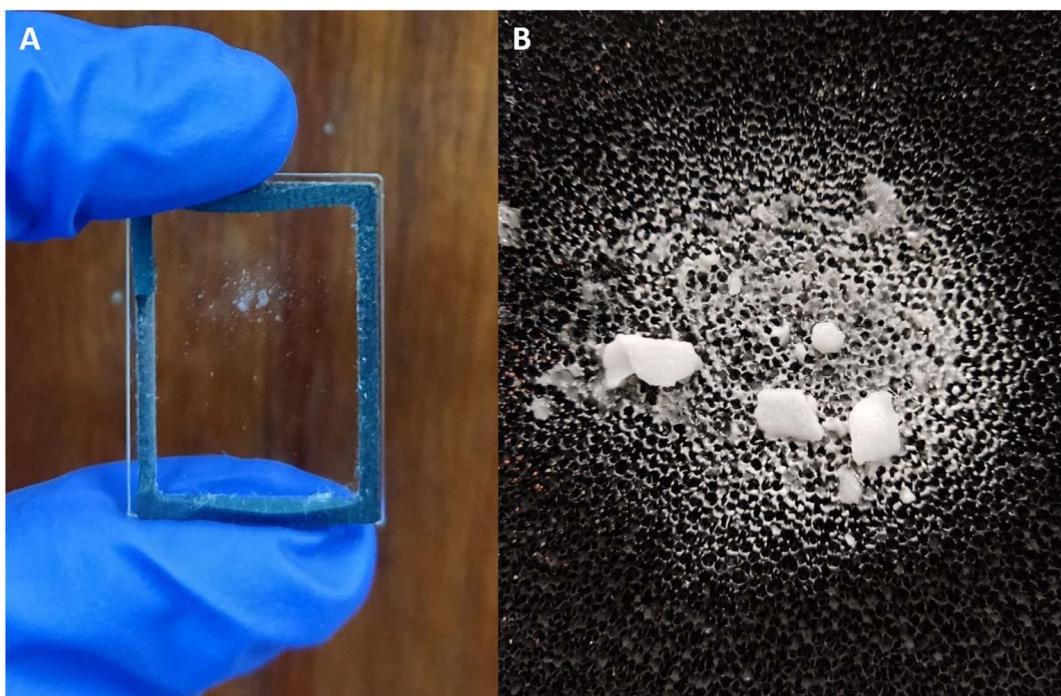


Fig. 5 Salt residues after the analysis of high viscosity brine samples using handheld LIBS. (A): Method 1 quartz window. (B): Method 2 forced evacuation unit filter.



RSD lower than 1.5%²⁶ and is similar to the work of Zhang *et al.* with an % RSD between 1.5–4.5%.¹⁷

As observed in Table 5, counterintuitively, repeatability yielded worse precision than reproducibility. Our interpretation of these results is based on two aspects. The first is that the laser impact on sample droplets would be the step that has the highest error in the analysis. In the case of repeatability, only three measurements were taken. However, reproducibility is an average of nine measurements, with three measurements for each of the 3 analyses, and it is a larger sample size in this case that improved precision.

3.3 Memory effects

Under the best working conditions, a sequence of brine analyses was carried out. A typical quality control sequence using method 1 tends to fail after two samples because the high surface tension of the brines generates severe splashing that contaminates the quartz window (Fig. 5A), increasing errors and forcing the analysis to be stopped for the window to be cleaned or replaced. However, with the Venturi system in LIBS method 2, these salt residues remain in the filter of the forced evacuation unit, as shown in Fig. 5B.

Under optimal operating conditions for LIBS method 2, a series of 15 measurements were conducted on one brine. Measurements were iterated until the bias exceeded $\pm 20\%$. As illustrated in Fig. 6, the determination of Li content remains within the $\pm 20\%$ bias range for up to 17 measurements until the injection tube became blocked for Brine L5. This experiment was repeated with two additional brines, and the performance remained within the $\pm 20\%$ error range for 7 and 10 measurements, respectively. Notably, cleaning the injection system is a straightforward process, enabling the analysis sequence to swiftly resume while maintaining result quality within these specified margins.

3.4 Trueness

Given that method 2 yielded superior results, trueness was assessed in this method by analyzing a set of 13 brine samples, utilizing values obtained from a flame atomic absorption

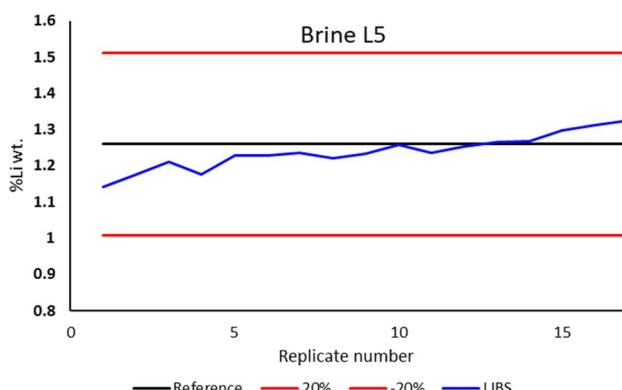


Fig. 6 Sequence of analysis for the determination Li content in a real brine sample using LIBS method 2.

Table 6 Determination of accuracy and precision for the determination of Li content in real brines from industrial processes using method 2 (Venturi) LIBS

Brine code	Lithium content % wt			
	FAAS	Average	% RSD	% Bias
A	1.32	1.19	4	-10
B	1.34	1.26	2	-6
C	1.27	1.18	2	-7
D	1.29	1.18	1	-9
E	1.28	1.17	1	-8
F	1.28	1.18	2	-7
G	1.26	1.21	1	-4
H	1.28	1.01	0	-21
I	1.26	1.12	4	-11
J	4.55	4.75	16 ^a	4
K	4.54	4.30	9	-5
L	4.53	3.93	2	-13
M	4.56	4.67	9	2

^a clogged tip.

spectroscopy (FAAS) analysis as reference values based on the ASTM standard.²² Table 6 shows that by working in the best linear range and operational conditions for LIBS method 2, it is possible to determine the Li content in brines with precision below 10% RSD. Conversely, the bias obtained is, in most cases, less than 20%, so we can obtain reliable results within a relative margin of error of 20%.

When applying a paired-sample *t*-test to the same dataset from Table 6, it yields a calculated *t*-statistic of 2.36, meeting a reliability criterion at a 90% confidence level. This allows us to state that the results of Li content determination using LIBS method 2 are statistically similar to the ASTM reference method with 90% confidence (*t* critical value: 1.78).

4 Conclusions

From our results, we can conclude that the direct determination of lithium in brine is feasible using our portable LIBS system. Our findings demonstrate that employing an injection system based on the Venturi effect effectively mitigates splashing, leading to improvements in precision, accuracy, and memory effect. In summary, our novel LIBS device, incorporating sample injection using the Venturi effect, represents a significant technological advancement in analytical atomic spectroscopy. This innovation enables *in situ* analysis of brines *via* a handheld LIBS system with errors of less than 20%.

Conflicts of interest

Dave Day, Morgan Jennings and Agustin Loureiro are SciAps employees. Christopher Green and Loverchio Gallardo are SQM employees. Waldo Quiroz has been hired as a consultant by SQM as a part of this investigation.

Author contributions

Nayadet López: writing, investigation, and validation. Gonzalo Puebla: writing, investigation, and validation. Dave Day: conceptualization and resources. Morgan Jennings: conceptualization and resources. Agustín Loureiro: conceptualization and resources. Christopher Green: resources, methodology, and supervision. Loverchio Gallardo: resources, methodology, and supervision. Waldo Quiroz: writing – review & editing, visualization, and supervision.

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References

- 1 E. Polanco Valenzuela, "Historia de SOQUIMICH, una revisión", *Congreso Geológico Chileno*, La Serena (Chile), 4–8 Octubre 2015.
- 2 T. Han, X. P. Yu, Y. F. Guo, M. L. Li, J. Duo, T. L. Deng, G. Pu, X. Yu, G. Pu and F. Xi, *Spectrosc. Spectral Anal.*, 2020, **40**, 1214–1220.
- 3 B. Baraj, L. F. H. Niencheski, R. D. Trapaga, R. G. França, V. Cocoli and D. Robinson, *Fresenius' J. Anal. Chem.*, 1999, **364**, 678–681.
- 4 B. Lemière, *J. Geochem. Explor.*, 2018, **188**, 350–363.
- 5 R. Van Grieken and A. Markowicz, *Handbook of X-Ray Spectrometry*, CRC Press, Boca Raton, USA, 2001.
- 6 B. Zawisza, *Anal. Chem.*, 2008, **80**, 1696–1701.
- 7 B. Zawisza and R. Sitko, *Appl. Spectrosc.*, 2011, **65**, 1218–1221.
- 8 J. F. Araneda, P. Hui, G. M. Leskowitz, S. D. Riegel, R. Mercado and C. Green, *Analyst*, 2021, **146**, 882–888.
- 9 R. S. Harmon, F. C. DeLucia, C. E. McManus, N. J. McMillan, T. F. Jenkins, M. E. Walsh and A. Mizolek, *Appl. Geochem.*, 2006, **21**, 730–747.
- 10 J. Huidobro, J. Aramendia, G. Arana and J. M. Madariaga, *Anal. Chim. Acta*, 2022, **1197**, 339499.
- 11 W. Li, X. Li, X. Li, Z. Hao, Y. Lu and X. Zeng, *Appl. Spectrosc. Rev.*, 2020, **55**, 1–25.
- 12 K. Keerthi, S. D. George, S. D. Kulkarni, S. Chidangil and V. K. Unnikrishnan, *Opt. Laser Technol.*, 2022, **147**, 107622.
- 13 Q. Wang, A. Chen, Y. Chen, Y. Jiang, S. Li and M. Jin, *J. Anal. At. Spectrom.*, 2021, **36**, 1889–1894.
- 14 Z. You, X. Li, J. Huang, R. Chen, J. Peng, W. Kong and F. Liu, *Molecules*, 2023, **28**, 2777.
- 15 C. Eum, J. Park, S. Kumar, E. Jang, Y. Lee, S. H. Nam, D. Choi and H. Chung, *J. Anal. At. Spectrom.*, 2022, **37**, 823–832.
- 16 Y. Wang, Y. Bu, Y. Cai and X. Wang, *J. Anal. At. Spectrom.*, 2022, **37**, 1023–1031.
- 17 D. Zhang, A. Chen, Q. Wang, H. Zhang, S. Li and M. Jin, *Opt. Express*, 2021, **29**, 9897–9906.
- 18 Z. Wei, W. Ye, C. Zhai, Y. Tian, Y. Lu, J. Guo and R. Zheng, *Spectrochim. Acta, Part B*, 2023, **208**, 106780.
- 19 P. Xing, J. Dong, P. Yu, H. Zheng, X. Liu, S. Hu and Z. Zhu, *Anal. Chim. Acta*, 2021, **1178**, 338799.
- 20 D. R. Day, "Lithium Brine Analysis Using Handheld LIBS", 9th Euro-Mediterranean LIBS Symposium (EMSLIBS), Pisa (Italy), 11–16 June 2017.
- 21 D. S. K. Karunasingha, *Inf. Sci.*, 2022, **585**, 609–629.
- 22 ASTM, *Standard Test Method for Lithium, Potassium, and Sodium Ions in Brackish Water, Seawater, and Brines by Atomic Absorption Spectrophotometry*, 2021, pp. 1–6.
- 23 M. Thompson, S. L. R. Ellison and R. Wood, *Pure Appl. Chem.*, 2002, **74**, 835–855.
- 24 'repeatability' in IUPAC Compendium of Chemical Terminology, International Union of Pure and Applied Chemistry, 3rd edn, 2006, Online version 3.0.1, 2019.
- 25 'reproducibility' in IUPAC Compendium of Chemical Terminology, International Union of Pure and Applied Chemistry, 3rd edn, 2006, Online version 3.0.1, 2019.
- 26 A. A. Bol'shakov, S. J. Pandey, X. Mao and C. Liu, *Spectrochim. Acta, Part B*, 2021, **179**, 106094.

