Article

Detection of Low Lithium Concentrations Using Laser-Induced Breakdown Spectroscopy (LIBS) in High-Pressure and High-Flow Conditions

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Abstract

This paper describes the effects of laser pulse rate and solution flow rate on the determination of lithium at high pressure for water and 2.5% sodium chloride solutions using laser-induced breakdown spectroscopy (LIBS). Preliminary studies were performed with 0–40 mg L^{-1} Li solutions, at ambient pressure and at 210 bar, and in static and flowing (6 mL · min^{-1}) regimes, for a combination of four different measurement conditions. The sensitivity of calibration curves depended on the pressure and the flow rate, as well as the laser pulse rate. The sensitivity of the calibration curve increased about 10% and 18% when the pressure was changed from 1 to 210 bar for static and flowing conditions, respectively. However, an effect of flow rate at high pressure for both 2 and 10 Hz laser pulse rates was observed. At ambient pressure, the effect of flow rate was negligible, as the sensitivity of the calibration curve decreased around 2%, while at high pressure the sensitivity increased around 4% when measurements were performed in a flow regime. Therefore, it seems there is a synergistic effect between pressure and flow rate, as the sensitivity increases significantly when both changes are considered. When the pulse rate is changed from 2 to 10 Hz, the sensitivity increases 26–31%, depending on the pressure and flow conditions. For lithium detection limit studies, performed with a laser pulse energy of 2.5 mJ, repetition rate of 10 Hz, gate delay of 500 ns, gate width of 1000 ns, and 1000 accumulations, a value around 40 μg L^{-1} was achieved for Li solutions in pure water for all four measurement conditions, while a detection limit of about 92 μg L^{-1} was determined for Li in 2.5% sodium chloride solutions, when high pressure and flowing conditions were employed. The results obtained in the present work demonstrate that LIBS is a powerful tool for the determination of Li in deep ocean conditions such as those found around hydrothermal vent systems.

Introduction

In situ measurements in deep-ocean hydrothermal vents are a great challenge, due to harsh conditions such as high pressure, high temperature, and corrosive environment.[1,2] Usually, analyses are performed in the laboratory after sampling, bringing a series of disadvantages, as a mixture between the sampled fluid and sea water occurs, changing its physico-chemical characteristics, and other parameters are changed due to the removal from the high pressure and high temperature environment.[1] Furthermore, sampling provides limited temporal and spatial information that are of vital importance for a complete understanding of hydrothermal vent systems.[1] Laser-induced breakdown spectroscopy (LIBS) is a promising

tool for real-time analysis and has the proper sensitivity to study these processes. Analysis can also be performed in situ, as the sample interrogation occurs by means of a high energy laser pulse, producing a plasma, whose emission can be collected far away from the point of analysis. Several contributions can be found in the literature, addressing different fundamental aspects regarding LIBS

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measurements in high pressure water.[1,3–10] Michel et al.[3] verified that intensities of atomic lines for alkali and alkaline-earth metal ions do not change for pressures up to 270 bar when low-energy laser pulses are employed, findings that agree with those obtained by Hou et al.[4] Lawrence-Snyder et al.[1] verified that the effect of pressure is dependent on the laser pulse energy as well as on the gate delay and gate width employed for data acquisition. The double pulse LIBS strategy can be utilized to enhance the sensitivity of underwater measurements, but there are contradictory results described in the literature, stating that the increase in sensitivity is not substantial under pressure,[5–8] although being advantageous for alkali and alkaline-earth metal ions in depth up to 2800 m.[1,3,4,9,10] The above-mentioned contributions[1,3–5,8–10] employed static high-pressure cells (up to 35–400 bar), which did not allow for the evaluation of the effect of flow rate on the emission signals. As a means of mimicking the currents that occur in the deep ocean, the effect of flow rate is important, as the bubbles formed in the sample by incidence of the laser pulse can be removed from the interrogated area by the flowing fluid, which changes the conditions for plasma formation. There are contributions in the literature that deal with the effect of flow rate on the LIBS sensitivity, where measurements are performed in solution films,[11] jets,[11,12] focusing the laser pulse on the surface of a flowing solution,[13,14] and sprays.[15]. Barreda et al.[11] evaluated the determination of platinum in silicone oil in static, liquid jet, and flowing liquid conditions, concluding that results obtained with liquid jet and flowing liquid are similar, providing lower detection limits than in static liquid. In addition, it was found that flow rates in the range from 6 to 14 mL min^{-1} produce a stable film, having no effect on the LIBS signal. Ohba et al.[12] produced liquid sheets in air with thicknesses from 5 to 80 μm by pumping water and sodium chloride solution through a slit-type nozzle and verified that the best signal-to-noise ratio was obtained for 20 μm thick sheets, in which the laser pulse was focused. St-Onge et al.[13] used NaCl isotonic solutions to demonstrate that measurements performed by focusing the laser at the surface of a flowing solution provide a relative standard deviation (RSD) of 0.5%, while a value of 1.8% is obtained with non-flowing solution. This result explained the interaction between the laser beam and the sample, which impaired the reproducibility of the measurements demonstrating the surface perturbations and bubbles formation in previous laser shots. Similarly, Loudyi et al.[14] verified that RSD for determination of Pb decreased from 15.1% to 6.7% for measurements performed in a static fluid and a flowing fluid at a flow rate of 130 mL min^{-1}. These studies were performed at ambient pressure, which do not significantly elucidate the effects of flow rate in solution under high pressure.

Lithium ions are found in sea water in concentrations around 0.2 mg L^{-1},[16] reaching higher concentrations in hydrothermal vent fluids (10 mg L^{-1} or higher), as it is leached from rocks by the action of hot vent fluids.[17] Therefore, this ion can be considered a valuable tracer for hydrothermal fluids, indicating the evolution of the plume and its extension.[17] It was demonstrated that Li(I) ion can be determined in pressures as high as 276 bar, with no significant pressure effect on the emission signal intensity, while the laser pulse energy, gate delay, and gate width do affect the sensitivity.[1] Recently, it was also demonstrated that emission signals of oxygen and hydrogen can be employed as a reference for intensity correction, increasing the precision of the measurements.[2] Regarding the detectability of lithium ions, studies in water employing single pulses describe detection limits of 60 μg L^{-1} [18] and 13 μg L^{-1},[19] while values of 6 μg L^{-1} [20] and 0.8 μg L^{-1} [19] were obtained with the double pulse technique. A recent contribution describes a limit of detection of 10.5 mg L^{-1} in water, while this value decreases to 18.4 μg L^{-1} after enrichment in filter paper.[21]

The present work describes the effects of pressure, flow rate, and laser pulse repetition rate on the emission signal of lithium in order to optimize the experimental conditions for obtaining higher sensitivity, demonstrating the usefulness of LIBS for oceanographic studies.

Experimental

A LIBS system furnished with a high-pressure flow cell similar to those previously described[1] was employed in this study and is shown in Fig. 1. The laser pulse was focused on the center of a homemade stainless-steel flow cell with an internal volume of 40 mL, furnished with a sapphire window (diameter 25 mm, thickness 6.35 mm). The flow rate was orthogonal to laser pulse and collected plasma emission. Stainless-steel tubing with diameter of 3.175 mm (1/8 in.) was employed to connect the sample cell to a high performance liquid chromatography (HPLC) pump (LC5000, Isco) to maintain the cell pressure and sample flow rate. The system pressure was adjusted with a proportional relief valve (Swagelok R3A series), which was automatically opened when pressure was higher than the back-pressure provided by an internal spring.

The optical setup shown in Fig. 1 consisted of a pulsed laser source (5 ns, Continuum Surelite III neodymium-doped yttrium aluminum garnet, or Nd:YAG, with a frequency doubling crystal for 532 nm), a polychromator (Chromex Model 250IS/RF, f/4300 grooves/mm, blazed at 1000 nm, slit of 100 μm), and an intensified charge-coupled device (ICCD) detector (Princeton Instruments I-Max 1024-E, 1064 × 256 pixels). The diameter of the laser beam was expanded to 50.8 mm, by employing a plano-concave lens (25.4 mm diameter, focal distance −25.4 mm), collimated with a biconvex lens (57.2 mm diameter, focal distance 76.2 mm) and then conducted to the sample by employing a dichroic mirror (Thorlabs DMLP550L). A biconvex lens (50.8 mm diameter, focal distance of
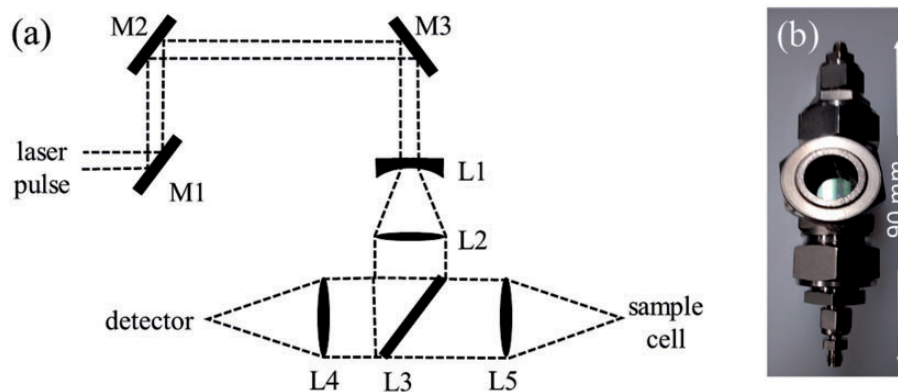
Figure 1. Schematic diagram of the optical setup: M1, M2, and M3 mirrors (25.4 mm diameter); L1 plano-concave lens (25.4 mm diameter, focal distance −25.4 mm), L2 biconvex lens (57.2 mm diameter, focal distance 76.2 mm), L3 dichroic mirror; L4 and L5 biconvex lenses (50.8 mm diameter, focal distance 76.2 mm) (a) and flow cell (b).

76.2 mm) was used to focus the laser pulse (average irradiance of approximately $2–3 \times 10^{12}$ W cm^{-2}) and collect plasma emission. The collected signal was then focused onto the tip of a 2 mm core optical fiber transmitted into the polychromator by using another biconvex lens (50.8 mm diameter, focal distance of 76.2 mm). The laser pulse energy was adjusted in the laser power control unit, while the repetition rate, gate delay, and gate width were controlled by a pulse generator (BNC model 555). Spectra were acquired with the aid of software (Winspec32), which aided in adjusting the number of pulses for obtaining a spectrum, number of spectra, and ICCD detector gain, among other parameters.

Initially, measurements with solutions containing 0–40 mg L^{-1} of NaCl (Fisher Chemical), lithium chloride (Acros Organics), and potassium chloride (Baker) were performed to evaluate the pressure and flow rate (0–6.7 mL min^{-1}) effects on the sensitivity. After this preliminary evaluation, measurements were carried out using LiCl solutions in the concentration ranges of 0–1 mg L^{-1} and 0–5 mg L^{-1}, prepared in water and in 2.5% NaCl, respectively.

Results and Discussion

The evaluation of LIBS as a tool for oceanographic studies has been performed under various aspects, encompassing variables such as temperature, pressure, and salinity.[3] However, the effects of flow rate and systematic studies regarding the laser repetition rate on the analytical signal have not been performed yet.

Preliminary studies were carried out with solutions containing lithium chloride, sodium chloride, and potassium chloride at the same concentrations. The gate width was fixed at 1000 ns and each spectrum was obtained with an accumulation of 100 runs at pulse frequencies (repetition rate) of 2 Hz. A 532 nm laser source was employed, as this wavelength is less absorbed by water than 1064 nm,[22]

which is an important point for remote measurements in deep sea. A gate delay of 340 ns was determined to be adequate, as the baseline was minimized, without significantly impairing the intensity of the emission peaks. A pulse energy of 3.4 mJ provided the highest peak intensities, although its effect was less significant for potassium (Figure S1, Supplemental Material). Similar experiments were performed with repetition rates of 10 Hz and gate delays of 380 ns, producing the most intense signals for a laser energy of 3.1 mJ.

After these preliminary studies were performed at ambient pressures and static conditions, experiments were then carried out to verify the effects of laser repetition rates, high pressures, and flow rates on the sensitivity of the analytical curves for the three metal ions. For both repetition rates of 2 and 10 Hz, analytical curves were constructed with data obtained in four different conditions: (i) 1 bar, static flow rate; (ii) 1 bar, 6.7 mL min^{-1} flow rate; (iii) 210 bar, static flow rate, and (iv) 210 bar, 6.7 mL min^{-1} flow rate. The value of 6.7 mL min^{-1} was the highest flow rate provided by the pump which is why higher flow rates were not tested. The pulse energies were set at 3.4 mJ (2 Hz repetition rate) and 3.1 mJ (10 Hz repetition rate), the gate delay was set at 380 ns while keeping a gate width of 1000 ns and an accumulation of 100 shots for each spectrum that was obtained. Thus, analytical curves up to 40 mg L^{-1} were constructed, which presented correlation coefficient (R^2) that remained higher than 0.99. Table 1 shows the sensitivities (slope of the analytical curves) obtained for each ion in the different experimental conditions evaluated.

Different scenarios seem to be evident at low and high pressures when the values of the SDs and their RSDs are considered. When the pulse rate is increased from 2 to 10 Hz, at the same conditions of pressure and flow rate, the SD usually increases at low pressures, while almost the same SD values are observed at high pressures. This result arises from the fact that bubbles formed by the laser pulses

Table I. Sensitivities, standard deviations (SDs), and relative standard deviations (RSDs) for analytical curves obtained in different conditions (laser pulse energy: 3.4 mJ at 2 Hz and 3.1 mJ at 10 Hz; LP (low pressure): 1 bar; HP (high pressure): 210 bar; S: static; F: 6.7 mL min^{-1}).

	Na	SD	RSD (%)	R^2	Li	SD	RSD (%)	R^2	K	SD	RSD (%)	R^2
2 Hz LPS	657	13	2.0	0.9984	813	18	2.2	0.9981	156	19	12.1	0.9446
10 Hz LPS	1413	63	4.5	0.9920	1862	66	3.5	0.9950	287	3	1.0	0.9995
2 Hz LPF	646	4	0.6	0.9999	795	5	0.6	0.9998	141	8	5.6	0.9880
10 Hz LPF	1407	25	1.8	0.9988	1814	41	2.2	0.9979	280	11	3.9	0.9941
2 Hz HPS	778	18	2.3	0.9979	896	20	2.2	0.9981	149	5	3.4	0.9948
10 Hz HPS	1616	15	0.9	0.9996	2068	11	0.5	0.9999	281	13	4.6	0.9911
2 Hz HPF	822	31	3.8	0.9944	947	13	1.4	0.9992	147	5	3.4	0.9953
10 Hz HPF	1702	24	1.4	0.9992	2138	28	1.3	0.9993	297	11	3.7	0.9944

are larger at ambient pressure and the number of bubbles formed is related to the pulse rate, that is, higher rates produce more bubbles. Therefore, these laser pulses can then be deviated by the bubbles more easily, varying the focus of the laser beam, which affects the laser pulse energy and, consequently, affects the repeatability of the measurements. In addition, the deviation of emitted radiation by bubbles also affect the repeatability of the measurements, as the beams can be directed towards the detection system or away from it. However, these effects are less pronounced at high pressures, as bubbles cannot expand in the same extension, providing almost the same SD values for 2 and 10 Hz. The increase in pressure does not significantly affect the RSD, a small increase in %RSD is observed at 2 Hz, while the reverse is observed at 10 Hz. If the low-pressure measurements are considered, there is an increase in the RSD values for Na and Li when the pulse rate is changed from 2 to 10 Hz, while the opposite trend is observed at high pressure. The same statement regarding the bubble size can explain this behavior, but the RSD value considers the sensitivity, which overall is higher at high pressures than in low pressures. For K, the RSD does not significantly vary with changing the laser pulse rate, because its signal intensity is almost the same as the laser pulse energy is varied. The effect of the flow rate on the precision of the results is also different at low and high pressures; while, on average, the flow rate caused an increase in the precision of measurements at low pressures, the SD and RSD increased at high pressures, independent of the pulse rate. Better RSD values were obtained when a flow regime was employed at low pressures which is in accordance with the results described by St-Onge et al.[13] and Loudyi et al.[14]

The effects of each variable on the sensitivity were also evaluated, based on the values of the slopes of the analytical curves. Tables II to IV show the effect of increasing the flow rate, pressure, and laser repetition rate, respectively, when the other two parameters were kept constant. Variations in the sensitivity of the analytical curves listed in these tables were calculated with data extracted from Table I.

Table II. Variation in the sensitivity (%) of the analytical curves when the flow rate was varied from 0 to 6.7 mL min^{-1}, keeping constant the laser repetition rate and pressure.

	Na	Li	K
2 Hz LP	−1.7	−2.3	−9.1
10 Hz LP	−0.4	−2.6	−2.5
2 Hz HP	5.7	5.7	−1.9
10 Hz HP	5.3	3.4	5.8

Table III. Variation in the sensitivity (%) of the analytical curves when the pressure was varied from 1 to 210 bar, keeping constant laser repetition rate and flow rate.

	Na	Li	K
2 Hz S	18.4	10.1	−4.0
10 Hz S	14.3	11.1	−2.4
2 Hz F	27.3	19.1	3.6
10 Hz F	20.9	17.8	5.9

The flow rate (shown in Table II) seems to cause little effect on the signal intensity, producing a slight decrease at ambient pressure (1 bar) and an increase in high pressure (210 bar). This result is important for measurements in deep sea, as it eliminates a fundamental variable for obtaining reliable and consistent results on in situ measurements. The increase of the pressure (shown in Table III) causes an increase in the sensitivity; in addition, it seems that a synergistic effect between this variable and flow rate occurs, which agrees with the results showed in Table II. However, Michel et al.[3] reported a different result, concluding that effect of pressure is minimal in a range of 1 to 270 bar for Na and Li, when a 1064 nm laser source was employed, operating at a frequency of 5 Hz. It is clear that repetition rate of the laser pulses (Table IV) caused the most significant variation in the sensitivity. The sensitivity enhancement

is related to the formation of bubbles in bulk solution, which can act as preferential centers for the occurrence of breakdown.[23] Since the bubble formation is higher when a repetition rate of 10 Hz in employed, the signal intensity tends to be higher in this condition. It seems that higher pulse rate forms a kind of emulsion of microbubbles in the fluid, which lasts for a long interval of time, being more difficult to remove at high pressure, as shown in Table II. Although the laser beam can be deviated by a bubble, there are many other bubbles that can act as preferential centers for breakdown, increasing the sensitivity. Similar results were obtained with a double pulse approach, by substituting the first laser pulse with a sequence of pulses of lower energy, which caused the formation of a higher number of bubbles.[24,25] For lithium, measurements in flow conditions or in high pressure did not significantly influence the effect of the repetition rate. However, the change in pressure seems to decrease this effect for Na, while the flowing solution increments the effect of the repetition rate for K.

The studies above described indicate the possibility of determining these species in concentrations below $1\,mg\,L^{-1}$, which is not very usual for LIBS in solution.

Table IV. Variation in the sensitivity (%) of the analytical curves when the repetition rate was varied from 2 to 10 Hz, keeping constant pressure and flow rate.

	Na	Li	K
LPS	115.2	128.9	84.6
LPF	117.9	128.2	98.0
HPS	107.7	130.9	87.7
HPF	106.9	125.9	102.3

Lithium was chosen for this evaluation, due to its importance for oceanography, especially the study of hydrothermal vents, as it is leached from the rocks, therefore being a proper tracer for the understanding of the plumes formed in these regions of the oceans.[17] The evaluation of Li determination below $1\,mg\,L^{-1}$ was performed by employing a repetition rate of laser pulses of 10 Hz, as it provided higher sensitivity and the number of accumulations for obtaining one spectrum was increased, as a mean of increasing the signal-to-noise ratio.

Initially, the pulse energy and the gate delay were re-evaluated, keeping the gate width as 1000 ns. A 2.5 mJ pulse provided better results than at 3.1 mJ pulse, which was employed in the previous studies, because both an intense signal and a more adequate baseline above 670 nm are obtained (Figure S2). The variation of the gate delay (Figure S3) indicated that a value between 450 and 500 ns (500 ns was chosen) is more adequate for minimizing the baseline signal and the emission of H(α) signal, which appeared as a wide band centered around 656 nm, when a gate delay of 380 was employed.

The evaluation of LIBS for the determination of Li in concentrations below $1.0\,mg\,L^{-1}$ was carried out by means of analytical curves constructed in four different conditions. These conditions considered pressures of 1 and 210 bar and flow rates of 0 and $6.7\,mL\,min^{-1}$. Figure 2 shows the emission signals obtained at ambient pressures and static conditions as well as the analytical curves obtained in the above-mentioned four conditions. Each spectrum was obtained as an accumulation of 1000 laser shots and measurements were performed in quintuplicate, presenting SDs lower than 1.5%. The limits of detection were estimated to be 44, 50, 36, and $38\,\mu g\,L^{-1}$ for measurements performed in the following conditions: (1 bar and static), (1 bar and
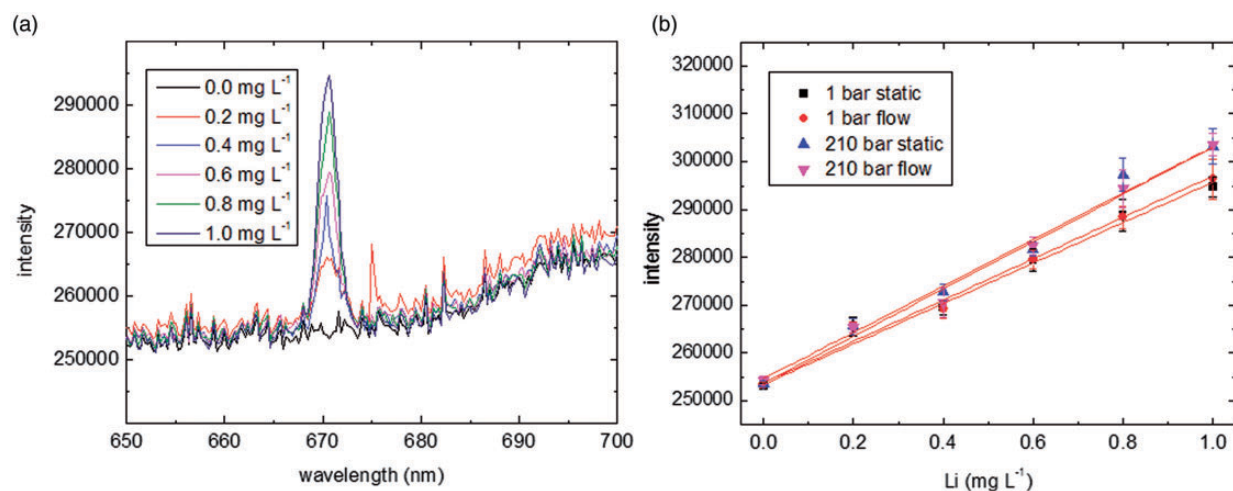

Figure 2. (a) Spectra obtained with Li aqueous solutions ranging from 0 to $1.0\,mg\,L^{-1}$ (1 bar, static condition). (b) Analytical curves obtained in different conditions of pressure and flow rate (pulse energy 2.5 mJ, repetition rate 10 Hz, gate delay 500 ns, gate width 1000 ns, 1000 accumulations, $n = 5$).
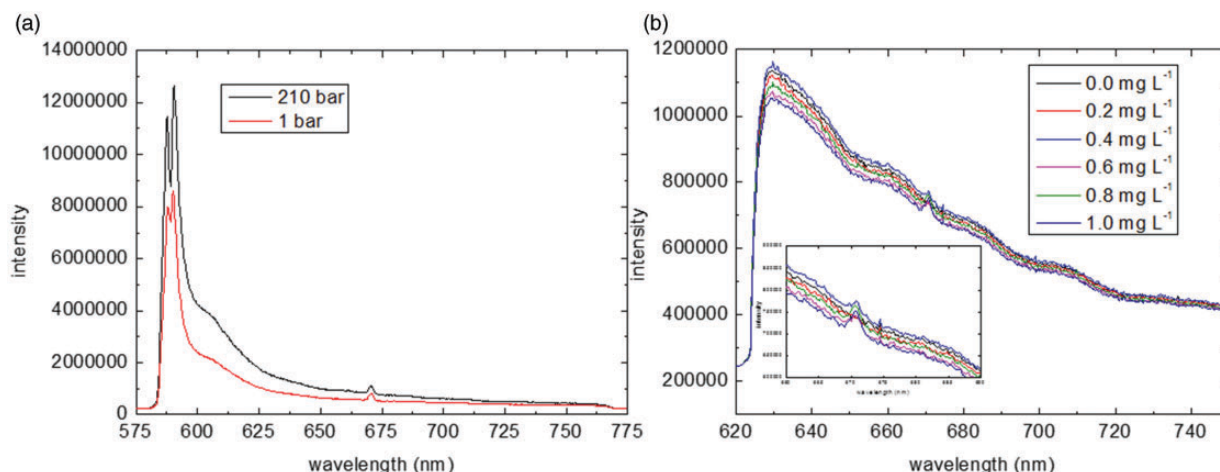
Figure 3. Spectra obtained with a $5.0\,mg\,L^{-1}$ LiCl in 2.5% NaCl solution at ambient pressure (1 bar) and high pressure (210 bar) and static condition (a) and spectra of LiCl solutions in the concentration range from 0.2 to $1.0\,mg\,L^{-1}$ in 2.5% NaCl (average of five spectra) (b). The inset shows a zoom of the Li(I) peak, evidencing the baseline fluctuation.
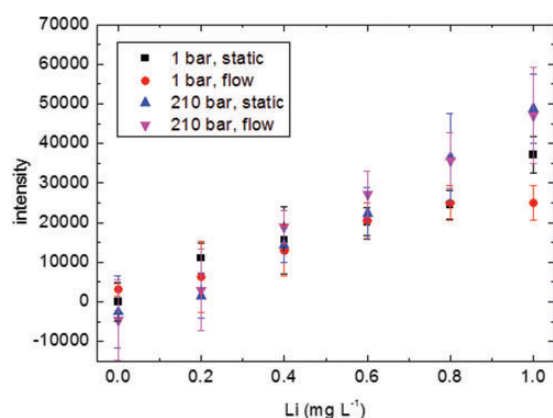

Figure 4. Analytical curves for Li in 2.5% NaCl solution, in the concentration range from 0 to $1.0\,mg\,L^{-1}$, obtained in different experimental conditions of flow rate (0 and $6.7\,mL\,min^{-1}$) and pressure (1 and 210 bar) ($n = 5$).

$6.7\,mL\,min^{-1}$), (210 bar and static), and (210 bar and $6.7\,mL\,min^{-1}$), respectively. These detection limits are very similar to $60\,\mu g\,L^{-1}$ described by Goueguel et al.,[18] $13\,\mu g\,L^{-1}$ reported by Knopp et al.,[19] and slightly higher than those obtained with the double pulse approach, e.g., $0.8\,\mu g\,L^{-1}$ and $6\,\mu g\,L^{-1}$.[19,20]

The evaluation for the determination of Li in 2.5% NaCl solution was carried out in the concentration range of 0 to $1.0\,mg\,L^{-1}$, employing the same experimental conditions for measurements in water. Figure 3 shows the spectra obtained with a $5.0\,mg\,L^{-1}$ Li(I) solution, acquired at ambient pressure and high pressure (210 bar), in which the intense peak for Na(I) which can be observed (Fig. 3a) as well as the spectra obtained with Li(I) solutions with concentrations below $1.0\,mg\,L^{-1}$ (Fig. 3b), acquired at 210 bar

and flow rate of $6.7\,mL\,min^{-1}$. It can be noted that peaks present low intensities and considerable baseline fluctuations occur due to the high concentration of sodium ion and the fluctuation of the laser source. The inset of Fig. 3b makes clear the fluctuation of the baseline and, therefore, the signal referred to each solution could not be inferred directly from their intensity at 671 nm, as in the case of measurements in water.

The strategy employed for obtaining peak heights consisted in taking baseline average values between the intensities of two adjacent points around the Li emission peak (intensities at 667.97 and 673.16 nm). The intensity of each peak was taken as the difference between the intensity at 670.56 nm (Li emission) and the average value obtained as described above. Figure 4 shows the analytical curves obtained, by taking the signal intensities as described.

Although it is possible to fit a linear curve with the intensity data, the SDs of the measurements are high, making the quality of the analytical curve not satisfactory, the fact that directed the studies for the concentration range of 0 to $5.0\,mg\,L^{-1}$ in 2.5% sodium chloride, whose results are shown in Fig. 5.

The strategy for the baseline correction allowed the measurement of the signal intensities in the concentration range of $0–5.0\,mg\,L^{-1}$, providing an SD around 10%, which can be considered acceptable as the concentration of sodium chloride is very high. The limits of detection were estimated as 266, 298, 204, and $92\,\mu g\,L^{-1}$ at (1 bar and static), (1 bar and $6.7\,mL\,min^{-1}$), (210 bar and static), and (210 bar and $6.7\,mL\,min^{-1}$) experimental conditions, respectively.

It is noticeable that measurements at high pressure provide curves with better sensitivity and linearity in both concentration ranges. The sensitivity is higher as pressure is increased, as shown in Table III. However, the flow rate
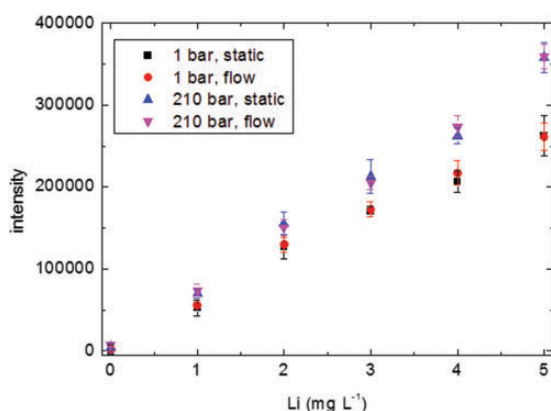
Figure 5. Analytical curves for Li in 2.5% NaCl solution, in the concentration range from 0 to 5.0 mg L^{-1}, obtained in different experimental conditions of flow rate (0 and 6.7 mL min^{-1}) and pressure (1 and 210 bar) ($n = 5$).

does not affect the sensitivity in sodium chloride solution as it does in water (as listed in Table III, sensitivity increases 11% in static condition and 18% in flowing condition when the pressure is increased from 1 to 210 bar). This result is promising, as the sensitivity seems to be unaffected by flow rate at high pressures in salty solutions, which can provide more reliable results in deep sea monitoring. As far as the linearity is concerned, an explanation can be based on the supposition that lithium ionization decreases as pressure increases, enhancing the linearity or the small bubbles formed at high pressure does not significantly affect the laser pulse focus, maintaining almost constant the pulse energy. However, these statements must be demonstrated with more experiments, which is not the aim of the present work.

Conclusion

The results obtained in the present work demonstrated that LIBS is a powerful technique for the determination of Li in deep sea and can be employed to monitor Li ions in the hydrothermal vents. The effect of the three experimental variables on LIBS signal was investigated and the measurements were carried out in eight different experimental conditions, by combining static and flow (6 mL min^{-1}) regimes, low (1 bar) and high (210 bar) pressures, and low (2 Hz) and high (10 Hz) pulse rates. For pulse rates of 2 and 10 Hz, the effect of flow rate seemed to be negligible at ambient pressure. The sensitivity, expressed as the slope of the calibration curve, increased around 10% and 18% when the pressure was changed from 1 to 210 bar in both static and flowing conditions, respectively, indicating a synergistic effect between pressure and flow rate, as the sensitivity increases significantly when both changes are considered. Increasing the pulse rate from 2 to 10 Hz increased the sensitivity from 26 to 31%, depending on

the pressure and flow conditions. The determination of Li in low concentrations was performed in water and 2.5% NaCl solution, employing with a laser pulse energy of 2.5 mJ, repetition rate of 10 Hz, gate delay of 500 ns, gate width of 1000 ns, and 1000 accumulations, allowed to achieve detection limits as low as 40 and 92 µg L^{-1}, respectively.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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Supplemental Material

The supplemental material mentioned in the text, consisting of three figures, is available in the online version of the journal.

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