

# Rapid and Reliable Detection of Lithium in Water Sources Using Surface Enhanced Laser Induced Breakdown Spectroscopy (SENLIBS) on Aluminium Substrate

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**Abstract**—Lithium is one of the most important materials in re-chargeable battery as well as pharmaceutical and automotive industry. Due to the increasing demand for lithium for industrial production and daily usage, the reliable detection and recovery of lithium, a non-renewable metal, from water resources is an essential requirement. In this work, we performed lithium detection using surface enhanced laser induced breakdown spectroscopy on aluminium (Al) substrate for three different matrices, sea, river and municipal water. We also examined the matrix effect on sensitivity of lithium detection. Lithium spiked samples in different concentration (0-100 ppm) was dried on an Al surface. The specific emission line of Li 670 nm was used for quantitative analysis. The intensity of Li was obtained about 15 times on Al substrate better than microscope glass. The limit of detection (LOD) value achieved to 0.138 ppm. No significant matrix effect was observed in the different water sources. Good reliability was obtained for intra and inter-day precision methods with RSD is <3.7% and <7.3% respectively in all water samples. Total analysis time including sample preparation is approximately in 1 min. We demonstrated that SENLIBS method provides rapid, high accuracy and repeatability of sensitive Li detection in different water sources.

**Index Terms**—Aluminium, lithium, SENLIBS, sensor, water sources

## I. INTRODUCTION

Lithium (Li) is an alkaline metal which has great importance due to its wide range of industrial usage (pharmaceutical, portable electronic devices, automobile, batteries) [1–3]. The important applications of Li can be listed as tracer and groundwater and geothermal research, gas exploration, microbiological and geoscientific studies [4–12]. Nevertheless, Li is considered as one of the 31 rare metal elements. Because of its wide range of use and difficulty in its production from brine, a shortage of Li might be faced in commodity market [13]. Therefore, different sources of Li have been studied in the literature. Sea water is considered as a promising resource due to its rich Li reserve which is much higher than minerals and brine [14]. Lithium concentration in different water sources were described in the literature [13]. It is a well-known fact that concentration of elements in sea water can vary widely between locations depending on geographical location and climate conditions.

Manuscript received September 30, 2022; revised October 14, 2022; accepted December 14, 2022.

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Conventional methods for lithium enrichment contain certain processes which are solar evaporation, adsorption and co-precipitation of metal cations. These were very significant procedures; however, it takes a lot of time, money and effort. Therefore, it is important to decide Li level in the water source before the process. In addition, lithium plays an important role in the treatment of bipolar disorder, a mental disorder that causes unusual changes in mood, concentration, and ability to perform daily tasks [15, 16] It has been reported how lithium is associated with a reduced risk of suicide and death in people with mood disorders [17, 18] To prevent suicides, the proposal of keeping the Li concentration at a certain level in the public water sources and/or addition it to the waters was discussed by Barros *et al.* [19]. For all these reasons, it is crucial to evaluate Li amount with a rapid and high accuracy method in a water source.

Laser-induced breakdown spectroscopy (LIBS) has become one of the popular techniques for assessment of liquid quality/control due to its important advantages such as multi-elemental, in situ, rapid and real-time analysis measurement capacity in any environment on any material type (solid, liquid, gas, aerosols) [20, 21]. Another advantage of LIBS with respect to other conventional analytical measurements is the direct determination of some elements with minimal sample preparation. In the case of liquid analysis, in particular, complex sample digestion is not necessary [22]. Direct LIBS analysis of liquids has several disadvantages such as quenching of intensity, surface ripples, splashing and shorter plasma duration, which adversely affects the signal quality, measurement repeatability and sensitivity [23]. Recently, many studies have been reported in the literature for successful application of LIBS for liquids. The techniques can be listed as double-pulse LIBS (DP-LIBS) for bulk samples, use of liquid flow, jet flow, droplets, and transformation of the liquid sample to solid, liquid samples in the form of static surfaces, liquids substrates and aerosols [24–33], [34–36]. Surface-enhanced LIBS (SENLIBS) is also one of the important methods used in liquid analyses. In many SENLIBS applications, a small volume of liquid is dropped on a solid surface such as metals and then dried. The results obtained from SENLIBS applications are promising compared to direct drop analysis. In SENLIBS, solid substrate plays a host role and doesn't absorb the analyte. Results of the SENLIBS in previous applications showed that a dried liquid on a solid substrate provides a better limit of detection (LOD) value and sensitivity than direct drop analysis with LIBS [37–40]. Since SENLIBS is a relatively new method, there are only a limited number of studies in the literature. Until quite recently, the common approach was to implement SENLIBS method to detect the analyte and to search the physics behind. To the best of our knowledge,

validation performance of the SENLIBS at inter/intra-day studies hasn't been reported.

The aim of this work is to investigate accurate measurement of the Li content in different water sources to determine the composition by using SENLIBS and to evaluate the repeatability performance of the method. In this work, municipal water ( $n=1$ ), river ( $n=2$ ) and sea ( $n=3$ ) samples were dropped on the surface of the aluminum substrate and then dried before analysis. Quantitative measurement was performed according to the LIBS spectra. The obtained spectra were evaluated based on peak intensity. For validation, inter-day and intra-day measurements were carried out to detect the repeatability and reproducibility.

## II. MATERIALS AND METHODS

### A. Materials

Lithium chloride (LiCl), was obtained from Merck. 1050 series commercial aluminium (99.5% Al) sheet was purchased from Ankara Aluminium Metal AS (Ankara Turkey).

### B. Sample Preparation

Lithium solutions with different concentration were prepared from Lithium perchlorate (Merck KGaA, Darmstadt, Germany). Lithium sample solutions were prepared in three different matrices; which were municipal water ( $n=1$ ), river ( $n=2$ ) and sea ( $n=3$ ) samples. Calibration sample group was prepared by using municipal water which contains spiked Li in range of 0-100 ppm. Validation sample group were prepared by using river and sea samples which contain spiked Li in the range of 0-100 ppm. For LIBS experiment, 2  $\mu$ L of sample solution was deposited on microscope glass and aluminum (Al) substrate which has 2 cm width and 10 cm length. To obtain better sensitivity, micro-droplets were left to dry for 10 min in drying oven.

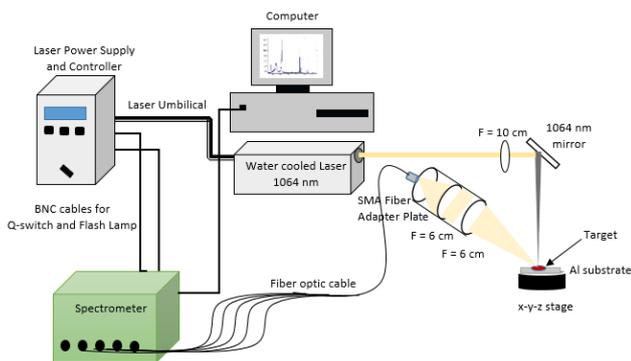


Fig. 1. Experimental setup of the LIBS system.

### C. LIBS Instruments and Operating Conditions

The setup of LIBS measurement was shown in Fig. 1. Q-switched Nd:YAG laser (Litron Nano SG, Litron Lasers, Warwickshire, UK) with a wavelength of 1064 nm and a repetition rate of 8 Hz was used to ablate the sample. The ablation took place in the air. Five channel LIBS spectrometer (Aurora, Applied Spectra, Fremont, CA), which records the spectrum between 186-888 nm was used. Laser pulses passed through plano convex focusing lens with a focal distance (FL)

of 10 cm and were directed onto the sample surface. Plasma optical emission was collected with a cage system composed of a pair of lenses with FL= 6 cm and fiber optic cable. The laser was operated at 13 mJ/pulse, while the spectrometer was operated at 1.05 ms integration time and 650 ns gate delay. Each concentration was scanned at five different regions and analyzed in duplicate.

### D. Data Analysis

LIBS spectra were associated with Li content by using univariate data analysis techniques. In the univariate method, peak intensities of Li element at 670 nm were correlated with known concentrations to obtain the calibration curve. The aluminum emission line (Al I 396.15 nm) from the substrate was used as an internal standard. This Al standard was internal for the plasma that doesn't pre-exist in the micro-droplet itself. In this study, the presented signal value is the average of five different measurements obtained from the same drop and two replicate measurements obtained from the same concentration.

In order to evaluate the measurement sensitivity and precision, LOD, LOQ, RSD and bias values of PLS method were calculated using the following Eqs (1)–(4) [41].

$$LOD = 3.3 \times \frac{S.D.}{S} \quad (1)$$

$$LOQ = 10 \times \frac{S.D.}{S} \quad (2)$$

LOD = limit of detection

S.D. = standard deviation of the predicted lithium content

S = slope of the calibration curve

$$RSD(\%) = \frac{100}{N_{conc}} \sum_{k=1}^{N_{conc}} \frac{\sigma_{C_k}}{C_k} \quad \text{with } \sigma_{C_k}^2 = \sum_{i=1}^p \frac{(\hat{c}_{ik} - c_k)^2}{p-1} \quad (3)$$

$N_{conc}$  = number of different concentrations in the validation set

$p$  = number of spectra per concentration

$\sigma$  = standard deviation

$$Bias(\%) = \frac{(Mean\ concentration - Real\ concentration)}{Real\ concentration} \times 100 \quad (4)$$

## III. RESULTS AND DISCUSSION

### A. Evaluation of LIBS Spectra

In this study, detection of lithium using surface enhanced laser induced breakdown spectroscopy on aluminium substrate for three different matrices, sea, river and municipal water was investigated. The laser beam was focused on the sample surface to obtain the LIBS spectra of the micro-volumes of samples. To determine enhancement factor, the LIBS measurements were performed both aluminium substrate and microscope glass. In analysis of micro-droplet, the main aim was to determine the spectral peak and intensity of the lithium element. The results obtained from early studies show that the spectral lines of lithium are observed at 670 nm [42]. In this study, the intensity of the Li was attributed to the concentration to Li element. Fig. 2(a) demonstrates the full LIBS spectra of the municipal water ( $n=1$ ), river ( $n=2$ ), and sea ( $n=3$ ) samples. Also, the increase in intensity due to the increase in lithium concentrations at

670 nm can be seen in Fig. 2 (b, c, d, e, f, g). It should be noted that the term surface-enhanced was selected in this study to explain the effect of the metallic surface as in the paper reported by Aguirre *et al.* [38]. This paper describes that the metallic substrate creates a hot and dense plasma on the substrate surface which absorb the droplet which enhances the LIBS signal. As a result, atoms in the droplet reach the thermal equilibrium of the plasma within a short period of time. It is a well-known fact that direct analysis of the droplet is not able to reach such a high electron density and temperature, which is the main reason of the lower intensity of the analyte. The term “enhanced” is not used to describe the signal enhancement caused by the interaction with the surface plasmons. Additionally, there are some other studies in the literature which describes this effect as SENLIBS [37–40], [43]. In this context, we showed that the Li density on the aluminum substrate is approximately 15 times higher by comparing with microscope glass for both two concentrations (50 and 100 ppm) of Li as seen graphs in Fig. 3.

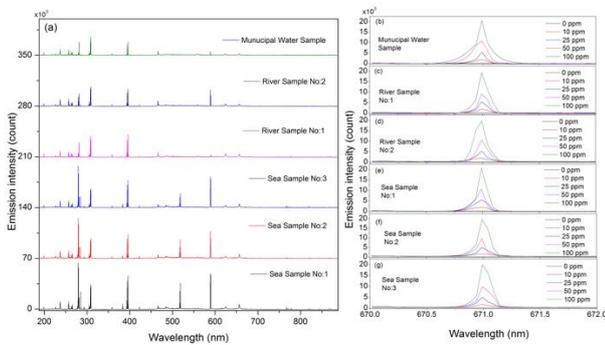


Fig. 2. Full spectrum of the different water sources (a) and increase in the lithium emission of the municipal water (b), river sample no:1 (c), river sample no:2 (d), sea sample no:1 (e), sea sample no:2 (f), sea sample no:3 (g).

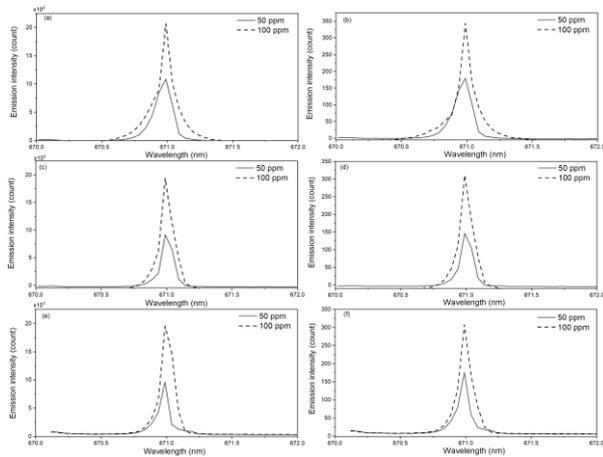


Fig. 3. The lithium emission line at 670 nm for two concentrations of Li.

### B. Calibration Study and Method Validation on Aluminum Substrate

The quantification study is conducted by generating a calibration curve based on a set of samples that contain different known concentration(s) of analyte. In order to study quantitative SENLIBS analysis of Li and to determine analytical performance, calibration curves were created. In quantitative SENLIBS analysis, the spectral intensity of any

Li emission line obtained from LIBS spectra of all samples increases as the Li concentration increases, which is the evidence of the linearity between LIBS emission intensity of Li and its concentration.

Calibration curve of the SENLIBS analysis was shown in the Fig. 4. The presented signal in the calibration curve was an average of the two replicate measurements each of which were obtained from averaging five different shots from five different locations of the same droplet. As can be seen in Fig. 4, calibration curve showed a good linear fit ( $R^2=0.998$ ). A good linear relationship was obtained between Li-spiked water samples and SENLIBS intensity. For validation study, prediction ability of the calibration equation was tested for river and sea samples, and the results were presented in Table I.

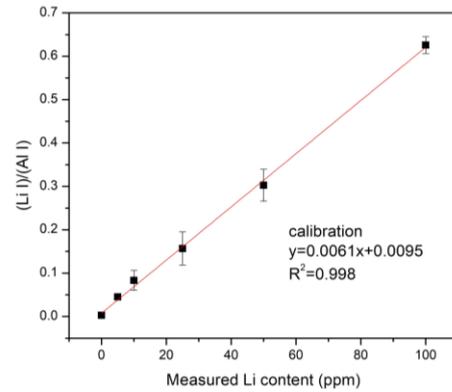


Fig. 4. Calibration of the lithium emission line at 670 nm.

TABLE I: RESULTS OBTAINED FROM VALIDATION STUDY

Sample Name	Spiked concentrations (%)	Average predicted concentrations (%)	Standard deviation (%)
River	0	0.02	0.003
	5	3.14	1.45
	10	7.60	1.59
	20	17.39	3.32
	25	22.46	2.91
	50	52.70	1.44
	75	76.05	0.17
Sea	100	96.83	3.41
	0	0.01	0.01
	5	5.35	0.96
	10	12.32	2.11
	20	18.50	3.41
	25	22.61	3.98
	50	48.27	1.74
	75	78.17	4.38
	100	102.59	3.77

For lithium analysis, LOD and LOQ values were calculated as 0.138 ppm and 0.459 ppm, respectively. These values indicate that SENLIBS is a reliable and sensitive method for Li analysis in water samples and has good prediction ability. The accuracy and precision of the method were calculated for municipal water spiked with 10 ppm and 50 ppm lithium. Precision was shown as RSD, and accuracy was explained by calculating the bias value. Accuracy and precision are the

closeness of the independent results of the true value and method respectively. The results from accuracy and precision measurements are shown in Table II. Based on the overall results, it can be said that the method had good reproducibility, repeatability and accuracy for lithium detection in different water samples. In the literature, complexity, homogeneity,

composition surface condition, and particle size of the sample as well as the reproducibility of the laser shots are reported to be the major parameters affecting RSD values. Typical RSD values for SENLIBS are in the range of 1-10%, and the calculated RSD value in the present study was in this range [44].

TABLE II: DESCRIPTIVE STATICS OF THE LIBS MEASUREMENT

Analyses	Measurements	Spiked concentrations (ppm)	Amount found (ppm)	Average Band area (a.u.)	Precision as RSD (%)	Accuracy (bias)%	RSD (%)
Intra-day	Day 1	10	9.22±0.24	7545	2.6	-7.8	3.66
	Day 1	10	10.68±0.47	7733	4.4	6.8	
	Day 1	10	11.40±0.42	7818	4.6	14	
	Day 1	10	10.82±0.41	7795	3.8	8.2	
	Day 1	50	50.24±1.21	34945	2.4	0.48	2.85
	Day 1	50	50.55±1.36	35182	2.7	1.1	
	Day 1	50	49.79±1.54	33394	3.1	-0.42	
	Day 1	50	50.06±1.60	34014	3.2	0.12	
Inter-day	Day 1	10	9.96±0.58	7589	5.8	-0.4	5.98
	Day 2	10	10.48±0.62	7625	5.9	4.8	
	Day 3	10	9.67±0.42	7558	4.3	-3.3	
	Day 1	50	50.27±3.07	34984	6.1	0.54	7.25
	Day 2	50	49.82±4.35	33456	8.7	-0.36	
	Day 3	50	50.60±3.51	35428	6.9	1.2	

Lithium concentration in the different water sources were in the range of 0.1-1.2 ppm, which implies that SENLIBS can be used as a rapid analysis technique for Li detection of water matrix. It is also useful for detection of the drilling tracer in liquid matrix. And this method can also be applied to detect Li contamination in drinking water or surface water in the case of environmental pollution. Besides, validation performance of SENLIBS at inter/intra-day studies has been reported for the first time in the literature, which presents the analytical performance of SENLIBS. As seen in Table II, RSD is <3.7% and <7.3% respectively in all water samples obtained at inter/intra-day studies. The results are in good agreement with previous studies indicated that SENLIBS provides good reproducibility [31, 45].

One of the most critical points for the SENLIBS method is the selection of the appropriate metal substrate. The aluminum substrate used for this purpose is inert to both solvent and solute, reduces interference in the spectrum, and has good electrical and thermal conductivity. By utilizing this property of the aluminum substrate, the determination of lithium has been carried out successfully since it is possible to get rid of the disadvantages of fluctuation, absorption, sputtering and quenching effects in the analysis of liquid samples and to increase the signal.

#### IV. CONCLUSIONS

In the paper, a fast and quantitative measurement of lithium content was demonstrated in three different water sources such as municipal water, river water and sea water by using surface-enhanced laser induced breakdown spectroscopy. No significant matrix effect was observed in the different water sources. The good reproducibility for lithium ion spiked into the water resources has been obtained. In contrast to conventional methods, LIBS is a practical and rapid method

which requires minimum sample preparation and no aggressive chemicals. Besides, with this technique, the time and effort spend on the analysis was also reduced significantly. The method is a relatively rapid technique for lithium quantification in different water sources, and the obtained results have showed that the developed method has potential to be a used as an accurate analysis technique as well as a useful tool for quality control laboratories. The proposed aluminum can be a good candidate as LIBS substrate due to its ability to enhance the signal of the target analyte and its low cost.

#### CONFLICT OF INTEREST

The authors declare no conflict of interest.

#### AUTHOR CONTRIBUTIONS

Tugba Tezcan has done investigation, methodology, data curation, validation, visualization, writing—original draft preparation; Banu Sezer has done investigation, validation, visualization, writing—original draft preparation; Ugur Tamer has done investigation, resources, writing—review and editing; Ismail Hakki Boyaci has done investigation, methodology, supervision, writing—review and editing.

All authors have read and agreed to the published version of the manuscript.

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