Application of Laser-Induced Breakdown Spectroscopy to Monitor Fission Products in LiCl-KCl Eutectic

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ABSTRACT

In the Molten Salt Reactor (MSR), nuclear fuel dissolves directly into the coolant, thereby leading to an immediate release of fission products. Regular extraction of these fission products from the coolant is crucial to maintaining the reactor's performance efficiency, safety, and to facilitate more efficient waste storage and disposal procedures. Similarly, an accumulation of fission products within a molten salt bath during the electrorefining stage of pyroprocessing significantly impedes the efficiency of the separation process. Thus, it is necessary to remove these fission products at optimal intervals to preserve the integrity of the bath and reduce the generation of excessive nuclear waste. To manage these challenges effectively, real-time monitoring of the fission product concentrations in the molten salt is required. In this study, we have proposed the use of Laser-Induced Breakdown Spectroscopy (LIBS) to monitor and measure the concentrations of fission products such as strontium (Sr) and barium (Ba) in a LiCl-KCl eutectic at 823K. We obtained LIBS spectra from LiCl-KCl samples, which contained individual elements spanning a wide concentration range. Subsequently, we calculated the limits of detection and maximum detectable concentrations for Sr and Ba using highly accurate calibration curves. In addition to performing a univariate analysis, we also applied Partial Least Squares Regression (PLSR) to the data to establish superior calibration models for a more precise quantitative analysis. This was achieved by using the LIBS data measured when Sr and Ba were simultaneously dissolved in the molten salt. Consequently, we obtained low values for both Root Mean Square Error of Calibration (RMSEC) and Root Mean Square Error of Cross-Validation (RMSECV).

Introduction

In Molten Salt Reactors (MSRs), nuclear fuels are dissolved directly into the coolant, resulting in the release of fission products such as Sr and Ba into the coolant. This necessitates periodic replacement or purification of the coolant to maintain the reactor's operational efficiency and safety [1, 2]. Therefore, the development and deployment of real-time monitoring technology are critical to effectively manage the quality of the coolant. This would involve perpetually monitoring and analyzing the concentrations of Sr and Ba in the coolant to maintain its integrity, optimize reactor performance, and minimize associated risks.

Simultaneously, during the electrorefining stage of pyroprocessing, the presence of fission products in a LiCl-KCl eutectic molten salt presents significant challenges [3-6]. The accumulation of these products induces excessive heat generation and diminishes uranium capture, thereby impacting the efficiency of the separation process adversely. As a result, the timely and efficient removal of these fission products from the salt bath becomes crucial to enabling its reuse and mitigating additional nuclear waste production.

To address these challenges, we propose the application of Laser-Induced Breakdown Spectroscopy (LIBS) as an innovative solution. LIBS offers a promising technology for real-time monitoring, designed to effectively manage the quality of the coolant and ensure the efficient operation of MSRs. With its capability to perform in-situ measurements, LIBS allows for continuous monitoring and comprehensive analysis of concentrations of fission products in the coolant [7, 8]. This technology not only aids in maintaining coolant integrity and optimizing reactor performance but also plays a pivotal role in minimizing potential risks associated with the MSR operations. In addition, during the electrorefining process of pyroprocessing, LIBS can be instrumental in overcoming the challenges posed by the accumulation of fission products in a LiCl-KCl eutectic molten salt. By providing accurate and real-time data on fission product concentrations, LIBS facilitates timely and efficient removal of these elements from the salt bath. This directly contributes to enhancing the efficiency of the separation process, enabling salt bath reuse, and ultimately reducing additional nuclear waste production.

In this study, we aim to undertake a detailed investigation using Laser-Induced Breakdown Spectroscopy (LIBS) to quantitatively analyze strontium (Sr) and barium (Ba) that are dissolved in LiCl-KCl at a temperature of 823K.

Methods

In this experiment, a eutectic solution was prepared by mixing LiCl (99.9%) and KCl (99.9%), which was employed as the molten salt. The temperature of the molten salt was maintained at 823K. To set conditions similar to those in nuclear applications, $SrCl_2$ (99.999%) and $BaCl_2$ (99.999%) were dissolved in the molten salt. The LIBS measurement was conducted inside a glove box to maintain an oxygen concentration below 5 ppm and a moisture concentration below 2 ppm, thereby simulating the low-oxygen, low-humidity environment typical of MSR operations.

As depicted in Figure 1, the Laser-Induced Breakdown Spectroscopy (LIBS) system was installed both inside and outside the glove box. A Q-switched Nd:YAG (Q-smart 450, Quantel) laser located outside the glove box emitted a beam of 532 nm wavelength. The beam was directed into the glove box through a series of mirrors and lenses, finally entering through a quartz window at the rear of the glove box. The beam was then focused onto the surface of the molten salt by a lens with a focal length of 50 cm, generating a plasma. Light emanating from this plasma was collected and transmitted via an optical fiber to a spectrometer (Mechelle 5000, Andor) coupled with an intensified charge-coupled device camera (iStar 334T CCD, Andor), enabling a detailed analysis of the light.
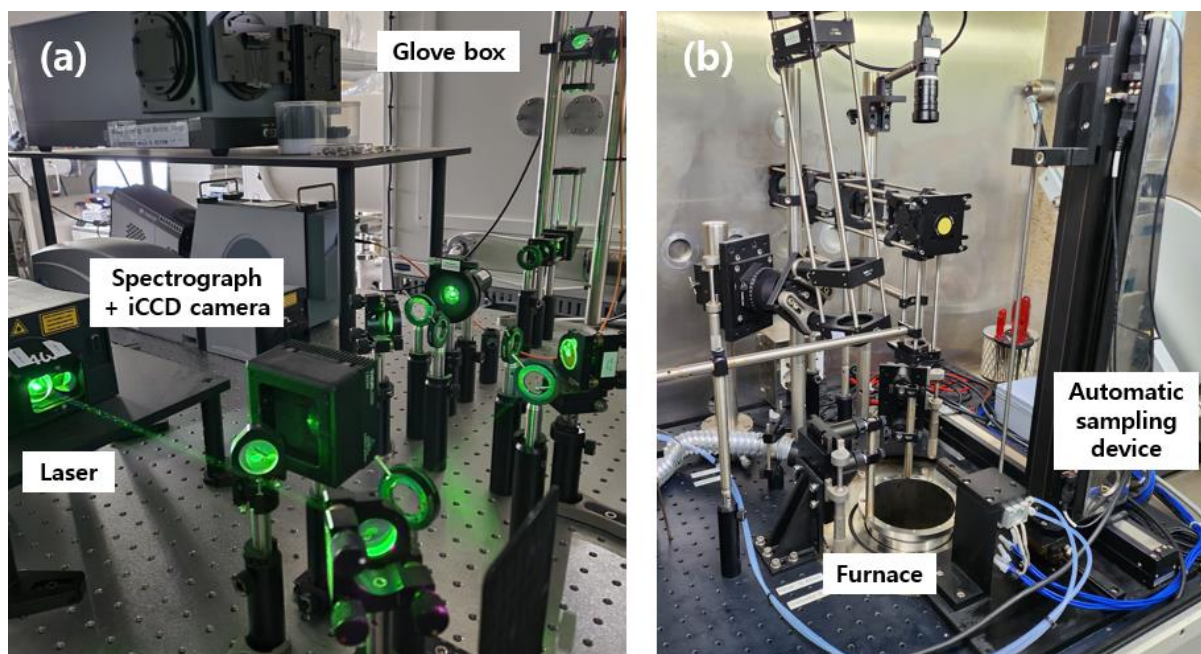
Fig 1. The LIBS system (a) outside and (b) inside the glove box.

To perform LIBS analysis, it is essential to select appropriate characteristic peaks of the target elements. These characteristic peaks should not overlap with each other, exhibit sufficient intensity, and should not induce significant self-absorption. Using the National Institute of Standards and Technology (NIST) database, the characteristic peaks selected for Sr were identified at 407.771 nm and 421.552 nm, while the characteristic peaks for Ba were identified at 455.403 nm and 493.408 nm.

The quality of LIBS data is influenced by several parameters, such as laser pulse energy, delay time, and gate width. These parameters were optimized for Sr and Ba by analyzing characteristic peaks in the LIBS data obtained when Sr and Ba were dissolved in the molten salt. The objective was to achieve the maximum Signal-to-Noise Ratio (SNR). As a result of this optimization, the laser pulse energy was set at 21.2 mJ, delay time was determined to be 1 μs, and the gate width was set at 1 μs. Through such meticulous parameter optimization, we were able to enhance the quality of the molten salt component analysis, ultimately improving the performance of the LIBS system in monitoring the concentrations of Sr and Ba in the molten salt in real-time.

Results and Discussions

The process started by deriving calibration curves, which were obtained through LIBS measurements of the dissolved elemental species. These curves were crucial for ascertaining both the maximum concentration and the limit of detection for Sr and Ba within the molten salt medium. Each data point in the calibration curve corresponded to the mean value of 15 spectra, ensuring statistical robustness by averaging out potential outliers and noise. Further enhancing the reliability of the results, each individual spectrum was acquired through a series of 30 shot accumulations. This meticulous accumulation process served to heighten the signal-to-noise ratio, thereby refining the precision of the measurement.

The data points derived from the calibration curves represented the relationship between characteristic peak intensity and concentration for each element. When subjected to a linear fitting algorithm, these points generated a regression line that had an R^2 value very close to 1. The strong correlation highlighted the reliable linearity of the relationship between peak intensity and concentration, which is crucial for ensuring the dependability of LIBS in elemental concentration measurements. For Sr, the maximum detectable concentration was determined to be 15,000 ppm, while for Ba, it could reach up to 35,000 ppm. This demonstrated the capability of LIBS to detect substantial concentrations of these elements, lending credence to its applicability in reactor conditions where high concentrations of fission products may be expected.
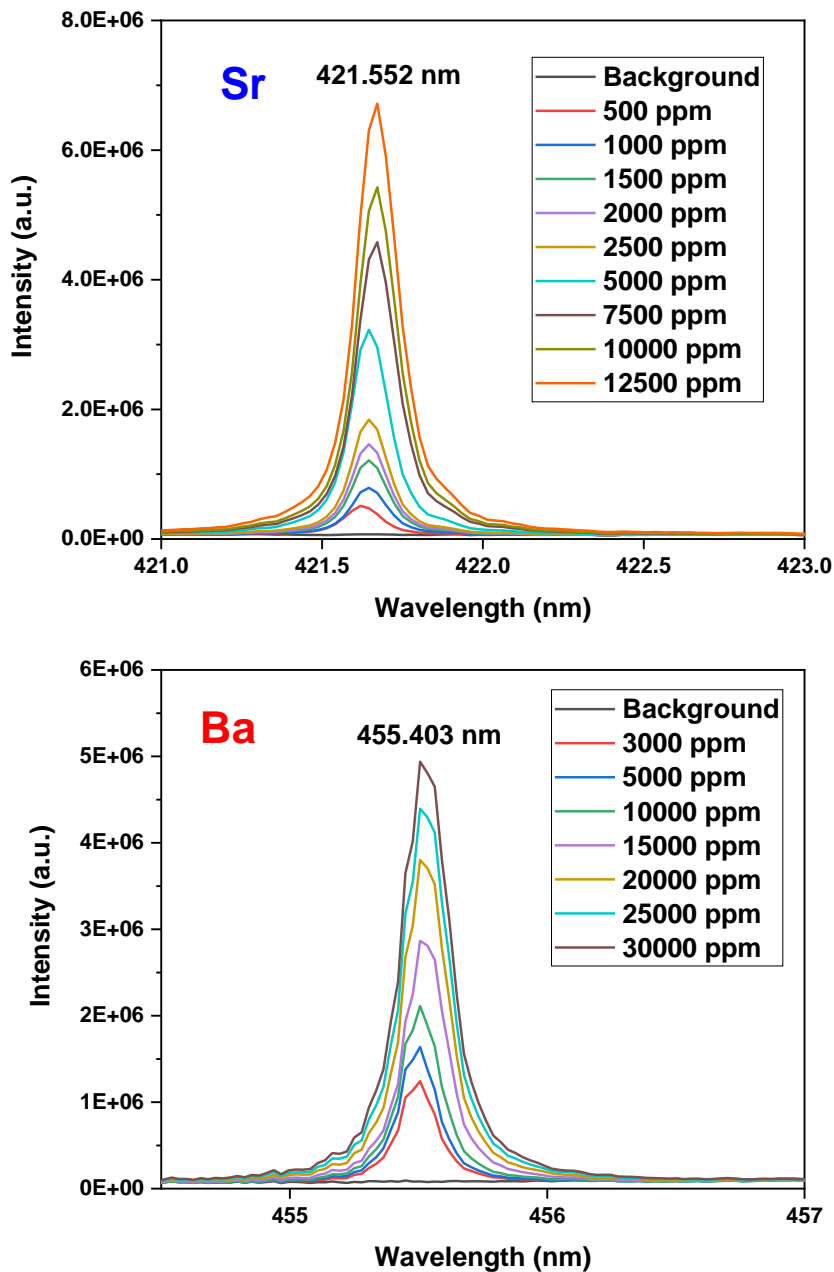

Fig 2. Comparison of characteristic peak intensities depending on the concentrations of Sr and Ba dissolved in LiCl-KCl eutectic.

Finally, the limit of detection (LOD) for Sr and Ba was calculated. This measurement is of paramount importance as it provides an indication of the minimum concentration of a substance that can be confidently distinguished from the background signal. By applying the equation below the LOD was computed.

$$Limit\ of\ detection\ (LOD) = \frac{3\sigma_B}{S}$$

σ_B: standard deviation of the background, S: slope of the calibration curve

For Sr, the LODs were found to be 46.55 ppm and 19.23 ppm, while for Ba, they were ascertained to be 80.02 ppm and 52.41 ppm. These LODs confirm that LIBS can facilitate the detection of relatively low concentrations of these elements, further enhancing its potential for real-time monitoring and quantitative analysis in MSRs and electrorefining of pyroprocessing.
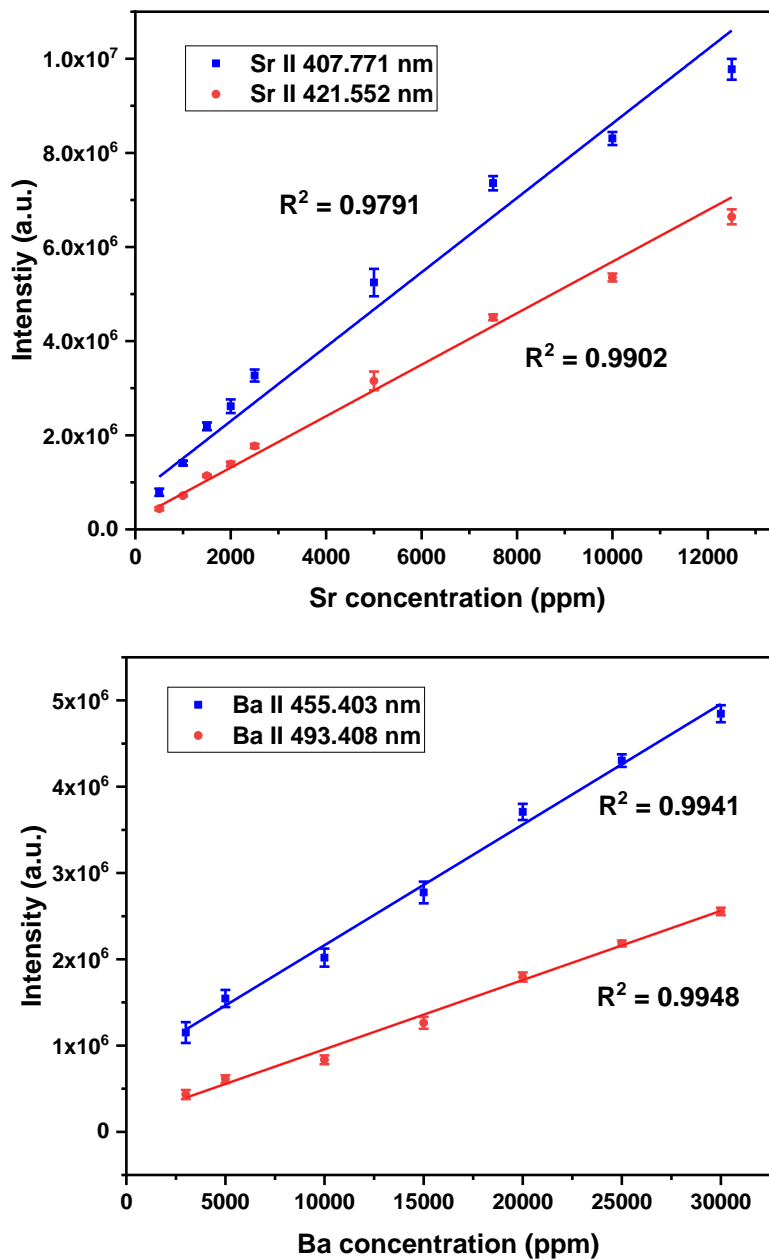

Fig 3. Calibration curves of Sr and Ba for the calculation of LOD.

Transitioning from the analysis of single-element measurements, the research now embarks upon the examination of multi-element measurements, leveraging the technique of Partial Least Square Regression (PLSR) applied to Laser-Induced Breakdown Spectroscopy (LIBS) spectra. This technique was employed to develop more comprehensive calibration models contingent on the concentration of each targeted element. A systematic evaluation was conducted to ascertain the accuracy and reliability of the constructed calibration models. Essential to this process was the computation of multiple key indicators, namely the R^2 values of both the calibration and prediction lines, as well as the Root Mean Square Error of Calibration (RMSEC) and the Root Mean Square Error of Cross-Validation (RMSECV) for each element.

In a practical application of the model, for each sample, four spectra were randomly chosen from a total of fifteen spectra obtained. This selection served as the empirical base for the exercise. Three of these spectra were utilized as training sets to calibrate the model, and the remaining spectrum was then used as an unknown sample to test the validity and predictive power of the model.

When examining Sr, the R^2 value of the calibration line was recorded at an impressive 0.975, and that of the prediction line was nearly as high at 0.951. Furthermore, the RMSEC and RMSECV values were computed to be 262.50 ppm and 368.31 ppm, respectively. For the case of Ba, the results were even more promising. The R^2 value of the calibration line was close to the ideal at 0.986, and that of the prediction line was 0.983. The RMSEC and RMSECV values for Ba were slightly lower than for Sr, at 195.57 ppm and 247.38 ppm respectively.

Upon inspection of these results, the close proximity of the R^2 values to the ideal score of 1 signifies an excellent level of prediction accuracy. Additionally, the relatively low RMSEC and RMSECV values in relation to the range of measured concentration highlight the high precision of the model. The parallelism between the RMSEC and RMSECV values also suggests a well-generalized model that is capable of accurately predicting new, unseen data. Thus, the combined implications of these results clearly illustrate the robustness and reliability of the calibration models developed via PLSR, further establishing the feasibility of utilizing the LIBS technique for accurate multi-element analysis in molten LiCl-KCl.
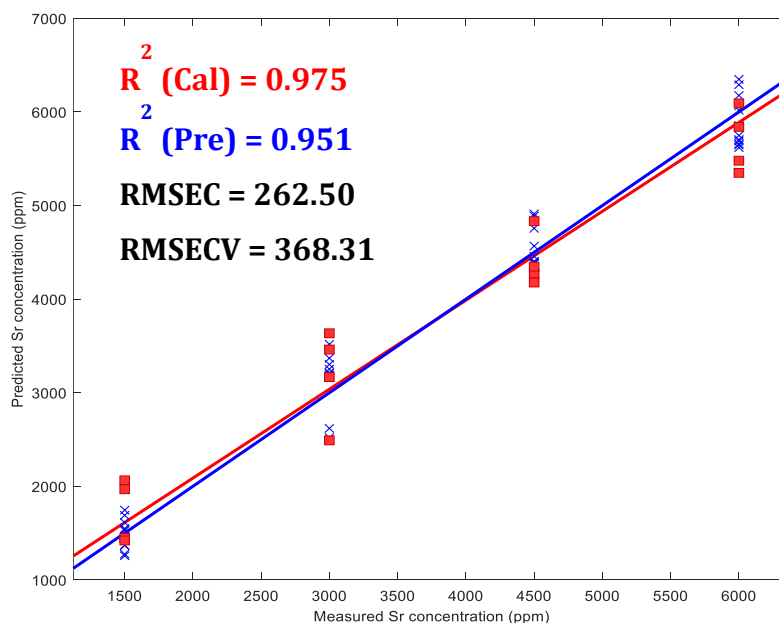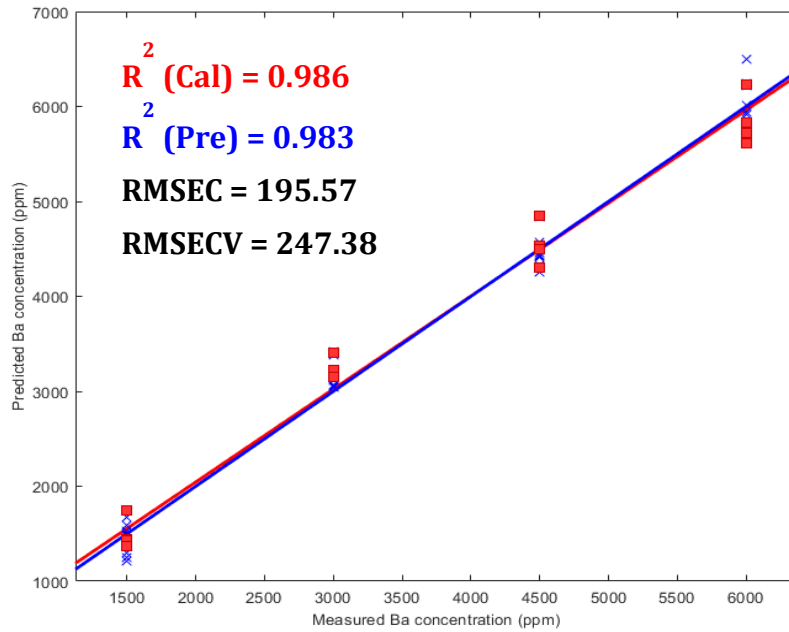
Fig 4. Linear fitting results of the PLSR model using LIBS spectrum depending on Sr and Ba concentrations.

Conclusions

In this study, we employed LIBS to quantitatively measure the concentrations of Sr and Ba, both individually and simultaneously, dissolved in a high-temperature LiCl-KCl eutectic. This comprehensive assessment was undertaken with an objective to harness the potential of LIBS in tracking and monitoring nuclear applications, such as the coolant of MSR or the molten salt bath in pyroprocessing, which demand precise evaluations.

Our findings indicate that in the case of single element measurements, Sr in a concentration range of approximately 20 to 15,000 ppm and Ba in a concentration range of roughly 50 to 35,000 ppm could be measured with minimal error. The efficiency of these measurements within the specified concentration range underscores the applicability of LIBS in various nuclear settings, thereby broadening its scope of usage. Furthermore, we extended our investigation to multi-element measurements, wherein we developed a reliable calibration model for the concentrations of Sr and Ba. This model, predicated on the implementation of Partial Least Square Regression (PLSR), showed a substantial degree of accuracy. This highlights the proficiency of LIBS in enabling the quantitative measurement of each element even in situations where fission products are simultaneously dissolved in the molten salt.

In summary, the results of this investigation authenticate the feasibility of LIBS as a robust monitoring technology for nuclear fission products in molten salts. The outcomes of our study mark a significant step forward in the domain of nuclear monitoring, underlining the potency of LIBS to operate under complex multi-element conditions. We are encouraged by our findings and are in the process of developing a fiber-optic LIBS methodology that is aimed at further refining the system for remote measurements in real-world applications. Our endeavor represents a critical advancement in nuclear safety and monitoring, positioning LIBS as an effective tool for future nuclear applications.

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