



LASER-INDUCED BREAKDOWN SPECTROSCOPY - MULTIVARIATE METHODS FOR ANALYSIS OF ENVIRONMENTAL REFERENCE MATERIALS

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Abstract

The use of laser-induced plasma emission analysis provides a unique way to measure major and minor elements in various types of samples under optimal conditions. To accurately quantify multiple components in complex matrices, chemometric techniques are highly reliable and effective tools. To examine the feasibility of laser-induced breakdown spectroscopy (LIBS) in combination with multivariate analysis, researchers investigated the analysis of environmental reference materials (RMs). In this study, LIBS was used to analyze different types of soil and plant-based reference materials, and the presence of Al, Ca, Mg, Fe, K, Mn, and Si were detected in their LIBS spectra. To quantitatively analyze the constituent elements using the LIBS spectral data, multivariate statistical methods such as Partial Least Square Regression and Partial Least Square Discriminant Analysis were employed. To verify the accuracy of models, calibration models were employed to forecast the concentrations of various elements in test samples. The projected concentrations were compared to certified concentrations to ensure the reliability of the models. Additionally, Instrumental Neutron Activation Analysis (INAA), a non-destructive analytical technique that utilizes high flux reactor neutrons and high-resolution gamma-ray spectrometry, was used to compare the results of two reference materials through Laser-Induced Breakdown Spectroscopy (LIBS).

Introduction

Validation of an analytical method is crucial and can be achieved by analyzing certified/standard reference materials (CRMs/SRMs). The use of CRMs can evaluate the accuracy of the technique and methodology, thus increasing confidence when analyzing

unknown samples. However, accessing CRMs for various matrices in different labs can be challenging. Therefore, it is important to use suitable methodologies to evaluate the accuracy of analytical methods. The detection of essential elements in various materials is vital in several scenarios, and analytical techniques such as ICP-AES, ICP-MS, XRF, INAA, etc. have been extensively researched for compositional analysis. The analytical methods available are highly effective, but many of them involve destroying a significant amount of the sample. Additionally, preparing samples for analysis can be a time-consuming process. Non-destructive nuclear techniques like INAA and IBA have the ability to determine multiple elements, but they require specialized equipment such as a high flux research reactor for INAA and a tandem particle accelerator for IBA, which are not readily available for routine material analysis.

The process of laser-induced breakdown spectroscopy (LIBS) involves emission spectroscopy and is used to analyze multiple elements at once. LIBS has several benefits over traditional techniques, such as not requiring pretreatment and being minimally invasive. This approach has a straightforward and compact experimental setup that avoids the need for sample preparation. Additionally, it is relatively non-destructive and can provide in-situ analysis remotely in harsh environments or inaccessible targets with appropriate experimental arrangements.

This technique employs a strong laser beam to focus on the surface of a sample, leading to the creation of a plasma plume that disintegrates all molecules and tiny particles within the energetic micro plasma. The plasma emission resulting from this process can be used to measure the concentration of elements present on the sample surface, providing a comprehensive elemental analysis of the material. To assess the accuracy of the technique, it's crucial to examine appropriate certified reference materials with similar matrices. For quantitative analysis, standards similar to the matrix of the unknown sample must be prepared, and a calibration curve for various elements obtained.

The spectra obtained from LIBS are typically intricate and provide a considerable amount of information. These spectra consist of numerous data points that can be gathered in under one second. In the case of complicated spectra such as those from soil and plants, it is not always feasible to analyze the results of every emission line for a given element within such a chemically complex matrix. Therefore, an effective method is required to address these difficulties and avoid the loss of valuable spectral information. Multivariate analysis (MVA) is a reliable analytical tool that considers all possible variables, removes redundant and correlated variables, and makes full use of the LIBS spectral information. Many research

studies have utilized MVA on LIBS to extract extensive spectral information from the sample's elemental composition. Multivariate techniques such as partial least square regression (PLSR) and partial least square discriminant analysis (PLSDA) are helpful methods for compensating data points for various deviations. The study discusses the use of various statistical analytical methods in conjunction with Laser-Induced Breakdown Spectroscopy (LIBS) to develop calibration models for predicting the concentrations of different elements in unknown samples. The advancements in these analytical methods have made LIBS a promising tool for both qualitative and quantitative analysis of various elements in a wide range of samples. The study involved obtaining LIBS spectra of environmental samples such as plant and soil reference materials (RMs), followed by chemometric analysis using Partial Least Squares Regression (PLSR) and Partial Least Squares Discriminant Analysis (PLSDA). The results were then compared with those obtained through Instrumental Neutron Activation Analysis (INAA) using the Dhruva Research reactor's higher neutron flux irradiation position for IAEA RM SL-1 and NIST SRM 1632a. The predicted concentrations for test samples using these methods were then compared with their certified values.

Material and Methods

Experimental Setup

The LIBS spectra were obtained by creating pellets of each sample and RM using a hydraulic press machine. To make the pellets, a gram of each sample was placed in a pellet die that was 20 mm in diameter and 3 mm high. The samples were then compressed using 6 tons of pressure for one minute. The experimental setup used to obtain the LIBS spectra is illustrated in Figure 1. A pulsed laser source Nd: YAG with a frequency doubled Q switch was used, which had a pulse width FWHM of 4 ns, a variable repetition rate of 1e10 Hz, and a maximum laser energy delivery of 425 mJ per pulse. The laser was focused on the sample's surface with a converging lens (f 15 cm) using a 532 nm laser beam. The pulse repetition rate and laser pulse energy were optimized, and the best signal to background ratio was obtained at an energy of 20 mJ and a repetition rate of 4 Hz. The laser beam's focal spot, calculated using $[D \ 4f/pd]$, where l is the wavelength, f is the focal length of the lens, and d is the aperture, is about 11 mm for a laser beam of diameter 9 mm. The laser beam's power density, or fluence, is $5.24 \times 10^{12} \text{ Wcm}^{-2}$ for a laser pulse with an energy of 20 mJ and a pulse width of 4 ns. The plasma emission was collected by a lens (diameter 5 mm, f-number is $f/2$) attached to the optical fiber bundle's tip and positioned to collect the emission signal at an

angle of about 45 degrees with respect to the laser beam. At the entrance slit of the CzernyeTurner spectrometer (Ocean Optics LIBS 2000 with a fixed gate delay of 1.5 ms), the opposite end of the optical fiber was situated. The spectrometer is made up of four modules, with the first three modules covering the spectral range of 200 nm to 510 nm and providing high resolution with a spectral resolution of 0.1 nm (FWHM). The fourth module, which covers the spectral range of 200 nm to 900 nm, has a lower resolution of 0.75 nm (FWHM). A gated charge coupled device (CCD) with 14,336 pixels was used as a detector to capture the spectra.

The experimental conditions were fine-tuned and used for analyzing all the samples in the study. This paper describes the analysis of a total of five environmental samples, which included three soil samples and two plant samples. To improve the signal quality, an average of 20 laser shots was taken for each sample. In order to account for variations in laser shots and sample heterogeneity, seven spectra were recorded for each sample to minimize statistical errors. Finally, the OOI LIBS 2000 software was used to analyze the resulting spectra.

The process involved irradiating powder samples (known as RMs) in polythene pouches, along with a reference standard of approximately 10 mg, for 1 minute using the Pneumatic Carrier Facility (PCF) at the Dhruva reactor located in BARC, Trombay, Mumbai. This irradiation was conducted to detect the presence of Al, Ca, K, and Mn in the samples. In addition, a separate set of samples weighing 100 mg each, along with reference standards, were irradiated for 1 day in the tray rod facility of the Dhruva reactor to determine the concentration of Fe. Following irradiation, gamma activity of the samples was assessed using a 30% relative efficiency HPGe detector. Peak areas were calculated using the PHAST peak fit software, and the concentration was determined using the standard relative method.

Statistical Treatment

The spectral emission lines corresponding to various wavelengths of different samples were collected and arranged in the form of a matrix for statistical comparison using LIBS. The software used for multivariate analysis of this data was Unscrambler-X by CAMO software India Pvt. Ltd. Two types of samples, plants, and soils, were studied separately resulting in two matrices, one containing data for plants (14 5855) and the other for soil samples (21 5855). Multivariate techniques such as PLS-DA and PLS-R were employed to analyze both matrices using the principle of partial least square (PLS) which is often used for analyzing large data. To improve the accuracy of a calibration model and avoid overfitting, spectral

information can be effectively utilized through the use of Partial Least Squares (PLS). PLS models a linear relationship between input and output variables, but it only considers the mathematical correlation in the data, ignoring any physical principles. PLSR, on the other hand, is a data decomposition method that creates latent variables or factors through a mathematical procedure. These factors reduce the number of correlated independent variables into a smaller set of uncorrelated independent variables. PLSR can uncover unknown trends and interpret interrelationships among different variables. The PLSR technique establishes a linear relationship between the independent variables and dependent variables, which is particularly effective when the independent variables are correlated. This simplifies the interpretation of the connection between the two variables. The PLSR model's performance is assessed using a set of unidentified samples, by constructing a PLSDA model based on the PLSR calibration model. This method allows prediction of unknown sample classes and determines optimal variance between each class. The PLSDA model's effectiveness is compared using validation test sets. The primary objective of this study is to build sturdy calibration models that relate to the concentration of diverse elements in different samples, and use the models to predict unknown sample element concentrations. Using MVA in extracting and analyzing LIBS spectral information will enhance the quantitative analytical capability of LIBS and make it more viable.

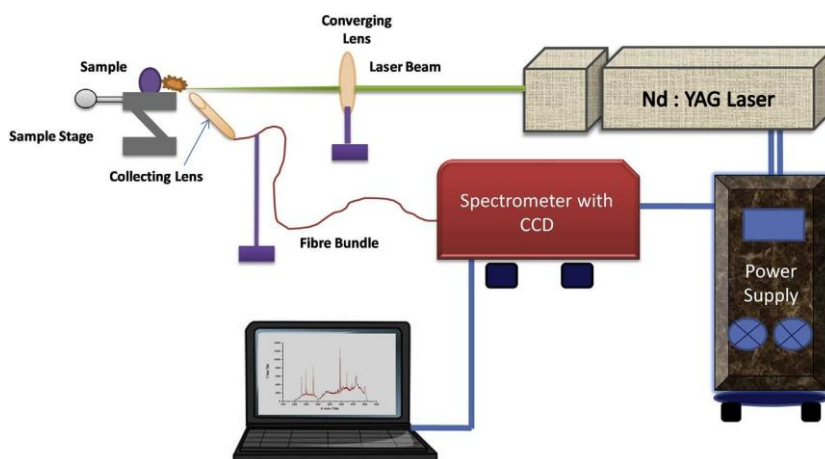


Fig. 1. Schematic diagram of LIBS experimental setup.

Results and Discussion

Table 1 provides information about the samples that were examined using LIBS for multivariate analysis. Fig. 2 displays the typical LIBS spectrum of a cabbage leaf CRM, which was collected in the spectral range of 200 nm to 500 nm. The spectrum clearly indicates the presence of significant lines of various elements such as Mg, Ca, Fe, K, Al, Si, and others.

The LIBS spectra of all other standard RMs that were analyzed also showed the presence of spectral lines of Mg, Ca, Fe, K, Al, Mn, and other elements. The wavelengths of different atomic and ionic species present in the spectra were determined using the atomic spectroscopy database of NIST and chemical spectroscopy by WR Brode. The certified values of element concentrations for plant and soil RMs are presented in Table 2 and Table 3, respectively.

In this study, PLSR is utilized to create a calibration model for RMs. The PLSR model is represented by plots that compare predicted values to reference values. To develop calibration models for different elements with varying concentrations, specific wavelength regions are chosen that contain the majority of the emission lines of the corresponding elements for each sample. Figure 3 (a) and (b) display typical PLSR calibration models of Al for plant and soil samples, respectively. Calibration models using PLSR are generated for all other elements as well. To evaluate the model's performance, the coefficient of determination (R^2) and root mean square error (RMSE) are used. The R^2 values are found to be nearly 1, while the RMSE is close to 0, indicating a strong correlation between the predicted and reference values. Ideally, the predicted values should match the reference values. As the slopes tend toward 1, this model can be considered good enough for conducting regression. We collected 14 spectra for two plant samples, with 7 spectra per sample. To develop a PLSR model, 10 of the spectra were chosen as the training set, while the remaining 4 were set aside as the test set. We also collected 21 spectra for three soil samples, with 7 spectra per sample. Of these, 15 were selected as the known training set, while the other 6 were used as the unknown test set. To validate the PLS model, a cross-validation strategy was employed, and the test sets were used to identify the model's strengths and weaknesses. Tables 2 and 3 were used to construct the PLSR model, using concentrations of various elements. The calibration (blue) and validation (red) best-fit lines were close together, indicating a high R^2 value and reliable model. The model's root-mean-square error of calibration and prediction (RMSEC&P) was nearly 0 for all elements in both matrices. It is not trustworthy if there are significant differences between Cal and Val. The PLSR calibration model is evaluated using RMSEC, and the resulting calibration models are used to predict test sets. To assess the prediction capabilities of the PLSR calibration models, RMSEP is used. If the matrix of measured samples does not deviate significantly from that of the calibration sample set, the accuracy of the determination can be evaluated based on predictions from a PLS model. The proposed PLSR model is more accurate and reliable for all samples, as indicated by the low RMSE and high R^2 values, demonstrating its overall robustness (see Fig. 3(a) and (b)). This

method can compensate for matrix effects and overcome the limitations of conventional internal standard calibration methods.

Table 1
Description of different reference materials used for analysis

S. No.	RM code	Matrix	Sample code	Approved by
1	NCSZC73012	Cabbage leaf	P1	China National Analysis Center for Iron and Steel
2	NCSZC73014	Tea Leaf	P2	China National Analysis Center for Iron and Steel
3	SRM 2704	River Sediment	S1	National Bureau of Standards (NBS)/NIST
4	SRM 1632a	Bituminous Coal	S2	National Bureau of Standards (NBS)/NIST
5	RM SL-1	Buffalo River Sediment	S3	International Atomic Energy Agency (IAEA)

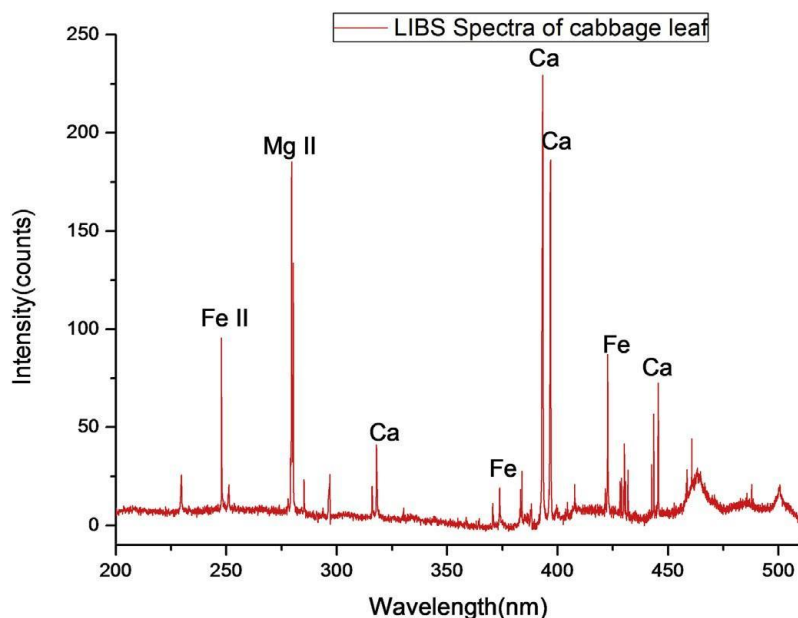


Fig. 2. LIBS spectra of cabbage leaf in spectral range 200e500 nm.

Table 2

Certified concentrations of different elements for plant RMs with predicted concentrations of unknown plant samples (in which Fe is in ppm & others are in wt %).

Element	Cabbage (P1)		Tea (P2)	
	Certified	Predicted	Certified	Predicted
Al (%)	0.0166 ± 0.0022	0.0184 ± 0.0076	0.094 ± 0.009	0.092 ± 0.006
Ca (%)	0.70 ± 0.02	0.70 ± 0.04	0.326 ± 0.008	0.296 ± 0.037
Fe(ppm)	98 ± 10	104 ± 10	242 ± 18	246 ± 10
K (%)	1.55 ± 0.06	1.56 ± 0.01	1.63 ± 0.07	1.60 ± 0.01
Mg (%)	0.241 ± 0.015	0.242 ± 0.007	0.186 ± 0.011	0.181 ± 0.005
Si (%)	0.024 ± 0.005	0.024 ± 0.006	0.099 ± 0.008	0.099 ± 0.006

Table 3

Certified concentrations (wt %) of different elements for soil CRMs with predicted concentrations of unknown soil samples.

Uncertainties quoted on certified values are at 95.5% confidence level.

Element	SRM 2704 (S1)		SRM 1632a (S2)		IAEA-RM-SL-1 (S3)	
	Certified	Predicted	Certified*	Predicted	Certified**	Predicted
Al	6.11 ± 0.16	6.14 ± 0.26	(3.1)	2.9 ± 0.20	(8.9)	9.02 ± 0.50
Ca	2.60 ± 0.03	2.36 ± 0.16	0.23 ± 0.03	0.29 ± 0.11	(0.25)	0.26 ± 0.01
Fe	4.11 ± 0.10	3.74 ± 0.39	1.11 ± 0.02	1.45 ± 0.40	6.74 ± 0.20	6.75 ± 0.75
K	2.00 ± 0.04	1.93 ± 0.15	0.42 ± 0.02	0.33 ± 0.18	(1.5)	1.87 ± 0.30
Mg	1.20 ± 0.02	1.10 ± 0.11	(0.1)	0.12 ± 0.02	(2.9)	2.82 ± 0.22
Mn	0.0555 ± 0.0019	0.0307 ± 0.0127	0.0028 ± 0.0002	0.0029 ± 0.0001	0.346 ± 0.017	0.339 ± 0.031

* Values given in () are recommended values from NIST.

** Values given in () are recommended values from IAEA.

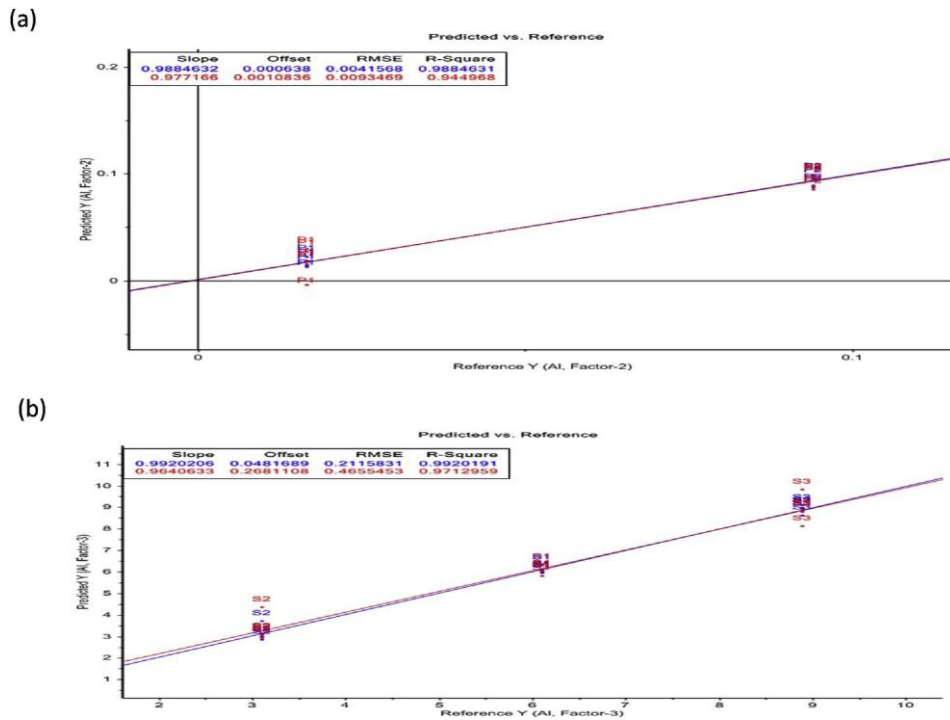


Fig. 3. (a & b). Predicted vs. Reference plots for concentration of Al for plant and soil RMs.

The figure labeled as Fig. 4 displays a three-dimensional scatter plot representing three specified factors for two types of samples. By analyzing the score plot, we can deduce that samples that are closer in proximity to each other on the plot are more alike in comparison. In the first matrix, samples are classified into two clusters, whereas in the second matrix, they are classified into three clusters. Although most of the components present in the samples are similar in both matrices, they are divided into separate clusters. This suggests that the composition of samples is different, with varying concentrations of elements, as evidenced by the concentration data in Tables 2 and 3. These plots (Fig. 4) provide insights into sample patterns by analyzing the factors.

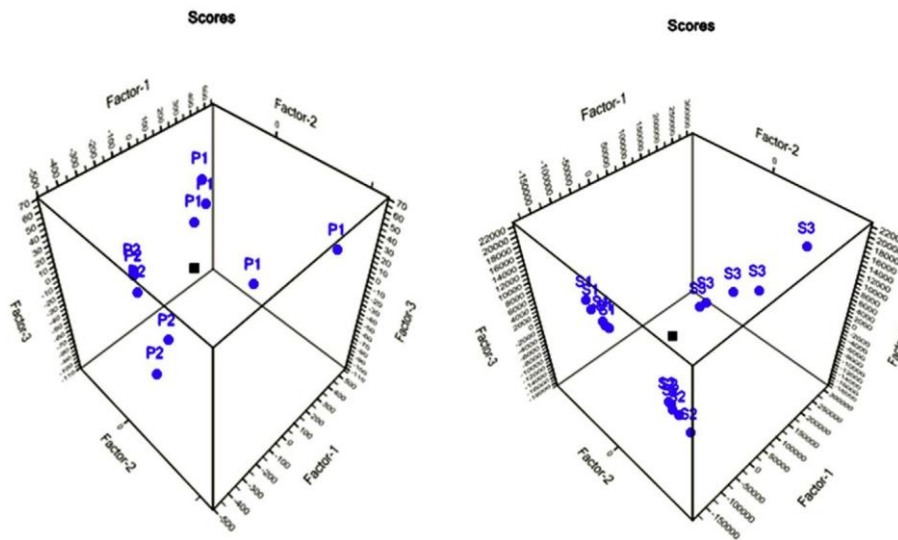


Fig. 4. Three-dimensional score plots for plant and soil CRMs.

The 5th figure illustrates the regression coefficients associated with the wavelength used in the spectral range chosen for Magnesium (Mg) in soil samples, and a similar plot was created for other elements. The peaks displayed in the figure strongly affect the variation of Mg concentrations and are used to construct Partial Least Squares (PLS) calibration models. The regression coefficients indicate a direct linear relationship between the Laser-Induced Breakdown Spectroscopy (LIBS) spectra and the elemental concentrations. The peaks identified in this study correspond to the emission lines that are relevant to the changes in the elemental concentrations. To make the PLS models practical and minimize the interference of irrelevant emission lines, a smaller spectral range is selected based on the regression coefficient plot, where the most intense peaks of the particular element are displayed.

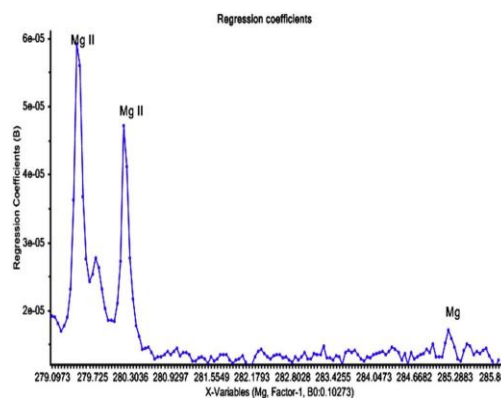


Fig. 5. Regression coefficient vs. wavelength plot for Mg element in soil samples.

The 6th figure illustrates how the cumulative explained variance changes depending on the number of factors included in the model. This curve shows how much variance of an individual variable can be explained by the model with different numbers of factors. The

figure suggests that a model with two factors would yield the most accurate predictions. It also displays two types of variances: the calibration variance (shown in blue) is calculated by fitting the calibration data to the model used to build the model, while the validation variance (shown in red) is obtained by testing the model with new data. If the validation variance is significantly smaller than the calibration variance, the model is not reliable for new data. Conversely, if the two curves are similar, the model is valid. In this case, the validation variance is almost identical to the calibration variance, indicating that the model is accurate for new data.

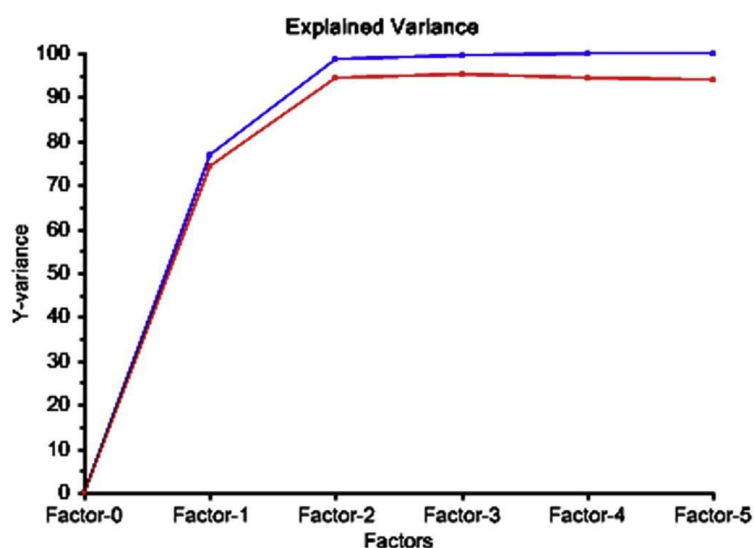


Fig. 6. Explained variance plot in PLSR model.

After observing the strength of the PLSR model, it was employed to forecast the concentrations of the test samples. The outcomes presented in Figure 7(a) and (b) represent the PLSDA models for the test dataset of Al for soil and plant samples correspondingly. Similarly, these models were plotted for all other elements. These graphs demonstrate the anticipated concentrations for all the test (unfamiliar) samples. To assess the effectiveness of the calibration model, test sets were employed to determine the concentrations of various elements. The expected values are indicated by horizontal lines, and the boxes surrounding them indicate the differences from the training set of the data (refer to Figure 7(a) & (b)). If the training sets used to create the calibration model differ greatly from the test sets in which predictions are made, there will be a significant deviation. Tables 2 and 3 display the expected concentrations of all elements for soil and plant samples, along with their relative standard deviation (RSD). The findings indicate that the predicted concentrations of different

elements for unknown samples are nearly identical to the certified concentrations provided in Tables 2 and 3, with only slight variations in values. This indicates that the proposed model is robust for unknown samples and closely resembles the known samples.

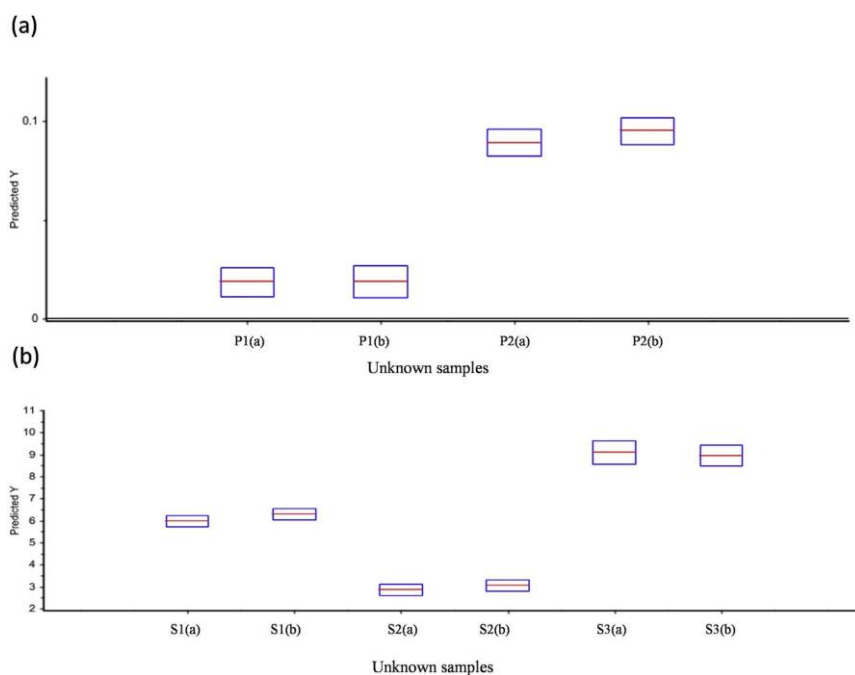


Fig. 7. (a & b). PLSDA models for test set of Al for plant and soil samples.

Table 4 presents a comparison between the results obtained from Laser-Induced Breakdown Spectroscopy (LIBS) and Instrumental Neutron Activation Analysis (INAA), which is also a widely used non-destructive analytical method. The uncertainty percentage of the results obtained by INAA from four independent samples analyzed ranges from 3.0e to 9.5%. The results obtained by INAA for the IAEA RM SL-1 and NIST SRM 1632a are in good agreement with the certified values, with a difference of less than 3.3% for SL-1 and less than 10% for 1632a, and are also consistent with each other (within 10% except for a few elements in 1632a). INAA can provide data on various elements simultaneously, but it requires a high flux neutron source like a nuclear reactor for conducting the experiments. LIBS, on the other hand, has the advantage of obtaining data in a reasonably compact experimental system and a non-destructive way.

Table 4

Comparison of elemental concentration (wt %) results of IAEA RM SL-1 and NIST SRM 1632a by LIBS with INAA.

Element	IAEA RM SL-1			NIST SRM 1632a		
	LIBS	INAA	Certified ^b	LIBS	INAA	Certified ^a
Al	9.02 0.50	$\pm 9.0 \pm 0.3$	(8.9)	2.9 ± 0.2	3.3 ± 0.2	(3.1)
Ca	0.26 0.01	$\pm 0.24 \pm 0.01$	(0.25)	0.38 ± 0.17	0.21 ± 0.02	0.23 ± 0.03
Fe	6.75 0.75	$\pm 6.81 \pm 0.19$	6.74 ± 0.20	1.45 ± 0.40	1.15 ± 0.05	1.11 ± 0.02
K	1.87 0.30	$\pm 1.45 \pm 0.11$	(1.5)	0.33 ± 0.18	0.46 ± 0.02	0.42 ± 0.02
Mn	0.339 0.031	$\pm 0.35 \pm 0.01$	0.346 ± 0.017	0.0029 0.0001	± 0.0027 0.0002	± 0.0028 0.0002

^a Values given in () are recommended values from NIST.

^b Values given in () are recommended values from IAEA.

Conclusion

This research focuses on using Laser-Induced Breakdown Spectroscopy (LIBS) as a quick method for analyzing environmental samples by using multivariate statistical analysis of data. The study builds a model for multivariate analysis based on certified reference materials and applies it to unknown samples. The study shows that Partial Least Squares Regression (PLSR) and Partial Least Squares Discriminant Analysis (PLSDA) are effective for implementing multivariate approaches in analyzing LIBS spectral data. The study also develops calibration models to relate concentrations of different elements. The LIBS predicted concentrations of the certified reference materials are comparable to the certified concentrations. This approach provides a practical way to determine elemental concentrations in samples that are otherwise difficult to analyze using traditional calibration curve methods. The methodology can also check the technique's robustness, even in the absence of certified reference materials for the same matrix. Because multivariate methods have powerful analytical abilities, they can yield better results.

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