



Multivariate methods for analysis of environmental reference materials using laser-induced breakdown spectroscopy



Shikha Awasthi ^a, Rohit Kumar ^a, Alamelu Devanathan ^b, R. Acharya ^c, A.K. Rai ^{a,*}

^a Laser Spectroscopy Research Laboratory, Department of Physics, University of Allahabad, Allahabad 211002, India

^b Fuel Chemistry Division, Bhabha Atomic Research Center, Trombay, Mumbai 400085, India

^c Radiochemistry Division, Bhabha Atomic Research Center, Trombay, Mumbai 400085, India

ARTICLE INFO

Article history:

Received 30 November 2016

Accepted 9 January 2017

Available online 16 January 2017

Keywords:

LIBS
RMs
INAA
MVA
PLSR
PLSDA

ABSTRACT

Analysis of emission from laser-induced plasma has a unique capability for quantifying the major and minor elements present in any type of samples under optimal analysis conditions. Chemometric techniques are very effective and reliable tools for quantification of multiple components in complex matrices. The feasibility of laser-induced breakdown spectroscopy (LIBS) in combination with multivariate analysis was investigated for the analysis of environmental reference materials (RMs). In the present work, different (Certified/Standard) Reference Materials of soil and plant origin were analyzed using LIBS and the presence of Al, Ca, Mg, Fe, K, Mn and Si were identified in the LIBS spectra of these materials. Multivariate statistical methods (Partial Least Square Regression and Partial Least Square Discriminant Analysis) were employed for quantitative analysis of the constituent elements using the LIBS spectral data. Calibration models were used to predict the concentrations of the different elements of test samples and subsequently, the concentrations were compared with certified concentrations to check the authenticity of models. The non-destructive analytical method namely Instrumental Neutron Activation Analysis (INAA) using high flux reactor neutrons and high resolution gamma-ray spectrometry was also used for intercomparison of results of two RMs by LIBS.

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1. Introduction

Analysis of certified/standard reference materials (CRMs/SRMs) is essential to validate an analytical method. The accuracy of the technique and methodology can be evaluated using CRMs which enhances the confidence when the same is employed for unknown samples. Since CRMs are not easily accessible for a number of matrices in various laboratories, it is necessary to employ suitable methodologies to evaluate the accuracy of analytical methods. The analytical techniques play a major role for detecting essential elements in a variety of materials that are of key importance for direct analysis of materials in diverse scenarios. Numerous analytical techniques like Inductively Coupled Plasma Emission Spectrometry (ICPAES), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), X-ray Fluorescence (XRF), Instrumental Neutron Activation Analysis (INAA) etc have been extensively explored for the compositional analysis [1–4]. These techniques have excellent analytical

performance, but most of the techniques are destructive as a significant amount of the samples are consumed. Furthermore, the sample preparation methods are also time-demanding. On the otherhand, nuclear analytical techniques like INAA and IBA are non-destructive in nature and have multielement determination capabilities. However, INAA needs high flux research reactor and IBA needs tandem particle accelerator, which are not easily accessible for routine analysis of materials.

Laser induced breakdown spectroscopy (LIBS) is a multi-elemental analytical technique based on emission spectroscopy for obtaining the data on various elements simultaneously. This technique has certain potential advantages over conventional techniques that require pretreatment. The emission spectroscopy approach is minimally invasive having simple or compact experimental setup with avoiding sample preparation. It is relatively non-destructive in nature and can also provide remote *in-situ* analysis in hostile environments or inaccessible targets using suitable experimental arrangements [5–8].

In this method, a powerful laser pulse is focused on the sample surface, resulting in the formation of plasma plume, dissociating all molecules and fine particulates within the highly energetic micro

* Corresponding author.

E-mail address: awadheshkrai@rediffmail.com (A.K. Rai).

plasma. The resulting plasma emission can be correlated to the elemental concentration in the sample surface and LIBS spectrum can provide a detailed elemental fingerprint of the material being analyzed. The accuracy of the method can be evaluated by analyzing suitable matrix matched certified reference materials. For quantitative analysis, it is necessary to prepare standards that are similar to the matrix of the unknown (test) sample and obtain a calibration curve for the different elements.

The LIBS spectra usually very complex and contain significant information where the spectral information consists of thousands of data points that can be collected in less than one second. For complex spectra such as that of soils and plants, it is always not possible to compare the analytical results for elements using every possible emission line for that element in such chemically-complex matrix. Thus a promising method is necessary to resolve these challenges in addition to prevent any loss of useful spectral information. Multivariate analysis (MVA) is a well-established chemometric analytical tool that takes into account all the possible variables, removes the redundant and correlated variables, and fully utilizes the LIBS spectral information. Many studies have applied MVA on LIBS to utilize the abundant spectral information from the elemental compositions of the sample [9,10]. Multivariate techniques like partial least square regression (PLSR) and partial least square discriminant analysis (PLSDA) are useful methods to compensate the data points for different deviations [11–13]. These methods are coupled with LIBS to build the calibration models and can be used to predict concentrations of different elements for unknown samples. With the development and optimization of various robust statistical analytical methods, LIBS is more promising for the qualitative and as well as the quantitative analysis of various elements in a wide range of samples [14–21]. In this study, LIBS spectra of environmental samples (plant and soil RMs) were obtained and the chemometric analysis was performed using PLSR and PLSDA. The results of IAEA RM SL-1 and NIST SRM 1632a were compared with the results obtained from INAA using higher neutron flux irradiation position of Dhruva Research reactor. The predicted concentrations for test samples by these approaches are compared with their certified values.

2. Material and methods

2.1. Experimental setup

For recording the LIBS spectra, pellets of each sample and RM were prepared using hydraulic press machine (H-Br Press MODEL M-15). To form the pellets, one grams of each sample was poured into a pellet die (20 mm diameter and 3 mm high) and then compressed with 6 tons of pressure for one minute. Experimental setup for obtaining the LIBS spectra is shown in Fig. 1. A frequency doubled Q switched pulsed laser source Nd: YAG (continuum surelite III-10), pulse width FWHM (full width at half maximum) of 4 ns (variable repetition rate 1–10 Hz) with maximum deliverable laser energy of 425 mJ per pulse was used. A beam of 532 nm laser was focused on the surface of sample using a converging lens ($f = 15$ cm). The laser pulse energy (measured with an energy meter, Genetec-e model UP19K- 30 H-VM-DO) and pulse repetition rate were optimized and the best signal to background ratio were observed with an energy of 20 mJ at repetition rate of 4 Hz. Focal spot for a laser beam of diameter 9 mm is about 11 μm calculated by $[D = 4\lambda f/\pi d]$, where λ is the wavelength, f is the focal length of the lens, and d is the aperture, i.e. unfocused (original) beam diameter]. The power density of the laser beam (fluence) is $5.24 \times 10^{12} \text{ Wcm}^{-2}$ (laser pulse with energy of 20 mJ and a pulse width of 4 ns). The emission from plasma was first collected by lens (diameter 5 mm, f -number is $f/2$) fixed at the tip of the optical fiber bundle, adjusted to

maximize the collection of emission signal (at about 45° with respect to the laser beam). The other end of the optical fiber was at the entrance slit of the Czerny–Turner (C–Z) spectrometer (Ocean Optics LIBS 2000 + with fixed gate delay of 1.5 μs). The spectrometer has four modules. The first three modules covering the spectral range of 200 nm–510 nm have spectral resolution of 0.1 nm (FWHM) to provide high resolution, while the fourth module covering the spectral range 200–900 nm has low resolution of 0.75 nm (FWHM). A gated charge coupled device (CCD) equipped with the spectrometer having 14,336 pixels was employed as a detector to obtain the spectra.

The experimental parameters were optimized and the optimized parameters were employed for the analysis of all samples in the experiment. In this manuscript total five environmental samples (three soils and two plants) have been analyzed. An average of 20 laser shots was recorded to enhance the signal-to-noise ratio. Seven spectra of each sample are recorded to reduce statistical error due to laser shot-to-shot fluctuations as well as to account for the sample heterogeneity. The resultant spectra were analyzed using OOI LIBS 2000 + software.

Powder samples (RMs) were sealed in polythene pouches along with a reference standard each of about 10 mg and were irradiated for 1 min in Pneumatic Carrier Facility (PCF) of Dhruva reactor, BARC, Trombay, Mumbai. This irradiation helped to get Al, Ca, K and Mn in samples. Another set of samples 100 mg each with reference standard were irradiated for 1d irradiation in tray rod facility of Dhruva reactor for obtaining Fe concentration. After irradiation, samples were assayed for gamma activity using a 30% relative efficiency HPGe detector. Peak areas were determined using peak fit software PHAST and concentration calculation was carried out by standard relative method.

2.2. Statistical treatment

LIBS spectra of different samples were arranged in form of a matrix containing several variables (spectral emission lines corresponding to various wavelengths) for statistical comparison. The Unscrambler-X software (CAMO software India Pvt. Ltd.) was used for performing the multivariate methods using this LIBS spectral data matrix. We have two types of samples (plants and soils) therefore data sets were further divided into two matrices, one for plants (14×5855) and another for soil samples (21×5855). Multivariate techniques are applied for both matrices. PLSDA and PLSR are the most often used multivariate approaches for analysis of data. These techniques work on the principle of partial least square (PLS), which is widely employed for analysis of large data. PLS is used to minimize the residuals of the calibration model for effectively utilizing the spectral information to reduce the possibility of over fitting and thus improving the accuracy of the model. In essence, PLS is a technique for modeling a linear relationship between input and output variables. The fundamental limitation for applying the PLS technique on the spectral data is that it neglects any underlying physical principles and focus purely on the mathematical correlation in the data. PLSR is a data decomposition method that involves a mathematical procedure for creating latent variables (factors). Latent variables transform a large number of correlated independent variables into a smaller number of uncorrelated independent variables orthogonally. PLSR can interpret the interrelationships among different variables and uncover unknown trends. PLSR linearly relates the variations of dependent variables to the independent variables, which works especially well when independent variables carry common information like correlations. It simplifies the interpretation of the relationship between independent variables and dependent variables. The performance of the PLSR model is then validated using a set of unknown samples. For

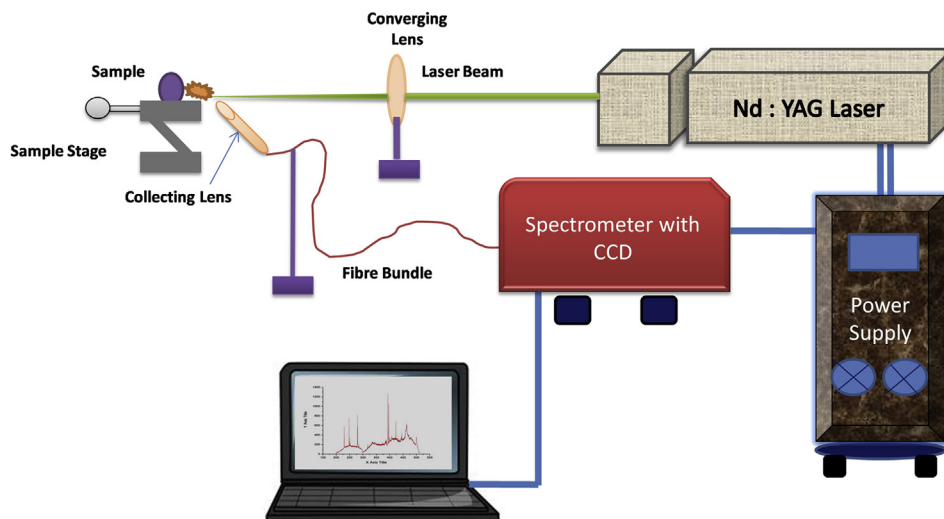


Fig. 1. Schematic diagram of LIBS experimental setup.

this PLSDA model is constructed based on the PLSR calibration model. In this technique classes of unknown samples can be predicted. It determines the optimal variance between each class. Validation test sets are used to compare the effectiveness of PLSDA model. The main purpose of this work is to construct robust calibration models relating concentration of different elements in a variety of samples and to use the model to predict concentrations of these elements in unknown samples. The application of MVA in extracting and analyzing the LIBS spectral information will definitely improve the quantitative analytical ability of LIBS and make it more promising.

3. Results and discussion

Table 1 shows the description of samples analyzed by LIBS for the multivariate analysis. Fig. 2 shows the typical LIBS spectrum of cabbage leaf CRM in spectral range of 200 nm–500 nm which clearly shows the presence of prominent lines of Mg, Ca, Fe, K, Al, Si etc. Similarly spectral lines of Mg, Ca, Fe, K, Al, Mn etc. are present in the LIBS spectra of all other analyzed standard RMs. The wavelengths of different atomic and ionic species present in the spectra were identified using atomic spectroscopy database of NIST [22] and chemical spectroscopy by W R Brode [23]. Certified values of concentrations of different elements for RMs are given in Table 2 and Table 3 for plant and soil RMs respectively.

PLSR is employed here to construct the calibration model for RMs. These are predicted vs. reference plots of PLSR model. To draw the calibration models of various elements having different concentrations, typical wavelength regions containing the majority of the emission lines of corresponding elements are chosen for each sample. Fig. 3(a) and (b) show typical PLSR calibration models of Al for plant and soil samples respectively. Similarly PLSR models are plotted for all other elements. The performance of the model is

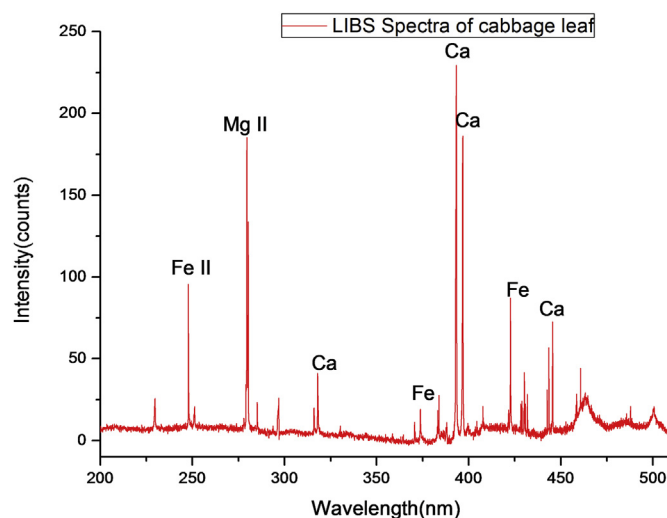


Fig. 2. LIBS spectra of cabbage leaf in spectral range 200–500 nm.

Table 2

Certified concentrations of different elements for plant RMs with predicted concentrations of unknown plant samples (in which Fe is in ppm and 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 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) |

Table 3

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

| 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 |

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

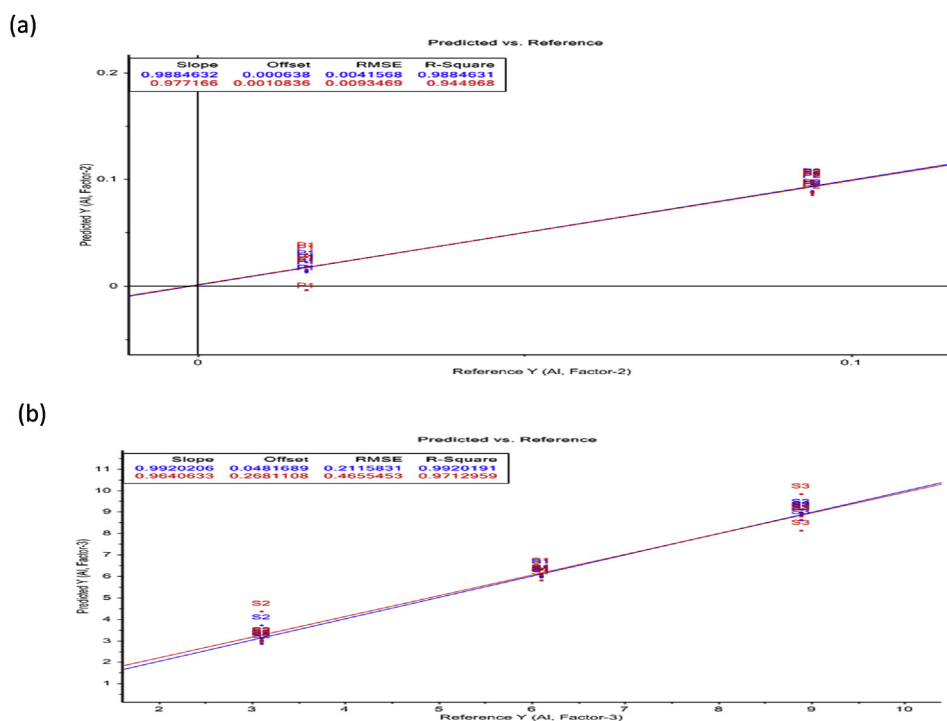
* Values given in () are recommended values from NIST.

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

assessed by the coefficient of determination (R^2) and root mean square error (RMSE). It is observed that the R^2 values are almost equal to 1 while RMSE is close to 0, revealing a strong correlation between the predictions and references. Ideally, the predicted values should be equal to the reference values. With slopes tending to 1 one can qualify this model as good enough for running the regression. We have recorded 14 spectra of two plant samples (7 spectra of each). Out of 14 spectra, 10 spectra are chosen as training set to prepare PLSR model and rest 4 spectra are chosen as test set. For soil samples 21 spectra of three soil samples (7 spectra of each) are recorded. Out of 21 spectra, 15 spectra are chosen as training (known) set and rest 6 spectra as test (unknown) set. Cross-validation strategy is used to validate the PLS model. Test sets give the indications about strengths and weakness of the model. We used the concentrations of different elements given in Tables 2 and 3 to construct the PLSR model. Furthermore, the best fits of calibration (blue one) and validation (red one) deviate very little from each other due to the high value of R^2 , showing that R^2 for calibration (Cal) is close to the validation (Val). If there are large differences between Cal and Val, the model cannot be trusted. The root-mean square error of calibration and prediction (RMSEC&P)

for the model is close to 0 for all elements in both matrices. RMSEC for the model are used to evaluate the PLSR calibration model and using these calibration models, test sets are predicted. RMSEP is used to verify the prediction capabilities of these PLSR calibration models. As a result, we can evaluate the accuracy of the determination based on the predictions from a PLS model if the matrix of the measured samples is not varying away from that of the calibration sample set. It is seen that the PLSR model is more accurate and reliable for all samples as RMSE is low while R^2 remains high, showing the overall robustness of the proposed model (Fig. 3(a) and (b)). This approach is capable of compensating for matrix effects as well as to overcome the issues of conventional internal standard calibration methods.

Fig. 4 shows the three dimensional scatter plot of three specified factors for both types of samples. From score plot, we get a map about samples such that closer the samples are in this plot, the more similar they are with respect to each other. Samples are clustered into two groups in first matrix and in second matrix, the samples are divided into three clusters. It can be seen that most of the elements are the same in all the samples in both matrices but they are clustered separately. This, interestingly, shows the

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

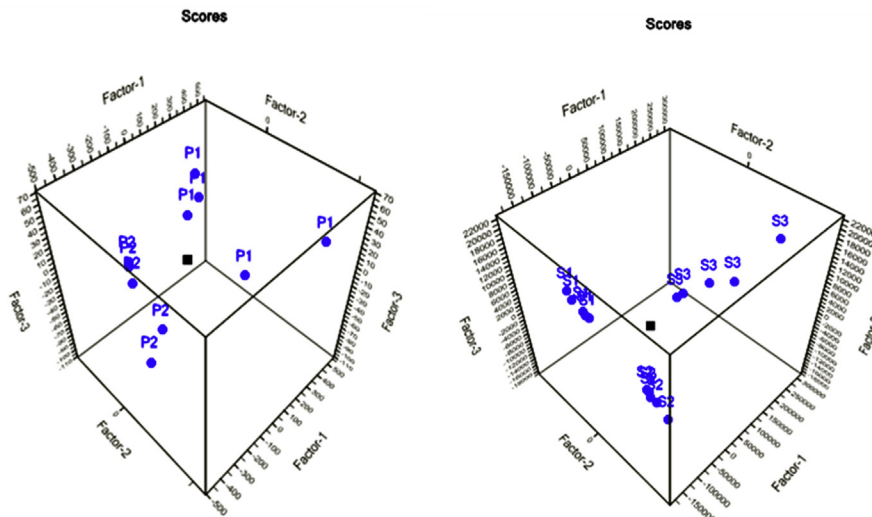


Fig. 4. Three dimensional score plots for plant and soil CRMs.

dissimilar composition of samples as the elements present in the samples differ in terms of concentration, as can be seen from the concentration data in Tables 2 and 3 of samples. These plots (Fig. 4) give the information about patterns in samples by computing the factors.

Fig. 5 depicts the regression coefficient corresponding to the wavelength performed on the spectral range chosen for Mg for soil samples; similarly this plot was also drawn for other elements. The peaks shown in Fig. 5 have strong influence on the variation of Mg concentrations and are used to build the PLS calibration models. The regression coefficients represent a direct linear relationship between the LIBS spectra and the elemental concentrations. The peaks assigned here show the emission lines that are relevant to the changes of the elemental concentrations. In order to reduce the interference of irrelevant emission lines and to make the PLS models practically reasonable, a smaller spectral range is selected to build the PLS models where the most intense peaks of particular element are shown based on the regression coefficient plot.

Fig. 6 describes the relationship of the cumulative explained variance as a function of the number of factors. This variance curve describes how explained variance of an individual variable evolves

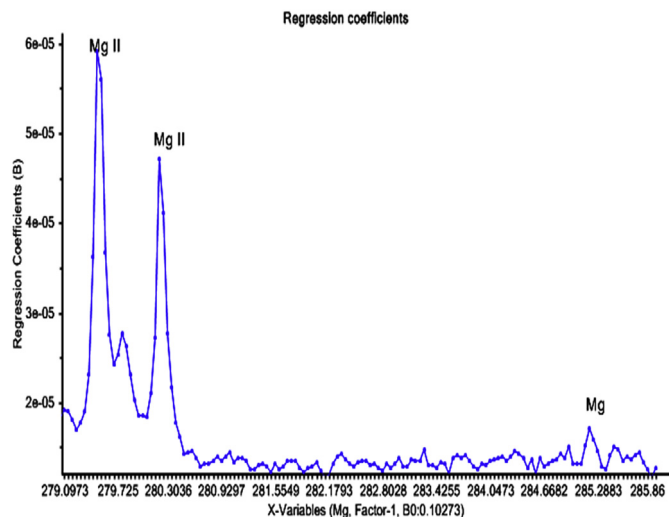


Fig. 5. Regression coefficient vs. wavelength plot for Mg element in soil samples.

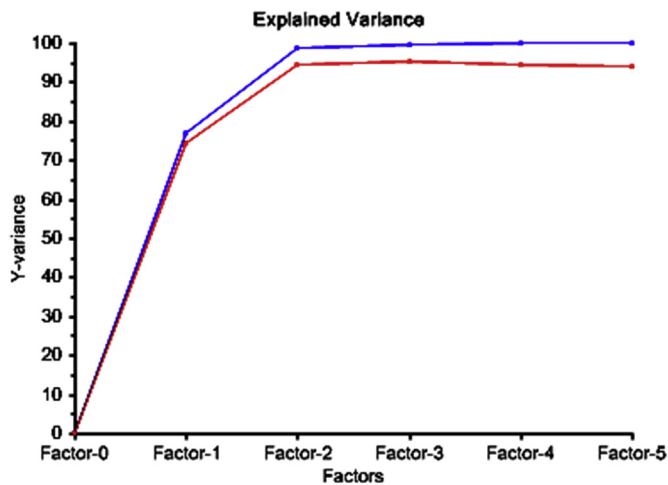


Fig. 6. Explained variance plot in PLSR model.

with the number of factors in the model. This figure indicates that two factors are enough to obtain a calibration model with the optimum predictability. From this plot we can obtain the variation in the responses that is described by each of the component. Two types of variance are shown: The blue line is the calibration variance and the red line is the validation variance. Calibration variance is based on fitting the calibration data to the model that were used to build the model. Validation variance is computed by testing the model on data. If the validation variance is different or much smaller than the calibration variance, the model does not describe new data clearly. On the contrary, if these curves are close together, the model is representative. From the plot it can be seen that the validation variance is close to the calibration variance.

On seeing the robustness of PLSR model it is applied to predict the concentrations of test samples. Results shown in Fig. 7(a) and (b) are PLSDA models for test set of Al for plant and soil samples respectively. Similarly these models are plotted for all other elements. These plots show the predicted concentrations for all test (unknown) samples. To evaluate the performance of the calibration model, test sets are used here then determine the concentrations of different elements. The predicted values are shown by horizontal lines and the boxes around the values indicate the deviations from

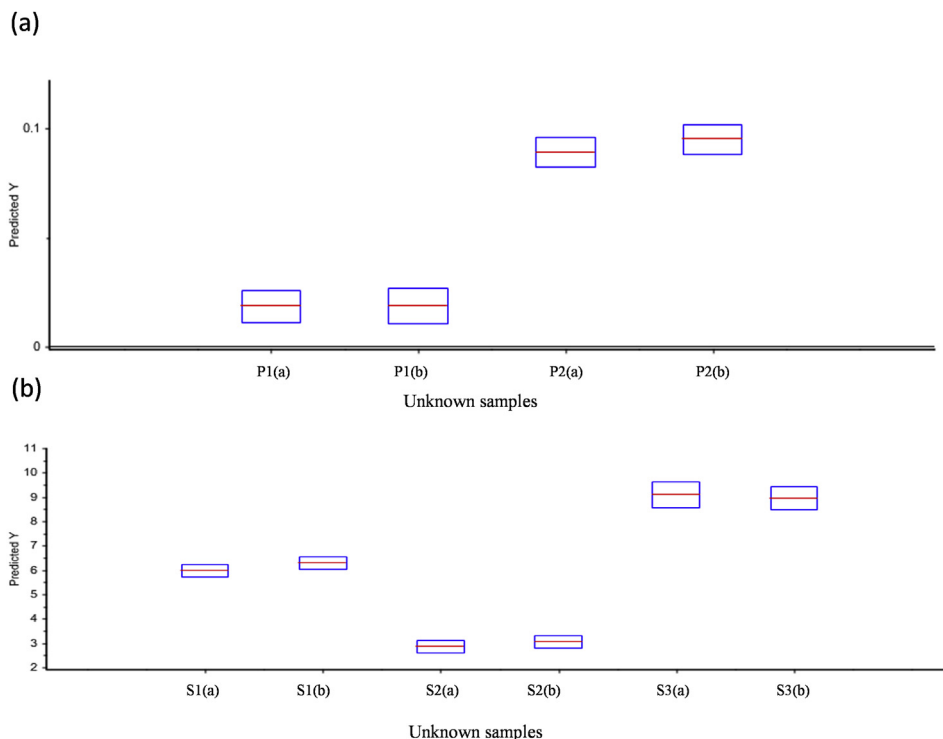


Fig. 7. (a & b). PLSDA models for test set of Al for plant and soil samples.

training set of the data (Fig. 7 (a) & (b)). If training sets used to form calibration model are not very similar to the test sets in which the predictions are applied, boxes indicate the large deviation. Tables 2 and 3 show the predicted concentrations of all elements with RSD for plant and soil samples. It is noticed here that the concentration values of different elements predicted for unknown samples are almost similar to the certified concentrations given in Tables 2 and 3 with small deviations in values. This shows the robustness of the proposed model for unknown samples that they are very similar to the known samples.

Table 4 gives a comparison of results of LIBS with that obtained by instrumental NAA (INAA), which is also one of the non-destructive analytical methods employed widely. The % uncertainties on results from four independent sample analyzed by INAA are in the range of 3.0–9.5%. It can be seen that the INAA results obtained for the IAEA RM SL-1 and NIST SRM 1632a are in good agreement (within 3.3% for SL-1 and within 10% for 1632a) with the certified values as well as with respect to each other (within 10% except for a few elements of 1632a). INAA has a capability of providing data on various elements with widely varying concentration range simultaneously, but a high flux neutron source like nuclear reactor is necessary for conducting the

experiments. LIBS is advantageous since the data can be obtained with a reasonably compact experimental system as well as on non-destructive way.

4. Conclusion

In this study, the ability of LIBS as a rapid technique for analysis of RMs of environmental samples based on multivariate statistical analysis of data is addressed. The model for the multivariate analysis was built using certified reference materials. The developed model was then applied to unknown samples. The results clearly demonstrate that PLSR and PLSDA are powerful for implementation of multivariate approaches in analyzing the LIBS spectral data. The calibration models are developed here relating concentrations of different elements. In case of the RMs, the predicted concentrations by LIBS are comparable to the certified concentrations. This methodology provides a viable approach for the determination of elemental concentrations in a variety of samples which is extremely difficult to achieve in case of the traditional calibration curve method. The methodology also is helpful to check the robustness of the technique, even in the absence of the RMs for the same matrix. Due to the robust and powerful analytical ability of

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 | 9.0 ± 0.3 | (8.9) | 2.9 ± 0.2 | 3.3 ± 0.2 | (3.1) |
| Ca | 0.26 ± 0.01 | 0.24 ± 0.01 | (0.25) | 0.38 ± 0.17 | 0.21 ± 0.02 | 0.23 ± 0.03 |
| Fe | 6.75 ± 0.75 | 6.81 ± 0.19 | 6.74 ± 0.20 | 1.45 ± 0.40 | 1.15 ± 0.05 | 1.11 ± 0.02 |
| K | 1.87 ± 0.30 | 1.45 ± 0.11 | (1.5) | 0.33 ± 0.18 | 0.46 ± 0.02 | 0.42 ± 0.02 |
| Mn | 0.339 ± 0.031 | 0.35 ± 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.

multivariate methods, these approaches yield better results.

Acknowledgments

The authors are heartily thankful to Dr. A K Pathak and Dr. Abhimanyu Kumar Singh for their valuable discussion and suggestions. Ms. Shikha Awasthi is grateful to UGC, New Delhi for D.Phil. Fellowship. The authors express their sincere thanks to BRNS (No.2009/37/30/BRNS/2063), DAE, India for financial support.

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