CHAPTER 5

In-situ analysis of fireworks
5.1 Introduction

These days lights and sounds have become so inseparable parts of many festivals, functions etc. that it is tough to resist the fun and excitement of playing with the fireworks. In modern times fireworks have become an integral part of celebrations for all of us around the globe. In fact, these aesthetic forms of light seem very much appropriate and the most essential when celebrating the festival of lights in India and New Year celebration. Such limitless use of fireworks plays a big role in polluting our environment [1-3]. The toxic substances used in them release toxic gases that are harmful to the health of all living beings. Materials that are used for making fireworks contain different elements like Ba, Na, Sr, Al, Ca, Li etc. to impart various colors. For example green color is due to the presence of Ba, red color of light is due to Sr, Ca and Li, yellow is due to Na and Li, silver is due to Ca, Al, Mg etc. They produce spark because of the presence of elements like Al, P, Fe and Mg which cause air pollution after burning. Some toxic elements also remain in byproduct after burning which get disposed in bins or poured down in outdoor drains flowing directly into rivers and lakes etc. thus polluting the water. Waste is hazardous when it has properties that make it harmful to human health or to the environment [4, 5]. Hazardous does not always mean that such waste is immediately harmful (though some can be) but it may become harmful after reacting with other materials present in the environment. To protect our environment, proper analysis of these elements is very important and needs rapid detection.

For identification/quantification of elements generally conventional methods are used [6-9]. These techniques are time consuming, costly and require a complicated sample pretreatment procedure prior to the analysis. Therefore to overcome the drawbacks of these conventional methods, there is a strong motivation to develop reliable analytical methods to provide quality information of elemental compositions in real time. LIBS is a quick, eco-friendly, efficient and useful analytical technique for the detection of the trace elements present in any environment [10-13].

Chemometric methods have been shown to significantly improve the analytical performances of spectroscopic techniques and used for several years in LIBS for quantitative and qualitative analyses [14, 15]. In the present study,
chemometric techniques are applied along with LIBS to improve the capability of discrimination, regression and prediction. In this chapter common chemometric techniques such as PCA and PLSR have been applied for the analysis of LIBS spectral data of fireworks which help us in the identification and differentiation of different fireworks and to build models that describe the relationship between the known and unknown samples [16-18]. The main objective of the present study is to evaluate the feasibility of LIBS technique for rapid analysis of fireworks and chemometric method is used for discrimination of these.

5.2 Material and Methods

5.2.1 Experimental setup

LIBS spectra of all samples have been recorded using the experimental setup shown in Figure 5.1. For experiment we have used Nd:YAG laser and laser beam is focused using a plano convex (f = 15 cm) lens. Maximum signal intensity and signal to background ratio is observed at 60 mJ laser energy at 2 Hz repetition rate. At focal point laser irradiance is $1.6 \times 10^{13}$ W/cm$^2$. Collection optics (CC 52, Andor) is arranged in such manner so that maximum emission from the plasma plume is collected. The collected emission is guided through optical fiber, dispersed by Mechelle spectrometer and recorded with ICCD. Gate delay and gate width are also optimized and the values are 1 µs and 5 µs, respectively. A single LIBS spectrum represents the average from fifty consecutive laser-induced plasma events and such ten spectra of each sample are recorded.

5.2.2 Statistical treatment

LIBS spectra obtained from different firework samples have been used as input data. It is organized in a form of matrix (23 x 25456) containing lots of variables which are spectral emission lines corresponding to various wavelengths in columns and the spectral responses (observations) in rows. Variables are mean centered using a common pretreatment before processing with the help of Unscrambler-X software.
5.3 Results and Discussion

The description about the samples analyzed in the present chapter is given in Table 5.1. These samples are collected from local market of Allahabad, India. Five types of fireworks are taken for the analysis in which first three samples (S1, S2, S3) are the sparklers which produce different colors while burning though they look similar before burning. Fourth sample (S4) is another type of firework which is generally called Mehtab in local language. The last one (S5) is the firecracker. Sparklers are used for experiment in their original form while for samples S4 and S5, the constituent material is taken out and pellets are made with the help of hydraulic pressure machine (H-Br Press MODEL M-15).

Table 5.1: Description of different firework samples used for the LIBS analysis

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample Name</th>
<th>Color while burning</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Sparkler 1</td>
<td>Yellowish</td>
</tr>
<tr>
<td>S2</td>
<td>Sparkler 2</td>
<td>Reddish</td>
</tr>
<tr>
<td>S3</td>
<td>Sparkler 3</td>
<td>Greenish</td>
</tr>
<tr>
<td>S4</td>
<td>Firework (Mehtab)</td>
<td>Yellowish</td>
</tr>
<tr>
<td>S5</td>
<td>Cracker</td>
<td>Yellowish</td>
</tr>
</tbody>
</table>
Figure 5.2 (a-e) depict the emission spectra of all samples in different spectral ranges. These regions are chosen to show the maximum appearance of spectral lines in the LIBS spectra for all samples. Spectral signatures of Sr, Ca, Al, Fe, Ba, Na, Mg and Si are clearly observed in the LIBS spectrum of different samples. Wavelengths of different spectral lines have been identified using National Institute of Standards and Technology (NIST) atomic spectroscopic database [19] and W. R. Brode, Chemical Spectroscopy [20]. Elements present in Firework samples might be hazardous up to a certain level of concentrations into environment. These elements are found in many compartments of the environment, including rocks, soil, water, and air etc. These compounds may dissolve easily in water and are found in lakes, rivers, and streams. The elements mentioned above are hazardous to the environment in their original form or in the form of some compounds. [21-24].

![LIBS spectra of sample 1 in the spectral range 510-590 nm](image-url)
Figure 5.2 (b) LIBS spectra of sample 2 in the spectral range 330-430 nm

Figure 5.2 (c) LIBS spectra of sample 3 in the spectral ranges 360-470 nm and 640-730 nm
Figure 5.2 (d) LIBS spectra of sample 4 in the spectral ranges 300-400 nm and 584-594 nm

Figure 5.2 (e) LIBS spectra of sample 5 in the spectral ranges 300-400 nm and 581-591 nm
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Compositional analysis is important to interrogate samples for direct analysis of materials. Multivariate analysis of the LIBS spectra are used to discriminate the different samples qualitatively. In PCA spectrally similar materials are grouped together that is why we have analyzed the all LIBS spectral data of fireworks using PCA. Figure 5.3 (a) shows a two dimensional score plot of PCA. PC1 and PC2 explain respectively 87 \% and 9 \% of variance in data matrix.

![Two dimensional PCA Score Plot of five different Fireworks](image)

\textbf{Figure 5.3 (a): Two dimensional PCA Score Plot of five different Fireworks}

Appearance of clustering is clearer in three dimensional view of score plot shown in Figure 5.3 (b). This plot includes the calculation of PC3 and also has better reliability in discrimination between samples. Higher order PCs do not give any other relevant information or evidence about clustering. A set of 23 LIBS spectra of five different fireworks is classified in five distinct groups using PCA, which indicates the existence of dissimilar composition of fireworks. It is observed from the score plot of PCA that samples S1, S4 and S5 are close to each other, this indicates that elemental composition of these samples are similar. This also interestingly verifies the fact that they produce same color (yellowish, Table 5.1) while burning so they appear close to each other and appear far from those
samples which produce different color while burning. This work also demonstrates the capability of PCA to differentiate between similar samples but having different spectral response due to presence of minor impurities. The multivariate data analysis (PCA) has been used to analyze LIBS data. This method is used to discriminate/differentiate between various samples. PCA score plot on LIBS data of various types of samples is shown in Figure 5.3. The chosen samples appear to make good training samples to include in further MVA models. The model classification results for each sample are presented in this figure.

Figure 5.3 (b): Three dimensional Score Plot of PCA

After classification PLSR model is developed using sample spectral data to predict unknown sample. The Predicted vs. Reference plot of PLSR model are shown in Figure 5.4 (a). The calibration (blue one) and prediction (red one) performance of the model is assessed by the coefficient of determination ($R^2$) and root mean square error (RMSE). For an ideal model, $R^2$ should be close to 1 while RMSE to 0. Ideally the predicted values should be equal to the reference values.
and this model is used to check whether it can predict new sample well or not. The PLSR model is always suggested to be cross-validated, for this each spectrum is removed from the model and treated as an unknown. After that a model is generated with the remaining spectra and the elemental composition of the unknown is calculated. This process is repeated as each spectrum in the model is successively removed from the training set. 23 spectra of known samples are chosen as a training set to build the calibration model and 10 spectra are selected as a test set for model prediction. The response variables or predicted values are set as 1 referring to S1 similarly 2, 3, 4 and 5 referring to S2, S3, S4 and S5 respectively, thus randomly choosing the classes of samples to predict the classes of unknown ones of the model. The correlation between predicted value and reference value of these samples is shown in Figure 5.4 (a). The determination coefficient $R^2$ using PLSR model is 0.95 for calibration and 0.93 for prediction. The root-mean square error of calibration and prediction (RMSEC & RMSEP) for the model is 0.29 and 0.39 respectively. RMSEC for the model samples are used to evaluate the PLSR model. Using developed models, the test set is predicted. RMSEP for the test samples are used to verify the prediction capabilities of these PLSR models. The results (Figure 5.4 a) showed that the PLSR model is more accurate and reliable for all samples. Based on dominant factor across a broad range of sample matrices the prediction range is chosen purposely to test the robustness of the PLSR model. Results show that for the proposed PLSR model RMSE is low (0.29) while $R^2$ remains high (0.95), showing the overall robustness of the proposed model. This method can compensate the influence of matrix effects on the conventional calibration curve method.

The established PLSR model using the training set of data is then applied to predict the classes of test samples as shown in Figure 5.4 (b). In order to evaluate the performance of the calibration model, ten samples (each of five sample are predicted twice) of unknown composition are predicted. This plot shows the predicted values for all unknown samples and the boxes around the predicted value indicate the deviation. If there is large deviation in boxes it indicates that the samples used for prediction are not similar to the samples used to make calibration set. In Figure 5.4 (b) it is shown that unknown samples 1 contain the predicted value 1 with small deviations corresponding to class of S1.
Similarly unknown samples 2, 3, 4 and 5, belong to the classes of S2, S3, S4 and S5 respectively with small deviations. It is clear from Figure 5.4 (b) that unknown samples 3 show large deviation as compared to other unknown samples indicating that chosen samples 3 are not very much similar to reference samples S3.

Table 5.2 shows the predicted and deviated values of unknown samples corresponding to each class of known samples. Results show a well discriminated prediction of unknown samples. It is shown that the spectroscopic analysis of plasma emission would be a promising technique for unknown samples using prediction by PLSR model.
Table 5.2: Predicted and Deviated values of unknown samples

<table>
<thead>
<tr>
<th>Unknown Samples</th>
<th>Predicted Values</th>
<th>Deviated Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unknown 1</td>
<td>1.1893</td>
<td>0.2474</td>
</tr>
<tr>
<td>Unknown 2</td>
<td>0.8983</td>
<td>0.2276</td>
</tr>
<tr>
<td>Unknown 2</td>
<td>1.6838</td>
<td>0.2771</td>
</tr>
<tr>
<td>Unknown 3</td>
<td>2.4979</td>
<td>0.2475</td>
</tr>
<tr>
<td>Unknown 3</td>
<td>3.4453</td>
<td>0.3808</td>
</tr>
<tr>
<td>Unknown 3</td>
<td>3.0567</td>
<td>0.4878</td>
</tr>
<tr>
<td>Unknown 4</td>
<td>4.0843</td>
<td>0.2146</td>
</tr>
<tr>
<td>Unknown 4</td>
<td>4.0486</td>
<td>0.2283</td>
</tr>
<tr>
<td>Unknown 5</td>
<td>4.8861</td>
<td>0.2082</td>
</tr>
<tr>
<td>Unknown 5</td>
<td>4.9237</td>
<td>0.2110</td>
</tr>
</tbody>
</table>

5.4 Conclusion

In this study, the ability of LIBS as a rapid technique for material analysis of fireworks is addressed and the impact of these elements on environment and human health is also discussed. Chemometrics techniques that are considered here are used as an effective and reliable tool for multiple components in complex matrices. Reasonable discrimination and prediction have been achieved with all sample types using PCA and PLSR. Here it can be concluded that without knowing concentration or any other information about samples, only on the basis of random classes, we can develop a model for unknown samples. Results show good performances on classification, regression, prediction and provide promising principles for the elaboration of methods which could be used to discriminate the fireworks in various groups. In conclusion, the results presented in this chapter demonstrate the ability of the LIBS technique coupled with multivariate analysis for the classification and prediction of firework samples.
References


14. WANG Qian-Qian, LIU Kai and ZHAO Hua, CHIN. PHYS. LETT. 29 (2012) 044206.


