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In situ ANALYSIS OF FIREWORKS USING LASER-INDUCED BREAKDOWN SPECTROSCOPY AND CHEMOMETRICS

S. Awasthi, R. Kumar, A. K. Rai *

University of Allahabad, Allahabad-211002, India; e-mail: awadheshkrai@rediffmail.com

Different types of fireworks are analyzed using the laser-induced breakdown spectroscopy (LIBS) technique. The system employed for spectral acquisition consists of a Nd:YAG laser (532 nm, FWHM = 4 ns) and an Andor Mechelle ME 5000 echelle spectrometer. The presence of Ba, Ca, Mg, Fe, Na, Sr, Si, and Al is identified in the LIBS spectra of different fireworks. These elements can mix easily into the surroundings and thus pollute the environment. In combination with LIBS, multivariate statistical methods, such as principal component analysis and partial least square discriminant analysis, are employed for qualitative classification, regression, and prediction purposes. These methods show good applicability for the classification and prediction of a large data set.

Keywords: *laser-induced breakdown spectroscopy, fireworks, elemental analysis, multivariate analysis, environmental hazards.*

In situ АНАЛИЗ ФЕЙЕРВЕРКОВ МЕТОДАМИ ЛАЗЕРНО-ИНДУЦИРОВАННОЙ СПЕКТРОСКОПИИ И ХЕМОМЕТРИИ

S. Awasthi, R. Kumar, A. K. Rai *

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Университет Аллахабада, Аллахабад, 211002, Индия; e-mail: awadheshkrai@rediffmail.com

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С помощью методов лазерно-индуцированной спектроскопии (ЛИС) анализируются различные типы доступных в продаже фейерверков. Для спектральных измерений использована система, включающая в себя импульсный Nd:YAG-лазер (λ = 532 нм, длительность импульса 4 нс), а также спектрометр AndorMechelle ME 5000 Echelle. В спектрах различных фейерверков обнаружены Ba, Ca, Mg, Fe, Na, Sr, Si и Al. Эти элементы легко смешиваются и могут загрязнять окружающую среду. Для количественной оценки и выявления регрессии в сочетании с ЛИС использованы многовариантные статистические методы, такие как частичный квадратичный дискриминантный анализ, который перспективен для анализа большого количества данных.

Ключевые слова: *лазерно-индуцированная спектроскопия, фейерверк, элементный анализ, многовариантный анализ, экологические риски.*

Introduction. The use of fireworks has become these days an inseparable part of festivities. However, the toxic substances present in them release toxic gases, thus polluting the environment and posing a potential threat to human health [1–3]. The materials used for manufacturing fireworks contain different elements, such as Ba, Na, Sr, Al, Ca, and Li, to impart various colors. For example, green is due to the presence of Ba; red is due to Sr, Ca, and Li; yellow is due to Na and Li; silver is due to Ca, Al, Mg, etc. Fireworks produce sparks because of the presence of elements like Al, P, Fe, and Mg, which cause air and water contamination after burning [4, 5]. Hazardous waste can be harmful immediately or after reacting with other materials in the environment. Therefore, rapid and sensitive elemental analysis of fireworks is paramount.

For identification/quantification of elements, conventional methods such as inductively coupled plasma mass spectrometry (ICP-MS), electron dispersion X-ray florescence (EDXRF), atomic absorption spectroscopy (AAS), instrumental neutron activation analysis (INAA), and particle-induced X-ray emission (PIXE) are used [6–9]. These techniques are time-consuming, costly, and require a complicated sample pretreatment procedure prior to the analysis. In order to overcome the drawbacks of these methods, there is a need to develop reliable analytical methods able to provide quality information on elemental compositions in real time. LIBS is a quick, eco-friendly, efficient, and useful analytical tool for the detection of trace elements in any environment [10, 11]. It is known as an atomic emission spectroscopy (AES) technique, based on the analysis of the subsequent dissociation and ionization of small amounts of material, which leads to the generation of a continuum and atomic/ionic emission in the plasma obtained by focusing a pulsed laser beam onto a sample [12, 13]. The main objective of the present study is to evaluate the feasibility of LIBS for rapid analysis of fireworks.

In the field of chemometrics, many multivariate tools are available for data description, classification, regression, and prediction. Chemometric methods are known to significantly improve the analytical performances of spectroscopic techniques and have been used for several years along with LIBS for quantitative and qualitative analyses [14, 15]. LIBS spectra usually contain a number of variables (in terms of wavelengths), so multivariate analysis (MVA) is clearly a promising method to resolve these challenges. The purpose of using MVA is to reduce the dimensions of the spectral data into fewer factors describing the data. In such a case, chemometric techniques are usually applied along with LIBS to improve the capability of discrimination, regression, and prediction. In the present report, common chemometric techniques such as PCA and PLSR are applied to the LIBS spectral data of fireworks to identify the distinguishing characteristics of the samples and to build models that describe the relationship between the known and unknown samples [16–18].

Experimental. ***LIBS Setup*****.** The experimental setup to record the LIBS spectra of the samples is the same as used in references [12, 13]. A Q-switched, pulsed Nd:YAG laser (continuum surelite III-10, pulse width FWHM = 5 ns at 1064 nm, maximum deliverable laser energy 950 mJ per pulse, variable repetition rate 1–10 Hz) is used as an excitation source. For the experiment, we use a second harmonic 532 nm Nd:YAG laser (FWHM = 4 ns at 532 nm, maximum deliverable laser energy 425 mJ per pulse). To create the plasma on the surface of the samples, the laser beam is focused using a planoconvex (f = 15 cm) lens. The maximum signal intensity and signal-to-background ratio are observed at a laser energy of 60 mJ, measured with an energy meter (model UP19K-30H-VM-DO), at a repetition rate of 2 Hz. At the focal point, the laser irradiance is 6.3×10^4 J/cm^2 and the fluence is 1.6×10^{13} W/cm^2. Collection optics (CC 52, Andor) is so arranged that the maximum emission from the plasma plume is collected. The collected emission is guided through a UV-VIS optical fiber, dispersed by a Echelle spectrometer (Mechelle ME 5000, Andor), and recorded with an ICCD (iStar DH334T, Andor). Before the collection of spectral data, the wavelength calibration of the ICCD is carried out with an Hg-Ar lamp (Ocean Optics), and after that the intensity calibration is performed with a D-W-H (Ocean Optics CAL-500). The spectral resolution ($\lambda/\Delta\lambda$) of the spectrograph is 6000. The experimental set-up is optimized for maximum signal-to-noise LIBS spectra, and these experimental parameters are maintained during the whole experiment. The gate delay and gate width are also optimized and the values are 1 and 5 μs. A single recorded LIBS spectrum represents the average from 50 consecutive laser-induced plasma events, and as such ten spectra of each sample are recorded.

Statistical treatment. Herein, two chemometric methods are employed for statistical comparison. LIBS spectra obtained from different fireworks are used as input data, organized as a matrix (23×25456) containing variables which represent spectral emission lines corresponding to various wavelengths (in columns) and spectral responses (in rows). Before processing, the variables are mean centered using a common pretreatment with Unscrambler-X software (CAMO software India Pvt. Ltd.). PCA intends to identify the clustering of the samples in different groups, and the variables are responsible for those differences on the basis of their compositional similarities and differences. For classification in PCA, principal components (PCs) are computed and weighted linear combinations of the variables describing major trends in the data are found.

PLSR extracts information about specific sample matrixes to establish a robust calibration model. In this study, we develop a model that describes a statistical correlation between the intensities of the spectral lines corresponding to different wavelengths in the LIBS spectra and the variations in the elemental compositions. It includes the noise reduction and variable selection advantages of partial least squares (PLS). PLS maximizes the covariance between latent variables so that the relationship of the predicted and certified values can be found out.

We predict unknown samples based on the PLSR calibration model of fireworks, and the performance of the PLSR model is validated using a set of test samples. Validation test sets are used to compare the effectiveness of the prediction model. In this technique, the class of the calibration set is known. It determines the optimal variance between each class. The calibration set is used to calculate the model, which tries to fit the relationship between the spectra and their corresponding classes.

Results and discussion. The description of the samples is given in Table 1. These samples are collected from the local market in Allahabad, India. Five types of fireworks are taken for the analysis, among which the first three (S1, S2, S3) produce different colors despite looking similar. The fourth (S4) is another type of firework, generally called *Mehtab* in the local language. The last one (S5) is a firecracker. The sparklers are used for the 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 a hydraulic pressure machine (H-Br Press MODEL M-15). We have performed the experiment and recorded the LIBS spectra of all the samples. The spectral signatures of Sr, Ca, Al, Fe, Ba, Na, Mg, and Si are found in the LIBS spectra of different samples. The wavelengths of different spectral lines have been identified using [19, 20].

TABLE 1. Description of Different Firework Samples Used for the LIBS Analysis

Sample	Sample Name	Color while burning
S1	Sparkler 1	Yellowish
S2	Sparkler 2	Reddish
S3	Sparkler 3	Greenish
S4	Firework (Mehtab)	Yellowish
S5	Cracker	Yellowish

The elements present in the firework samples might be hazardous in their original form or in the form of some compounds [21–24].

We have analyzed the all LIBS spectral data of the fireworks using PCA. Figure 1 shows the three-dimensional score plot of PCA. PC1, PC2, and PC3 explain 87 %, 9%, and 3% of the variance in the data matrix, respectively. 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, which indicates the dissimilar composition of the fireworks. It is observed that samples S1, S4, and S5 are close to each other, which indicates that the elemental composition of these samples is similar. This also verifies the fact that they produce the same color (yellowish) while burning. This work also demonstrates how PCA can be used to identify spectral differences between similar sample types based on minor impurities. The multivariate data analysis tools used to analyze the LIBS data appear to compensate for some of the chemical matrix effects and differentiate between various sample types, as shown in Fig. 1. The chosen samples make good training samples to include in further MVA models. The model classification results for each sample are presented, and the influence of the variables on these results is discussed.

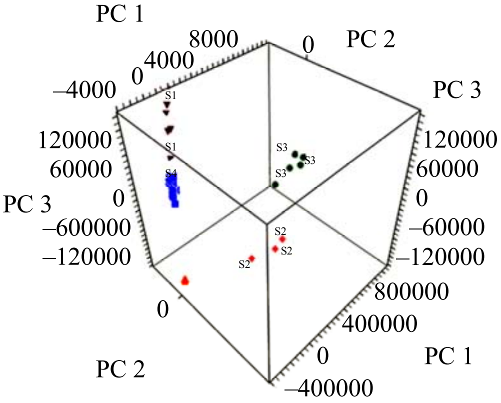

Fig. 1. Three dimensional score plot of five different fireworks.

PLSR is a multivariate projection method for modeling the relationship between dependent variables and independent variables. The predicted vs. reference plot of the PLSR model can be seen in Fig. 2a. The same samples are used to construct the PLSR calibration models for making predictions. The calibration (blue) and prediction (red) performance of the model is assessed by the determination coefficient (R^2), and the root mean square error (RMSE), as for an ideal model, R^2 should be close to 1, and RMSE to 0. The PLS model is cross-validated by the leave-one-out cross-validation strategy. Twenty-three spectra of the known samples are chosen as a training set to build the calibration model, and 10 spectra are selected as a test set for the model prediction. The response variables or predicted values are set as 1 referring to S1; similarly, 2, 3, 4, and 5 refer to S2, S3, S4, and S5, respectively. The correlation between the predicted value and the reference value of these samples is shown in Fig. 2a. The determination coefficient R^2 using the PLSR model is 0.95 for calibration and 0.93 for prediction. The root-mean square error of calibration and prediction (RMSEC&P) for the model is 0.29 and 0.39, respectively. The results show that the PLSR models are more accurate and reliable than traditional calibration curve methods. Based on the dominant factor across a broad range of sample matrices, the prediction range is chosen purposely to test the robustness of the PLSR model. The results show that for the proposed PLSR model, the RMSE is low while R^2 remains high, showing the overall robustness of the proposed model. This method can compensate for the influence of matrix effects over the conventional internal standard calibration.

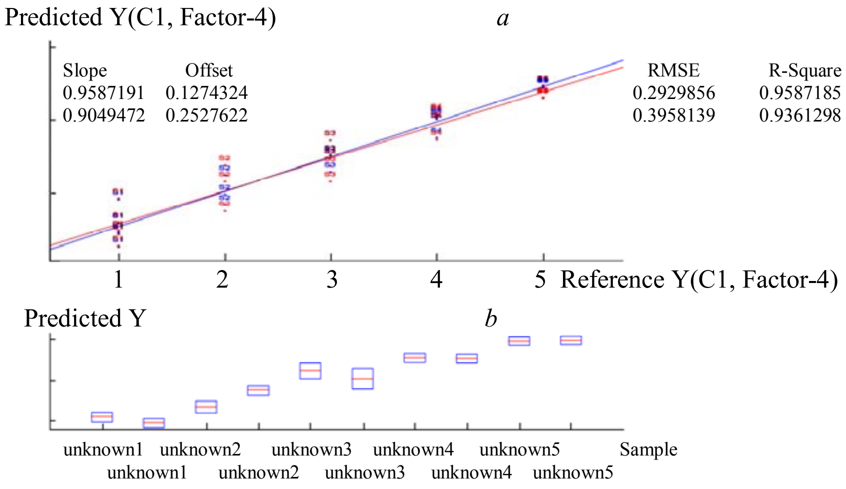

Fig. 2. Predicted vs. reference plot for S1, S2, S3, S4, and S5 of PLSR model (a) and PLSDA model for unknown samples (b).

TABLE 2. Predicted and Deviated Values of Unknown Samples Calculated by PLSDA Model [*]

Samples	Predicted Values	Deviated Values
1	1.1893 0.8983	0.2474 0.2276
2	1.6838 2.4979	0.2771 0.2475
3	3.4453 3.0567	0.3808 0.4878
4	4.0843 4.0486	0.2146 0.2283
5	4.8861 4.9237	0.2082 0.2110

[*] One unknown sample predicted twice.

The established PLSR model using the training data set is then applied to predict the classes of test samples, as shown in Fig. 2b. In order to evaluate the performance of the calibration model, ten samples 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 the calibration set. In Fig. 2b, it is shown that unknown samples 1 contain the predicted value 1 with small deviations corresponding to the class of S1. Similarly, unknown samples 2, 3, 4, and 5 with small deviations belong to the classes of S2, S3, S4, and S5, respectively. It is also observed that unknown samples 3 show large deviation compared to other unknown samples, indicating that samples 3 are not very much similar to reference samples S3. Table 2 shows the predicted and deviated values of the unknown samples, corresponding to each class of known samples. The results show that the spectroscopic analysis of plasma emission can be a promising technique for unknown samples using the PLS method.

Conclusion. The ability of LIBS as a rapid technique for the analysis of fireworks is addressed and the impact of these elements on the environment and human health is also discussed. The chemometrics techniques 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. It can be concluded that without knowing concentration or any other information about the samples, only on the basis of random classes we can develop a model for any unknown samples. The results show good performances on classification, regression, and prediction and provide promising principles for the elaboration of methods, which could be used to discriminate fireworks in various groups and predict quality parameters based on appropriate algorithms for the data. In conclusion, the results presented in this paper demonstrate the applicability of the LIBS technique coupled with multivariate analysis for the analysis of firework samples.

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REFERENCES

1. Ravindra Khaiwal, Suman Morand, C. P. Kaushik, *J. Environ. Monit*., **5**, 260–264 (2003).
2. Min Zhang, Xuemei Wang, Jianmin Chen, Tiantao Cheng, Tao Wang, Xin Yang, Youguo Gong, Fuhai Geng, Changhong Chen, *Atmos. Environ*., **44**, 5191–5198 (2010).
3. Hsieh-Hung Tsai, Li-Hsing Chien, Chung-Shin Yuan, Yuan-Chung Lin, Yi-Hsiu Jen, Iau-Ren Ie, *Atmos. Environ*., **62**, 256–264 (2012).
4. LingxiaoYang China, Xiaomei Gao, Xinfeng Wang, Wei Nie, Jing Wang, Rui Gao, Pengju Xu, Youping Shou, Qingzhu Zhang, Wenxing Wang, *Sci. Total Environ*., **476**, 57–64 (2014).
5. Ying Wanga, Guoshun Zhuanga, Chang Xua, Zhisheng Ana, *Atmos. Environ*., **41**, 417–431 (2007).
6. N. S. Rajurkarand, M. M. Damame, *J. Radioanal. Nucl. Chem*., **219**, 77–80 (1997).
7. C. G. Ryan, *Int. J. Imag. System. Technol*., **11**, 219–230 (2000).
8. Shuenn-Chin Chang, Ta-Hsiung Lin, Chea-Yuan Young, Chung-TeLee, *Environ. Monit. Assess*, **172**, 463–479 (2011).
9. N. Civici, Sh. Gjongecaj, F. Stamati, T. Dilo, E. Pavlidou, E. K. Polychroniadis, Z. Smit, *Nucl. Instrum. Methods Phys. Res. B*, **258**, 414–420 (2007).
10. Prasanthi Inakollu, Thomas Philip, Awadhesh K. Rai, Fang-Yu Yuehand, Jagdish P. Singh, *Spectrochim. Acta B*, **64**, 99–104 (2009).
11. J. E. Carranza, B. T. Fisher, G. D. Yoder, D. W. Hahn, *Spectrochim. Acta B*, **56**, 851–864 (2001).
12. Rohit Kumar, Awadhesh K. Rai. *Environ. Monit. Assess*, **185**, 171–180 (2013).
13. Shikha Awasthi, Rohit Kumar, G. K. Rai, A. K. Rai, *Opt. Laser. Eng*., **79**, 29–38 (2016).
14. Qian-Qian Wang, Kai Liu, Hua Zhao, *Chin. Phys. Lett*., **29**, 044206 (2012).
15. J. L. Gottfried, R. S. Harmon, F. C., Lucia De, Jr., A. W. Miziolek, *Spectrochim. Acta B*, **64**, 1009–1019 (2009).
16. J.-B. Sirven, B. Salle, P. Mauchien, J.-L. Lacour, S. Maurice, G. Manhe, *J. Anal. At. Spectrom*., **22**, 1471–1480 (2007).
17. Shanshan Qiu, Liping Gaoand, Jun Wangn, *J. Food Eng*., **144**, 77–85 (2015).
18. A. Sarkar, V. Karki, S. K. Aggarwal, G. S. Maurya, R. Kumar, A. K. Rai, X. Mao, R. E. Russo, *Spectrochim. Acta B*, **108**, 8–14 (2015).
19. National Institute of Standards and Technology Electronic database http://physics.nist.gov/PhysRefData/ASD/lines form.html
20. W. R. Brode, *Chemical Spectroscopy*, Wiley, New York (1958).
21. G. Steinhauser, J. H. Sterba, M. Foster, F. Grass, M. Bichler, *Atmos. Environ*., **42**, 8616–8622 (2008).
22. W. H. Kojola, G. R. Brenniman, B. W. Carnow. *Rev. Environ. Health*, **3**, 79–95 (1979).
23. T. Moreno, X. Querol, A. Alastuey, F. Amato, J. Pey, M. Pandolfi, N. Kuenzli, L. Bouso, M. Rivera, W. Gibbons, *J. Hazard. Mater*., **183**, 945–949 (2010).
24. Caroline Gouderand Stephen Montefort, *Lung India*, **31**, 375–379 (2014).