Implementation of statistical methods on LIBS data for classification of residues of energetic materials (nitro compounds)

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ABSTRACT

Our key aim is to validate the use of statistical methods for analysis of Laser-Induced Breakdown Spectroscopy (LIBS) datasets of pure nitro compounds (4-nitroaniline and 4-nitrotoluene) and of test samples formed in Cu matrix. Laser-Induced Breakdown Spectroscopy (LIBS) provides the spectral lines of the constituent elements. The interest behind this study is to establish the essence behind the supplementation of LIBS analysis with statistical methods. When the energetic materials were doped with the interferents, such as Cu metal powder it leads to the alteration of the spectral profile of both the target samples, which have similar constituent elements such as C, H, N and O. So, for this situation, it is difficult to classify the test samples from their pure samples only on the basis of its spectral signatures. Hence, in order to classify these sets, we have applied sophisticated chemometric techniques such as linear correlation and Principal Components Analysis (PCA) to familiar LIBS datasets and found that 50% test samples of 4-nitroaniline and 70% test samples of 4-nitrotoluene were successfully discriminated. The causes for partial classification for both the samples have also been discussed in detail. Copyright © 2011 VBRI press.

Keywords: LIBS; nitro compounds; linear correlation; principal component analysis.

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Introduction

Residue detection of energetic materials, which may be either organic or inorganic, has become a key aim for national security as well as prevention of loss of lives and property. The importance of the present work lies in the fact that discrimination and recognition of suspected area soil like soil of battle field or millatry sites that includes energetic material residue can be carried out and is an important task in the present scenario for onsite energetic material residue and environmental contamination detection. Currently for their detection, several spectroscopic techniques [1-10] are available, such as ion mobility spectroscopy, gas chromatography, Raman spectroscopy, and Laser- Induced Breakdown Spectroscopy (LIBS). Among these techniques, LIBS has the capability of multi-elemental analysis of any type of material present in any phase (solid, liquid and gas) [11-16] with minimal sample preparation, with real-time, *in situ*, remote detection, and with the capability of non-destructive determination of elemental composition. It is suitable for rapid identification of nitro compounds by excitation with a single laser shot and subsequent data analysis, taking place almost instantly within a second. Therefore LIBS is promising technique for the detection (identification/ classification) of energetic materials.

LIBS are an emerging spectroscopic technique that operates with high-power laser pulses focused onto a small spot of the sample material. The interaction of the pulsed laser beam with the target sample produces high temperature ionized plasma, containing excited elements which radiate the characteristic emission lines of the corresponding elements. These emission lines are collected by a fiber optic cable with a collecting lens at the tip and on the other end a spectrometer equipped with a Charge coupled device (CCD) detector (gate delay 1.5 μs), whose output is finally displayed on the computer screen. These emission lines provide valuable information about the composition of the sample.

The purpose of this paper is to examine the feasibility of using the LIBS technique together with chemometric techniques, such as linear correlation and Principal Component Analysis, for detection of nitro compounds namely 4-nitroaniline, 4-nitrotoluene and their residues in a Cu matrix. Relative intensity of atomic lines of elements present in the LIBS spectra of the target material has been taken as the prime parameter for spectral matching with a predetermined spectral library. Eight averaged LIBS spectra of 4-nitroaniline and 4-nitrotoluene have been recorded to form the library of pure samples. Eight averaged spectra of their residue in a Cu matrix have been recorded as library of test samples. Each LIBS spectrum is average of ten laser shot. We have employed chemometric techniques to analyze the data sets after formation of the LIBS library.

Experimental

Nitro compounds, such as 4-nitroaniline (99%) and 4-nitrotoluene (99%) and copper metal powder (99.5%) were purchased from the Central Drug House Ltd., India. Test samples were prepared by homogeneously mixing 0.5 g powder of pure nitro compounds in 5 g Cu metal powder. Copper matrix has been used to avoid a matrix containing any element present in compound of interest. Pellets of this powder mixture were formed by applying a pressure of approximately 2×10^8 Pa by a hydraulic machine (supplied by Midvale - Heppenstall Company, Philadelphia, Model no. 341-20). Similarly, pellets of pure 4-nitroaniline and pure 4-nitrotoluene were prepared.

LIBS spectra have been recorded by foucsing Nd:YAG laser (Continuum Surelite III-10, 10 Hz, 425 mJ at 532 nm, 4 ns pulse width) onto the surface of the pellet by using a 150 mm focal-length lens (quartz). More detail related with the experimentation described by the authors elsewhere [17]. The optimum value of the laser energy during this experimentation is found to 18 mJ and resolution of spectrometer is 0.1 nm (from 200-500 nm) and 0.75 nm (from 200-900 nm).Each spectrum is an average of ten laser shots. Finally eight such spectra for pure nitro compounds and eight spectra for residues of these nitro compounds in a Cu matrix were obtained. The library of the intensities of the atomic lines of different elements present in the LIBS spectra of 4-nitroanilie and 4-nitrotoluene was prepared. Similarly, a library of test samples was also produced.

Results and discussion

The averaged spectra of 4-nitroaniline, 4-nitrotoluene, and the residues of these samples in Cu matrix recorded in air are shown in **Fig. 1** (**a, b**) and **2** (**a, b**). Here I and II denotes neutral atom and first ionization state respectively. We have shown the spectra in two distinct spectral regions (from 200-550 nm and 650-780 nm) to observe the peak of emission lines of our interest. It is clear from these Figures that these spectra contain C, H, N, O, Mg and K atomic lines C_2 and CN molecular bands. Magnesium and potassium were the only impurities observed in the spectra of nitro compounds [18]. Using **Fig. 1** and **2**, it is very difficult to make a clear distinction between the LIBS spectra of these compounds because of the fact that spectral profile of LIBS spectra of pure nitro compounds does not remain exactly the same when it is embedded into some matrix, like Cu metal powder, because of the matrix effect. It is only possible when we apply some efficient statistical methods/ chemometric techniques on the LIBS datasets of pure and test samples of nitro compounds. A chemometric technique is the application of mathematical or statistical methods to the experimental data. Therefore the supplementation of statistical methods with LIBS datasets is essential. Therefore, we have used chemometric

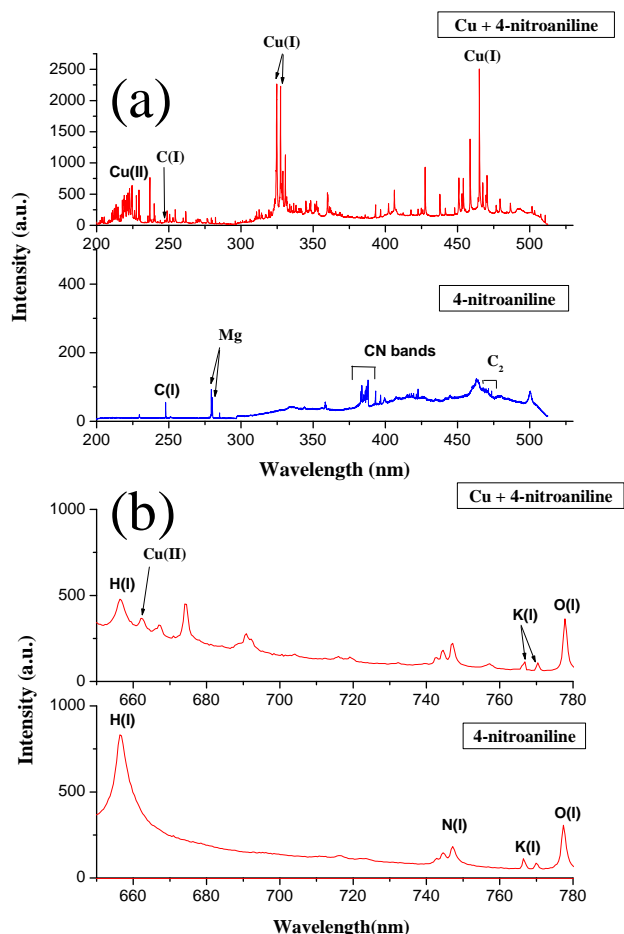techniques to distinguish the LIBS spectra of these compounds.

Fig. 1. Laser-induced breakdown spectra of 4-nitroaniline and test sample which contain traces of 4-nitroaniline in Cu matrix from the spectral range of (a) 200-550 nm and **(b)** 650-780 nm.

Identification of the nitro compounds was done on the basis of the prepared libraries of pure samples (4-nitroaniline, 4-nitrotoluene) and their test samples with the aid of linear correlation [**3**]. The library provides the basis for the comparison of the spectrum of a test sample with the spectra of the pure samples already present in the library. The library consists of 32 spectra (8 spectra of each pure sample and 8 spectra of each test samples). Each sample spectrum exhibits identical molecular bands and atomic lines of elements/species. The intensities of discrete atomic lines and molecular bands were measured from area under the line profile. Therefore, the intensity ratios of elements C (I), H(I), N(I), O(I), and ratios of these atomic line to the molecular bands (i.e. C_2 (swan bands) and CN (violet bands)) were computed for identification of LIBS spectra of the compounds present in the Cu matrix. Fourteen sets of intensity ratios of atomic and molecular bands have been calculated (**Table 1**) and were used as input data for linear correlation. Here the emission line corresponding to elements (C, H, N, O) and molecular bands CN violet and C_2 swan in **Table 1** corresponds to wavelength at 247.8, 656.2, 744.2, 777.1 and 388.34, 473.7 nm, respectively.
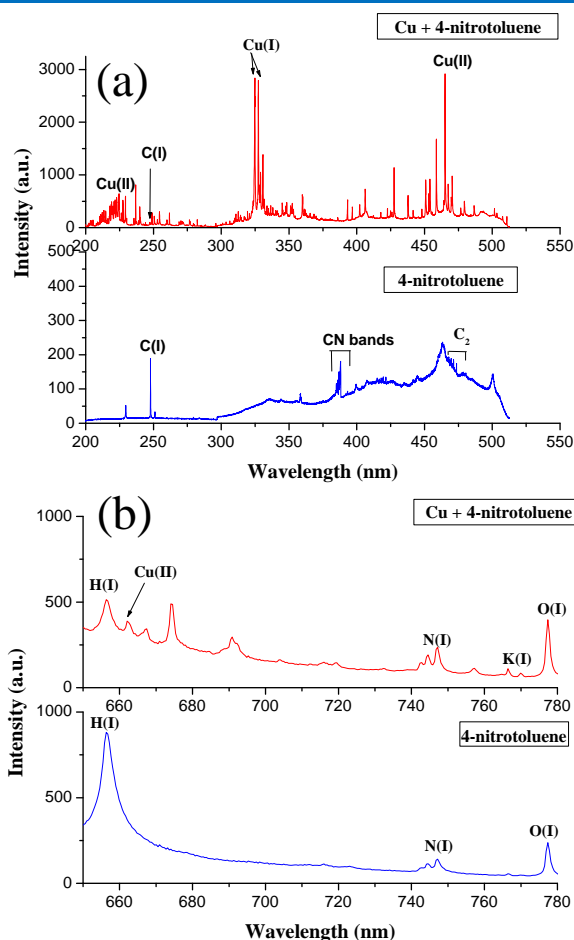

Fig. 2. Laser-induced breakdown spectra of 4-nitrotoluene and test sample which contain traces of 4-nitrotoluene in Cu matrix from the spectral range of (a) 200 - 550 nm and (b) 650-780 nm.

Table 1. Different sets of ratios atomic lines and ratios of atomic to molecular bands.

H(I)/C(I)	C(I)/CN
N(I)/C(I)	O(I)/CN
O(I)/C(I)	H(I)/CN
C_2/C(I)	N(I)/CN
N(I)/H(I)	C_2/CN
O(I)/H(I)	O(I)+N(I)/H(I)+C(I)
O(I)/N(I)	O(I)/N(I)/H/C(I)

To measure relationship between two variables, we have applied linear correlation [**19**] to the above data sets. Each LIBS intensity ratio (y_i) from the library of test samples is examined for correlation with every intensity ratio (x_i) of all the LIBS spectra in the previously constructed library of pure samples (nitro compounds). The correlation coefficient (r) is calculated with the help of data analysis feature of Microsoft Excel and is defined as

$$r = \frac{\sum[(x_i - \bar{x})(y_i - \bar{y})]}{[\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2]^{1/2}} \quad (1)$$

where $\bar{x}$ and $\bar{y}$ are the mean of $x_{i's}$ and $y_{i's}$.

The results of linear correlation analysis of pure nitro compounds with their test samples are shown in **Table 2**. The correlation of each sample with another is indicated by a correlation coefficient r, ranging from -1 to 1, with r = 1 indicating an exact spectral match. In this Table, the reported value of r is the average of ten correlation coefficients evaluated by correlating ten spectra of each test samples individually against all 8 spectra of each nitro compound simultaneously. The highest values of r will occur for the correlation of each sample with itself, indicating a positive identification of the sample.

Table 2. Correlation coefficient (r) of nitro compounds.

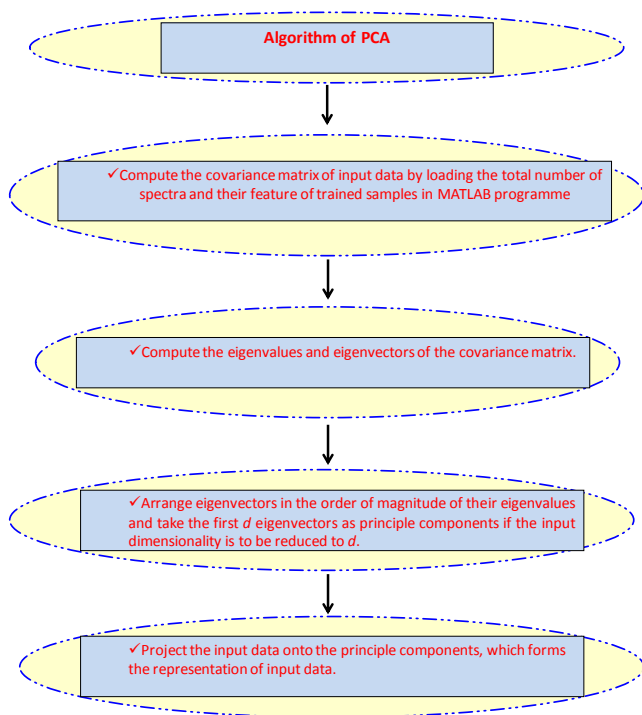| Pure nitro compounds → Test sample of nitro compounds ↓	$C_6H_6N_2O_2$ (4-nitroaniline)	$C_7H_7NO_2$ (4-nitrotoluene)
$Cu+C_6H_6N_2O_2$	.987	.980
$Cu+C_7H_7NO_2$	.976	.985

Fig. 3. Set of instructions used in the PCA programme running under MATLAB version 7.0.

Table 2 indicates that the test sample of 4-nitroaniline is correlated almost equally well with respect to 4-nitroaniline and 4-nitrotoluene. Thus, identification of an unknown sample is not always possible with this method. The limitations associated with this analysis include the fact that when we have multivariate data sets having similar elemental nature/similar constituents, use of this analysis become very lengthy and time consuming and also it does not have the capability of characterizing and mapping interrelationships between data sets of pure and test samples. Hence, in order to overcome these difficulties, alternative ways are required to fulfill the requirements to correlate the data sets of pure and test samples. This alternative method is a dimension reduction technique based on a dispersion (covariance) matrix, which transforms the input space into a lower-dimensional feature space, such that the feature space retains the maximum characteristics of the input space. This method is known as Principal Component Analysis (PCA) [**20-22**]. The algorithm of the PCA is summarized in flow chart (**Fig. 3**).

Therefore, here we have applied PCA [**4**] to overcome the limitation involved in linear correlation which is most frequently used for measuring the association between two variables among categorized samples. As compared to linear correlation PCA have several other capabilities: it is suitable for data sets in multiple dimensions, for extracting the trend of data set which ease the task of characterization of several class of the samples and hence also use in pattern recognition. It is based on the orthonormal eigenvectors and eigenvalues of the covariance matrix of the original features or variables. These orthonormal eigenvectors are used for constructing the principal components, and the eigen - values are the variances of the corresponding principal components. Finally, the LIBS intensities are projected onto the eigen - vectors of the covariance matrix of the pure spectra which are linear combinations of the intensity levels in the input space themselves. These projections are called the principal components.
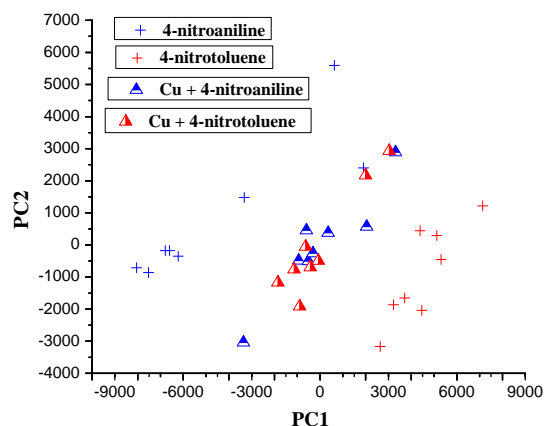

Fig. 4. PCA scores plots of nitro compounds and their test samples in selected spectral regions (200-800) nm. (+ and ▲) are used for distinction of trained and test samples.

In the present work, PCA has been performed on the data related to the intensities of atomic lines of each pixel in the spectral region from 200 to 800 nm. This analysis has been carried out by dividing the sample sets into two different categories such as training set (4- nitroaniline and 4-nitrotoluene) and test set (nitro compounds residue in Cu matrix).The methodology consists of applying PCA on the training set which consists of 16 spectra, 8 from each nitro compounds (4-nitroaniline and 4-nitrotoluene). There are 1325 pixels with different wavelengths in the wavelength range mentioned above. Each of these wavelengths corresponds to one dimension in the multi - dimensional representation of the spectra of 16 data points. This gives a data matrix of dimensions 16×1325, i.e., a row matrix composed of data set of 16 spectra each with 1325

dimensions (column). Each column in this matrix is referred to as feature. Thus we have 1325 features and 16 spectra represented by these features. The visualization of 1325 dimensions is very difficult to represent pictorially and it is almost impossible to interpret the relationships between the training and test data sets. PCA is done to reduce the dimensionality of the data matrix by identifying the directions of maximum variances in the data set so that the features that have minimum or no variance may be neglected. The first two principal components explain 85.7% (PC1) and 12.3% (PC2) of the total variance within the dataset. A 2-dimensional PCA scores plot for the trained samples is shown in **Fig. 4**. The data sets for the test samples have also been projected on the two eigen - vectors (corresponding to PC1 and PC2) as shown in **Fig. 4**. It can be seen that the training samples of 4-nitroaniline and 4-nitrotoluene form clearly separable clusters. This clustering of samples can be used for classification of test samples.
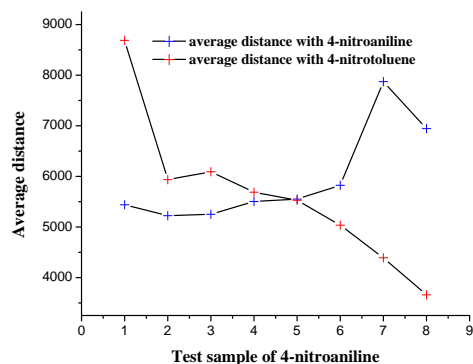
classification of test samples of 4-nitroaniline indicates that the clusters of the 4-nitroaniline have linear discrimination boundary as compared to 4-nitrotoluene, causing less distinction for test samples of 4-nitroaniline

Conclusion

We have successfully examined the efficacy of statistical methods using LIBS datasets. Here we have preferred LIBS technique rather than other techniques like AAS, ICP etc because of the fact that in other technique; sample is introduced into the instrument in the form of solution only and applicable for trace metal detection only. In AAS we can only determine only one element at a time. As comparison of it, LIBS is applicable to all samples from whatever its nature (solid, liquid or gas) and also possessing ability of multi-elemental analysis. Present study infers that PCA is very efficient tool for the discrimination of the samples in contrast to the linear correlation. Examination of average distance plot in PCA provides distinct features about the category of test sample classes. Work is in progress to perform the PCA for particular sets of intensity ratios for improvement of results related with the classification of samples. We are also trying to perform the aforesaid experimentation in an argon atmosphere in order to study the comparative effect of this atmosphere over the constituent elements of nitro compounds and percentage of classification.

Fig. 5. Plot of average distance from the each data points of test sample of 4-nitroaniline with respect to all data points of trained data sets.
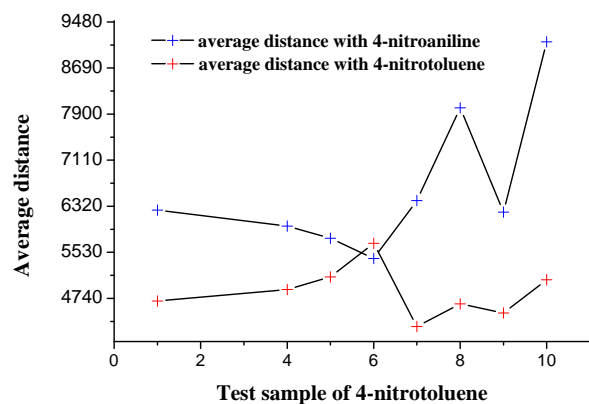

Fig. 6. Plot of average distance from the each data points of test sample of 4-nitrotoluene with respect to all data points of trained data sets.

Classification of the test samples is based on fact that the test samples belongs to that class with which its average Euclidean distance is minimum, shown in **Fig. 5** and **6**. A close observation of **Fig. 6** shows that test samples of 4-nitrotoluene are classified correctly almost for every sample whereas the test samples of 4-nitroaniline are comparatively less separable in a few cases. The relatively lower

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