Rapid Analysis of Energetic and Geo-Materials Using Laser Induced Breakdown Spectroscopy

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**Abstract:**
The laser induced breakdown spectroscopy (LIBS) technique has been used to analyze a diverse array of materials for several decades. LIBS is ideal for rapid materials analysis since data can be collected in real time with no sample preparation. The coupling of LIBS with multivariate analysis has increased in recent years and allows for rapid processing of spectral information for qualitative or quantitative analysis. We discuss several examples of how LIBS and multivariate analysis has been used to classify geological and energetic materials at the U. S. Army Research Laboratory. It is important to understand the parameters that influence the results and the limitations of multivariate analysis for LIBS applications.

**Subject Terms:**
LIBS, qualitative, multivariate analysis, geological materials, energetic materials
Rapid analysis of energetic and geo-materials using LIBS

The laser induced breakdown spectroscopy (LIBS) technique has been used to analyze a diverse array of materials for several decades. LIBS is ideal for rapid materials analysis since data can be collected in real time with no sample preparation. The coupling of LIBS with multivariate analysis has increased in recent years and allows for rapid processing of spectral information for qualitative or quantitative analysis. We will discuss several examples of how LIBS and multivariate analysis has been used to classify geological and energetic materials at the United States Army Research Laboratory. It is important to understand the parameters that influence the results and the limitations of multivariate analysis for LIBS applications.

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Laser-induced breakdown spectroscopy (LIBS) has been used for a wide range of materials analysis applications ever since the inception of the term “LIBS” in 19811,2. Specific applications include analysis of metal alloys3-6, plastics7-9, ceramics10-12, biological material13-16, and geological materials17-20. LIBS is an optical spectroscopic technique that uses a focused laser pulse, of the order of tens to hundreds of millijoules, to generate a microplasma that subsequently vaporizes a small amount of the target sample. A dispersive spectrometer and detector is used to collect the light from the plasma in order to resolve the signatures of the excited atomic, ionic, and some molecular species. A selection of books and review articles describe the breadth and growth of LIBS materials analysis over the past few decades21-32.

LIBS has several attributes that make it an attractive tool for rapid materials analysis: (i) no sample preparation is required; (ii) it provides a real-time (< 1 second) response; (iii) only nanograms – picograms of the material is required for production of a usable LIBS spectrum; and (iv) relatively simple components (i.e., laser, optics, detector, computer, etc.) are used for experiments. This last attribute makes LIBS useful for different types of application in the laboratory, portable field systems, and standoff analysis. Field-portable LIBS instruments have been used for many applications, including the determination of lead (Pb) in soil and paint33, the online sorting of wood34, and the analysis of paints and coatings35.

LIBS instruments at a distance, or standoff LIBS, have been demonstrated at distances up to 100 meters for environmental36, industrial37,38, cultural heritage39, and geological applications18,40.

A typical LIBS experiment (example setup shown in Fig. 1) uses a focused laser pulse at the fundamental wavelength from a Nd:YAG laser. However, there are numerous studies that have investigated...
the influence of different laser parameters such as wavelength, pulse width (femto-, pico-, nanosecond), energy, and number of pulses. Focusing optics are used to generate the microplasma on the sample. Next, collection optics are used to capture the emission from the microplasma and direct it towards the collection device. Typically, a dispersive spectrometer and an intensified charge coupled device (ICCD) are used for detection; however a wide range of spectrometers and detectors (CCDs, electron multiplying CCDs, photomultiplier tubes and photodiode arrays) have been employed.

The most common types of analysis performed using LIBS spectra are qualitative classification and quantification. A typical LIBS spectrum is made up of multiple emission lines primarily due to atomic species. The specific wavelength of the atomic emission line corresponds to a particular element. Most elements have multiple emission lines; iron for example has hundreds. Fig. 2 shows the LIBS spectrum of a stainless steel standard reference material (SRM 1155). Multiple atomic emission lines of iron are present, as well as chromium and nickel. The nitrogen and oxygen atomic emission lines are due to the surrounding atmosphere. These can be eliminated by blowing a bath gas across the surface if desired. In the inset, we focus on a small section of the spectrum from 335 – 375 nm that contains multiple atomic emission lines due to iron, nickel, and chromium. LIBS used in conjunction with broadband detectors (ultraviolet – visible – near-infrared spectral range) can determine the elemental composition of any target material since every element on the periodic table has characteristic atomic emission lines in the UV-VIS-NIR spectral range. Therefore, an elemental inventory can be obtained of any sample of interest using a LIBS spectrum. Beyond tabulating the elements present in a sample, the intensity of an atomic emission line can be correlated to the amount of the material present in the sample. LIBS has been used in numerous quantification studies for steel, aluminum alloys, bronze, ceramics, surface mapping, and many more applications.

Fig. 1 LIBS experimental setup (a) Nd:YAG laser, (b) focusing optics, (c) pierced mirror, (d) microplasma, (e) sample, (f) collection optics, and (g) spectrometer/detector.

Fig. 2 Broadband LIBS spectrum of stainless steel (NIST standard reference material 1155). Inset. Sub-section of steel spectrum from 335 – 375 nm.
Rapid analysis of energetic and geo-materials using LIBS

In general, limits of detection (LOD) for LIBS are in the parts per million (ppm) range. However, the LOD value of a given element will depend on experimental parameters such as laser energy, surrounding matrix, and the experimental setup. Reported LODs in the literature are intrinsically related to the particular application and experimental apparatus described in the article.

There are several difficulties associated with the collection and analysis of LIBS spectra. Even though the experimental setup of a LIBS system is relatively simple, the non-linear processes underlying the formation of the microplasma are highly complex. Therefore, the shot-to-shot variation is an inherent issue with all LIBS experiments due to the laser material interaction. The properties of the material being interrogated by the laser will influence the LIBS signal due to matrix effects. In addition, if the material is heterogeneous, the microplasma will sample regions in the material with different compositions.

Identifying molecular compounds with similar elemental composition is also difficult since LIBS is fundamentally an elemental technique. Some molecular information, such as relative stoichiometries, can be determined from relative atomic peak emission intensities, but it is not a straightforward analysis. In addition, each LIBS experimental setup is intrinsically tied to the application for which it is designed. The data analysis method must be revisited if the experimental setup or application is altered. LIBS is a versatile tool for materials analysis, capable of providing large amounts of data quickly using a relatively simple experimental setup. However, obtaining useful information and analyzing that information requires careful experimentation and an understanding of the underlying system being investigated.

Analysis of LIBS spectra using multivariate analysis

High-resolution, broadband LIBS spectra can contain as many as 100,000 variables as seen in the LIBS spectrum of stainless steel shown in Fig. 2. These variables include atomic emission lines, ionic emission lines, molecular bands, and background emission. Depending on the application, multiple spectral regions may need to be analyzed simultaneously. The ability to quickly process all of the data in a useful manner is a challenge. Multivariate analysis is a technique used to reduce or compress the spectral data into fewer combinations of variables that still retain the essential information describing the data set. Furthermore, the essential information must then be extracted in a manner that can be easily displayed. The coupling of LIBS spectral data with multivariate analysis techniques has been a major advance for LIBS analysis of materials over the past decade. The increase in LIBS publications using multivariate techniques over the last few years is shown in Fig. 3. The use of multivariate analysis with LIBS for data analysis includes quantitative analysis and classification.

One of the earliest combinations of LIBS with a multivariate technique utilized a principal components regression (PCR) calibration model to determine detection limits of trace heavy metals in soils, sands, and sewage sludge. Another early study used neural networks to classify polymers based on nine spectral regions of interest in the LIBS spectra. Multivariate techniques for classification and quantification have been used for a variety of LIBS material analysis applications. Amador-Hernandez et al. used principal components analysis (PCA) to obtain sample composition plots of screen-printed electrodes. Another classification technique, soft independent modeling of class analogy (SIMCA), was used to differentiate between bacterial spores, molds, pollens, and nerve agent simulants. Partial least squares discriminant analysis (PLS-DA) was used to test the feasibility of classifying rocks based on LIBS spectra for eventual use on the Mars Science Laboratory rover. LIBS spectral data was used for the multivariate calibration technique partial least squares (PLS) regression in order to quantify the amount of gold and silver in gold-silver-copper alloys. In addition to trace heavy metal analysis, PCR has been used to measure the composition of iron ore samples.

At the US Army Research Laboratory (ARL), we have primarily used the multivariate techniques PCA, SIMCA, and PLS-DA to classify hazardous materials such as explosives, biological and chemical weapon simulants. PCA is an unsupervised multivariate technique that compresses large data sets in order to extract useful information by finding combinations of variables that describe major trends in the data. The large data set is reduced to weighted sums of the original variables. These weighted sums, or scores, are used to describe variations in the data. Since PCA is unsupervised, it seeks to describe the overall variation in the data. This may not be useful for differentiating between different classes of samples. Therefore classification techniques such as SIMCA and PLS-DA are more useful for describing data sets that consist of many measurements of several samples or classes. A SIMCA model consists of a collection of PCA models. Each PCA model within the SIMCA model describes a particular sample type or class from the data set. SIMCA incorporates the properties of PCA models with...
information about the types of classes incorporated in the sample data set. The SIMCA model is then used to determine the nearest class for unknown test samples. For material analysis performed at ARL, we have found that PLS-DA offers the best classification results. PLS-DA is a supervised, inverse least-squares discrimination method used to classify samples. In PLS-DA, the predictor variables or latent variables (LV) are generated from the input variables to determine the maximum variance between each sample class, unlike other techniques such as PCA and SIMCA. PLS-DA maximizes the inter-class variance while minimizing the intra-class variance. For LIBS this is important due to the inherent shot-to-shot variability. If the variance in shot-to-shot variability approaches the inter-class variance, then unsupervised techniques like PCA will not be able to separate the different samples. The PLS-DA model calculates the probability that a test sample belongs to a particular class in the model. Parameters that will influence model performance include the chosen spectral regions of interest, the types of samples in a class, the number of classes, and the number of latent variables. It is important to determine the variables that most contribute to the separation between classes in the model. This will assure that the separation is due to the physical or chemical properties of the underlying system. Further iterative testing with independent test sets are needed to optimize the model.

At ARL, we have used LIBS to qualitatively analyze a wide variety of materials. We have analyzed metals to determine the trace impurities in aluminum alloys, the composition of steel parts, and solder compositions. We have used LIBS to analyze thermoplastic polymers, painted surfaces, and plastic land mine casings. In this paper, we will focus in detail on implementation of multivariate analysis to characterize and classify geomaterials and explosive materials at ARL. Even though we are focusing on two types of material of interest to ARL, the methods we describe can be applied to all types of material classification applications with LIBS.

Materials analysis at ARL

Geomaterials

Using LIBS to analyze geomaterials at ARL began with the desire to detect lead contamination in soil from military installations. The potential of LIBS as a field portable instrument for in situ geochemical analysis has been explored. More recently, LIBS spectra were collected from a wide variety of geomaterials, including garnet samples collected worldwide, obsidian samples from the southwestern United States, and a survey of carbonates, fluorites, silicate rocks, and soils. In general, all of the geomaterials analyzed with PLS-DA and LIBS were classified correctly by the most optimized multivariate model.

The garnet samples consisted of six different types that could be discriminated based on their composition. Interestingly LIBS demonstrated promise for identifying the geographic origin of garnets of the same type. Broadband spectra of each garnet type were used as variable inputs for the PLS-DA models. It was assumed that the PLS-DA model would use the emission wavelengths that were most capable of separating the six garnet types. Subsequent analysis of the model using variable importance in projection (VIP) scores confirmed this assumption. The VIP scores are used to determine how much each variable in a model contributes to the separation between the classes. Generally, a variable with a VIP score greater than 1.0 is important to a model. In addition, to determine what variables are influencing the classification in a particular model, the variables that do contribute to classification should have physical meaning for the system being investigated. The VIP scores from the composition model and the origin models are displayed in Fig. 4. In this case, the major variables that contribute to classification correspond to the expected chemical properties. For the classification of the six garnet types based on composition, atomic spectral intensities due to the major elements in each garnet composition (Ca, Mg, Al, Fe, Mn, Cr) were responsible for the separation between the classes. For origin determination, atomic spectral intensities from contaminants and impurities (Na, K, Li, H), likely associated with surrounding environment, were largely responsible for the separation. The variables that most influence classification are dependent on how the samples are classified in a particular multivariate model. In this case, we observe the most influential variables for the model based on composition classification differs from the most influential variables for the models based on geographical origin classification.

The obsidian samples were collected from multiple sites at the Coso Volcanic Field (CVF) in California and single sites at four other locations. Remus et al. constructed multiple PLS-DA models to analyze different facets of the sample set, primarily to determine the provenance of each sample. Broadband spectra were compared to pre-selected atomic emission intensities and atomic emission intensity ratios from the LIBS spectra as variable inputs. Minimal differences...
in model performance were found for this application. In a study of the subset of obsidians collected from CVF, models were constructed based on eight different collection sites, i.e., each collection site was represented by a class in the model. However, these models were outperformed by subsequent PLS-DA models consisting of four classes based on geological evidence that grouped some of the sites together. The obsidians were ~70 – 80 % correctly classified based on the models that grouped sites together based on geography. By contrast, the obsidians were only classified correctly ~40 – 50 % of the time based on the models that used the eight different sites as classes. This result demonstrates the importance of designing and constructing a model based on the actual properties of a set of samples.

Finally, multivariate analysis was used on a series of geomaterials: carbonates, fluorites, silicate rocks, and soils, in order to classify samples. In this case, Gottfried et al. used several different experimental configurations to collect spectra of the geomaterials: single pulse LIBS, double pulse LIBS, and standoff LIBS. An example of LIBS spectra collected from the same obsidian sample using each experimental configuration is shown in Fig. 5. As expected, the spectra have different features and intensities due to differences in laser intensity, spectrometer response, and light collection optics. These differences clearly illustrate that any multivariate predictive model created from data from one experimental configuration cannot be used successfully with another experimental setup. However, excellent classification was achieved for each of the geological sample groups studied as long as the multivariate models designed for a particular experimental setup were used.

Explosives
The primary focus of LIBS at ARL has been on the detection of explosive residue and the subsequent discrimination from benign background clutter. This is a challenging problem since the majority of military explosives are organic and thus only contain carbon, hydrogen, oxygen, and nitrogen. These same elements can be present in non-explosive interferents and substrate materials making discrimination and classification difficult. In addition, since trace amounts of sample are being interrogated, weaker elemental emissions from the LIBS spectra are expected. Both laboratory and standoff experimental configurations and several multivariate techniques have been used to classify materials as either explosive materials or as interferents based on LIBS spectral signatures. The initial coupling of LIBS with multivariate analysis at ARL involved using principal components analysis (PCA) to determine the feasibility of separating cyclotrimethylenetrinitramine (RDX) from diesel fuel. Gottfried et al. used a standoff LIBS instrument to collect LIBS spectra from a variety of explosive and non-explosive samples. Several multivariate techniques including linear correlation, PCA, SIMCA, and PLS-DA were used to determine if a sample was an explosive or a non-explosive.
Rapid analysis of energetic and geo-materials using LIBS

PLS-DA was determined to be the most effective analysis technique for correctly classifying test samples as either explosive or non-explosive, including explosives and interferents that were not in the model and mixtures of explosives and interferents. De Lucia et al. constructed PLS-DA models based on LIBS spectral signatures collected at standoff distances of 20 and 30 meters of RDX, dust, oil, and blank substrate. A typical standoff, broadband LIBS spectrum of RDX is shown in Fig. 6. Multiple test samples, including three types of explosives, four interferents, several different mixtures of explosives and interferents, and samples collected at 50 meters were tested against the optimized PLS-DA model. The number of individual test samples that classified as explosives is displayed in Table 1. Overall the model performed well against samples collected at 20 and 30 meters with an 87 % true positive rate (TPR) and a 1.2 % false positive rate (FPR). The trace fingerprints and mixtures were the poorest performers for explosives determination. Since, the mixtures were heterogeneous, the microplasma might not interrogate any explosive at all for some of the test shots. The ability to prepare samples in such a way that one would know the exact sample composition in the microplasma is difficult, especially for mixtures, but it would be beneficial for model building and validation. In addition, the model performed poorly against the test set collected at 50 meters, 15 % TPR and 8 % FPR. Originally, the standoff instrument was designed with the intent of collecting spectra out to 30 meters. So at 50 meters, the spectra quality will be obviously diminished. Subsequently, a new PLS-DA model was constructed using input variables from LIBS spectra collected at 50 meters instead of 20 – 30 meters. This model

Table 1 Results from PLS-DA model for determining if a test sample belongs to the explosive class.

<table>
<thead>
<tr>
<th>Samples at 20 – 30 meters</th>
<th># classified as explosives</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>69/70</td>
</tr>
<tr>
<td>RDX trace fingerprints</td>
<td>38/50</td>
</tr>
<tr>
<td>TNT</td>
<td>50/50</td>
</tr>
<tr>
<td>Comp-B</td>
<td>50/50</td>
</tr>
<tr>
<td>RDX+ road dust</td>
<td>201/250</td>
</tr>
<tr>
<td>RDX+oil</td>
<td>195/225</td>
</tr>
<tr>
<td><strong>True Positive Rate</strong></td>
<td>87 %</td>
</tr>
<tr>
<td>House dust</td>
<td>1/50</td>
</tr>
<tr>
<td>Fingerprints</td>
<td>0/100</td>
</tr>
<tr>
<td>Oil + road dust</td>
<td>3/150</td>
</tr>
<tr>
<td>Oil</td>
<td>0/10</td>
</tr>
<tr>
<td>Road dust</td>
<td>0/10</td>
</tr>
<tr>
<td><strong>False Positive Rate</strong></td>
<td>1.2 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Samples at 50 meters</th>
<th># classified as explosives</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 – 30 meter PLS-DA model</td>
<td></td>
</tr>
<tr>
<td>RDX+ road dust</td>
<td>3/20  TPR 15 %</td>
</tr>
<tr>
<td>Oil+ road dust</td>
<td>3/18  FPR 8 %</td>
</tr>
<tr>
<td>Fingerprints</td>
<td>0/20</td>
</tr>
<tr>
<td>50 meter PLS-DA model</td>
<td></td>
</tr>
<tr>
<td>RDX+ road dust</td>
<td>16/20 TPR 80 %</td>
</tr>
<tr>
<td>Oil+ road dust</td>
<td>1/18 FPR 8 %</td>
</tr>
<tr>
<td>Fingerprints</td>
<td>2/20</td>
</tr>
</tbody>
</table>

Fig. 6 Broadband LIBS spectra of RDX obtained at 20 meters with a double-pulse standoff LIBS system. Labeled emission lines of compositional elements (C, H, N, O) and impurities (Ca, Na, K).
was tested against a validation sample set that included additional spectra collected at 50 meters and improved the TPR to 80%. These experiments demonstrated the importance of knowing the underlying composition of the test samples as well as experimental parameters such as distance to target when validating a model. It is also essential to understand the limits of the LIBS instrumentation when building a robust predictive model for a particular application.

In the first study of its kind, Gottfried et al. developed a PLS-DA model to test the ability to discriminate explosive residues from interferents on a variety of surfaces\(^9\). The PLS-DA model was based on LIBS spectral signatures from a small set of residues: RDX, oil, and dust, placed on six different surfaces including aluminum, white rubber, red silicone, wood, cardboard, and travertine. A validation set composed of the residues on each surface was used to test the model returning a true positive rate (TPR) of 88.6% and a false positive rate (FPR) of 12.7%. A second validation set that included the explosive residues on surfaces not included in the model (tan silicone, clay tile, slate, and blue plastic) was also used to test the model. The classification of the explosive on the tan silicone and the slate surface performed poorly (TPR of 56.7% and 5% respectively). For this particular model and LIBS system, it is important to understand the limits of the application. Only a certain set of surfaces can be interrogated for explosive residues using this particular model. Gottfried et al. also showed that the model could be altered in order to incorporate residues on slate. Input variables collected from LIBS spectra of the various residues on slate were added to the model. Subsequent analysis of the new model using the explosive on slate validation set increased the TPR from 5% to 50%. These results demonstrated that LIBS and multivariate analysis can classify successfully as long the boundaries and limitations of the model and LIBS system are clearly defined.

These results have shown the feasibility of using LIBS and multivariate analysis to separate explosive residues from non-explosive interferent materials based on the chemical composition of explosives. The TPR and FPR values described above are useful for comparing different models and testing the feasibility of discriminating between explosives and non-explosives. However, as predictive values for describing how well LIBS can detect trace explosive residues, further refinement of the model and quantifying the trace residues would be necessary. The results from any of the PLS-DA models are dependent on experimental configurations, model input variables, and model parameters. It is also observed that while the multivariate models can correctly classify some samples not included in a model, other samples not defined in the model will be misclassified. In order to define the scope of materials a model can successfully classify, it must be optimized by iteratively testing with independent validation sets that include samples identical to those used as model inputs, similar samples to those used as model inputs, and samples not included in the model.

**Conclusions and discussions**

In the field of LIBS, a wide range of materials for many diverse applications have been analyzed demonstrating its versatility. LIBS has been used for capturing a simple inventory of a material’s elemental composition and for more complex quantitative and classification analysis. Rapid analysis of samples is one of the reasons LIBS is an ideal technique for materials analysis. The collection of numerous high-resolution, broadband spectra can be achieved quickly since data collection occurs in real time and no sample preparation is required. In order to get real time analysis such as classification or quantification, the high dimensional data set acquired from a LIBS spectrum must be processed in a timely manner. For this reason, we expect research coupling multivariate analysis with LIBS to continue to increase in the future. Multivariate analysis can process large data sets in a computationally efficient manner by reducing high dimensional data to lower dimensional factors that describe the variance between sample sets. A predictive model, derived from LIBS spectra, is developed to elucidate information about a sample set based on its LIBS spectral signatures. Once an effective predictive model is produced, it can rapidly return the desired information about the sample set. The major challenge is producing an effective predictive model that is both accurate and robust.

One of the most important aspects of a predictive model is the quality of the data used to populate the model. The predictive ability of the model is entirely dependent on having a high quality set of data that is representative of the system being investigated. For building a model based on LIBS spectra, the spectra should be representative of the system being studied and classed together in a way that is aligned with the underlying physical or chemical properties of the system. Having an understanding of the composition of a sample whose LIBS spectra will populate a predictive model is desirable. Once the model is populated with high quality data, the variable inputs responsible for separation between the classes need to be determined to ensure that the separation is due to the underlying chemistry or physical properties of the system. Finally, the model needs to be iteratively tested and optimized with independent data sets that include a wide range of samples that could be encountered for a particular application. Once the multivariate model has been developed, the true potential of LIBS as a rapid, versatile sensor technique can be achieved.
The coupling of LIBS with multivariate analysis will continue to expand for materials analysis, especially into industrial and field applications where rapid analysis is essential. Even though this manuscript focused on materials of interest to the Army, the advantages and limitations of multivariate analysis described can be applied to all types of material analysis. As the development of turn-key LIBS instruments for materials analysis continues to grow, it is important to define the capabilities of each instrument, not only in terms of the LIBS hardware parameters but also in terms of the application and analysis software parameters and limitations.
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