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## **Laser-Induced Breakdown Spectroscopy: A Review of Applied Explosive Detection**

**by John J. Brady, Stephen D. Roberson, Mikella E. Farrell, Ellen L. Holthoff,  
Dimitra N. Stratis-Cullum, and Paul M. Pellegrino**

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**ARL-TR-6649**

**September 2013**

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# REPORT DOCUMENTATION PAGE

*Form Approved*  
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<b>1. REPORT DATE (DD-MM-YYYY)</b> September 2013		<b>2. REPORT TYPE</b> Final		<b>3. DATES COVERED (From - To)</b>	
<b>4. TITLE AND SUBTITLE</b> Laser-Induced Breakdown Spectroscopy: A Review of Applied Explosive Detection				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> John J. Brady, Stephen D. Roberson, Mikella E. Farrell, Ellen L. Holthoff, Dimitra N. Stratis-Cullum, and Paul M. Pellegrino				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> U.S. Army Research Laboratory ATTN: RDRL-SEE-E 2800 Powder Mill Road Adelphi, MD 20783-1198				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>  ARL-TR-6649	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> Approved for public release; distribution unlimited.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The complex chemical nature of the current military environment complicates the ability of the Warfighter to detect an explosive threat prior to detonation. The challenge is further complicated when standoff or proximal detection is needed. In this report, results from a survey of current literature and available industry data are used to provide an assessment of laser-induced breakdown spectroscopy (LIBS) phenomenology for explosives detection, as well as recognize potential gaps in knowledge. Examination of the literature reveals that there are many strengths and challenges associated with the LIBS techniques and its variants. These challenges, such as varied signal intensities due to matrix effects, are being addressed by examining the role of pulse duration, wavelength, and fluence in LIBS and by developing parallel techniques (e.g., dual-pulse LIBS) to reduce or nearly eliminate interferences. Despite advances in the LIBS research to mitigate these matrix effects, sample analysis remains arduous due to the complex emission spectra obtained. Therefore, the use of chemometrics to aid in the discrimination of hazardous material has recently been examined with some limited success. Based on the information gathered from this report, a list of recommendations for future research and/or development to increase the utility of the technique for trace standoff explosive detection is provided.					
<b>15. SUBJECT TERMS</b> LIBS, explosive detection, standoff					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
<b>a. REPORT</b> Unclassified	<b>b. ABSTRACT</b> Unclassified	<b>c. THIS PAGE</b> Unclassified	UU	58	Ellen L. Holthoff
					<b>19b. TELEPHONE NUMBER (Include area code)</b> (301) 394-0939

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## Contents

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<b>List of Figures</b>	<b>v</b>
<b>List of Tables</b>	<b>vi</b>
<b>Acknowledgments</b>	<b>vii</b>
<b>1. Introduction</b>	<b>1</b>
<b>2. Trace Explosive Detection Techniques</b>	<b>3</b>
2.1 Chromatographic Techniques.....	6
2.2 Colorimetric Techniques .....	6
2.3 Amplifying Fluorescent Polymers.....	6
2.4 Biological-Based Techniques.....	7
2.5 Ion Mobility and Mass Spectrometry Techniques .....	7
2.6 Laser-Based Techniques.....	8
2.6.1 Photodesorption and Photofragmentation .....	8
2.6.2 Spontaneous Raman Scattering .....	8
2.6.3 Infrared Laser-Based Techniques .....	9
<b>3. Laser-Induced Breakdown Spectroscopy</b>	<b>10</b>
3.1 Laser-Induced Breakdown Spectroscopy Basics .....	10
3.2 Qualitative And Quantitative Laser-Induced Breakdown Spectroscopy .....	13
3.3 Chemometric-Based Approaches for Material Identification .....	14
3.4 Modeling Plasmas in Laser-Induced Breakdown Spectroscopy .....	15
3.5 Common Difficulties in Laser-Induced Breakdown Spectroscopy .....	17
3.5.1 Matrix Effects in Laser-Induced Breakdown Spectroscopy.....	17
3.5.2 Frequency Dependence in Laser-Induced Breakdown Spectroscopy .....	19
3.5.3 Robust Algorithms for Material Identification.....	20
<b>4. Laser-Induced Breakdown Spectroscopy Techniques for Enhanced Detection of Hazardous Materials</b>	<b>20</b>
4.1 Enhancement of the Laser-Induced Plasma .....	21
4.1.1 Dual-pulse Laser-Induced Breakdown Spectroscopy .....	21

4.1.2	Townsend Effect Plasma Spectroscopy .....	22
4.1.3	Microwave-Enhanced Laser-Induced Breakdown Spectroscopy.....	23
4.2	Orthogonal Laser-Induced Breakdown Spectroscopy Techniques .....	23
4.2.1	Raman-Laser-Induced Breakdown Spectroscopy .....	24
4.2.2	Laser-Induced Breakdown Spectroscopy-Laser-Induced Fluorescence .....	25
4.3	Short Pulse Laser-Induced Breakdown Spectroscopy.....	27
<b>5.</b>	<b>Industry Review</b>	<b>29</b>
<b>6.</b>	<b>Conclusions and Future Recommendations</b>	<b>32</b>
<b>7.</b>	<b>References</b>	<b>33</b>
	<b>List of Symbols, Abbreviations, and Acronyms</b>	<b>46</b>
	<b>Distribution List</b>	<b>48</b>

---

## List of Figures

---

- Figure 1. A schematic depicting a typical LIBS experimental setup.....11
- Figure 2. (a) The number of publications, as compiled from Science Citation Index Search 11Sept2012, with keywords: laser-induced breakdown spectroscopy/plasma and explosive. This demonstrates an increase in the number of LIBS publications as a function of time. (b) The total number of LIBS publications, related to all sample types, per year.....11
- Figure 3. The life cycle diagram showing the main events in the LIBS process. Taken from V. P. Andrzej W. Miziolek, I. Schechter, *Laser-Induced Breakdown Spectroscopy*. (Cambridge University Press, 2006).....12
- Figure 4. Net intensity of the LIBS signal in air from several organic compounds, 2-mononitrotoulene ( $C_7H_7NO_2$ , MNT), DNT ( $C_7H_6N_2O_4$ ), TNT ( $C_7H_5N_3O_6$ ), RDX ( $C_3H_8N_6O_6$ ), anthracene ( $C_{14}H_{10}$ ), 2,4-diminitoulene ( $C_7H_{10}N_2$ , DAT), 4-methyl-3-nitroaniline ( $C_7H_8N_2O_2$ , MNA), and pentaerythritol ( $C_5H_{12}O_4$ , PENT). Figure taken from P. Lucena, A. Doña, L. M. Tobaría, J. J. Laserna, *Spectrochim. Acta B*: 66, 12 (2011).....18
- Figure 5. Spectra that illustrate the large neutral atomic and ionic emission and S/N enhancements that can be obtained with orthogonal (a) pre-ablative dual-pulse LIBS of sodium in aqueous solution and (b) collinear dual-pulse LIBS of an aluminum standard in air. (c) Single-pulse LIBS of an aluminum standard in air where the right-hand y-axis applies to (b) and left-hand y-axis applies to (c). The lower trace in (a) is a single-pulse spectrum for comparison with the upper, dual-pulse spectra. The above spectra were taken from Scaffidi, J., Angel, S. M., Cremers, D. A., *Anal. Chem.* 78, 24 (2006). .....22
- Figure 6. A comparison of plasma lifetime with and without enhancement from a microwave. The microwave-enhanced plasma is observed for the entire 20 ms lifetime of the microwave pulse. Figure was taken from Liu, Y., Baudelet, M., Richardson, M., *J. Anal. Atom Spectrom.* 25, 1316 (2010). .....23
- Figure 7. Paired (a) standoff-LIBS and (b) Raman spectra for RDX. Figures were taken from Moros, J., Lorenzo, J. A., Laserna, J. J., *Anal. Bioanal. Chem.* 400, 3353 (2011).....24
- Figure 8. The LIBS-LIF spectra of (a) egg white and (b) rabbit glue acquired using an excitation wavelength of 266 nm which is resonant with an electronic transition in both tyrosine and tryptophan. The LIBS (lower traces) and LIF spectra (upper traces) have been recorded using the same laser and grating 600 g/mm. The spectra were taken from Osticioli, I., Mendes, N. F. C., Nevin, A., Zoppi, A., Lofrumento, C., Becucci, M., Castellucci, E. M., *Rev. Sci. Instrum.* **80**, 076109 (2009).....26
- Figure 9. The distance dependence of the range-corrected remote FIBS signal for the 521.8 nm copper line versus a simulated traditionally focused beam. Taken from Stelmaszczyk, K., Rohwetter, P., Mejean, G., Yu, J., Salmon, E., Kasparian, J., Ackermann, R., Wolf, J.-P., Woste, L., *Appl. Phys. Lett.* 85, 3977 (2004). .....29

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## List of Tables

---

Table 1. Examples of common explosives [ethylene glycol dinitrate (EGDN), RDX, 2,4,6-trinitrotoulene (TNT), 2,4-dinitrotoluene (DNT), pentaerythritol tetranitrate (PETN), HMX, triacetone triperoxide (TATP)], precursor materials (sucrose and ammonium nitrate (AN)), and explosive primers and propellants (potassium chlorate and ammonium perchlorate). .....	4
Table 2. Examples of some techniques used for hazard detection. *Note: The degree of sensitivity and specificity will change depending on the laser-based technique utilized. ....	5
Table 3. List of LIBS systems that are commercially available or in development. ....	30



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## **Acknowledgments**

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This work was sponsored by the U.S. Army Research Laboratory and the Army Technology Objective (ATO) Detection of Unknown Bulk Explosives R.ECB.2010.01 and was accomplished under cooperative agreement number W911NF-12-2-0019 and AB03.34C.

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## 1. Introduction

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The detection of energetic material is of great interest to the Department of Defense (DOD) and coalition forces for the protection and continued operation of the Warfighter. Of the many hazards commonly encountered by Warfighters, energetics in the form of improvised explosive devices (IEDs) and homemade explosives (HMEs) remain the primary threat to military and civilian personnel. Unfortunately, the energetic materials used to construct these devices are notoriously difficult to detect. For this reason, IEDs and HMEs continue to be one of the main methods of attack in terrorist and criminal offensives. According to the “Report on the Progress Toward Security and Stability in Afghanistan” issued by the DOD in April 2012, the average number of IED attacks per month ranges in the 100’s and account for nearly half of all casualties in Iraq and Afghanistan (1). The number of casualties emphasizes the necessity to develop technology to detect and identify energetic materials for the continued support and safety of the Warfighter. Therefore, renewed research efforts have focused on using existing technologies or developing innovative systems for detecting these hazards (trace and bulk) in many states at a variety of ranges (point and long range) dependent on the concept of operation.

Typically, explosive detection is based on matching a particular physical or chemical property of the sample to an ever-expanding threat library. For example, many x-ray interrogation systems determine if an object is hazardous based on the material’s density as determined from the attenuation of radiation either from scattering or absorption by the unknown object (2). However, explosives can be difficult to distinguish from non-hazardous materials based on physical properties alone, due to the lack of specificity. In addition, such a physical-based method is typically limited to bulk or visible quantities of material. The use of chemical properties may allow for higher specificity and sensitivity, enabling the trace detection and identification of explosive material.

It has been shown that handling and transporting hazardous materials often results in the generation of trace amounts of sample on surfaces. Trace energetic vapors and particle samples can be found on a variety of surfaces including baggage, cargo, person-borne IEDs, or even vehicle-borne IEDs. Trace quantities of explosives are typically non-visible and can be present in the nanogram to picogram range, making detection challenging for several reasons. Current trace explosive detection devices (TEDDs) mainly rely on vapor detection or the collection of particles (e.g., swabbing); therefore, successful and efficient collection and transfer of materials to a TEDD can prove difficult. The trace detection challenge is also in part due to the wide range of chemical structures, inherently low vapor pressures (e.g., the high explosive 1,3,5-trinitroperhydro-1,3,5-triazine [RDX] has a vapor pressure of  $\sim 6.3 \times 10^{-7}$  Pa at 25 °C and urea nitrate has a vapor pressure of  $\sim 8.8 \times 10^{-7}$  Pa at 25 °C), and possible sample degradation, hydrolysis or polymerization demonstrated by many of these energetic (2). Other challenges

associated with some trace detection systems include nuisance alarms (analyte detected below threat level), contamination ease (malicious or inadvertent), and modest spatial or quantitative information provided for decision making. Also such materials are often poorly suited for low volatility threats (e.g., black powder). For example, at a civilian airport the detection and discrimination of trace explosive materials among background containments (e.g., perfume, lotions, hand sanitizers, etc.) would be more straightforward than the detection of energetics on the battlefield due to the various differences in the compounds. Discrimination of undetonated IEDs on the battlefield is severely hindered due to the complex, highly similar background (i.e., residue from exploded ordinance, gunpowder residue, fuel, fertilizers, etc.) that is observed. The similar chemical and physical properties of the background in an operationally significant environment will typically lead to false positives or false negatives. The challenge is further complicated when standoff or proximal detection is needed.

For the detection of hazards, a system that embodies the following ideal attributes is needed. The system should be able to do the following:

1. detect many types of explosives and be adaptable/expandable to new targets;
2. demonstrate low analyte detection limits (lowest quantity detectable);
3. have standoff/proximal detection capabilities;
4. have a high probability of positive detection and a low probability of false alarm;
5. demonstrate good throughput or areal coverage;
6. have limited vulnerabilities to countermeasures;
7. be rugged, robust, and have limited maintenance needs;
8. be operationally easy to use; and
9. have low cost, space, and power requirements.

In the last decade, many technologies have been explored for direct detection and identification of bulk and trace explosives analysis, with emphasis on near-term transition, characterized by limited capabilities. In 2010, an Army Technology Objective (ATO), Detection of Unknown Bulk Explosives R.ECB.2010.01, was initiated. The purpose of the ATO was to develop an understanding of signatures and algorithms required to provide improved point, proximity, and standoff detection of explosives and precursor materials to enable the warfighter to integrate chemical and explosive hazard detection equipment. An important attribute of this ATO involved taking a phenomenology-based approach to determining what detection methods have the potential to address the detection and analysis of unknown explosives in complex environments. A spectroscopic-based technique that was recognized as a possible method capable of detecting and identifying energetic materials is known as laser-induced breakdown spectroscopy (LIBS). LIBS most commonly uses a high energy, nanosecond laser to create a plasma and breakdown

the unknown material into its atomic constituents. The emission spectrum from the plasma containing the various excited and ionized atomic species is analyzed to determine the elemental composition, and in some cases, quantify the target material. However, none of the core Government research organizations supporting the ATO had in-house LIBS research programs. Therefore, a foundation to assess previous research, development, and testing claims was necessary.

In supporting the goals of this ATO, this review surveys the current literature and available industry data to assess LIBS phenomenology for explosives detection under ambient conditions and determine potential gaps in knowledge. A thorough examination of the literature reveals that the LIBS techniques and its variants have many strengths, such as Raman-LIBS or LIBS-laser-induced fluorescence (LIF), and challenges, such as varied signal intensities due to matrix effects, which are being addressed by examining the role of pulse duration, wavelength, and fluence in LIBS and developing parallel techniques (e.g., dual-pulse LIBS) to reduce or nearly eliminate interferences. Despite advances in the LIBS research to mitigate these matrix effects, qualitative and quantitative sample analysis remains arduous due to the complex emission spectra obtained. Therefore, chemometrics are used to identify and discriminate hazardous materials. These chemometric-based approaches have been successful, but more robust detection algorithms are still needed.

This report briefly discusses the current technologies used for trace hazard detection, focusing on emerging laser-based efforts for standoff/proximal trace detection. We show that the algorithms for material identification could be improved by including the critical signatures (e.g., C2 and CN emission lines) required for discrimination and advanced plasma diagnostics (e.g., plasma temperature and electron density). Finally, based on the information gathered in this report, suggestions of areas where more research efforts could be focused to make LIBS a viable technology for trace standoff explosive detection for the Army and DOD are also presented.

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## **2. Trace Explosive Detection Techniques**

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There are numerous examples of explosives and precursor materials encountered by the U.S. military. Example explosive materials and precursors, and their chemical compositions, are listed in table 1. Explosives are organic or inorganic compounds primarily composed of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) in various ratios. As compared to other classes of compounds, explosives are characterized as being both rich in nitrogen and oxygen and poor in carbon and hydrogen. For example, high-velocity military explosive (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine [HMX]) is composed of approximately 37.8% nitrogen, 43.2% oxygen, 16.2 % of carbon, and 2.7% of hydrogen by weight. The similarities in chemical composition among explosive material and other subtle nuances of data collection can cause various challenges associated with their accurate detection.

Table 1. Examples of common explosives, precursor materials, and explosive primers and propellants.

<b>Material</b>	<b>Composition</b>	<b>Application</b>
EGDN	$C_2H_4N_2O_6$	Explosive
RDX	$C_3H_6N_6O_6$	Explosive
TNT	$C_7H_5N_3O_6$	Explosive
DNT	$C_7H_6N_2O_4$	Explosive
PETN	$C_6H_8N_4O_{12}$	Explosive
HMX	$C_4H_8N_8O_8$	Explosive
TATP	$C_9H_{18}O_6$	Explosive
AN	$NH_4NO_3$	Precursor Material
Sucrose	$C_{12}H_{22}O_{11}$	Precursor Material
Chlorate	$KClO_3, NH_4ClO_4$	Primer, Propellant

Note: EGDM = ethylene glycol dinitrate, TNT = 2,4,6- trinitrotoulene, DNT = 2,4-dinitrotoluene, PETN = pentaerythritol tetranitrate, TATP = triacetone triperoxide, AN = ammonium nitrate,  $KClO_3$  = potassium chlorate, and  $NH_4ClO_4$  = ammonium perchlorate.

There are several technologies under consideration for trace energetic detection (point and/or range). These TEDDs include, but are not limited to, various forms of chromatography, colorimetric indicators, capillary electrophoresis, ion mobility spectrometry (IMS), desorption electrospray ionization (DESI), laser electrospray mass spectrometry (LEMS), emerging efforts like antibody/antigen-based efforts, and laser-based techniques like LIBS. While most of these techniques are laboratory-based, some have demonstrated real-world application (e.g., colorimetric, IMS-based efforts, and laser-based efforts). Table 2 shows examples of some techniques used for trace hazard detection and a summary of their pros and cons.

Table 2. Examples of some techniques used for hazard detection.

Technique	Trace Detection	Example(s)	Pros	Cons
Chromatographic techniques	Vapor and particle	Gas chromatography (GC) and high performance liquid chromatography (HPLC)	Can be miniaturized, good specificity, applicable to several sample types	Inefficient sample transfer, requires solubility in mobile phase, limited to remote or point detection
Colorimetric indicators	Vapor and particle	M256A1 chemical agent detector kit & colorimetric reconnaissance explosive squad screening (CRESS) detector kit	Easy sample analysis due to color change	Limited to few threats, point analysis for visible quantities, low specificity, typically requires handling of chemicals stored in a bulky kit
Amplifying fluorescent polymers	Vapor and particle	FIDO®	High response and sensitivity to certain hazards	Limited to few threats, high false alarm rate, lack of spatial information, limited to remote or point detection
Biological-based sensors	Vapor and particle	BioThreat Alert® Kit	High sensitivity and specificity for a specific threat	Inefficient sample transfer, needs large sample volume (vapor), limited to few threats, no <i>in situ</i> analysis, point analysis only, still in development
Ion mobility spectrometry	Vapor and particle	M4 joint chemical agent detector (JCAD) and Ionscan 500DT®	Miniaturized, automated, applicable to several sample types, high sensitivity	Inefficient sample transfer, needs large sample volume (vapor), maintenance, prone interferents, radiation safety training
Mass spectrometric-based	Vapor and particle	DESI and LEMS	Rapid, <i>in situ</i> detection, high specificity from multiple surfaces, applicable to several sample types	May require the use of solvents, limited to remote or point detection, still in development
Laser-based methods	Vapor and particle	ST-LIBS and FirstDefender RM®	Rapid, sensitive* and accurate, point, remote or standoff detection, good to high specificity*, applicable to several sample types	Laser safety training, “eye safe” requirement, still in development

\*The degree of sensitivity and specificity will change depending on the laser-based technique used.

## 2.1 Chromatographic Techniques

In chromatographic-based techniques, an analyte is identified by the interaction of the sample with stationary and mobile phases in the instrument. This interaction can be achieved primarily by injection of the solubilized analyte into the instrument and separation of the sample as it interacts with the column, and finally as the analyte is carried by the mobile phase through the stationary phase, detection is achieved. Chromatographic-based techniques can analyze samples that have been collected from the vapor phase as well as particulates. For gas phase samples, large volumes of air are often collected (3, 4) and pre-concentrated using various methods such as solid phase extraction to increase the sensitivity of these techniques. This is a somewhat inefficient sample transfer technique, and instead collection of the condensed phase energetic material is performed using swabs. In a typical analysis, a swab is taken of the item to be interrogated (e.g., suitcase, laptop, etc.) transferring any adsorbed molecules onto the swab (5). Once collected, the adsorbed sample is either eluted or thermally desorbed enabling analysis of the threat agent. Currently, the predominant methods used in forensic laboratories for the detection and identification of energetic materials are GC (6, 7) and HPLC (8). Another chromatographic-based method commonly used for energetic detection is thin-layer chromatography (9).

## 2.2 Colorimetric Techniques

There have also been some limited demonstrations of trace energetic sensing using colorimetric indicators (10, 11). Colorimetric trace explosive technology relies on a series of chemical reactions that produce a visual response (identifiable color change) when in the presence of a specific functional group or chemical category. Thus, in some cases specificity to differentiate benign material (e.g., nitrates for treatment of angina) from hazardous substances (e.g., nitrates from an IED) using only a color change can be challenging. While some of these systems have been successfully utilized for trace detection, most often they work best with visible bulk quantities. Some examples of commercially available colorimetric kits commonly used in the field for the detection of chemical or energetic hazardous materials are the HazCat<sup>®</sup> Kit, the M256A1 Chemical Agent Detector Kit, and the Heinz 5-step<sup>™</sup> Field Identification Method\*.

## 2.3 Amplifying Fluorescent Polymers

Another tool that is used in the field, the FIDO<sup>®</sup> explosives detector, uses amplifying fluorescent polymers (12–14). This technology links chromophores together in a chain producing a single polymer molecule. When this polymer is exposed to light at a particular wavelength, it begins to fluoresce. When a hazardous material is introduced to the polymer, it binds to the fluorescent material, quenching the fluorescence of the entire polymer chain, effectively amplifying the quenching process. This is unlike traditional chemosensor technology, where an analyte

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molecule will quench only the chromophore to which it is bound. These amplifying fluorescent polymers allow for dramatic increases in both response and sensitivity (14). However, the polymers have been designed for a limited number of explosive threats and are not easily adaptable to new targets. In addition, the limited ranged detection capabilities, the relatively low probability of detection (89%), and high probability of false alarms (27%) (14) decrease the versatility of the technique.

## 2.4 Biological-Based Techniques

Emerging biological-based techniques for trace energetic detection use antibodies, antigens, or peptide-based approaches for specific interaction with the energetic target. Commonly, the solubilized explosive sample is introduced to a system with an antibody, antigen, or peptide fixed to a surface. After introduction, the sample interacts with the bound an antibody, antigen, or peptide causing a change in the system (i.e., electrochemical, optical, mass, etc.) producing a measurable signal. In the case of a mass-based transduction, the explosive sample will then interact with the bound antibody, antigen, or peptide either displacing a labeled antigen (15), causing a shift in the resonant frequency of an acoustic resonator (16), or altering the system's mass as measured using a quartz crystal micro-balance (17). Although these biological-based approaches offer relatively high sensitivity and selectivity, the techniques are unsuited for *in situ* analysis or ranged detection limiting these approaches in their applications.

## 2.5 Ion Mobility and Mass Spectrometry Techniques

Thermal energy activation systems and IMS (18, 19) are other common analytical techniques used to separate and identify energetic material. For example, in IMS, ionized molecules in the gas phase are separated, detected, and identified based on their mobility through a carrier gas. In the IMS process, molecules are thermally desorbed prior to being ionized. Ions drift through a buffer gas under the influence of an electric field. The rate of drift depends on the electronic and physical properties of the ions. IMS is a common point detection method currently used by military and airport security personnel. For example, one commonly employed IMS system adopted for military use is the portable JCAD for the detection of chemical warfare agents and toxic industrial chemicals. IMS is a popular method for the detection of hazardous material because it is rapid (8–10 s), it demonstrates high sensitivity (nanogram to picogram) to energetic (20, 21), and the interpretation of the mobility spectrum can be completely automated. However, despite these advantages, IMS systems typically have a lower chemical specificity than other analytical techniques, decreasing the system's capability to differentiate between threat agents and background interferents (22–24), thus producing false positives and negatives (25).

Several mass spectrometry-based methods, such as DESI (26–28) and LEMS (29–31), have also been developed to directly analyze condensed phase explosive residues adsorbed onto external surfaces at ambient temperature and pressure. These mass spectrometry-based techniques have enabled the rapid, *in situ* detection and identification of energetic material with high chemical specificity from multiple surfaces, thus no sample preparation is required. The *in situ* analysis of

trace energetic material has the potential to decrease complications in the analysis process caused by either incomplete transfer to the sample swab (32) or thermal degradation. Despite the possible advantages for both DESI and LEMS, the use of a mass spectrometric-based approach inherently limits the analysis to proximate or point detection.

## **2.6 Laser-Based Techniques**

Pure, laser-based methods could enable the rapid, sensitive, and accurate point, proximate, or standoff detection of energetic materials. Commonly, laser-based approaches focus and irradiate a gas phase or condensed phase sample with a nanosecond laser beam. Light that is emitted, reflected, or scattered is collected and directed into a detector for analysis. The light is analyzed allowing for determination of the electronic structure, vibrational structure, or atomic constituents of the adsorbed species.

### **2.6.1 Photodesorption and Photofragmentation**

Explosive molecules have low vapor pressures causing difficulty in the detection process for vapor phase TEDDs. Increasing the vapor pressure of the energetic molecules would ease these detection difficulties. One way to increase the vapor pressure of the adsorbed molecule is to irradiate the sample using a laser. The laser causes desorption of the analyte through a variety of mechanisms increasing its vapor pressure several orders in magnitude. However, intact desorption is uncommon for such laser-desorption techniques. Excess energy from the laser can be deposited into internal modes of the molecule leading to extensive fragmentation of the desorbed species. These fragments are subsequently detected with a number of techniques such as LIF (33) or resonance-enhanced multiphoton ionization (REMPI). These photodesorption/photofragmentation techniques have been used to detect a variety of nitro-based energetic materials with one- and two-laser configurations. For example, Wynn et al. used photodesorption LIF to detect TNT, DNT, RDX, and PETN (34). This research group used a 236-nm laser pulse to desorb and photofragment the adsorbed nitro-based explosive molecule. The rotationally and vibrationally excited nitric oxide (NO) fragments were resonantly excited by the same laser pulse producing a blue-shifted fluorescence signal allowing for detection and discrimination from background NO and nitrogen dioxide (NO<sub>2</sub>). In another example, Roberson and Sausa resonantly excited a sample of laser dye containing trace quantities of RDX or TNT (35). The energy absorbed from the laser pulse lead to desorption and photofragmentation of the energetic molecule allowing for the resultant NO fragments to be detected by a second laser using REMPI.

### **2.6.2 Spontaneous Raman Scattering**

One vibrational spectroscopy technique, spontaneous or incoherent Raman scattering (36–38), allows for the detection of vapor and condensed phase material with high chemical specificity. The atoms/bonds that compose a molecule are oscillating and therefore the polarizability of that bond is periodically oscillating in time (39). In addition, the refractive index of the

medium/molecule will also be modulated in time, since the refractive index of the medium is related to the polarizability of the molecule (39). Thus, if a laser beam were to interact with the molecule, frequency sidebands of  $\pm\nu_{\text{vib}}$  will be imparted on to the laser beam of frequency  $\nu_0$ , producing peaks of  $\nu_0 \pm \nu_{\text{vib}}$ . In this manner, spontaneous Raman scattering has been used for the proximal detection of materials at a distance of approximately 50 m (40). However, incoherent Raman scattering has difficulty in meeting the sensitivity requirement meant for standoff detection for trace threat agents due to its low signal-to-noise, particularly in the presence of interferences commonly found in the field. This low sensitivity is due to the small Raman Stokes scattering cross section, which is approximately  $10^{-30} \text{ cm}^{-2}/\text{molecule}$  (41).

### 2.6.3 Infrared Laser-Based Techniques

Optical detection techniques based on infrared (IR) laser spectroscopy are a promising approach as organic molecules typically exhibit strong characteristic absorbance features in the mid-IR spectral region (i.e., the fingerprint region). The introduction of the quantum cascade laser (QCL) in 1994 changed the prospects of IR spectroscopy and IR laser-based techniques. Since that time, the QCL has matured to a level at which numerous companies can produce gain material for these laser systems. Along with this production, several companies have manufactured laser systems which are suitable for spectroscopic purposes. External cavity (EC) grating QCL systems have demonstrated up to  $350 \text{ cm}^{-1}$  of continuous tunability from a single-chip platform, allowing for collection of vibrational spectra in the fingerprint region for various materials (42).

Standoff detection in the IR is more challenging than traditional IR spectroscopy. The surface investigated in standoff measurements is unlikely to be oriented such that the light originating from the specular reflection can be collected. Furthermore, the spatial composition can vary based on surface contamination. IR reflectance spectroscopy has demonstrated capability to overcome these problems (43). For example, Fuchs et al. used widely tunable EC-QCLs to irradiate artificial fingerprints of TNT, RDX, and PETN on various substrates (44). The authors measured the diffuse backscattered light from the sample via the use of a mercury-cadmium-telluride focal plane array IR camera. Spectra were obtained by integrating the backscattered laser light from the region in the camera image where the sample was located and corrected for the thermal background allowing for the imaging standoff detection (20 m distance) of trace explosives. This backscattering laser spectroscopy technique has been further developed into commercially available items. One of these items, the Block Engineering LaserScan<sup>TM</sup> is a handheld instrument where the light source, a QCL, and detector are integrated. This allows for the portable detection of trace explosives (e.g.,  $1\text{--}100 \mu\text{g}/\text{cm}^2$ ) on a variety of surfaces at standoff distances ranging from 6 in to 3 ft via the use of diffuse reflectance and off-normal specular reflection (43).

Photoacoustic spectroscopy (PAS), another IR laser-based spectroscopy technique, takes advantage of the photoacoustic (PA) effect. The PA or optoacoustic effect is the generation of

acoustic waves in a sample due to the absorption of radiation, including laser radiation. Periodic heating and cooling of the sample via the use of modulated or pulsed excitation sources produces pressure fluctuations (i.e., acoustic waves). The acoustic wave produced is subsequently detected by a pressure transducer, in most cases a microphone, of the appropriate frequency response. The signal generated by the microphone is proportional to the amplitude of the pressure wave. Modern PAS research uses widely tunable QCL sources that can achieve full spectroscopic discrimination of gaseous and condensed phase analytes, due to their large tuning ranges. However, due to the higher sensitivities achieved with *in situ* PA methods as well as the numerous challenges associated with PAS of samples in open air (e.g., acoustic waves spreading, influence of wind effects), reports of *in situ* and short-range PA experiments are more prevalent in the literature than standoff PA techniques (42). Perrett et al. attempted to overcome these challenges using a pulsed indirect PA spectroscopy technique, which employed a stronger light source and a parabolic focusing mirror (45). The authors suggested a more powerful light source would increase the amplitude of the acoustic waves as the parabolic mirror captured and refocused the sound back onto a microphone; however, significant losses in the system and field environment ultimately effects the range and sensitivity of this technique. Although the acoustic waves generated at standoff distances are affected by atmospheric conditions, the reflected or scattered light is unaffected. Van Neste et al. demonstrated a standoff hybrid PA reflectance technique used for analyzing surface adsorbed chemicals, including tributyl phosphate, RDX, TNT, and PETN as targets (46, 47). The authors employed an EC-QCL to illuminate a target located at standoff distances of 0.5, 4, 10, and 20 m. The light reflected or scattered off the target was collected using a spherical mirror and focused onto a quartz crystal tuning fork (TF), producing an acoustic wave on the TF surface. A detection limit on the order of 100 ng/cm<sup>2</sup> was achieved with this standoff detection system.

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### **3. Laser-Induced Breakdown Spectroscopy**

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#### **3.1 Laser-Induced Breakdown Spectroscopy Basics**

Laser-based methods used for trace standoff detection of hazardous material include LIBS and associated laser-induced plasma techniques. One reason LIBS is an attractive technique to perform energetic material detection is due to its simplicity in operation and design. For example, LIBS analysis allows for sampling (ablation), plasma formation, and elemental emission analysis to all be performed in a single-step enabling point, proximal, and standoff detection of material. This rapid, analysis is partly enabled by its experimental design. LIBS requires six main components to enable analysis and detection: (1) a pulsed laser; (2) optics to steer and focus the laser beam; (3) a sample; (4) optics to collect the emission produced by the laser-matter interaction; (5) a monochromator or a spectrometer to analyze the light; and (6) a computer and timing electronics (figure 1) (48).

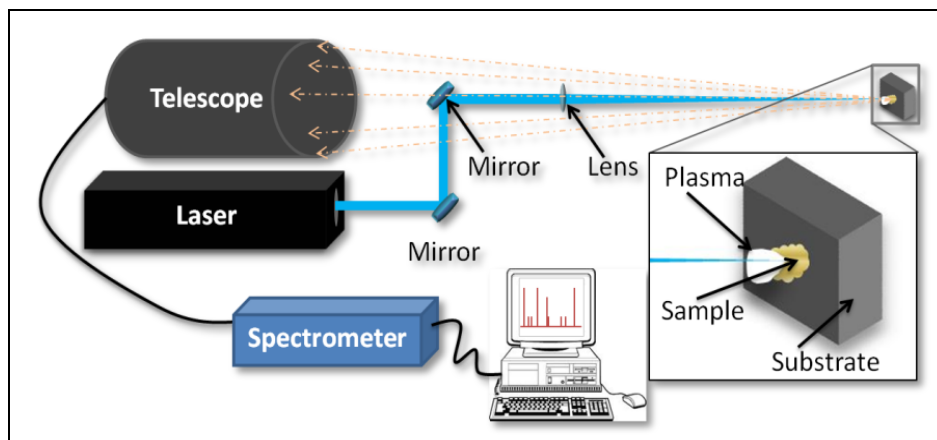


Figure 1. A schematic depicting a typical LIBS experimental setup.

The LIBS analysis method is also advantageous as it is a pure optical technique that only requires optical access of the laser beam to the target. As a result, any sample could be investigated by the LIBS technique without the necessity of preparation prior to analysis, provided the laser's fluence is high enough to exceed the dielectric breakdown of the sample. This lack of sample preparation is critical as it allows for direct analysis of surfaces without any sample pre-concentration, elution, or swabbing. Another advantage of the LIBS technique is that it can be performed on condensed phase and gas phase samples further enhancing its utility. These advantages for the LIBS technique enable the proximate and standoff detection of explosive materials (49–55), potentially making LIBS a valued tool for the protection of Warfighters in hostile or hard to reach environments. It is because of these advantages that there has been a steady increase in the literature demonstrating the detection of explosive samples using LIBS, representing approximately 3% of the publications (figure 2).

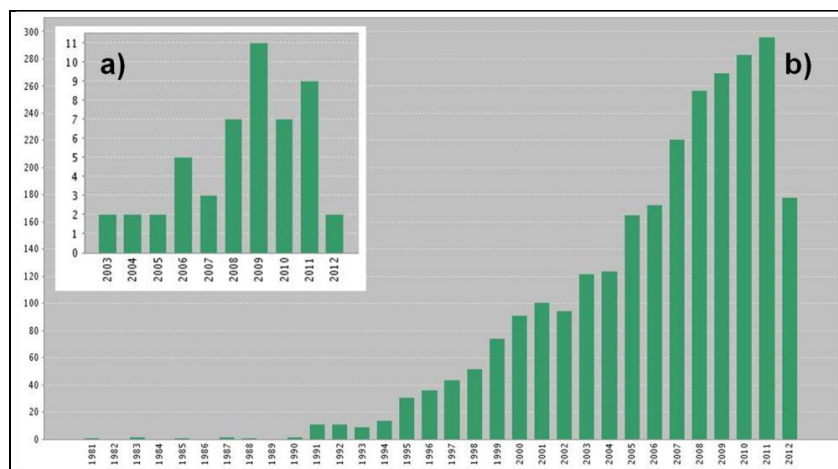


Figure 2. (a) The number of publications, as compiled from Science Citation Index Search 11Sept2012, with keywords: laser-induced breakdown spectroscopy/plasma and explosive. This demonstrates an increase in the number of LIBS publications as a function of time. (b) The total number of LIBS publications, related to all sample types, per year.

LIBS is an optical detection technique based on plasma generation from a laser (figure 3) (54). The majority of LIBS research has generally been performed with high energy, nonresonant nanosecond lasers, but the technique can be done with any pulsed laser that is capable of delivering the necessary conditions for plasma formation, including picosecond (53, 55) and femtosecond (52, 56–58) lasers. For long pulse durations (i.e., nanosecond), the focused laser contains sufficient enough energy to produce free electrons in the medium via one of two mechanisms; multiphoton ionization or by a thermionic process (i). The free electrons in the medium allow for further absorption of the laser pulse's energy, enabling additional heating of the sample and avalanche ionization. These processes allow for the subsequent breakdown of the material (48, 49, 59) into its atomic constituents producing electron dense plasmas ( $10^{17}$ – $10^{19}$  cm<sup>-3</sup>) at high temperatures (6000–20000 K) (60, 61). The formed plasma extends in all directions at a rate of  $10^5$  m/s producing an audible shock wave (49). In addition, it should be noted that this high temperature can cause latent heating of the surrounding surface leading to the thermal desorption of molecules and molecular fragments similar to that seen in laser desorption mass spectrometry (62).

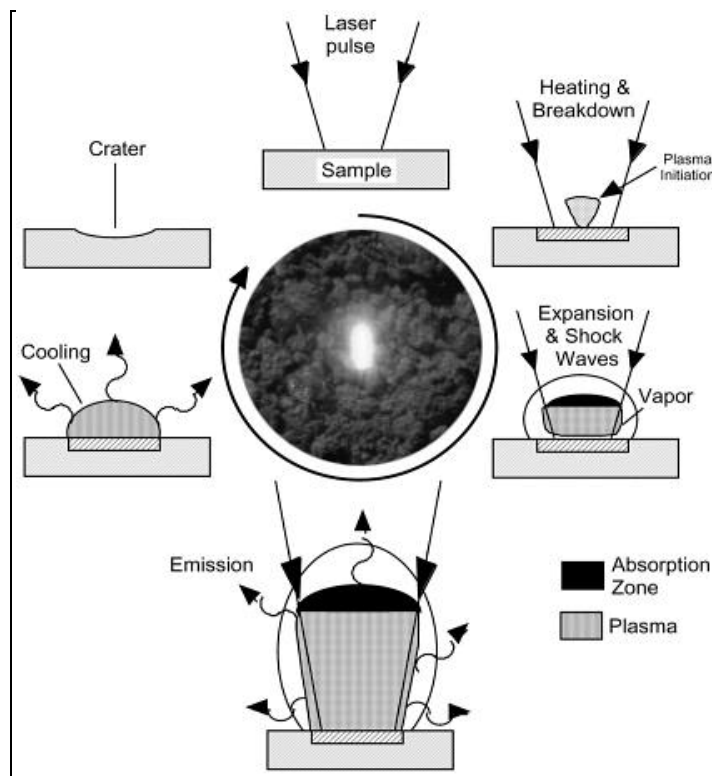


Figure 3. The life-cycle diagram showing the main events in the LIBS process. Taken from V. P. Andrzej W. Miziolek, I. Schechter, Laser-Induced Breakdown Spectroscopy. (Cambridge University Press, 2006).

Initially, the plasma's emission spectrum, generated by a nanosecond laser, is dominated by a continuum caused by Bremsstrahlung and recombination radiation from the plasma as the

electrons and ions recombine thus cooling the plasma (49). As time evolves, the continuum emission decreases allowing for the ionic emission lines to be observed. After a few microseconds, the excited atomic emission lines are able to be detected. Typically, the continuum emission is electronically filtered out using a gated intensified charge-coupled device (CCD) array set to a particular time delay, allowing for observation of the emission spectrum from these excited atoms and ions. The emission spectrum from the plasma's constituents is recorded and analyzed to determine the elemental composition and in some cases the eventual quantification of the targeted material. In this manner, LIBS has been successful at detecting and analyzing a wide range of materials such as highly radioactive substances (63–66), biological aerosols (67), heavy metals (68, 69), and explosive threats (70–73).

### **3.2 Qualitative and Quantitative Laser-Induced Breakdown Spectroscopy**

LIBS analysis falls under two main categories: qualitative LIBS and quantitative LIBS (48, 74). Qualitative LIBS analysis is able to determine whether a hazardous material is present at the LIBS analysis region (i.e., the plasma spark). This determination is commonly performed by the analysis of spectral lines from the sample and the measurement of ratios of emission bands such as the C/H, C/O, C/N, C<sub>2</sub>/C, C<sub>2</sub>/CN, and O/N. Once the emission lines have been obtained, the difficult task of assignment occurs. Typically, accurate assignment of the observed emission requires knowledge of the sample, knowledge of the intensities of the emission lines from wavelength tables, and understanding of the ionization state of the element and information of operational conditions. Emission line assignment can be quite arduous, increasing the difficulty in its automation. However, patterns in the emission line spectrum formed from element line intensities can be useful for identifying a hazardous material (48). For example, standard spectra can be acquired for specific samples under particular sampling conditions and compared to unknown spectra to match the observed pattern of element line intensities for identification or determine if there is surface contamination (48). It is possible that from the obtained ratios, emission lines and element line intensity patterns that indicate the presence of an energetic material can be determined; however, establishing the hazardous materials quantity is difficult without calibration procedures.

Conversely, quantitative LIBS analysis allows for both material identification and the determination of its quantity from the plasma (48, 74, 75). This capability is due to the creation of calibration curves using various amounts of material deposited on the target. However, the creation of the calibration curve is dependent on the sample, the laser, the detector, and the sampling parameters. For example, it has been shown that the resulting emission intensity varies as a function of laser pulse energy, lens-to-sample distance (76), sample uniformity effects (48), and atmospheric pressure (77). Because plasma excitation is a Boltzmann-driven process, when these parameters change, relative excitation conditions (e.g., temperature, electron density) can change substantially. This wide range of factors can therefore affect the dynamic range and the quality of the calibration affecting the quantitative capabilities of the technique. Therefore, the use of calibration standards, identical calibration, and sampling procedures has been put into

place to try to overcome such issues. Yet these solutions may poorly translate to the analysis of real-life samples, which can vary widely in sample concentration yielding high variability in the determined concentrations. In addition, when such calibration is performed it is commonly done in a lab for standardized samples and may be unsuitable for field analysis when the chemical, its concentration, and its substrate are unknown at range. The use of calibration-free LIBS (CF-LIBS) has begun to be explored as a method to mitigate such effects (78). To perform CF-LIBS, a family of Boltzmann distributions is created for all the constituents leading to the observed emission lines in the plasma. The concentration of the constituents, determined from the intercepts of the lines on the  $y$ -axis, is forced to add up 100%. In addition, it is also assumed that the plasma is in local thermodynamic equilibrium and is spatially narrow. This information, along with self-absorption estimates, is fed into an iterative algorithm allowing for the constituent concentrations to be determined with high accuracy within 10–15 cycles (79). However, a common difficulty with this technique is accounting for all neutral and ionic species related to the constituents in the plasma as they all contribute to the plasma. Therefore, other equations, such as the Saha equation, may have to be used to determine the concentration of a missing species increasing the difficulty in the technique.

### **3.3 Chemometric-Based Approaches for Material Identification**

As stated earlier, LIBS breaks the sample of interest and underlying matrix down to its atomic constituents and some possible molecular fragments due to the inherent use of a plasma. The obtained emission spectrum is complex making identification of the hazardous material by eye arduous. However, one of the most difficult problems for energetics detection is distinguishing the subtle changes in the carbon, hydrogen, nitrogen, and oxygen emission lines, resulting from breakdown of the explosive, from the matrix/background emission lines. However, researchers have shown that multivariate analysis of these complex plasma emission spectra can help aid in the identification process (80–82). Recently, such chemometric-based approaches have begun to be implemented to aid the user in the explosives materials identification (70, 73, 83). To perform such a chemometric-based analysis, a large number of LIBS spectra are acquired to build a “training set.” This training set serves as a standard allowing for new data or “testing sets” to be accurately classified. Initially, the data contained in the collected training sets are reduced in its number of dimensions to reduce its complexity and extract significant emission features. Common techniques used to reduce the dimensionality of the original emission spectra include, principal component analysis (PCA) and partial least squares discriminate analysis (PLS-DA). PCA works by maximizing the variance between the different samples, and in the process transforms the raw data (i.e., wavelengths and intensity) into a few new variables called principal components (PCs). These PCs are linear combinations of the original spectra (84–86). In addition, PCs are orthogonal functions that contain the maximum amount of variance in the data set with a minimum number of functions. Partial least squares or nonlinear iterative partial least squares, the supervised complement of PCA (87), is another method to reduce the dimensionality of the original dataset (88, 89). The reduction occurs by maximizing the variance between the



dependent variables (e.g., the class) and the independent variables (e.g., atomic emission lines) by constructing a new set of variables known as latent variables (70, 90). These latent variables are linear combinations of the independent variables that capture information contained by the independent variables and their relationship to the dependent variables. The PLS solution can later be applied to unknown data allowing for its identification and discrimination to determine whether a material is an explosive. These dimensionality reduction methods are normally complemented by a discrimination technique, such as discriminant analysis (DA) or a nearest neighbor approach, allowing for automatic discrimination. However, each technique makes certain assumptions regarding the initial training data set. For example, the parametric linear DA method assumes that the input data has a Gaussian probability distribution while the non-parametric nearest neighbor classifier makes no prior assumptions about the training data (91).

Using techniques such as those listed above, accurate identification and discrimination of explosive material has been achieved (70, 73, 83). For example, using PLS LIBS spectra of the explosive 1,3,5-triaminoguanidinium dinitramide (TAG-DN) were positively classified with 100% accuracy, resulting in 0% misclassifications, using a particular discrimination model (70). However, when the discrimination model is altered for the *same* data set 55% of the TAG-DN spectra were accurately identified, 0% were misclassified as another explosive, and 45% were unclassified (70). This suggests that there might be some drawbacks when using chemometric approaches for the discrimination of explosive material. One of the initial obstacles that must be overcome is that a large training set must be compiled of *all* classes of explosive material to prevent the detection system from misclassifying the investigated surface. If all explosive material was analyzed at a range of concentrations, from a wide *variety* of surfaces, with and without interferences, an accurate training set could be built allowing for more accurate identifications. However, if the unknown data are taken under different experimental conditions (i.e., the field vs. the laboratory environment used for training), the trained algorithms may not hold. The existing complex chemometric protocols are difficult to train because of this variability in the background and plasma generation in that particular set of environmental conditions/sample/background are not consistent. This suggests that more research needs to be performed to enable the rapid discrimination of samples with 100% accuracy using chemometric-based approaches.

### **3.4 Modeling Plasmas in Laser-Induced Breakdown Spectroscopy**

The capability to accurately model emission spectra from LIBS would (1) contribute to a better overall understanding of the parameters impacting the collected data, (2) lead to an accurate quantitative interpretation of data, and (3) aid in the chemometric-based analysis for the identification of energetics. The physics and chemistry dealing with these short-lived plasmas is very complex resulting in a wide variety of models that may inaccurately predict the behavior of a laser-induced plasma from first principles (54) While the scope of discussing all the various models is beyond this report, we instead focus on basic models (physical, heuristic, and kinetic) for modeling the plasma emission observed in LIBS.

The physical model of a plasma is used to calculate the entire temporal and spatial evolution of a plasma, including the emission spectrum. To create a physical model of a laser-induced plasma, one uses the Navier-Stokes equations that are used to model the fluid flow of the plasma when subjected to a laser pulse (92). These Navier-Stokes equations are normally solved numerically using computational fluid dynamics computer packages. Complete determination of a laser-induced plasma evolution using the physical model of the plasma requires laser beam parameters, such as the irradiance as a function of location and time, the center wavelength of the laser, and the energy of the laser beam; ambient gas parameters, such as the composition and pressure; and material parameters, such as the concentration, specific heat, and thermal diffusivity (75). This model uses these parameters to simulate the interaction of the laser pulse with the condensed phase material, the resultant material vapor and plasma, and the atomic emission from the material vapor and plasma.

Computational fluid dynamics is computationally intensive even for small, short-lived events like a laser-induced plasma. Additionally, some of the required parameters needed to solve the equations for the physical model of the plasma may be unknown. When some of the necessary information is unavailable, the heuristic model can be used to solve for the spectra of the laser-induced plasma (75). The heuristic model assumes the composition of the target molecule, the plasma, and the plasma state (e.g., the plasma is in a constant spherical geometry with only electrons, atoms, and ions present) are known. These assumptions reduce the complexity of the problem and allow for an emission spectrum to be obtained for an inhomogeneous plasma surrounded by an ambient atmosphere. However, these assumptions can also lead to some shortcomings in the obtained results. For example, molecules in the plasma are unaccounted for when calculating the spectrum with the heuristic model and therefore the obtained emission spectrum is misrepresented. In addition, the assumption that the plasma is in a constant spherical geometry is a fallacy as many laser-induced plasmas exhibit a lack of radial and axial symmetry.

Another approach that LIBS researchers use is kinetic modeling. Kinetic modeling uses the obtained emission spectrum generated from the LIBS event at specific time intervals as the data to generate a model for the plasma evolution. The kinetic modeling technique reverse engineers the plasma model by using the temporally-dependent LIBS emission spectrum and all possible reactions with the ejected material plume and the ambient atmosphere. For example, Babushok et al. used this method to model the interaction of a laser pulse with metallic lead in ambient atmosphere (93). In doing so, 38 different chemical species (e.g., lead oxide [PbO], H<sup>+</sup>, NO, etc.) and 220 different reactions, such as ion chemistry, air reactions, and oxidation reactions, were included in the model to determine the evolution of the excitation, ionization, and oxidation processes within the plasma leading to the observed atomic emission lines for lead. These results were then included into a two-dimensional computational fluid dynamics model allowing for more accurate results.

### 3.5 Common Difficulties in Laser-Induced Breakdown Spectroscopy

Explosive material determination using LIBS is straightforward to perform: irradiate a sample with a pulsed laser and measure the emission lines from the resulting plasma. However, as with any technique, there are subtle nuances that can occur making such measurements challenging to apply. For example, the plasma generated by the LIBS technique can vary tremendously from one laser to another depending on the pulse duration of the laser shot, the wavelength of the laser, the energy of each laser shot, etc. Additionally, the shot-to-shot variability in the laser, the laser-matter interaction, and the highly non-uniform nature of the plasma will also affect the resultant emission signal. The effects of these various complications in obtaining a “standardized” emission signal was shown when ancient bronze metals were irradiated with a 355-nm laser pulse as opposed to a 1064-nm laser pulse (94). The inability to obtain reproducible data in terms of line strength and emission features has the potential to decrease LIBS capability to positively identify trace amounts of energetic materials. These and other common challenges are discussed in more detail below.

#### 3.5.1 Matrix Effects in Laser-Induced Breakdown Spectroscopy

LIBS is particularly appealing for explosive detection measurements for several reasons. The LIBS technique requires no sample preparation enabling *in situ* analysis at long range with the only requirement being optical access to the target. In addition, measurements can be collected rapidly enabling real-time analysis of condensed phase or gas phase material with good sensitivity. However, for LIBS to become a standard analytical technique used for trace explosive detection there must be a thorough understanding of the parameters that go into and can influence a measurement.

A LIBS “matrix effect” is a term used to generally describe the physical and chemical effects of “non-target host elements” (e.g., atmospheric, underlying surface, etc.) on the plasma reaction. Even under fixed experimental conditions, adverse affects from the environment and/or the chemical composition of the targeted sample, can result in both physical and chemical matrix effects. Generally, physical matrix effects are closely related to the physical properties of the sample, and if observed, occur in the ablation step of LIBS. Specifically, physical sample properties like different specific heats, absorption properties, and even varied matrixes (even with all other parameters kept steady) can result in varied signal intensities or even the amount of material ablated, which ultimately affects the overall analytical figures of merit (detection limits, precision, and accuracy). Chemical matrix effects are generally observed in the presence of the target sample and any other “interfering” species. For example, as noted above, one of the most difficult problems in the qualitative LIBS analysis of explosive material is distinguishing the energetic’s carbon, hydrogen, nitrogen, and oxygen emission lines from of the background air. Ultimately, chemical matrix effects can make accurate quantification of analyte species challenging, and thus also affect the utility of LIBS as a trace energetic sample detection technique. The interaction of the plasma with the material can be influenced by several factors

that include the sample's composition, atmospheric changes, and varying surface conditions. Even if a thorough understanding of the support matrix exists, there can still be concentration variance from the sample analyte spot-to-spot (different quantities deposited across the surface). Such an effect is specifically seen when working with trace quantities of material. Additionally, spectral line masking, analyte blocking, and shot-to-shot instability can increase with the physical ejection of granular particles, commonly observed when measuring spectra from trace explosives.

There are a few examples in the literature highlighting novel research conducted to try to better understand some of the challenges faced when applying LIBS for explosive detection (57, 95–97). The matrix effect can even occur when working in ambient air, largely comprised of O<sub>2</sub> and N<sub>2</sub> at 21% and 78%, respectively. Lazic et al. studied the matrix effect by observing variations in the characteristic atomic (C, H, N, and O) and molecular (C<sub>2</sub> and CN) LIBS emission lines obtained from heterogeneously dispersed organic residues (pure explosives and interferents) on clean aluminum supports (97). Secondary ionization events can occur in air leading to complication of the LIBS emission spectra (98). For example, when several organic compounds were investigated using LIBS, it was found that the strength of the carbon emission line was uncorrelated with the amount of carbon in the molecular structure. A similar trend was also observed for the nitrogen and oxygen emission lines (figure 4) (98). Even when the same species were analyzed in a background of helium, it was found that the carbon emission line had no correlation to the structure and the nitrogen emission line was virtually absent.

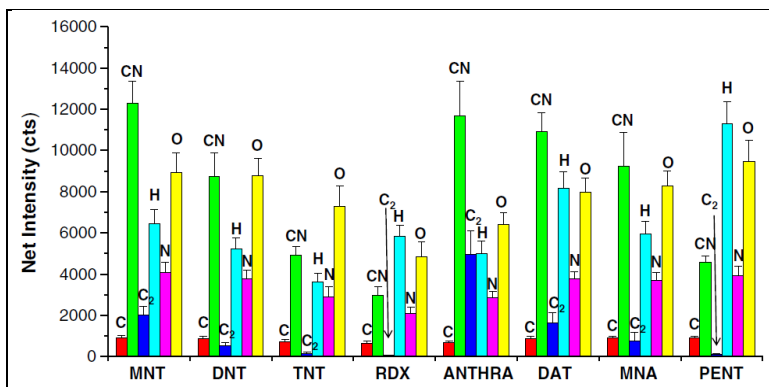


Figure 4. Net intensity of the LIBS signal in air from several organic compounds, 2-mononitrotoulene (C<sub>7</sub>H<sub>7</sub>NO<sub>2</sub>, MNT), DNT (C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O<sub>4</sub>), TNT (C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>6</sub>), RDX (C<sub>3</sub>H<sub>8</sub>N<sub>6</sub>O<sub>6</sub>), anthracene (C<sub>14</sub>H<sub>10</sub>), 2,4-diminotoulene (C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>, DAT), 4-methyl-3-nitroaniline (C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>, MNA), and pentaerythritol (C<sub>5</sub>H<sub>12</sub>O<sub>4</sub>, PENT). Figure taken from Lucena, P.; Doña, A.; Tobaría, L. M.; Laserna, J. J. *Spectrochim. Acta B* **2001**, *66*, 12.

From this informative work and others (97, 98), conclusions regarding trace explosive detection using LIBS can be drawn. The data collected demonstrated the following: (1) measurements collected in air displayed significant changes in H emission intensity (up to a 50% reduction);

(2) atomic line ratio intensities were observed to vary widely (almost an order of magnitude) and appeared unrelated to the molecular structure; (3) in the presence of other organic residues, a portion of O and N is lost due to chemical reactions; (4) atomic and molecular line intensities vary significantly as a function of the amount of sample residue; and (5) the CN and C<sub>2</sub> spectral lines are the only reliable molecular fragment emissions, which may be independent of buffer gas. Therefore, the elemental ratios and molecular fragments commonly used in PCA or PLS analysis may be ineffective as the carbon and nitrogen emission lines appear to be uncorrelated to energetic material investigated. In addition, as noted earlier, if new data are taken under different experimental conditions, the “trained” algorithms may not identify the material properly due to the inconsistency in the background and/or plasma generation. For example, as noted earlier there are four main elemental constituents in an explosive molecule (C, H, N, and O). However, in a recent publication 28 preselected atomic emission lines and 104 ratios had to be used to enable discrimination of LIBS spectra from energetic materials (99). This clearly illustrates how the matrix can complicate the identification process. The atmospheric interferences and chemical reactions that occur in the plume affect the observed ratios in the obtained LIBS spectra, affecting the material’s discrimination.

### **3.5.2 Frequency Dependence in Laser-Induced Breakdown Spectroscopy**

Laser-based spectroscopy commonly uses pulsed, nanosecond neodymium (Nd): yttrium aluminum garnet (YAG) lasers. The fundamental of these Nd:YAG lasers is 1064 nm; however, its various harmonics at 532, 355, and 266 nm have also been used for spectroscopic studies. The results obtained from various studies suggest that there might be frequency dependence for certain laser-based techniques. For example, spontaneous Raman scattering has a frequency dependence of  $\nu^4$  causing an increase in the scattering efficiency as the frequency increases (100). In addition, if the laser source’s central frequency is close to a particular electronic resonance, the scattering efficiency will also increase (100). Such a frequency dependence may also occur in LIBS (82, 101–105). For example, Wang et al. showed in a recent paper that lower breakdown thresholds were observed when the plasma was initiated using ultraviolet (UV) laser pulses (266 nm) (104). However, when near-IR (NIR) pulses (1064 nm) were used, higher signal-to-noise (S/N) ratio was obtained (104). A similar observation was observed for LIBS studies (105) when the fundamental wavelength 1064 nm was compared to 1470 nm. The overall emission intensities and ratios of molecular to atomic emissions were found to be greater when a 1064-nm nanosecond laser pulse was used to initiate the plasma as compared to a 1470 nm pulse (105). From these studies and others (106), it is found that NIR nanosecond laser pulses are ill suited for organic residue analysis at low fluence due to low molecular fragment production and also at high fluence due to plasma shielding. Low fluence, short wavelength (i.e., UV), nanosecond lasers appeared to work best, but if the fluence is increased, a higher atomization rate was observed producing less emission from molecular fragments.

Another manifestation of the frequency dependence is LIBS is demonstrated through a technique known as resonance-enhanced LIBS (RELIBS) (107–110). RELIBS is capable of enhancing spectral lines by using a laser pulse that is resonant with a transition in the target. This tuned excitation leads to enhancement in a specific spectral region of the LIBS spectrum for a particular target element. One drawback is that the laser pulse's frequency is tuned so that only an analyte with a particular electronic transition will strongly absorb the energy of the laser enabling this enhancement. Therefore, a tunable laser is typically required for implementation. Nevertheless, further research needs to be conducted to determine the optimal wavelength and fluence to yield the unique signatures that are required for identification of explosive materials.

### **3.5.3 Robust Algorithms for Material Identification**

There is a need for additional research studies analyzing the detection capabilities of LIBS as applied to explosive residues. It has been shown that matrix effects, different chemical reactions occurring in the plasma, variation in sample amount from spot-to-spot, and unknown support composition information can affect the observed emission spectrum. In addition, it was also found that there was a strong dependence of line intensities and ratios based on the plasma temperature, and averaging the data may prevent a full data description unless all measurements are collected under the same ablation rates. Therefore, to enable the accurate and rapid identification several factors have to be included in the developed detection algorithms. The first factor to include is to determine and incorporate the critical signatures required for discrimination, such as the C<sub>2</sub> and CN emission lines. The second factor would be to assimilate kinetic information regarding the plasma into the algorithm. The third factor would be to include advanced plasma diagnostics, such as plasma temperature and electron density, into the detection code. These parameter inclusions would lead to more robust discrimination using chemometric-based models.

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## **4. Laser-Induced Breakdown Spectroscopy Techniques for Enhanced Detection of Hazardous Materials**

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The identification of energetic material using LIBS can be challenging due to interferences in the environment that hinder detection. When a plasma is created by the laser, the initial molecular structure of the analyte is completely lost as the molecule is decomposed into its elemental components, mainly carbon, hydrogen, oxygen, nitrogen, etc. The material's determination is performed by measuring the obtained emission spectrum and comparing the atomic lines to a library. However, the elemental constituents from the sample are also naturally abundant in many materials in the immediate vicinity of the energetic material, including the atmosphere and the surface upon which the energetic is resting (i.e., matrix). Any researcher using LIBS for energetic material detection must be able to determine conclusively whether an elemental emission line is a result of the target material or from the surrounding matrix. LIBS researchers

tackle this problem in many ways. For example, Babushuk et al. was able to determine via a kinetic model that the time an emission line is observed relative plasma initiation is an indicator of whether the emission line came from the target, the substrate, surrounding atmosphere, or a chemical reaction within the plasma (111). Such information would enable more accurate identification of emission lines and eventual discrimination of target material.

It can be seen that there are various challenges and gaps in literature that require additional studies to be performed. However, research has begun in the required areas to determine if techniques like dual-pulse LIBS, microwave-enhanced LIBS, Raman-LIBS, LIBS-LIF, or the use of ultrashort pulses may be able to minimize background effects or provide additional molecular information adding in the identification of energetic material.

## **4.1 Enhancement of the Laser-Induced Plasma**

### **4.1.1 Dual-Pulse Laser-Induced Breakdown Spectroscopy**

One widely adopted technique that has been used to mitigate atmospheric contributions (i.e., N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>) to the plasma's emission signature is dual-pulse LIBS. In dual-pulse LIBS, two laser pulses interact with the target at a predetermined time delay. These two laser pulses can be generated from two separate lasers or from one laser that has been modified to generate multiple laser pulses with a short time delay between pulses (112). The use of two separate lasers allows for additional and independent control of the center wavelength, pulse duration, laser power, and pulse delay of each laser. However, the use of two lasers for dual-pulse LIBS results in a more complex optical setup that may be unsuited for studies performed outside of the laboratory. For example, a crossing or collinear configuration may be used when performing dual-pulse LIBS (75). In addition, the flexibility in the optical scheme may actually increase the difficulty of assuring that both beams will overlap at their respective foci. This issue can be mitigated by using one laser to generate two pulses. Although it can be guaranteed that the generated laser pulses will be collinear, there is a significant reduction in the control that the user has over pulse parameters.

Nevertheless, the dual-pulse LIBS technique has been shown to increase the ablation yield when using two laser pulses. The use of two laser pulses allows for one laser pulse to be optimized for ablation, resulting in the maximum amount of material to be ejected from the surface, and the other laser pulse to be optimized for plasma excitation resulting in increased signal intensity (101, 113) (figure 5). This increase was only observed for dual pulses as the emission intensity remained unchanged for single pulses with the same total pulse energy (48). Therefore, the laser-matter interaction is altered in the dual-pulse scheme leading to enhanced emission even for materials deposited on dielectric substrates. Some work suggests that a reduced pressure environment is created above the target surface minimizing interferences from the matrix (i.e., nitrogen, oxygen, and carbon dioxide) (114, 115). The dual-pulse configuration caused a reduction in the O/N ratio for bare metals, better reflecting the true stoichiometric ratio of nitrogen and oxygen contained in the air. However, when explosive-coated metals were sampled,

a modest enhancement in the O/N ratio was observed reflecting RDX's stoichiometric ratio (114). Although this preliminary data using a dual-pulse configuration have shown to decrease emission resulting from nitrogen and oxygen contained in the atmosphere, effectively increasing emission contributions relevant to the trace species (113), the reproducibility and potential complications in protocol transfer to the field may limit the technique's utility. Nevertheless, the potential benefits of dual-pulse LIBS have lead researchers to begin investigations with the multi-pulse LIBS as a function of various parameters (116). This research should include studies aimed at gathering more data at examining the effect of wavelength, pulse duration (nanosecond and nanosecond, nanosecond and femtosecond, or femtosecond and nanosecond), fluence, pulse separation, matrix, and spatial effects on the observed emission lines.

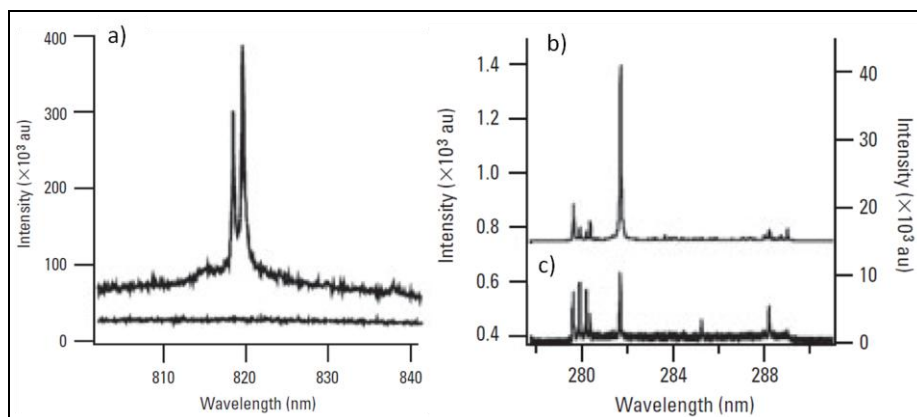


Figure 5. Spectra that illustrate the large neutral atomic and ionic emission and S/N enhancements that can be obtained with orthogonal (a) pre-ablative dual-pulse LIBS of sodium in aqueous solution and (b) collinear dual-pulse LIBS of an aluminum standard in air. (c) Single-pulse LIBS of an aluminum standard in air where the right-hand y-axis applies to (b) and left-hand y-axis applies to (c). The lower trace in (a) is a single-pulse spectrum for comparison with the upper, dual-pulse spectra. The above spectra were taken from Scaffidi, J.; Angel, S. M.; Cremers, D. A. *Anal. Chem.* **2006**, *78*, 24.

#### 4.1.2 Townsend Effect Plasma Spectroscopy

Townsend effect plasma spectroscopy (TEPS), also known as CO<sub>2</sub> laser-enhanced LIBS, uses a pulsed CO<sub>2</sub> laser to interact with the LIBS plasma 1–2 μs after its formation. During this 1–2 μs timeframe, the plasma continuum reaches the peak number of free electrons (117). The free electrons in the plasma absorb the CO<sub>2</sub> laser radiation via inverse Bremsstrahlung absorption reheating the plasma. Coons et al. showed this increase in temperature when there was a large increase in the electron temperature of the plasma after a Nd:YAG laser-generated plasma was irradiated by a CO<sub>2</sub> laser (118). The reheated plasma causes the excited states to emit for longer periods, enhancing signal intensity by a factor of 25 to 300 times, therefore, increasing detection (119). To date, research in the area of TEPS has shown that UV lasers are best for the ablation and plasma generation step when coupled with pulsed CO<sub>2</sub> lasers for plasma heating (120, 121). However, additional studies still need to be performed.



### 4.1.3 Microwave-Enhanced Laser-Induced Breakdown Spectroscopy

The plasma generated in LIBS will undergo rapid oscillations in its electron density. The frequency at which these oscillations occur is known as the plasma frequency and is dependent on the electron density of the plasma. Resonant enhancement of the plasma can occur if a source, set to the plasma frequency, is used to irradiate the LIBS plasma. Such a resonant enhancement occurs with microwave-enhanced LIBS. Matching the microwave frequency to the plasma frequency of the laser-induced plasma couples the two, allowing the microwave to become a resonant source of energy for the plasma. When the plasma becomes resonantly coupled to the microwave, the free electrons in the plasma are excited. These “hot” electrons collisionally excite the atoms and ions in the plasma (92) leading to an increase in the plasma lifetime (122) and enhanced sensitivity (figure 6). For example, Liu et al. measured a 23-fold increase in the detection sensitivity of copper in soil samples using microwave-enhanced LIBS (123). In addition, laser-induced plasmas that are resonantly coupled to microwaves can be used to detect certain molecular species within the plasma (124). Ikeda and Tsuruoka were able to detect nitrogen and OH with their microwave-enhanced LIBS system demonstrating enhancement of molecular and atomic signatures. The microwaves allow for resonant stimulation of the plasma where as the plasma is enhanced in a non-resonant manner with traditional dual-pulse LIBS or TEPS. However, there are certain limitations that occur with microwaves. The microwaves that are used in conjunction with LIBS are created in cavities and are transmitted over short distances via antennas or waveguides. This limitation would make remote interrogation of a target using microwave-enhanced LIBS more complicated than analysis using other laser-based techniques.

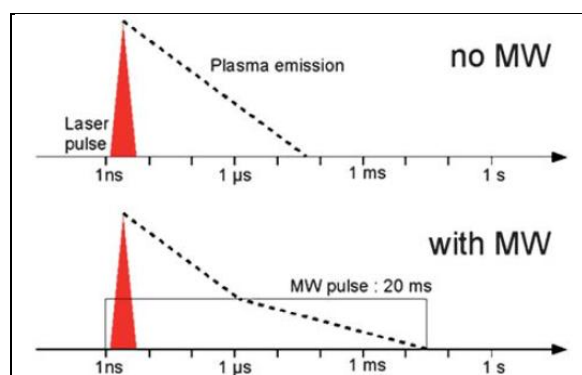


Figure 6. A comparison of plasma lifetime with and without enhancement from a microwave. The microwave-enhanced plasma is observed for the entire 20-ms lifetime of the microwave pulse. Figure was taken from Liu, Y.; Baudelet, M.; Richardson, M.; *J. Anal. Atom Spectrom.* **2010**, *25*, 1316.

## 4.2 Orthogonal Laser-Induced Breakdown Spectroscopy Techniques

Enhancement of the plasma does lead to the production of stronger emission lines from the analyte under investigation causing an increase in the observed S/N. However, the only information provided by such techniques is the atomic emission lines. Additional information

(e.g., vibrational information) regarding the molecule is unavailable using LIBS techniques alone. Techniques that allow for additional structural information or electronic state information to be gained about the molecule could allow for better target material discrimination. Research groups have begun to investigate the use of LIBS in conjunction with other detection techniques, such as Raman and LIF, to reduce interferences from the matrix and allow for better material identification due to the information gleaned.

#### 4.2.1 Raman-Laser-Induced Breakdown Spectroscopy

To develop a suitable technique or technology for standoff explosive detection, the detection system must be sensitive, demonstrating detection of target material from small/trace sample quantities from several meters, and be selective to accurately identify the hazard information clearly to the operator. One technique that meets these goals merges Raman with LIBS (Raman-LIBS) (125). Employing a Raman-LIBS system is advantageous as both molecular and atomic information about the target of interest can be collected (126). Due to the potential of this technique, interest in applying Raman-LIBS for explosive detection is rising, as demonstrated with the increased research funding in industry and Government. To demonstrate the utility of a Raman-LIBS system, analysis of the energetic molecule RDX is shown in figure 7. The spectra obtained allow for both atomic and molecular information to be collected from the same instrument leading to enhanced identification and discrimination. However, the utility of Raman-LIBS is unlimited as the technique has also been used the study of works of art (127, 128) and extraterrestrial exploration (129, 130).

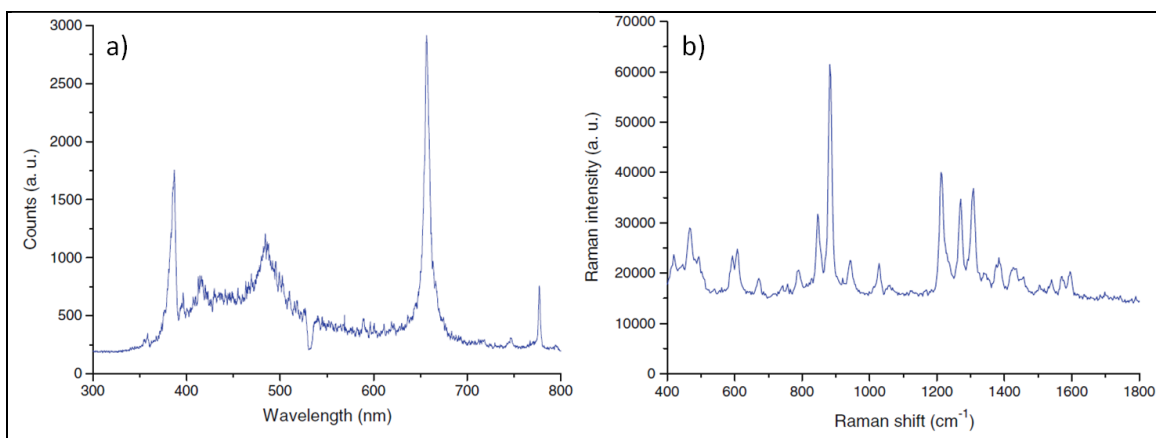


Figure 7. Paired (a) standoff-LIBS and (b) Raman spectra for RDX. Figures were taken from Moros, J.; Lorenzo, J. A.; Laserna, J. J. *Anal. Bioanal. Chem.* **2011**, *400*, 3353.

Raman-LIBS technology demonstrates considerable advantages as a combined sensing platform for the standoff detection of explosive materials. One significant advantage is the complementary spectral information provided from these two techniques which allows for the determination of the elemental composition (LIBS) and also differentiation between hazardous and benign targets (Raman) via the collected vibrational fingerprint from the scattered light. Additionally, a Raman-

LIBS system can rely on a single high energy laser excitation source to interrogate the target of interest. A single laser can be used at different fluence levels to obtain either the Raman spectrum (low fluence) or LIBS spectrum (high fluence) as the techniques rely on scattering and atomic emission, respectively, for signal generation. Another advantage of Raman-LIBS is that both the Raman and LIBS techniques require a similar level of spectral resolution. Therefore, comparable spectrographs can be used for signal dispersion and detection. Giakoumaki et al. demonstrated this capability by using the same hardware (i.e., a single 532-nm Nd:YAG laser and optical collection arrangement) to analyze a number of substances using both Raman and LIBS spectroscopy (131). Using this optical arrangement, both techniques were performed in succession allowing for the same point in space to be sampled, simply by increasing the power of the laser for LIBS analysis after Raman spectroscopy was performed.

However, despite the intriguing possibilities of using similar sources and detectors for a Raman-LIBS system, there are some limitations with these systems that would be pertinent to energetic material detection. One such limitation is the difference in the amount of time needed to collect a Raman spectrum versus that needed to collect a LIBS spectrum. The collection of a spontaneous Raman spectrum requires the detector to integrate the collected signal for one second up to hundreds of seconds depending on the scattering cross section for the target molecule. Therefore, if during the light collection process the spatial positioning of the laser/sample is altered, or decomposition of the target occurs, the resulting Raman spectra will be altered either in intensity or spectral features. This time requirement is more relaxed for LIBS analysis as collection can be performed in a single shot with a very short integration time (microsecond to millisecond). Another limitation in the Raman-LIBS technique is the difference in sensitivities. Spontaneous Raman scattering is less sensitive having a theoretical amount of analyte exposed to the laser pulse within the focal volume or limit of detection (LOD) in the microgram per pulse range as opposed to LIBS with a LOD in the nanogram per pulse range (132).

#### **4.2.2 Laser-Induced Breakdown Spectroscopy-Laser-Induced Fluorescence**

Laser-induced fluorescence has been used to perform diagnostics in plasmas such as number density and electron temperature (133). However, recently LIF has begun to be used to enhance the detection capabilities of a specific target when used in conjunction with LIBS (134). When using LIF along with LIBS, two laser pulses from either one or two lasers interact with the target area. The first laser pulse creates the plasma that is ordinarily analyzed with LIBS along with a plume of material caused from target ablation. The second laser pulse is delayed a few microseconds with respect to the first laser pulse allowing enough time for the constituents of the laser plume to return to the ground state. The second laser pulse, which is tuned to a specific wavelength to resonantly excite a target molecule, is focused into the plasma plume containing the ablated material. The fluorescence from the gas phase target molecule is then captured and analyzed with a CCD or spectrometer. For example, figure 8 shows the LIF spectra of protein-based binding media: egg white and collagen-based rabbit skin glue, which both have similar LIBS spectra (135). However, differentiation between the two binding agents commonly found

in works of art is able to be achieved by the differences observed in the fluorescence spectra due to the different amino acids present in the protein-based binding media.

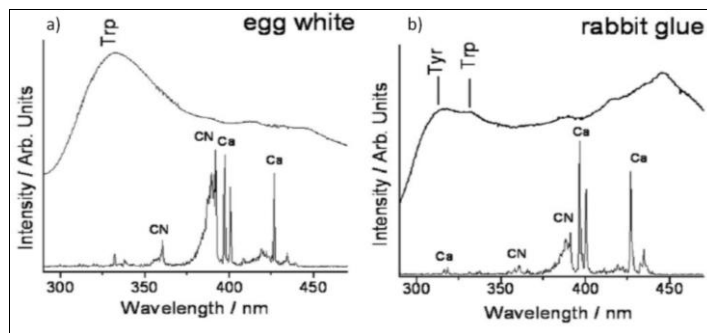


Figure 8. The LIBS-LIF spectra of (a) egg white and (b) rabbit glue acquired using an excitation wavelength of 266 nm, which is resonant with an electronic transition in both tyrosine and tryptophan. The LIBS (lower traces) and LIF spectra (upper traces) have been recorded using the same laser and grating 600 g/mm. The spectra were taken from Osticioli, I.; Mendes, N. F. C.; Nevin, A.; Zoppi, A.; Lofrumento, C.; Becucci, M.; Castellucci, E. M. *Rev. Sci. Instrum.* **80**, 076109 (2009).

Some of the earliest work on this technique was done by Kwong and Measures to study the effect of plasma component interference on the capability to detect trace amounts of material (134). They studied LIBS-LIF on materials inside of vacuum chambers with inert buffer gases at low pressures to reduce collisional quenching, improve detection limits, and create conditions for more reproducible plasma generation(134). Niemax and Sdorra found that when using LIBS-LIF for trace detection, the measured concentration of the target is independent of the matrix (136). Under atmospheric conditions, LIBS-LIF has been found to increase sensitivity and specificity beyond traditional LIBS alone (137). The LIBS-LIF technique, also known as RELIBS, is also capable of enhancing spectral lines that are normally unable to be resolved due to their spectral interference from other elements. The second laser pulse is typically tuned to transfer a population from a specific species back up to an excited state. This reexcitation allows for additional emission to occur enhancing the observed LIBS spectrum in a specific spectral region for a particular target element. This idea was demonstrated by enhancing the UV emission lines of phosphorus ablated from a steel target using the RELIBS technique (107). Despite the successes that LIBS-LIF has achieved in the area of material identification, there are some drawbacks to the technique. One drawback to using LIBS-LIF technique is that LIF can only be used for one target species at a time. The second laser pulse is tuned so that only analytes with a particular electronic transition will strongly absorb the energy of the laser enabling fluorescence. However, such a drawback could be overcome if the second laser pulse is generated by a tunable laser that can be moved to optimal excitation wavelengths for any species allowing for customization of the LIBS-LIF system for a wide range of target molecules. Another drawback to this technique, as it pertains to energetic material detection, is that LIF can only be used with

elements and small molecules with easily distinguishable fluorescence spectra. For example, Phifer et al. showed that no distinctive fluorescence spectra were obtained when using LIF to detect TNT, RDX, HMX, or PETN (138). Therefore LIBS-LIF technique would have difficulty in yielding any additional information allowing for accurate identification of any one of these four nitro-based explosives in its current manifestation.

### 4.3 Short Pulse Laser-Induced Breakdown Spectroscopy

Traditional LIBS research uses nanosecond lasers to initiate plasma generation at the target. The high temperature electron dense plasma that is formed continues to interact with the laser pulse through plasma shielding. This process allows for the laser pulse energy to be further absorbed via inverse Bremsstrahlung or scattered off the electron dense plasma preventing the laser pulse from interacting with the target. As a result, the plasma can reach higher temperatures and higher electron densities. Time-resolved measurements in metallic systems reveal that after the initial electronic excitation, the internal modes of the condensed phase system thermalize on the picosecond to nanosecond timescale (139). Therefore, when nanosecond lasers are used to perform the LIBS technique, there is enough time for the system to come to thermal equilibrium with the plasma temperature. This heating leads to increased atomic emissions but also higher intensity background with prolonged continuum emission. In addition, the supplementary heating causes additional melting and ablation (53), leaving large craters at the target's surface.

Recent work with femtosecond laser pulses suggests that the laser-matter interaction is fundamentally different with ultrashort lasers. For example, femtosecond laser pulses have the capability to exceed the ionization threshold of the target molecule without using a large amount of laser pulse energy. Therefore, femtosecond pulses have sufficient intensity ( $>10^{13}$  W/cm<sup>2</sup>) to form the free electrons necessary for plasma formation via a multiphoton excitation. However, it should be noted that the femtosecond pulse is gone by the time the plasma is formed, eliminating the interaction between the laser pulse and the resultant plasma, preventing plasma shielding in the sample, and allowing for all energy to be deposited prior to material removal. In addition, the lower pulse energy thresholds (140) and the fact that the laser pulse is deposited into the system on a timescale much faster than that required for any ensuing thermal response may prevent thermal damage from occurring to the system. Less damage to the sample prevents layer mixing in the sample and results in cleaner ablation profiles (140–142), enabling depth profiling (49). Additionally, the plasma that is formed is temporally shorter (53) and spatially smaller than the plasmas formed with nanosecond lasers. The temporally short plasma can enable gate-free analysis of the sample (49, 58, 141), reducing cost of the optical system and enabling higher repetition rate lasers. These advantages suggest that femtosecond lasers may offer unique advantages over traditional nanosecond lasers in LIBS studies and researchers have begun to explore what they may be (72, 143–148). Femtosecond laser pulses have been found to yield more molecular fragments than elemental constituents when compared to nanosecond lasers at low fluence (72, 106, 148). The increased yield of molecular components could serve as signatures for energetics and possibly eliminate background matrix effects from the substrate and

the atmosphere. In addition, Piñon et al. showed that dual-pulse LIBS using femtosecond duration lasers provides a similar enhancement that one would expect in a dual-pulse experiment with nanosecond laser pulses. This research (149) and work by De Lucia Jr. et al. (148) showed that as the energy of the femtosecond laser pulses was decreased, the effectiveness increased. However, it was also found that the advantages that femtosecond pulses provided were easily negated when the fluence of the laser was increased (148).

Although there are a number of advantages that one can experience when using a femtosecond laser to produce plasma for LIBS, there are a number of challenges as well. One drawback to femtosecond lasers is the complexity of the lasers themselves. Femtosecond laser pulses are enabled due to mode-locking within the cavity of an oscillator. Ruggedization of these oscillators and amplifiers still has to be performed; therefore, it is rather easy to break mode-lock within the laser, preventing its operation. However, it should be noted that laser manufacturers are working to resolve these problems with ruggedized femtosecond lasers and fiber-based femtosecond lasers. Another challenge is due to the ultrashort pulse duration of the laser. All material has dispersion associated with it, including air. Therefore, as the ultrashort laser pulse propagates through the air, the pulse will become chirped and the degree of dispersion is dependent on the amount of material through which the pulse propagates. This dispersion can be pre-compensated for to a certain extent, but there may be some variability of the laser beams pulse duration at the target unlike nanosecond laser pulses. Such dispersion effects can be controlled by altering the phase of the laser pulse via a spatial light modulator (150) prior to its interaction with the target.

Another issue with femtosecond lasers is due to their high energy and the ultrashort pulse duration. Due to the high energy and short pulse duration, the irradiance or intensity of the beam is several orders of magnitude higher than that of nanosecond lasers. Therefore, nonlinear effects such as Kerr lensing, self-phase modulation (151), and filamentation (151, 152) can occur, which is uncommon with nanosecond laser pulses. When a femtosecond laser beam of sufficient power travels through the air towards the target, Kerr lensing can begin to overwhelm the diffraction effects. The Kerr lensing leads to a self-focusing of the laser beam due to the intensity-dependent refractive index of the material:  $n(I) = n_o + n_2I$ , where  $n_o$  is the linear refractive index and  $n_2$  is the second-order refractive index ( $n_2 = 3 \times 10^{-19} \text{ W/cm}^2$  for air). However, once the intensity of the pulse reaches approximately  $10^{13} \text{ W/cm}^2$ , ionization of the air will occur causing a negative lens effect on the laser pulse (151), essentially limiting the intensity of the pulse to  $5 \times 10^{13} \text{ W/cm}^2$  (153, 154). When the two processes, Kerr lensing and plasma defocusing, are in balance, the plasma channel or filament can propagate for several hundred meters (155) to kilometers (156). Therefore, this filamentation process can enable the delivery of ultrashort pulses to a target at virtually any distance by altering the phase (157), power, or divergence angle of the pulse (158). This allows for the filament to be initiated anywhere close to the desired target without the need for focusing optics. This is unlike the use of nanosecond laser pulses in which the standoff distance for a LIBS analysis is determined by the numerical aperture of the focusing optic and the available laser power (159). For example, a LIBS analysis using a

nanosecond laser would require alteration of the system’s optical components to enable 100-m detection instead of 50 m. However, if a femtosecond laser was used to perform remote filament-induced breakdown spectroscopy (R-FIBS) (160–162) no alteration of the optical components would be necessary. The use of R-FIBS instead of traditional nanosecond LIBS could allow for kilometer-ranged detection in theory (161, 163), eliminate the effect of the lens-to-target distance (figure 9) (161), and may produce higher S/N measurements due to the intensity clamping effect of the filament (164). Using this method of R-FIBS, preliminary investigations have begun allowing for the remote detection of DNT with IR and UV filaments (160). In addition, since the femtosecond pulses are maintained at “low” intensities within the filament, an increase of molecular fragments relative to elemental constituents should be observed. This increase in molecular fragments would minimize matrix effects in a similar manner as that seen with traditionally focused, low fluence, femtosecond laser pulses.

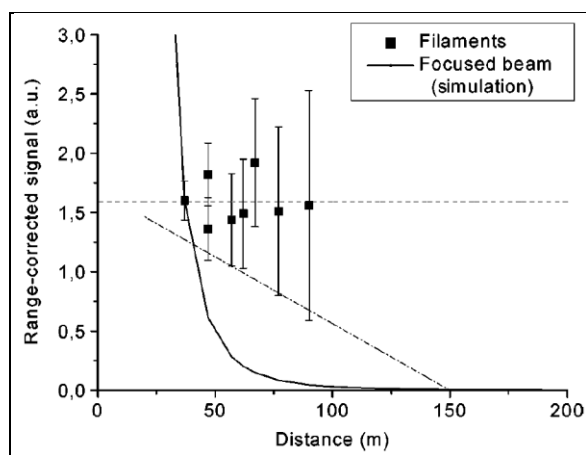


Figure 9. The distance dependence of the range-corrected remote FIBS signal for the 521.8-nm copper line versus a simulated traditionally focused beam. Taken from Stelmaszczyk, K.; Rohwetter, P.; Mejean, G.; Yu, J.; Salmon, E.; Kasparian, J.; Ackermann, R.; Wolf, J.-P.; Woste, L. *Appl. Phys. Lett.* **2004**, 85, 3977.

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## 5. Industry Review

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One contributing factor often overlooked by researchers within a technology space is the health and activity associated with industrial counterparts’ ability to bring the technology to market as a commercial product. In an effort to address the state of LIBS within the industrial community, this report attempted to identify all commercial entities that list LIBS as a technology area being pursued. Table 3 lists all companies found with investments in LIBS technology. Examination of this table reveals that the number of companies that list LIBS as a technology area is moderate (15) with even fewer companies (8) with fully developed and marketed products. Even with

these moderate numbers, it can be seen that a large fraction (>70%) of the companies are attempting to take advantage of LIBS for standoff detection applications, which fits well into the use of LIBS for energetic material detection at range.

Table 3. List of LIBS systems that are commercially available or in development.

<b>Company Name</b>	<b>Range</b>	<b>Part Number</b>
<a href="#"><u>Alakai</u></a>	Standoff	In Development
<a href="#"><u>Ameasol</u></a>	Point	In Development
	Standoff	In Development
<a href="#"><u>Applied Photonics</u></a>	Standoff	ST-LIBS (in conjunction with Ocean Optics)
<a href="#"><u>Applied Research Associates</u></a>	Point	In Development
	Standoff	In Development
	Standoff	In Development
<a href="#"><u>Applied Spectra</u></a>	Point	RT100 (HP, B and EC)
	Point	Portable LIBS
	Standoff	Mini-ST/In Development
<a href="#"><u>BAE Systems</u></a>	Standoff	In Development
<a href="#"><u>ChemImage</u></a>	Standoff	In Development
<a href="#"><u>Energy Research Company</u></a>	Point	LIBSCAN 25
	Point	LIBSCAN 50
	Point	LIBSCAN 100 (3 $\omega_0$ and 4 $\omega_0$ )
	Point	LIBSCAN 200
	Point	LIBSSCAN 400
	Standoff	In Development
<a href="#"><u>P&amp;P Optica</u></a>	Standoff	PPOLIBS
	Standoff	In Development
<a href="#"><u>Pharma Laser</u></a>	Point	PharmaLIBS™250
<a href="#"><u>Photon-Machines</u></a>	Point	SpectroLaser
	Point	Insight
<a href="#"><u>Physical Sciences Inc.</u></a>	Point	In Development
<a href="#"><u>Progression</u></a>	Point	Titan CCA
	Point	MagnePulse AT
	Point	iPulse
<a href="#"><u>SAIC</u></a>	Standoff	In Development
<a href="#"><u>StellarNet Inc.</u></a>	Point	Porta-LIBS-2000
	Standoff	LIBS System

In an effort to further examine this possibility, the authors used their direct relationship with several companies to survey them as to their investments and outlook for LIBS in general and for the use of the technology for detection of energetic materials. Although each individual company has differing outlooks on LIBS, there were several trends that became apparent when analyzed. First, as this report is being written, there is little to no investment for development of standoff LIBS for explosives detection within the United States. All companies interviewed had



previously received funding for this type of work from DOD or other Government sources, but these programs had concluded and no follow-on programs were expected. Given the statements of the companies interviewed, it became clear that progress toward the end goal of energetic detection at range had been arduous and lack of technical maturity had ended most programmatic efforts. Several of these vendors either had commercial systems for sale or were expecting initial release of products soon. However in all cases, the products being marketed were not targeting the area of hazardous material detection, but were focused on industrial processing applications. Second, there was a clear confidence to address industrial processing types of applications and full confidence in LIBS as an analytic tool among the interviewed companies. On the contrary, LIBS as a technology to address standoff explosive detection needs of the military environment was viewed as a difficult problem that would require research and development investment to overcome. Although all companies interviewed indicated they would pursue LIBS for standoff detection of explosives if given the chance, that is where the similarities stop. All respondents suggested numerous focus areas including, but not limited to, fluence control, plasma temperature stability, general signal reproducibility, pre-measurements on expected substrates, time-resolved plasma emissions, and increase in optical engineering of systems. These same themes of shortcomings have been mentioned numerous times within this report and again, even within commercial entities, are recognized as technical hurdles for use of LIBS as a DOD capability. There are common aspects of these remarked areas that can be addressed by dedicated optical engineering, but several could be characterized as fundamental limitations of the technology with no obvious solutions within reach. As called out earlier, investigations into use of chemometrics, temporal and in situ calibration techniques are a step in the right direction, but challenges still remain.

In conclusion, it is clear that LIBS technology is being pursued by a handful of companies as an analytic technique and that these companies are actively producing products that have market pull due to several unique features associated with LIBS and the promise of analytic capability without sample preparation and at standoff ranges. This base market could be advantageous, because the other obvious trend is that LIBS technology is not ready to be commercialized for explosive hazard detection. All agree that commercialization will require development of the technique or methodology to push beyond its current laboratory or early prototype level of performance to a level of reliability not seen as of yet in LIBS directed at field environment task. This state of the commercial sector mirrors the opinions generated in the portions of the DOD community and reflect the open question of whether continued development for LIBS as a hazardous material detection capability is warranted for DOD applications.

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## 6. Conclusions and Future Recommendations

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It has been demonstrated throughout this review that LIBS is a promising technique for the trace detection of explosive materials. However, several challenges have to be overcome to allow for the complete transition of LIBS to the field for practical explosive detection applications. The main research goal needs to focus on minimizing matrix effects (i.e., atmospheric and substrate). Due to the matrix effects, quantitative and qualitative analysis of organic species is quite difficult. The data suggest that the CN and C<sub>2</sub> spectral lines are the only reliable molecular fragment emissions, which may be independent of buffer gas. In addition, the research suggests that the use of short wavelength, femtosecond laser pulses may minimize fragmentation in the target molecule reducing atmospheric chemistry (i.e., recombination) and allow for more robust identification. As a result, advanced plasma spectroscopies such as femtosecond LIBS and FIBS should continue to be studied, particularly in the low fluence regime where sample matrix interferences may be minimized. Other recommendations include (1) use reproducible sample residue preparation (*I65*) on various substrates to accurately benchmark performance; (2) perform additional temporal studies/kinetics to facilitate the development of more robust analysis tools; and (3) conduct experiments on the conditions (e.g., single or dual-pulse) that yield robust “matrix independent” results. From such studies, the minimization of matrix effects and accurate determination of these critical signatures would be determined, leading to the development of a more robust detection algorithm allowing for quantitative analysis.

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## List of Symbols, Abbreviations, and Acronyms

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AN	ammonium nitrate
ATO	Army technology office
CCD	charge-coupled device
CF-LIBS	calibration-free LIBS
CRESS	colorimetric reconnaissance explosive squad screening
DA	discriminate analysis
DAT	2,4-dinitrotoulene
DESI	desorption electrospray ionization
DNT	2,4-dinitrotoluene
DOD	Department of Defense
EC	external cavity
EGDN	ethylene glycol dinitrate
GC	gas chromatography
HMEs	homemade explosives
HMX	high-velocity military explosive
HPLC	high performance liquid chromatography
IEDs	improvised explosive devices
IMS	Ion mobility spectrometry
IR	infrared
JCAD	joint chemical agent detector
LEMS	laser electrospray mass spectrometry
LIBS	laser-induced breakdown spectroscopy
LIF	Laser-induced fluorescence
LOD	Limit-of-detection
MNA	4-methyl-3-nitroaniline
MNT	2-mononitrotoulene
Nd:YAG	neodymium-doped yttrium aluminum garnet



NIR	near infrared
PA	photoacoustic
PAS	photoacoustic spectroscopy
PCA	principal component analysis
PCs	principal components
PENT	pentaerythritol
PETN	pentaerythritol tetranitrate
PLS	partial least squares
QCL	quantum cascade laser
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
REMPI	resonance-enhanced multiphoton ionization
R-FIBS	remote filament-induced breakdown spectroscopy
TAG-DN	1,3,5,-triaminoguanidinium dinitramide
TATP	triacetone triperoxide
TEDDs	trace explosive detection devices
TEPS	Townsend effect plasma spectroscopy
TF	tuning fork
TNT	2,4,6- trinitrotoulene
UV	ultraviolet
$\nu$	frequency
$\nu_o$	fundamental frequency
$\nu_{vib}$	vibrational frequency
$n(I)$	intensity-dependent index of refraction
$I$	intensity
$n_o$	linear refractive index
$n_2$	second-order nonlinear refractive index

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