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of Explosives Residues: A Review of Recent Advances,
Challenges, and Future Prospects**

**by Jennifer L. Gottfried, Frank C. De Lucia Jr., Chase A. Munson, and
Andrzej W. Miziolek**

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Laser-induced breakdown spectroscopy for detection of explosives residues: a review of recent advances, challenges, and future prospects

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Abstract In this review we discuss the application of laser-induced breakdown spectroscopy (LIBS) to the problem of detection of residues of explosives. Research in this area presented in open literature is reviewed. Both laboratory and field-tested standoff LIBS instruments have been used to detect explosive materials. Recent advances in instrumentation and data analysis techniques are discussed, including the use of double-pulse LIBS to reduce air entrainment in the analytical plasma and the application of advanced chemometric techniques such as partial least-squares discriminant analysis to discriminate between residues of explosives and non-explosives on various surfaces. A number of challenges associated with detection of explosives residues using LIBS have been identified, along with their possible solutions. Several groups have investigated methods for improving the sensitivity and selectivity of LIBS for detection of explosives, including the use of femtosecond-pulse lasers, supplemental enhancement of the laser-induced plasma emission, and complementary orthogonal techniques. Despite the associated challenges, researchers have demonstrated the tremendous potential of LIBS for real-time detection of explosives residues at standoff distances.

Keywords Explosives detection · Laser-induced breakdown spectroscopy · Double-pulse LIBS · Chemometric analysis

Introduction

The direct chemical detection of energetic materials and residues of explosives in real-time is a particularly challenging problem. Interest in overcoming the difficulties associated with the detection of explosives has grown over the past decade and is now shared by many government organizations. The military has a vital interest in the development of field-portable sensors to detect landmines, improvised explosive devices, remotely detonated munitions, hidden armaments, and unexploded ordnance. Homeland security requires an analytical capability for the detection of trace amounts of explosives or their residues in a variety of different situations (e.g., in airplane, train, or ship passenger luggage, in vehicles, and within transport containers). In addition, the ability to detect trace amounts of residues of explosives would greatly benefit forensic investigations of destructive explosive events.

Most widely accepted techniques for detection of traces of explosives, for example ion-mobility spectrometry and gas chromatography, rely on vapor detection. Unfortunately, at room temperatures the vapor pressures of many common explosives are extremely small (ppb_v or less) and attempts to conceal the explosives by sealing them in packaging materials can reduce the vapor concentrations by up to three orders of magnitude [1]. A single first generation C-4 (91% RDX, 9% plasticizer and binder) fingerprint, however, can contain several milligrams of the secondary explosive cyclotrimethylene-trinitramine (RDX) [2]. Surface sampling is therefore an important pathway for indirectly detecting explosive devices; because explosive particulate matter strongly adheres to surfaces, even careful handling is likely to result in the transfer of explosive material to surfaces such as door knobs, walkways, and vehicle surfaces [3]. One of the most pressing needs for the

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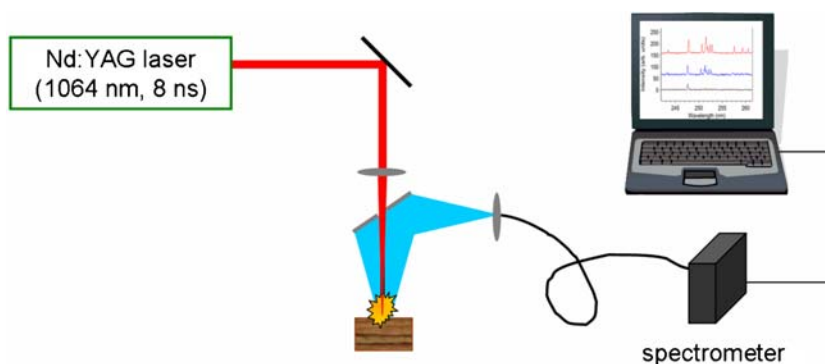
military is the standoff detection of explosives (~100 m), in which the screeners and equipment remain a safe distance from the screening area. Laser-based optical techniques provide the capability for true standoff detection [4].

One promising optical technique for detection of explosives is laser-induced breakdown spectroscopy (LIBS). LIBS is a spectroscopic analysis technique that uses the light emitted from a laser-generated microplasma to determine the composition of the sample on the basis of elemental and molecular emission intensities [5]. The ability of LIBS to provide rapid, multi-element microanalysis of bulk samples (solid, liquid, gas, and aerosol) in the parts-per-million range with little or no sample preparation has been widely demonstrated [6–13]. LIBS holds particular promise for the detection and identification of explosives because of its intrinsic capability for minimally destructive, in situ, real-time detection and analysis of a broad range of chemical species. The ability of LIBS to detect trace amounts of materials with a single laser shot is especially important for residue detection, because the first shot can ablate all or most of the residue. Figure 1 shows a diagram of a simple LIBS system and lists several key advantages.

LIBS has the following properties:

1. no sample preparation is required;
2. it is very sensitive, e.g. only a very small sample is required (nanograms–picograms) for production of a usable LIBS spectrum;
3. it is fast, providing real-time (<1 s) response;
4. LIBS sensors can be made rugged and field-portable;
5. all components (i.e., laser, detector, computer, etc.) can be miniaturized; and

Fig. 1 Diagram of a typical LIBS system. The laser (~GW cm^{-2}) is focused on to the sample surface with a lens, resulting in the ablation of a small amount of material and the subsequent formation of microplasma above the sample surface. The light emitted from the plasma is collected and focused on to a fiber optic attached to a spectrometer, which spectrally and temporally resolves the light. A PC displays and analyzes the recorded spectra, which are characteristic of the target material



- real-time sensor technology, no sample preparation
- bulk and residue solid, gas, and liquid detection
- broadband spectrometers (~100–1000 nm)
→ universal materials detection (hazardous and benign)
- potential for ruggedized instrumentation in a variety of configurations, including standoff

6. LIBS offers the flexibility of point detection or standoff mode operation.

With recent advances in broadband detectors (multi-spectrometer or echelle), LIBS can be used to determine the elemental composition of any target material, because every element in the periodic table has characteristic atomic emission lines that emit in the UV–VIS–NIR spectral region. Although most early LIBS applications involved metal targets, LIBS can be applied to a variety of materials including plastics and other organic compounds, biological materials, and hazardous substances. Here we review the recent advances in LIBS as a technique for detection of residues of explosives and discuss the feasibility of LIBS for this application.

LIBS for explosives detection

The carbon, hydrogen, oxygen, and nitrogen atomic emission lines (which span the UV to NIR spectral regions) are commonly used to identify organic compounds such as plastics [14–19], nitroaromatic molecules, and polycyclic aromatic hydrocarbon samples in ambient air [20]. Atomic emission lines associated with C, H, N, and O, and molecular fragments associated with the $\text{CN}(B^2 \Sigma^- - X^2 \Sigma^+)$ violet system and the $\text{C}_2(d^3 \Pi_g - a^3 \Pi_u)$ Swan system were used to successfully show differences between the compounds studied. Peak intensity ratios of these lines have also been used to analyze samples; the C/H ratio was found to be particularly important for discrimination [14, 15, 17]. Both Anzano et al. [18] and Tran et al. [21] analyzed the emission intensity ratios of several organic compounds for classification and quantification, respectively.

The successful detection and discrimination of organic material with LIBS based on atomic and molecular emission intensity ratios led researchers at the US Army Research Laboratory (ARL) to investigate characteristics of the LIBS spectra of explosive materials. LIBS spectra were collected from various energetic materials, including highly purified RDX, cyclotetramethylene tetranitramine (HMX), trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), and nitrocellulose (NC), and from operational explosives and propellants C-4, A-5, M-43, LX-14, and JA2 [22]. The observed LIBS spectra contained the expected C, H, N, and O emission lines, and atomic and ionic emission resulting from impurities (Ca, Na, K, and Mg). Table 1 lists the emission lines observed by ARL in the LIBS spectra of research-grade nitroamine explosives, including RDX and TNT (see Fig. 2 for chemical structures). Although the C₂ and CN molecular emission peaks are primarily due to recombination in the plasma [23, 24], they serve as an indication of the amount of carbon present in the explosive material (the source of the nitrogen for CN formation in single-pulse LIBS is primarily air). Elemental emission lines listed in Table 1 are from the NIST database [25] and molecular emission lines are from Pearse and Gaydon [26]. A kinetic model for the LIBS plume of RDX has recently been developed in order to study the processes responsible for the LIBS signature of explosives [27], but the complex nature of the laser interaction with energetic materials is not well understood.

The energy required for direct initiation of explosives with a laser (leading to detonation) increases as pulse length is reduced [28], and the short-pulse lasers used for LIBS (typically <10 nanosecond pulse widths) are generally not sufficient to initiate the energetic materials with a reactive shock wave. The plasma formation (and subsequent shielding of the surface from the laser by the plasma) occurs too fast for significant thermal energy transfer to the remaining material, and the small amount of material removed results in negligible shock imparted to the

remaining material. Ultrashort-pulse lasers have even been used to safely machine a variety of high explosives [29, 30]. Ignition (i.e. burning) of an explosive residue has occasionally been observed in our laboratory (primarily with TNT particles), but initiation of an energetic material with a LIBS laser has not been observed for the secondary explosives commonly used by the military.

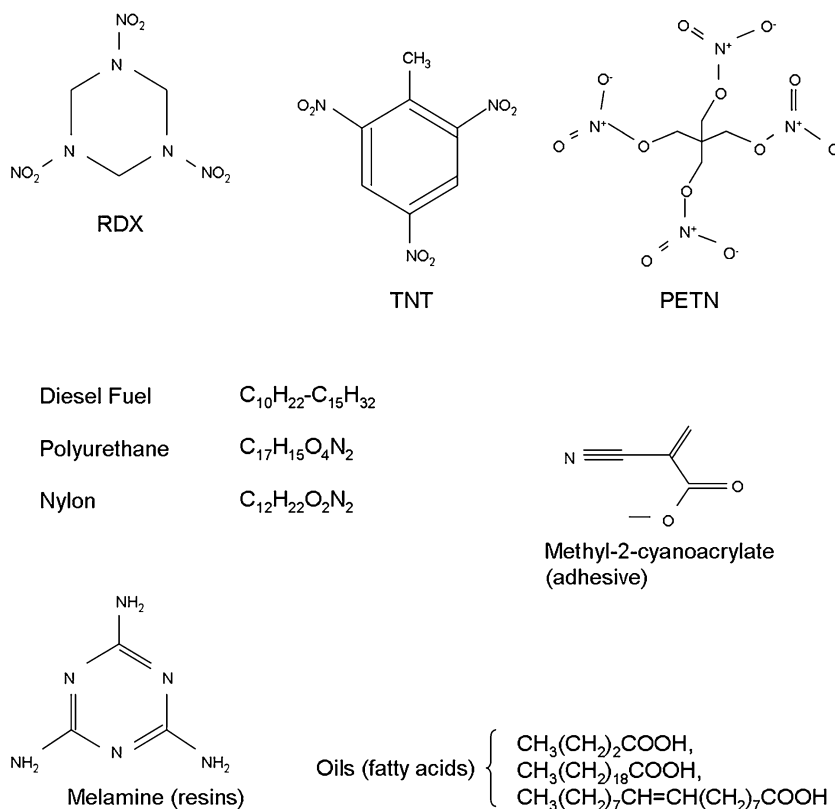
Recent research efforts in this area have been focused on optimizing the sensitivity and selectivity of LIBS for the detection of residues of explosives. LIBS is a relatively sensitive technique capable of detecting elemental emission in the low ppm or ppb range [12], however determining the limit of detection (LOD) of molecular compounds such as explosives is extremely complicated; because identification depends on more than a single tracer element, multivariate analysis is required for discrimination of explosives from other organic materials. In addition, because a small amount of substrate is ablated into the laser-induced plasma with the residue of interest, the LOD will also depend on the type of substrate and the extent of surface coverage for the residue, and on experimental conditions such as the laser energy, pulse width, and wavelength, the efficiency of the collection optics and spectrometer, and the distance to the target. Discrimination of residues of explosives applied to aluminium foil has been demonstrated for concentrations of approximately a few hundred nanograms per square centimeter or less [31, 32].

A common characteristic of most explosives is their high nitrogen and oxygen content relative to the amount of carbon and hydrogen [33]. By tracking the amounts of oxygen and nitrogen in a sample relative to the other elements it is possible to determine if a compound is energetic or non-energetic [34]. Figure 2 shows the molecular formulas or structures of several explosives and potential interferents. The interferents have a much higher carbon and hydrogen content relative to the oxygen and nitrogen than the explosives. Some of the interferents contain no nitrogen; however, their oxygen content is still

Table 1 Observed LIBS emission lines in research-grade military explosives

Species	Emission lines (nm)
C	247.856, 833.515, 906.247, 907.828, 908.851, 909.483, 911.180, 940.573
CN	385.09, 385.47, 386.19, 387.14, 388.34, 415.24, 415.81, 416.78, 418.10, 419.72, 421.60
C ₂	467.86, 469.76, 471.52, 473.71, 512.93, 516.52, 550.19, 554.07, 558.55, 563.55
H	486, 656
N	742.364, 744.229, 746.831, 818.487, 818.802, 820.036, 821.072, 821.634, 822.314, 824.239, 856.774, 859.400, 862.924, 865.589, 867.608, 868.028, 870.325, 871.054, 871.883, 872.889, 874.736, 938.680, 939.279, 946.068
O	715.670, 777.194, 777.417, 794.755, 795.216, 822.182, 842.616, 844.636, 882.043, 926.084
Ca	315.887, 317.933, 370.603, 373.690, 393.366, 396.847, 422.672, 585.745, 849.802, 854.209, 866.214
K	766.490, 769.896
Na	568.263, 568.821, 588.995, 589.592, 819.482

Fig. 2 Structures or formulas of several explosive and non-energetic organic compounds



low relative to hydrogen and carbon. Furthermore, the diesel fuel interferent is a combination of chains of hydrogen and carbon with no oxygen or nitrogen content. These differences can be exploited using LIBS in order to improve discrimination (i.e. selectivity) between energetic and non-energetic materials.

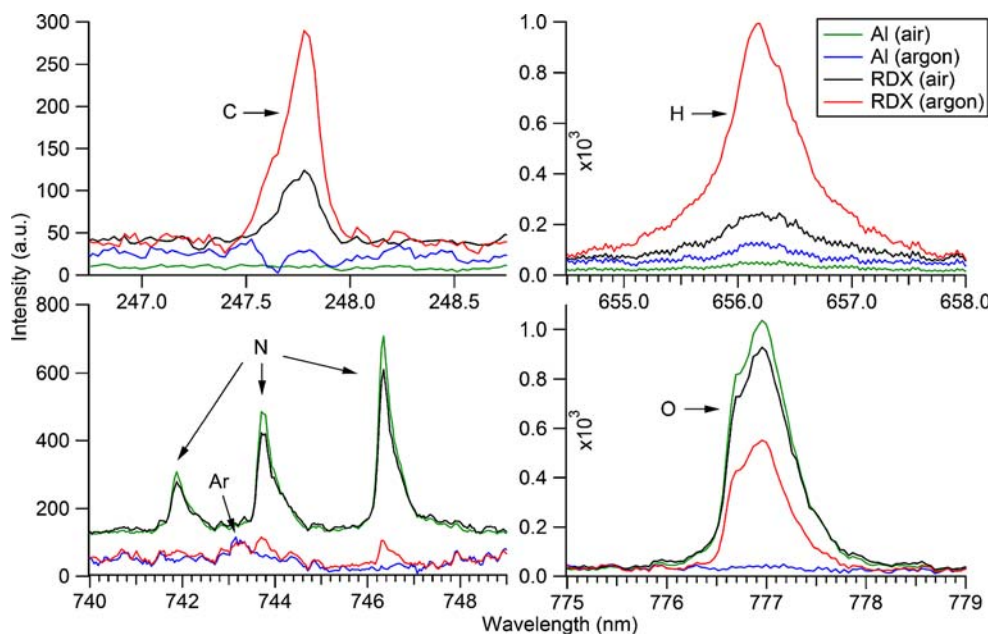
Although explosives residues can be identified on the basis of C:H:N:O elemental ratios, entrainment of atmospheric oxygen and nitrogen into the laser-induced plasma complicates the discrimination of energetic and non-energetic materials. Minimizing the oxygen and nitrogen contribution from the atmosphere is necessary to track the true value of oxygen and nitrogen relative to carbon and hydrogen in a LIBS spectrum. The formulation of RDX, for example, has equal amounts of O and N. Air alone has more nitrogen (80%) relative to oxygen (20%). Eliminating the nitrogen and oxygen contribution from air therefore results in a larger O:N ratio characteristic of the explosive material [22].

In a laboratory setting, argon can be used to displace the ambient atmosphere from the surface of the sample. As an added benefit, the use of argon as a buffer gas at atmospheric pressures also results in an increase in emission signal compared with air (e.g. Ref. [35]). Enhanced discrimination of explosives residues under argon has been demonstrated with a man-portable LIBS (MP-LIBS) prototype system [32] and with laboratory

close-contact systems [32, 36]. Figure 3 shows the improvement in the signal-to-noise ratio for the C and H lines with the addition of an argon flow across the sample surface, and the reduction in atmospheric O and N. Although using an inert gas to displace the air above the sample is effective for close-contact studies, it cannot be used practically for standoff applications.

As an alternative to atmospheric displacement with a buffer gas, multiple laser pulses can be used to interrogate the sample. Double-pulse LIBS, which is known to reduce the amount of air entrained in the laser-induced plasma, has recently been demonstrated to improve the discrimination of energetic and non-energetic materials [31, 32, 36]. In double-pulse LIBS, two successive laser pulses are used to generate the microplasma. Typically, the laser pulses are separated by a few microseconds. Researchers have used a variety of double-pulse LIBS experimental configurations ranging from collinear nanosecond laser pulses to orthogonal laser schemes utilizing both a femtosecond pulse and a nanosecond pulse [37–42]. The collinear double pulse configuration with identical laser pulses is the simplest to implement for standoff LIBS. The main advantage of double-pulse LIBS for most applications is the observed increase in signal; consequently, studies of double-pulse LIBS have increased in recent years [42]. The extent of the reported signal increases depend on many factors including pulse separation times, wavelength, pulse energies, sample,

Fig. 3 Single-shot spectra of aluminium and RDX residue ($\sim 400 \text{ ng mm}^{-2}$) on Al in air and under argon. The spectra were acquired with a portable back-pack LIBS system [32] and demonstrate the enhancement of the C and H emission from RDX under argon, and the reduction in atmospheric O and N (the source of the O and N emission from the blank Al substrate is air)



and experimental configuration. Several theoretical models have recently been developed to model the plume dynamics and understand the signal enhancement in double-pulse LIBS [43, 44]. Another advantage of using two pulses is that the ablation pulse is separate from the analytical pulse, thus improving reproducibility in most cases.

A combination of several factors is thought to increase the emission signal in double-pulse LIBS. These factors include greater mass ablation, larger plasma volume (more atoms are excited) and less laser shielding of the second pulse resulting from the decrease in gas density following the first pulse [39–42]. When the first laser pulse hits, it impacts the sample and the resulting shock wave displaces the surrounding gas. The second pulse arrives and interacts with the material within the first plasma in a reduced-density environment. Researchers at ARL have exploited this decrease in gas density for explosives detection. The reduced-air-density environment within the analytical (second) plasma diminishes the effects of oxygen and nitrogen from the atmosphere on the LIBS emission signals. The oxygen and nitrogen signal obtained is therefore more representative of the sample composition than the surrounding air, and better determination of whether or not an unknown material is an explosive can be achieved.

Figure 4 compares the receiver operating characteristic (ROC) curves for the discrimination of RDX and diesel fuel residues on aluminium using single and double-pulse LIBS (at 320 mJ total laser energy). ROC curves show the probability of detection (i.e. sensitivity, or true positives) versus the false alarm rate (i.e. 1-specificity, or false positives) and are useful for comparing the performance of different systems. Using principal components analysis (see section on *Chemometric Analysis*), the first principle

component (PC1) was calculated for each single-shot spectrum based on the O:C, O:H, N:C, N:H, and O:N peak emission intensity ratios and the samples were classified as explosive or non-explosive on the basis of the PC1 scores relative to a detection threshold (i.e. samples with PC1 scores above the threshold are considered explosive) [36]. Each point in the ROC curve corresponds to a specific threshold value. Whereas single-pulse LIBS resulted in 5.1% false positives at 100% sensitivity and only 61% sensitivity with 0% false positives, double-pulse LIBS resulted in perfect discrimination of the RDX and diesel fuel residues.

The improvement in discrimination of explosives residues with two laser pulses has also been demonstrated for standoff LIBS [31]. Spectra of blank aluminium and RDX residue on aluminium were acquired at 20 m with both

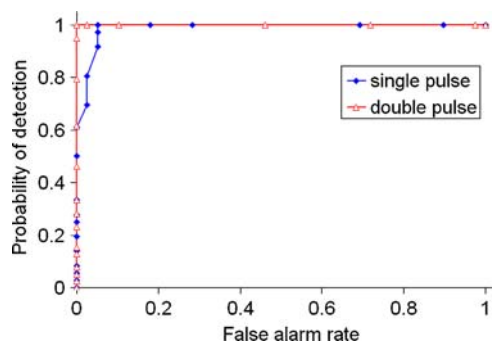


Fig. 4 ROC curves for the discrimination of RDX and diesel fuel residues on aluminium generated from the first principal-component scores based on atomic emission ratios for both single and double-pulse LIBS [36]. The double-pulse ROC curve represents complete discrimination between the two residues (100% true positives with 0% false positives)

single and double-pulse LIBS (interpulse delay $\Delta t=3\mu\text{s}$, 275 mJ). As shown in Fig. 5, the aluminium and RDX residue spectra are virtually indistinguishable on the basis of the O:N, O:C, and O:H ratios for single-pulse LIBS (within \pm one standard deviation), but there is no overlap between the two sample types with double-pulse LIBS. The enhancement of the overall spectral intensity with double-pulse LIBS (Fig. 5) is particularly striking for the standoff LIBS instrument, because the laser is not as tightly focused at longer distances as it is in typical laboratory LIBS setups (i.e. the laser energy density is lower at the target). It is important to note that while comparing the two cases (275 mJ single pulse vs. two 137.5 mJ pulses), the total laser energy used to generate the LIBS event was the same. Simply adding additional energy to the plasma with a second laser pulse always increases the LIBS signal; in this case, however, the signal enhancement is clearly caused by the double pulse effect rather than an overall increase in laser energy imparted to the LIBS plasma. In addition, the distinction between increased signal intensity (with a corresponding increase in noise) and actual improvement in sample discrimination must be made, because they do not necessarily go together.

Detection of landmines

Researchers have also applied LIBS to the problem of landmine detection. Unlike conventional landmine detection techniques utilizing hand-held metal detectors or thin, tapered prodding devices, LIBS is capable of detecting plastic and metal landmine casings and any explosive material in or around the buried landmine [45]. In addition

to the carbon and hydrogen backbone of the plastic casings and any residual metal content, chemicals such as binders, fillers, and additives (anti-statics, flame retardants, lubricants, pigments, stabilizers, etc.) will contribute to the LIBS emission signal, thus enabling discrimination of landmines from other subsurface clutter objects.

In early work at ARL, a bench-top LIBS system was used to discriminate more than a dozen anti-personnel and anti-tank mines manufactured in four countries from a set of natural and anthropogenic clutter objects (plastic, wood, rocks, metal, etc.) [46]. A subsequent study employing the backpack MP-LIBS system demonstrated discrimination of landmine casings and plastic or wood mine simulants using linear correlation [45]. Bohling et al. have also recently demonstrated the detection of landmine casings with a fiber-optic LIBS sensor combined with a conventional mine prodder [47–49]. They were able to show that different materials with identical atomic composition (e.g. plastic mine casings and TNT) can be classified by comparing the time evolution of the various LIBS emission lines [47].

More recently, ARL has obtained laboratory LIBS spectra (~ 100 mJ laser energy at 1064 nm) of 39 anti-personnel and anti-tank mines from four different countries, and several wood and plastic mine simulants [50]. As shown in Fig. 6, although many of the mines can be easily distinguished by their metal content, some of the plastic mines have relatively simple spectra containing mostly C, CN, C₂, H, O, and N emission lines. A library model of 1000 broadband, single-shot LIBS spectra was constructed using partial least-squares discriminant analysis (described in the *Chemometric Analysis* section), and 1485 out of 1500 test spectra were correctly classified by the model. These results show that not only can landmines be discriminated

Fig. 5 Comparison of single and double pulse ($\Delta t=3\mu\text{s}$) standoff LIBS at 20 m with 275 mJ total laser energy [31]. The average values for the O:N, O:C, and O:H ratios for blank aluminium and RDX residue on aluminium overlap for single-pulse LIBS (within \pm one standard deviation of the values for 20 spectra) but not with double-pulse LIBS (*top*). In addition to the decrease in air entrainment, double-pulse LIBS also significantly enhances the intensity of the RDX residue emission spectra (*bottom*)

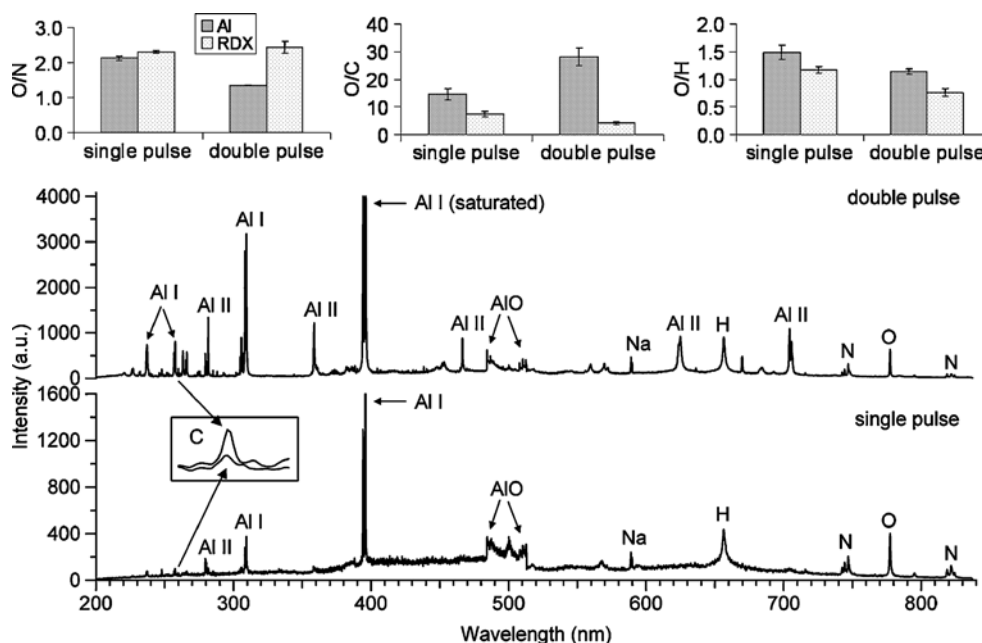
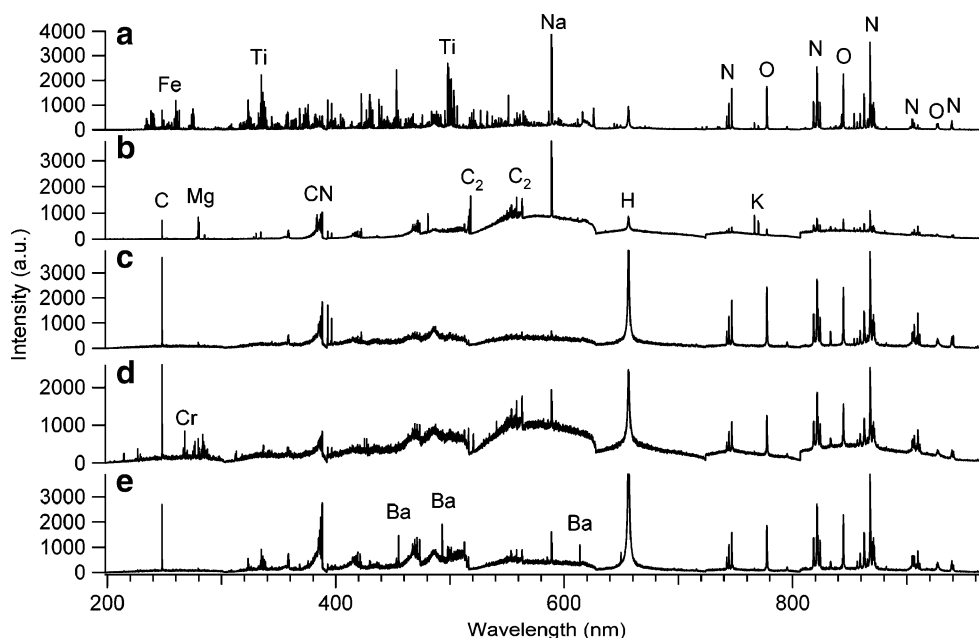


Fig. 6 Single-shot LIBS spectra (~100 mJ Nd:YAG laser in air, 1064 nm) (a) PMN-1 anti-personnel mine (Russia), (b) VS-MK2 anti-personnel mine (Italy), (c) nylon mine simulant ($C_6H_{11}NO$), (d) M14 anti-personnel mine (USA), and (e) PMA-1A anti-personnel mine (Yugoslavia)



from clutter objects by use of LIBS, different types of mines can be discriminated from each other with a high degree of success.

Enhancement of the LIBS signal

The performance of LIBS in discriminating residues of explosives from other interfering materials is strongly affected by the physics of the laser–plasma–substrate interaction. The depth of laser penetration into the residue and surface, and the relative amount of atomized material (emitting species within the plasma) will vary with laser conditions such as laser energy and wavelength, the substrate material physical properties, and the extent to which the sample adheres to the substrate – fine, loose particulate matter will often scatter instead of becoming atomized within the plasma. These variables can lead to a large LIBS signal contribution from the substrate relative to the residue, complicating residue discrimination.

An increase in the analyte LIBS signal, which aids identification of the sampled material, can sometimes be achieved by boosting the laser energy; however for residue detection this also leads to increased substrate penetration with an associated increase in substrate signal and damage to the target surface. A method to enhance the residue LIBS signal with minimal ablation of the substrate material is therefore required. Such a scheme would reduce detection limits for residues of explosives and also reduce the substrate imprint – a requirement for the use of LIBS on high-value property. For standoff applications, tradeoffs between detection limit and range must be made. Selectively enhancing the residue signal in these applications

will enable improved performance at longer ranges. Such enhancement will also enable detection at shorter distances using lower energy, eye-safer laser wavelengths. Several techniques have been identified that might produce this desired enhancement effect – preferential ablation of the residue using specific laser wavelengths, the use of ultrashort laser pulses, sustainment of the LIBS plasma through the addition of non-ablating energy, or resonance signal enhancement of the ablated material in the laser-induced plasma.

Wavelength dependence of LIBS

The choice of laser wavelength affects the mechanism responsible for material ablation, the sample penetration depth, and many other experimental conditions. The ability of a material to absorb radiation varies as a function of the wavelength of the laser. By tuning the laser to a wavelength that is preferentially absorbed by the explosive molecules in the residue rather than the substrate material, it may be possible to minimize the contribution of the substrate to the plasma emission and reduce the amount of damage to the substrate. Explosive materials absorb radiation most strongly in the ultraviolet (electronic $\pi \rightarrow \pi^*$ transitions of nitroaromatics) and mid-infrared regions (vibrational transitions) [4]. In general, the shortest wavelengths (UV) have been shown to result in reduced fractionation and increased ablation efficiency [51–53]. At infrared wavelengths the absorption depth of the irradiated material is small and reaction occurs at the surface. At high laser fluences, the plasma formed by the ablated material efficiently attenuates the incoming laser radiation (i.e. plasma shielding) and reduces the ablation rate. The extent of this shielding effect

depends on the laser wavelength and other experimental conditions [54, 55]. In addition to the laser–target and laser–plasma interactions, the plasma–target interactions must also be considered, because the presence of the plasma changes the optical properties of the surface. The plasma can actually enhance the amount of laser pulse energy deposited in a solid (i.e. plasma-enhanced coupling), e.g. metals that do not normally absorb IR radiation see increased coupling of the laser energy to the target surface [56, 57]. The effect of geometry and material refractive indices on the transmission, reflection, and refraction of the radiation must also be considered when choosing an appropriate laser wavelength [28]. Because the laser ablation processes are so complex, the optimum laser wavelength for a particular application is usually determined empirically.

Several groups have investigated the wavelength dependence of LIBS for explosives detection in recent years. Bauer et al. measured a 20% increase in absorption by explosive materials at 1470 nm (compared with 1064 nm), which resulted in a smaller LIBS breakdown threshold for TNT at the longer wavelength (0.15 GW cm^{-2} at 1470 nm vs. 0.5 GW cm^{-2} at 1064 nm) [58]. Because the absorbed laser energy is distributed in a very small volume close to the surface, the laser interacts primarily with the residue molecules rather than the substrate material and laser-induced fragmentation of surface contamination was enhanced at 1470 nm. Wong and Dagdigian also compared the LIBS signatures of organic residues including dinitrobenzene and dinitrotoluene (DNT) on aluminium at 1064 nm and 1500 nm [59]. Unlike the earlier study, they compared the LIBS spectra of the explosives residues at the same laser energy (above the breakdown threshold). Despite higher observed temperatures and electron densities, the overall LIBS intensity was significantly smaller at 1500 nm. The ratios of the atomic and molecular emission intensities were also very different at the two wavelengths. They attributed these differences to the increase in inverse bremsstrahlung absorption by the plasma at the longer wavelength, which would increase shielding by the plasma at 1500 nm (resulting in less material ablated from the surface). The advantages of using the wavelength more strongly absorbed by the residues of the explosives, i.e. lower breakdown threshold and less substrate interaction, seem to be at least partially negated by the reduction in the LIBS emission signal at the relatively low laser energies studied ($\sim 7 \text{ mJ}$). Further studies are necessary to explore the affect of using different wavelengths and laser pulse energies on the ability of LIBS to discriminate explosives residues from other materials.

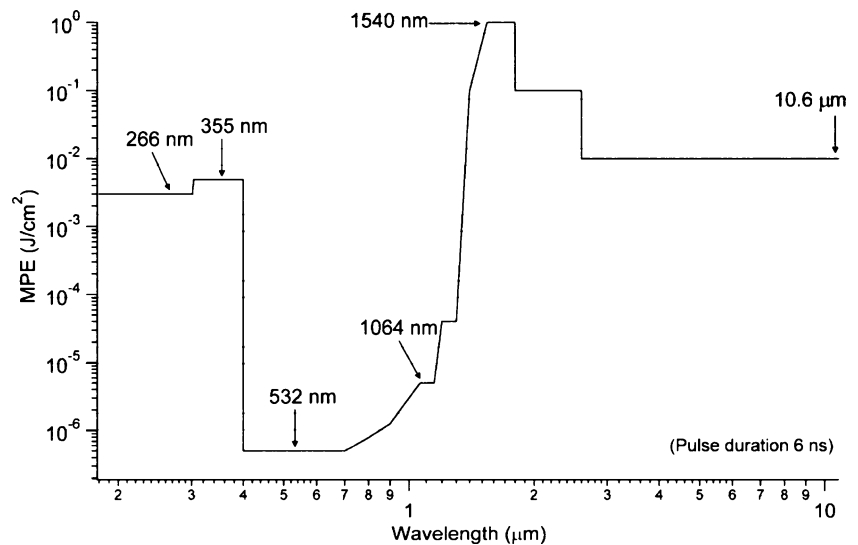
The most widely used laser wavelength for LIBS, 1064 nm, is the fundamental of a flashlamp-pumped, Q-switched Nd:YAG laser. The Nd:YAG laser has been used in industrial

applications for a number of years and commercially available systems can provide laser pulse energies $> 2 \text{ J}$ (5–9 ns pulse width) at 1064 nm. The fundamental wavelength can be frequency-doubled (532 nm), trebled (355 nm) or quadrupled (266 nm) to lower wavelengths, at a cost in efficiency (i.e. lower pulse energy). Because of the maturity of the technology, the harmonics of the Nd:YAG laser are of great interest for LIBS applications in general, and many studies have compared LIBS performance at those wavelengths [20, 55, 60–67]. Noll's group at the Fraunhofer Institute compared 1064 nm and 266 nm excitation of laser-induced plasmas for several plastics and TNT [19]. They concluded that both the UV and NIR lasers provided some advantages for detection of explosives residues; the breakdown threshold energy is less dependent on the substrate material for 266 nm, but the 1064 nm laser yields a higher signal-to-noise ratio (SNR), because the laser heats the plasma more efficiently. In an earlier work, Sabsabi and co-workers demonstrated a moderate improvement in sensitivity for a metallic target (Al) using sequential UV (266 nm)–NIR (1064 nm) double pulses [63]. The results of these studies suggest that using a double-pulse method where the first pulse is efficiently absorbed by the explosives residues (minimizing substrate interference) followed by a second pulse which efficiently heats the plasma (increasing the emission signal) may provide significant enhancement for discrimination of explosives residues with LIBS.

An important concern for fielding a standoff LIBS system is laser eye safety [68]. High-power lasers such as those required for standoff applications can burn skin or the retina of the eye, especially near the focus of the laser (at the target). Infrared lasers (e.g. 1064 nm) are particularly hazardous, because the blink reflex response is triggered only by visible light. In this case, thermal damage occurs when the tissues are heated to the point where proteins are denatured, either at the retina for near-infrared wavelengths or near the front of the eye at longer wavelengths. Ultraviolet wavelengths are absorbed in the cornea and lens; photochemical damage occurs when the laser triggers chemical reactions in the tissue.

While the LIBS laser will never be completely safe in the direct path of the focused beam, diffuse reflections will be less of a problem at some wavelengths. The ANSI Z 136.1 “Safe Use of Lasers” Standard (1993) provides maximum permissible exposure (MPE) limits derived from biological research studies. The MPE is the highest energy density (J cm^{-2}) of a light source that is considered safe. Figure 7 shows the calculated MPE for different laser wavelengths with an exposure time of 6 ns (a single laser pulse). The most dangerous laser wavelength is 532 nm, followed by the Nd:YAG fundamental at 1064 nm. The ultraviolet wavelengths have higher MPE levels, while wavelengths near 1500 nm are the safest. The nominal

Fig. 7 Maximum permissible exposure (MPE) as a function of laser wavelength for a 6-ns pulsed laser (derived from ANSI Z 136.1 Standard)



hazard zone (NHZ) describes the distance within which the direct, reflected, or scattered radiation exceeds the MPE level. The NHZ for a single-pulse (6 ns, 9 mm diameter, 0.5 mrad divergence), 1 J laser is 45.1 km at 532 nm, 14.3 km at 1064 nm, 454 m at 355 nm, 582 m at 266 nm, and only 26.4 m at 1540 nm; these distances will be significantly shorter at the lower pulse energies more likely to be used at wavelengths other than 1064 nm. Clearly, the NHZ must be considered when choosing a laser wavelength for standoff LIBS. The ongoing development of new lasers at longer wavelengths, such as those based on thulium (Tm^{3+}) with emission around $1.95\ \mu\text{m}$ [69], will present new opportunities for designing more eye-safe LIBS systems. Protective eye wear and implementation of standard operating procedures designed to minimize risk to operators and other personnel can also help mitigate the problems associated with outdoor laser usage.

An additional consideration for standoff LIBS is the atmospheric attenuation of the laser over long distances. Variables that can affect the beam characteristics include wind, humidity, atmospheric pressure, and thermal radiation. Extinction processes such as particle scattering and absorption can reduce the energy of the laser pulse at the target and block the transmission of the plasma light. Ferrero and Laserna [70] have developed a model for calculating the practical transmittance as a function of wavelength for distances less than 200 m. They concluded that in the absence of severe weather conditions, the laser is well-transmitted through the atmosphere and that atmospheric extinction of the return plasma light is small compared with the attenuation with range resulting from the inverse square law. Breakdown of the focused laser beam on particulates in the path of the standoff laser may occur near the intended target at high peak laser intensities, however detailed studies of this phenomenon have not been

performed for LIBS measurements and it is unclear what concentration of particulate matter begins to affect the ability to discriminate target materials. This phenomenon is also dependent on laser wavelength, because of the decrease of aerosol breakdown thresholds with decreasing wavelength [71].

Femtosecond LIBS

Replacing conventional nanosecond pulses with femtosecond pulses potentially offers several advantages for LIBS detection of explosives. Because of the short time scale of the femtosecond pulse ($10^{-15}\ \text{s}$), all of the energy is deposited into the material in the focal volume before it can be translated to the surrounding lattice. As a result, material is rapidly ionized and thermal and mechanical damage is diminished around the ablation crater [72, 73]. These characteristics make femtosecond pulses ideal for precise laser ablation applications.

Femtosecond pulses have been used for micromachining of explosive materials [29, 30]. Beyond laser ablation, femtosecond LIBS may have several attractive features for explosives detection. Because the ablation is more efficient, smaller amounts of an explosive can be sampled and still be detected. This is particularly desirable, because most explosives detection applications involve detecting trace amounts ($\sim 1\ \mu\text{g}\ \text{cm}^{-2}$). Because less damage occurs to surrounding material and the sampled area is more precise, less substrate or other benign materials that could potentially interfere with the LIBS emission from explosives will be entrained in the plasma. In addition, leaving a smaller imprint on the substrate could be important for certain applications involving detection of residues of explosives.

There are a handful of published studies that use femtosecond pulses to detect explosives. Spicer's group

has used femtosecond pulses to investigate LIBS spectra of TNT. They observed small molecular fragments (C_2 and CN) with 1 mJ laser pulses, but no atomic emission [74]. Similar results were obtained on different substrates [75]. Researchers at ARL have also used femtosecond pulses to study explosive samples [76]. They used much higher laser fluences (10 mJ per pulse, $\sim 30 \text{ J cm}^{-2}$) on a variety of bulk explosive materials, RDX, C-4, and Composition-B (36% TNT, 63% RDX, and 1% wax). As shown in Fig. 8, all of the expected atomic constituents (C, H, N, O) were observed in addition to the CN and C_2 fragments. At fluences comparable with Spicer's (1 mJ per pulse, $\sim 3 \text{ J cm}^{-2}$), the explosives spectra generated by ARL were similar, i.e. no atomic emission was observed (only molecular fragment emission). The researchers at ARL also observed that at higher laser fluences the desirable attributes of femtosecond pulses (including minimized background continuum and negligible atmospheric entrainment) were not realized for explosives detection. However, because femtosecond pulses enable use of lower laser fluences to generate the laser-induced plasma than those needed for nanosecond pulses, minimal damage to the substrate can be achieved. The disadvantage of using the lower-fluence pulses is that the LIBS emission signal is greatly reduced. Improvements in light collection achieved by optimizing the collection optics, using higher throughput spectrometers, or employing more sensitive detectors are needed to detect the low levels of light emission from the femtosecond-generated plasma at lower laser fluences.

Use of femtosecond pulses is not limited to the conventional LIBS experimental setup for explosives detection. A more recent technique that is being investigated is the use of filaments. Filaments are formed through a balance between two nonlinear physical effects—Kerr self-focusing and defocusing caused by multiphoton absorption

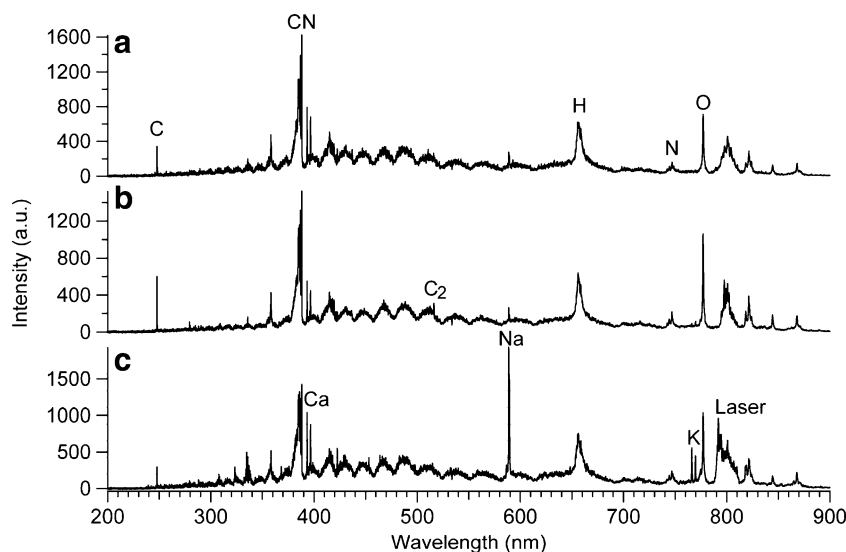
in the resulting plasma [77, 78]. The advantage of using filaments is that no focusing optics are needed and, depending on the femtosecond beam profile, the filament can be formed in air over long distances (up to several km). LIBS spectra of metallic targets have been obtained at 90 m with NIR filaments (795 nm) [79, 80], and UV filaments at 248 nm have been used to distinguish between different stone samples at 6 m [81]. Currently, only one group has published work on using filaments to detect explosive-related material. Mirell et al. have used filaments generated with UV (266 nm) and NIR (795 nm) pulses to remotely detect DNT and ammonium perchlorate residues; the parabolic mirror focusing the plasma emission on the entrance slit of the spectrometer was placed 3 m from the target [82].

In addition to the relatively weak LIBS signal resulting from femtosecond laser pulses (for both focused lasers and filaments), one of the biggest disadvantages is the size, expense and complexity of the laser systems required to generate ultrashort pulses of sufficient energy. For more practical applications of LIBS with femtosecond lasers, these shortcomings must be addressed. Moreover, despite some promising results in initial studies, no one has demonstrated improvement in the analytical performance of LIBS for explosives detection with femtosecond lasers.

Microwave-enhanced LIBS emission

One method recently developed for augmenting the laser-induced plasma is laser-assisted microwave plasma spectroscopy (LAMPS) [83–85]. In this technique, the laser-induced plasma is formed adjacent to a microwave cavity. The laser-induced plasma initiates a microwave plasma that is sustainable up to 30 ms, as opposed to the 10–20 μs plasma lifetime usually observed with conven-

Fig. 8 Femtosecond spectra (10 mJ) of bulk explosives (a) C-4, (b) Composition-B, and (c) RDX. Atomic (C, H, N, O) and molecular (CN, C_2) emission from the explosive was observed in addition to the impurities (Ca, Na, K) and the laser line at 800 nm



tional LIBS. Only the minimal laser energy required to breakdown the target material is needed to initiate the microwave plasma; consequently lower laser energies can be used – e.g. tens of mJ per pulse compared with 50 mJ per pulse or greater using a conventional nanosecond Nd:YAG laser – and little or no substrate imprint can be achieved in combination with significant enhancement of the LIBS emission. Kearton and Mattley report that using this technique developed by Ocean Optics and EnviroMetrics can result in LIBS sensitivity enhancements of 10 to 1000-fold, depending on the sample material [83]. A similar enhancement technique developed by Killinger et al. uses a long-pulsed CO₂ laser to deliver additional energy to an existing laser-produced plasma [86]. Using alumina ceramic targets, Killinger et al. demonstrated signal enhancements of 25–60 fold for neutral atomic lines and 50 to 300 fold for ionized species. The authors attribute these gains to plasma reheating caused by the CO₂ laser during the lifetime of the initial laser plasma.

Both of these techniques are still in development and little has been reported on their application to explosives detection and identification in close-contact or standoff configurations. Microwave enhancement of the LIBS plasma has been used to investigate DNT signatures in a laboratory setting [85]. Devices capable of projecting focused microwaves at a distance are available and might be employed in future standoff detection applications using this technique. The CO₂ enhancement technique has been demonstrated using DNT and TNT on aluminium and ceramic substrates at distances up to 40 m [87].

Resonance-enhanced LIBS emission

In addition to increasing the overall LIBS signal, a second approach for increasing the sensitivity of LIBS for explosives detection is to maximize the SNR for particular emission lines relevant to explosives. Maximizing the SNR will improve the ability to detect the explosive material and discriminate explosives from interferent materials. One method to increase the SNR of LIBS emission that has not been thoroughly explored for explosives detection applications is resonance-enhanced LIBS. Resonant laser ablation (RLA) has been studied for many years, but most of these studies have focused on mass spectrometry as the detector [88–91]. Several papers by Cheung and co-workers have explored resonant laser ablation specifically coupled with LIBS [92–96]. The experimental configuration, which uses two lasers, is slightly different from previous RLA experiments. The first laser ablates the material and creates a plasma; the second laser is tuned to a resonant wavelength of the material being studied and interacts with the ablated material in the plasma. Cheung et al. have observed that the mechanism involved allows reheating of the entire plasma,

thus emission from all of the atomic species is increased [93]. These studies were performed at much lower laser energies (<1 mJ) than those typically used for LIBS experiments. Both Lui and Cheung [92] and Cleveland et al. [91] note that as the ablation laser energy increases the enhancement in emission they observe resulting from the resonant laser disappears.

By contrast, Shen et al. have generated enhanced emission with laser energies typical of LIBS experiments (>10 mJ) [97]. The technique is called LIBS-LIF (laser-induced fluorescence). Enhancement only occurs in the emission lines for the species of interest based on the atomic or ionic transition that the laser is resonantly tuned to match. In this case only specific uranium lines were enhanced. LIBS-LIF has been used to improve the limits of detection of heavy metals in soil [98] and remote detection of several metallic species [99].

Resonance-enhanced LIBS should be investigated for explosives detection applications. Studies need to be undertaken to determine the effect of a resonantly tuned laser on explosive emission line intensities. As Cheung et al. observed, a low-energy laser pulse will cause minimal damage to the sample [92]. For explosives residues on different types of substrates, a low-energy laser would be beneficial for two reasons. There would be minimal imprint left on the substrate and more importantly less substrate would be entrained in the plasma. A second resonantly tuned laser could enhance the signal observed from the low-energy plasma. One could also envisage coupling the resonance enhancement technique with low-energy femto-second pulses. Using the resonance enhancement technique thus offers several potential advantages for LIBS detection of explosives.

Multi-sensor techniques

Many past investigations have clearly demonstrated the benefit of combining different, but complementary (or orthogonal) data from multiple sensors to obtain greater information from a sample. In the case of detection schemes, combining data from orthogonal techniques can lead to increased probability of detection with a reduced number of false-positive detection events. The benefits of sensor data fusion have been most clearly observed in the field of analytical separations, where optical and mass spectrometric techniques have been combined with chromatography or capillary electrophoresis to separate and then identify analytes in a mixture. In combination with LIBS, several optical spectroscopy techniques have the potential to provide complementary data useful in the detection and identification of explosive materials. Several examples are discussed in the following sections.

Raman/LIBS

Raman spectroscopy is a light-scattering method that provides vibrational information about the molecule being analyzed. Unlike LIBS, which provides information on the relative elemental content of molecules within the laser plasma, the vibrational frequencies measured using Raman spectroscopy are related to the mass of the atoms within the molecule and the bonds joining them. The theory of the Raman spectroscopy is beyond the scope of this work; however, additional information may be found in several reviews [100, 101].

The molecular nature of the information provided by Raman spectroscopy makes it a good candidate for the detection of many analytes and materials, including the detection of energetic materials [4]. Raman spectra of nitro-based explosives are readily identifiable by vibrational features associated with symmetric and asymmetric stretching of the NO₂ groups [4, 102]. Using a prototype standoff system, Sharma et al. collected Raman spectra of milligram quantities of cyclotetramethylene tetranitramine (HMX) and triaminotrinitrobenzene (TATB) at a distance of 10 m [103]. In a later study, Carter and colleagues collected Raman spectra of TNT, RDX, pentaerythritol tetranitrate (PETN), and nitrate and chlorate simulants mixed with sand (8%) at a distance of 50 m [104].

Early results for LIBS/Raman data originated in the art and cultural heritage communities [105, 106]. More recently, combined Raman and LIBS spectroscopy developments have arisen from the need to refine technologies for space exploration [107, 108]. This has led a push to develop simplified instruments incorporating Raman and LIBS components into a single device. Various efforts have been made to reduce the size and complexity of instrumentation by combining Raman and LIBS in single instruments through sharing of lasers, spectrometers, and optic light paths [107–110]. To date, limited work using combined LIBS/Raman for explosives detection has been published [111].

Photofragmentation-laser induced fluorescence (PF-LIF)/LIBS

A second technique that may have potential for combination with LIBS is photofragmentation-laser induced fluorescence (PF-LIF). In this technique, a laser source is used to first vaporize molecules on a surface, resulting in the dissociation of the molecules into molecular fragments. These fragments are then excited by a laser tuned to an absorption line of some atom or molecule of interest. As these molecules relax from the electronically excited state, characteristic fluorescence is emitted. In the case of nitro-based energetic materials, these fragments are typically NO

and NO₂. PF-LIF has been applied to many explosives materials and simulants such as RDX, nitrobenzene, DNT, TNT, PETN, and C-4 [4, 112]. PF-LIF also has the potential to be developed into a standoff technology [112, 113].

The combination of LIF techniques with LIBS for the detection of explosives has not yet been reported. Unlike the atomic fluorescence enhancement technique described in the section on resonance-enhanced LIBS, LIBS/PF-LIF has the potential to combine atomic spectral information from LIBS with supplemental molecular fluorescence information. The ability to identify nitrate-containing molecules, for example nitro-based explosives or home-made explosive precursors should be useful in reducing false alarms and increasing positive identifications.

Photoacoustic spectroscopy (PAS)/LIBS

A final example of a technique that may share complementary data with LIBS is that of photoacoustic spectroscopy (PAS). PAS measures an acoustic effect created by the absorption of light by sample molecules. In the typical PAS experiment, sample materials in a closed cell are irradiated using a modulated light source. The sample species absorb the light and are thermally excited, causing expansion and contraction of the gas within the cell in synchronization with the modulation frequency. The resulting dynamic motion of the gas creates an acoustic pressure front that can be monitored by microphone or piezoelectric crystal [114].

Many energetic materials have been studied using the PAS technique. Photoacoustic spectra of 18 different energetic material powders were investigated to determine optimal sources for laser ignition of these materials [115]. Using a tunable CW quantum cascade laser (QCL), Pushkarsky and others collected PAS spectra of TNT in the region 7300–7500 nm [116]. From their measurements, they estimated detection limits for TNT at 0.1 ppb ($\approx 1.01 \text{ pg cm}^{-2}$). Measurement of the LIBS spectrum of the sample within the PAS cell could be implemented if the cell is optically transparent to the ablation laser and collection optics.

The traditional scheme for PAS is not suitable for standoff applications because of the requirement for containing the sample in the specialized sample cell. However, a recently developed variant of the PAS technique has exhibited strong potential for use as a standoff detector for energetic materials. Researchers at Oak Ridge National Laboratory and the University of Tennessee have used QCL lasers in conjunction with quartz crystal tuning fork (QCTF) resonators to measure photoacoustic spectra of RDX, PETN, TNT and tributyl phosphate (TBP) absorbed on to surfaces at a distance of 20 m with a detection limit of

100 ng cm⁻² [117]. In this variant, the QCLs and QCTFs are modulated at matched frequencies. Light from the QCL is directed on the target and is reflected back to the QCTF. The light stimulating the QCTF is diminished by the amount absorbed by the target, and the contribution of the residue is determined by subtraction of the substrate background. Combination of this variant of PAS with LIBS for standoff detection could be readily implemented by interrogating the same sample space with the QCL laser followed by the LIBS laser.

Chemometric analysis for discrimination

In addition to advances in instrumentation and experimental methods, recent progress in the analysis of LIBS data for detection of residues of explosives has resulted in dramatic improvements in sensitivity and selectivity. The most straightforward approach for identification of materials is through spectral matching based on a predetermined and assembled spectral library of reference materials of interest. The feasibility of this approach for explosive materials was first demonstrated using linear correlation with a small library consisting of black powder and its principle components (charcoal, sulfur, calcium sulfate, potassium nitrate, and ammonium nitrate) [22]. Although this approach was successful for bulk explosives, it has the obvious limitation of needing a pre-existing library containing the spectra of any unknown materials likely to be encountered. In addition, a recent study has demonstrated that unknown residue spectra can be identified by linear correlation with a high degree of accuracy only as long as the library contains spectra of the same sample types (i.e. identical residue and substrate). Spectra of residues not included in the library resulted in a large number of false positives and false negatives [32]. Because the primary application of LIBS for detection of explosives is residue identification where the substrate may not be known a priori, a more sophisticated chemometric approach is needed.

As described earlier, the ratios of key atomic emission lines can be used to discriminate explosive and non-explosive materials. Several groups have used ratios to discriminate explosive materials, including the initial work by ARL [22], the initial testing of a standoff LIBS system for detection of residues of explosives [118], and more recent work involving laboratory close-contact [36, 119] and standoff systems [31]. While these results were quite encouraging, the successful application of multivariate analysis techniques to LIBS data has demonstrated dramatic improvement in the discrimination capability of LIBS for industrial [120, 121], cultural heritage [122, 123], environmental [124–126], geological [127, 128], biological [129–

133], and chemical [134, 135] applications. Principal-components analysis (PCA) [136], soft independent method of class analogy (SIMCA) [137], partial least-squares discriminant analysis (PLS-DA) [138], and neural networks [139] are multivariate chemometric techniques that have been applied to the problem of detection of explosives with LIBS.

PCA is a multivariate technique which finds weighted linear combinations of variables that describe major trends in the data. Preliminary results on explosives discrimination with PCA demonstrated how the ratios of the emission intensities for the key elements C, H, N, and O can be used to distinguish RDX, oil, dust, and fingerprint residues [31]. Analysis of the PCA loadings revealed that the O/N and H/C ratios were the most important for discriminating the explosives and non-explosives residues in the model [32]. PCA was also used to demonstrate the improvement in discrimination of double-pulse LIBS over single-pulse LIBS (Fig. 4) [36]. Bohling et al. used software to combine PCA with neural networks to classify land mines and other objects hidden in soil on the basis of the LIBS spectra and the decay times of selected emission lines [49]. More recently, researchers at ARL demonstrated how PCA can be used to identify components of mixtures containing explosives [140].

Although PCA describes the total variability of the entire data set, it does not distinguish between group-to-group variability and within-group variability [138]. PCA works well when the variability within each group or sample class is much smaller than the variability among the groups. However, if the variability within a group is of the same order as the group-to-group variability, as is the case with LIBS, because of the large shot-to-shot variability and heterogeneous residue samples, the discrimination of sample types (i.e. groups) will be poorer. In addition, while PCA is a useful tool for identifying whether samples are the same or different and what variables are responsible for those differences, PCA is not a classification technique.

For the SIMCA technique, a PCA model is developed for each sample class in the data set. New samples are identified by calculating the distance between the test spectrum and the center of each PCA model in order to predict the nearest class. A SIMCA model built using spectra of RDX, TNT, dust, and lubricating oil residues and the aluminium substrate was tested with “unknown” spectra of Composition-B, fingerprint residue, and several explosive and non-explosive dust mixtures [32]. While the Composition-B was correctly identified as explosive, the other sample types resulted in a large number of false positives and false negatives.

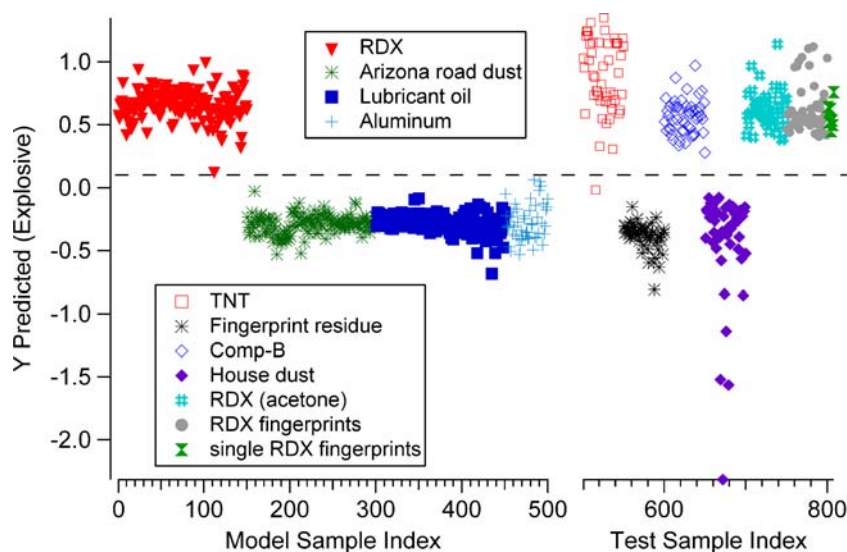
PLS-DA is an inverse least-squares discrimination method used to classify samples. Unlike PCA and SIMCA, the predictor variables (based on linear combinations of the

spectral features) are calculated while simultaneously considering both intraclass and interclass variance. In a comparison of linear correlation, PCA, SIMCA, and PLS-DA, the most promising chemometric technique for discrimination of explosives residues was found to be PLS-DA [32]. The ARL group was able to demonstrate the discrimination of several types of explosives residues (RDX, TNT, and Composition-B) on aluminium with LIBS and PLS-DA. In addition, test spectra of residues included in a PLS-DA model containing explosive and non-explosives residues were correctly classified as explosive/non-explosive, as were additional spectra of residue types not included in the model. Discrimination of explosives residues, biological warfare agent surrogates, and chemical warfare agent simulants at 20 m with a single PLS-DA model has also been demonstrated [135].

The initial work describing the discrimination of explosives with PLS-DA has recently been extended to include more complex sample types [140]. Samples of residues of the explosive RDX with different preparation methods (crushed, suspended in solution, fingerprint transfer), sample types not included in the chemometric model (house dust, fingerprint residue, TNT, and Composition-B), explosives mixed with non-explosives (RDX/dust, RDX/oil), mixtures of non-explosives (dust/oil), and sample spectra acquired at different standoff distances (20, 30, and 50 m) were all tested against a simple PLS-DA model including RDX, dust, and oil residues and the blank aluminium substrate [140].

Figure 9 shows the PLS-DA results from residue spectra acquired at 20 m. The y-axis gives the class prediction; a threshold (above which a sample is considered in the class) is automatically calculated by the software using Bayesian statistics in order to minimize the number of false positives and false negatives. The x-axis is simply a sample index.

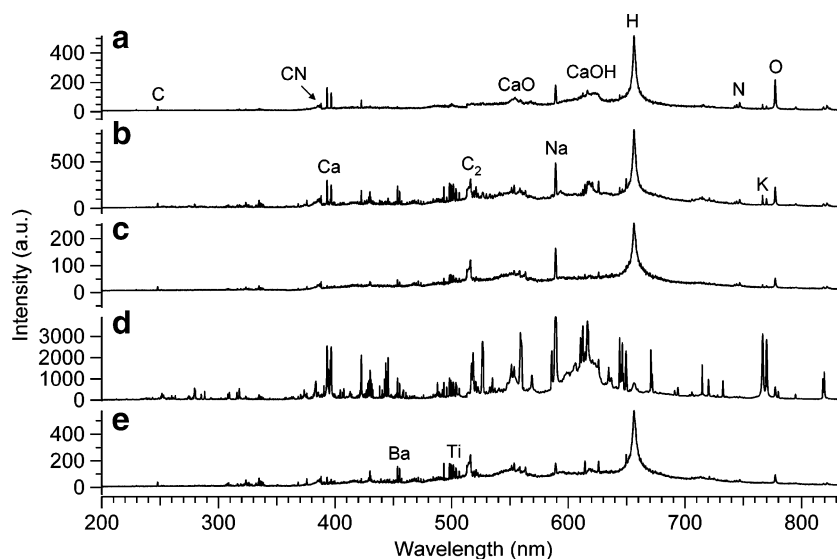
Fig. 9 PLS-DA model built with RDX residue (samples 1 through 150), Arizona road dust (151 through 300), lubricating oil (301 through 450), and Al (451 through 500) acquired at 20 m on several different days. Residues of TNT (501–550), fingerprint oil (551–600), Composition-B (601–650), house dust (651–700), RDX suspended in acetone (701–750), RDX applied via repeated fingerprint transfer (751–800), and RDX applied via single fingerprint transfer (801–808) were tested against the model generated using the data presented in Ref. [140]



The model contains single-shot spectra from RDX crushed in a thin layer on aluminium, oil and dust residues, and the blank substrate. For the test spectra, 49/50 of the TNT residue single-shot spectra were correctly classified as explosive, as were 50/50 Composition-B residue samples, 50/50 of the RDX samples prepared by suspending the explosive in acetone, 50/50 of the RDX samples applied by repeatedly pressing a fingertip coated in RDX on the substrate, and 8/8 of the RDX samples applied by a single fingerprint. In addition, 0/50 of the fingerprint oil residue spectra and 0/50 of the house dust residue spectra were classified as explosive. All 50 of the fingerprint oil spectra classified with the lubricating oil in the model, and 50/50 of the house dust spectra classified with the Arizona road dust in the model. The addition of residue mixtures and different standoff distances results in poorer discrimination, as described in Ref. [140].

While most published studies on discrimination of explosives residues utilize a simple aluminium substrate, discrimination of explosives residues on both organic and inorganic substrates has recently been explored [141]. Detection of organic residues on organic substrates is a challenge for LIBS, because atomic and molecular emission lines caused by the substrate are observed in the plasma, in addition to those from the residue. RDX, dust, and oil residues were applied to numerous substrates including aluminium, white rubber, red silicone, wood, cardboard, and travertine. Figure 10 shows the standoff LIBS spectra (acquired at 25 m) of the residues on the white rubber substrate; although the relative intensities vary, all of the atomic and molecular emission lines observed in RDX (a, b) are also present in the blank white coaster spectra (e). Individual PLS-DA models generated for each substrate resulted in >90% true positives for detection of explosives

Fig. 10 Standoff LIBS spectra (25 m) of (a) RDX pellet, (b) RDX residue on white rubber, (c) oil residue on white rubber, (d) dust residue on white rubber, (e) white rubber



for all substrates and <10% false positives for all the substrates except the travertine (22.5% false positives).

PLS-DA models consisting of nine classes (RDX, oil, dust, and the six blank substrates) were constructed [141]. Two methods for input variable selection were compared. Background corrected, summed emission intensities of the atomic and molecular species present in the LIBS spectra of RDX (C, C₂, CN, H, N, O, Ca, Na, and K) were calculated for each spectrum. The nine summed intensities were then used to calculate 20 ratios: (O/C, H/C, O/N, N/C, O/H, N/H, C/CN, O/CN, H/CN, N/CN, C₂/CN, C₂/C, (O+N)/(H+C), Ca/H, Ca/C, Ca/O, Ca/N, (O+N)/(C+C₂+CN+H), (O/N)/(H/C), and CN/(N/C)). One model was constructed using the set of pre-selected input variables (intensities and ratios); a second model was constructed using the full broadband spectra for each single-shot analysis. While the full spectra model resulted in higher true positive and true negative rates for test spectra of residues on substrates included in the model, the intensity/ratio model resulted in a significantly lower false positive rate for residues on unknown substrates. It was suggested that the fusion of the results for the two models may enhance the capability for discrimination of explosives residues with LIBS in cases where a complete library model cannot be developed.

Outlook

LIBS as a true analytical technique is less than 30 years old, and the application of LIBS to detection of explosives was first demonstrated only six years ago (in 2003) [22]. In those six years, a tremendous number of advances in the development of LIBS hardware and data analysis have resulted from increasing interest in the unique advantages

of the LIBS technique. Although the past several years have seen significant advances in the chemometric analysis of LIBS spectra, the problem of detection of residues of explosives is extremely challenging. While discrimination of residues on individual organic and inorganic substrates has been demonstrated, much improvement is still needed to make LIBS a viable sensor for explosives residues in a field environment.

LIBS is not as sensitive as vapor-based techniques, some of which can detect explosives at ppt levels [142]. The LOD for explosives residues with LIBS depends on numerous factors including the distance to the target material, laser properties (energy, wavelength, pulse duration), light collection and spectrometer efficiency, substrate material, and presence of interferents. Sample preparation for algorithm development and LOD determination is an area that still needs to be addressed; preparing homogenous layers of explosives residues of known concentration on realistic substrates is difficult. Substrate signal interference in the LIBS emission and matrix effects resulting from those substrates affect the sensitivity and selectivity of LIBS. The powerful lasers used for standoff LIBS detection present eye-safety concerns, and result in the necessity for line-of-sight point detection. Although the laser can pass through transparent materials at certain wavelengths, it cannot detect explosive material outside the beam path. Appropriate selection of the wavelength for detection of explosives with LIBS has not yet been determined. Advances in instrumentation needed for building rugged, fieldable systems include improvements in both the lasers and spectrometers. The lasers currently used in the field are expensive and generally designed for laboratory environments. Commercially available, highly sensitive, rugged, broadband gated spectrometers are also needed.

The biggest advantage of LIBS for detection of explosives is its capability for real-time, standoff detection. Enhancement of the analytical plasma through techniques such as double-pulse LIBS, plasma re-heating, or resonance enhancement can improve the sensitivity of LIBS. The combination of LIBS with complementary techniques (Raman, LIF, etc.) improves the selectivity. The proper choice of laser wavelength and operational procedures will minimize the risk of eye or skin damage to personnel. The relatively high cost of LIBS systems compared with other, non-laser-based explosive detectors is offset by the potential for universal hazardous material detection (i.e. a LIBS system can replace multiple pieces of equipment). Not only is LIBS not limited to specific classes of explosives, the same system can also be programmed for detection of chemical and biological warfare agents [31, 46, 135]. LIBS can also be used to identify otherwise innocuous materials that might indicate the presence of a hidden explosive device, e.g. painted foam disguised as a rock.

LIBS is an evolving technique with tremendous potential for detection of residues of explosives; the difficulties in implementation are outweighed by its unique advantages and capabilities. In the near future, commercial LIBS systems developed for specific, well-defined applications are most likely to gain widespread acceptance and usage. With improvements in instrumentation and data-analysis techniques, LIBS systems in multiple configurations (portable, standoff, robot-mounted, etc.) capable of universal material detection in any environment may some day be possible.

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