Femtosecond laser induced breakdown spectroscopy based standoff detection of explosives and discrimination using principal component analysis

ABDUL KALAM SHAIK, NAGESWARA RAO EPURU, HAMAD SYED, CHANDU BYRAM, AND VENUGOPAL RAO SOMA

Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad 500046, Telangana, India
’soma_venu@uohyd.ac.in

Abstract: We report the standoff (up to ~2 m) and remote (~8.5 m) detection of novel high energy materials/explosive molecules (Nitromidazoles and Nitropyrazoles) using the technique of femtosecond laser induced breakdown spectroscopy (LIBS). We utilized two different collection systems (a) ME-OCT-0007 (commercially available) and (b) Schmidt-Cassegrain telescope for these experiments. In conjunction with LIBS data, principal component analysis was employed to discriminate/classify the explosives and the obtained results in both configurations are compared. Different aspects influencing the LIBS signal strength at far distances such as fluence at target, efficiency of collection system etc. are discussed.

OCIS codes: (140.3440) Laser-induced breakdown; (300.6365) Spectroscopy, laser induced breakdown; (140.7090) Ultrafast lasers; (170.1580) Chemometrics.

References and links


1. Introduction

The development of rapid, reliable and real-time techniques to anticipate/dissolve the threats from nefarious elements by identifying high energy materials (HEMs), improvised explosive devices (IEDs) and special nuclear materials is a top priority for many nations to safeguard their citizens. Though the existing lab-based explosive trace detection techniques (Ion mobility, Mass spectrometry etc.) are sensitive, they are not in situ, time-consuming and could be more helpful in different scenarios (e.g. post incident analysis) [1, 2]. In contrast, laser based spectroscopic techniques such as Raman spectroscopy, laser induced breakdown spectroscopy (LIBS), terahertz spectroscopy and laser induced fluorescence possess high...
potential for in situ remote/standoff detection of explosives, biological warfare agents and hazardous substances [3–9]. Laser induced breakdown spectroscopy has been extensively used in various fields owing to its robust in situ elemental analysis, such as space exploration, pharmaceutical, soil and nutrient analysis and identification/discrimination of explosives [10–18]. To this end, nanosecond (ns) LIBS has been extensively used in analysing aerosols [19], process control and monitoring in metallurgical industry [20], planetary missions and detection of explosive residues [21–24] at standoff distances. Lazic et al. have utilized intensity ratios C/H, C/O, C/N, N/H and correlation between atomic intensities with Al’ intensity to classify explosive traces [25]. Gottfried et al. utilized nanosecond double pulse standoff LIBS system (ST-LIBS) for detecting explosive residues and chemical warfare agents on Aluminum at a distance of 20 m [21]. Further, they have utilized PLS-DA model to discriminate explosive residues on organic and inorganic substrates obtained at 25 m [26] and RDX traces on various metallic substrates in near field and suggested approaches to improve PLS-DA model as well [27]. Cristina et al. employed a portable ns ST-LIBS system for detection of explosive residues at 30 m [28]. Sustained efforts are in progress to increase sensitivity and selectivity for explosive detection by combining LIBS and Raman spectroscopy onto a single platform. Efforts for the development of portable LIBS systems for field applications have been multiplied by various research communities over the last decade [29–32]. ST-LIBS spectra of a few explosive residues were recorded from 30 m distance, which were kept behind the transparent barriers such as PMMA and colourless glasses [33].

Though the advantages of femtosecond (fs) pulses over ns pulses are well documented, the technique of ST-LIBS with fs pulses has not been explored fully and only petite literature is available [34–37]. Fs pulses are rewarding when compared to ns pulses for LIBS studies since these short laser pulses offer lesser Continuum, smaller heat effected zones, lesser plasma-ambiance interaction and ideally minimal plasma–plume interaction [38, 39]. These pulses are ideal for remote/standoff detection as they can be formed into filaments through the phenomenon of filamentation and capable of delivering high energies over the long distances and has been used in atmospheric sensing [40, 41], cultural heritage monitoring [42], analyzing metals [43, 44], chemical and biological agents [45], organic samples [46], labeling of radioactive isotopes [47] and in detection of explosives [48, 49]. Femtosecond filaments can be generated at distances even hundreds of meters to few kilometers [50] in harsh environments and are barely influenced by turbulence. Fischer et al. recently demonstrated that fs filaments can be controlled to achieve highly stable, repeatable spatial and temporal distributions by use of a vortex phase plate which in turn provided better signal in remote LIBS (R-LIBS) [51]. In contrary, conventional ns pulses suffer from diffraction, beam wandering (severely affected by turbulence) which adversely influences the signal to noise ratio (SNR) and fail to deliver high intensities to remote locations [52]. Small crater depth attained in fs filament ablation compared to tight focused fs/ns pulses, as revealed from the recent studies by Harilal et al. is a certain advantage in minimizing substrate signal [53]. Fuji et al. have demonstrated in situ remote detection of salt water aerosols using fs laser pulses at 16 m [54]. Rohwetter et al. have used terawatt mobile laser system to obtain R-LIBS signal of Cu, Al at 25, 90 m and compared the utility of fs, picosecond and ns pulses towards ST-LIBS applications [55]. Effect of pulse chirp has been examined and demonstrated that detection limit can be improved by the use of chirped fs pulses, which provide better contrast compared to classical LIBS [56, 57]. For standoff applications, collection system plays a vital role as equal to the excitation wavelength and pulse duration of the laser. There have been several modifications executed to improve the efficiency of collection system [58]. Patrick et al. have proposed a spatial heterodyne spectrometer for ST-LIBS measurements up to 20 m which offers a very large field of view [59]. Recently, Li et al. have shown that a multi-collector lens system could outperform the Newtonian telescope of similar dimensions for ST-LIBS measurements [60]. Multivariate techniques such as PCA, PLSDA, SIMCA and ANN
algorithms have been used to assist LIBS in identifying and discriminating explosives, soil, bacteria and classification of polymers etc. Gottfried et al. utilized PCA scores of various atomic intensities to distinguish explosives RDX, TNT, and Composition-B [61]. There remain several challenges for explosives detection using LIBS in general, and fs pulses in particular. Detailed studies on diverse molecules (including traces) using various optical configurations is essential to arrive at a field-usable instrument for unambiguous detection. In this work, fs LIBS technique was utilized to carry out ST-LIBS experiments of explosive molecules (nitropyrazoles and nitroimidazoles) and R-LIBS experiments of the explosive molecules as well as metals. Results from both the configurations are compared and complexities in obtaining standoff LIBS spectra are addressed.

2. Experimental details

An ultrafast Ti: Sapphire laser system (LIBRA, ~4 mJ, 1 kHz) delivering ~50 fs laser pulses and operating at 800 nm was employed to perform the fs LIBS experiments in two different configurations and ambient air. Figure 1 depicts the schematic of two configurations used in the present work: (i) fs standoff LIBS setup (fs ST-LIBS, up to 2 m) with D1 (collection optics, ME-OPT-0007, ANDOR) and (ii) fs remote LIBS setup (fs R-LIBS, ~8.5 m) with D2 (Schmidt-Cassegrain telescope) as collection systems.

![Fig. 1. Femtosecond standoff (up to 2 m, configuration 1) and remote (~8.5 m, configuration 2) LIBS setup. In figure M, A, HWP, BP, L, D, P and T stands for mirror, aperture, half wave plate, Brewster plate, lens, collection system, plasma and target, respectively.](image)

<table>
<thead>
<tr>
<th>Compound name</th>
<th>IUPAC name</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-LIBS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-NIm</td>
<td>4-nitroimidaole</td>
<td>C₃H₃N₃O₂</td>
</tr>
<tr>
<td>1M-4NIm</td>
<td>1-methyl-4-nitroimidazole</td>
<td>C₄H₅N₄O₃</td>
</tr>
<tr>
<td>2,4-DNIm</td>
<td>2,4-dinitroimidazole</td>
<td>C₆H₈N₄O₄</td>
</tr>
<tr>
<td>1M-2,4-DNIm</td>
<td>1-methyl-2,4-dinitroimidazole</td>
<td>C₆H₈N₄O₄</td>
</tr>
<tr>
<td>2M-(5)-NIm</td>
<td>2-methyl-(5)-nitromidazole</td>
<td>C₅H₇N₃O₃</td>
</tr>
<tr>
<td>4-NIm</td>
<td>4-nitroimidazole</td>
<td>C₅H₇N₃O₃</td>
</tr>
<tr>
<td>1M-2,4-DNPY</td>
<td>1-methyl-2,4-dinitropyrazole</td>
<td>C₇H₈N₄O₄</td>
</tr>
<tr>
<td>4-NPY</td>
<td>4-nitropyrazole</td>
<td>C₅H₈N₄O₄</td>
</tr>
<tr>
<td>1,3-DNPY</td>
<td>1,3-dinitropyrazole</td>
<td>C₆H₆N₃O₂</td>
</tr>
<tr>
<td>1M-3,4,5-TNPY</td>
<td>1-Methyl-3,4,5-trinitropyrazole</td>
<td>C₇H₁₀N₄O₆</td>
</tr>
<tr>
<td>Metals &amp; Alloys</td>
<td>Aluminum (Al), Copper (Cu), Brass (Br), Stainless Steel (SS) (not standard samples)</td>
<td></td>
</tr>
</tbody>
</table>
D1(ME-OPT-0007) from M/s Andor is a patented UV-NIR achromatic collecting/collimating lens/mirror system, which is optimized to ensure that all wavelengths in the range 200 - 1100 nm are collected evenly into the entrance fiber. It has one mirror and two lens fixed in an external body which makes it rugged and portable. In ST-LIBS, lenses of five different focal lengths i.e. 10, 30, 50, 100, and 200 cm were used to focus the fs pulses on to the sample and the emissions were collected by D1. The position of D1 was fixed besides the focusing lens and was optimized for each standoff distance by tilting/adjusting such that the collection distance is equal to focusing distance. Beyond the focusing length of 30 cm the point plasma stretched into filament. For example, a short filament of ~10 cm length was observed for the f = 200 cm focal length lens. The typical length of the filament varied from ~2 cm to ~10 cm (observed with naked eye). Due to several optical elements in the elaborate experimental setup we expect broadening of the fs pulses from ~50 fs to ~80 fs (estimated from calculations using dispersion relations). There is also possibility of the pulses being chirped. The present work did not investigate the effect of chirp on the LIBS emission. At each standoff position, an aluminum plate was interrogated in order to estimate spot-size and fluence delivered. In case of R-LIBS, plasma was produced by focusing the fs laser pulses using a 10 cm focal length lens and emissions were detected at 8.5 m away using a (6", f/10) Schmidt-Cassegrain telescope (D2) whose construction is explained elsewhere [62] where 6” corresponds to the diameter of corrector plate and f/10 is the f-number. The incident pulse energy was ~2 mJ in both the configurations. The optical emissions collected from plasma were coupled to ANDOR Mechelle spectrometer (resolution of 0.05 nm @ 500 nm and the spectral window is 200-880 nm) attached with ICCD via an optical fiber (600 µm).

Fs ST-LIBS spectra of a set of five HEMs (nitroimidazoles) were recorded at five standoff distances of 10, 30, 50, 100 and, 200 cm. The spectra were acquired using a gate delay 50 ns, gate width 2 µs, gain 4000 (3000 at 10 cm was used to avoid ICCD saturation) with 1.5 s exposure time. Each spectrum is the resultant of 6 accumulations (which effectively means that each spectrum recorded is accumulation of the data from 9000 laser pulses). At a given standoff distance, 10-15 spectra per sample were recorded. All the spectrum acquisition conditions for HEMs and metals in R-LIBS case are as same as in ST-LIBS case, except ICCD gain of 1000 in case of metals. In R-LIBS, 10-15 spectra of HEMs and 20-25 spectra of metals were recorded. Pure HEMs powder (~300 mg) was ground and pressed at 3 tonnes pressure using a manual hydraulic press (Carver Co.) for 10 minutes to form a pellet of 12 mm diameter and thickness of ~3 mm. The pellets were translated in the plane transverse to the laser incident direction using Newport ESP 300 motion controller. Table 1 lists the details of all the samples that were investigated in both standoff and remote configurations.

3. Results and discussion

3.1 Standoff LIBS studies of nitroimidazoles

Figures 2(a)-2(e) illustrate the stack plots of representative fs ST-LIBS spectra of a set of five nitroimidazoles obtained at five different standoff distances i.e. ~10, ~30, ~50, ~100 and ~200 cm, respectively. Nitroimidazoles and nitropyrazoles are nitro rich energetic molecules, systematically studied and reported by Rao et al. in near fs LIBS configuration [63, 64]. The essential spectral features of these molecules are CN, C₂ molecular bands and C, H, N, O atomic emissions. Three CN bands were observed in the spectral region of 358-360 nm, 386-390 nm, 410-422 nm corresponding to \( \Delta \nu \) values of 1, 0, −1, respectively. The CN violet band (\( \Delta \nu = 0, B^2\Sigma^- \rightarrow X^2\Sigma^+ \)) had the maximum intensity. Three C₂ bands (\( \Delta \nu = -1, 0, +1 \)) were observed in the spectral range of 465-475 nm, 510-518 nm, 555-565 nm with maximum intensity at C₂ Swan band (\( \Delta \nu = 0, d^3\Pi_g \rightarrow a^3\Pi_u \)). In standoff spectra CN, C₂, NH (336 nm) molecular emissions were observed along with C, H, N, O atomic emissions though their
intensity decreased as the standoff/working distance increased. Figure 2(f) represents the typical fs standoff Aluminum spectra recorded at all working distances.

Fig. 2. Typical fs standoff LIBS spectra of nitroimidazoles at (a) 10 cm (b) 30 cm (c) 50 cm (d) 100 cm (e) 200 cm acquired in ST-LIBS (configuration 1) and (f) Stack plot of the fs standoff LIBS spectra of Al at all distances.

Few Fe I impurities were identified (305.79 nm, 305.90 nm, 386.91 nm and 388.71 nm) in aluminum along with Al I transitions at 308.2 nm, 309.27 nm, 394.40 nm and 396.15 nm and AlO molecular bands in the spectral region of 440-550 nm. From Fig. 2 it is evident that the
spectral intensity varies in case of each sample at a given position. This can be attributed to their molecular structure and the numerous complex plasma recombination reactions. In laser produced plasmas (LPP), it has been proved that co-existence of several reactions between excited radicles, atomic and molecular fragments from plasma as well as ambience leads to the formation or depletion of species [65, 66]. In our previous works we have discussed and elucidated few plasma reactions and their thermodynamic feasibility through which they conduit in formation and depletion of CN and C₂ molecules in a laser induced plasma. Good correlation observed between CN spectral intensity and %C-N, %C = N linkages of samples investigated indicating lesser intrusion of air with fs pulse interrogation in comparison with the ns case [67].

Moreover, in LPP, the input pulse duration [15] as well as the focusing conditions [53] significantly influence the persistence of plasma species. Comparative ns and fs LIBS studies of TNT residue on Al substrate by Dikmelik et al. [68] have again illustrated that lower background signal from substrate is observed in case of fs pulses with CN and C₂ being identified as markers for explosives whereas C, H, N, O atomic lines were suggested as markers in case of ns pulses. The change in focal length affects the spot size, filament generation conditions and, hence, has significant influence in the LIBS plume emission properties. Harilal et al. [53] have identified that the filament generation conditions can significantly influence the plasma properties including (a) atomic and molecular emission features (b) persistence and (c) plasma temperature and electron density. For short focal length focusing (say f = 10 cm), the physical conditions of the plasma will be hotter at early times which will obscure the molecular formation. Similarly, cooler plasma will be generated when the plasma is produced using fs laser filaments and thus leading to limited persistence of plasma species. Further, gate delay and gate width are also should be optimized for better spectral intensity.

3.2 Principal Component Analysis (PCA)

LIBS spectral analysis combined with chemometric techniques enhances the accuracy in discrimination of samples compared to the standard ratiometric approaches, where ratios of neutral and ionic species are utilized in the latter case. Principal component analysis (PCA), is
a simple though powerful chemometric technique which is capable of grouping or classifying various materials by correlating their spectral features. PCA has been used in various fields such as face recognition and image compression, drug and pharmaceutical, soil analysis and explosive discrimination owing to its capability of finding patterns (the similarities and differences) in high dimensional data sets [69–72]. In this technique, original data set \( X_{mxn} \) \([\text{‘m’ observations (no. of spectra) and ‘n’ variables (wavelengths)}]\) is transformed into a new data set through a mathematical change of basis (e.g. via singular value decomposition) which can be represented in the space of the principal components (PCs), where each PC represents the variance in data set. Wang et al. have used principal component analysis to distinguish an organic explosive (TNT, trinitrotoluene) among plastics [73]. PCA used in conjunction with laser photo acoustic spectroscopy (LPAS) has resulted in classification of explosive traces [74]. De Lucia et al. classified different explosive traces on organic explosives using PLS-DA and obtained high true classification rates (TCR) and low false classification rates (LCR) through selective data input models [75, 76].

Here, the LIBS spectra of nitroimidazoles obtained at five different standoff distances were merged and processed for impurities such as sodium, calcium which are not the spectral signatures of HEMs and analyzed through PCA program written in a MATLAB code. Figures 3(a)-3(e) depict the PC score plots of processed LIBS spectra of nitroimidazoles at different distances. First three principal components together account for 99%, 97%, 91%, 82%, 52% of the total variance associated with in each data set. It is evident that as the standoff distance increases first three PCs could not account for the total variance in the data set. Figure 4 shows the stack plots of first three PCs at 10 cm, 100 cm and 200 cm. The important spectral features are C, CN and other atomic and molecular peaks. At farther distances, PCs couldn’t account for the complete variance in the data set. This could be attributed to reduction in signal strength which in turn decreases the signal to noise ratio (SNR). The decrease in SNR with the increase in distance can be attributed to the following factors (a) the solid angle subtended by the collection system at the plasma, (b) intensity of the laser beam (fluence/time) at the sample due to change in spot size and (c) change in filament generation conditions due to different focusing conditions, which are discussed below in detail.

The amount of plasma emissions (flux) collected can be expressed as 
\[ d\Phi = I \, d\Omega, \]
where \( I \) is the luminous intensity of the plasma and 
\[ d\Omega = dA / (r^2), \]
is the solid angle which varies square inverse with the distance, with collection area (dA) being constant. Thus, for D1 with input aperture of 1.57” (4 cm) diameter, the solid angle subtended by it at plasma source varies from 0.126 sr to 0.00031 sr from 10 cm to 200 cm, with \( 1/r^2 \) dependence. Thus,
the signal entering collection system decreases and evidently results in decrease in signal strength. The average spot sizes at different working distances were estimated by analysing the interacted portions on an Aluminum target using optical microscopic data. It is well-known that the spot size (at focus) increases as the focal length of focusing lens increases and, hence, the fluence/intensity also decreases. The observed spot size (diameter, $2\omega_0$) was estimated to be in the range of 230-330 µm (246 µm at 10 cm and 324 µm at 200 cm) which is apparently different from estimated values of 50-100 µm. This is because the repetition rate of the laser being 1 kHz the number of pulses incident on a particular spot of the sample is more than one leading to cumulative effects and thereby an increase in the observed feature size (from which the beam diameter was calculated). Thus an increase in the spot size leads to decrease in the peak intensity. Moreover, the reduction in spectral intensity could also be due to reduced laser energy coupled to the target because of the interaction of filaments. Filaments carry a small fraction of laser energy and bulk of the laser energy is carried by the energy reservoir [77]. The ablation efficiency is governed by the filaments as well as the energy reservoir around the filaments. For lenses with larger focal lengths, especially with $f > 50$ cm, the ablation process could be due to filaments and the process can be termed as filament ablation. With increasing focal length, though the filament holds the same energy and diameter (~100 microns), the energy density of the energy reservoir may change and hence the ablation efficiency along with the SNR of the LIBS spectrum is affected.

4. Remote LIBS of explosives and metals

As shown and described in experimental section, R-LIBS experiments of HEMs and metals were carried out by focusing fs pulses with a 10 cm lens and a Schmidt- Cassegrain telescope (D2) was used to collect plasma emissions at a distance of ~8.5 m. The collection capability of any telescope depends on various factors such as size of aperture, optical quality, contrast and alignment. Size of the aperture affects light gathering power of telescope and quality, coatings of the optics decides the reflection and transmission range of light through the telescope. Telescopes with large f-number (f/8 and above) possess high magnification capability, suffer less chromatic aberrations and deliver high power with a narrow field of view. The transmission range of this telescope is entirely in the visible range (400 nm- 700 nm) and quickly falls off towards the UV region, thus prohibiting to capture the emission in UV region (C I 247.8 nm, Al 308 nm doublet, etc.).

Figure 5 depicts typical remote LIBS spectra of HEMs (220-870 nm) and metals (300-700 nm) at a remote distance of ~8.5 m with important peaks identified and labelled. All HEMs exhibited CN violet (B$^2\Sigma^+$–X$^2\Sigma^+$) and C$_2$ swan band. In CN violet band, $\Delta\nu = 0$ band was dominantly visible compared $\Delta\nu = -1$ while $\Delta\nu = + 1$ (358 –359 nm) band is absent in all HEMs. In C$_2$ swan band (d$^3\Pi_u / a^3\Pi_u$), $\Delta\nu = 0$ band head at 516.53 nm was observed in all HEMs. Few Fe I impurities were identified at 386.91 nm and 388.71 nm in aluminum along with Al I transitions at 394.40 nm and 396.15 nm. Copper and Zinc peaks were observed in the LIBS spectra of Copper and Brass targets. The lower intensity of Zinc spectral lines in the LIBS spectrum of Copper target suggests that Zn is an impurity. However, quantitative analysis of Zn in brass and copper is beyond the scope of this article.
Figure 6(a) shows the PCs score plot of R-LIBS spectra of HEMs and Fig. 6(b) shows the corresponding PCs. First three principal components together accounts for 88% of the variance present in the data set, with PC1 being the strongest with 82%, followed by PC2 with 5% and PC3 with 1%. The essential spectral features in classification are C, H, N, O atomic peaks and CN, C\textsubscript{2} molecular bands. Major spectral features from PC1 are CN, C\textsubscript{2} and hydrogen. CN, O, N, H are prominent features in PC2, whereas CN, O, and N in PC3. Figure 6(c) shows the PC scores plot for R-LIBS spectra of aluminum, copper, brass and stainless steel. From the data presented it is apparent that aluminum and stainless steel are well separated and easily distinguished. Brass and Copper clusters are also clearly grouped though they are slightly together and this could be attributed to the low purity of Copper with Zinc rendering the LIBS spectra being similar with Brass. Figure 6(d) shows the first three PCs, from R-LIBS spectra of metals and alloys, which accounts for most of the variance present in the data set. The PCs thus obtained through the analysis explain the important spectral features from various samples. The first three PCs together accounted for 69% (43%, 21%, 5%) of variance. Out of these PCs, first PC is similar to SS with transitions of Fe and has also Cu and, Zn thus indicating the spectral features of either Cu or brass, or both and SS. However, the data is dominated by SS spectral features. Second PC has lines of Al with maximum magnitude, followed by Cu, Zn and Fe. Therefore, it has spectral features from all the investigated targets. Thus, first and second PCs possess spectral features of all the samples considered. Third PC has Zn lines with maximum magnitude and followed by Cu and Al. Contribution of spectral features from stainless steel are very feeble and thus can be ignored. Other higher PCs (fourth, fifth, etc.) are insignificant as they account for minimal variance (less than the third PC) and thus can be neglected. All the samples demonstrated a long dispersion along PC3 but seem to be adjacent when viewed with first two PCs (2D-plot, not shown here). Minimal (2-3) outliers were observed in PC scores plot of metals, which attributes to replication of metals spectra. These results conduit to these possible conclusions: (i) The R-LIBS spectra can be utilized in identification of constituents of metals and alloys (with impurities) even at large standoff distances and (ii) PCA, though a unsupervised chemometric technique, can potentially be employed to identify the critical spectral signatures to classify or group the samples. In future, various standard samples will be procured and will
be analyzed for class classification by using the supervised techniques such as SIMCA, PLS-DA models, which gives improved classification and identification.

Fig. 6. (a) PC scores plot and (b) first three PCs for the processed LIBS spectra of explosives (nitroimidazoles and nitropyrazoles) obtained at 8.5 m. (c) PC scores plot and (d) first three PCs for R-LIBS spectra of different metals obtained at 8.5 m.

5. Conclusions

We have investigated the feasibility of fs LIBS technique for explosives detection in two configurations i.e. ST-LIBS (up to 2 m) and R-LIBS (at 8.5 m). Finely ground powders of energy rich nitroimidazoles, nitropyrazoles were pressed into pellets and then used in these studies. Two collection systems i.e. ME-OPT-0007 (ANDOR) and Schmidt-Cassegrain telescope of different sizes, aperture window and transmission capabilities were used in standoff and remote configuration respectively to capture the LIBS emissions. Along with HEMs, metal and alloy targets were recorded in R-LIBS configuration. Prominent spectral features of HEMs i.e. C, H, N, O atomic transitions and CN, C2, NH molecular bands were readily identified. A decrease in the LIBS intensity with increase in standoff distance could be attributed to the different plasma generation conditions with interaction of filaments involved in certain cases. Filaments carry a fraction of incident energy and thus results in reduced laser energy coupling to the target. Filaments produce a cooler plasma as compared to tightly
focused fs pulses thus limiting the persistence of plasma species. However, focusing the fs pulses after expanding the beam, could result in narrowing the filament length and minimizing the energy redistribution. Further, the decrease in solid angle subtended by the collection system at the plasma source, decrease in intensity due to increase in spot size also influence the LIBS signal strength. At each standoff distance, explosives were classified using a PCA code written in MATLAB. 3D PC scores plot exhibited robust clustering in the case of nitroimidazoles. As the standoff distance increased, the contribution of first three PCs has decreased from 99% to 52%, which indicates that half the information from data is unaccounted for. However, when the PCA was performed on R-LIBS spectra of HEMs, the first three PCs accounted for 88% of variance, which is similar to the result obtained at 50 cm standoff distance. The superior result was possible due to the deployment of a Schmidt-Cassegrain telescope which has large aperture (6") and improved collection arrangement. A combination of two or three lenses can be used to focus fs pulses at desired standoff position and thus the working distance can be changed by adjusting the distance between lenses. However, it is crucial to understand the complex focusing dynamics of fs pulses [78] and optimize the pulse energy as they affect LIBS signal strength. Recently, it has also been demonstrated that either part of the LIBS spectra [79] or part of the echellograms [80] itself can be utilized effectively in discrimination/classification studies implying the reduction in algorithm time, complexity and increase in the sampling rate. Further, Ultra-short pulse fiber lasers can also be used for portable applications owing their compact size, minimized background emission [81].

Thus, in conclusion, fs laser pulses can be potentially deployed in field for standoff detection due to their appealing features such as (i) lesser intrusion of air, stoichiometric ablation with fs pulses (ii) minimized contribution from the substrate (crater depth attained in fs filament ablation is smaller in comparison with those obtained using fs/ns pulses) (iii) formation of filaments and when augmented with telescopes of large f-number, efficient pulse delivery with an easy user interface assisted with superior multivariate analysis algorithm will result in efficient trace detection of hazardous materials of interest.

We strongly believe that the future studies on fs ST- LIBS technique (including ours) should focus on

(a) Acquiring the fs ST-LIBS spectra of all common/standard explosives.

(b) Utilize superior supervised algorithms such as PLS-DA, ANN, etc. for exemplary and unambiguous detection.

(c) Optimize the acquisition parameters (e.g. gate delay, gate width, gain of the ICCD) to enhance the SNR at each standoff position.

(d) Investigate some of the hybrid techniques such as LIBS-Raman technique to embrace the advantages of both the methodologies for effective explosives detection.

Our future LIBS work with fs pulses and in standoff configuration will focus on

(a) Improving the collection efficiency by studying various optical (focusing and collection) configurations.

(b) Extend these studies to trace level detection. For this one also need to explore the single-shot LIBS technique so as to eliminate any detrimental substrate effects.

We believe that with latest developments in the sources (of fs pulses) and the detectors it will not be a difficult task to make compact (portable) LIBS systems for field deployment.

**Funding**

DRDO, India (ERIP/ER/1501138/M/01/319/D(R&D)); Board of Research in Nuclear Sciences (BRNS), India (34/14/48/2014-BRNS/2084).
Acknowledgments

Authors acknowledge the technical support of Mr. Krishna Kumar and his team at LightMotif (Hyderabad, India) for designing and delivering the standoff optics. Authors also acknowledge Dr. Dibakar Das (and his group), School of Engineering Sciences & Technology (SEST), University of Hyderabad for permitting us to utilize the Carver hydraulic press facility.