Rilevamento di tracce di esplosivo mediante spettroscopia di plasma indotto da laser

Sono stati eseguiti studi comparativi delle righe spettrali del plasma prodotto su residui di esplosivi o interferenti organici. La distribuzione e lo spessore dei residui non erano uniformi, proprio come ci si deve aspettare nelle condizioni operative di interesse per la *security*, nelle quali lo strumento sarà testato durante le prossime campagne di misura. Questi studi hanno permesso di identificare i parametri spettrali che portano a una corretta classificazione dei residui per i dati acquisiti. In tutti i casi, la soglia di rilevamento stimata per gli esplosivi è compresa tra 0,1 e 1 ng.

Explosive's trace detection by laser-induced breakdown spectroscopy

Comparative studies of the line intensities from the plasma produced on residues from explosives or organic interferents were performed. The residues had not uniform distribution and thickness, as expected in real conditions for security applications, to be tested in forthcoming campaigns. These studies allowed identifying the spectral parameters for the correct residue classification within the acquired data set. In all the cases, the estimated detection threshold was between 0.1 ng and 1 ng of explosives.

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Introduction

Field explosive detection is extremely important for homeland security. Although many explosive's detection techniques are well established, there is still the need and technological challenge for development of fast, in-situ screening sensors. One of the possibilities to recognize hidden explosives is through the detection of their dispersed particles. The handling and transportation of explosives has been shown to generate explosive traces on surfaces, which may subsequently be detected [1]. One of the most promising techniques for ultra-rapid, in-situ identification of materials is the laser-induced breakdown spectroscopy (LIBS) [2, 3], as it does not require any sample preparation. LIBS analyses demand no contact, making stand-off detection possible from up to 130 m [3].

LIBS is based on plasma generation by an intense laser pulse, which leads to atomization and ionization of the sample material. Spectral emission from the excited species in plasma is used for the identification and eventual quantification of the sample composition. Explosives are organic compounds, containing carbon, hydrogen, and oxygen, while nitrogen is present in almost all high explosives. Commonly, explosives are rich in N and O, and poor in H and C, with respect to

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other organic substances. LIBS spectra from energetic materials normally contain atomic lines from these four elements and molecular bands of CN and C_2 [3-6]. Molecular emission can be attributed both to the native C=C and C-N bonds [7, 8] and to recombination in plasma [9]. Rapid LIBS detection of energetic materials is normally performed in air surroundings, so the interference from air components on the spectra must be taken into account. Classification of organic compounds by LIBS can be performed by comparison between the sample spectra and the previously established library, or by comparing line intensity ratios from H, C, N and O [3-6]. In this latter case, a procedure for explosive recognition is based on properly constructed algorithms, or on chemometric methods.

Similarly to LIBS, Raman spectroscopy might be applied for stand-off explosive detection. The Raman technique is highly discriminant, being based on molecular detection where each substance has its characteristic spectra. However, the Raman technique deals with low-signal intensities and the estimated explosive detection limit is in the order of 1-100 μg, which is not always sufficient for trace detection. Differently, LIBS is highly sensitive with respect to Raman, but it is less selective and requires further fundamental studies in order to understand and establish the most discriminant spectral features of explosives compared to the common organic materials.

The final scope of this work is to establish the most appropriate procedure for explosive trace recognition by LIBS, later to be exploited for in-field operation, as required by the FP7 project EDEN (End-user driven DEmo for cbrNe). The instrument for remote explosive detection is under construction and is illustrated in Figure 1. The LIBS sensor was designed to perform measurements at distances between 7.5 m and 30 m through the scanning of surface areas chosen by the operator, with the help of integrated viewing systems.

In the present work we present the results from LIBS measurements on residues of nine types of explosives and of some common organic materials. The random presence of residues on the target corresponds to conditions expected in real situations.

Experimental

Measurements were performed by the LIBS prototype system developed by the industrial company IPAC (Austria) in the frame of the ISOTREX project (FP6). The system employs Nd:YAG laser from Quantel (Model Ultra 50) operated at 1064 nm. The laser pulse width was 8 ns and the laser energy was fixed at 50 mJ. The laser beam of a 3 mm diameter was focused onto the sample surface by two quartz lenses with effective focal length of about 90 mm, thus producing the laser spot of diameter 0.22 mm (Fig. 1). The corresponding energy density averaged across the laser spot was of about 130 J/cm^2, which is 3.6 times higher than in our previous experiment [6], with the advantage of achieving a higher degree of atomization of the organic compound in the plasma.

The plasma emission was collected by two optical systems containing focusing optics and fiber bundles [10]. At one end, the bundle was separated into single fibers, and each of them was connected to one of the six spectrometer channels (StellarNet). A single channel, with 0.1 nm spectral resolution, covers a bandwidth of about 100 nm, and it is equipped with a 2048 Photo-Diode Array (PDA). Each spectrometer channel was triggered externally and simultaneously with the laser flash lamp. The minimum integration time used here was 30 ms. The spectrometers cover the 200-800 nm spectral range. After one laser shot, the whole spectrum was saved for further analysis by custom written programs under Labview.

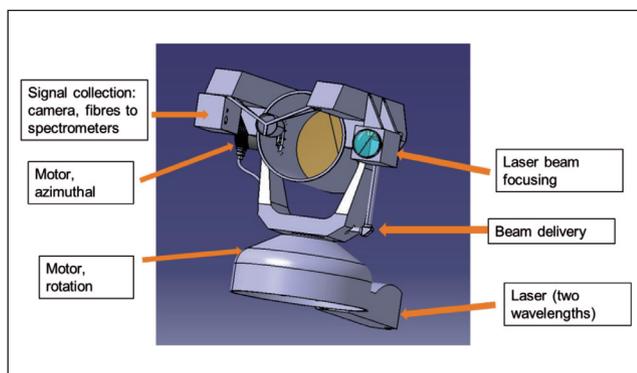A sample was placed on an X–Y micrometric table, and

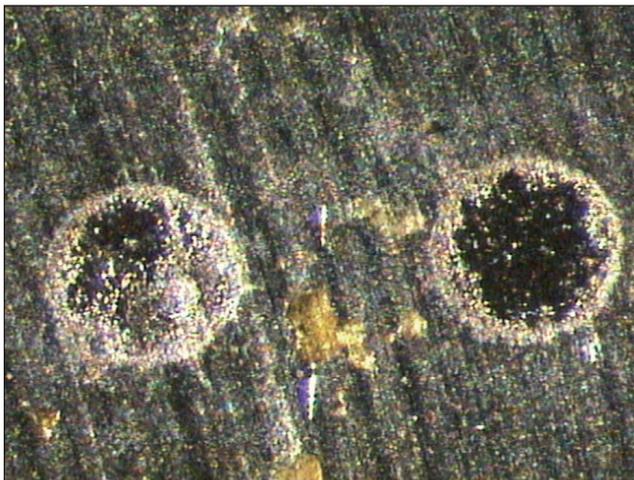**FIGURE 1** Laser system for remote explosive detection

FIGURE 2 Photo of laser-induced craters (0.22 mm diameter) in the presence of TETRYL residues, here yellow

FIGURE 3 Characteristic spectral parts of TNT traces on aluminium support; Si, Mg and Al lines belong to the support

shifted by 0.5 mm after each laser pulse. The support material for residues was aluminium (Anticorodal), roughly machined (Fig. 2) and cleaned in an ultrasound bath, first with pure acetone and then with distilled water. All the explosives considered, except DNT, are standard solutions with concentration of 1.0 mg/ml or 0.1 mg/ml (TATP) in methyl- or ethyl alcohol, or acetonitrile. DNT was purchased in the form of crystal grains and dissolved in pure acetone before placing it onto support. Small droplets of solution containing explosives spread themselves over the aluminum surface and were left to evaporate thermally, leaving unevenly distributed residues (Fig. 2). Other analyzed, not energetic materials (diesel, pure paraffin wax, and hand cream) were directly distributed over the support in thin layers of uncontrolled thickness. After the initial measurements on the interferents, the substrate was wiped out with a tissue in order to reduce the residue thickness. This operation was repeated a few times.

Results and discussion

The spectra obtained on organic residues always contained the emission lines of aluminium, thus indicating the support ablation, too. A typical LIBS spectrum on organic residues is shown in Figure 3. The
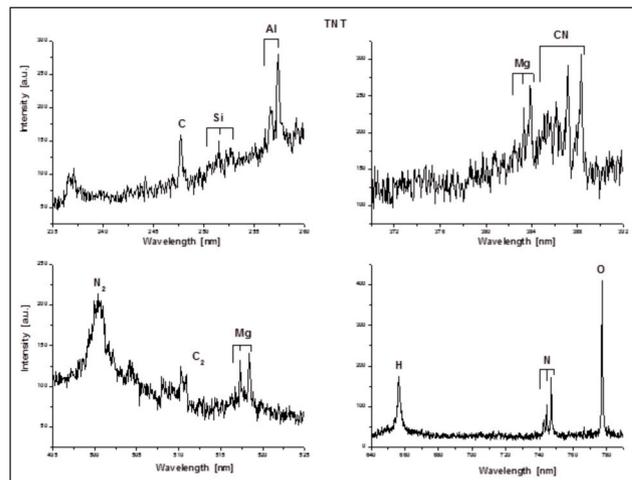
plasma intensity also from the clean support exhibits fluctuations [6, 10] due to the surface roughness with structures comparable to the spot size and due to laser energy instabilities. In case of the residues, a more intense LIBS signal corresponds to a smaller sample amount inside the laser focal spot.

In our previous work [6] the initial data set was elaborated in three different ways attempting to explosives from interferents:

1) Principal component analysis (PCA) which includes line ratios O/N, O/C, H/C, N/C, N/H and O/H
2) Plot of the line intensities H/N as a function of Al
3) PCA analysis with the line ratios (1) plus parameter A, which considers a possible recombination between C and N in the plasma, and is defined as:

$A = I(C_2) - 2*K_1 I(N) - I(CN) + K_2 I(C)$

Where coefficients K_1 and K_2 were weighted as 0.6 and 2.0, respectively, to produce similar contribution of the terms.

The results of the classification by the three methods are shown in Table 1, where the highest score is marked with red. From here, it could be noted that beside the interferents, five out of nine explosive could be 100% correctly classified by LIBS. Differently, EGDN and DNT produced a false negative of about 20%, while NG and TATP had a high error rate with all the three

methods applied. The false negatives always occurred for relatively thick residues; the corresponding plasma temperature, measured through the Boltzmann's plot, was also for 3000 K with respect to the plasma on thin residue [10]. The plasma temperature affects not only the excitation of the emission lines but is also related to the molecule fragmentation and chemical reactions in the plasma.

All the previous works by other research groups considered that the plasma produced on explosives was stoichiometric, i.e., the intensities of the characteristic lines from C, H, N, O, CN and C_2 were proportional to the sample amount. The corresponding classification procedures were based on this assumption, which also means that the ratios of the characteristic spectral lines are stable in the plasma.

In the present experiment, where the laser irradiance was relatively high and favorable to achieve a more complete fragmentation of organic molecules, we observed the following:

Name	Method 1	Method 2	Method 3
EGDN	65	81	68
NG	0	3	39
RDX	95	100	59
TNT	100	100	100
DNT	79	36	64
PETN	100	100	100
HMX	95	100	95
TETRYL	100	96	100
TATP	4	4	54
Diesel oil	100	100	100
Paraffin wax	100	100	100
Grease lubricant	100	100	100
Glue LOCTITE	100	100	100
Hand cream	100	100	100
Support	100	100	100

TABLE 1 Percentage of correct sample classification by LIBS (explosive or non-explosive) according to the methods 1-3 (cf. text above)
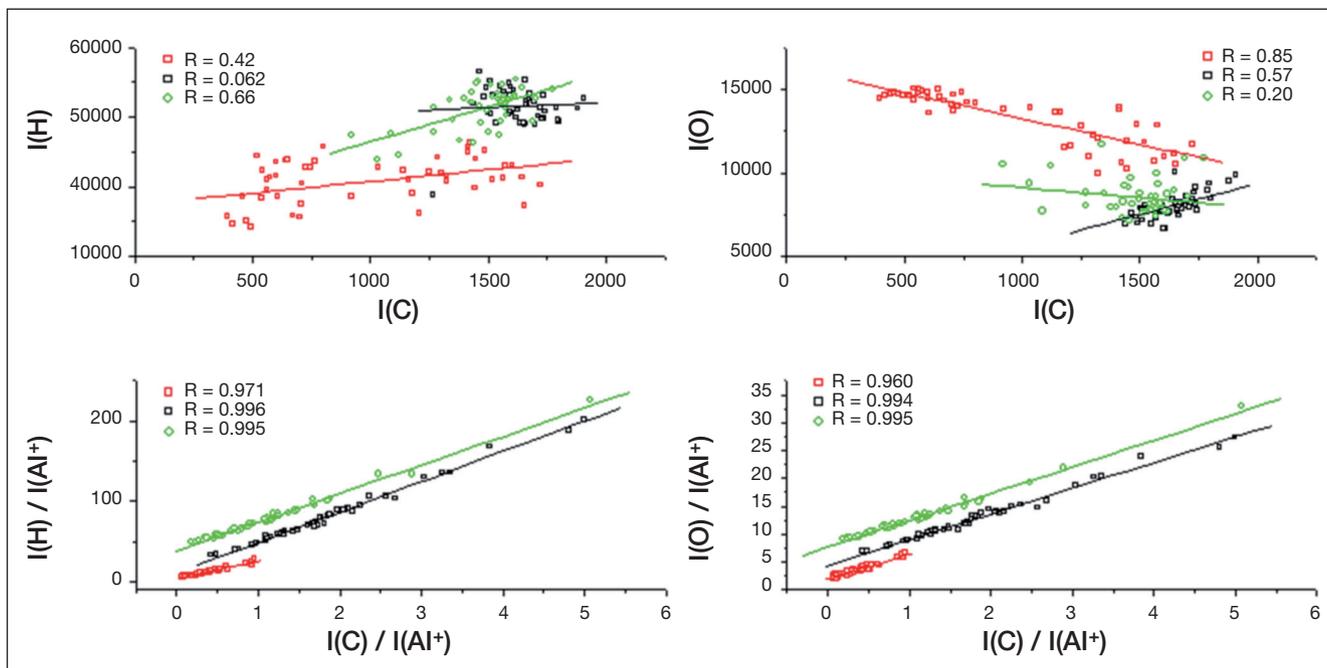

FIGURE 4 H and O emission intensities from TNT (red), diesel (black) and paraffin (green) residues as a function of atomic C emission: top — raw data; bottom – after normalization; the points of diesel and paraffin are shifted vertically [10]

Explosive	H(O)	N(O)	N(H)	O(C)	N(C)	H(C)	Total	% of correct classif.
TATP	- / -	- / -	- / -	+ / -	- / -	- / -	1 / 0	4
NG	- / -	- / -	- / -	- / -	+ / -	- / -	1 / 0	0
EGDN	- / -	- / -	- / -	+ / -	+ / +	+ / -	3 / 1	65
RDX	+ / +	- / -	- / -	- / -	+ / -	+ / -	3 / 1	95
DNT	+ / +	- / -	- / -	- / -	+ / -	+ / +	3 / 2	79
HMX	+ / +	- / -	+ / -	+ / -	+ / -	+ / +	5 / 1	95
TETRYL	- / +	- / -	- / -	+ / -	+ / +	+ / +	3 / 3	100
PETN	+ / +	- / -	- / -	+ / -	+ / +	+ / +	4 / 3	100
TNT	+ / +	- / -	+ / -	+ / -	+ / +	+ / +	5 / 3	100

TABLE 2 Capability to discriminate explosives (+ for yes, - for no) through the intercepts/slopes, respectively, of the linearly fitted functions involving different emission lines; the last column compares the percentage of correct classifications previously obtained by PCA (Table 1, method 1)

1) In the presence of carbon in the plasma, atomic emissions from O and N are clearly reduced; this indicates that O and N atoms are lost in some chemical reactions involving products of fragmented organic molecule.

2) There is a striking anti-correlation between line intensities from N, O, and Al^+ (from the support) with respect to the emission from atomic carbon. Simultaneously, H emission follows fluctuations of C line intensity, as expected from the residue molecular formula.

3) The line intensity ratios change even for one order of magnitude from one sampling point to another; consequently, averaging the spectra in the attempt to classify organic residues is not meaningful.

4) The LIBS plasma generated on organic samples is not stoichiometric; this was particularly evident from very different line intensity ratios (up to 60%) on RDX and HMX, which have the same stoichiometry in the molecular formula.

5) Ionic emission intensity, here of Al^+, is a good indicator of the plasma temperature and the electron density. The line intensity ratio of Al^+/Al changes with the residue thickness, and the measured electron density was always lower in the spectra with more intense Al^+ lines, corresponding to a smaller quantity of the residue, see point 2) [10].

Based on the facts above, it was possible to establish the normalization procedure which linearizes the data set

(Fig. 4 bottom) starting from weakly correlated data (Fig. 4 top). The slopes and intercepts of different linearized functions, related to H, N, O and C emission lines, were calculated both for explosives and interferents, and those marking the difference among them are shown in Table 2. The intercept indicates the function value for very thin residues.

From Table 2, it can be observed that the functions H(O), H(C) and N(C) are the most important features for explosive classification. Although the LIBS-measured ratio O/N was also considered as an indicator of the presence of explosives [3, 11-12], the results shown in Table 2 demonstrate that the function O(N) does not contribute to the discrimination at all. Both atomic oxygen and nitrogen are depleted in the presence of carbon in the plasma, and anomalous O/N ratio in the molecules of the explosives is not reproduced in the LIBS spectra. From the intercepts of the function N(C), all residues containing nitrogen are clearly distinguished from interferents. This was true also for nitroglycerin, which is difficult to discriminate by LIBS. From the slopes of O(C) it was not possible to discriminate the residues; however, the intercepts are again indicative of most of the explosives, including TATP. Hydrogen emission was always more intense on thicker residues. It is well known in literature that detaching hydrogen needs less energy than fragmenting the whole organic molecule [13]. For most of the explosives examined here, the slope of H(C) is lower than for interferents,

indicating that a detachment of hydrogen from the mother molecule in the weak plasma (thick residue) is less efficient.

The results summarized in Table 2 show that some intercepts of the considered atomic functions allow distinguishing all the examined explosives from the interferents; the corresponding slopes are less indicative. This also signifies that the organic residues can be more easily classified when present in very thin layers (close to the intercept points) or under high laser irradiance, where the plasma temperature is high and molecular fragmentation is efficient. The TNT residue is the easiest to discriminate by LIBS as it differs from the interferents in eight of the examined twelve functions. Differently, TATP and NG are very difficult to detect by LIBS since they have only one function intercept out of the ranges belonging to the interferents. These results are in good agreement with the percentages of correct classifications previously obtained on residues of the same explosives [6], where PCA analyses were performed considering the next line intensity ratios: O/N, O/C, H/C, N/C and O/H.

When probing the residues by laser, the non-uniform distribution of the sample must be taken into account, and this generates LIBS spectra with strongly variable line intensities and their respective ratios. However, thanks to a good correlation between the characteristic line intensities after proper normalization (Fig. 4, bottom row), a 100% correct classification of all the residues here considered was obtained by the simple procedure described in the following:

1) acquisition of a sufficient number of single-shot spectra (for example, more than 30 spectra);
2) normalization of C, H, N and O line intensities on ionic emission (here on Al^+) in all the individual spectra;
3) linear fitting of the normalized functions H(O), N(H), O(C), N(C) and H(C), and retrieving of their slopes and intercepts;
4) verifying if one or more of the calculated slopes and intercepts fall inside the limits for explosives.

For the organic residues distributed over support materials other than here, the data linearization could be performed by involving different parameters related to the plasma condition, as for example other ionic lines (like C^+) or continuum spectral distribution. Each type of normalization requires evaluating the errors in the fitting, before placing the limits that separate explosives from interferents.

Conclusions

In the presence of non-uniform organic residues, as expected in real-field conditions, the LIBS plasma parameters vary from one sampling point to another. This also leads to changes in the laser-induced fragmentation pathways and in chemical reactions inside the plasma. The characteristic line intensities and their ratios change up to one order of magnitude from one spectrum to another. The plasma induced on organic materials is not stoichiometric.

The organic residues can be more easily classified by LIBS when present in very thin layers or exposed to high laser irradiance, where the plasma temperature is high and molecular fragmentation is efficient. Among the examined explosives, the easiest to identify in air by LIBS is TNT, followed by HMX, PETN and TETRYL. The most difficult to discern are NG and TATP, having only one function each that distinguish them from other organic residues.

These results of the present studies will be exploited for building up the classification procedure for the stand-off LIBS instrument under development. The chosen approach will be tested and validated over a larger number of residues, and placed on different substrates than here.

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