Standoff LIBS Sensor Technology. Fieldable, Remotely Operated Platforms for Detection of Explosive Residues

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ABSTRACT

Laser induced breakdown spectrometry (LIBS) offers unique capabilities for investigating the elemental composition of solid samples. One of the key aspects of LIBS relies in its ability for non-intrusive analysis of targets located at several tens of meters from the instrument. Thus, complex scenarios and hazardous materials can be inspected from safe, remote locations. This paper discusses the capabilities of LIBS to detect, identify, and measure concentrations of explosives at operationally significant ranges. Fieldable platforms for this task will be presented, including new solutions for autonomous instrument operation.

1.0   INTRODUCTION

Laser Induced plasma spectrometry (LIBS) is an analytical technique based on atomic emission spectrometry. A plasma with high electron temperature and electron density is generated as a consequence of the action of a laser pulse with sufficient energy in a sample. The plasma formed can be used to determine the chemical species that constitute the sample matrix. Laser ablation can be used as a method of vaporization and excitation of the material for subsequent analysis with other techniques, such as atomic emission spectrometry in an inductively coupled plasma (LAICPAES) or by mass spectrometry (LAMS). Direct spectral analysis of the emission produced by the plasma is known as LIBS. A large number of acronyms exists in literature for the same method of analysis. Among them, LIBS (laser-induced plasmas spectrometry), LIBS (laser-induced breakdown spectrometry), LIESA (laser induced emission spectral analysis) and LA-AES (laser ablation-atomic emission spectroscopy) are often used. Although LIBS was first described in the nineteen sixties, it took more than three decades for fully development of the technique, due mainly to the low stability and reliability of the available lasers and to the high cost of lasers at that time. Improvement in the optics and the electronics of the lasers along with the reduction in price and maintenance costs caused that LIBS resurged fundamentally during years 1990, first as a technique for direct analysis of solid samples and, later, for analysis of liquids, gases, and aerosols [1-8]. Due to its versatility, the technique covers at the present time a great variety of applications in a broad front of disciplines including life sciences [9, 10], cultural heritage [11-13], environment [14, 15], industrial processes [16-23], among many others.

With analytical sensitivity in the range of parts per million and precision better than 5% in most of the cases, the potential of the technique is comparable to that offered by other methods of atomic emission spectrometry. Universal experimental conditions allowing the satisfactory analysis of all sample types do not exist and consequently each application requires the careful selection of the working parameters and the best experimental configuration. These parameters include irradiance at the sample, beam focalconditions, laser wavelength, pulse repetition rate, pulse width, synchronization between laser pulse

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and detector integration, among others. Several research groups have proposed the use of double-pulse excitation in an attempt to increase sensitivity and consequently to improve the detection limits [24-27]. Improvements by at least one order of magnitude in LODs are routinely reported with double pulse systems. Other groups are exploring the processes of interaction of ultrashort laser pulses with matter. The interaction processes taking place in the femtosecond and picosecond regimes are not linked to thermal effects in contrast to the interaction on the nanosecond scale [28]. Active research is also devoted to development of new LIBS instruments. Considerable attention is paid to development of fieldable systems capable of providing analytical data in real time. Such instruments can be used for fast decision making in scenarios that require an immediate intervention such as plants of industrial production or environmental reservoirs affected by severe pollution.

A unique capacity of LIBS is that it can remotely analyze the elemental composition of solids, liquids, aerosols and gases by means of the guidance towards the sample of interest of a laser beam through the free atmosphere (direct sensing), or through optical fibers (indirect sensing). Panne [29] reviewed the techniques of remote analysis with laser, some of which use optical fiber for the guidance of the laser radiation or the analytical signal. Although the use of optical fibers certainly makes the analysis in some unattainable locations viable [30], there are practical limitations to the energy level that can be delivered through optical fibers to the sample. Noll at al. [31] applied LIBS to certain distance for the multielemental liquid steel analysis using optical fibers. The limits of detection reported for some elements were below 21 ppm.

Figure 1: Photograph of the stand-off LIBS system prototype

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The authors of the present work have pioneered the development of remote LIBS in open path configurations, the so called TELELIBS technique [32, 33]. The technique was applied to the sorting of steel classes. The analysis at a distance of 45 m of the sample was demonstrated for the first time. In successive works [34-40], the research group that presents this proposal developed LIBS remote analysis and demonstrated many of the unique capabilities of the technology for environmental analysis, analysis of objects at high temperature, and analysis of organic materials. Cremers and Salle [41-45] evaluated the capabilities of LIBS analysis in a Martian atmosphere, in view to a possible mission to Mars. Ultrashort laser pulses (picosecond or femtosecond) are an attractive approach for remote systems and several groups have reported in this field [46-48]. Nevertheless, femtolasers are still complex and delicate instruments which impose severe limitations to their use in fieldable remote applications. Integration and operation of LIBS with another technique such as laser induced fluorescence [49] or Raman spectroscopy [50] in remote conditions have been recently reported. Recent applications of remote LIBS include the analysis and verification of mine casings [51], the conservation of objects belonging to the cultural heritage [52-53], meteorite analysis [54] and the detection and extraction of salt in metals and polymers [55].

One of the most promising capabilities of TELELIBS is the analysis of energetic materials at a distance, a hot topic that requires much attention by the scientific community. Conventional methods for the detection of explosive at a distance go from colorimetric screening to speciation methods using spectroscopic measurements [56-58]. Recent analytical methods of remote explosive detection are based on Raman spectroscopy [59-60]. Raman scattering provides information on the composition and molecular structure, that may complement the elemental information provided by TELELIBS. Our research group has recently demonstrated the viability of TELELIBS detection of explosive residues to a distance of up to 30 m [40]. This study has initiated a large, world-wide interest by security officials in the capabilities of the technology. Also, a large number of research groups are exploring the capabilities of the technology for this application.

This research work evaluates the capacity of stand-off LIBS to discriminate between explosive and non explosive substances. The used stand-off optical system allows to explore and to analyse samples located at more than 30 meters (30 m- 50 m). The results in this work were obtained at the maximum distance (50 m). A simple chart flow gives very promising results in distinguishing organic compounds from inorganic compounds, between explosive and non explosive substances (in case of organic compounds), and in identifying sodium chlorate and ammonium nitrate (in case of inorganic compounds), which are the most important inorganic explosives.

2.0   INSTRUMENT DESCRIPTION

2.1 Experimental setup

The instrument used is a stand-off LIBS system prototype designed by the University of Malaga, that is capable to work at maximum distance of 50 m. A Q-Switched pulsed Nd:YAG laser operating at infrared wavelength (1064nm) was used. This laser can emit a pulse of energy 1600mJ at a maximum repetition rate of 10Hz. The pulse width is 5.5ns, and the spatial energy distribution of the beam is Gaussian. The laser pulse energy can be controlled by the delay of the Q-switched laser relative to the flash lamps. The optical system is used to emit laser and receive plasma light in the same axis. It must focus the laser beam in the remote sample surface in order to provide the necessary irradiance to produce plasma. The plasma emission is remotely collected by a fibre optic cable, located in the own instrument. The diameter of the receiver aperture is 203.2mm. The end of this fibre is connected to the entrance slit of spectrograph. The plasma light was detected using a gated intensified charge-coupled device (i-CCD).

The system is installed in portable platform that allows to working in field (Fig. 1). The weight of the complete system is about 300kg. A wireless high speed network connection allows to controlling the most important actions of the system from a remote location (ca. 50 m) (Fig. 2).

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2.2 Samples

Eleven samples were used for studying the discrimination capacity of our experimental system: (1) aluminium foil, 2mm thick, commercial aluminium (Al); (2) 4-nitrotoluene (MNT) with a purity of 98%; (3) 2,4-dinitrotoluene (DNT) with a purity 97%; (4) sodium chlorate ($NaClO_3$) with a purity >99%; (5) ammonium nitrate (NH_4NO_3) with a purity of >99.5%; (6) 4-methyl-3nitroaniline with a purity of 97%; (7) pentaerythritol with a purity >99%; (8) cellulose, microgranular; (9) 1,3,5-trimethylhexahydro-1,3,5-triazine with a purity of 97%; (10) sodium chloride (NaCl) with a purity of >99.5; (11) zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) with a purity of 98%. The samples are provided by Sigma-Aldrich, Fluka and Scharlau.
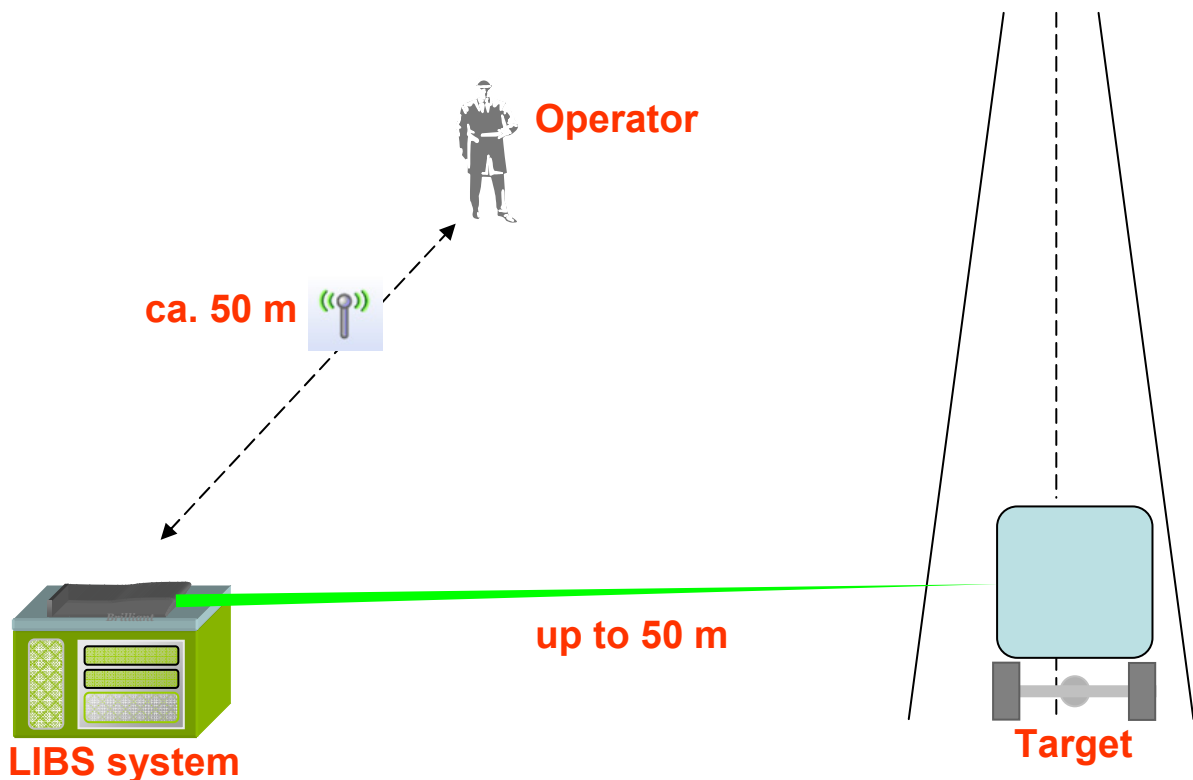

Figure 2: Diagram of remote operation using high speed network connection

In order to obtain residues on solid surfaces (aluminium foil), we prepared dissolutions in acetone or water (depending on the analyte) at the same concentration (10% w/w). The foils are immersed in the dissolution and then it is dried to obtain a residue film on the foil surface. When we are intended to quantitatively know the amount of the sample, we pour a known volume of the dissolution on the foil. The surface density of the residue is directly calculated from the surface occupied by this volume.

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3.0 RESULTS AND DISCUSSION

The typical emissions used to the identification of explosive organic compounds by LIBS are C_2 (516.5 nm, 558.5 nm), CN (388.30 nm) molecular bans and C (247.93 nm), H_α (656.45 nm. 656.47 nm), O (777.27 nm, 777.42 nm), N (742.757 nm, 744.43 nm, 747.04 nm) atomic lines. A Stand-off LIBS spectrum obtained by the prototype, corresponding to an organic explosive substance (a MNT pellet), is shown in Figure 3 where C_2 (516.5 nm, 558.5 nm) molecular band and H_α (656.45 nm. 656.47 nm), O (777.27 nm, 777.42 nm), N (742.757 nm, 744.43 nm, 747.04 nm) emission lines are labeled in the spectrum.
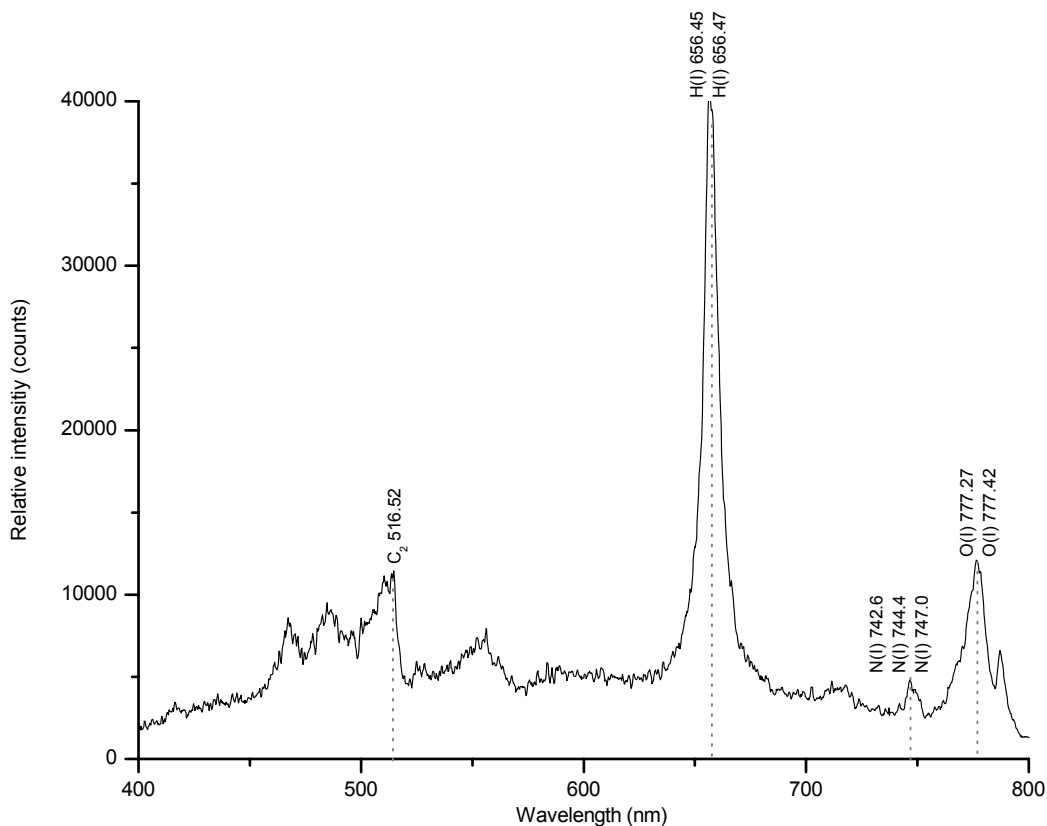

Figure 3: Stand-off LIBS spectrum corresponding to an organic compound (MNT pellet)

The explosive detection capacity with our system is shown in Figure 4 and Figure 5. In Figure 4, it is shown three single-shot LIBS spectra of an explosive organic residue (DNT) on aluminium foil, an non explosive organic residue (1,3,5-trimethylhexahydro-1,3,5-triazine) on aluminium foil and an aluminium foil. With the spectra obtained by stand-off LIBS, we can distinguish with the naked eye between an explosive organic residue and a non explosive organic residue. In this case the organic explosive can be detected principally because C_2 and CN bands appear in its spectrum. In Figure 5, it is shown three single-shot LIBS spectra of an organic explosive residue (DNT) on aluminium foil, an inorganic explosive residue ($NaClO_3$) on aluminium foil and an aluminium foil, that is material used as subtract in our experiment. With the spectra obtained by stand-off LIBS, we can distinguish with the naked eye between

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an organic explosive residue and an inorganic explosive residue. The absence of the molecular bands and the high intensity of Na emission line allow to discriminating between both explosives.

It is necessary to point out the difficulties to measure concentrations with this system. The most critical difficulty is that the absolute intensity of the lines and the ratios between several lines and bands are very instable at the same conditions. Perhaps, this instability is due to have used an irradiance very close to the ionisation threshold.

100 spectra for each sample are acquired by stand-off LIBS (50m), using a fresh surface between each acquisition. The identification of explosive substances is carried out by obtaining relations between atomic and ionic lines and molecular bands in acquired spectra. Presence of CN and C_2 bands help to distinguish between organic and inorganic substances. For the discrimination between non explosive and explosive organic substances, it is important to study the presence of the N atomic line and the CN band, because of the NO_2 group presence in this kind of explosives. It is considered as explosive organic the organic substances with the NO_2 group. Finally, in the explosive inorganic substances case, it is studied the relations that distinguish the two most important inorganic explosives: ammonium nitrate ($NH_4 NO_3$) and sodium chlorate ($NaClO_3$).
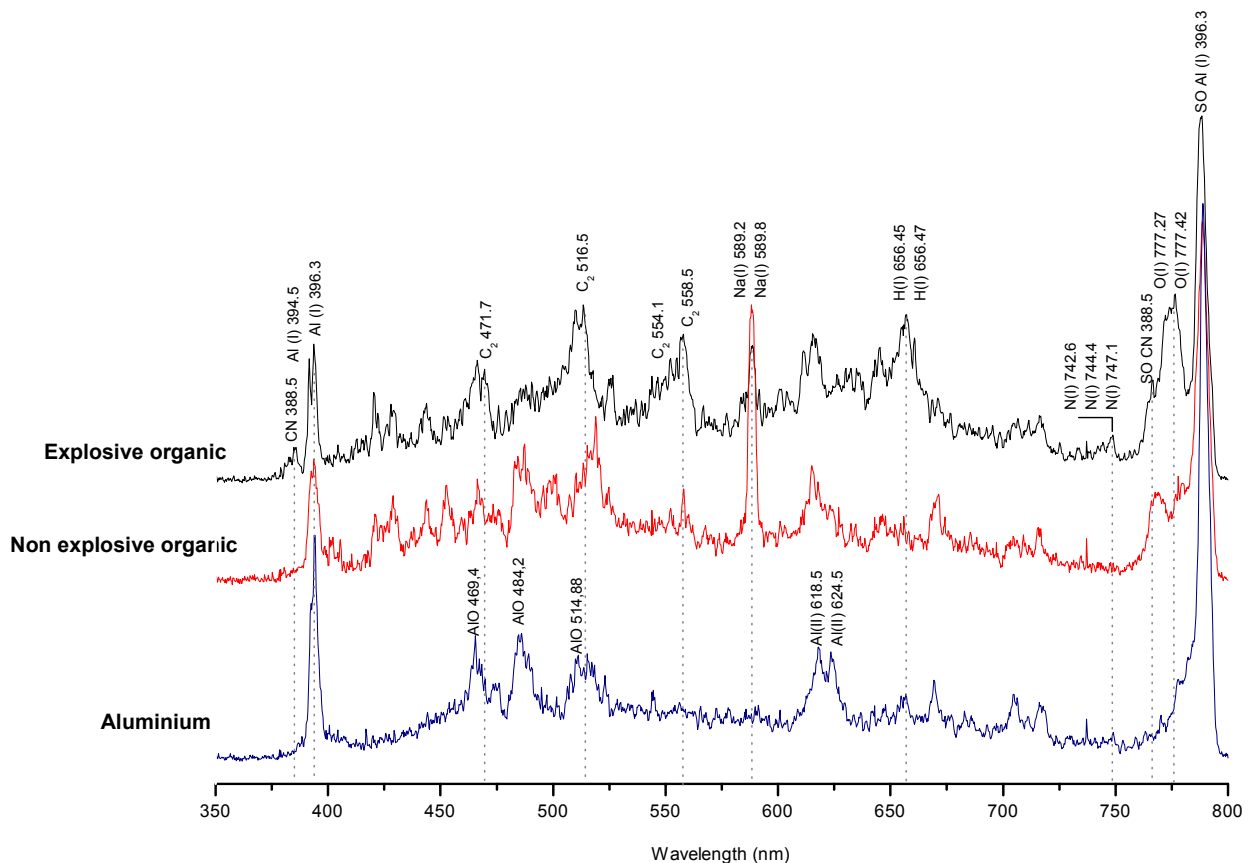

Figure 4: Organic explosive vs organic non explosive

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In Fig. 6, it is shown the flow chart used for the discrimination between explosive and non explosive substances. The decisions within the flow chart depend on several threshold values. In some cases, the threshold values in the chart are chosen values of the contribution of the atomic lines or molecular bands to the spectrum (N, C2, CN) or values of the contribution of the fixed pattern noise of the i-CCD (Ro). In other cases, these thresholds are chosen values of ratios between atomic lines contributions (Na/O, H/O, N/O). The contributions are calculated from an algebraic algorithm that evaluate the contribution of the spectrum respect a set of spectra (library), where spectra of Hα (656.45 nm. 656.47 nm), O (777.27 nm, 777.42 nm), N (742.757 nm, 744.43 nm, 747.04 nm), C2 (516.5 nm, 558.5 nm), CN (388.30 nm), Al (394.51 nm, 396.26 nm), Na (589.16 nm, 589.76 nm), Ca (393.80 nm 396.96 nm) and the spectral representation of Ro are included [61]. The Ca spectrum is included in the library in order to considering calcium impurities, and the Al spectrum is included for considering the aluminium substrate. At the beginning of the discrimination flow chart we have included the condition of a low contribution of Ro. If this condition is not fulfilled, the spectrum is never evaluated, reducing the false positive number. The discrimination strategy was based in the inspection of a scenario of 1100 spectra, where organic explosive (MNT (100 samples), DNT (100), 4-methyl-3-nitroaniline (100 samples)), inorganic explosive (NH4 NO3 (100 samples), NaClO3 (100 samples)), organic non explosives (pentaerythritol (100 samples), cellulose (100 samples), 1,3,5-trimethylhexahydro-1,3,5-triazine (100 samples)) and inorganic non explosives (Al (100 samples), NaCl (100 samples), Zn (NO3)2 (100 samples)) spectra were included. The threshold values were chosen in order to have a high specificity (probability that the detector does not alarm when it should not [62]), because the sensitivity (probability that the detector alarms when it should [62]) can be increased using more than one single-shot. According to the probability rules (disjunction and addition of independent events), the variation of the specificity and the sensitivity with the number of single-shots can be expressed as:

$$p_{sens}(i+1) = p_{sens}(i) + p_{sens}(1) - p_{sexs}(i)p_{sens}(1) \tag{1}$$

$$p_{spec}(i) = p_{spec}(1)^i \tag{2}$$

where psens(i) and pspec(i) are the sensitivity and specificity using i single shots, respectively. In Fig. 7, it is shown, as an example, how change sensitivity and specificity of organic discrimination with the number of single-shots. When the sensitivity increases, the specificity decreases. Therefore, it is necessary to reach a tradeoff between both variables. In Table 1, it is shown how change sensitivity and specificity of organic discrimination, explosive and non explosive organic discrimination, sodium chlorate identification and ammonium nitrate identification with the number of single-shots.

The results that we present in this work are based in 8 single-shot, because at this condition we obtain high sensitivity and specificity. A chart flow result as explosive in one of the 8 single-shots is enough to consider that the detection is positive.

In Table 2, it is shown the result of applying the chart flow in Fig.6 to the 1100 spectra for discrimination between organic and inorganic substances, discrimination between non explosive and explosive organic substances, identification of NaClO3 and identification of NH4 NO3, respectively. The results in this table are for a 8 single-shot based sampling. The identification of organic substances is very sensitive (91%). It was obtained a 14% of false positives. This is due to the low threshold values that we have chosen in order to obtain a high specificity (86%). In the 90% of the cases we distinguished between organic explosives and organic non explosives, what is a very promising result for this preliminary study. In this case, it is obtained only a 8% of false positives. Apparently the result of identification of the NaClO3 should be much better than the obtained result (93%), because of the strong emission of the sodium at 589.16 nm and 589.76 nm. But the restrictions on the threshold values are very exigent, in order to distinguish between NaClO3 and NaCl or substances with presence of sodium impurities. We have to notice that, with these restrictions, we never confuse NaCl with NaClO3. In the case of NH4NO3, we obtain the worst

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sensitivity and specificity (57% and 80%, respectively). The 82% of the samples used for this study have got hydrogen, therefore, the identification of NH4NO3 is particularly complex within the chosen population. A less exigent population would provide a much better specificity.

5.0   CONCLUSIONS

The development of an instrument that allows to identifying explosives on a solid surface, by the stand-off Laser-induced Breakdown Spectroscopy technique (distance to target up to 50 m, experiments now under experimental control, sampling speed from single-shot to 10 Hz) is presented. The capacity of working in field and the presence of new solutions for autonomous instrument operation are included in the instrument. In the present state of development, it is difficult to assure to carry out measurements of concentration with this technique. However, it has been proven that this instrument obtains a good discrimination of explosive and non explosive substances.

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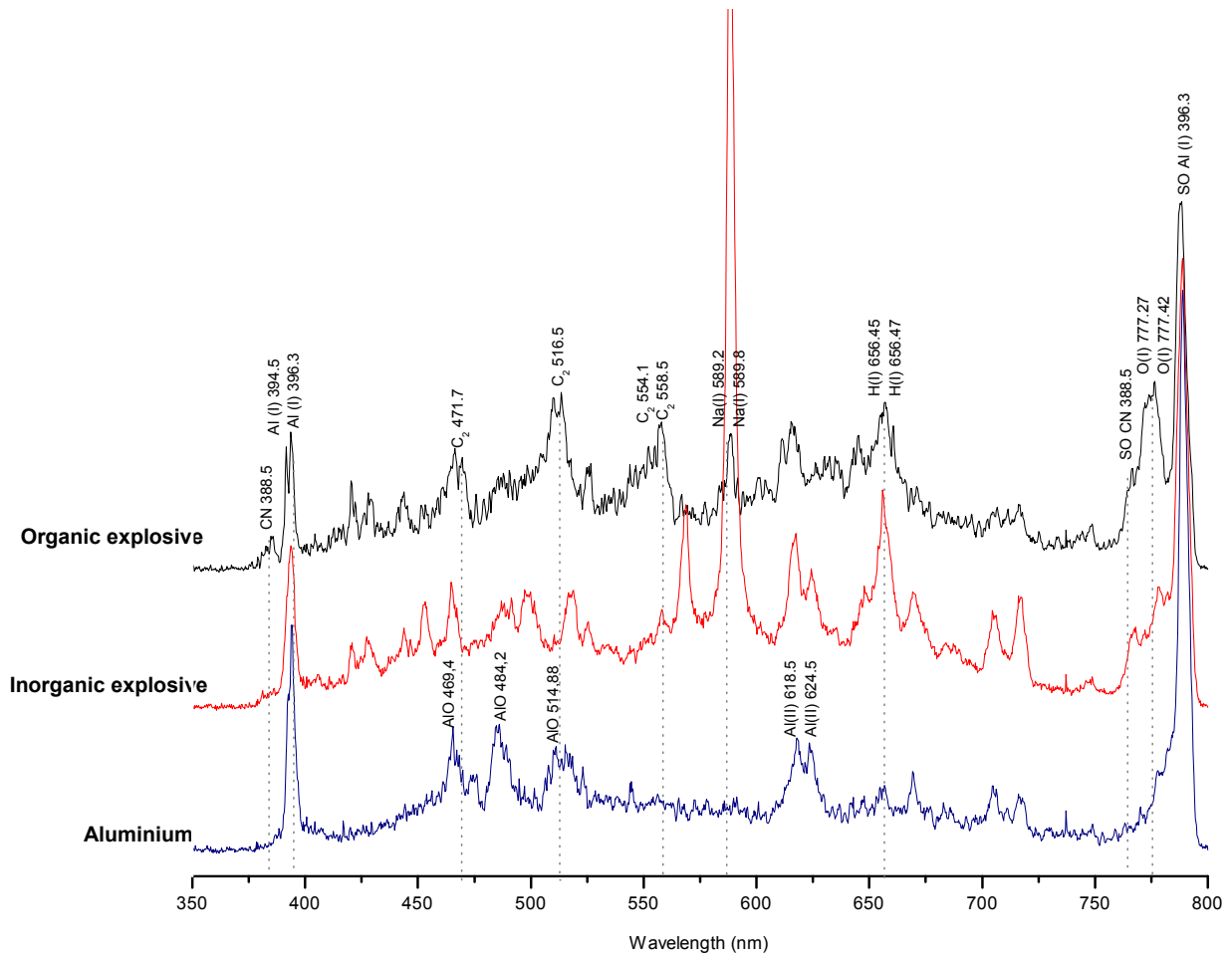
Figure 5: Organic vs inorganic explosive

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Figure 6: Flow chart for detection of explosives

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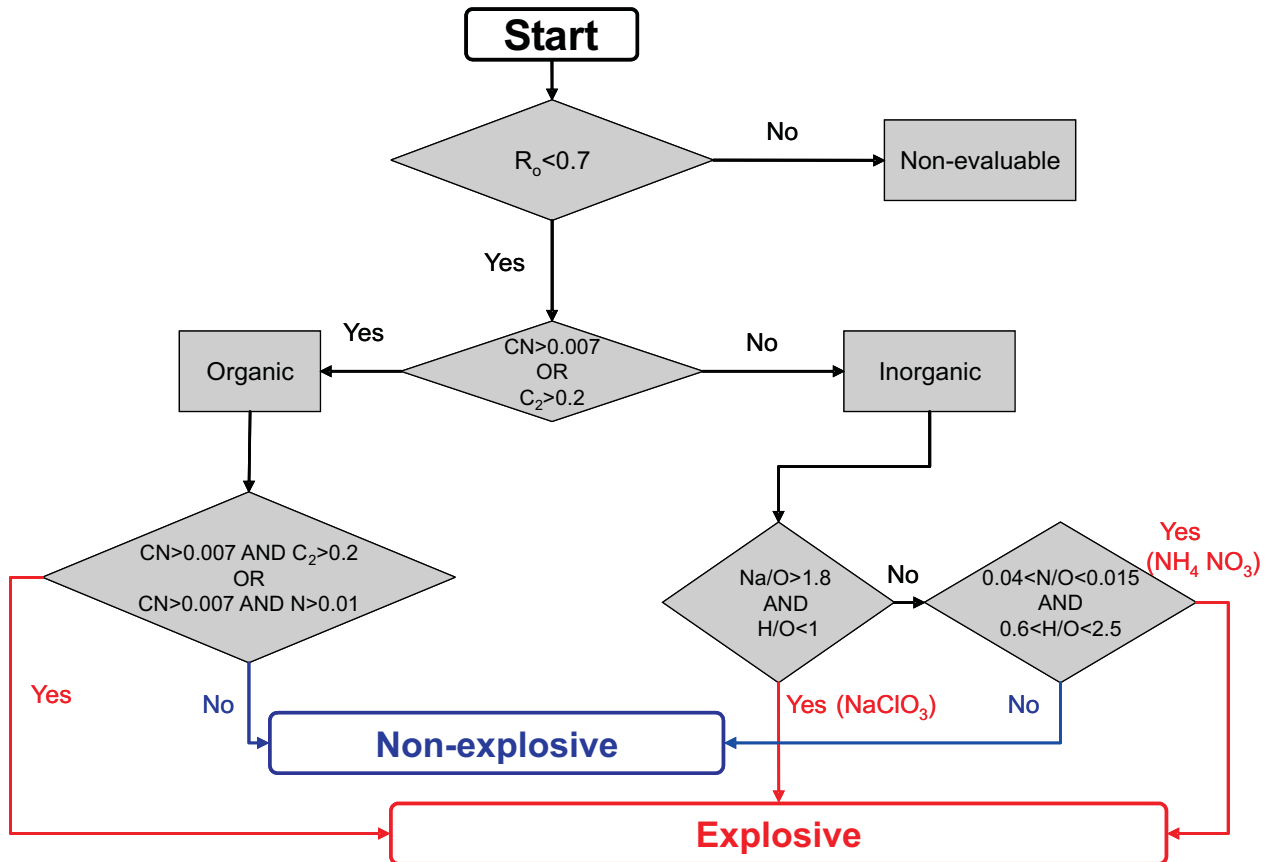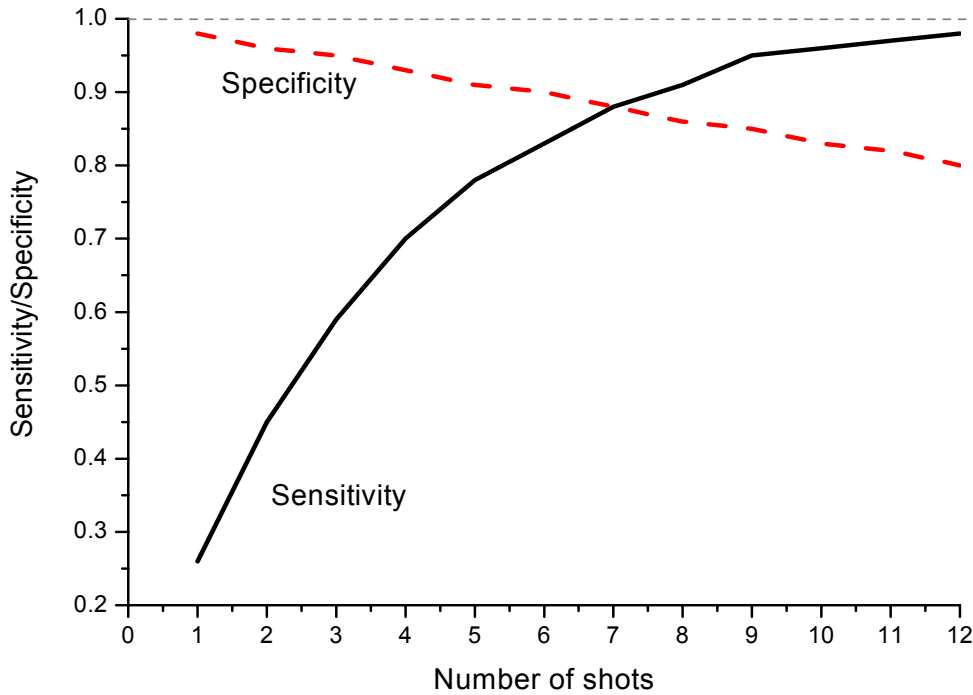Operated Platforms for Detection of Explosive Residues**

**Figure 7: Specificity and sensitivity variation for organic discrimination with the number of
single shots**

# single-shots	Organic		Explosive organic		Sodium Chlorate		Amonium Nitrate	
	Sensit.	Spec.	Sensit.	Spec.	Sensit.	Spec.	Sensit.	Spec.
1	0.26	0.98	0.25	0.99	0.28	0.99	0.10	0.97
2	0.45	0.96	0.43	0.98	0.48	0.98	0.19	0.94
3	0.59	0.95	0.57	0.97	0.63	0.96	0.27	0.92
4	0.70	0.93	0.68	0.96	0.73	0.95	0.34	0.89
5	0.78	0.91	0.76	0.95	0.81	0.94	0.41	0.87
6	0.83	0.90	0.82	0.94	0.86	0.93	0.47	0.84
7	0.88	0.88	0.86	0.93	0.90	0.92	0.52	0.82
8	0.91	0.86	0.90	0.92	0.93	0.91	0.57	0.80
9	0.95	0.85	0.94	0.91	0.96	0.90	0.65	0.77
10	0.96	0.83	0.96	0.90	0.97	0.89	0.69	0.75
11	0.97	0.82	0.97	0.90	0.98	0.88	0.72	0.73
12	0.98	0.80	0.97	0.89	0.99	0.87	0.75	0.71

**Table 1: Variation of sensitivity and specificity of organic discrimination, explosive and non explosive organic
discrimination, sodium chlorate identification and ammonium nitrate identification with the number of single-shot.**

RESULTS

	Organic	Inorganic	Number of samples
Organic	91%	9%	600
Inorganic	14%	86%	500
	Organic explosive	**Organic non explosive**	**Number of samples**
Organic explosive	90%	10%	300
Organic non explosive	8%	92%	300
	NaClO$_3$	**Other**	**Number of samples**
NaClO$_3$	93%	7%	100
Other	9%	91%	1000
	NH$_4$NO$_3$	**Other**	**Number of samples**
NH$_4$NO$_3$	57%	43%	100
Other	20%	80%	1000

(Row label at left, rotated: **TRUTH**)

Table 2: Results for a 8 single-shot based sampling

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