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Recognition of explosives fingerprints on objects for courier services using machine learning methods and laser-induced breakdown spectroscopy

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ABSTRACT

During recent years laser-induced breakdown spectroscopy (LIBS) has been considered one of the techniques with larger ability for trace detection of explosives. However, despite of the high sensitivity exhibited for this application, LIBS suffers from a limited selectivity due to difficulties in assigning the molecular origin of the spectral emissions observed. This circumstance makes the recognition of fingerprints a latent challenging problem. In the present manuscript the sorting of six explosives (*chloratite*, *ammonal*, *DNT*, *TNT*, *RDX* and *PETN*) against a broad list of potential harmless interferents (butter, fuel oil, hand cream, olive oil, ...), all of them in the form of fingerprints deposited on the surfaces of objects for courier services, has been carried out. When LIBS information is processed through a multi-stage architecture algorithm built from a suitable combination of 3 learning classifiers, an unknown fingerprint may be labeled into a particular class. Neural network classifiers trained by the *Levenberg–Marquardt* rule were decided within 3D scatter plots projected onto the subspace of the most useful features extracted from the LIBS spectra. Experimental results demonstrate that the presented algorithm sorts fingerprints according to their hazardous character, although its spectral information is virtually identical in appearance, with rates of false negatives and false positives not beyond of 10%. These reported achievements mean a step forward in the technology readiness level of LIBS for this complex application related to defense, homeland security and force protection.

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1. Introduction

In recent times, laser-induced breakdown spectroscopy (LIBS) has been demonstrated to be a powerful analytical tool to cope the direct chemical detection of energetic materials and residues of explosives in real-time [1–3]. However, despite all the efforts and the gains achieved in recent years when using LIBS for this last topic [4,5], a particularly challenging problem still needs to be overcome for offering greater assurances in this matter. From the identification point of view, the recognition aspects of LIBS are considered one of its *Achilles' heels*, because compounds sharing a similar chemical composition also have virtually the same LIBS signature. Difficulties on discrimination issues are increasing when residues and also the support where they are left are from the same nature. The situation is further complicated due to the fact that for heterogeneous residues their particular emissions and their characteristic intensity ratios, which are usually used in classification of explosives by LIBS, may fluctuate in a random manner. Finally, to round off the problem, the varying influence

of the surrounding atmosphere may also contribute to these cited fluctuations.

For all these reasons, a broad range of powerful chemometric tools have been applied for dealing with this issue of assigning an identity to a residue, or at least, for its sorting into as hazardous or harmless. Table 1 summarizes the state-of-the-art of statistical and mathematical tools applied to LIBS information in order to improve its discrimination capability. The most relevant aspects involved in the successful application of these multivariate analysis techniques, namely, the evaluated materials (not only explosives but also potential interferents), the supports where the residues are left, the way used to prepare the experimental targets, and supplied quantities, are provided. In any case, readers interested in detailed information are invited to consult the references cited.

Among the multivariate techniques demonstrated to be viable to classify an unknown sample as an explosive or a harmless product, the most widely used has been the principal component analysis (PCA) [6–9]. This technique works well when the variability within a group is much smaller than the variability among groups. However, this circumstance is unlikely when account is taken of the heterogeneous deposition of a fingerprint and the large *shot-to-shot* variability of LIBS spectra. For these reasons, the deposition of discrete volumes of acetone solutions and the

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Table 1
State-of-the-art in the combination of LIBS with chemometric tools for the detection of explosive residues.

Explosives	Potential interferents	Support/s	Sample preparation/form	Modeling approach	Ref.
<ul style="list-style-type: none"> ● RDX (Cyclotrimethylenetrinitramine) ● Composition-B (36% TNT, 63% RDX, and 1% wax) 	<ul style="list-style-type: none"> ● Diesel fuel 	Aluminum foil	<ul style="list-style-type: none"> ● Depositing of a discrete volume of solutions (powdered explosives in acetone) that then is allowed to evaporate. ● Spreading of diesel fuel on the support surface as a thin film. 	Principal component analysis (PCA)	[6]
<ul style="list-style-type: none"> ● RDX ● TNT (Trinitrotoluene) ● Composition-B 	<ul style="list-style-type: none"> ● Arizona road dust ● Commercial lubricant (WD-40) ● Oil from the surface of the skin in a fingerprint pattern 	Aluminum foil	<ul style="list-style-type: none"> ● Depositing of a discrete volume of solutions (powdered explosives in acetone) that then is allowed to evaporate (~500 ng/cm²). ● Spreading of interferents on the support surface as a thin layer/film (< 2 μg/cm²). 	PCA	[7]
<ul style="list-style-type: none"> ● RDX ● TNT (Trinitrotoluene) ● Composition-B 	<ul style="list-style-type: none"> ● Arizona road dust ● Commercial lubricant (WD-40) ● Oil from the surface of the skin in a fingerprint pattern 	Aluminum foil	<ul style="list-style-type: none"> ● Depositing of a discrete volume of solutions (powdered explosives in acetone) that then is allowed to evaporate (~500 ng/cm²). ● Spreading of interferents on the support surface as a thin layer/film (< 2 μg/cm²) 	<ul style="list-style-type: none"> ● Linear correlation ● PCA ● Soft independent method of class analogy (SIMCA) ● Partial least squares–discriminant analysis (PLS–DA) 	[8]
<ul style="list-style-type: none"> ● EGDN (Ethylene glycol dinitrate) ● NG (Nitro glycol) ● RDX ● TNT ● DNT (Dinitrotoluene) ● PETN (Pentaerythritol tetranitrate) ● HMX (Cyclotetramethylene tetranitramine) ● TETRYL (2,4,6-Trinitrophenylmethylnitramine) ● TATP (Triacetone triperoxide) 	<ul style="list-style-type: none"> ● Diesel oil ● Paraffin wax ● Grease ● Lubricant ● Coal ● NIST 1632b ● Glue LOCTITE ● Hand cream 	Aluminum discs	<ul style="list-style-type: none"> ● Spreading, over support surface, of small droplets of commercial solutions of explosives (0.1–1.0 mg/ml in methyl or ethyl alcohol, or acetonitrile) that then are allowed to evaporate thermally, leaving unevenly distributed residues. ● Spreading of interferents on the support surface as thin layers/films of uncontrolled thickness. 	PCA	[9]
<ul style="list-style-type: none"> ● RDX ● TNT ● Composition-B 	<ul style="list-style-type: none"> ● Arizona road dust ● Commercial lubricant (WD-40) ● Oil from the surface of the skin in a fingerprint pattern 	Aluminum foil	<ul style="list-style-type: none"> ● Depositing of a discrete volume (10 μL) of solutions (~1 mg/mL powdered explosives in acetone) that then is allowed to evaporate. Crushing and spreading of small amounts (< 1 mg) of RDX powder with a Teflon block. Direct transferring of RDX powder from the fingertips to the support. ● Spreading of interferents on the support surface as a thin film. Printing of grease from skin by handling repeatedly the surface of the support. 	PLS–DA	[10]
RDX	<ul style="list-style-type: none"> ● Arizona road dust ● Commercial lubricant (WD-40) 	<ul style="list-style-type: none"> ● White rubber (drink coaster) ● Red silicone (pot-holder) ● Blue plastic (floppy disk case) 	Spreading of several milligrams of the dry, powdered explosive on the surfaces of the different supports with a Teflon block,	PLS–DA	[11]

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