Unveiling the identity of distant targets through advanced Raman-laser-induced breakdown spectroscopy data fusion strategies

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A B S T R A C T

Data fusion is the process of combining data gathered from two or more sensors to produce a more specific, comprehensive and unified dataset of the inspected target. On this basis, much has been said about the possible benefits resulting from the use of molecular and atomic information for the detection of explosives. The orthogonal nature of the spectral and compositional information provided by Raman spectroscopy and laser-induced breakdown spectroscopy (LIBS) makes them suitable candidates for an optimal combination of their data, thus achieving inferences that are not feasible using a single sensor. The present manuscript evaluates several architectures for the combination of spectral outputs from these two sensors in order to compare the benefits and drawbacks of data fusion for improving the overall identification performance. From the simple assembling (concatenation or addition) of Raman and LIBS spectra to signals' processing on the basis of linear algebra (either the outer product or the outer sum), different identification patterns of several compounds (explosives, potential confusants and supports) have been built. The efficiency on target differentiation by using each of the architectures has been evaluated by comparing the identification yield obtained for all the inspected targets from correlation and similarity measurements. Additionally, a specific code integrated by several of these patterns to identify each compound has also been evaluated. This approach permits to obtain a better knowledge about the identity of an interrogated target, mainly in those decisive cases in which LIBS or Raman cannot be effective separately to reach a decision.

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1. Introduction

Data fusion commonly refers to a process of combining synergistically or integrating, in the most effective way, observed data that gather from two or more sensors to produce a more specific, comprehensive and unified dataset of an interrogated target [1]. The benefits of data fusion have been used in a wide range of application fields. For instance, in the area of chemoinformatics, data fusion experiments have been made to combine several binary similarity coefficients to get an overall estimate of similarity for searching databases of bioactive molecules [2]. In environmental monitoring, spectral and structural datasets gathered from CASI (compact airborne spectrographic imager) and LIDAR (light detection and ranging) sensors, respectively, have been fused on a pixel level to improve the classification of the floodplain vegetation [3]. Similarly, ^{1}H NMR (nuclear magnetic resonance) information has been recently combined with mass spectrometry data from liquid [4] and gas [5] chromatography to generate metabolic profiles from analysis of rat urine as well as of cerebrospinal fluid of multiple sclerosis individuals,

respectively. Information obtained by ^{1}H NMR has been also combined with UV–visible spectroscopy data [6] and with isotopic figures [7] to determine banned dyes in culinary spices and to improve the authenticity of wines, correspondingly.

New data fusion structures from chromatographic and spectroscopic data have been also proposed for improving the capability to identify the photoproducts formed and the accuracy in the description of the mechanism driving the photodegradation process [8]. The synergy of Raman and FT-NIR microscopies to enable a more complete visualization of any solid dosage pharmaceutical form has been demonstrated [9]. Likewise, in cultural heritage issues, data-fusion strategies based on the outputs of a Raman/X-ray fluorescence combined instrument, has been investigated for dealing with the classification of ochre pigments [10]. Furthermore, complementary spectra from Raman, IR (infrared) and NMR sources have been assembled for giving a "fused" dataset to an increased understanding and control of an industrial process [11]. Also for solving problems related to food authentication, data collected from near (NIR) and middle (MIR) infrared spectrometers have been processed both, separately and jointly, using chemometrics to demonstrate the synergistic effect from fused spectroscopic datasets for dealing with classification problems [12,13]. In the same vein, data from mass spectra (MS)-based electronic nose (E-nose), a mid-IR optical-tongue

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and a UV–visible sensor have been assembled to deal with differences from sensory properties on beer samples of the same brand and commercialized as a same product, but brewed in four different factories [14]. Equally, a data fusion strategy of combining multiple spectroscopic techniques (NIR, Raman, 2D fluorescence and X-ray fluorescence) has been also investigated for the characterization of soy hydrolysates in mammalian cell cultures [15]. In the area of homeland security, an approach for the combination of the spectral outputs of sensors based on Raman and LIBS (Laser-Induced Breakdown Spectroscopy) in order to improve the identification of explosives and related compounds has been developed [16]. However, despite the improvement on materials distinction from each other by simple linear correlation when molecular information is merged to atomic data, the progress of selectivity towards specificity is still being pursued.

Detection of explosives has attracted considerable attention in recent years [17]. From the standpoint of sensor fusion, the most appealing tools to tackling this scenario have proved to be LIBS [18] and Raman spectroscopy [19]. Together with their versatility to operate under a standoff scheme, both sensing modes offer complete information on the constitution of the sample, that is, elemental composition from the emission spectra and molecular information extracted from scattered radiation. Commonly, to deal with such challenge both techniques are used separately. At these circumstances, that is, when findings are judged on the basis of particular spectral information, the decision about target's identity might be limited. For instance, LIBS has a restricted ability on identify those inspected targets that share elemental composition, as organics [20]. Similarly, although interaction between excitation light and the target might lead to a unique spectral fingerprinting of the material, selectivity of Raman suffers when the same functional group is involved in the composition of the interrogated targets [21]. Clearly, these particular scenarios entail a deficit for each spectroscopic technique, notably when trying to differentiate between explosive and harmless materials.

Assembling and integration of such techniques into a mobile sensor platform using the same laser pulses and gated multi-channel detectors to improve identification confidence has been demonstrated [22]. Despite that this fitting of the two sensors allows to simultaneously gather both spectral data coming from the same laser events, the manner in how such information may be manipulated and also associated has still a lot of grounds for concern. The reason is due to some technical incompatibilities, especially when it comes to residue analysis [23]. Indeed, to date, only a few attempts on fusion of these data, although acquired from a sequential interrogation of bulk targets, have been recently published [16,24].

In order to progress, in the present manuscript, several novel architectures on assembling data from Raman and LIBS sensors are described. The strengths and the weaknesses of several estimators built to provide a precise identification of pure materials have been evaluated through correlation and dissimilarity measurements. Results on the implementation of such assets in order to enhance the differentiation and recognition of inspected targets have been discussed. Findings have revealed that the combination of different bidimensional assembling frameworks fused into a unique estimator may provide a reliable attribute to confidently label the identity of each interrogated target.

2. Experimental

2.1. Sensor set-up

The versatile Raman and LIBS configurable set-up for standoff analysis consisted of twins Q-switched Nd:YAG lasers (10 Hz, 532 nm, 400 mJ pulse^{-1}, 5.5 ns pulse width) that were utilized as irradiative sources. A beam expander ($10\times$ large output) was employed for first expanding and then focusing the laser beam on the target. Scattered and emitted light from the target was gathered through a home-made Cassegrain telescope (167 cm in length and 24 cm in diameter), which permits converging light on the tip of an optical fiber 600 μm in diameter mounted on a precision linear stage. After collection, light was guided to the entrance port of the proper detection system.

For Raman data collection, a holographic imaging spectrograph (85 mm focal length, f/1.8i, 25 μm slit) equipped with a volume phase holographic (VPH) grating (model HSG-532-LF) and fitted with an iCCD detector (intensifier tube diameter of 18 mm) was used. For LIBS signal detection, a Czerny–Turner spectrograph (303 mm focal length, f/4, 10 μm slit) fitted with a 150 lines per mm diffraction grating blazed at 500 nm and an iCCD detector (intensifier tube diameter of 25 mm) was employed.

Raman and LIBS measurements were sequentially obtained for each target after focusing a number of laser pulses of 440 mJ each on sections of ca. 1.00 cm^2 and 0.02 cm^2, thus achieving irradiance values of 0.11 GW cm^{-2} and 4.73 GW cm^{-2}, respectively. For Raman data collection, the delay time was set to zero ns, whereas the gate width was set to 800 ns. For LIBS data acquisition, a delay time of 900 ns and an integration time of 9 μs were established as timing parameters. Experiments were all carried out at standoff distances of 20 m inside a 50 m long partially closed corridor. Data obtained from Andor were exported in text format and analyzed using Matlab$^{®}$ (The Mathworks Inc., South Natick, MA, USA). In any case, readers requiring more details are requested to check the reference [23].

2.2. Samples

In order to evaluate the strength and weaknesses on the implementation on data fusion from different strategies, Raman and LIBS representative spectra from pure explosive materials, including 2,6-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), pentaerythritoltetranitrate (PETN) as well as some explosive related compounds (ERCs) such as sodium chlorate ($NaClO_3$) and potassium chlorate ($KClO_3$), were registered. In parallel, several non-energetic materials, but subject to confusion with the previous ones from their LIBS responses, such as nylon, wood, riblene (low density polyethylene), anthracene (anth), sodium chloride (NaCl) and potassium chloride (KCl) were also considered.

Samples were primed and arranged for the analysis in their most appropriate bulk form. Thus, DNT, $NaClO_3$, $KClO_3$, anth, NaCl and KCl were used as cylindrical pellets of ca. 200 mm^2 in area and 6 mm in thickness. In addition, RDX base paste explosive was prepared as a sticky mass on the surface of a glass microscope slide (76 mm × 26 mm), at all times, helping to safeguard dimensions (thickness and area) similar to those achieved for the previously cited pellets. Similar case held true for TNT, from its melted solid form. Finally, PETN, extracted as a ring from a booster, as well as Nylon, wood and Riblene, all them as plates (40 mm × 40 mm × 4 mm), were analyzed in their raw state. In this way, all the targets were tested as bulk materials.

2.3. Raman-LIBS data fusion approaches

The fusion process at the feature level of spectral responses from sensor measurements consists in the generation of a new attribute, that is, a new identity which aims to more clearly identify the interrogated target. To this end, a global descriptor of the compound is generated by fusing the molecular and atomic outputs of a compound when interrogated by Raman and LIBS sensors.