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Near infrared spectral imaging for the analysis of dynamite residues on human handprints

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ABSTRACT

This study examines the utility of near infrared hyperspectral imaging (NIR-HSI) combined with chemometrics for the detection of dynamite residues on human handprints. Polyvinyl sheets containing dynamite residues were then analysed with the NIR-HSI system. A spectral library was developed by using partial least squares-discriminant analysis model (PLS-DA) to detect and classify the pixels contaminated with the dynamite residues. Values of sensitivity and specificity of 100% were obtained for both calibration and cross validation of dynamite and ammonium nitrate. The results were tested in real human handprints. Seven volunteers deposited their handprints into polyvinyl transparent sheets after the manipulation of a common type of dynamite which was mainly composed by ammonium nitrate. These results highlight the extremely high potential and capability of NIR-HSI combined with chemometrics for the fast and easy identification of explosive residues and additionally, its potential competence to detect the explosive manipulation.

1. Introduction

Developments in explosive identification are constantly being presented. Unfortunately, the continuous threat of worldwide terrorist activities are becoming necessary to design new analytical methodologies for fast and robust explosive detection and identification methods, strongly demanding specific requirements for those novel methodologies. Requirements such as minimizing the risk of analysts and operators during sample manipulation and analysis, reducing the possibility of sample contamination or destruction by developing non-contact and non-destructive, and when possible, portable technologies to place in the crime scene, are now the main target in forensic science [1–4].

Focusing on explosives, dynamites are normally used for mining, construction and demolition industries, that is to say, civilian purposes. However, since its invention by Nobel in 1867 [5], dynamites have been frequently used in military conflicts and, more recently, also present in terrorist actions. Despite different dynamite compositions have been described, ethylene glycol dinitrate and ammonium nitrate are normally the major components of dynamites. Additionally, nitrocellulose, calcium carbonate, flour or sawdust and plasticizers are regularly incorporated to the dynamite composition as minor components [4].

Although few works were focused on the study of dynamite, the analysis of every single dynamite component has been reported by different analytical approaches [6,7]. Regarding vibrational spectroscopy techniques, both infrared (IR) and Raman spectroscopy have provided information on the main constituents of dynamite with the utilization of minimal sample pretreatments or even avoiding sample pretreatment procedures [8–10].

The civilian usage of explosives usually does not represent any danger to the contemporary society and, in consequence, the posterior identification or detection of explosives is not object of interest. On the contrary, the identification of explosives in a crime scene is still nowadays a challenge. Specifically, when that identification must be carried out directly from human handprint residues. Analysis of sweat, latent human fingerprints as well as drug and organic explosive residues on fingerprints have been successfully approached in the last years [11–19]. However, to our knowledge, the identification of explosive residues on human handprints had never been approached.

Conventional IR spectroscopy, and more specifically near infrared spectroscopy (NIR) offers the advantages of a fast, robust and non-destructive technique but is limited to the analysis of very small area of sample during each single measurement. Therefore, a plausible solution to analyse larger surfaces is the use of NIR hyperspectral imaging (HSI). HSI combines the non-contact, non-destructive properties of NIR analysis with the conventional

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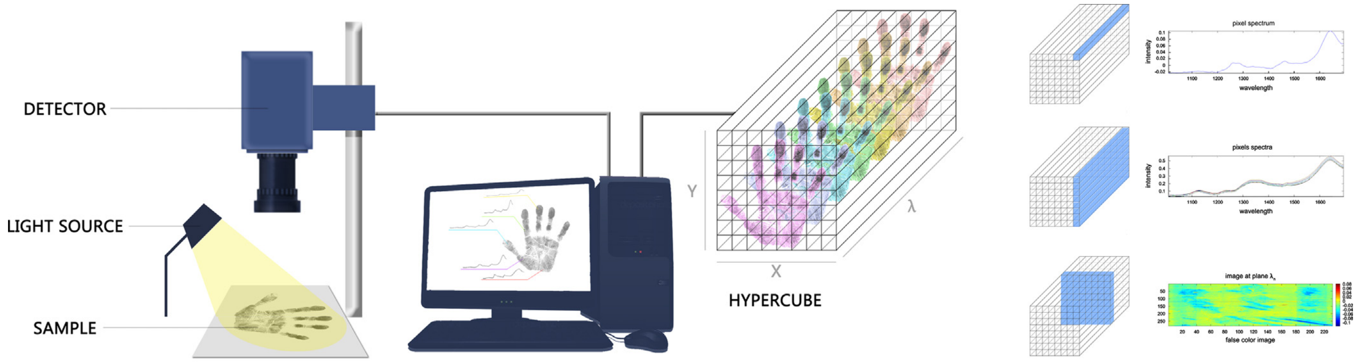

Fig. 1. Schematic representation of the configuration in the HSI system and the 3D structure ($XY\lambda$) of the final hypercube data obtained.

chemical imaging techniques to generate a three-dimensional image (known as spectral hypercube) containing spatial and spectral information of the sample [20]. Moreover, NIR-HSI cameras found in the market nowadays have the ability of scanning wide areas (e.g. human handprint area) in a very fast way, using push-broom technology [20], characteristics that makes NIR-HSI a proper methodology for, e.g. in-situ analysis of handprints.

The spatial information of a NIR-HSI image corresponds to the digital image of the sample (X and Y axes) while the spectral data contain the NIR spectra in the complete wavelength range (λ axis) for every single pixel presents in the digital image, defining a pixel as the minimal sub-units of an image. Therefore, each hypercube can comprise thousands of spectra (see Fig. 1). This, together with the spatial data and number of samples and their repetitions in measurement, widely increase the amount of total data, becoming indispensable the use of powerful mathematical treatments for data exploration [21,22]. Among all possible multivariate data analysis methodologies, one of the most commonly used for sample exploring and classifying of NIR-HSI data is partial least squares-discriminant analysis (PLS-DA). PLS-DA is a supervised technique for classification of unknown samples in different classes by comparison with a previously created calibration set [23,24].

Hyperspectral set-ups combined with infrared spectroscopy are still nowadays an emerging tool with few applications in forensics and scarcely applied to the forensic investigation of explosives [25,26]. Among them, works focused on the study of explosive residues found on human fingerprints present special interest. On this respect, both teams Chen et al. [27] and Bhargava et al. [28], proposed the detection of traces of RDX (hexogen) within a latent fingerprints by using middle infrared hyperspectral imaging (MIR-HSI), while Ng et al. [29] were able to identify the presence of PETN (pentaerythritol tetranitrate) traces deposited on a fingerprint. MIR-HSI has also been applied for the identification of explosives on other several surfaces. Blake et al. [30] deals with the standoff detection of RDX, HMX (octogen) and TNT (trinitrotoluene) on metallic surfaces and at distances from 14 to 50 m. Finally, hyperspectral imaging has also been applied for the standoff detection of TNT, RDX and PETN on packages [31].

Therefore, the main goal of this work is to develop a fast, non-destructive and non-contact approach for studying the presence of explosive residues on large surfaces of interests like the human handprints. To this aim, NIR-HSI and PLS-DA were first applied to study specifically the presence of dynamite residues on human handprints deposited on adhesive polyvinyl films. Hyperspectral images for the dynamite main component, ammonium nitrate, were collected to be used as standards. Once hyperspectral images of standards and all human handprint samples had been registered, these images were preprocessed with the aim to extract the relevant information. Finally, the PLS-DA model constructed was applied to identify the presence of dynamite residues on human handprints.

2. Materials and methods

2.1. Samples

Dynamite and ammonium nitrate samples were kindly provided by the Criminalistic Service of *Guardia Civil* (Spanish civil police, Madrid, Spain). Dynamite samples used in this work were gelatinous formulations of pink colour whose quantitative composition was not specified by the manufacturer but ammonium nitrate and ethylene glycol dinitrate were declared as its major components. Plasticizers, dies, flour, sawdust, nitrocellulose and $CaCO_3$ are also included as minor components of this kind of dynamite sample. Both, dynamite and ammonium nitrate samples were directly used through this study avoiding any sample treatment.

The analysis of handprints from seven participants, five women and two men with ages from 20 to 30 years, was performed. In order to detect if sweat or common dirtiness may influence the spectra different procedures were studied. With the aim of regenerating the sweat as was proposed by Gilchrist et al. [18] the participants washed their hands in Milli-Q water 15 min prior to sampling. During this time, they were not allowed to manipulate anything. Then, the handprints were deposited by application of slight pressure on the adhesive side of a 50 μm thick clear self-adhesive polyvinyl film of $22 \times 38\ \text{cm}^2$ size (Sadipal, Gerona, Spain). For sample protection, films were covered with another piece of film of the same characteristics. Additionally, to test the influence of common dirtiness presented in human handprints, the handprints corresponding to participants who had not washed their hands in at least 3 h and had performed common tasks such as driving, eating, write tipping or mobile using, were collected.

Finally, approximately 5 g of dynamite was manipulated by each participant during 10 min and handprints were deposited in a self-adhesive film by placing hands on the adhesive side of the film. Excessive dynamite residues were rubbed off from both hands in spite of residues not being visible by the naked eye. Prior dynamite manipulation, all participants cleaned their hands as above, respecting the 15 min of no-manipulation period time.

Note that, sample burning or ignition was not observed during any dynamite or ammonium nitrate analysis at the applied experimental conditions. Dynamites should be handled and stored carefully but they are stable in the range of -15 to $+60\ ^\circ\text{C}$; therefore, for personal safety it is only required to ensure the product is kept away from flames, extreme heat sources, or methane environments.

2.2. Hyperspectral imaging

The NIR-Hyperspectral images were obtained with a spectrometer (Headwall photonics model 1002A-00371) working in the wavelength range of 1000–1700 nm with a spectral resolution of 7 nm (total of 142 bands recorded for each spectrum).