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Detection of residues from explosive manipulation by near infrared hyperspectral imaging: A promising forensic tool

Mª Ángeles Fernández de la Ossa [a], José Manuel Amigo [b], Carmen García-Ruiz [a,*]

[a] Inquifor Research Group, Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering and University Institute of Research in Police Sciences (IUICP), University of Alcalá, Ctra. Madrid-Barcelona km 33.600, 28871 Alcalá de Henares, Madrid, Spain[1]
[b] Department of Food Sciences, Faculty of Life Sciences, University of Copenhagen, Rolighedsvej 30, DK-1958 Frederiksberg C, Denmark

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ABSTRACT

In this study near infrared hyperspectral imaging (NIR-HSI) is used to provide a fast, non-contact, non-invasive and non-destructive method for the analysis of explosive residues on human handprints. Volunteers manipulated individually each of these explosives and after deposited their handprints on plastic sheets. For this purpose, classical explosives, potentially used as part of improvised explosive devices (IEDs) as ammonium nitrate, blackpowder, single- and double-base smokeless gunpowders and dynamite were studied. A partial-least squares discriminant analysis (PLS-DA) model was built to detect and classify the presence of explosive residues in handprints. High levels of sensitivity and specificity for the PLS-DA classification model created to identify ammonium nitrate, blackpowder, single- and double-base smokeless gunpowders and dynamite residues were obtained, allowing the development of a preliminary library and facilitating the direct and in situ detection of explosives by NIR-HSI. Consequently, this technique is showed as a promising forensic tool for the detection of explosive residues and other related samples.

1. Introduction

An improvised explosive device (IED) is a device placed or fabricated in an improvised manner, which incorporates destructive, lethal, noxious, pyrotechnic or incendiary chemical substances and it is designed to destroy, incapacitate, harass or distract. It may incorporate military stores, but is normally constructed from non-military components. IEDs are weapons designed to cause as much damage as possible and usually employed on military conflicts or terrorist activities worldwide. Unfortunately, during the last years the use of IEDs against civilian populations has been intensely increased [1,2]. This fact can be due to the production of IEDs is relatively easy and cheap, founding detailed text and even videos of free access on Internet explaining their preparation. Consequently, their use is quickly spread and the information related to their development and improvements is also published on Internet.

Since these types of weapons are built in an improvised manner and with the aim to be camouflaged in different environments, their designs are highly varied. However, all IEDs are formed by three essential elements: detonator system for initiating the devices, explosive charge to produce the damage associated to the use of any weapon and container to transport or camouflage the explosive charge and the detonator system. Among these elements, the explosive charge presents the higher destruction capacity and therefore, its investigation with the aim to obtain rapid, sensitive and reliable detection methods is an extremely important priority in security fields [1].

Varied explosives such as RDX (hexogen), TATP (triacetone triperoxide), TNT (trinitrotoluene), pyrotechnic charge, dynamite, smokeless gunpowders, blackpowder, among others, have been used on the preparation of IEDs throughout History. During last years, terrorist attacks as the Boston Marathon bombing in 2013 used blackpowder [3], while the train bombings in Madrid 2004 involved the use of dynamites [4]. Due to the increase on the use of these devices for attacks in public and populous locations (airports, public transports, restaurants, shopping centres, theatres, etc.), the detection of explosives present an intensely priority for public security and as a result, there is a great demand of analytical techniques specially designed for this objective [2,5–7].

The detection of explosive residues on human fingerprints is recently gaining attention [8–12]. The aim is to facilitate the forensic investigations by relating the presence of explosive residues on

* Corresponding author. Tel.: +34 918856431.
E-mail address: carmen.gruiz@uah.es (C. García-Ruiz).
[1] http://www.inquifor.com.

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fingerprints collected at crime scene. In such a way that fingerprint may identify the person presents at that crime scene and its potential manipulation of explosives. In this sense, vibrational spectroscopic methods represent a very interesting alternative to classical analysis since they have the advantage of the detection of explosives in solid, liquid or gas state, avoiding the sample pretreatments necessary for separation techniques. In addition, they are fast, non-contact, non-invasive and non-destructive techniques. All these characteristics are highly desirable for forensic investigations due to the sample contamination and destruction are avoided, allowing that the sample analysis can be repeated as many times as required. Additionally, the elimination of sample preparation procedures and the non-contact analysis improve the security of forensic analysts compared to the mandatory manipulation and chemical modification required in other analytical techniques that do not present these characteristics [13–15].

Hyperspectral imaging (HSI) presents the abovementioned advantages of classical spectroscopy combined with the usefulness provided by imaging techniques [8,16]. On one hand, spectroscopy provides chemical information specifically related to the chemical composition and properties of the sample studied. On the other hand, convectional imaging processes any form of signal (brightness, colour, spectroscopic absorbance, thermal energy, etc.) from an image (photograph or video frame) to improve or highlight some parameters or characteristics related to the original image and, consequently, related to its appearance [17,18]. On this respect, both Chen et al. [9] and Bhargava et al. [10] teams, proposed the detection of RDX traces within latent fingerprints, and Ng et al. [11] were able to identify the presence of PETN traces deposited on a fingerprint. Nevertheless, these studies focus on the examination of the human fingerprint for the traditional forensic identification of the person and simultaneously obtain information of the residues found in those latent fingerprints. Consequently, these works only approached the study of a little part of human hands, making desirable a methodology that allows the scanning of the whole handprint since may increase the possibility to detect the presence of explosive residues in case of the fingerprints had been exhaustively cleaned by the criminals knowing that this is the part of the hand more intensely examined for security aims. In addition, fingerprints are the part of the hands more used for routine tasks, being possible to find more interferences or a higher loss of residues than in other parts of the hand such as the palm. In addition, reported studies only approached the detection of two types of explosives, RDX and PETN, but any study has been published considering the detection of common and more "easy-finding" explosives as blackpowder, smokeless gunpowder or dynamite. In this respect, Near Infrared Hyperspectral imaging (NIR-HSI) represents a perfect alternative. The great advantage of NIR-Imaging technique over other vibrational Imaging techniques is its versatility, allowing the recording of a wide area in few seconds, and obtaining robust and reliable spectral information for every pixel. NIR-HSI is widely used in different scientific disciplines like remote sensing, pharmaceutical science or food science [19,20] due to its capability of providing spatial and chemical information of wide scanning areas (depending of the configuration of the camera) in a fast, robust and non-destructive manner. A method to cope the challenging detection of dynamite residues on human handprints by using NIR-HSI has been recently developed [12]. The fast, non-invasive, non-destructive and non-contact analysis characteristics of NIR-HSI systems may facilitate the forensic investigation of explosive residues because eliminate the risks of forensic analysts when explosives have to be collected, prepared and measured. Therefore, NIR-HSI could be considered as a promising forensic tool because, this technology presents the advantage to facilitate the remote and real-time measurements. Both characteristics are highly interesting for controlling the homeland and international security by adapting these systems to places where there are potential security threats related to the illegal use of explosives. Usually terrorist attacks occurs in public and crowded places as airports, transport stations, music halls, theatres, hospitals or shopping centres and may be possible to directly examine the handprints from a potential suspect who presents explosive residues from the preparation and/or transportation of an IED.

Therefore, in this work we propose the usage of NIR-HSI linked to multivariate classification model to detect the residues of explosives potentially used for the fabrication of IEDs, in full handprints. For this aim, different volunteers manipulated explosives as ammonium nitrate, blackpowder, single- and double-base smokeless gunpowders and dynamite. Then, in a process that consumes about 5 min, their handprints were collected and analyzed by NIR-HSI and finally, a partial-least squares discriminant analysis (PLS-DA) model was established to successfully detect the presence of explosive residues.

2. Experimental

2.1. Samples

The explosives studied were ammonium nitrate, blackpowder, nitrocellulose, single- and double-base smokeless gunpowders and dynamite, which were kindly provided by the Criminalistic Service of *Guardia Civil* (Spanish civil police, Madrid, Spain), except blackpowder that were extracted from a pyrotechnic device. Since the blackpowder studied in the present work was extracted from a pyrotechnic device, strictly speaking, a blackpowder substitute product where the potassium nitrate has been replaced by potassium perchlorate (blackpowder is technically defined as a mixture of sulphur, charcoal and potassium nitrate) was analyzed in this study. The charge of the pyrotechnic device was composed by sulphur, charcoal and $KClO_4$. Regarding smokeless gunpowders, the single-base gunpowder sample was composed by 94% of nitrocellulose whereas the double-base gunpowder sample contained 85% of nitrocellulose and 10% of dinitrotoluene (information from the official label [21]). Ammonium nitrate and ethylene glycol dinitrate were declared as dynamite major components [22]. According to its manufacturer, dynamite was composed by ethylene glycol dinitrate, ammonium nitrate, nitrocellulose, dynamite dye, sawdust, $CaCO_3$, guar gum and plasticizers.

2.2. Handprint collection

Volunteers were asked to wash their hands in Milli-Q water 15 min prior to handprint deposition. During this time, with the aim to regenerate the common sweat presents in human hands, they were not permitted to manipulate anything. Then, all the volunteers, five women and two men with ages from 20 to 30 years, deposited their handprints by application of slightly pressure on the adhesive side of a 50 μm thick clear self-adhesive polyvinyl film of 22 cm $\times$ 38 cm size (Sadipal, Gerona, Spain). Films were protected of dirty and possible contaminants by covering them with another piece of plastic film of same characteristics. In addition, handprints from volunteers who have been washed their hands at least 3 h before performing everyday activities as eating, mobile using, driving or manipulating common things (keys, money, books, etc.) were also collected.

Finally, volunteers carried out the manipulation of the different explosives. Explosives were directly manipulated avoiding any sample treatment, simulating the construction of an IED device. Approximately 5 g of each type of explosive, ammonium nitrate, blackpowder, single- and double-base smokeless gunpowders and dynamite were independently manipulated during 10 min. Following the previously described methodology, handprints were