



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.

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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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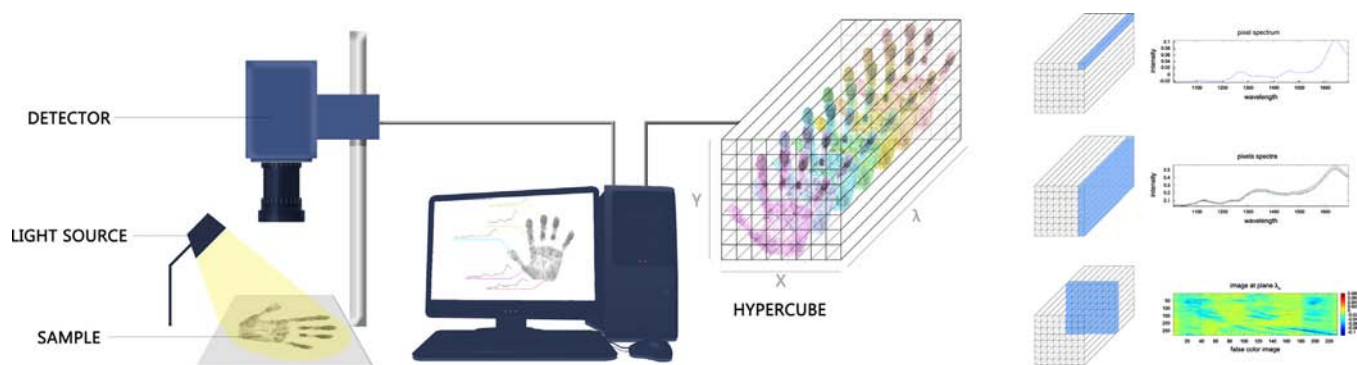


Fig. 1. Schematic representation of the configuration in the HSI system and the 3D structure ($XY\lambda$) of the final hypercube data obtained.

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, dyes, 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 $+60 \text{ }^\circ\text{C}$; 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).

The spectrometer was adapted to a line mapping configuration with a line of 320 pixels. This hyperspectral camera was kindly provided by FOSS (FOOS A/S, Denmark). The camera was calibrated using a *spectralon* plate. Spectra were recorded in the reflectance mode for 351 rows \times 320 columns referring to pixel (or spatial dimension) in the *X/Y* axis, giving a final pixel resolution of 300 μm .

2.3. Data analysis

The hyperspectral images were analysed by using home-made functions programmed in MatLab under the name of HYPER-Tools working under MatLab v. 8.1 (MathWorks, MA, USA) environment. They can be freely downloaded (www.models.life.ku.dk) and they are available upon request (jmar@life.ku.dk). Data pre-processing was composed by several steps, which were applied to the images prior to approach of the sample classification. First, all the images were cropped in order to eliminate the area left outside the sample (background) since they presented highly noisy spectra that could influence the classification. Final images of 281 rows \times 231 columns \times 142 bands were treated. Then, scattering and noise effects were corrected in all data by applying smoothing transformations by using Savitzky–Golay methodology with a second order polynomial and a window of 15 wavelengths and Standard Normal Variation (SNV).

2.3.1. Partial least squares-discriminant analysis (PLS-DA)

PLS-DA is a supervised class-modelling method to classify new and unknown samples in different classes. Starting from the required calibration set of sample, a classical PLS regression model is built, which creates an appropriate number of new latent variables to maximize the covariance and achieving in this way, the discrimination among classes. This PLS model relates the independent variables to a vector containing the categorical classes, zero or one. The value one is attributed to the class of interest while zero value is related to a different class in such a way that, an unknown sample is classified according to the categorical class predicted by the PLS model. This predicted value is a real number distributed between zero and one, therefore, to determine if an unknown sample belongs to the class of interest it is necessary to define a threshold. Samples containing values above the defined threshold will be considered to belong to the class of interest (class 1) while samples providing prediction values below the threshold will be assigned to other class (class 0) [32,33].

The PLS-DA computation was performed using the PLS-toolbox v. 7.0.3 (Eigenvector Research, WA, USA) working under MatLab environment. The calibration set was created from an individual image of a cross section of about 5 g of the studied dynamite, approximately 3 g of ammonium nitrate and a sheet of polyvinyl plastic ($10 \times 10 \text{ cm}^2$) used to recover the handprints. Therefore, this calibration set was composed by three classes, ammonium nitrate, dynamite and plastic, and it was made considering a Region of Interest (ROI) from each individual image of every single explosive and clean plastic. ROIs were manually selected by manually cropping the image to select the central part of the samples and to avoid the noisy background and edge regions. Then, data were pre-processed as mentioned before (SNV and smoothing). The ROIs of each standard was composed by 50 pixels and joined in a final matrix with dimensions of 150 rows \times 142 columns. Random subsets cross-validation with 10 data splits was used to select the number of latent variables for PLS-DA model. In addition, the model was validated in both calibration and cross-validation models through the examination of sensitivity, specificity and classification error parameters.

3. Results and discussion

As a proof of concept, the analysis of the hyperspectral images of handprints obtained from participants who, as explained in the experimental section, had cleaned their hands or just followed everyday activities, was first performed. Results showed that many of the wavelength signals recorded along the samples was different to the characteristic signal corresponding to plastic used as the substrate for the handprint collection. Either hand sweat or common dirtiness did not present absorption in the NIR region, and they were not registered as interferences in this study, since their presence did not influence the final results.

Fig. 2 shows the NIR spectra corresponding to dynamite, ammonium nitrate and plastic after preprocessing. As can be seen, the spectral shape of dynamite and ammonium nitrate are basically identical, having one intense band at 1650 nm which possibly corresponds to the presence of primary amine groups (NH_3 bending). This spectral similarity was expected as ammonium nitrate is the major component of dynamite. Together with ammonium nitrate, ethylene glycol dinitrate is the other principal component of dynamite. However, ethylene glycol dinitrate presents a high vapour pressure (7.0×10^{-2} Torr at 25 °C) [7] and, consequently, is volatilized at room conditions used in this research (dynamite manipulation during 10 min), making difficult its detection by NIR-HSI. The plastic sample, on the contrary, presents a completely different spectrum with two intense bands that occurred at 1280 nm and 1490 nm. Bands probably due to the C–H vibrational overtones from the polyvinyl plastic and to the presence of residuary water or humidity on handprints.

The complete calibration model was built by using the ROIs previously selected from the image recorded for ammonium nitrate, dynamite and plastic standard samples and consequently, was composed of three classes. Data were pre-processed as previously indicated in the PLS-DA section (smoothing and SNV) and mean centring, and cross-validated with random subsets. The figures of merit obtained for the PLS-DA calibration model described by four latent variables with 99.09% of explained variance (sensitivity, specificity of 100%, classification error of 0% for both calibration and cross-validation, and a threshold of 0.4 for dynamite) denote the high dissimilarity that exists in the spectra for the different classes, allowing a robust and accurate classification of dynamite in further real samples.

Once the classification model was constructed and assessed, the presence or absence of dynamite residues on different parts of handprint samples collected from the seven volunteers was determined.

Fig. 3 shows the results corresponding to three different parts of handprints (thumb, fingers and hand palm). Dynamite residues were successfully identified in all of them. In addition, comparing the dynamite and ammonium nitrate spectra (see Fig. 2) with those corresponding to a one pixel randomly selected of each handprint picture (see Fig. 3, pixels coloured in red) from pixels identified as dynamite by the PLS-DA model, it can be observed how they perfectly match and therefore, the corresponding spectral bands were registered at the same wavelengths (intense band at 1650 nm). To assess the significance of the reported spectra, examples of spectra obtained from neighbouring regions of the handprint outside of the edge of the region that is classified as containing dynamite are also included in this figure. As can be seen, only signal corresponding to the plastic substrate or background were obtained. Therefore, it was concluded that dynamite residues or its main component, the ammonium nitrate, were well identified by the PLS-DA model. Consequently, the proposed HSI-PLS-DA approach will be able to determine if a person has been manipulating dynamite explosives by directly analysing her/his handprints.

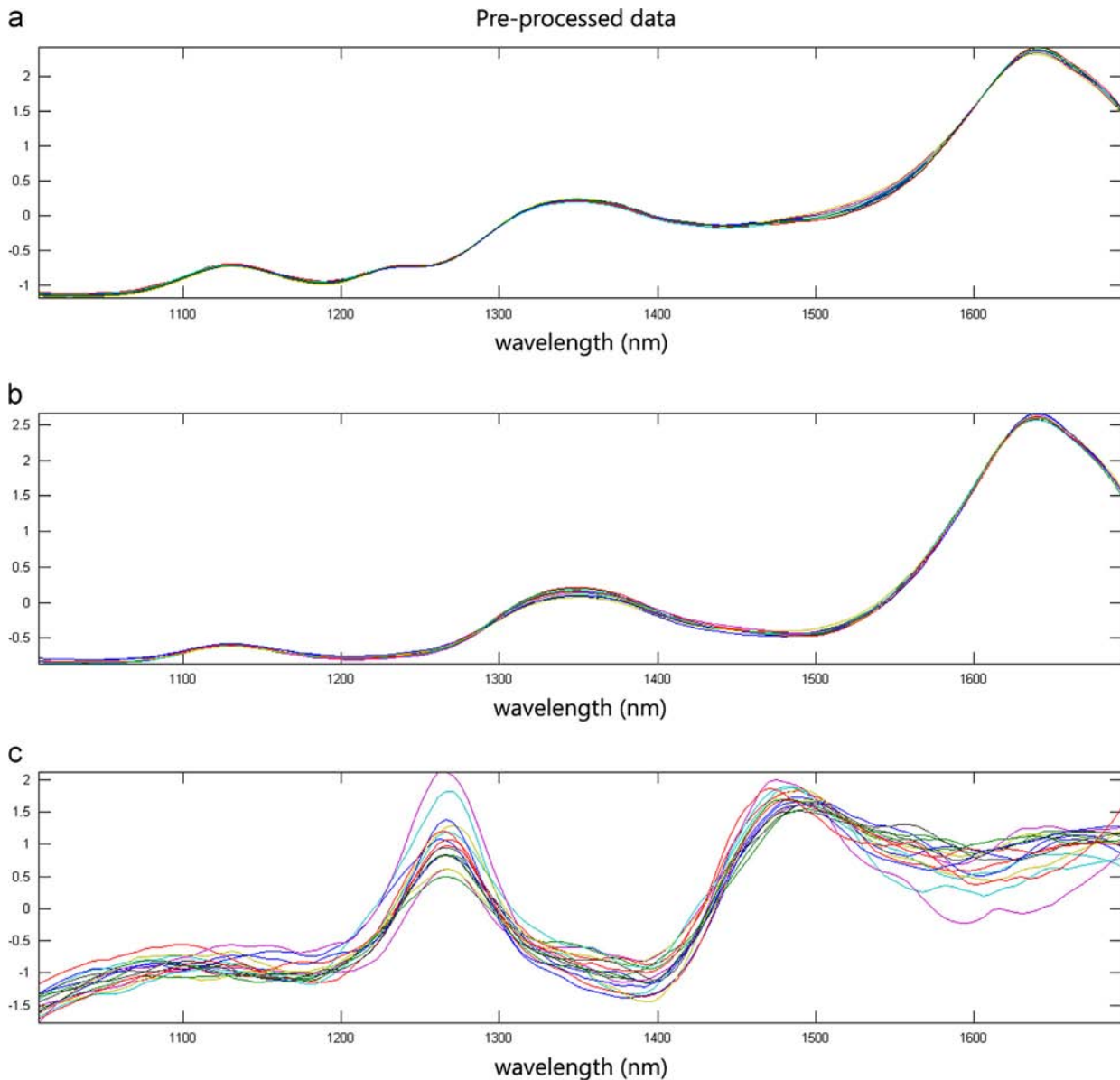


Fig. 2. Pre-processed spectra of (a) dynamite, (b) ammonium nitrate and (c) plastic (polyvinyl sheet) analysed by using the NIR-HSI system showed in Fig. 1.

These observations were also repeated by the study of the rest of handprint samples. Fig. 4 depicts a batch of hyperspectral images compared with the false colour hyperspectral images for highlighting the presence of dynamite residues and corresponding to different parts of handprints and several participants who had been manipulating this explosive. In addition, a zoom region to highlight the red pixels identified in the hand palms is shown in Fig. 4c. Interestingly, dynamite residues were identified in all cases studied. The limit of detection (LoD) should be divided into spectral LoD and spatial LoD. Based on the resolution of the camera, the spatial LoD must be set at 300 μm . Therefore, it can be only assessed to find particles of that size. It is noteworthy, though, that a positive identification can be based in the identification of the explosive in just one pixel.

4. Conclusions

This paper first proves the direct, fast and easy identification of dynamite residues from human handprints supported by combining the use of NIR-HSI and the posterior application

of a supervised class-modelling methodology (PLS-DA). The proposed method also has the advantage of simplicity, avoiding sample pre-treatment procedures and non-contact, non-invasive and non-destructive measurements, which is considered as the optimal technological characteristics for the analysis of an explosive, or any forensic sample. The PLS-DA model described for both dynamite and its principal component, ammonium nitrate, was excellent, achieving specificity and selectivity values of 100% for calibration and cross-validation.

Since the PLS-DA model presented for dynamite was of a perfect accuracy and robust, the building of a larger database to create a spectral library containing more dynamite samples, different explosives and also combinations of different explosives, should be extraordinarily attractive and useful for forensic investigations. This, together with the proposed methodology, can be easily adaptable and used as an automated method in public places such as airports, stations, auditoriums, hospitals and populous public events with the aim to detect and control the potential criminal use of explosives, which may represent a breakthrough for public security.

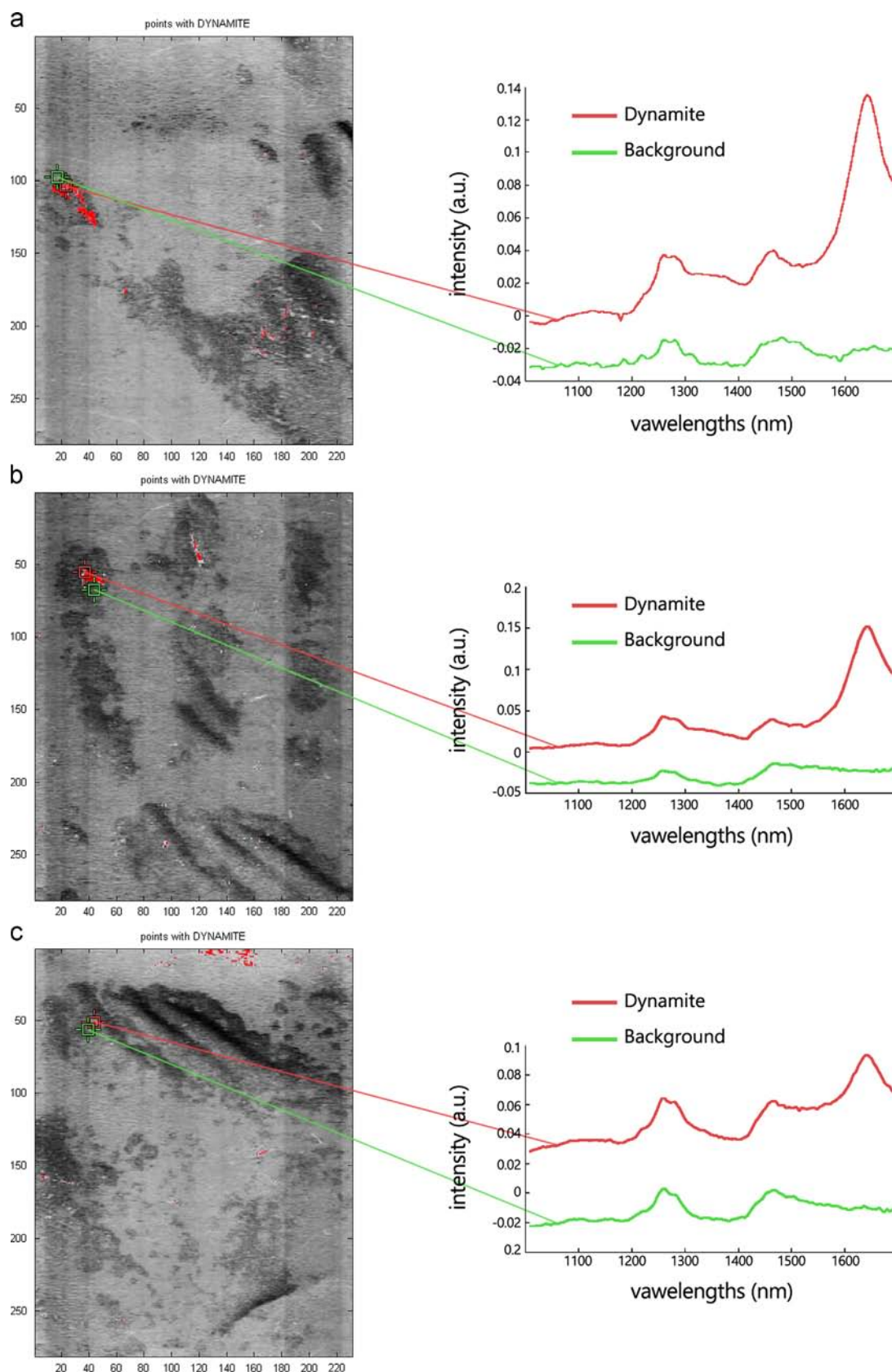


Fig. 3. NIR false colour hyperspectral image showing the presence of dynamite residues (red) and neighbouring regions (green) in different parts of a handprint: (a) thumb; (b) fingers; and (c) hand palm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

To fully implement the proposed methodology further investigations must be carried taking into account different variables (e.g. the persistence of the explosives with time, the potential influence of

common hand care products such as creams or soaps, the study of limits of detections and potential interferences that may generate false positive errors caused by other common, legal and frequently

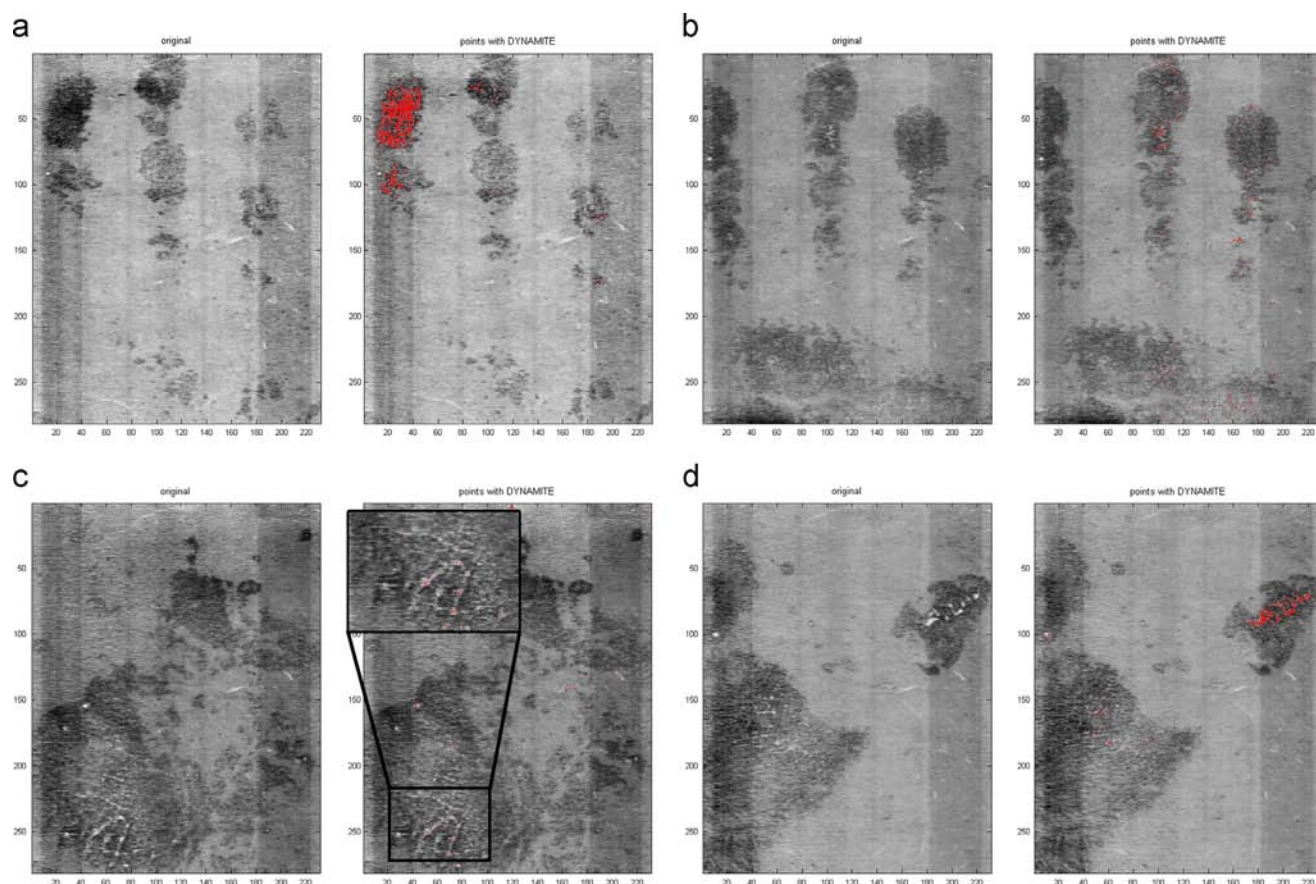


Fig. 4. NIR false colour hyperspectral images from different parts of handprints deposited by the volunteers who collaborated in this study, showing the presence of dynamite residues as highlighted pixels in red colour: (a) 910 pixels for a fingers sample; (b) 277 pixels for a fingers sample; (c) 57 pixels for a hand palm sample with a zoom to facilitate visualize red pixels related to the presence of dynamite residues; and (d) 229 pixels for a thumb finger sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

used nitrated compounds such as fertilizers, as well as the consideration of more samples and other spectral wavelengths).

Author contributions

The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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