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Detection of explosives on the surface of banknotes by Raman hyperspectral imaging and independent component analysis

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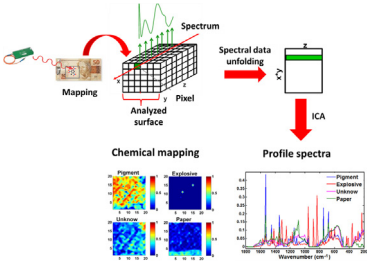
HIGHLIGHTS

- Raman imaging and ICA were used for detection of explosives in banknotes.
- Use of MF-ICA algorithm without initial estimates.
- Comparison of performance of ICA and MCR-ALS.
- Chemical information without manipulation or destruction of the sample.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to develop a methodology using Raman hyperspectral imaging and chemometric methods for identification of pre- and post-blast explosive residues on banknote surfaces. The explosives studied were of military, commercial and propellant uses. After the acquisition of the hyperspectral imaging, independent component analysis (ICA) was applied to extract the pure spectra and the distribution of the corresponding image constituents. The performance of the methodology was evaluated by the explained variance and the lack of fit of the models, by comparing the ICA recovered spectra with the reference spectra using correlation coefficients and by the presence of rotational ambiguity in the ICA solutions. The methodology was applied to forensic samples to solve an automated teller machine explosion case. Independent component analysis proved to be a suitable method of resolving curves, achieving equivalent performance with the multivariate curve resolution with alternating least squares (MCR-ALS) method. At low concentrations, MCR-ALS presents some limitations, as it did not provide the correct solution. The detection limit of the methodology presented in this study was 50 $\mu g\,cm^{-2}$.

1. Introduction

The analysis of explosives and their residues on different surfaces is of great interest to the fields of forensic science, environmental chemistry and national security. The interest in forensic analysis relates to the use of these devices in criminal actions [1]. The explosives may be a combination of inexpensive components and homemade products such as hydrogen peroxide, perchlorates and acetone, which are easily obtained, transported, and hidden and possess a high destructive power.

The goal of analysis of explosives for forensic purposes is the identification of pre- and post-blast samples and residues. The

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identification is performed with the purpose of establishing links between suspects and crime scenes. Traditionally, this type of sample is analyzed for the presence of nitrite, which would be indicative of the presence of explosives. The most commonly used method of analysis is known as the Griess wet test [2]. However, this test is not selective because it identifies any source of nitrite, and the results are not always conclusive.

The identification of explosives using vibrational spectroscopic techniques such as infrared and Raman spectroscopy have been presented in the literature in the last few years [1,3–9]. Examples include in-situ analysis using confocal Raman spectroscopy for security applications [3] and analysis with a portable Raman spectrometer using a laser in the region of 785 and 1064 nm for identification of unknown materials in public places. The equipment with the laser in the near infrared region is of great relevance some types of applications require this type of technology due to the presence of fluorescence [4]. The use of Raman spectroscopy in the analysis of suspected improvised explosive manufacture such as peroxide-based explosives has also been reported in the literature [5,6]. In recent years, the stand-off detection of explosives by Raman spectroscopy has been the focus of research in this field [7,8]. The use of methodologies for signal processing and resolution is required to reduce background and interferences and to detect the analyte of interest better [7].

Raman spectroscopy is a well-established technique in the field of forensic chemistry, and its spectra provide specific and selective molecular information. One additional advantage of Raman spectroscopy is that sample preparation is either not required or minimal, allowing for non-destructive analysis, which is of great importance in forensic judicial cases. Another important feature of the technique is its versatility regarding the presentation of samples.

Raman hyperspectral imaging is an extension of Raman spectroscopy that combines spectral and spatial information about the sample. The sample area is delimited, and a spectrum is obtained at each point (pixel) on the *xy* surface. Finally, a three-dimensional array is obtained, where *xy* represents the pixel coordinates and the third dimension *z* corresponds to the wavenumber spectrum. The addition of the spatial dimension has greatly benefited the use of Raman spectroscopy due to the increase in understanding of areas already established by the technique. The use of Raman hyperspectral imaging has been used in the detection of trace amounts of explosives on fingerprints [9]. Raman hyperspectral imaging has been shown to be a powerful tool in the detection of explosives in trace amounts, even in the presence of interferents and without destroying the sample, leaving the sample available for forensic evidence or further analysis.

To extract information collected by Raman imaging, the use of chemometric tools is essential. Chemometric tools enable complete extraction of information and allow for simultaneous processing of large amounts of data, even with low spectral resolution, overlapping bands and low intensity of the analytical signal.

The aim of this study was to develop a methodology using Raman spectroscopy imaging and independent component analysis (ICA) as a multivariate curve resolution method for identification of pre- and post-blast explosives on banknote surfaces. The motivation for this work was the increase in attacks on automated teller machines (ATMs) for purposes of banknote theft using combustion-based substances to cause explosions. ATM theft by blow up is a reality in Brazil and anywhere there is an ATM will be a thief's target. According to the national survey on attacks on banks in Brazil, general enforced banks break in has increased from 838 cases in half 2011 to 1693 cases in half 2014 – a total increase of 102% in this period. Unequivocal analytical methods that can identify explosives residues on any surface (crime scene and related crime utensils) help the criminal investigation tracking thieves [10].

The study was conducted in the following steps: first, spot Raman spectra of different explosives were obtained. Then, Raman images of banknotes contaminated with explosives in the laboratory were obtained, and independent component analysis was applied to extract the pure explosive spectrum and the distribution of the explosive on the surface analyzed. Finally, the methodology was applied to forensic samples in an attempt to find post-blast explosive residues on suspect banknotes.

2. Theory

Independent component analysis (ICA) is a blind source separation method that has been used for multivariate resolution purposes in analytical chemistry [11,12]. ICA assumes that the original sources are statistically independent and estimates the components as independently as possible. The goal of ICA is to retrieve the pure sources of the mixed signals.

In ICA, a matrix of spectra can be considered as a collection of signals with a certain number of common sources. Then, the algorithm is applied to extract the pure source signals and their concentration in each mixture. Considering that the mixture signal is a linear combination of pure signals, the ICA linear model can be written as:

$$X = AS^T + E \tag{1}$$

In this study, X (IxJ) is the matrix of the observed spectra, A (IxN) is the mixing matrix (concentration), S (NxJ) is the matrix of pure source signals (spectra) that contains independent components, and E is the error matrix (I*x*J). The mixing vectors in A are independent and components in S^T are mutually statistically independent.

For the ICA, the independence between all components is the only important condition. The ICA estimates a linear transformation matrix W that, when applied to X, produces a matrix S of independent component spectra:

$$S^T = WX \tag{2}$$

The estimate of W can be performed by different algorithms, which will maximize or minimize a given function.

After estimation of W, the matrix S can be defined as:

$$S = W(AS) \tag{3}$$

where W should be the inverse of A. Finally, the mixing matrix A can be calculated as:

$$A = XS^T(SS^T)^{-1} \tag{4}$$

The ICA solutions may present some ambiguities; it is not possible to determine the variances of the independent components, and as a consequence, their order cannot be determined [13]. The choice of the number of components is also a critical step, and various methods such as the ICA-by-block, Durbin–Watson test [14] and the square root of the sum of the residues [12] have been proposed in the literature. However, some of these methods require prior knowledge of the matrix A. Another important issue is the choice of the ICA algorithm. Several algorithms are available to execute ICA, and these algorithms are based on different criteria of independence and mathematical procedures to maximize it [12].In this work, mean field ICA (MF-ICA), which estimates A and S based on Bayesian statistics, was used. In MF-ICA, the source profiles are estimated by integration over the source posterior, and the mixing matrix and noise covariance are estimated by