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Design of a Virtual Sensor Data Array for the Analysis of RDX, HMX and DMNB Using Metal-Doped Screen Printed Electrodes and Chemometric Analysis

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The detection of explosive substances is a subject of high importance in several areas including environmental health, de-mining efforts (land and sea) and security and defence against terrorist activity. The use of electrochemical methods for the detection of these substances has increased in recent years but still is quite restricted to the most common explosives. The electrochemical detection of explosive nitroamines and taggant substances in solution using a virtual sensor array of metal-doped screen printed electrodes and differential pulse voltammetry was achieved. The multiple sets of voltammetric data from the different electrodic systems using Differential Pulse Voltammetry (DPV) were integrated using multivariate analysis (PCA, NIPALS and LDA) and matched with known substances present in explosives. These combinations created a mathematical array which separated the explosives, even if the electrochemical information is buried or mixed with the background noise. Two explosive substances: octogen (HMX- 1,3,5-Trinitroperhydro-1,3,5-triazine) and cyclonite (RDX-Hexahydro-1,3,5-trinitro-1,3,5-triazine) and a taggant agent 2,3-dimethyl-2,3-dinitrobutane (DMNB) were subjected to electrochemical analysis using a solid carbon- based screen printed electrode modified with silver, gold and platinum in aqueous solutions.

Keywords: Explosives, Chemometrics, Voltammetry, Electrochemistry, Octogen, RDX, Cyclonite, HMX, DMNB.

1. INTRODUCTION

Aside from the obvious dangers of explosive compounds, they also pose a problem when released into the environment. Nitroaromatic and nitramine compounds are mutagenic and toxic. They are associated with a wide range of health issues including liver damage, aplastic anaemia, cardiac irregularities and renal problems. Explosive compounds persist in the biosphere, and represent a danger to humans, fish and microorganism life [1].

Separation techniques associated to electrochemical detectors such as liquid chromatography [2] or even more sophisticated ones using micro capillary electrophoresis chips [3] have been used in conjunction with electrochemical detection techniques to discriminate and quantify explosive mixtures. These techniques are very efficient, but in the last 10 years they have not yet been able to be integrated in operational portable instruments, due to the complex needs of such systems. However simpler electrochemical devices based on carbon fibres as working electrodes have been recently used for the successful analysis of TNT in seawater [4] and even integrated in autonomous underwater vehicles [5]. Electrochemical sensors offer the sensitivity, selectivity, minimal space and power requirements needed to fulfill the required tasks in the detection of explosives and to be integrated in portable instruments [5].

The analysis of two explosive substances such as RDX and HMX from soil samples has been previously attempted using square-wave voltammetry and a glassy carbon electrode [6]. This method can be seen as precise and sensitive but the selectivity achieved is seriously compromised as both RDX and HMX rely on the reduction of nitro groups and the reduction potential for both substances was found to be very similar and close to -0.78V. This implies that RDX and HMX cannot be selectively identified as the peaks will necessarily overlap if both explosives are present in the sample. This problem can be easily solved through the use of multivariate analysis and data fusion. Attempts in this sense were performed by Polsky et al. for the analysis of TNT and DNT [7]. They combined the voltammetric responses to resolve mixtures of nitroaromatic compounds using two chemically modified and an unmodified glassy carbon electrodes. This combined data set, based on the combined response of the multiple working electrodes, was then analysed by multivariate discriminant analysis techniques; Principal component analysis was used to discriminate the responses of 4 nitro aromatic compounds, and Partial Least Squares regression was used to construct models to predict the concentration of the components in a binary sample.

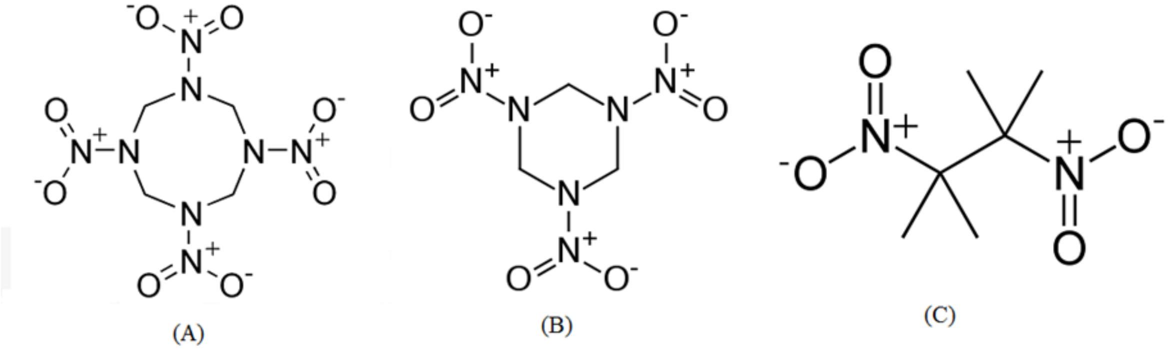

Figure 1. Chemical structures for (a) RDX, (b) HMX and (c) DMNB.

Many papers have concentrated on the analysis of TNT and DNT isomers, given their importance, but the number of publications on the electrochemical analysis of explosive nitroamines (RDX and MX) and taggants, such as DMNB (2,3 Dimethyl 2,3 Dinitrobutane) is less abundant. This is particularly surprising, especially when their chemical structures are full of electroactive nitro groups (see figure 1). In this sense is worth mentioning the work performed by Prabu et al [8] using bare glassy carbon electrodes and Berger et al [9] who used gold electrodes to obtain electrochemical signals using unmodified electrodes for HMX and RDX. Modified glassy carbon electrodes were used by Ly et al [10], who used mercury-film plated electrodes, and Rezaei et al [11], using multi-walled carbon nanotubes, for the determination of RDX.

Another important development for the use of solid electrodes in the analysis of explosive substances is the use of carbon-based screen printed electrodes (SPE) for the detection of TNT [12] and DNT [13]. In some cases these SPEs were attached to clothing showing good detection levels and demonstrating their usability as portable sensors for different applications [14]. The use of SPE for explosive analysis presents a similar scenario as that reported before for solid electrodes with few reports on the analysis of HMX, RDX or taggants even when different combinations of DMNB and RDX can be found in military plastic explosives such as C-4.

The aim of the work presented here is to fill a gap in the existing research and to open a window of opportunity for the analysis of different explosive substances with special focus on nitro amines and taggant substances. To the best of our knowledge there is no previously published work regarding the analysis of HMX, RDX or DMNB using electrochemical virtual sensors or showing the potential use of metal-doped SPEs for the analysis of explosive substances involving the use of data fusion or virtual sensors.

2. MATERIALS AND METHODS

The Screen Printed Electrode (SPE) measurements were performed using a µstat 400 portable BiPotentiostat/Galvanostat from DropSens (Oviedo, Spain). The C110 Screen-printed Carbon electrodes from DropSense were also used in conjunction with the µstat 400. Before using the unmodified SPE the surface was polished with filter paper and washed with de-ionised water. The working surface was activated through 40 cycles between +2 and -2 V, at a scan rate of 100 mV/s in a 0.1 KCl solution. The area of the carbon electrode was calculated experimentally by using a $K_3Fe(CN)_6$ 1mM solution in KCl 1 M. The equation used for the determination of the experimental area was:

$$i_p=(2.69x10^5)\ n^{3/2}AD_o^{1/2}v^{1/2}c_o \qquad (1)$$

being (1) the typical equation for a reversible process where i_p= peak intensity, n=number of electrons exchanged, A=area, D_o= coefficient of diffusion, v=scan rate, α=coefficient of the electronic transfer and C_o=concentration. As the value for the coefficient of diffusion for $K_3Fe(CN)_6$ is $Do=7.84x10^{-6}cm^2/s$, the average (n=8) calculated area value for (1) was 0.0489±0.0038 cm^2. This analysis served the purpose of guaranteeing that the active carbon surface offered an homogeneous substrate for the doping of the electrodes.

The electrochemical deposition of Ag, Au and Pt particles on the surface of the electrode followed the following procedure: Britton-Robinson buffer was used to favour the reduction of nanoparticles on the surface of carbon electrodes (0.04 M H_3PO_4 +0.04M H_3BO_3 + 0.04 M CH_3COOH + NaOH to pH=2). Phosphoric, boric and acetic acids were purchased from Sigma. In order to deposit the silver nanoparticles on the surface of the electrode 10 µL of a 1.15 mM silver nitrate aqueous solution (Sigma-Aldrich, Dorset, UK) was used and the potential of the cell set at -1.20 V for 120 s. In order to produce the gold nanoparticles,10 µL of a 1mM hydrogen tetrachloroaurate (III) trihydrate ($AuCl_3$ $3H_2O$) solution was used together with a 0.1M HCl, both from Sigma. The potential was set at -0.4 V. and maintained for 200 s. Platinum coating was achieved by using 10 µL of a 1mM $PtCl_4$ solution in a 0.1M HCl both from Sigma was deposited on the surface of the electrode set at a potential of -0.4V. for 200 s.

In order to obtain mechanically silver-doped electrodes an electrochemical cleaning was performed followed by the addition of 10 µL of a 1 mM silver nanoparticle solution [15] on the working electrode and left for 24 h for the particles to physically attach to the surface.

As a result five different electrodes were used to build the virtual array: carbon SPE, mechanically Ag-doped carbon SPE, Ag-electrochemically doped carbon SPE, Au-electrochemically doped carbon SPE and Pt-electrochemically doped SPE.

Multivariate Analysis was performed using Tanagra software [16] (University Of Lyon, France). A set of 48 samples (16 samples per explosive/taggant type) were used to perform the tests. The virtual voltammograms generated as input for the multivariate analysis software (Tanagra) were created as an average of the different signals obtained from the bare SPE (blank), mechanically silver-doped SPE, electrochemically silver-doped SPE, gold-doped SPE and platinum-doped SPE.

3. RESULTS AND DISCUSSION

3.1. Electrochemical analysis

Explosive substances are molecules with great potential to release huge amounts of energy very fast. This characteristic is given by the presence in the molecular structure of certain functional groups able to deliver this energy. Nitro groups are one of these types of functional groups. It is well known that the presence of nitro groups in a molecule greatly influences their electrochemical behaviour due to their electron acceptor properties. So, in principle an electrochemical reduction is expected to occur when a compound rich in these molecules is presented to an electrode able to donate the required electrons. This is highly dependent on pH and the presence of multiple nitro groups in the structure of the molecule [2]. It is also well known that nitro amines are more difficult to reduce than other molecules containing nitro-aromatics and nitro-esters, such as TNT or DNT [5], which makes them a challenge for electrochemical sensor systems. This may explain why most of the work developed in electrochemical sensing has been devoted to nitro aromatics and not much has been done for RDX or HMX even when they have molecules present in many explosive compounds.

Previous work from our group [17] has shown that there is a good response from RDX, HMX and DMNB when presented to commercial silver, platinum or glassy carbon electrodes showing that standard electrodes have potential to be used in a sensor array. The problem posed by using such commercial electrodes to create a virtual array is their size and selectivity. This can be overcome by using the new generation of commercially available miniaturised screen printed electrodes (SPE). The SPE can be modified to present properties different from those of the base material they were manufactured with (usually carbon). Our previous work showed that when the different electrode responses were combined, improved detection accuracy could be achieved by using Principal Component Analysis but selectivity needed to be improved. An added advantage of the present work, together with the miniaturisation of the array, was the use of the same base material for the electrode (carbon) which could be modified easily for different analytes.

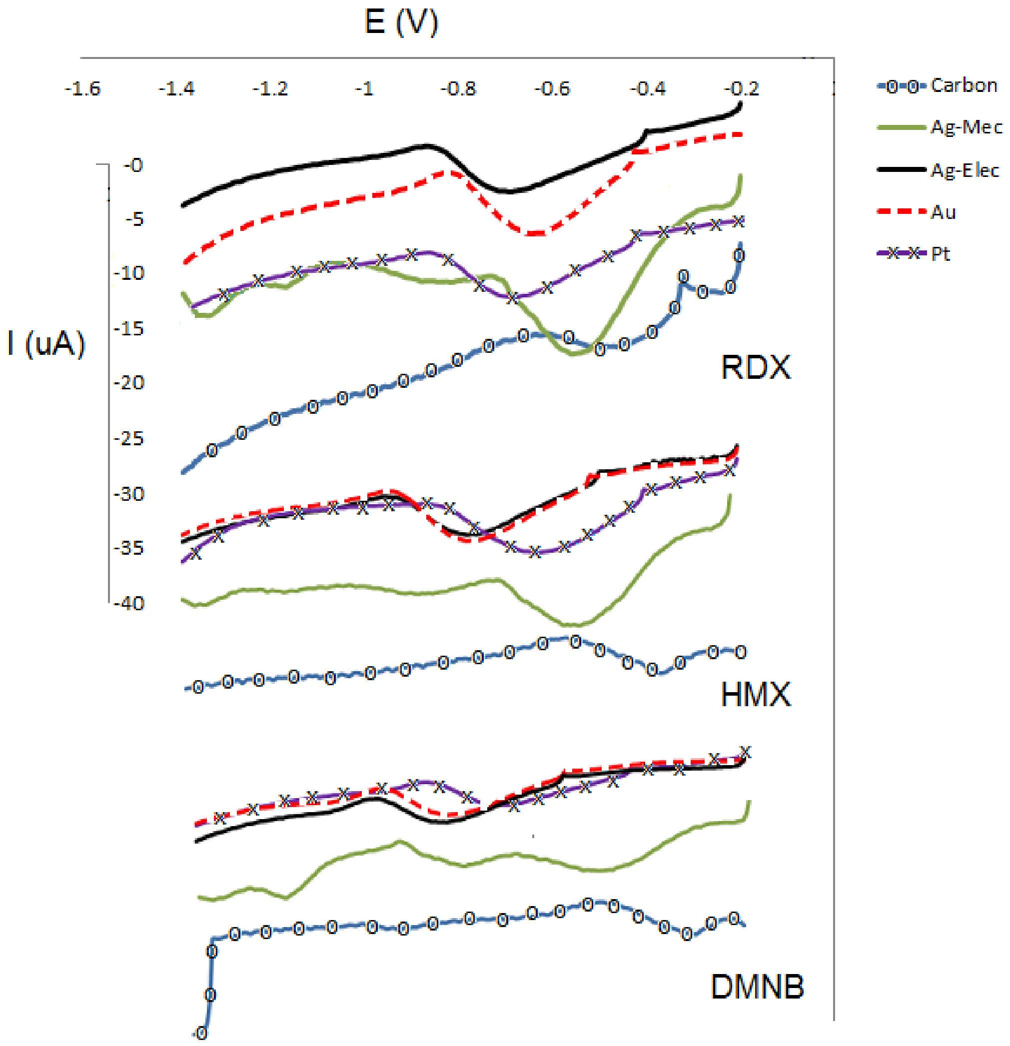

Figure 2. Different electrochemical responses obtained from the different metal-doped screen printed electrodes: carbon (-o-o-), mechanically doped silver SPE (——), electrochemically modified silver SPE (——) and electrochemically modified gold (— —) and platinum (-x-x-) SPEs.

In our present work, carbon-based SPEs were modified with metal nanoparticles as described in the materials and methods section. The responses obtained by the different modified and unmodified electrodes are shown in figure 2. The first noticeable feature of these voltammograms is the lack of clearly defined Gaussian peaks. For most of them, we can observe consistent broad reduction waves in the range -0.4 and -0.9V. For all substances under study, the carbon electrode, base material of the SPE used, offered the least responsive and featureless signal presenting the higher electrodic discharge currents. The mechanically silver-doped electrode also presented high discharge currents but presented more electrochemical activity when presented to the different analytes under study. This effect can be explained taking into account the deposition pattern observed on the surface of the electrode.

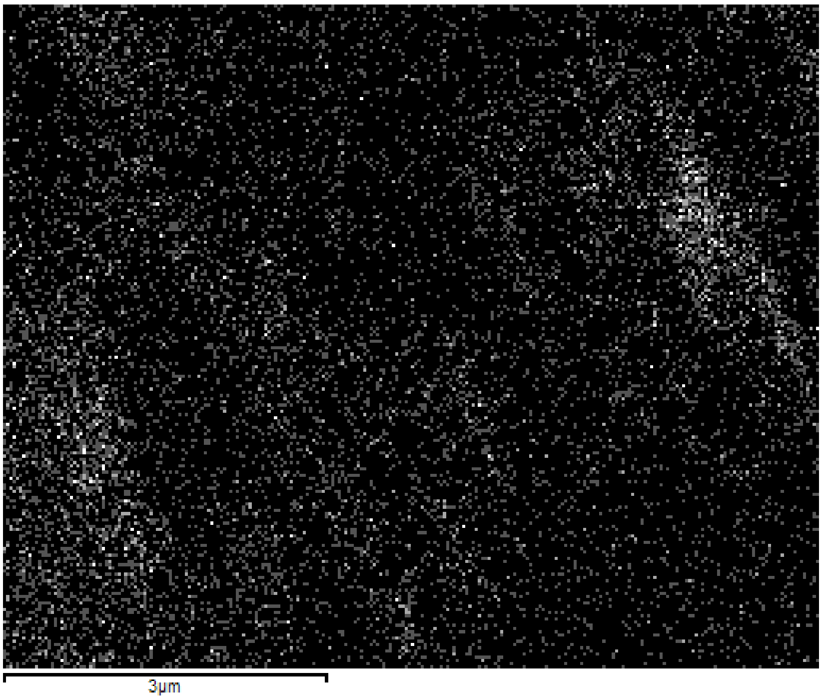

Figure 3. EDX-SEM image of a mechanically modified silver SPE at a magnification level of 3µm. White spots represent the signal obtained for silver in the EDX analysis.

Figure 3 shows an SEM-EDX image where the silver particles deposited on the carbon surface can be clearly observed and identified as metallic silver from their EDX spectrum. The average size of these clusters is around 153 nm showing a deviation in size of 15.8% (in terms of RSD(%) n=18). These silver metal clusters may act as AgNP aggregates formed from colloidal Ag for the reduction of the different analytes but also enough of the carbon substrate is still available to transfer electrons and participate in the reduction of the different explosives offering a mixed response. This behaviour greatly differs from that observed when electrochemically silver-doped SPEs were analysed by SEM-EDX where a thin homogenous silver layer was deposited on the carbon electrodes, similar to that obtained through electroplating. This is consistent with the lower background current obtained due to a greater influence from the metal particles is present.

When the different substances were analysed DMNB offered an almost featureless shape for all electrodes compared with the rest of the substances. It can also be observed that in the case of both gold and silver-doped electrodes, there is a shift toward more negative reduction potentials with decreasing number of nitro groups in the molecule (E(V) DMNB<HMX<RDX). A similar behaviour has been previously reported in nitro aromatic explosives in which tri-nitro compounds are more easily reduced than di- or mono-nitro compounds, with TNT more easily reduced (less negative E) than, for example, DNT or NT (more negative E) [5].

Table 1. Electro analytical values for the SPE silver mechanically-modified (Ag-Mec) and electrochemically-modified (Ag-Elec) electrodes, SPE platinum-doped (Pt) and SPE gold-doped (Au). E(V): reduction potential; correlation coefficient of the calibration curve; % accuracy (%Ac) and precision (n=3) expressed as %RSD.

	Ag-Mec				Ag-Elec				Pt				Au			
	E(V)	R^2	%Ac	%RSD	E(V)	R^2	%Ac	%RSD	E(V)	R^2	%Ac	%RSD	E(V)	R^2	%Ac	%RSD
RDX	-0.70	0.86	19.0	0.51	-0.92	0.998	6.69	2.62	-0.71	0.882	17.3	9.21	-0.63	0.990	8.33	6.68
HMX	-0.59	0.96	14.4	3.86	-0.89	0.920	6.61	3.15	-0.62	0.992	9.45	3.49	-0.80	0.950	12.3	8.16
DMNB	-0.51	0.98	8.58	4.06	-0.87	0.986	5.26	2.96	-0.73	0.978	10.3	1.33	-0.90	0.948	9.18	7.10

Table 1 shows the different electroanalytical variables obtained from the analysis of the different explosives. The linear range studied for all electrodes was from 0.1 mgL^{-1} to 10 mgL^{-1}. As can be observed, all electrodes and compounds present relatively acceptable linearity for the calibration curves as demonstrated by the correlation coefficients. The reduction potential is also relatively different for all of them, but still close enough to make them overlap if they are present in the same solution, which poses the greatest problem when trying to obtain selective analysis. For all the electrodes and explosives the precision of the analyses is below 10% (%RSD) and for many of the analyses (66%) below 5%. Inter-day average accuracy (n=3) was 10.6%. These results indicate that the doped sensors could be used for screening of explosives with relatively good precision and accuracy.

3.2. Chemometric analysis

Principal Component Analysis (PCA) and Non-Iterative Partial Least Squares-Linear Discriminant Analysis (NIPALS-LDA) of the different electrochemical responses obtained for the different compounds for each individual metal-doped electrode were performed. The PCA results provided exploratory information on how well the different explosives clustered when analysed with the supervised learning tool, NIPALS-LDA. The leave-one-out algorithm was then used to evaluate the robustness of this classification.

NIPALS produces factors (latent variables) similar to those produced in principal component analysis (PCA) but with a much faster processing time. As with PCA, NIPALS can be used for exploratory data analysis looking for hidden data structures within a dataset [18]. It can also be used as a method of data reduction prior to the use of supervised learning tools such as linear discriminant analysis (LDA) [19]. This approach is commonly used with PCA [20] and offers the advantages of significant data reduction allowing the use of tools such as LDA (not possible with the initial dataset) and providing orthogonal variables which removes problems due to variable co-linearity observed in voltammogram data.

HMX, RDX and DMNB responses from the electrochemically silver-doped electrodes were analysed firstly with NIPALS as a method of data reduction before using the principal components as input to Linear Discriminant Analysis (LDA). The model was validated with the ‘leave-one-out’ algorithm which gave 50% of the RDX, 17% of the DMNB and 67% HMX as correctly classified. When a mechanically silver-doped SPE electrode was used for the analysis 100% DMNB, 80% HMX and 83% RDX were correctly classified. The electrochemically gold-doped SPE correctly classified 33% of DMNB and 67% of both HMX and RDX. Finally the platinum-doped SPE gave as correctly classified 67% DMNB, 50% of HMX and 83% RDX. From this analysis it is clear that single metal-doped SPE do not provide sufficient differentiation for accurate classification. However, there is enough evidence to suggest that sufficient chemical differences lay in the electrochemical signals obtained for the different individual electrodes and compounds.

These chemical differences buried in the voltammograms when combined together may provide enough differentiation power to produce a successful separation in the PCA. In order to prove this, the voltammograms were combined as described in the materials and methods section and, a new virtual voltammogram was created.

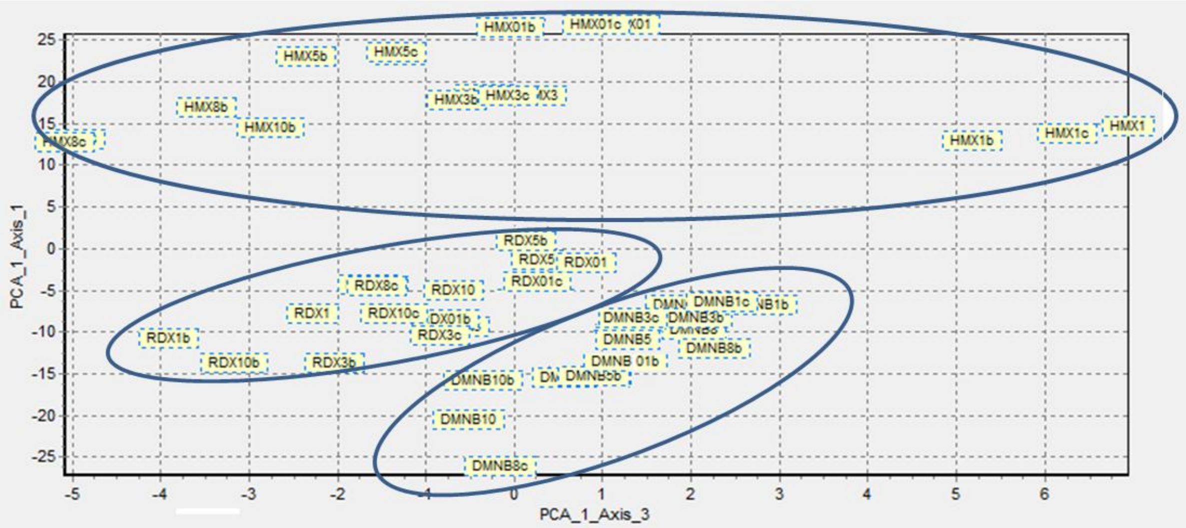

Figure 4. PCA analysis from the data fusion of the voltammograms from the bare SPE (blank), mechanically silver-doped SPE, electrochemically silver-doped SPE, gold-doped SPE and platinum-doped SPE electrodes.

Figure 4 shows PC1 vs PC3 score plot from the PCA analysis of the virtual array. A previous step to standardise the data used in the virtual array did not have any effect on the quality of the data obtained and therefore raw data were used throughout the analyses. The score plot shows good separation of the different explosive substances, which seems to indicate that the virtual array can provide enough chemical information to obtain good separation. From the analysis of the eigen values

PC1 explains 86.12% of the variability, PC2 8.37% and PC3 2.54% obtaining a cumulative variability of 97.03%. In the figure it can also be observed that PC1 presents the greatest discrimination power, which explains the separation of HMX from the rest of the explosives. The importance of PC1 to explain the discrimination power for the different explosives is also corroborated by the factor loadings.

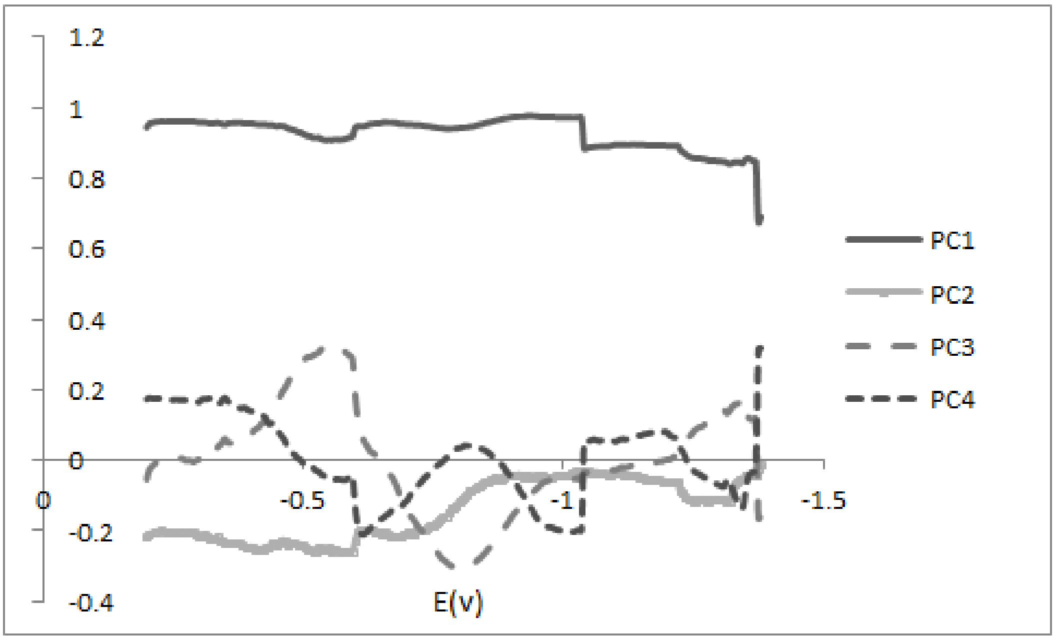

Figure 5. Factor loadings for the virtual data array when plotted versus the reduction potentials

Figure 5 shows that the higher statistical weight is obtained for PC1 (factor closer to 1) compared to those obtained for the rest of the PCs. It is also interesting noting how the pattern obtained for PC3 resembles the voltammograms obtained for the different substances under study and seems to be correlated to a certain extent to the explosive concentration. The potential range (-0.4 to -0.9V.) in which we could observe most of the electrochemical features for these voltammograms in figure 1 presents a relative increase in the factor loadings for PC3 when compared to PC2 and PC4, which can be associated to the presence of chemical information in this range. We also performed a 'stepdisc' analysis, a statistical test in order to identify the most significant variables used in LDA [19]. The stepdisc analysis showed that there is a set of variables concentrated in this potential range which play a vital role in the discrimination of the compounds. This is supporting evidence that vital chemical information associated with the reduction potentials of these substances for the different electrodes is buried in the individual signals and remained after the recombination playing an important role in the clustering.

To finally prove the efficacy of the virtual array, validation of the NIPALS-LDA model with the 'leave-one-out' test was performed. The results gave 100% correct classification for all substances (RDX, HMX and DMNB). This clearly confirms that the combination of different electrodes does contribute to increase the chemical information contained in the data fusion allowing a successful separation due to increased selectivity.

4. CONCLUSIONS

The electrochemical detection of nitroamines used as explosives and taggant substances in solution using a virtual sensor array of metal-doped screen printed electrodes and differential pulse voltammetry was achieved.

The PCA of the results showed that the use of single metal-doped electrodes was not able to provide enough differentiation power to separate the chemically similar structures. The single modified electrodes presented good eletroanalytical properties in order to combine them to form a virtual array though.

The separation achieved and the information obtained from the different multivariate validation tools is evidence that chemical information associated with the reduction of these substances in the range of potential -0.4 to -0.9 V. remained after the data fusion and plays an important role in the clustering obtained under PCA.

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