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Simultaneous identification and quantification of nitro-containing explosives by advanced chemometric data treatment of cyclic voltammetry at screen-printed electrodes

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ABSTRACT

The simultaneous determination of three nitro-containing compounds found in the majority of explosive mixtures, namely hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT) and pentaerythritol tetranitrate (PETN), is demonstrated using both qualitative and quantitative approaches involving the coupling of electrochemical measurements and advanced chemometric data processing. Voltammetric responses were obtained from a single bare screen-printed carbon electrode (SPCE), which exhibited marked mix-responses towards the compounds examined. The responses obtained were then preprocessed employing discrete wavelet transform (DWT) and the resulting coefficients were input to an artificial neural network (ANN) model. Subsequently, meaningful data was extracted from the complex voltammetric readings, achieving either the correct discrimination of the different commercial mixtures (100% of accuracy, sensitivity and specificity) or the individual quantification of each of the compounds under study (total NRMSE of 0.162 for the external test subset).

1. Introduction

With the surge of international terrorism and the increased use of explosives in terrorist attacks, law enforcement agencies throughout the world are faced with the problem of detecting hidden improvised explosive devices (IEDs) in luggage, mail, vehicles, and aircraft, as well as on suspects. This has become a major analytical problem, which requires highly sensitive, specific, fast and reliable field-deployable sensors [1,2].

There has been a huge increase in research within this area, through both the development of new, innovative detection approaches and the improvement of existing techniques [3]. The most common analytical techniques include ion mobility spectrometry (IMS), mass spectrometry (MS) and gas chromatography (GC). Most of these devices are, however, rather bulky, expensive, and require time-consuming procedures [4]. Over those, IMS is one of the most widely adopted detection techniques in routine use due to its ability to characterize the sample both qualitatively and quantitatively [5]. Because of the above limitations, such systems are deployed only at strategic locations, e.g. airports or government buildings. Nevertheless, further complications arise when one considers not only these placements, where there is a reasonably controlled environment for sensing and detection, but also the virtually uncontrollable entry points to public places, transportation, etc. or in-field applications. Thus, to ensure security over those scenarios, mass deployment of miniature sensors that are sufficiently sensitive and selective, inexpensive, and amenable for mass production is required.

The in-field detection of explosive compounds requires miniaturized low-cost measurement systems, with high probability of detection. In addition, such systems should provide a rapid response with a low rate of false alarms. In this sense, electrochemical devices are advantageous for addressing the growing need for detection of various explosives [2]. The advantages of electrochemical systems for on-site measurements include high sensitivity and selectivity, a wide linear range, minimal space and power requirements, and low-cost instrumentation. Moreover, both the sensor and the controlled instrumentation can be readily miniaturized to yield compact and user-friendly hand-held meters for on-site (indoor and outdoor) testing [6,7]. In addition, the inherent redox activity of commercial explosives [8], such as nitroaromatic or nitramine compounds, namely the presence of easily-reducible nitro groups, makes them ideal candidates for electrochemical (voltammetric) monitoring. Therefore, electrochemical devices represent a promising solution for on-site explosive detection.

Previous attempts were made to voltammetrically detect the aforementioned compounds employing different types of electrodes

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such as a bare screen-printed electrode (SPCE) [8], unmodified [5] or modified [9] gold electrodes and modified glassy carbon electrodes (GCE) [10–12]. Although the detection of such compounds can be achieved even at very low-concentration levels (e.g. ppb levels for 2,4,6-trinitrotoluene (TNT) [12]), it should be taken into account that common real-life explosives are usually mixtures of two or more different explosive species [13,14]. Table 1 outlines the compositions of some very well-known commercial explosive mixtures, although many variations in those compositions should be considered due to the specific preparation of IEDs. The main challenge encountered with these mixtures is the discrimination between individual compounds present, given that the voltammetric signals produced by these electrochemical methods correspond to a global overlapped, multiple peak voltammogram; i.e. there is a lack of specificity or identification of differentiated peaks for each of the compounds. Thus, in order to more accurately determine which type of explosive combination is used, ability to discern between different explosive compounds in a mixture is necessary, specially for security issues.

In this sense, the use of chemometric tools such as principal component analysis (PCA) or artificial neural networks (ANNs) can help to overcome this limitation [15–17], by identifying and processing the electrochemical fingerprint shown by the explosive mixture. The concept consists in the integration of a sensor (with marked mix-response towards the desired species) and a chemometric processing tool (able to interpret and extract meaningful data from the complex readings); an existing approach known as electronic tongue (ET) when an array of voltammetric sensors with a complementary response is used instead of a single sensor [18,19]. These principles have already been applied to the discrimination of some mixtures by means of PCA [5,20] or Linear Discriminant Analysis (LDA) [21]; even the quantification of 2,4-dinitrotoluene (2,4-DNT) in the presence of 2,6-dinitrotoluene (2,6-DNT) and vice versa has been addressed by Partial Least Squares regression (PLS) [11].

Also, in a related work, simultaneous detection of some toxic nitro-phenols in waste–water has been achieved through coupling of chemometrics and voltammetric measurements [22]. Concretely in that case, data obtained from a hanging mercury drop electrode (HMDE) were modeled employing linear methods such as principal components regression (PCR) and PLS. Nevertheless, despite the power of such an approach and good results obtained, the use of HDME demotes its field-application.

The method proposed herein couples field-deployable electrochemical measurements with multivariate calibration models obtained by ANNs [17]. However, processing a set of voltammetric signals with ANN requires a preprocessing stage of data reduction such as fast Fourier transform (FFT) [23] or discrete wavelet transform (DWT) [24] given its high dimensionality. This data preprocessing is required due to the extreme complexity of these signals in order to gain advantages in training time, to avoid redundancy in input data, and to obtain a model with better generalization ability. In particular, processing with DWT is particularly interesting because of its ability to compress and denoise data [25].

The aim of the present work is to examine the potential of a voltammetric device employing electronic tongue principles for the detection of explosive compounds and their mixtures, either through its qualitative discrimination or quantitative determination. The proposed approach is based on the coupling of cyclic

Table 1
Composition of common and well-known commercial explosives mixtures (obtained from [13]).

	RDX (%)	TNT (%)	PETN (%)	Tetryl (%)	HMX (%)	Other (%)			
Amatol		20/60				80/40 ammonium nitrate			
Baratol		25-33				Barium nitrate	1 Wax		
Comp. A	91					9 Plasticizing oil			
Comp.						1 Wax			
Comp. B-2	60	40							
Comp. C-1	88.3					11.7 Plasticizing oil			
Comp. C-2	80	4				5 MNT (mononitrotoluol)	10 DNT (dinitrotoluol)	1 NC (Nitrocellulose)	
Comp. C-3 or C-3	77	4		3		5 MNT (mononitrotoluol)	10 DNT (dinitrotoluol)	1 NC (Nitrocellulose)	
Comp. C-4 or C-4	91					2.1 Polyisobutylene	1.6 motor oil	5.3 2-ethylhexyl sebacate	
Cyclotol	70	30							
DBX	21	40				21 Aluminum Nitrate	18 Aluminum		
Detasheet C	–	–	63	–	–	8 NC (Nitrocellulose)	29 ATBC (acetyl tributyl citrate)		
Ednatol		43				57 EDNA (ethylenedinitramine)			
HBX	40	38				17 Aluminum powder	5 Desensitizer		
Octol		30/25			70/75				
PBXN-5					95	5 Fluoroelastomers			
Pentolite		50	50						
PEP-3			86			14 Plasticizing oil			
PTX-1	30	20		50					
PTX-2	43.2	28.8	28						
Semtex 1A (B1)	4.6		76			9 n-octyl phthalate, tributyl citrate	9.4 Styrene-butadiene	0.5 N-phenyl-2-naphthylamine	0.5 Sudan IV
Semtex H	41.2		40.9			7.9 n-octyl phthalate, tributyl citrate	9 Styrene-butadiene	0.5 N-phenyl-2-naphthylamine	0.5 Sudan I
Semtex 2P	22.9		58.45			8.45 n-octyl phthalate, tributyl citrate	9.2 Styrene-butadiene	0.5 N-phenyl-2-naphthylamine	0.5 Sudan III
Tetrytol		30		70					
Torpex 1	45	37				18 Aluminum powder	1 Wax added		
Torpex 2	42	40				18 Aluminum powder	1 Wax added		
Tritonal		80				20 Aluminum powder			

voltammetric responses obtained from a single bare SPCE with chemometric tools such as DWT for feature extraction, PCA for visualization of sample similarities and ANNs for building the quantitative prediction models.

2. Experimental

2.1. Reagents and solutions

Reference standard solutions (1000 μg mL^{-1} in acetonitrile) of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), *N*-methyl-*N*,2,4,6-tetranitroaniline and (Tetryl) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were purchased from Cerilliant Corp. (Round Rock, TX). Acetonitrile was purchased from Fisher Scientific (Pittsburgh, PA). Phosphate buffer solution (PBS) was obtained from Sigma-Aldrich (St. Louis, MO). Deionized water (18 MΩ-cm) was obtained from a NANOpure Diamond system (Thermo Scientific Barnstead) and used to prepare all solutions.

2.2. Samples under study

2.2.1. Qualitative discrimination of explosives

In order to evaluate the capabilities of the proposed system to distinguish between different explosives, stock solutions of each of the pure compounds were analyzed. Additionally, some mixtures based on usual commercial explosives (taking into account only the energetic composition, i.e. without addition of the plasticizers, binders or dyes; Table 1) were also prepared and measured. In all cases, the sum of the concentration of the explosive compounds was kept to the same level to ensure that the discrimination was not due to the different amount of compounds present. Hence, in this manner 10 different explosives mixtures were considered, the concentrations of which are detailed in Table 2. To confirm that discrimination between different compounds and mixtures is due to its differentiated electrochemical fingerprint and grouping is not a consequence of any other factor, all samples were prepared in triplicate and randomly measured, considering each replicate as a new sample and employing a new sensor each time to ensure the robustness of the approach. Therefore, the total set of samples under study was formed by 30 samples distributed in 10 different classes.

2.2.2. Quantitative resolution of explosives mixtures

The quantitative resolution of mixtures of three explosive compounds was evaluated (i.e. RDX, TNT and PETN) to provide a tool that would allow the identification of the type of explosive, its quantification, and its specific composition. For this, a total set of 42 samples were manually prepared with a concentration range for the three species from 0 to 200 μg mL^{-1} for each of the nitro-containing explosive compounds (i.e. using the wider concentration range possible based on the stock concentrations and the experimental design; details on Supplementary information Table S1 and S2).

The set of samples was divided into two data subsets: a training subset formed by 27 samples (64%), which were distributed in a cubic design and used to establish the response model [26]; plus 15 additional samples (36%) for the testing subset, randomly distributed along the experimental domain, and used to evaluate the model's predictive response.

Table 2
Detailed concentration of the samples used for the qualitative analysis.

Sample	**Concentration (μg mL^{-1})**				
	RDX	TNT	PETN	Tetryl	HMX
RDX	50	–	–	–	–
TNT	–	50	–	–	–
PETN	–	–	50	–	–
Tetryl	–	–	–	50	–
HMX	–	–	–	–	50
Semtex H	25	–	25	–	–
Comp. B	30	20	–	–	–
Comp. C-3	46	2	–	2	–
Pentolite	–	25	25	–	–
Tetrytol	–	15	–	35	–

2.3. Voltammetric measurements

2.3.1. Electrochemical cell and measurement conditions

SPCE electrodes were prepared following the conventional methodology previously described [8]. The electrochemical cell was formed by a carbon working electrode (geometric area ca. 10 mm^2; effective area of 8.7 ± 0.3 mm^2, with an RSD value of 3.37% for the latter with $n=6$; see Supplementary material), a carbon counter electrode and a silver pseudo-reference electrode. Cyclic Voltammetry (CV) measurements were implemented using a μAutolab Type II (Ecochemie, Netherlands) controlled by GPES Multichannel 4.7 software package, employing a new electrode for each sample.

Electrochemical measurements were performed at room temperature (21 °C) following previously established conditions [8]: the potential was cycled between +1.1 V and −1.4 V *vs.* Ag/AgCl, with a scan rate of 100 mV s^{-1} and a step potential of 4 mV, without applying any preconditioning potential or accumulation time. All electrochemical measurements were carried out using a 50 mM phosphate buffer solution (pH 6.5) to prepare the samples, without requiring the addition of any supporting electrolyte.

2.3.2. Sample measurement

Given the solutions of the explosive compounds were all supplied as an ACN solution, and to ensure that the variation of its proportion does not affect sensor's response, its volume was kept constant throughout all the measurements. For this, the right amount of each compound was mixed, adding the remaining volume of ACN up to 50 μL. Then, this was mixed with 50 μL of PBS buffer pH 6.5 to stabilize the pH and to ensure enough conductivity of the media. The importance of the pH cannot be overstated given that the electrochemical signals for the reduction potentials of nitroaromatics decrease sharply when the pH of the electrolyte increases above 7.0, indicating that high proton concentration favours the reduction [8].

2.4. Data processing

Chemometric processing of the data was performed by specific routines in MATLAB 7.1 (MathWorks, Natick, MA) written by the authors using its Neural Network and Wavelet toolboxes. DWT was used as the feature extraction tool in all cases; PCA was used for qualitative analysis of the results, while quantitative analysis was achieved by means of ANNs. Additionally, Sigmaplot 2000 (Systat Software Inc, California, USA) was used for graphic representations of data and results.

DWT is a high performance signal processing technique developed from Fourier transform, with the key advantage over the latter due to its temporal resolution: it captures both frequency and location information (location in time). DWT is used for signal decomposition onto a set of basis functions, obtained from dilations and translations of a unique function called mother wavelet, the most commonly used being Daubechies wavelets [27]. Transform is implemented using

Mallat's pyramidal algorithm [28], which operates over a single discrete signal of length M by decomposing it into orthogonal subspaces of length ca. M/2 in each step [25]. In this way, by repeating this decomposition process *k* times, the signal compression ratio can be increased; although it is at the expense of signal reconstruction, given signal reconstruction accuracy is degraded for each step.

PCA allows the projection of the information carried by the original variables onto a smaller number of underlying ("latent") variables called principal components (PCs) with new coordinates called scores, obtained after data transformation. Subsequently, by plotting the PCs, one can view interrelationships between different variables, and detect and interpret sample patterns, groupings, similarities or differences [29]. It should be noted that PCA just provides a visualization tool to check whether the samples group together in some regions, and cannot be fully considered as a pattern recognition method. Hence, it should be coupled with a modeling tool such as ANNs to be used as a classifier; subsequently, quantification of the classification performance of the system is accomplished.

ANNs are powerful modelers, that consist of a number of simple processing units (or neurons) linked by weighted modifiable interconnections [30], originally designed to mimic the function of the human brain and applied to quantitative and qualitative analysis during the last two decades [19]. ANNs work by imitating the biological learning task, i.e. requiring a training process where the weights of those connections are adjusted, and build a model that will allow the prediction of the desired parameters (either qualitative or quantitative). Such methods are known as supervised methods; the training data consists of a set of training examples (a fraction of the set cases) which are used to build the model plus the desired output for these cases, viz. the test subset. Thus, the model is built taking into account the parameters that best predict the desired output, whereupon its performance is evaluated employing the remaining cases not used in the training step. The main advantages of ANNs include a high modeling performance tool, particularly suited to non-linear sensor responses, and significant likeness to human pattern recognition.

3. Results and discussion

The characterization of the electrode response towards individual standard solutions of the explosives outlined in this work has been reported recently [8,31]. As guidance, the analytical performance for PETN for example, was a limit of detection of 0.2 ppm and a reproducibility of 4.5% RSD in the determination of a 10 ppm solution. Nevertheless, in there, discrimination between different compounds was not evaluated given the significant overlapping regions between the obtained voltammetric responses of the individual compounds. There, square-wave voltammetry (SWV) coupled with an adsorptive accumulation period was favoured given its improved performance.

In the work reported herein, we demonstrate the combination of CV and chemometric data treatment such as PCA or ANNs to maximize the information extracted from each measurement. This allows the identification of each compound's voltammetric fingerprint and overcomes signal overlapping. Nevertheless, to facilitate data treatment of information contained in each voltammogram, a compression step is required as stated in the introduction [30]. In this report, reduction of the large data record generated for each sample was achieved by means of DWT [25], employing Daubechies wavelet mother function and a fourth decomposition level. This allowed the reduction of signals from each voltammogram down to 82 coefficients without any loss of relevant information, attaining a compression ratio of 93.2%. The obtained coefficients were used to build a model that allows the prediction of the desired parameters, either the qualitative distinction of the different samples or the quantitative resolution of the mixtures composition.

3.1. Qualitative analysis of explosives

Under the conditions described in Section 2.3, a total of 30 samples were analyzed, corresponding to triplicate measurements of 5 explosive compounds (HMX, PETN, RDX, Tetryl, TNT) and triplicate measurements of 5 typical commercial mixtures (C-3, Comp. B, Pentolite, Semtex, Tetrytol), with one complete voltammogram for each sample. Afterwards, responses were preprocessed employing DWT and the obtained coefficients were analyzed by means of PCA analysis and were grouped using cluster analysis tools. After the initial representation of data, an ANN model used with its binary output was used as classifier, which allowed quantification of the classification performance of the system in contrast to the PCA analysis which just provides a visualization of the grouping regions.

Upon completion of the PCA analysis, the accumulated explained variance was calculated with the three first PCs as ca. 94.3%. This large value shows that nearly all the variance contained in the original data can be explained by just using the first new coordinates. Different clusters were obtained and plotted, outlined in Fig. 1; patterns in the figure show evidence that samples are clearly grouped based on explosives mixtures composition. These well established clusters separate the main classes of samples corresponding to: RDX, TNT, PETN, Tetryl, HMX, Semtex H, Comp. B, Comp. C-3, Pentolite and Tetrytol.

Analyzing the plot more thoroughly, some expected trends could be observed; i.e. the fact that clusters corresponding to mixtures are located close to the compounds forming those mixtures. For example, Comp. B samples are clustered between RDX and TNT groups, or Tetrytol samples close to TNT and Tetryl groups, etc. Hence, despite some overlapping regions between the different pure compounds signals are observed, their fingerprints can be still distinguished due to the differentiated sensitivity shown by the electrode. Therefore, these two facts suggest the possibility that even the resolution and individual quantification of explosives compounds from mixtures may be achieved by employing multivariate calibration methods.

To confirm the discrimination of the samples shown in the PCA plot, an actual classifier based on a PCA-ANN model was built. The output of the ANN model was formed by binary predictors

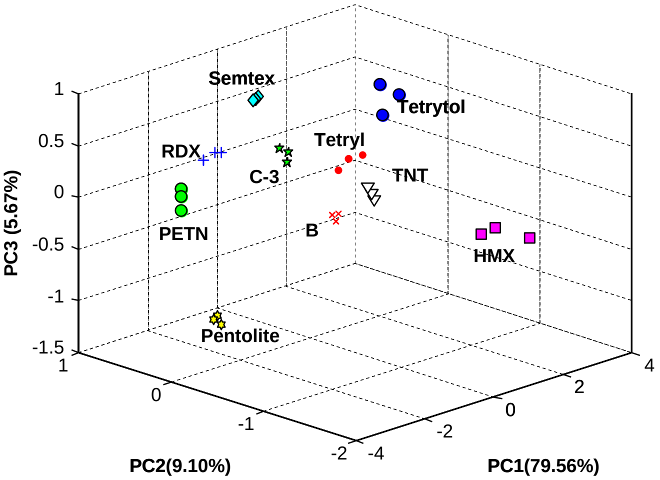

Fig. 1. Score plot of the first three components obtained after PCA analysis. A total of 30 samples were analyzed corresponding to triplicate determinations of: RDX, TNT, PETN, Tetryl, HMX, Semtex H, Comp. B, Comp. C-3, Pentolite and Tetrytol.

(1/0) for each of the classes. As usual, the ANN configuration first needed to be optimized. After some preliminary tests, the final ANN architecture model had 3 neurons (corresponding to the first three components of the PCA, with explained variance accumulated ca. 94.3%) in the input layer, 6 neurons in the hidden layer and 11 binary (1/0) neurons in the output layer (one for each class plus an unknown class) with *logsig* transfer function connecting the three layers. The aim of including an unknown class in the classifier model was to somehow avoid that other explosive compounds could result in a miss-classification [32].

The PCA–ANN model was trained with 67% of the data (20 samples) and evaluated using the information of the testing set (remaining 33% of the data; 10 samples) in order to characterize the accuracy of the identification model and obtain unbiased data. From the classification results, the corresponding confusion matrix was built. Correct classification for all the classes was obtained (i.e., a classification rate of 100% for each of the groups), as indicated from the direct visualization of the PCA analysis. The percentage of correct classifications was estimated, from individual sample calculation in the test subset, as 100%. The efficiency of the classification obtained was also evaluated according to its sensitivity, i.e., the percentage of objects of each class identified by the classifier model, and to its specificity, the percentage of objects from different classes correctly rejected by the classifier model. The value of sensitivity, averaged for the classes considered, was 100%, and that of specificity was 100%.

3.2. *Quantitative analysis of explosive mixtures*

Table 1 shows that while even the most common commercial mixtures were distinguished in the previous section, variations of the commercial formulations may lead to erroneous identification of substances or wrong authorizations of hazardous products. That is, the detection of IEDs, where qualitative analysis may result in a miss-classification or improper identification. Hence, it may be more useful to achieve the quantification of the individual compounds which form the mixture, which, in addition to qualitative identification of the explosive itself, would further allow the quantification of the amount of explosive material present. The most common explosive compounds encountered commercially are RDX, TNT and PETN; therefore, their quantification would allow the detection of the majority of commercial mixtures.

In order to prove the capabilities of the proposed approach to achieve the quantification of the explosive compounds, besides the qualitative identification of the commercial explosive, mixtures of the main common compounds (i.e. RDX, TNT and PETN) were analyzed. As before, mixtures were prepared and analyzed by means of CV, obtaining an entire voltammogram for each sample. The voltammograms, as before, were compressed employing DWT and obtained coefficients were used as inputs in an ANN model which implemented the quantification of the compounds overcoming signal overlapping [33].

Fig. 2 shows some of the obtained voltammograms for the different mixtures of explosive compounds. Concretely, Fig. 2(a) shows the voltammograms of the individual explosive compounds, and Fig. 2(b) outlines the voltammetric signature of different mixture ratios of these three compounds. Complex and highly overlapped signals are observed along the whole voltammogram, although some characteristic features of each compound response are still observed; e.g. cathodic peak around −1.0 V due to the reduction of TNT and/or RDX nitro groups. This data, with marked distinct features and sensitivity for the different analytes, is an ideal departure point to be used in an ANN application.

The first step in building the ANN model is selecting the topology of the neural network used. This is a trial-and-error process where several parameters (training algorithm, number of hidden layers, number of neurons, transfer functions, etc.) are fine-tuned in order to find the best configuration that optimizes the performance of the model [30]. Upon completion of an extensive study varying its configurations, the final ANN architecture had 82 neurons (corresponding to the coefficients obtained from the DWT analysis) in the input layer, 5 neurons and *tansig* transfer function in the unique hidden layer and 3 neurons and *purelin* transfer function in the output layer (one for each compound). Despite the number of neurons used in the input layer, only a few seconds of calculation were required for the construction of the model.

The accuracy of the generated model was then evaluated towards samples on the external test subset by using it to predict the concentrations of explosives on those samples. Subsequently, comparison graphs of predicted *vs.* expected concentration for the three compounds were built, both for training and test subsets, to easily check the prediction ability of the obtained ANN model (Fig. 3). A satisfactory trend is obtained for the three compounds observed in Fig. 3, with regression lines almost indistinguishable from the theoretical ones. Also, as is usual in ANN models, lower dispersion and uncertainties are obtained for the training subsets, as expected taking into account that the external test subset data is not

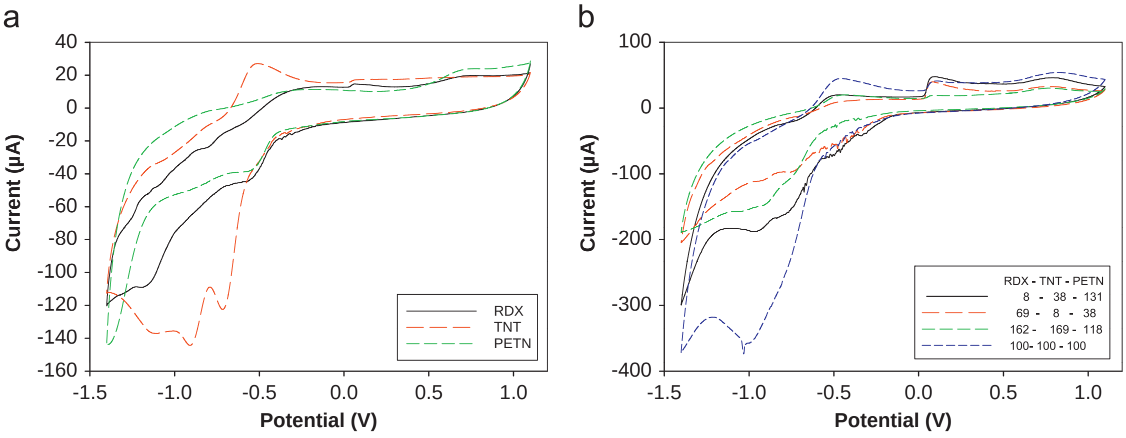

Fig. 2. Example of the different voltammograms obtained for (a) 50 µg mL^{-1} standard solutions of each of the three explosive pure compounds under study and (b) certain arbitrary mixtures of the three explosive compounds (all concentrations are expressed in µg mL^{-1} and correspond to RDX, TNT and PETN, respectively). Conditions: CV: $E_{start/end}=+1.1$ V; $E_{second}=-1.4$ V; $E_{step}=4$ mV, scan rate: 100 mV s^{-1}; Medium: 50 µL 0.05 M PBS pH 6.5+50 µL ACN. Note: no accumulation before and during measurement.

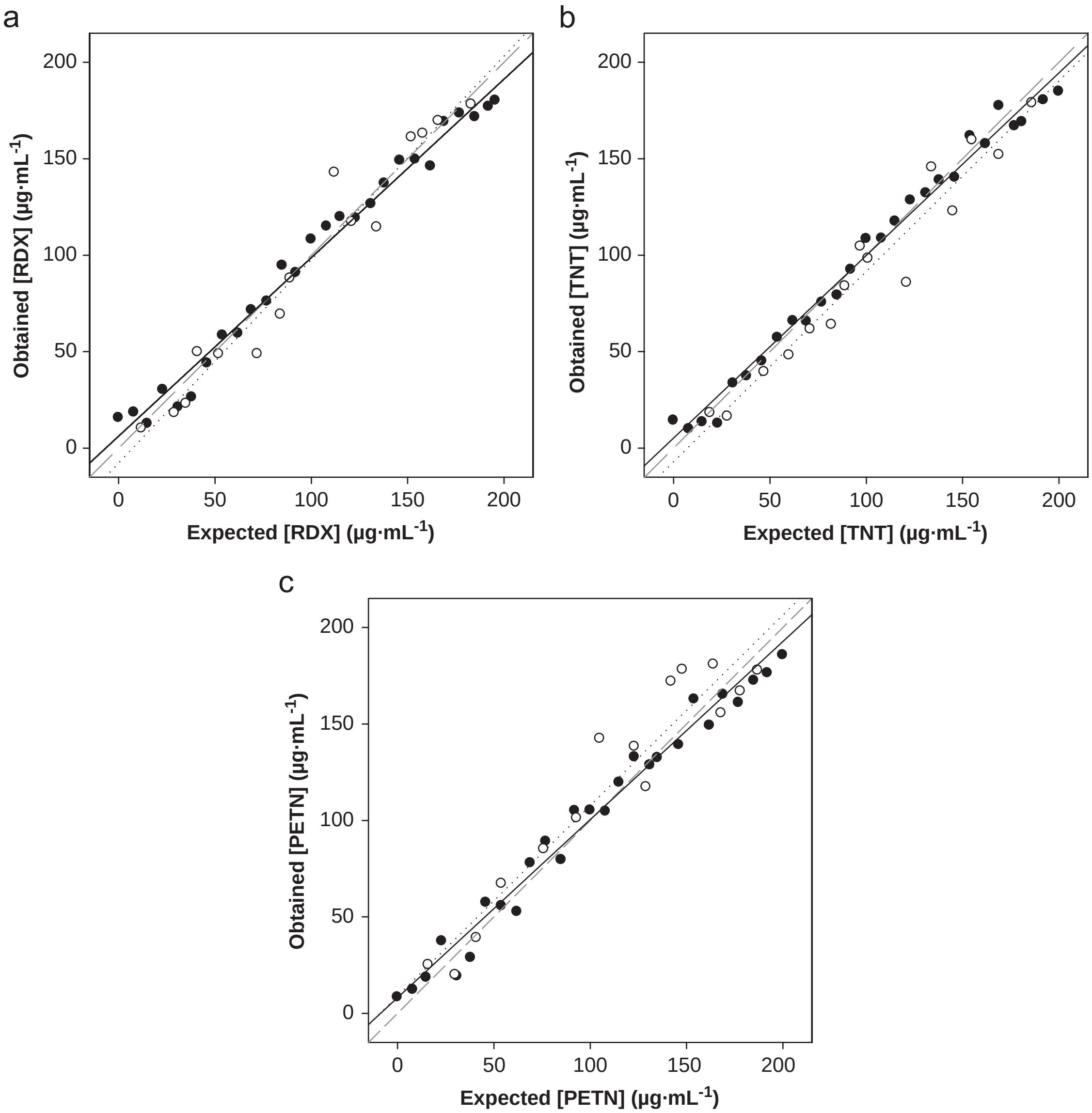

Fig. 3. Modeling ability of the optimized ANN. Sets adjustments of obtained *vs.* expected concentrations for (A) RDX, (B) TNT and (C) PETN, both for training (●, solid line) and testing subsets (○, dotted line). Dashed line corresponds to theoretical diagonal line.

employed at all for the modeling, so its goodness of fit is a measure of the accomplished modeling performance.

Table 3 summarizes the resulting regression parameters. As expected from the comparison graphs, a good linear trend is attained for all the cases, but with improved correlation coefficients in the training subsets due to the lower dispersion. Despite this, the results obtained for both subsets are close to the ideal values, with intercepts close to 0, and slopes and correlation coefficients close to 1.

Therefore, it has been demonstrated that the combination of CV with chemometric tools is an analytically powerful approach for the characterization and detection of individual explosive substances and its mixtures commercially available. This is particularly useful since it does not only allow the identification of typical commercial mixtures, but also the quantification of the amount present and the ratio of the mixtures analyzed. Hence, in this manner home-made nitro-containing explosives and IEDs might be properly identified; this represents a major advantage compared to the qualitative approach.

We therefore present this tool as an attractive alternative to other classical methods for security screening of explosives. We propose this as a qualitative a method to provide the identification of the voltammetric fingerprint of different explosive mixtures commercially or otherwise manufactured, such as home-made mixtures/IEDs.

With the same experimental setup, the approach proposed herein may be alternatively applied for the quantification of analogous or different explosive mixtures, even quaternary or more complex mixtures, with a proper retraining set of samples. This is due to if the specific compound is not included in the set of samples used to build the model, it might not be able to extrapolate its presence, while in addition it could originate certain errors in the estimation of the rest of compounds. However, as it has also been demonstrated by recent works from our laboratory [34], the use of mutliway processing methods, thanks to their "second order advantage" permits even the correction of the presence of an interfering species, even if not initially considered in the response model.

This represents a viable system with significant promise for in-field measurements given its simplicity, rapidity and portability. Furthermore, next step will also be the implementation of the ET approach as defined; i.e. coupling the responses obtained from an array of sensors with marked mix-response towards the desired species and applying the same chemometric data treatment.

Table 3
Results of the fitted regression lines for the comparison between obtained *vs.* expected values, both for the training and testing subsets of samples and the three considered explosive compounds (intervals calculated at the 95% confidence level).

Explosive	Correlation	Slope	Intercept (μg mL^{-1})	NRMSE	Total NRMSE
Training subset					
RDX	0.992	0.925 ± 0.048	6.20 ± 5.61	0.067	0.065
TNT	0.994	0.954 ± 0.043	3.83 ± 5.06	0.053	
PETN	0.989	0.916 ± 0.056	7.65 ± 6.57	0.073	
Testing subset					
RDX	0.976	1.054 ± 0.141	-7.65 ± 15.52	0.078	0.093
TNT	0.973	0.987 ± 0.142	-7.07 ± 15.81	0.088	
PETN	0.958	0.988 ± 0.177	8.85 ± 21.77	0.110	

NRMSE: Normalized Root Mean Square Error.

Nevertheless, to fully achieve the correct identification of almost all types of explosives, application of the proposed approach to the detection of peroxide-based explosives is still required. Its increasing use has led to considerable research into the detection of this group of improvised explosive substances; the challenge being that many current chemical identification techniques are based on the nitrogen and carbon content of a substance for identification and this practice is not suitable for peroxide explosive. Besides, its detection is more complex due to the fact they do not fluoresce, have minimal UV absorption and a lack of nitro groups -all necessary parameters upon which traditional detection techniques are based [2]. In this context, electrochemical sensors offer an opportunity to detect peroxide-based explosives that would otherwise prove problematic.

4. Conclusions

In this work, we have demonstrated that the use of a single, bare, graphite SCPE is sufficient for the generation of distinct electrochemical signatures for commonly used nitro-containing explosives. Analysis of samples was based on the combination of cyclic voltammetry that offers fingerprints of the individual components and mixtures of these species, along with chemometric tools employing electronic tongue principles that allow resolution of signal overlapping and extraction of the characteristic fingerprints. Specifically, preliminary distinction of most common compounds and mixtures has been achieved by means of Wavelet transform + principal component analysis, with automated identification employing an ANN as the classifier; in a further approach, resolution and quantification of the mixtures composition was achieved employing a Wavelet transform + ANN model. In this sense, such strategy would allow field detection for major explosives (commercial or home-made) to be performed rapidly, reliably, and inexpensively, and should thus facilitate decentralized security screening applications.

Finally, future efforts with this approach may involve the detection of peroxide-based explosives given their increasing use in recent years, thereby obtaining a system capable of detecting almost all types of explosives.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.12.042.

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