

# Voltammetric Electronic Tongue for the Sensing of Explosives and Its Mixtures

Andreu González-Calabuig and Manel del Valle

**Abstract** This chapter presents recent work with electronic tongues, that is sensor analytical systems formed by an array of chemical sensors featuring low selectivity plus a chemometric tool to process the complex multivariate data that is generated. As the generic application covered is related to security, the described systems are those devised to identify and detect explosive compounds. These are characterized from their voltammetric features, whereas a particular fingerprint is used to identify particular compounds alone, or, in a more advanced application, to resolve mixtures of compounds, that is to quantify their presence in mixtures. Two are the main approaches shown, a first from the use of a voltammetric screen printed electrode, and a second one from an array of metallic electrodes. Detected compounds are different nitro-based energetic compounds, and later, also the identification of organic peroxide type compounds.

**Keywords** Electronic tongues · Voltammetry · Principal component analysis · Artificial neural networks · Explosives

## 1 Introduction

Concerns relating to homeland security have given rise to increased research into explosive detection as well as further developments for existing analytical techniques to enable faster, more sensitive, less expensive and simpler determinations to facilitate the trace identification of explosives.

Traditional security measures at airports include the use of metal detectors to identify concealed weapons in conjunction with X-ray machines to inspect baggage. One major problem is that explosive substances are not easily detectable using conventional approaches and that in this context terrorist groups may avoid

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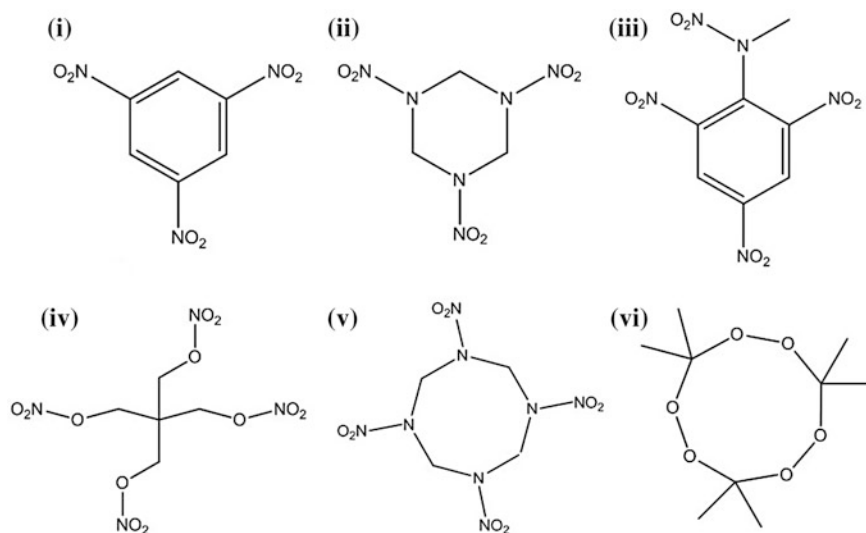
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the use of metallic objects. Approaches to detect volatile substances, such as ion mobility spectrometry in conjunction with swabbing, whilst in routine use, are largely only suitable for the screening of items of hand baggage.

Research in connection with security has received increased attention, through both the development of new, innovative detection approaches and through the improvement of existing techniques. The most commonly used techniques include Ion Mobility Spectrometry (IMS), Mass Spectrometry (MS), and Gas Chromatography (GC) followed by detection using a sensitive detector. Most of these devices are, however, rather bulky, expensive, and require time-consuming procedures. Over those, IMS is one of the most widely adopted detection techniques in routine use due to its ability to characterise the sample both qualitatively and quantitatively. 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 use. Thus, to ensure security over those scenarios, mass deployment of miniature sensors that are sufficiently sensitive and selective, inexpensive, and amenable for mass production may be required.

Explosive compounds are widely used in warfare, mining industries, civil constructions as well as terrorist attacks. Those are categorized in four major classes: nitroaromatics, nitroamines, nitrate esters and peroxides according to their chemical structures, as schematized on Fig. 1 [1]; from there, the most widely used being 2,4,6-trinitrotoluene (TNT) or 1,3,5-trinitroperhydro-1,3,5-triazine (RDX). Among them, special attention must be paid to peroxide explosives since those compounds contain neither nitro groups nor aromatic functionalities, what makes them difficult to be detected with the more established analytical methods used to determine explosives [2]. That is, the challenge is that many current chemical identification techniques are based on the nitrogen and carbon content of a substance for its identification, and this practice is not suitable for peroxide explosive. Furthermore, the peroxide explosives are also not suitable for UV detection [3] because of their lack of chromophores and their instability under illumination of UV light—all necessary conditions for traditional detection procedures.

As an alternative, electrochemical devices are advantageous for addressing the growing need for detection of various explosives, satisfying previously described requirements [4]. In this direction, previous attempts were made to voltammetrically detect the aforementioned compounds employing different types of electrodes such as a bare screen printed electrode (SPCE), unmodified or modified gold electrodes and modified glassy carbon electrodes (GCE). Although the detection of such compounds can be achieved even at very low concentration levels, the main challenge now is that common real-life explosives are usually mixtures of two or more different explosive species. Therefore, it is interesting to discriminate between individual compounds and to resolve their mixtures.



**Fig. 1** Chemical structures of important explosive compounds commercially available or used in terrorist acts. The different nitro- compounds (i) 2,4,6-trinitrotoluene (TNT); (ii) 1,3,5-trinitroperhydro-1,3,5-triazine (RDX); (iii) N-methyl-N,2,4,6-tetranitroaniline (Tetryl); (iv) Pentaerythritol tetranitrate (PETN); (v) octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and the peroxy- type (vi) triacetone triperoxide (TATP)

On the other hand, voltammetric signals produced by these electrochemical methods correspond normally 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, to correctly discover the relationships among all variables and samples efficiently and to overcome the limitations found when analyzing the data using only one or two variables at a time, it would be desirable to process all of the data simultaneously, in this case with help of chemometrics. Chemometrics is the discipline for extracting information from multivariate chemical data using tools of statistics and mathematics. In our case, the used techniques will be divided into two classes depending on the nature of the extracted information, either qualitative methods such as principal component analysis (PCA), linear discriminant analysis (LDA) or quantitative ones such as partial least squares (PLS) or artificial neural networks (ANNs).

The methodology needed for this kind of work consists, then, of two main parts: the development of the (bio)sensors responding to the species sought and the use of the processing tools for the data treatment. In the case of sensors, different alternatives, which will be detailed later, have raised; however, in all cases, voltammetric sensors are the preferred technology if explosives are the target analytes. In the case of the processing tools, the concept and principles of electronic tongues

will be used, which are a new relatively concept in analytical chemistry and on which our group has a wide experience [5].

These two blocks will also mark the roadmap of any investigation in this area. At an early stage we will mainly focus in the construction of the sensors first with response towards the nitro and later to the peroxy compounds. After the selection of the sensors that will be part of the electronic tongue, the different data treatment options will be evaluated; finally, the applications will be devised, in which it can be the detection of explosive presence, the identification of different types of explosives and the resolution and quantification of mixtures of different explosive substances, alone or in mixtures.

### ***1.1 Detection of Explosives by Simple Voltammetry***

As already mentioned, the development of electrochemical sensors for the detection of explosive substances provides significant benefits and is experiencing constant growth [6]. The main advantages of these types of sensors for on-field detection include its high sensitivity and selectivity, a wide linear range, minimal space and power requirements, and low-cost instrumentation. Moreover, both the sensor and the instrumentation can be readily miniaturized to yield compact and user-friendly hand-held meters for on-site (indoor and outdoor) testing [7].

In voltammetric sensors, there is a sweep in the potential applied to the working electrode to generate an electron transfer reaction (usually the reduction) of the explosive substance of interest, during which the current is measured. 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 voltammetric monitoring. What is needed, is to obtain their particular voltammetric fingerprint, which is text used for its identification. Hence, electrochemical devices represent a promising solution for on-site explosives detection.

Upon selection of the measuring technique, the next step is the evaluation of the different strategies/technologies for the obtention of the sensor array that will allow the detection of the explosive compounds. In this direction, the most feasible options are the use of:

- Composites, in this case based on conductive phases dispersed in polymeric matrices. These materials combine the electrical properties of graphite with the ease of processing of plastics (epoxy, methacrylate, Teflon, etc.) and show attractive electrochemical, physical, mechanical and economical features compared to the classic conductors (gold, platinum, graphite, etc.) [9]. The main advantages derived from the use of composites include their ability to integrate different materials that allow to improve the sensitivity and selectivity, the flexibility in size and shape that they bring to their manufacture, the possibility of polishing its surface to obtain fresh material for the next measurements (obtaining reproducible results due to the composition of the “composite” being

homogeneous), higher S/N ratio compared to pure conductors, which allows lower detection limits to be achieved, etc. The electrodes in the sensor array may incorporate catalysts, conducting polymers or nanoparticles in the composite formulation, according to existing knowledge, in order to display differentiated response.

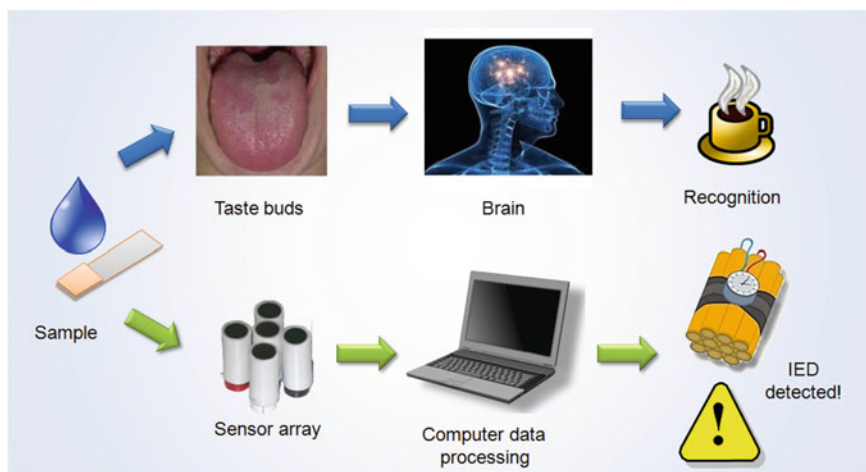
- Screen Printed Electrodes (SPEs), which allow the miniaturization of the previous described system through the use of screen printed electrodes instead of bulk composite electrodes; increasing in this manner, the portability of the system, allowing disposable use, reducing the amount of sample required and the manufacturing cost [10].
- Electropolymerized conducting polymers [11]. The high application potential of conducting polymers in chemical and biological sensors is one of the main reasons for the intensive investigation and development of these materials. Although conducting polymers show almost no conductivity in the neutral (uncharged) state, their intrinsic conductivity results from the formation of charge carriers upon oxidizing (p-doping) or reducing (n-doping) their conjugated backbone. A process that can be done electrochemically, which additionally provides fine tuning of the doping level by adjusting the electrical potential. Moreover, sensitivity of conducting polymers to organic molecules (explosive compounds in our case) can be fine tuned based on the intrinsic affinity of the polymer backbone, on the affinity of side groups or on binding to immobilized receptors.
- Molecularly Imprinted Polymers (MIPs), also known as artificial antibodies, are polymers formed in the presence of the molecule that we aim to determine (template) and that at a later stage is removed, leaving a complementary cavity in the polymer with affinity to the chosen template molecule [12]. Such polymers present a high affinity towards the template molecule and can be used to manufacture sensors with a similar recognition mechanism to antibodies, therefore with a very high selectivity. Molecular imprinting is, in fact, making an artificial tiny lock for a specific molecule that serve as miniature key. Integration of MIPs with voltammetric sensors is feasible when the detected molecules are electroactive, which is the selected case. Adsorptive stripping techniques will be the ideal choice for improving detection limits to the sub-ppb level.
- Molecularly imprinted Au nanoparticle composites. The idea in the construction of these sensors is very similar to the previous one, but replacing the polymer with gold nanoparticles [13]. The imprinting process involves the electropolymerization of thioaniline-functionalized gold nanoparticles on a thioaniline monolayer-modified electrode in the presence of a carboxylic acid, acting as a template analogue for the respective explosive. Then, the high affinity of gold with thiol groups lead to the formation of an array of gold nanoparticles (similar to the polymer matrix) in which cavities might be also generated due to the presence of the template molecule.

## 1.2 Improvement of Voltammetric Results with Use of Chemometrics

After the data collection task, which typically involves several measurements made on many samples, the next step is data processing. Voltammetric multivariate data has traditionally been analyzed using one or two variables at a time. However, this approach fails to discover the relationships among all variables and samples efficiently. To overcome this, we must process all of the data simultaneously, in this case with the help of chemometrics [14]. Therefore, in order to extract useful information from what is not, and be able to interpret the data so they can be used in useful prediction models, the use of multivariate processing tools such as in the case of electronic tongues is required.

Electronic tongues are inspired by the sensory ability of taste in mammals, where a few receptors can respond to a large variety of substances [5]. This principle functions thanks to the complex data treatment applied in the brain, which allows the quantification or classification of a large amount of substances. These biomimetic systems, opposed to conventional sensing approaches, are directed towards the combination of low selectivity sensors array response (or with cross response features) in order to obtain some added value in the generation of analytical information. Moreover, once implemented and trained, the usage of such systems facilitates its implementation as a screening/monitoring device since it does not require of any technician presence. The pictorial concepts intervening in an electronic tongue are sketched on Fig. 2.

Multivariate analysis techniques allow disclosing the contribution of different factors in a result [15]. These factors are related to the explanatory variables of the system; in the case of electronic tongues these variables are usually determined



**Fig. 2** The use of electronic tongue principles for the on-site detection of explosives and IEDs

experimentally and are related to each of the sensors' signals, while the response variable is related to the presence of a compound or the concentration value to be determined. The proposal and development of various methods based on mathematical, statistical and formal logic calculations are intended to establish procedures that allow to perform tasks such as the discrimination, quantification, classification and systems modelling trying to use the most relevant information from the analytical data available. On that account, data analysis and pattern recognition are a fundamental part of any electronic tongue system [5]. For the modelling, first, the data is preprocessed in order to make it independent from units, remove redundant information and to enhance signal-to-noise ratio. Following this, the model describing the relation between readings and outputs is then created. A known problem when voltammetric sensors are used is the large dimensionality of the generated data which hinders their treatment, that is, when a complete voltammogram is recorded for each sensor from the array. This is perhaps the main reason why this approach is not the most frequently used in the literature; especially if ANNs are to be used, in which case departure information needs to be preprocessed. Although signal preprocessing is not always strictly necessary (e.g. the whole data set may be employed in the case of PLS or PCA), it has been demonstrated that even in these cases, its use improves model predictive behaviour. In this sense, an attractive solution when dealing with a set of voltammograms is the use of a preprocessing stage for data reduction prior to modelling [5, 16]. The main objective of this step is to reduce the complexity of the input signal preserving the relevant information and making it compatible with ANN or other numeric modellers, which facilitates an advantageous reduction in training time, to avoid redundancy in input data and to obtain a model with better generalization ability. This compression stage may be achieved by the use of methods such as PCA [17], feature selection [18], "kernels" [19], discrete wavelet transform (DWT) [20] or even fast Fourier transform (FFT) [21].

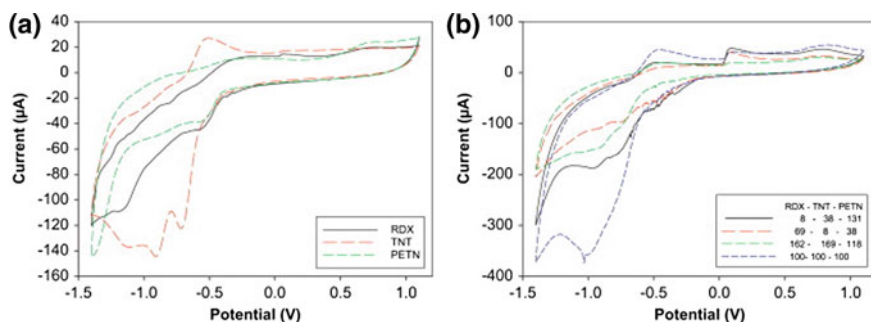
After applying the desired preprocessing method, the next step is the modelling of the target variables using the obtained coefficients as inputs into the model stage. Among the various numeric procedures that can be implemented, PCA, PLS and ANNs are the most widely used for electronic tongue applications [5, 22]. Concretely, PCA is the most common one being used either as a qualitative visualization tool or as a preprocessing step; whereas most advanced qualitative modelling may be achieved with the use of PLS discriminant analysis (PLS DA), linear discriminant analysis (LDA) or support vector machines (SVM) [23]. While in the case of quantitative applications, easier models can be built either using multiple linear regression (MLR) or principal components regression (PCR), although better results can be achieved by using more powerful methods such as PLS or ANNs. Lastly, the new trends in data analysis are mainly related to the use of trilinear approaches such as PARAFAC for qualitative analysis, and multi-way PLS (nPLS) for quantitative models.

## 2 Systems Using a Single Sensor

A first attempt to perform the detection of explosive compounds involving the coupling of electrochemical measurements and advanced chemometric data processing was realized from voltammetric signals obtained at a disposable carbon electrode, and with use of proper chemometric tools. 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) were identified as individual energetic chemicals, and next, a quantitative application was also illustrated with the resolution of their trinary mixtures.

Screen printed electrodes (SPCE) were prepared following the conventional methodology previously described [8]. The electrochemical cell was formed by a carbon working electrode, a carbon counter electrode and a silver pseudo-reference electrode. Cyclic Voltammetry (CV) was the technique employed and a new electrode was used for each sample. Figure 3 shows some of the obtained voltammograms for the different mixtures of explosive compounds, as can be seen complex and highly overlapped signals were observed. This kind of signals, which exhibit different sensibility and selectivity, are an ideal departure point to be used in an ANN application.

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, also mixtures based on usual commercial formulations were also prepared and measured. Hence, in this manner 10 different explosives mixtures were considered, the concentration of explosives was kept at 50 ppm for the case of pure compounds like TNT, RDX, HMX, Tetryl and PETN. For the commercial explosive mixtures like Semtex H (RDX:PETN at 1:1 ratio), Comp. B (RDX:TNT at 3:2 ratio), Comp. C-3 (RDX:TNT:Tetryl at 23:1:1 ratio), Pentolite (TNT:PETN at 1:1 ratio) and Tetrytol (TNT:Tetryl at 3:7 ratio) the total explosive concentration was



**Fig. 3** Example of the voltammograms obtained for (a)  $50 \mu\text{g}\cdot\text{mL}^{-1}$  standard solutions of each of the three explosive compounds under study and (b) mixtures of the three explosive compounds (all concentrations are expressed in  $\mu\text{g}\cdot\text{mL}^{-1}$ ). Reprinted from [24], with permission from Elsevier



kept at 50 ppm.. All samples were prepared in triplicate and randomly measured employing a new sensor each time. Therefore, the set of samples under study was formed by 30 samples distributed in 10 different classes.

It is important to note that DWT was used as the feature extraction tool; PCA was used for qualitative analysis of the results, while quantitative analysis and classification was achieved by means of ANNs. DWT is a high performance signal processing technique developed inspired in the Fourier transform, with the key advantage over the latter of its temporal resolution: it captures both frequency and location information (location in time). DWT is used for signal decomposition onto a set of basic functions, obtained from dilations and translations of a unique function called mother wavelet, the most commonly used being Daubechies wavelet [25]. Transform is implemented using Mallat's pyramidal algorithm [26], which operates over a single discrete signal of length  $M$  by decomposing it into orthogonal subspaces of length ca.  $M/2$  in each step [20]. In this way, by repeating this decomposition process  $n$  times, the signal compression ratio is increased at the expenses of the accuracy in the signal reconstruction.

Principal Component Analysis (PCA) allows the projection of the information contained in the original variables onto a smaller number of latent variables called principal components (PCs) with new coordinates called scores, obtained after data transformation. Plotting the PCs, one can view interrelationships between different variables, and detect and interpret sample patterns, groupings, similarities or differences [17]. As the PCA only is a visualization tool it has to be coupled with a modeling tool to be used as a classifier.

ANNs are excellent modellers, that consist of a number of simple processing units (also called neurons) linked by weighted modifiable interconnections [27], originally designed to mimic the function of the human brain. ANNs work by imitating the biological learning task, requiring a training process where the weights of those connections are adjusted, to build a model that will allow the prediction of the desired parameters. 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 an external set used to evaluate the performance of the model, the test subset. The main advantages of ANNs include a high modelling performance tool, particularly suited to non-linear sensor responses, and significant likeness to human pattern recognition [5].

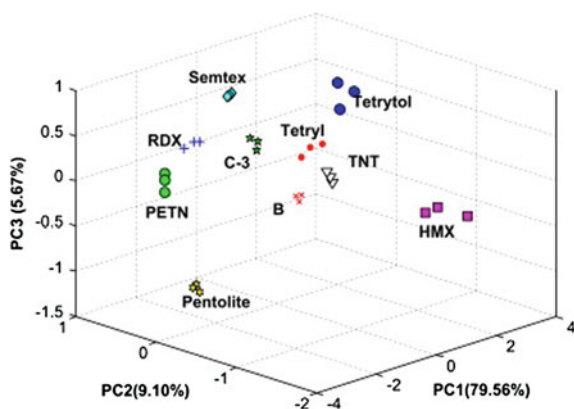
The combination of CV and chemometric data treatment such as PCA or ANNs allowed the identification of each compound's voltammetric fingerprint and solved the problem of signal overlapping. To facilitate data treatment of information contained in each voltammogram, a compression step was selected [30]. In this specific case the reduction of the large data generated was achieved by means of DWT [20]. This allowed the reduction of signals from each voltammogram down to 82 coefficients without any loss of relevant information and achieving a compression ratio of 93.2 %. The obtained coefficients were used to build a model that predicts the desired parameters, either the discrimination of different samples or the quantitative resolution of the mixtures composition.

As was previously commented 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.

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. 4; in this, observed patterns show evidence that samples are clearly grouped based on explosives mixtures composition.

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 pure 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.

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



**Fig. 4** 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). Reprinted from [24], with permission from Elsevier

PCA) 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 misclassification [28].

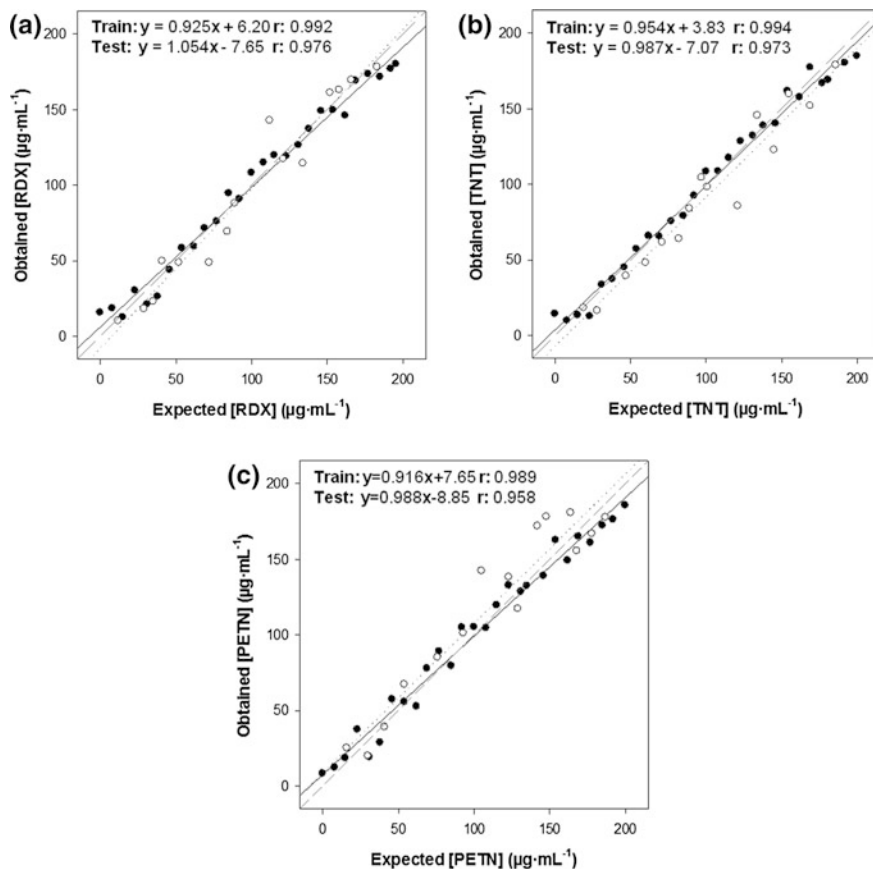
The PCA-ANN model was trained with 67 % of the data (20 samples) and evaluated using the information of the testing set (remaining 33 % of the data; 10 samples) in order to characterize the accuracy of the identification model and obtain unbiased data. From the classification results, the corresponding 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 %.

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  $\mu\text{g}\cdot\text{mL}^{-1}$  for each of the nitro-containing explosive compounds. 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 [18]; plus 15 additional samples (36 %) for the testing subset, randomly distributed along the experimental domain, and used to evaluate the model's predictive response.

In order to prove the capabilities of the approach to achieve the quantification of the explosive compounds, in addition to the qualitative identification of the commercial explosive, mixtures of the main constituents (i.e. RDX, TNT and PETN) were analyzed by means of CV. The voltammograms, as before, were compressed employing DWT and obtained coefficients were used as inputs to an ANN model [29].

The first step in building the ANN model is selecting the topology of the network used. This is a trial-and-error process where several parameters (number of neurons, transfer functions, etc.) are fine-tuned in order to find the best configuration that optimizes the performance of the model [27]. 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 hidden layer and 3 neurons and purelin transfer function in the output layer (one for each compound).

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



**Fig. 5** Modeling ability of the optimized ANN. Sets adjustments of obtained versus 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. Figure adapted from [24], with permission from Elsevier

check the prediction ability of the obtained ANN model (Fig. 5). A satisfactory trend is obtained for the three compounds observed in the figure, with regression lines almost indistinguishable from the theoretical ones. 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 employed at all for the modeling, so its goodness of fit is a measure of the model performance.

The figure also displays the resulting regression parameters of the obtained vs. expected 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 ca. 0, and slopes and correlation coefficients ca. 1.

In this way, it has been demonstrated how 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. In this manner home-made nitro-containing explosives and IEDs might be properly identified; this represents a major advantage compared to the qualitative approach.

The proposed sensor coupled with chemometrics represents a qualitative method to provide the identification of the voltammetric fingerprint of different explosive mixtures commercially or manufactured, such as IEDs. This represents a viable system with significant promise for in-field measurements given its simplicity, rapidity and portability. 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. In this context, electrochemical sensors offer an opportunity to detect peroxide-based explosives that would otherwise prove problematic.

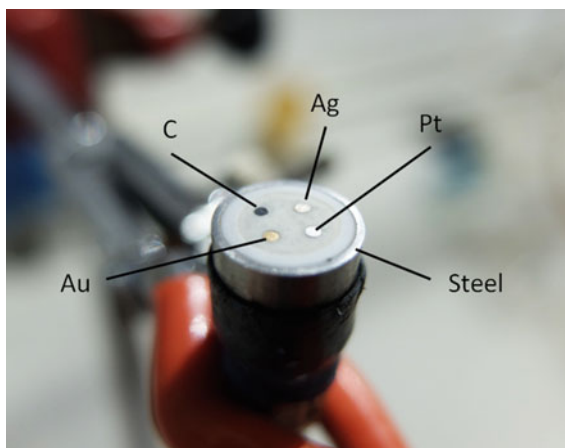
### 3 Systems Using a Sensor Array

In a second application study, a voltammetric electronic tongue (ET) was developed towards the simultaneous determination of both nitro-containing and peroxide-based explosive compounds, two families that represent the vast majority of compounds employed either in commercial mixtures or in improvised explosive devices. The electronic tongue was formed by a multielectrode array constituted by graphite, gold and platinum electrodes, which exhibited marked mix responses towards the compounds examined; namely RDX, HMX, PETN, TNT, Tetryl and triacetone triperoxide (TATP).

In this particular study, our aim was to obtain a miniaturized sensor array. Thus the use of a quatrielectrode with inner counter and reference electrodes was proposed. Platinum, silver, gold and epoxy-graphite 1 mm diameter discs were used as electrodes. The metal electrodes were fabricated from its metal wires, the epoxy graphite electrode was done mixing epoxy and carbon; the electrodes were encased in inert epoxy resin using a PVC tube as the body [30].

To complete the electrochemical cell, a stainless steel tube was glued to the cylinder multi-electrode and used as a counter electrode while, the Ag electrode was converted into a Ag/AgCl pseudo-reference electrode. Figure 6 illustrates the design of the quatrielectrode used. Thus, with this adaptation all the electrodes are integrated in a small device suitable to be used in field applications, which in turn

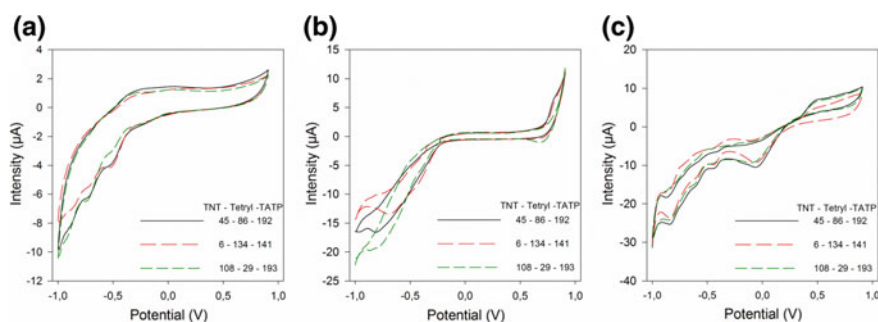
**Fig. 6** Quatrielectrode used during the measurements



allows using a smaller sample volume, also making possible to perform drop analysis.

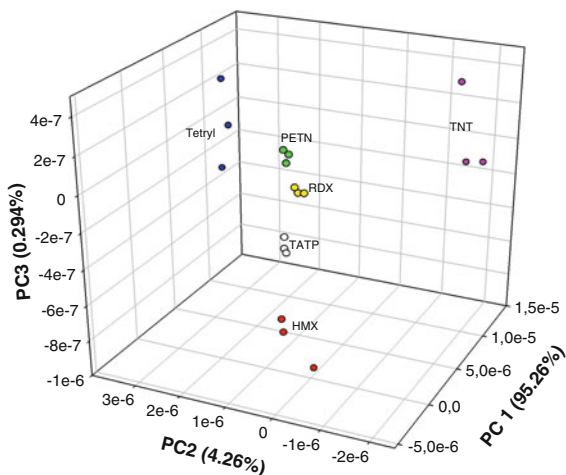
As in the previous case, the set of samples was measured employing the multi-electrode array to obtain a whole cyclic voltammogram for each of the sensors. The electrochemical measurements were carried out at room temperature (25 °C) under quiescent conditions. Some of those results are shown on Fig. 7. As can be seen, complex and overlapped signals are obtained along the whole voltammogram with differentiated signals obtained for the different kinds of sensors; this situation is ideal to implement the electronic tongue approach.

In a first experiment, discrimination of different explosive compounds by means of the electronic tongue was attempted. That is, to asses if the system presented herein was able to carry out the identification of the most common explosive compounds. For such purposes, we measured 18 samples, corresponding to 3 replicates of each explosive compound (RDX, HMX, TNT, TATP, PETN and tetryl).



**Fig. 7** Cyclic voltammograms for arbitrary mixtures of the three explosive compounds (all concentrations are expressed in  $\mu\text{g}\cdot\text{mL}^{-1}$ ) for the graphite epoxy electrode (a), gold electrode (b) and platinum electrode (c)

**Fig. 8** Score plot of the first three components obtained after PCA analysis



To this aim, voltammetric responses obtained for the stock solutions of each of the pure compounds were analyzed by means of PCA and grouped using cluster analysis tools.

Upon the completion of the PCA analysis (Fig. 8), the accumulated explained variance was calculated with the three first PCs as ca. 99.81 %. This large value shows that nearly all the variance contained in the original data can be explained by just using the first new coordinates. In addition, patterns in the figure evidence that samples are clearly grouped based on each explosive compound, with replicas for the same class one to each other. Moreover, the low dispersion of PETN, TATP and RDX clusters shows a more reproducible behaviour. Nevertheless, despite the bigger dispersion obtained for the others compounds there is no overlap between clusters.

After the initial representation of the data, a fuzzy ARTMAP ANN model with binary inputs (1/0) was used as classifier, which allowed quantification of the classification performance system in contrast to PCA analysis which just provides a visualization of the grouping regions.

The PCA-ANN model was trained with the 67 % of the data (12 samples) and evaluated using the information of the testing set (remaining 33 % of the data; 6 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 visualizations of the PCA. 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 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

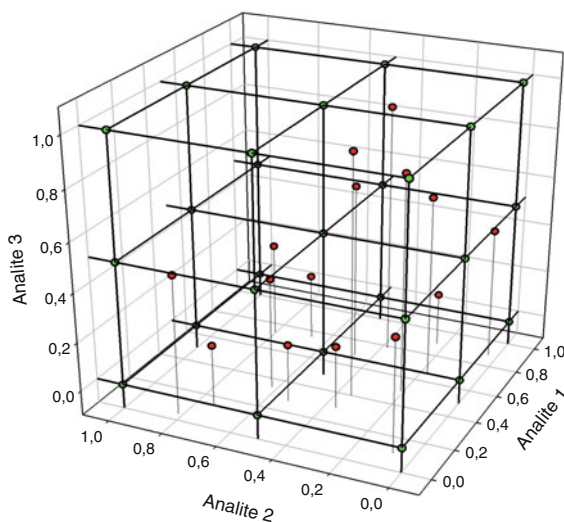
sensitivity, averaged for the classes considered, was 100 %, and that of specificity was 100 %.

Next, a quantification study case was also attempted. When designing an experiment involving quantification of compounds, a first consideration is the definition of the experimental domain, i.e. the range of concentrations for each analyte of interest. In our case, the experimental design used for the construction of the ANN model was a factorial design with three levels and three analytes ( $3^3$ ) which gives a total of 27 samples used to build the model (training subset). Once defined our experimental design and the number of samples required to build the model, its performance will be evaluated with an external subset of samples (testing subset). Those test samples are randomly distributed along inside the limits of the experimental domain as can be seen in Fig. 9. In this case the concentration ranged from 0–165  $\mu\text{g}\cdot\text{mL}^{-1}$  for TNT and tetryl, and 0–300  $\mu\text{g}\cdot\text{mL}^{-1}$  for TATP; 10 random samples were used for the testing subset.

A known problem when voltammetric sensors are involved is the large dimensionality of the generated data (samples  $\times$  sensors  $\times$  polarization potentials) which hinders their treatment: especially if ANNs are to be used, in which case departure information has to be preprocessed. In this fashion, prior to building the quantification model the removal of less significant coefficients that barely contribute to the network was carried out by means of causal index (CI) pruning inputs [16, 31].

Briefly, CI is based on the usage of ANNs as feature selection tools, aimed to the selection of an optimal set of inputs that can successfully classify or predict the desired outputs. To this end, an ANN model is built employing the whole set of variables, followed by the determination of the contribution and relevance of each of the network inputs to the variance in the output layer. This can be achieved with the analysis of its connection weights, which allows to easily identifying the

**Fig. 9** Factorial design  $3^3$ : training subset (*green*) and test subset (*red*)





important inputs since inputs that make relatively small contributions indicate that the input does not change significantly; and therefore, can be discarded, viz. pruned. Afterwards, selection of the most relevant inputs can proceed until a near-optimal, small, set of inputs is identified by repeating the training process of the ANN model with the reduced input set and selecting the most relevant ones each time. Finally, once the reduced set of inputs is identified, optimization of ANN architecture can proceed as usual [27].

The accuracy of the generated model was evaluated towards samples of the external test subset by using the built model to predict concentrations of the explosives of those samples. To evaluate the performance of the different models, its normalized root mean square error (NRMSE) for each combination of the transfer functions used in the hidden and output layers, and the number of neurons in the hidden layer.

$$NRMSE = \frac{\sqrt{\frac{\sum_{ij} (x_{expected} - x_{obtained})^2}{k \cdot n - 1}}}{x_{max} - x_{min}} \tag{1}$$

Thus, the optimum topology will be the one that also gives the lowest NRMSE value. As it can be seen in Fig. 10, by plotting the total NRMSE versus the number of inputs gives a clear view of the performance of the model.

Hence, once the predictors data matrix was obtained, the next step was the optimization of the ANN as previously done. In this case, the resulting ANN model has 48 neurons in the input layer (corresponding to the relevant data points previously selected), 8 neurons and *logsig* transfer function in the hidden layer, and 3 neurons and *purelin* transfer function in the output layer, providing the concentrations of the three species considered.

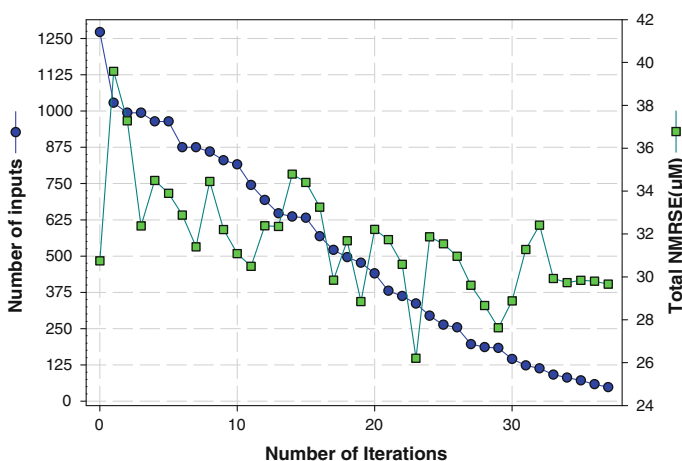


Fig. 10 Evolution of the total NRMSE as the number of inputs is decreased

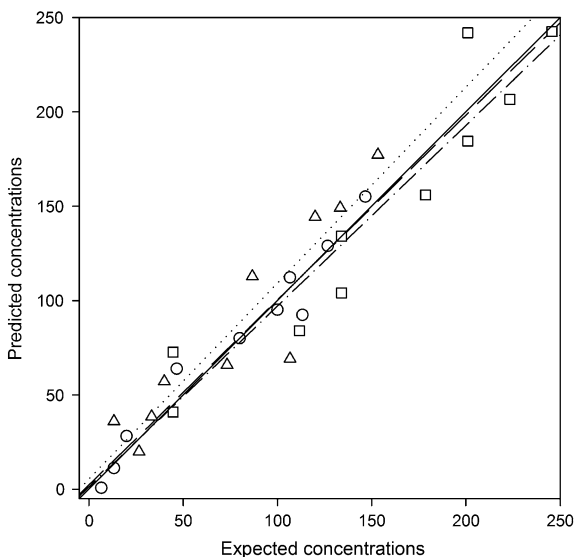
**Table 1** Results of the fitted regression lines for the obtained versus expected values for the samples of the training and testing subsets and the three considered explosive materials (intervals calculated at the 95 % confidence level)

Training subset					
Explosive	Correlation (r)	Slope	Intercept ( $\mu\text{g}\cdot\text{mL}^{-1}$ )	NRMSE	Total NRMSE
TNT	0.997	$0.984 \pm 0.030$	$1.4 \pm 3.2$	0.031	0.031
Tetryl	0.997	$0.980 \pm 0.030$	$1.7 \pm 3.2$	0.032	
TATP	0.998	$0.981 \pm 0.028$	$2.8 \pm 5.6$	0.030	
Testing subset					
Explosive	Correlation (r)	Slope	Intercept ( $\mu\text{g}\cdot\text{mL}^{-1}$ )	NRMSE	Total NRMSE
TNT	0.979	$0.981 \pm 0.166$	$2.2 \pm 14.9$	0.063	0.091
Tetryl	0.929	$1.038 \pm 0.337$	$5.4 \pm 30.8$	0.135	
TATP	0.945	$0.959 \pm 0.269$	$1.2 \pm 44.7$	0.080	

NRMSE Normalized root mean square error

Comparison graphs of predicted vs. expected concentration for the three compounds were built, both for training subset and testing subset. Table 1 shows the regression parameters for each compound in the training subset and the test subset. As can be seen in the plots (Fig. 11) a good linearity is achieved for all the cases, with better correlation in the training subset and less NRMSE. For the test subset, that is the one that really shows how the model is performing; the regression parameters are also close to the ideal values. Thus, in both subsets the intercepts are close to 0, and the slopes and the correlation coefficients close to 1.

**Fig. 11** Test plots of predicted versus expected concentrations for TNT (○, dashed line), Tetryl (Δ, dotted line) and TATP (□, dashed-dotted line)



Based on these results, we can confirm that the model is able to predict the concentration of the 3 individual compounds in a mixture sample with good performance. However, results show that the tetryl and the TATP show a bigger dispersion and that affects the regression parameters of these compounds.

The analysis of samples was based on the combination of cyclic voltammetry for the extraction of the fingerprints of the individual components and mixtures of these species, coupled with chemometric tools that allowed the resolution of signal overlapping and identification of the different compounds. The resolution and quantification of ternary mixtures was achieved employing an artificial neural network model. Obtained results suggest that voltammetric electronic tongues could be of application for the detection in real explosive formulation samples and a good candidate for homeland security applications.

## 4 Concluding Remarks

To summarize, these two application cases have shown how the voltammetric sensor systems used can be used as qualitative methods to provide the identification of the voltammetric fingerprint of different explosive mixtures commercially or manufactured, such as IEDs. The systems are also capable to detect peroxide compounds, due to their difficulty of detection its use has been increased and 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 explosives. In this context, electrochemical sensors offer an opportunity to detect peroxide-based explosives that would otherwise prove problematic. Alternatively, quantitative determination applications to determine explosives in mixtures can be also developed.

The results suggested that voltammetric electronic tongues could be of application for the detection of real explosive formulation samples and a good candidate for homeland security applications; leading to a new generation of on-site field deployable explosive detectors. These may be massively used, and with wireless communication allow for complete networked areas, even regions to prevent by their trace detection the approach of any of the considered substances. Alternatively, from environmental concerns, any affected area by these compounds may employ the described analytical systems a starting point for the monitoring of state and evolution of already polluted scenarios or the ones being remediated.

**Acknowledgements** Financial support from the Spanish Ministry of Economy and Innovation, MINECO (Madrid) through project CTQ2013-41577-P is gratefully acknowledged. M. del Valle thanks the support from program ICREA Academia. A. González-Calabuig thanks the Universitat Autònoma de Barcelona (UAB) for the award of PIF studentship.

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