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Electronic tongue for Nitro and Peroxide explosive sensing

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Abstract

This work reports the application of a voltammetric electronic tongue (ET) 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 multielectrode array was formed by graphite, gold and platinum electrodes, which exhibited marked mix-responses towards the compounds examined; namely, 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), pentaerythritol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT), *N*-methyl-*N*,2,4,6-tetranitroaniline (Tetryl) and triacetone triperoxide (TATP). Departure information was the set of voltammograms, which were first analyzed by means of principal component analysis (PCA) allowing the discrimination of the different individual compounds, while artificial neural networks (ANNs) were used for the resolution and individual quantification of some of their mixtures (total normalized root mean square error for the external test set of 0.108 and correlation of the obtained vs. expected concentrations comparison graphs r > 0.929).

Keywords: Electronic Tongue; Artificial Neural Network; voltammetric sensor; explosives; TNT; TATP

1. Introduction

The increased terrorism activities have brought the world’s attention on explosive compounds, and have given rise to increased research into explosive early detection as well as further developments in existing analytical techniques to enable faster, more sensitive, less expensive and simpler determinations to facilitate the trace identification of these energetic materials [1]. Specifically, the analyses of explosive compounds are demanded by the environmental monitoring and protection agencies, crime scene investigations and homeland securities.

Explosive chemicals are useful and widely used in warfare, mining industries and civil constructions; unfortunately also in terrorist attacks. These compounds are categorized in four major classes: nitroaromatics, nitroamines, nitrate esters and peroxides according to their chemical structures [2]. 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 detect with the analytical methods used to determine more established explosives [3], e.g. 2,4,6-trinitrotoluene (TNT) or 1,3,5-trinitroperhydro-1,3,5-triazine (RDX). That is, the challenge being 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 not suitable for spectroscopic detection [4] because of their lack of chromophores and their instability under illumination of UV light – all necessary parameters upon which traditional detection techniques are based [5].

These characteristics, as well as their large explosive power [6], have led to the increasing use of those by terrorists and criminals over the last few decades [3]. Concretely, triacetone triperoxide (TATP) became a well known explosive after its use by the thwarted “shoe bomber” in 2001 [7].

In this context, electrochemical sensors offer an opportunity to detect peroxide-based explosives that would otherwise prove problematic. The inherent redox activity of nitrogen-based commercial explosives [8, 9], such as nitroaromatic or nitroamine compounds, namely the presence of easily-reducible nitro groups, makes them ideal candidates for electrochemical (voltammetric) monitoring. Besides, 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. In addition, 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 [10]. Therefore, electrochemical devices represent a promising solution for on-site explosive detection.

Nevertheless, the presence of the reducible nitro groups on the aromatic ring, which differ only in their number and position, results in overlapping voltammetric signals and makes the simultaneous discrimination of mixtures of nitro-containing explosives problematic [8].

On that account, over the last years, a new concept in the field of sensors has appeared to tackle these problems: Electronic Tongues (ETs) [11]. These biomimetic systems, in opposition to conventional 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; and afterwards they are furnished with complex data treatment tools, which allows to identify or to quantify the substances under scrutiny. In this sense, the use of chemometric tools such as principal component analysis (PCA) or artificial neural networks (ANNs) can help to overcome limitations in data interpretation [12, 13], by identifying and processing the electrochemical fingerprint produced by the explosive mixture.

Herein, we propose the use of electronic tongue approach for the detection of different nitro- and peroxo- types of explosives utilizing voltammetric data acquired from a multielectrode array. The proposed approach is based on the coupling of cyclic voltammetric responses obtained from an array of graphite, gold and platinum electrodes with chemometric tools such as PCA for visualization of sample (dis)similarities and ANNs for building the quantitative prediction models. In this sense, the combination of fast voltammetric detection and chemometrics could possibly simplify measurements in security premises and lead to a new generation of on-site field deployable explosive detectors.

2. Experimental

2.1 Reagents and solutions

All reagents used were analytical reagent grade and all solutions were prepared using deionised water from a Milli-Q system (Millipore, Billerica, MA, USA). Reference standard solutions (1000 µg·mL^{-1} in acetonitrile) of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), pentaerythritol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT) and *N*-methyl-*N*,2,4,6-tetranitroaniline (Tetryl) were purchased from LGC standards (Teddington, Middlesex, UK). Acetone and Acetonitrile (ACN) were purchased from Scharlab (Barcelona, Spain). Potassium dihydrogenphosphate, potassium monohydrogenphosphate and H_2O_2 were purchased from Sigma-Aldrich (St. Louis, MO, USA). Sulphuric acid and KCl were purchased from Merck KGaA (Darmstadt, Germany).

2.2 TATP synthesis

The synthesis of triacetone triperoxide (TATP) was done following previously reported procedures [14, 15]. The peroxide can be easily synthesized by the acid catalyzed reaction between H_2O_2 and acetone at low temperatures (Figure S1, supplementary info). However, special care must be taken when synthesizing and handling TATP due to it is a primary explosive, but also to avoid the formation of the diacetone diperoxide (DADP). Thus, reaction was optimized, considering safety principles, to produce less than 1g of final product.

Synthesis was carried out according to the following procedure: a 0.68mL aliquot of chilled 30% H_2O_2 and 0.95mL of chilled acetone were placed in a 10mL beaker within an ice bath. The mixture was gently stirred and 20µL of chilled, concentrated H_2SO_4 (98% w/w) were added every 4min during 48min to give a total volume of 240µL of H_2SO_4 added. Special care was taken to add H_2SO_4, as adding it too quickly might cause a violent reaction or even an explosion. The mixture was kept during 24h without stirring or cooling to complete the precipitation of TATP.

2.3 Voltammetric measurements

2.3.1 Multielectrode array and measurement cell

Measurements were carried out using a previously developed arrangement [16], modified to incorporate the auxiliary element. The ET array consists in four discs of silver (acting as a pseudo reference electrode when chloridized), gold, platinum and graphite-epoxy composite of 1 mm diameter (acting as working electrodes), plus a stainless steel tube of 8 mm inner diameter acting as counter electrode. The four wire electrodes were cast in epoxy resin (Epotek H77, Epoxy Technologies) in a 8 mm outer diameter PVC tube used as body, which was afterwards stuck in the stainless steel tube (Figure 1).

<FIGURE 1>

2.3.2 Measurement procedure

Cyclic Voltammetry measurements were carried out at room temperature (25 ºC), in a multichannel configuration, using a 6-channel AUTOLAB PGSTAT20 (Ecochemie, Netherlands) controlled with GPES Multichannel 4.7 software package.

Firstly, prior to sample measurements, electrodes were cycled in saline solution in order to get stable voltammetric responses. For the measurements, potential was cycled between -1.0 V and +0.9V vs Ag/AgCl, with a scan rate of 100mV·s^{-1} and a step potential of 9mV. All experiments were carried out without performing any physical surface regeneration of the working electrodes. Thus, in order to prevent the accumulative effect of impurities on the working electrode surfaces, an electrochemical cleaning stage was done between each measurement applying a conditioning potential of +1.2V for 40s after each experiment, in a cell containing 150µL of 50mM KCl at pH=10 [17].

2.4 Samples under study

Firstly, voltammetric responses of the ET array towards the different explosive compounds were characterized. For this purpose, stock solutions of each of the pure compounds were analyzed. In all cases, same 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. Moreover, to confirm that discrimination between different compounds 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 to ensure the robustness of the approach.

Afterwards, in order to prove the capabilities of the ET to achieve the simultaneous quantification of different explosive compounds mixtures, resolution of TNT, tetryl and TATP mixtures was attempted. To this aim, a total set of 37 samples were manually prepared with a concentration range of 0 to 165µg·mL^{-1} for TNT ant tetryl, and 0 to 300µg·mL^{-1} for TATP. The set of samples was divided into two data subsets: a training subset formed by 27 samples (73%) which were distributed based on a factorial design (3^3) and used to build the response model, plus 10 additional samples (27%) for the testing subset, distributed randomly along the experimental domain and used to evaluate the model predictive ability.

In all cases, 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 75µL. Then, this was mixed with 75µL of phosphate buffer pH 6.5 to stabilize the pH and to ensure enough conductivity of the media.

2.5 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 toolbox; except, Simplified Fuzzy ARTMAP Neural Network which was already implemented by other authors (http://www.mathworks.com/, file ID: #11721) [18]. In this fashion, PCA was used for qualitative analysis of the results, while quantitative analysis was achieved by means of ANNs. Additionally, Sigmaplot (Systat Software Inc, California, USA) was used for graphic representations of data and results.

However, a known problem when voltammetric sensors are used is the large dimensionality of the generated data (samples x sensors x polarization potentials) which hinders their treatment; especially if ANNs are to be used, in which case departure information needs to be preprocessed. In this fashion, prior to building the quantification model, removal of less significant coefficients that barely contribute to the network was carried out by means of Causal Index (CI) pruning of the inputs [19, 20].

Briefly, this method 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 identify the 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 [21].

3. Results and Discussion

3.1. TATP synthesis

Although the conditions are optimized to produce the trimer, the reaction described previously can give the DADP and the TATP mixture. Consequently, a ^{1}H NMR spectrum (250MHz, $CDCl_3$) was acquired to ensure that the product resulting from the reaction was the trimer (Figure S1, Supplementary info). The resulting peaks in the ^{1}H NMR spectra were compared with the ones reported in previous works [22]. The NMR shows a very intense peak corresponding to TATP (δ=1.48 (s)) and various peaks corresponding to the $CDCl_3$ (δ=7.28), H_2O (δ=1.55), HDO (δ=1.37); meanwhile, no peaks corresponding to decomposition products were observed (δ=2.03, δ=1.82, δ=1.80, δ=1.31). Therefore, confirming that TATP was the product obtained.

3.2 Voltammetric responses

Following the described procedure, the set of samples was measured employing the multielectrode array, obtaining a whole cyclic voltammogram for each of the sensors from the array.

An extract of those results is shown on Figure 2. As it can be seen, complex and highly overlapped signals are obtained along the whole voltammogram, with differentiated signals obtained for the different kinds of sensors; a situation highly desirable for building an ET application, i.e. when the different sensors display marked distinct features for the different samples.

<FIGURE 2>

3.3 Qualitative analysis of explosives

In a first approach, discrimination of different explosive compounds by means of the ET was attempted. That is, to asses if the system presented herein was able to carry out the identification of the most common explosive compounds.

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 completion of the PCA analysis (Figure 3), the accumulated explained variance was calculated with the three first PCs as 99.85%. 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 close one to each other.

<FIGURE 3>

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

The PCA-ANN model was trained with 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 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%.

With the goal of providing a measure of performance for the identification, a Pearson's chi-squared test was calculated for the contingency table containing the test set samples alone; this calculation provided, for the six compounds considered, a calculated statistic of χ^2=90.0, significantly larger than the tabulated value at the 95% confidence level (37.7). This statistic also allowed calculation of the contingency coefficient (0.913), equal to the maximum achievable value for the number of samples and classes considered and that describes numerically the power of identification

In view of the good results obtained in the qualitative approach, and to further asses the capabilities of the ET to perform its individual quantitative determination, even in the presence of other explosive compounds, the next step was the resolution of ternary mixtures of TNT, tetryl and TATP.

3.4 Feature selection

As stated, when dealing with voltammetric sensor arrays, the main problem is the huge dimensionality of the recorded data (the set of voltammograms) which hinders the modelling step, especially if ANNs are to be used. Therefore, requiring a compression step, which in addition allows to gain advantages in training time, to avoid redundancy in input data and to obtain a model with better generalization ability [20]. In our case this was accomplished by the use of the causal index analysis (CI).

Main advantage of this method is the fact that allows the identification of the most relevant features, that is, not only the identification of which sensors most contribute to the discrimination and the quantification of the compounds under scrutiny, but also which points from the voltammograms (i.e. the currents associated to the applied potentials). However, its main drawbacks are the amount of time required for the feature extraction process, and the fact that the reduced sets are not unique and the arrival to an optimal set depends on the architecture of the ANN used.

As said, to carry out the selection of the most significant inputs by means of an ANN, first of all, the number of neurons in the hidden layer and the transfer functions (both in the hidden and output layers) are selected in advance to represent the intrinsic dimensionality of the dataset. In this case, and based on previous calculus, the selected ANN architecture to carry out the pruning of the inputs was formed by 5 neurons and *purelin* transfer function in the hidden layer, and 3 neurons and *logsig* transfer function in the output layer. Upon assignation of the weights by the ANN model, the most relevant features were identified, allowing the reduction of the number of inputs by repetitive pruning of the less significant inputs, without any loss of relevant information as can be seen in Figure 4.

<FIGURE 4>

After this, the final input set was formed by 48 inputs, which meant that a reduction of ca. 96.2% in the size of data to feed the ANN model was achieved. Hence, once the predictors data matrix was defined, the next step was the optimization of the neural network architecture with the reduced set of inputs by an iterative process varying its configuration (number of neurons in the hidden layer plus transfer functions in the hidden and output layers) in order to generate the best response model.

3.5 Quantitative analysis of explosive mixtures

Upon completion of an extensive study varying its configurations, the final architecture of the ANN model had 48 neurons (the ones previously selected during feature extraction stage) in the input layer, 8 neurons and *logsig* transfer function in the hidden layer and three neurons and *purelin* transfer function in the output layer, providing the concentrations of the three species considered.

The accuracy of the generated model was then evaluated towards samples of the external test subset by using the built model to predict the concentrations of the explosives of those samples. Since the external test subset data is not employed at all for the modelling, its goodness of fit is a measure of the accomplished modelling performance. To easily check the prediction ability of the obtained ANN model, comparison graphs of predicted vs. expected concentration for the three compounds were built, both for training subset and testing subsets.

As can be observed in Figure 5, a satisfactory trend is obtained for the three compounds, with regression lines close to the theoretical ones. Additionally, regression parameters were calculated (Table 1), and as expected from the graphs, a good linear trend is attained for all the cases, but, as usual, with improved behaviour for the training subsets due to this subset is the one used to build the model. 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.

<FIGURE 5>
<TABLE 1>

Although not considered in this case, individual ANN models may also be developed to separately predict the concentrations of the three species; what would lead to better prediction of the individual concentrations of the three species. However, this configuration was neglected as it does not represent the true nature of the approach and complicates its final application as three models would be used rather than a single one. Nevertheless, this option may represent an easy way to improve the performance of the final ET approach if required.

4. Conclusions

Proposed approach presented herein has demonstrated to be a useful tool for the detection of different explosive compounds, both nitro-containing and peroxide-based, representing the two main families of compounds employed either in commercial mixtures or in improvised explosive devices (IEDs).

Developed ET is based on a small multielectrode array formed by simple metallic electrodes plus a graphite one, which have exhibited marked mix-responses towards the compounds examined. 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. Specifically, PCA analysis showed the capability of the ET to discriminate most common explosive compounds, while in a further approach, resolution and quantification of ternary mixtures was achieved employing an artificial neural network model.

These results suggested that voltammetric electronic tongues could be useful for the detection of explosive compounds and pointed towards the possibility that this, or similar tongue-based systems, could be of application for their detection in real explosive formulation samples and a good candidate for homeland security applications; leading to a new generation of on-site field deployable explosive detectors.

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Table 1. Results of the fitted regression lines for the comparison between obtained vs. expected concentration values, both for the training and testing subsets of samples and the three considered explosive compounds (intervals calculated at the 95% confidence level).

Training subset					
Explosive	*Correlation*	*Slope*	*Intercept* ($\mu g \cdot mL^{-1}$)	*NRMSE*	*Total NRMSE*
TNT	0.997	0.984±0.030	1.4±3.2	0.027	0.028
Tetryl	0.997	0.980±0.030	1.7±3.2	0.030	
TATP	0.998	0.981±0.028	2.8±5.6	0.027	
Testing subset					
Explosive	*Correlation*	*Slope*	*Intercept* ($\mu g \cdot mL^{-1}$)	*NRMSE*	*Total NRMSE*
TNT	0.979	0.981±0.166	2.2±14.9	0.064	0.108
Tetryl	0.929	1.038±0.337	5.4±30.8	0.134	
TATP	0.945	0.959±0.269	1.2±44.7	0.113	

NRMSE: Normalized Root Mean Square Error

FIGURE CAPTIONS

Figure 1. Design of the multielectrode array: silver, gold, platinum and graphite wires were introduced into a PVC tube and casted into a resin, which additionally was stuck to a stainless steel tube. Silver was used as pseudoreference electrode and stainless steel tube as the counter electrode, while the others ones act as working electrodes.

Figure 2. Example of different voltammograms obtained for (a) epoxy graphite electrode, (b) Au electrode and (c) Pt electrode measuring 100 $\mu g \cdot mL^{-1}$ standard solutions of each of the explosive pure compounds under study (black for TATP, red for RDX, green for HMX, purple for TNT, blue for PETN and orange for Tetryl).

Figure 3. Score plot of the first three components obtained after PCA analysis. A total of 18 samples were analyzed corresponding to triplicate determinations of: (I) RDX, (II) HMX, (III) PETN, (IV) TNT, (V) Tetryl and (VI) TATP.

Figure 4. Feature selection and reduction of the number of inputs by means of CI-ANN method. In each iteration a model is fitted, its RMSE for testing subset is calculated and inputs to which model has assigned lower weights are discarded. This process is repeated until an increase in the RMSE is obtained for several successive iterations or desired reduction in the number of inputs is achieved.

Figure 5. Modelling ability of the optimized ANN. Sets adjustments of obtained vs. expected concentrations for (a) TNT, (b) Tetryl and (c) TATP, both for training (●, solid line) and testing subsets (○, dotted line). Dashed line corresponds to theoretical diagonal line.

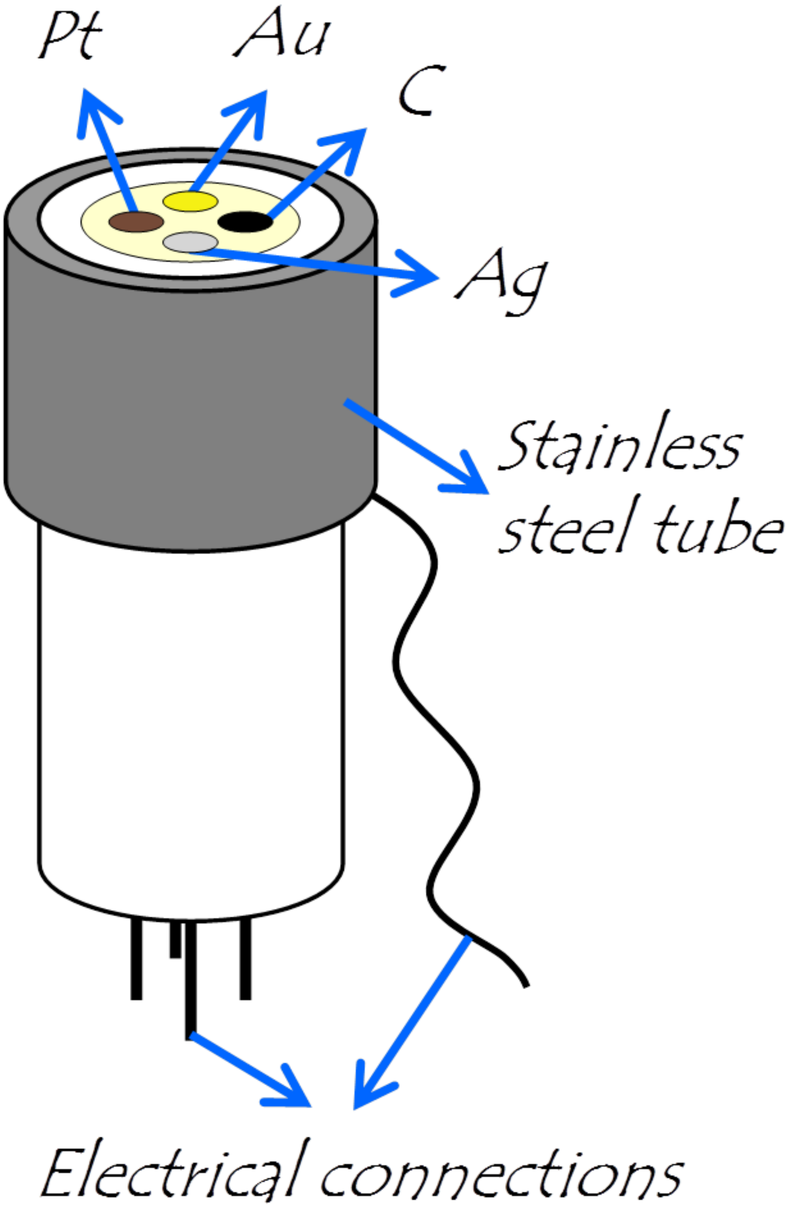

Figure 1

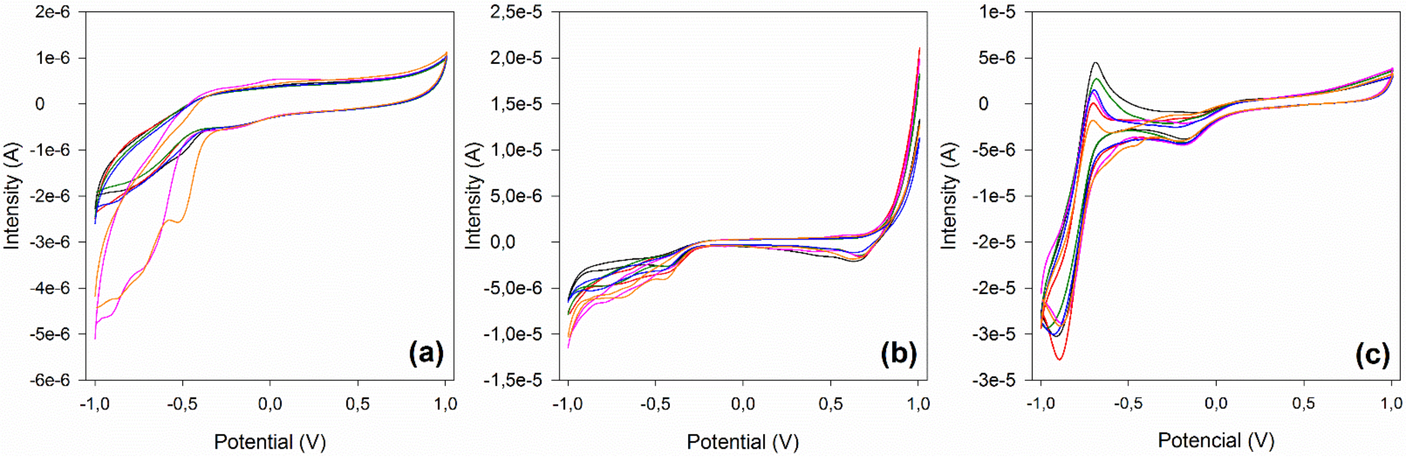
2e-6
1e-6
0
-1e-6
-2e-6
-3e-6
-4e-6
-5e-6
-6e-6
Intensity (A)
(a)
-1,0
-0,5
0,0
0,5
1,0
Potential (V)
2,5e-5
2,0e-5
1,5e-5
1,0e-5
5,0e-6
0,0
-5,0e-6
-1,0e-5
-1,5e-5
Intensity (A)
(b)
-1,0
-0,5
0,0
0,5
1,0
Potential (V)
1e-5
5e-6
0
-5e-6
-1e-5
-2e-5
-2e-5
-3e-5
-3e-5
Intensity (A)
(c)
-1,0
-0,5
0,0
0,5
1,0
Potencial (V)

Figure 2

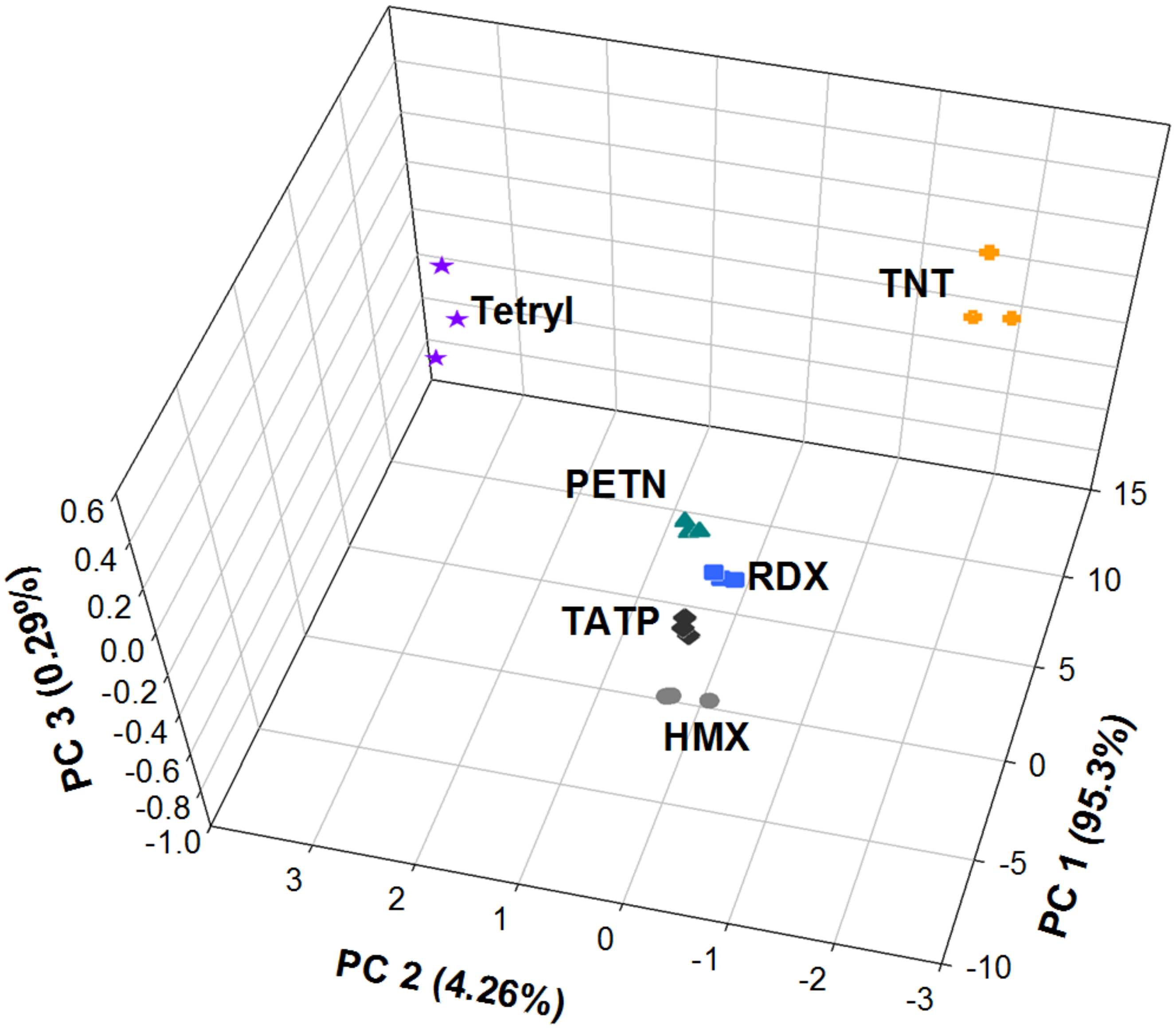
Tetryl
TNT
PETN
RDX
TATP
HMX
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
PC 3 (0.29%)
3
2
1
0
-1
-2
-3
PC 2 (4.26%)
15
10
5
0
-5
-10
PC 1 (95.3%)

Figure 3

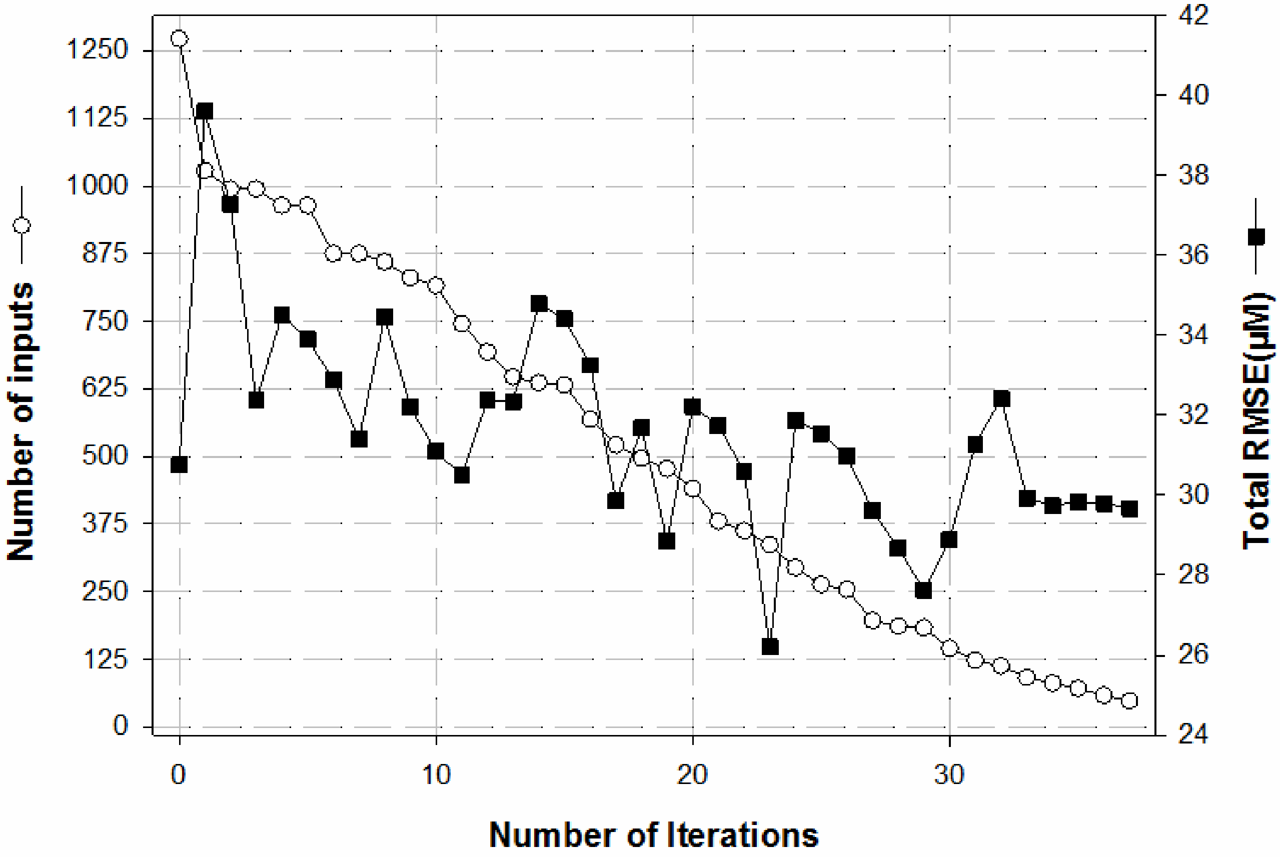
Number of inputs
1250
1125
1000
875
750
625
500
375
250
125
0
Total RMSE(μM)
42
40
38
36
34
32
30
28
26
24
0
10
20
30
Number of Iterations

Figure 4

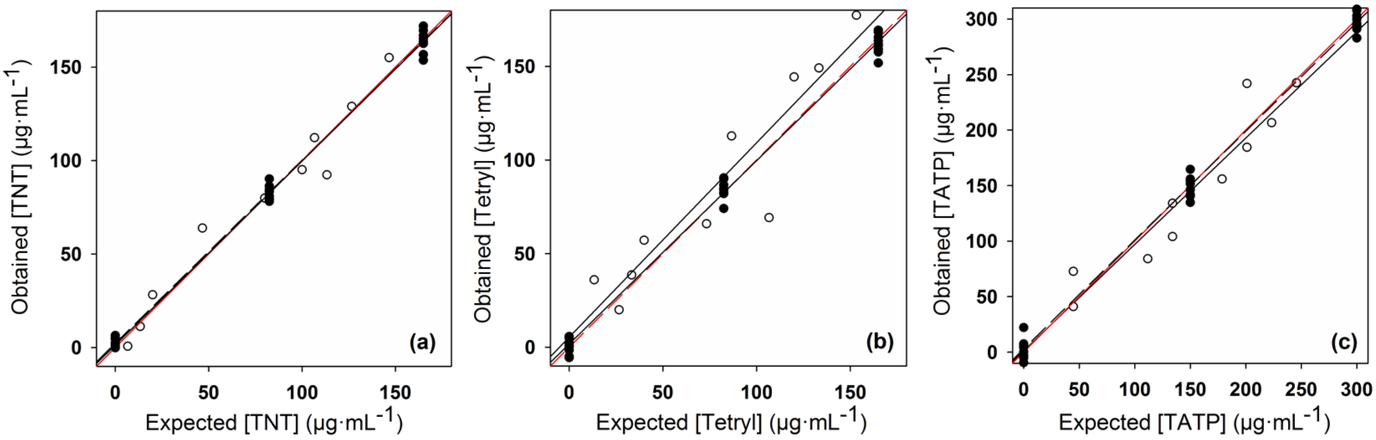
Obtained [TNT] (µg·mL^{-1})
150
100
50
0
0
50
100
150
Expected [TNT] (µg·mL^{-1})
(a)
Obtained [Tetryl] (µg·mL^{-1})
150
100
50
0
0
50
100
150
Expected [Tetryl] (µg·mL^{-1})
(b)
Obtained [TATP] (µg·mL^{-1})
300
250
200
150
100
50
0
0
50
100
150
200
250
300
Expected [TATP] (µg·mL^{-1})
(c)

Figure 5