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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 $r > 0.929$).

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 [8,9]. The inherent redox activity of nitrogen-based commercial explosives [10,11], 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 [12]. 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,

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results in overlapping voltammetric signals and makes the simultaneous discrimination of mixtures of nitro-containing explosives problematic [10].

On that account, over the last years, a new concept in the field of sensors has appeared to tackle these problems: Electronic Tongues (ETs) [13]. 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 coupled 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 [14,15], by identifying and processing the electrochemical fingerprint produced by the explosive mixture.

Initial attempts with such an approach have been directed to the discrimination of different nitroaromatic explosives [16–18]. Similarly, electronic noses (ENs) and colorimetric devices in conjunction with some chemometric methods have also been applied to the qualitative identification of some explosive compounds [19–22]. However, most of the works focus only on nitroaromatic or peroxide explosives separately, with almost none of them attempting its simultaneous quantification.

Herein, we propose the use of the 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.

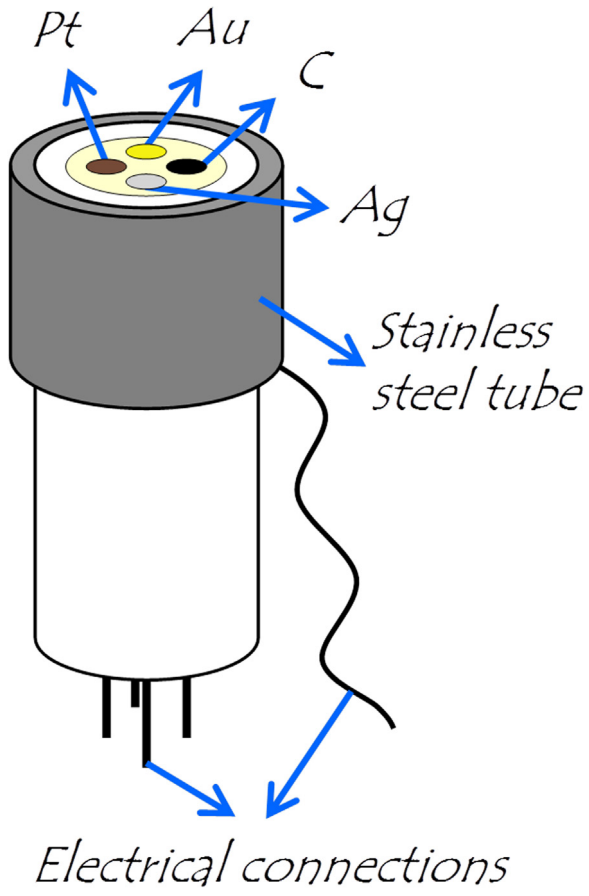

Fig. 1. Design of the multielectrode array: silver, gold, platinum and graphite wires were introduced into a PVC tube and casted into a resin, which additionally was stuck to a stainless steel tube. Silver was used as pseudoreference electrode and stainless steel tube as the counter electrode, while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

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). Sulfuric acid and Potassium chloride were purchased from Merck KGaA (Darmstadt, Germany).

2.2. TATP synthesis

The synthesis of triacetone triperoxide (TATP) was done following previously reported procedures [23,24]. The peroxide can be easily synthesized by the acid catalyzed reaction between H_2O_2 and acetone at low temperatures (see supplementary, Fig S1). 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 1 g of final product.

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

2.3. Voltammetric measurements

2.3.1. Multielectrode array and measurement cell

The ET array consists in four discs of silver, gold, platinum and graphite-epoxy composite of 1 mm diameter, plus a stainless steel tube of 8 mm inner diameter. The four wire electrodes were cast in epoxy resin (Epotek H77, Epoxy Technologies) in a 8 mm outer diameter PVC tube used as body [25], which was afterwards stuck in the stainless steel tube (Fig. 1). Platinum, gold and epoxy-graphite discs were used as working electrodes, whereas silver was used as pseudo-reference electrode (after proper chloridization) and the stainless steel tube as the auxiliary electrode.

Whereas graphite has already been demonstrated as an attractive material to achieve the detection of nitro-containing explosives [10,16,17]; platinum and gold were selected as it was found that metals such as gold, silver or platinum represent interesting electrodes that might provide a distinguished and characteristic fingerprint for each of the explosive compounds,