Available online at www.sciencedirect.com
ScienceDirect
Procedia Chemistry 1 (2009) 325–328
Procedia Chemistry
www.elsevier.com/locate/procedia

Proceedings of the Eurosensors XXIII conference

Use of a voltammetric electronic tongue for predicting levels of nerve agent mimics

Inmaculada Campos[a], Luis Gil[a], Ramón Martínez-Mañez[a], Juan Soto[a], José-Luis Vivancos[a]*

[a]*Instituto de Reconocimiento Molecular y Desarrollo Tecnológico, Universidad Politécnica de Valencia, Valencia, Spain*

Abstract

An electronic tongue (ET) based on pulse voltammetry containing a set of eight metallic electrodes (Au, Pt, Ir, Rh, Cu, Co, Ni and Ag) encapsulated on a stainless steel cylinder has been used to discriminate and predict levels of nerve agent mimics in aqueous environments. Analysis including principal component analysis (PCA) and partial least square techniques (PLS) have been applied for data management and prediction models. A good discrimination from other organophosphorous derivatives was found for the nerve agent simulants diethyl-chlorophosphate (DCP) and diethyl-cyanophosphate (DCNP).

Keywords: Electronic tongue; voltammetry; nerve agent mimics

1. Introduction

Chemical warfare agents are classified in several groups namely nerve agents, asphyxiant/blood agents, vesicant agents, choking/pulmonary agents, lachrymatory agents, incapacitating agents and cytotoxic proteins.[1,2] Among them, nerve agents are especially dangerous. They are hazards in their liquid and vapor states and can cause death within minutes after exposure. Nerve agents are phosphoric acid esters, structurally related to the larger family of organophosphate compounds. They are highly toxic and display severe effects on humans and animals via their ability to block the action of acetylcholinesterase. A number of detection systems have been developed most of them based on enzymatic and physical or chemical methodologies.[2-6] However; most of them still show limitations such as low selectivity, difficult portability and certain complexity in their use.

In the research we show herein we were interested in testing the detection of nerve agent mimics in aqueous medium through the use of a simple electronic tongue based on pulse voltammetry measurements. From the literature it is apparent that, although some electronic noses[7-10] and SAW[11-14] sensors have been reported to be able

* Corresponding author: José Luis Vivancos, Instituto de Reconocimiento Molecular y Desarrollo Tecnológico, Centro Mixto Universidad Politécnica de Valencia- Universidad de Valencia. Spain. Tel.: +34-96-387-9860; fax: 34-96-387-9869.
E-mail address: jvivanco@dpi.upv.es.

doi:10.1016/j.proche.2009.07.081

to detect certain chemical warfare agents in gas phase, the use of electronic tongues for the detection of these chemicals in water has never been used as far as we know.

2. Experimental

An experimental design is applied here to create a system of three compounds/four levels. This allows correlating the contribution and confounding when they were together in a mixture. All standards solutions were phosphate buffered at pH 7. All samples were measured two times and in random order to minimize possible error due to memory of the electrodes.

The electronic tongue device consists of an array of eight working electrodes (i.e. Au, Pt, Ir, Rh, Cu, Co, Ni and Ag)[15-17] with purity of 99.9 % and 1 mm diameter from ALDRICH that were housed inside a stainless steel cylinder used at the same time as both the body of the electronic tongue system and the counter/reference electrode. Generation of pulses and recording of current data were performed by using electronic equipment. All data management was carried out with Matlab (Version R2007b, MathWorks).

3. Results

The response of the electronic tongue was tested with diethylchlorophosphate (DCP) and diethylcyanophosphate (DCNP) in water (phosphate buffer 10^{-2} mol dm^{-3}). These organophosphates have been widely used as simulants as they display a similar reactivity that nerve agents such as Tabun, Sarin and Soman, yet they lack their toxicity. In this study we also included other organophosphorous (OP) shown in Fig. 1.

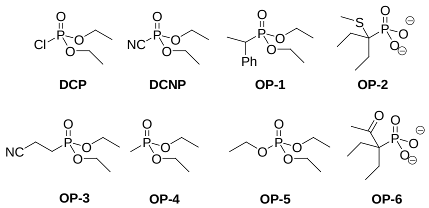

Fig. 1. Chemical structure of the nerve agent mimics and other organophosphorous derivatives.

The voltammetric response of a certain compound studied depends on the intrinsic chemical nature of the both the electrode and the electrochemical characteristics of the organophosphorous derivative. Subtle differences between compounds are reflected in the specific final voltammetric response of each electrode-compound ensemble. In fact it is expected that the redox properties of the derivatives (including chemical reactions coupled to electrochemical changes or modification of the electric double layer) may result in a differential response of the set of electrodes.

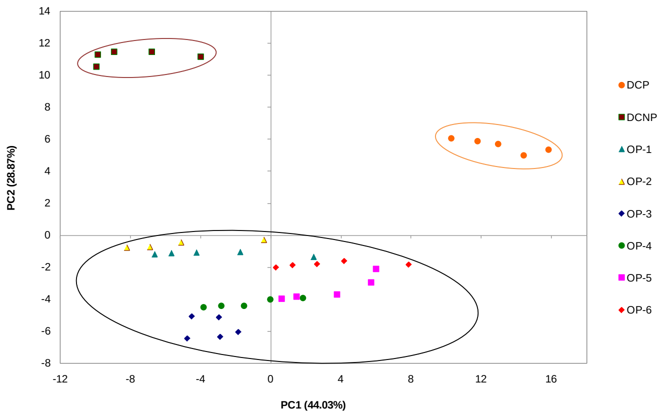

Fig. 2. Principal component analysis (PCA) score plot for the compounds shown in Fig.1. Data shown from five different trials. PC axes are calculated to lie along lines of diminishing levels of variance in the data set.

In order to study this differential response of the tongue with different nerve agent mimics and other organophosphorous derivatives the electrochemical response could be combined to form ensembles for pattern recognition in an attempt to find selectivity fingerprints. These studies can be carried out for instance when the matrix of data is analyzed by principal component analysis (PCA) algorithms. The PCA score plot of the results for the voltammetric tongue in the presence of the compounds in Fig. 1 is shown in Fig. 2 for five different trials. PCA analysis decomposes the data matrix into a new set of uncorrelated variables (Principal Components), by finding new directions in the pattern space in order to explain the maximum amount of variance within the data set. The figure shows clear clusters for DCP and DCNP whereas a similar response was observed for the remaining compounds studied.

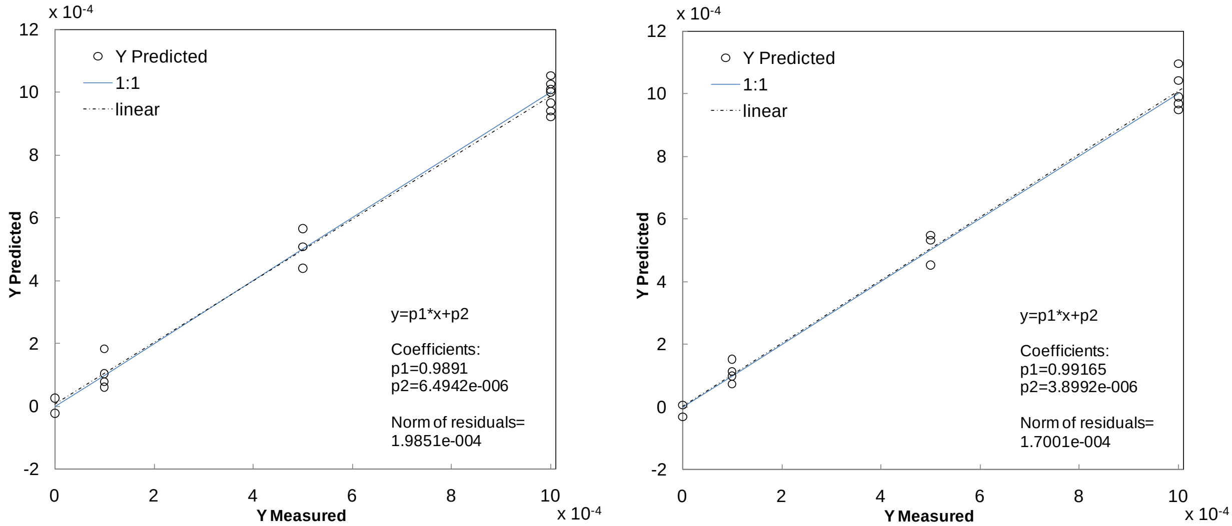

Fig. 3. (a) PLS plot of prediction of diethyl-chlorophosphate (DCP) with the ET, using noble electrodes (Au, Pt, Ir and Rh); (b) PLS plot of prediction of diethyl-cianophosphate (DCNP) with the ET, using noble electrodes (Au, Pt, Ir and Rh).

In a second step, by using a software of experimental design (MODDE 8.0), 18 standard solutions were prepared by addition of three selected compounds (DCP, DCNP and OP-2) into water (pH 7, phosphate buffer 10^{-2} mol dm^{-3}) in levels low (0), medium ($1x10^{-4}$ and $5x10^{-4}$ mol dm^{-3}) and high ($1x10^{-3}$ mol dm^{-3}). Results from the PLS model are shown in Fig. 3 that plots predicted vs. measured values of levels for DCP and DCNP. The linear fitting shown in the figures was calculated by using a linear model typed y = p1*x + p2. The results of the linear fitting display the values of coefficients p1 (slope of the curve fitting) and norm of residuals, which represents the goodness of the fit (see Table 1). The table also shows the different response found using the noble and no-noble electrodes. A simple visual inspection in Fig. 3 of the spread of the experimental points along the straight line (or reference line) in the figures shows a good prediction for the concentration of DCP and DCNP.

Table 1. Slopes of fitting line (SFT), norms of residuals (NR) and the R^2 value (RSQ) for the prediction of DCP and DCNP, using the ET.

	eight working electrodes			Noble working electrodes			Non-Noble working electrodes		
	SFT	NR	RSQ	SFT	NR	RSQ	SFT	NR	RSQ
DCP	0.94943	$4.15x10^{-4}$	0.949	0.9891	$1.98x10^{-4}$	0.989	0.95713	$3.89x10^{-4}$	0.956
DCNP	0.98951	$1.90x10^{-4}$	0.989	0.99165	$1.70x10^{-4}$	0.992	0.9811	$2.60x10^{-4}$	0.981

4. Conclusions

In summary we have shown that the use of a relatively simple voltammetric electronic tongue that uses metallic electrodes is able to discriminate the nerve agent simulants DCP and DCNP in water whereas the tongue shows a similar response to other organophosphorous derivatives. PLS data analysis using 3 compounds (DCP, DCNP and OP-2)/4 concentration levels system shows a good accuracy in concentration prediction for DCP and DCNP. These preliminary data suggest that this or similar voltammetric tongues could be used to detect moderate concentrations of nerve agents in aqueous environments.

Acknowledgements

We thank the Ministerio de Ciencia y Tecnología (project CTQ2006-15456-C04-01), and Universidad Politécnica de Valencia (project PAID-06-07-3243) for support. I.C. thanks the Universidad Politécnica de Valencia for a Doctoral Fellowship.

References

1. Angerson WS. *Chemical and Biological Warfare Agents*, Vol. 5, RAND Reports; 2000.
2. Walt DR, Franz DR. Biological warfare detection. *Anal Chem* 2000;**72**:738–46 A.
3. Royo S, Martínez-Máñez R, Sancenón F, Costero AM, Parra M, Gil, S. Chromogenic and fluorogenic reagents for chemical warfare agents' detection. *Chem Commun* 2007;**46**:4839–47.
4. Giordano BC, Collins GE. Synthetic methods applied to the detection of chemical warfare nerve agents. *Curr Org Chem* 2007;**11**:255–65.
5. Burnworth M, Rowan SJ, Werder C. Fluorescent sensors for the detection of chemical warfare agents. *Chem Eur J* 2007;**13**:7828–36.
6. Costero AM, Gil S, Parra M, Mancini PME, Martínez-Máñez R, Sancenón F, et al. Chromogenic detection of nerve agent mimics. *Chem Commun* 2008;**45**:6002–04.
7. Choi NJ, Kwak JH, Lim YT, Bahn TH, Yun KY, Kim JC, et al. Classification of chemical warfare agents using thick film gas sensor array. *Sensor Actuat B-Chem* 2005;**108**:298–304.
8. Brunol E, Berger F, Fromm M, Planade R. Detection of dimethyl methylphosphonate (DMMP) by tin dioxide-based gas sensor: Response curve and understanding of the reactional mechanism. *Sensor Actuat B-Chem* 2006;**120**:35–41.
9. Caihong W, Chu X, Wu M. Highly sensitive gas sensors based on hollow SnO_2 spheres prepared by carbon sphere template method. *Sensor Actuat B-Chem* 2007;**120**:508–13.
10. Lee SC, Choi HY, Lee SJ, Lee WS, Huh JS, Lee DD, et al. The development of SnO-based recoverable gas sensors for the detection of DMMP. *Sensor Actuat B-Chem* 2009;**137**:239–45.
11. Joo BS, Huh JS, Lee DD. Fabrication of polymer SAW sensor array to classify chemical warfare agents. *Sensor Actuat B-Chem* 2007;**121**:47–53.
12. Alizadeh T, Zeynali S. Electronic nose based on the polymer coated SAW sensors array for the warfare agent simulants classification, *Sensor Actuat B-Chem* 2008;**129**:412–23.
13. Du X, Ying Z, Jiang Y, Liu Z, Yang T, Xie G. Synthesis and evaluation of a new polysiloxane as SAW sensor coatings for DMMP detection. *Sensor Actuat B-Chem* 2008;**134**:409–13.
14. Nimal AT, Mittal U, Singh M, Khaneja M, Kannan GK, Kapoor JC, et al. Development of handheld SAW vapor sensors for explosives and CW agents. *Sensor Actuat B-Chem* 2009;**135**:399–410.
15. Labrador, RH, Olsson J, Winquist F, Martínez-Máñez R, Soto J. Determination of bisulfites in wines with an electronic tongue based on pulse voltammetry. *Electroanalysis* 2009;**21**;612-617.
16. Holmin S, Spangeus P, Krantz-Rulcker C, Winquist F. Compression of electronic tongue data based on voltammetry: a comparative study. *Sensor Actuat B-Chem* 2001;**76**:455–64.
17. Gutés A, Céspedes F, del Valle M, Louthander D, Krantz-Rulcker C, Winquist F. A flow injection voltammetric electronic tongue applied to paper mill industrial waters. *Sensor Actuat B-Chem* 2006;**115**:390–5.