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A “humid electronic nose” for the detection of nerve agent mimics; a case of selective sensing of DCNP (a Tabun mimic)

Lluís Pascual[a,b], Inmaculada Campos[a,b,c], Román Bataller[a,b], Cristian Olguín[a,d], Eduardo García-Breijo[a,d], Ramón Martínez-Mañez[a,b,c,*], Juan Soto[a,b]

[a] Centro de Reconocimiento Molecular y Desarrollo Tecnológico (IDM), Unidad Mixta Universidad Politécnica de Valencia – Universidad de Valencia, Valencia, Spain
[b] Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n, E-46022 Valencia, Spain
[c] CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Spain
[d] Departamento de Ingeniería Electrónica, Universidad Politécnica de Valencia, Camino de Vera, s/n, 46022 Valencia, Spain

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ABSTRACT

A “humid electronic nose” device based on pulse voltammetry has been applied to detect nerve agent simulants in gas phase. The “humid electronic nose” consists in a polypropylene piece which contains an array of eight metallic electrodes (i.e., Ir, Rh, Pt, Au Ag, Co, Cu and Ni) divided into two sets of four working electrodes housed inside a homemade steel cylinder, and a salt bridge connection to a reference electrode. The electrochemical system is fitted to a nylon membrane damped with a background solution of sodium tetraborate 0.01 M by a second polypropylene piece. The PCA analysis demonstrated that the system is able to discern principal organophosphorous nerve agent mimics (DCP, DCNP and DFP) from organophosphorous derivatives and some other potential interferents. Besides, the PLS quantification analysis showed sound accuracy in the concentration prediction for DCNP in air, good linearity and a limit of detection (LOD) of some a few ppm.

1. Introduction

An electronic nose consists in a device able to mimic the biological olfactory system. An array of non-specific sensors provides a characteristic response pattern which, treated by appropriate data analysis techniques, allows us to identify and quantify certain gas compounds. In the biological olfactory system, olfactory receptors respond non-specifically to smelly compounds and the overall response is interpreted by the brain by providing information about volatile derivatives. The first example of an electronic nose was reported by Dodd and Persaud who used three different metal oxide gas sensors to identify several substances in the gas phase [1]. Nowadays, a large number of transducer principles and techniques have been applied to electronic noses such as acoustic wave (SAW, BAW) sensors, metal oxide semiconductor field effect transistors (MOSFETs), conducting polymers (CP), optical sensors, gas chromatography, ion mobility spectroscopy, infrared spectroscopy, biosensors, etc. [2–5]. Besides there are many examples of amperometric electrochemical sensors to measure target gases. Some typical examples are sensors for oxygen or carbon dioxide [6–11]. In these systems, the gas sample permeates to the working electrode through the gas permeable membrane where it is detected. More recently, ionic liquids as solvents have been also reported [11] for the electrochemical detection of oxygen, carbon dioxide, ammonia [12–17] and hydrogen [15] through gas absorption processes.

The idea of developing a “humid electronic nose” is based on the concept that such a system may overcome the problems usually found in classical electronic noses based on metal oxides and resistive sensors, such as interference of water vapour. Another advantage of using “humid electronic nose” systems is the possibility of employing typical electrochemical techniques, such as potentiometry, coulometry or voltammetry, as used in electronic tongues [18,19], to analyse volatile derivatives. Recently, we showed the conceptual basis for designing a “humid electronic nose” using an array of potentiometric wire electrodes fitted to a wet nylon membrane [20]. That system was able to detect the volatile compounds generated during microbiological spoilage of wines. Moreover in another recent study, we used a “humid electronic nose” to discriminate between different food samples. The device was based on an array of noble metals electrodes which were in contact with a fabric mesh made of nylon that was damped with NaCl aqueous solution and the use of pulse voltammetry [21].

* Corresponding author.
E-mail address: rmaez@qim.upv.es (R. Martínez-Mañez).

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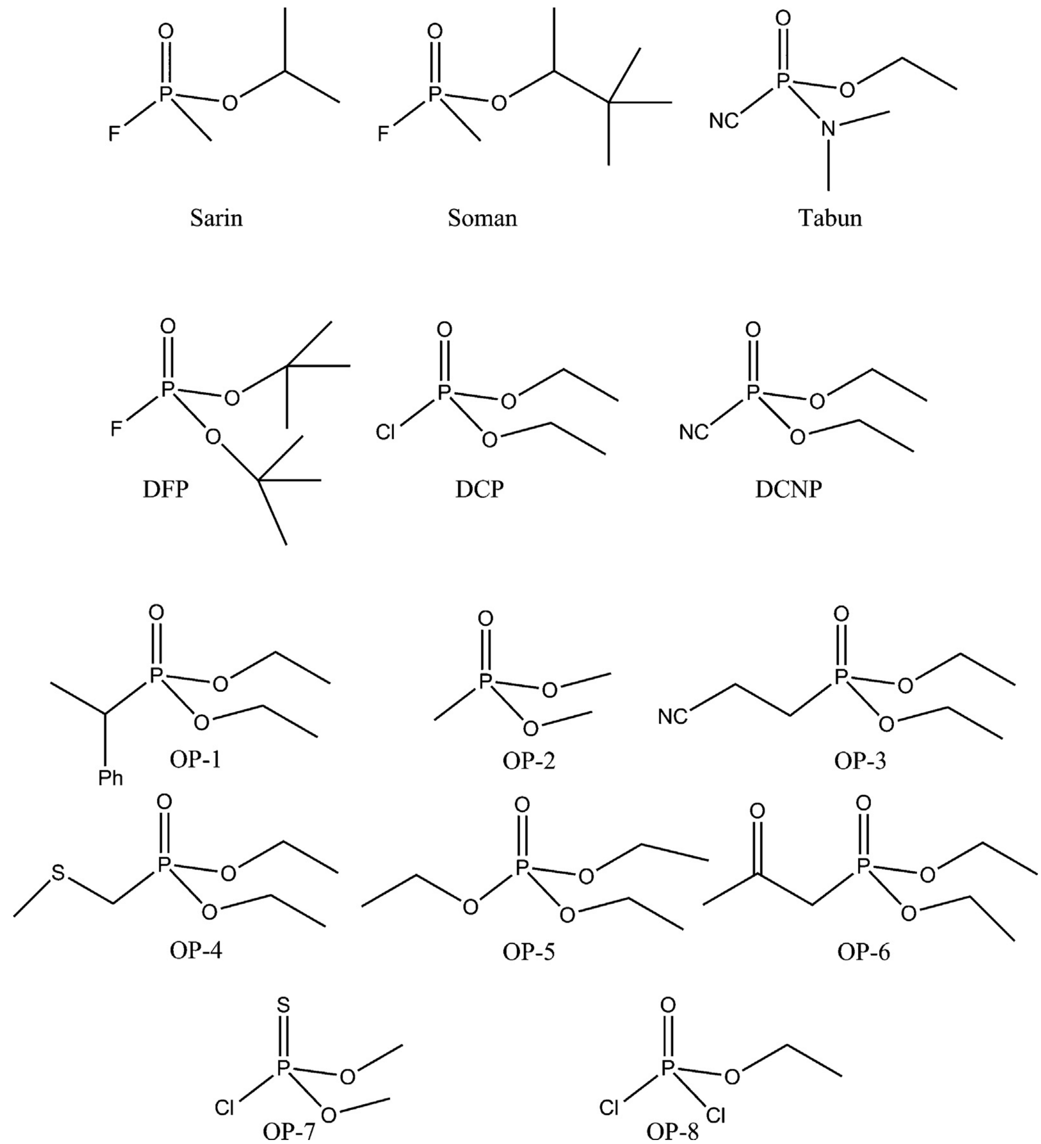

Fig. 1. Chemical structures of nerve agents, nerve agent mimics and other organophosphorus derivatives used in this study.

Furthermore, detection of chemical warfare agents concerns scientists and law enforcement agencies due to terrorist threads based on releasing these agents in public places. According to the Organisation for the Prohibition of Chemical Weapons and the Chemical Weapons Conventions, chemical weapons are "any chemical which through its chemical action on life processes can cause death, temporary incapacitation or permanent harm to humans or animals" [22]. In this context, we have recently shown interest in the design of sensing systems capable of detecting warfare agents. In particular, we focused our research on nerve agents, specifically G-type organophosphorous derivatives; i.e., Soman(GD), Sarin(GB) and Tabun(GA) [23]. Nerve agents have rapid, severe effects on human and animal health as either a gas or a liquid, and poisoning may occur through inhalation or consumption of liquids or foods contaminated with these agents. The effects of these gases are due to their ability to inhibit the action of acetylcholinesterase [24]. Given the high toxicity of these compounds, in these studies we used organophosphorous model compounds, such as diethyl chlorophosphonate (DCP), diethyl cyanophosphate (DCNP), diisipropyl fluoride (DFP), which have a similar structure and reactivity as nerve agents, but display less toxicity.

Several analytical methods and devices have been developed for the detection of nerve agents [25,26]. Current air monitoring systems for nerve agents are based mainly on ion mobility spectroscopy (IMS) or gas chromatography coupled with mass spectrometry (GC/MS). However these systems commonly present difficulties for being transported to test sites, are complex to operate, and are expensive to maintain and require relatively lengthy analyses and interpretation. Thus, alternative methods have been developed including surface acoustic wave (SAW) devices [27], enzymatic assays [28], electrochemical procedures [29,30], chromo-fluorogenic probes [31–34], chemiresistive sensors [35], liquid crystals [36], etc. Moreover, some are used as arrays and are based on principles of non-specific responses and multivariate analyses [37–42].

Following our interest in the development of electronic tongues and noses [43–46], we herein report the design of a "humid electronic nose" and its use for the discrimination and detection of nerve agent mimics in the gas phase.