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Additional Information

An Electronic Nose for the detection of Sarin, Soman and Tabun mimics and interfering agents.

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Abstract

An electronic nose system (E-nose) with metal oxide semiconductor sensors (MOS) has been designed to discriminate and quantify different chemical warfare agents (CWA) mimics. The E-nose consists of an array of commercial MOS sensors for different gases, two sensors for temperature sensing, a sample handling system, a data acquisition system and a laptop with the data acquisition system control. With this device, discrimination studies have been carried out to detect specific CWA simulants (diethyl chlorophosphate (DCP), diethyl cyanophosphate (DCNP), diisopropyl fluoride (DFP)), their derivatives (diethyl 1-phenylethyl phosphonate (OP-1), diethyl (2-cyanoethyl)phosphonate (OP-2), dimethyl methyl phosphonate (OP-3) and diethyl (2-oxopropyl)phosphonate (OP-4)) and some potential interfering substances (sulfuric acid, ammonia, ethanol and acetone). Principal Components Analyses (PCA) show that it is possible to discriminate the studied organophosphorous CWA mimics (DCP, DCNP and DFP) from the other studied derivatives and potential interfering agents. In addition, DCNP quantification studies have been done by using Partial Least Squares (PLS) and a mathematical model has been obtained to predict DCNP concentrations in air. In this model, the coefficient of determination (R^2) is 0.9567, the root mean square error of prediction (RMSEP) is 30 and the limit of detection (LOD) is 5 ppm so the model is considered valid. These results suggest that this E-nose system is capable to discriminate and quantify CWA mimics and it would be a feasible system to be used in a real scenario.

32 1. Introduction

33 The term "Electronic Nose" was first used in 1988 by Gardner and Bartlett, who defined it as
34 "an instrument which comprises an array of electronic chemical sensors with partial specificity
35 and appropriate pattern recognition system, capable of recognizing simple or complex odours"
36 [1, 2]. Due to the characteristic response pattern provided by the array of unspecific sensors,
37 this Electronic Nose System is capable to give information about the surrounding environment.
38 So, it is possible to identify and quantify certain gaseous compounds using an appropriate data
39 analysis technique.

40 The first electronic nose model was provided by Dodd and Persaud. Their system was based on
41 three different metal oxide sensors and it was able to identify several gases by using the
42 measured steady-state signals of these three sensors [3]. Nowadays, Electronic Noses have
43 evolved considerably and there are several technologies that can be applied in these devices
44 such as surface acoustic wave [4], metal oxide semiconductor field effect transistors [5],
45 conducting polymers [6], optical sensors [7], gas chromatography [8], ion mobility
46 spectroscopy [9], infrared spectroscopy [10], etc. [11, 12].

47 Due to the Biological and Toxic Weapons Conventions on the prohibition of the development,
48 production and stockpiling of bacteriological and toxin weapons and on their destruction
49 signed at London, Moscow and Washington on 10 April 1972 and revised in 1993, chemical
50 warfare agents (CWA) shouldn't be in use. However nowadays, the chemical warfare is still a
51 real problem. The threat of exposure to chemical warfare agents has been considered a
52 military issue. However, several recent events have demonstrated that civilians may also be
53 exposed to these agents. Chemical warfare agents are defined as "chemical substances,
54 gaseous, liquid or solid, which might injure humans or animals" [13, 14]. Chemical warfare
55 agents are extremely toxic and have severe effects on human and animal health, either as a
56 gas or liquid and poisoning may occur by gas inhalation, contact with skin or polluted
57 liquid/food consumption.

58 Our investigation reported herein focuses on G-type organophosphorous nerve agents as
59 Sarin(GB), Soman(GD) and Tabun(GA) whose effects in the organism are due to their ability to
60 inhibit the action of acetylcholinesterase [16]. Given the high toxicity of nerve gases,
61 organophosphorous model compounds, such as diethyl chlorophosphonate (DCP), diethyl
62 cyanophosphate (DCNP), diisopropyl fluoride (DFP), which has a similar structure and reactivity
63 as nerve agents but display less toxicity, are generally used in studies in the laboratory [34, 35].
64 The close reactivity is related with the presence of "similar" leaving groups (i.e. F, Cl and CN) in

65 DFP, DCP and DCNP to those found in Sarin, Soman and Tabun (i.e. F and CN). Moreover DFP,
66 DCP and DCNP are less toxic and in fact are not viable nerve agents because are readily
67 hydrolysed (poorly persistent) when compared with Sarin, Soman and Tabun. The mimics used
68 in the laboratory were also organophosphorous and organophosphate compounds such as
69 diisopropyl fluoride (DFP), diethyl chlorophosphonate (DCP), diethyl cyanophosphate (DCNP).

70 Nowadays, there are several equipments and analytical methods that have been approved by
71 the Chemical Weapons Convention in 1993 for chemical warfare agents in-situ detection and
72 quantification [16, 17]. Air monitoring systems for nerve agents are mainly based on ion
73 mobility spectroscopy (IMS) or gas chromatography coupled with mass spectrometry (GC/MS).
74 However, these systems commonly present several difficulties, for instance: Analyses have to
75 be carried out in a laboratory, qualified personnel is required to operate these devices,
76 instrumental and chemicals are complex, the equipment is expensive and the analyses are
77 time consuming. Due to these disadvantages, some alternative methods have been rising such
78 as surface acoustic wave devices [18], electrochemistry [19], spectrophotometric sensors [20],
79 immunochemical sensors [21], capillary electrophoresis [22], enzymatic assays [23], chromo-
80 fluorogenic probes [24, 25], chemiresistive sensors [26] and liquid crystals [27].

81 **2. Theory**

82 **2.1. Principle of operation**

83 Despite MOS sensors have problems with humidity (as water is an interfering compound for
84 this kind of sensors) we have used them in our system because MOS sensors are robust,
85 common and easy to buy everywhere. Therefore, in order to compensate the potential
86 interference of water, a humidity sensor has been included in the system. On the other hand,
87 as temperature is another potential interfering factor, two temperature sensors have also
88 been included in the system. A detailed explanation of the MOS sensors operation is provided
89 elsewhere [28].

90 **2.1.1. Chemical Principle**

91 MOS sensors use metal oxide-based sensing thick films deposited onto a silica substrate. The
92 substrate contains electrodes that measure the resistance of the sensing layer and a heater to
93 desorb any volatile compound remaining in sensing layer by increasing the temperature of the
94 sensor. The sensing layer is a porous thick film made of polycrystalline SnO₂. So the gases to be
95 measured are adsorbed in this surface.

96 In a clean atmosphere, both oxygen and water vapor-related species are adsorbed on the
97 surface of the SnO₂ grains but, when other pollutant gasses are present, a series of reactions
98 take place in the sensor's surface. In case of having reducing gases such as CO or H₂, a reaction
99 takes place with the pre-adsorbed oxygen and water vapor-related species which decreases
100 the resistance of the sensor. Instead, when oxidizing gases such as NO₂ and O₃ are present,
101 the resistance increases. The magnitude of the changes depends on the microstructure and
102 the composition/doping of the base material, on the morphology and the geometrical
103 characteristics of the sensing layer and substrate, **as well as on the temperature at which the**
104 **sensing takes place [28].**

105 In order to explain the resistance change in the sensor when measuring nerve agent mimics
106 the reaction mechanisms for DMMP sample is shown [29], (these mechanisms can be
107 extrapolated to other components and they help the understanding of how the MOS sensors
108 work). DMMP is quite thermally stable at temperatures between 300°C and 600°C. Its
109 degradation generates two compounds: carbon dioxide and methylphosphonic acid as shown
110 in Figure 1.

111 [Insert Figure 1]
112

113 The decrease in resistance obtained when DMMP is detected, takes place in two stages. First,
114 DMMP is adsorbed onto the SnO₂ surface, allowing it to react with an oxygen species (O⁻). This
115 reaction leads to the formation of methylphosphonic acid, which remains adsorbed onto the
116 SnO₂, CO₂ which does not react with the sensor, and H₂O. At the same time, electrons can be
117 released to the conduction band leading to a decrease in the SnO₂ resistance as shown in
118 Figure 2.

119 [Insert Figure 2]
120

121 Finally, the last stage of this mechanism leads to the formation of an ionic phosphorous
122 compound, which is adsorbed onto the SnO₂ (Figure 3).

123 [Insert Figure 3]
124

125 **2.1.2. Transducer Principle**

126 Composition changes in the environment will determine changes in resistance on the sensing
127 layers. The relationship between sensor resistance and the concentration of the target gas (the
128 gas or gases to which the sensor is designed) usually follows a power law described below:

129

$$R \approx K \times c^{\pm b}$$

130 Where 'c' is the concentration of the target gas, 'K' is a measurement constant and 'b' is a
131 value in the range [0.3-0.8]. The positive sign is used for oxidizing gases and the negative sign
132 for the reducing ones.

133 **3. Materials and methods**

134 **3.1. Chemicals**

135 All the chemical compounds have been purchased from Sigma-Aldrich. Discrimination studies
136 have been carried out at their respective saturated vapour concentrations (see Table 1). In
137 addition, quantification studies have been developed in the range [0-208(sat)] ppm.

138 **3.2. Experimental**

139 In this paper, two types of experiments have been done: First, a study has been carried out to
140 discriminate among the different mimic agent samples and some potential interfering
141 substances. Secondly, a quantification study of one of the mimics has been done in order to be
142 able to assess the concentration of this compound in a sample and obtain the limit of
143 detection (LOD).

144 First of all, discrimination studies have been carried out by using the selected nerve agent
145 simulants (diethyl chlorophosphate (DCP), diethyl cyanophosphate (DCNP), diisopropyl
146 fluoride (DFP)), and a set of four similar organophosphorous derivatives (diethyl 1-phenylethyl
147 phosphonate (OP-1), diethyl (2- cyanoethyl)phosphonate (OP-2), dimethyl methyl
148 phosphonate (OP-3), and diethyl (2-oxopropyl)phosphonate (OP-4)). On the other hand, a set
149 of different potential interfering samples were studied: Sulfuric acid and ammonia samples
150 were prepared and measured to analyze the system's response when acid and basic vapors are
151 present. The influence of ethanol and acetone was also studied using them as a reference of
152 the system's response to the presence of volatile solvents. All of them have been measured
153 independently using the same controlled environment and assay specifications in order to
154 avoid the effect of external factors.

155

[Insert Table 1]

156

157 The samples shown in Table 1 were measured under real conditions in order to study the
158 strength of the system. The evaporation chamber was the only part of the device that was
159 under control. In this way, it is possible to ensure that changes in the response signal are only

160 due to changes in the measured sample. The gas to be measured has been mixed with normal
161 air and not with a pattern gas. Next, measurements of the samples were carried out in
162 different seasons throughout the year in order to develop assays in a wide range of ambience
163 conditions. All the samples were measured randomly including the repetitions of each sample
164 as all of them were analyzed by triplicate. Consequently, all the analyses were carried out
165 completely random.

166 Quantification studies have been carried out using DCNP due to its higher response and
167 selectivity observed in discrimination studies previously conducted. A simple dosage system
168 was used to introduce different known concentrations of DCNP into the system (Table 2).

169 DCNP (500 μ L) were deposited and evaporated in a 500mL thermostated balloon at 25°C and
170 vacuum until gas saturation was reached. Then, a controlled volume was extracted with a
171 syringe and injected into the measurement chamber. First, an equal volume of air must be
172 extracted from the measurement chamber before the sample injection in order to avoid
173 overpressure. The injected volumes are those shown in Table 2.

174 [Insert Table 2]

175

176 **3.3. Equipment**

177 The equipment has been designed, developed and manufactured by the Group of Electronic
178 Development and Printed Sensors member of the Center of Molecular Recognition and
179 Technological Development (IDM) at the Polytechnic University of Valencia (UPV) and it was
180 previously used to detect maturation on fruit [30].

181 The equipment (named E-nose system) consists of an array of commercial MOS sensors
182 (FIGARO Engineering Inc., Japan) for different gases (hydrogen, carbon monoxide, butane,
183 methane, etc.), two LM35DZ for temperature sensing, a sample handling system, a data
184 acquisition system and a laptop with the data acquisition system control. The complete E-Nose
185 System is shown in Figure 4.

186 [Insert Figure 4]

187

188 **3.3.1. Sensors array**

189 This E-nose is capable to handle an array of 15 sensors. One of the advantages of the system is
190 that all the sensors can be configured independently (even different to those specified by the
191 manufacturer). So, there are several possible configurations for each sensor. The idea is to use
192 the nonspecific behavior of the sensor to recognize patterns. Therefore, the system has been
193 designed to be flexible and use the sensors as a complex array and not exclusively to detect
194 their corresponding specific gas.

195 Concerning the used sensors, Table 3 shows the list of the specific sensors in the E-Nose.

196 [Insert Table 3]

197

198 **3.3.2. Sample handling system**

199 The sample handling system includes two chambers: the concentration chamber (where
200 samples are placed) and the measurement chamber (where the sensors array is placed). The
201 concentration chamber has a cylindrical shape (12cm i.d x 16cm h.) and is connected to the
202 measurement chamber (12cm i.d x 14cm h.) through a BTC diaphragm pump (Brushless Motor
203 model H054B-11 from Hargraves) especially designed for gas flow and it has a diaphragm that
204 is compatible with this type of dangerous gasses. The sample handling system also includes
205 two stopcocks to control the gas flow. In this way, the sample handling system is flexible in
206 configuration.

207 When a measurement has finished, the heating process ensures desorption of all the
208 remaining molecules in the sensors. Vacuum is also applied to the system in order to assure
209 the removal of every volatile compound from the sample handling system. In this way, the
210 sensors become ready to be used again.

211 **3.3.3. Data acquisition system**

212 The data acquisition system includes the control for each sensor and the measuring electronic
213 system. It has a master–slave structure. All slave boards are controlled by the master board
214 that gather the data of the 15 slaves and send them to the PC. Each slave controls several
215 parameters of the sensor such as the supply voltage (V_C), heating voltage (V_H), load resistance
216 (R_L) and polarization pulses. These parameters can be configured through the PC by using an
217 own software. The slave is based on a PIC18F2580 microcontroller, a 12-bits analogical-digital
218 converter (AD7237A) and a 10-bits digital potentiometer (MAX5481). The master is based on a

219 PIC18F4550 microcontroller that controls the communication between the PC and the slaves;
220 furthermore it controls the whole gas flow system.

221 **3.3.4. Data acquisition system control**

222 In order to handle the entire system, a software interface has been designed. This software
223 **allows** the user to configure the sensors and control the parameters of the experiment. The
224 parameters are configured by the user via software and they are sent to the master through a
225 serial port. The master sends the configuration data to every slave by using an I²C bus. Next,
226 the slave-microcontroller configures the digital-analogical converter (DAC) to supply V_C and V_H
227 to the sensor. If pulses are required, the slave-microcontroller also configures these voltages
228 temporarily. Then, the microcontroller modifies the value of R_L through the digital
229 potentiometer by a serial peripheral interface (SPI) protocol. The implemented software has
230 three main parts.

231 The first one is the data acquisition control application, in which we can control the
232 parameters of every assay such as the time of the probe, the cleaning process, the diagnosis
233 test, etc.

234 The second part of the implemented software is a display showing the result of the measuring.

235 The last part of the software is the sensors configuration application. It makes the system
236 versatile and let the user configure all sensors separately and control the number of sensors
237 involved in our system. In addition, this application let the user define all the operating point
238 parameters: heater supply voltages, sensor supply voltages, heater heating/cooling times,
239 sensor connection/disconnection times, measurement time, test establishment time, as well
240 as the assignation of the sockets to the sensors. In fact, this important advantage let the user
241 chose among different configurations. Moreover, it supplies information of the manufacturer
242 about the nominal performance and security values of the different sensors.

243 **4. Results and discussion**

244 As a preliminary way to detect and discriminate nerve agent mimics and interfering
245 substances, a principal components analysis (PCA) has been done with the obtained data from
246 the studied samples. Next, an experiment to predict the concentration of DCNP was performed
247 by using the partial least square technique (PLS). All statistical analyses were performed using
248 the Solo (version 7.0.3, Eigenvector Research, Inc) software application.

249 **4.1. PCA Studies**

250 As PCA is an efficient approach to show a dataset in two dimensions, principal component 1
251 (PC1) and principal component 2 (PC2), with the maximum representativity, the responses of
252 different organophosphorous nerve agents simulants were analysed by this linear
253 unsupervised method. In addition, a set of potential environmental interferences such as
254 solvents, acid and basic compounds was also analysed in order to determine the hardness of
255 our system in a non-ideal environment.

256 Figure 5 shows a PCA analysis developed using data from all the measured samples. This PCA is
257 an approach of how the system might work in real conditions. It can be seen that there is an
258 effective discrimination among types of samples.

259 [Insert Figure 5]

260

261 Figure 6 shows a second PCA model developed including only organophosphorous compounds
262 in order to analyse the response of the system just with chemically similar samples. As shown,
263 there is a clear discrimination among types of samples.

264 [Insert Figure 6]

265

266 According to the obtained results our system is able to discriminate well among DCP, DFP,
267 DCNP, typical organophosphorous interfering agents with similar structure, and some potential
268 environmental interfering agents. Principally, DCNP is the easiest discriminated compound as
269 DCP and DFP are also easily detected but their discriminations are not as selective as DCNP's
270 discrimination is.

271 **4.2. PLS Quantification**

272 A quantification study using PLS was carried out [31, 32, 33] in order to evaluate the
273 performance of the system and determine the LOD for nerve agents simulants. According to
274 the obtained results in previous classification studies, DCNP was selected as quantification
275 analyte due to its high response.

276 The data collected was divided into two subsets; the first one was used to calibrate the model
277 and the second one to test it with independent data. The Leave-One-Out approach has been
278 used as cross-validation method, just using the training samples. According to the cross-
279 validation variance studies, 6 latent variables have been used to build the model. In order to
280 create this model, 33 samples of DCNP were measured in the concentration range of 0-208

281 ppm and then analysed by PLS. The calibration of the model was performed using 22 samples
282 so the remaining 11 samples were used to test the model. Figure 7 shows the predicted values
283 versus the real ones for DCNP. In this model, the coefficient of determination (R^2) is 0.9567
284 and the root mean square error of prediction (RMSEP) is 30 so the model is considered
285 statistically valid. In addition, the estimated LOD is 5 ppm. These values let us affirm that it is
286 feasible to quantify warfare gas mimics by combining an electronic nose and this kind of
287 mathematical models.

288 [Insert Figure 7]

289

290 **5. Conclusions**

291 A new method for nerve agents' mimics detection is introduced using a new device (E-Nose).
292 Classification studies by PCA analyses show that the E-Nose system is able to discriminate the
293 mimics of the main G-type nerve agents (DCP, DFP and DCNP) from typical organophosphorous
294 derivatives and some potential interfering compounds such as acids, bases and solvents. These
295 assays reveal that DCNP is the compound that shows a higher response. So, it was selected to
296 carry out quantification studies. These determinations were performed by using PLS analyses
297 and they showed statistically valid models. For the best of the obtained models, the coefficient
298 of determination is 0.9567, RMSEP is 30 and the LOD for DCNP is 5 ppm.

299 Finally, according to these preliminary obtained results, the introduced E-Nose seems to be a
300 reliable system to detect and quantify nerve agent mimics in complex samples with specific
301 potential interfering substances. This system provides a selective and statistically valid
302 response, in short measurement times; it is easy to use and cheap. These results give rise to
303 begin the development of specific easy to use equipment for early detection of CWA's.

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