Discrimination and classification of chemical warfare agent simulants using a Love-wave sensor array

D. Matatagui\textsuperscript{a}\textsuperscript{*}, M.J. Fernández\textsuperscript{a}, J. Fontecha\textsuperscript{a}, J.P. Santos\textsuperscript{a}, I. Gràcia\textsuperscript{b}, C. Cané\textsuperscript{b}, M.C. Horrillo\textsuperscript{a}

\textsuperscript{a}Instituto de Física Aplicada, CSIC, Serrano 144, 28006 Madrid, Spain
\textsuperscript{b}Instituto de Microelectrónica de Barcelona, CSIC, Campus UAB, 08193 Bellaterra, Spain

Abstract

An array made up of Love-wave sensors has been developed as a detection system for chemical warfare agents (CWAs). This array has been tested with well-known CWA simulants detecting very low concentrations, such as 40 ppb of DMMP, a simulant of sarin nerve gas, 250 ppb of DPGME, a simulant of nitrogen mustard and 15 ppm of DMA, a simulant of distilled mustard. Additionally, principal component analysis (PCA) as a data pre-processing and discrimination technique, and probabilistic neural networks (PNN) as a patterns classification technique, have been applied, obtaining good results concerning to discrimination and sensitivity.

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Keywords: Love wave, gas sensor, chemical warfare agent, sensor array;

1. Introduction

The chemical warfare agents are powerful weapons and a threat for civil safety, and as such, it is important to have an early detection for low concentrations, that is to say, concentrations below the median lethal dose (LD50: dose required to kill half the members of a tested population). In response to recent terrorist attacks there is an urgent interest to develop highly sensitive, selective and fast devices.

Array acoustic wave devices [1] have been widely used in sensing application. Some types of acoustic wave sensors are: quartz crystal microbalance [2], devices bases on Rayleigh waves [3] and Love waves [4]. Due to the high sensitivity, fast response, real time detection, stability and low cost, an array of Love wave sensor is suitable to detect CWAs.

* Corresponding author. Tel.: +34915618806; fax: +34915631794.
E-mail address: d.m@csic.es.
2. Materials and Methods

2.1. Love-wave devices

Our Love-wave sensors (Fig. 1a) are based on a shear horizontal surface acoustic wave (SH-SAW) propagated on the ST-cut quartz. This wave, with a wavelength $\lambda = 28 \mu m$, is generated and detected by interdigital transducers (IDTs) with a 200 nm thickness aluminum layer deposited by RF sputtering. A double electrode structure is repeated 75 times ($N=75$) to form each IDT. The spacing, center to center, between IDTs, $L_{cc}$, is $150 \lambda$ and the acoustic aperture, $W$, is $75 \lambda$. Finally, the SH-SAW is guided in a film of SiO$_2$ deposited by PECVD in order to obtain a Love-wave. The highest sensitivity is found for a thickness of SiO$_2$ of about 3 $\mu m$, being the synchronous frequency 163 MHz.

2.2. Sensitive layers

The CWA simulants are adsorbed on polymers, each one with different sorption properties. Six of these polymers [1] were deposited on the Love wave devices as sensitive layers by spray coating technique. Therefore, an array was made up of six sensors (Table 1).

Table 1. Sensor array composition.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>PMTFPS (Trifluoropropylmethylsiloxane dimethylsiloxane)</td>
</tr>
<tr>
<td>S2</td>
<td>CW (Carbowax)</td>
</tr>
<tr>
<td>S3</td>
<td>PEI (Polyethilenimine)</td>
</tr>
<tr>
<td>S4</td>
<td>PECH (Polyepichlorohydrin)</td>
</tr>
<tr>
<td>S5</td>
<td>PDMS (Polydimethylsiloxane)</td>
</tr>
<tr>
<td>S6</td>
<td>PCPMS (Polycyanopropylmethyisiloxane)</td>
</tr>
</tbody>
</table>

2.3. Samples and experimental setup.

The CWA simulants used in our experiment were: dimethylmethyl phosphonate (DMMP), dipropylene glycol methyl ether (DPGME), dimethylmethyl acetamide (DMA). The concentration of the simulant was calculated using Antoine’s Equation. The volatiles were extracted and diluted with synthetic air, controlled by a mass flow controller in order to provide the desired concentration. Volume of the samples was 10 ml. They were kept at constant temperature ($10^\circ C$) in a thermal bath for 30 minutes (headspace time) before being carried to the chamber. Air flow in the chamber was 200 ml/min and the exposition time 30 minutes. The experiment control and data acquisition in real time were implemented with a PC by means of software made at home. Experimental setup is shown in Fig. 1b.
2.4. Statistical treatment

Principal component analysis (PCA) and a probabilistic neural network (PNN) have been used for data analysis. PCA is a statistical method for reducing the number of dimensions of numerical dataset without much loss of information. Once the analysis is done, all data can be plotted in two or three axes. The neural networks were trained with the three principal components (PC1, PC2 and PC3) resulting from PCA and its performance was evaluated with leave-one-out cross validation.

3. Results and Discussion

The array sensor was exposed repeatedly to different concentrations of each simulant (Table 2), measuring the frequency in real time (Fig. 2a), in this case for DMMP. The sensors have a good linear correlation between the frequency shift and concentration as it is shown in Fig. 2b.
The maximum frequency shifts during exposure time were normalized to concentration and PCA was applied to these data, obtaining the principal components, then PC1 and PC2 were represented in Fig. 3. The ellipses include the measurements of each simulant, and therefore separated ellipses indicate that the CWA simulants can be clearly discriminated. In this case a good separation is observed among simulants. PC1, PC2 and PC3 were used to train the PNN and a 100% classification result was achieved.

Table 2. CWA simulants tested, concentrations measured and LD50 for each CWA

<table>
<thead>
<tr>
<th>Simulant</th>
<th>CWA</th>
<th>Concentrations (ppm)</th>
<th>LD50 (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMMP</td>
<td>Sarin (GB)</td>
<td>0.04, 0.05, 0.06, 0.08, 0.2, 0.4, 0.6, 0.8, 1</td>
<td>18</td>
</tr>
<tr>
<td>DPGME</td>
<td>Nitrogen Mustard (HN)</td>
<td>0.25, 0.5, 0.75, 1, 2.5, 7.5, 10</td>
<td>180</td>
</tr>
<tr>
<td>DMA</td>
<td>Distilled Mustard (HD)</td>
<td>15, 25, 50, 75, 125, 150, 175, 200</td>
<td>140</td>
</tr>
</tbody>
</table>

Fig. 3. PCA score plot of CWA simulants measurements.

4. Conclusions

In conclusion good linearity, stability, reversibility, accuracy, fast response, high sensitivity and selectivity have been achieved with the developed Love-wave sensor array. It has allowed us to detect low concentrations, discriminate, and classify the CWA simulants tested measured.

Acknowledgements

This work has been supported by the Spanish Science and Innovation Ministry under the project TEC2010-21357-C05-04.

References