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Optimized design of a SAW sensor array for chemical warfare agents simulants detection

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Abstract

Chemical warfare agent simulants detection is of great interest for security reasons. An electronic nose based on Surface Acoustic Wave (SAW) sensors has been developed and sensor polymer coatings have been optimized. These allowed us to detect very low concentrations of certain simulants. A good classification was achieved.
Keywords:SAW sensor ,Electronic nose, LSER, Chemical warfare agent.

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1. Introduction

Chemical Warfare Agents (CWA) are a very dangerous weapon, they are easily transported and hidden, highly mortal and effective. The samples measured are simulants of well known CWA such as Sarin (GB), Soman (GD), Distilled Mustard (HD) and Nitrogen Mustard (HN), which are nerve and blister agents [1,2,3].

1.1. SAW Sensors

A SAW sensor consist of an oscillator controlled by a Delay Line (DL) fabricated on ST-x quartz, which, in our case, have an oscillation frequency around 157 MHz. They were coated with different polymer thin films as a sensitive layer (Table 1a). The Interdigited Transducers (IDTs) were made of aluminium deposited by RF sputtering using photolithographic techniques, being the thickness 200 nm. Both the spacing between the fingers and their width were 5 µm, what means a 20 µm wavelength, λ,[4].

1.2. Theoretical background

Sensor responses are based on frequency shifts due to a mass loading. This mass loading depends on the polymer film volume, V_f and the concentration of the solute in the polymer phase C_s. A partition coefficient K represents the ratio between C_s, and the concentration of the vapour in the gas phase C_v. Consequently K depends on both the polymer and vapour properties.

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$$K = \frac{C_s}{C_v} \tag{1}$$

Also, by the linear solvation energy relationships (LSERs) equation, this partition coefficient is estimated:

$$\log K = c + rR_2 + s\pi_2^* + a\alpha_2^H + b\beta_2^H + l \cdot \log L^{16} \tag{2}$$

Where R_2, π_2^H, α_2^H, β_2^H and L^{16} are the solute vapour parameters, and r, s, a, b, l are the values which characterize the solubility properties of the polymer. The value c is the constant arising from the multiple linear regression method used to determine the LSER coefficients. The mass loading Δm may be easily calculated:

$$\Delta m = C_s \cdot V_f = K \cdot C_v \cdot V_f \tag{3}$$

Then, for a SAW oscillator, the expression for a frequency shift, due to a mass loading is:

$$\Delta f = (k_1 + k_2) \cdot f_o^2 \cdot \frac{\Delta m}{A} = (k_1 + k_2) \cdot f_o^2 \cdot h \cdot K \cdot C_v \tag{4}$$

Where k_1 and k_2 are constants of the piezoelectric substrate, h is the film thickness, f_o is the unperturbed resonant frequency of the SAW oscillator and A is the film area [5]. For a specific SAW oscillator and a given polymer and vapour, Δf is proportional to the vapour concentration.

1.3. Statistical treatment

Principal Component Analysis (PCA) and a Probabilistic Neural Network (PNN) have been used for data analysis. Both were implemented in Matlab®. PCA is a linear method to reduce the dimensionality of the data. Once the analysis is done, all data can be plotted in two axes. The neural networks were trained and the performance was evaluated with leave-one-out cross validation.

2. Array optimization

Our goal was to find the optimal polymers for coating the SAW devices to obtain the highest sensitivity and selectivity. The solute vapour parameters of DCE, DMA and DMMP have already been studied by several authors [6,7], as well as the solubility parameters of the most used polymers in gas sensing [8,9,10].

Table 1. (a) Chosen polymers for the array (b) Simulants data

Sensor number	POLYMER	THICKNESS (HZ)
0	Reference	-
1	PCPMS (Polycyanopropylmethylsiloxane)	150
2	PECH (Polyepichlorohydrin)	300
3	Carbowax	200
4	PDMS (Polydimethylsiloxane)	300
5	PEI (Polyethilenimin)	300
6	PMFTPMS (Trifluoropropylmethylsiloxane-dimethylsiloxane)	250

Simulant	Formula	Simulant	Concentration (ppm)
DMMP	$C_3H_9O_3P$	Dimethyl methylphosphonate	0.05-1
DPGME	C_7O_3	Dipropylene glycol monomethyl ether	0.5-10
DMA	C_4H_9NO	Dimethylacetamide	100-250
DCE	$C_2H_4Cl_2$	1,2-Dichloroethane	80-250

Using these parameters, the partition coefficient, K, for every pair polymer-simulant, was calculated by the LSER equation. Thus, the behaviour of a sensor array with different coatings sensing these simulants can be simulated in

Matlab®. Every polymer combination for an array of six sensors was studied, and the array with the highest sensitivity and selectivity properties was chosen.(Table 1a)

3. Experimental

3.1. Data acquisition and instrumentation

A thermal bath was used to keep liquid samples at constant temperature. The sensors responses, given by the frequency shifts, were measured with a frequency counter HP 53131 connected to a microwave switch system, Keithley S46, which switches the frequency display of the seven sensors. Vapour concentration in air was controlled by two mass flow controllers (10 and 200 ml/min). Data were acquired in a computer by a home-made software, which also measured the temperature in the sensor chamber and the room. Temperature in the sensor chamber was kept at 23° C by a Peltier device.

3.2. Samples

Using Antoine’s Equation we calculated the vapour pressure of the simulants. (Table 1b).The mass flow controllers were set to provide the desired concentration. Volume of the samples was 10 ml. They were kept at constant temperature (10ºC) in a thermal bath for 15 minutes (headspace time) before being carried to the chamber. Air flow in the chamber was 200 ml/min and the exposition time 30 minutes. Every simulant was measured repeatedly for each concentration.

4. Results

SAW sensors showed a fast and remarkable response to these simulants (Fig.1a). According to equation (4) sensors behave linearly with vapour concentration (Fig. 1b).

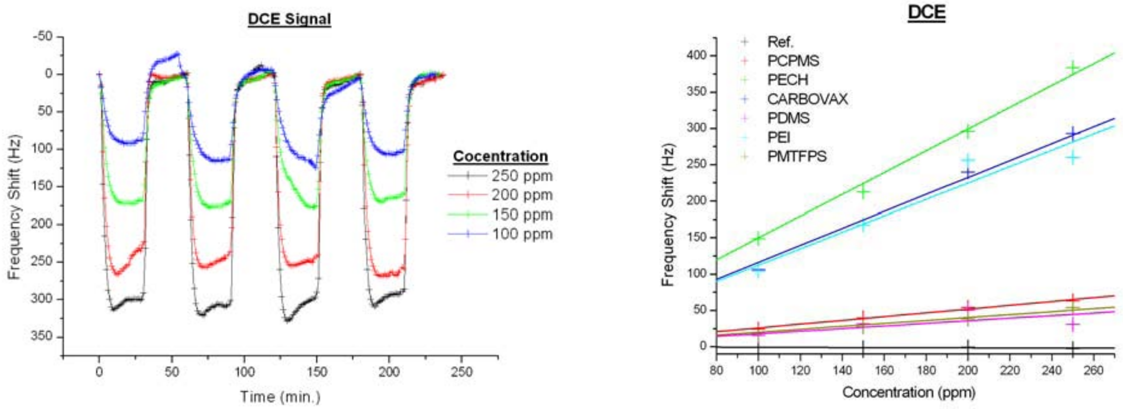

Fig. 1 (a) Response plot for DCE and different concentrations (b) Linear correlation between frequency shift and concentration

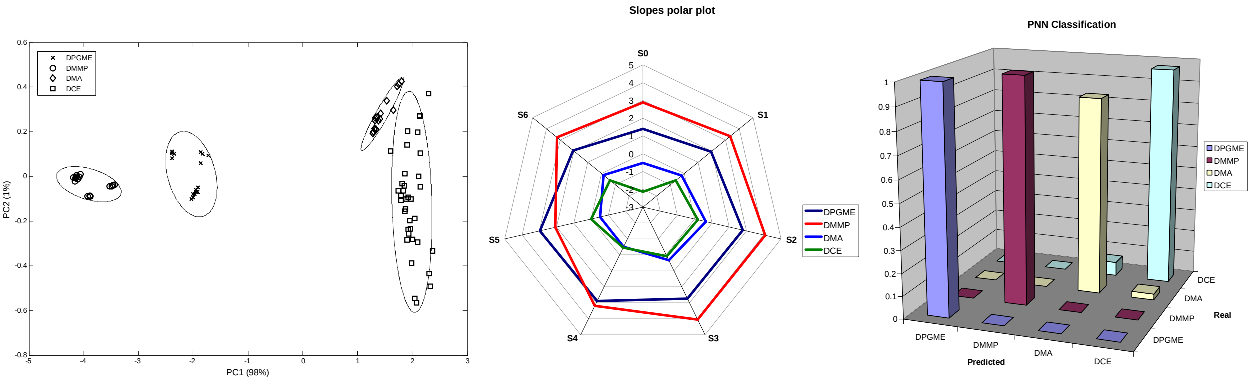

Fig.2 (a) Principal component analysis (b) Slopes composing a finger print (c) Probabilistic neural network results

The maximum frequency shifts during exposure time are normalized to concentration. PCA is applied to these data, and a good separation is observed among simulants (Fig. 2a).A radial plot of the slopes shows a specific finger print for each simulant which could be used for a visual differentiation between them (Fig. 2b).As data present very different magnitude orders, the logarithm of the slopes is presented. Classification results of the PNN are shown (Fig. 2c). In the X-axe are represented the real samples and the Y-axe represents predicted ones. Therefore, successful rates are plotted in the diagonal, where prediction matches the real gases. In the third axe is shown the rate of every event.

5. Conclusions

Interactions between VOCs and polymer coatings are predicted using LSER equation; therefore sensor array efficiency can be tested theoretically. This allowed us to choose between some of the most studied polymers and consequently good discrimination rates were achieved when measuring. Very low concentrations were detected in some cases, such as DMMP 0.05 ppm, and DPGME 0.5. Results could be improved by increasing the number of tested polymers.

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