SENSOR ARRAY ABLE TO DETECT AND RECOGNISE CHEMICAL WARFARE AGENTS

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Abstract

In this paper we studied a device based on array of six different sensors with surface acoustic wave for detections and recognition of three chemical warfare agents (chloropicrin, soman and lewisite). The sensors are "delay line" type with a center frequency of 69.4 MHz.

It presents an original algorithm to identify the nature and concentration of gas from a finite range of possible gases.

Numerical program developed to implement this algorithm, provides to operators all the particulars of gas and an indicator of credibility of the results provided as a measure of the degree of disturbance of the signals received from sensors.

Keywords: SAW, chemical warfare agent, array of sensors, algorithm.

1. Introduction

Perfect selectivity for a single analyte is virtually unattainable for a SAW sensor if we use a single sensitive material. To recognize an analyte it is necessary to use an array of several sensors with different coating materials with different sensitivities to various gases components.

Ability of array SAW sensors to discriminate between different analyte was demonstrated [2-9]. Generally it used an array of 3-6 elementary sensors to discriminate between a large area of target substances from chemical warfare agents (CWAs) [2, 4-8] to wine [3].

In this paper we studied a device based on array of six sensors with different coating materials for detections and recognize of three CWAs (chloropicrin, soman and lewisite).

The array of sensors has as sensitive layer polymers (polybutadiene (PBD), polyisoprene (PI), polydimethylsiloxane (PDMS), polyethylenimine (PEI)) and nanoparticles (Si/SiO_2, TiN) embedded in polymers.
The response of elementary sensors coated with polymer layer (PBD, PI, PDMS, PEI) at chloropicrin, soman and lewisite was presented by Viespe et. al. [10].

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The elementary sensor is a “delay line” type SAW device with a center frequency of 69.4 MHz. The SAW sensor consisted of two-port resonators with 50 electrodes pairs with an aperture of 2500 μm and a periodicity of 45.20 μm.

The interdigital transducers were made by RF magnetron sputtering, using standard photolithographic techniques.

The thickness of the ITD deposited on ST-X quartz substrate was of 150 nm gold on 10 nm chromium [10, 11]

The testing process of the sensor devices was carried out at the Scientific Research Center for NBC Defense and Ecology the only institute from Romania authorized to manipulate such CWAs.

The sensitivity of elementary sensors it is presented in table 1.

The frequency shift was proportional to concentrations for all the sensors between 30 - 4000 ppm [2].

2. Used Computing Structure

While establishing computing structure, as well as the adopted algorithm, it was assumed that from the three gases that would be possible (Chloropicrin, Soman and Lewisite) only one could be encountered.

Gas concentration, measured in *ppm*, could be any one and the sensor array will have six different sensors.

Computing procedure has as data input the frequency deviations, denoted with *f* [Hz], as them are determined by the six sensor array.

Table 1. Sensitivity of elementary sensors

CWA	SAWS no.	Polymer type	Sensitivity Δf/c Hz/ppm
chloropicrin	S_1	PBD	0.1
	S_2	PI	0.9
	S_3	PDMS	0.3
	S_4	PEI	0.4
	S_5	Si/SiO_2 -PEI	0.2
	S_6	TiN-PEI	0.1
soman	S_1	PBD	0.1
	S_2	PI	2.3

	S_3	PDMS	0.6
	S_4	PEI	1.6
	S_5	Si/SiO_2 -PEI	0.5
	S_6	TiN-PEI	0.3
lewisite	S_1	PBD	0.5
	S_2	PI	1.6
	S_3	PDMS	0.5
	S_4	PEI	2.7
	S_5	Si/SiO_2 -PEI	1.4
	S_6	TiN-PEI	1

Frequency deviations are analogical determined and then converted into numerical format, long integers or floating point simple precision.

It was experimental established that frequency deviations determined, by the sensors array, are linear in the entire used range of gas concentration.

Admitted error of each sensor is about ±10 [%]. Computing approach has to be flexible enough in order to support gas type and sensor parameter updates, such making sensor matrix adaptable in the future.

Following these general principles the structure of our approach is presented in figure 1.

3. Procedure Used To Identify Gas Type And Its Concentration

It was defined a deterministic procedure, based on the mean appearing absolute error. Each sensor has a linear characteristic as in Figure 2.

It means that each of the six sensors has a (linear) dependency algebraically expressed as in (1):

$$C_{jk} = \mu_{jk} \cdot \Delta f_k \qquad (1)$$

In relation (1) it was noted with:

- $C_{jk,}$ is the concentration of the gas j, ($m \geq j \geq 1$), m =3, measured with the sensor k ($n \geq k \geq 1$), n = 6.
- μ_{jk} is the sensibility of the sensor k for the gas j, and it is constant for each sensor in the array sensors (as can be seen in figure 2).
- Δf_k is frequency variation at the sensor k given the presence of gas j.

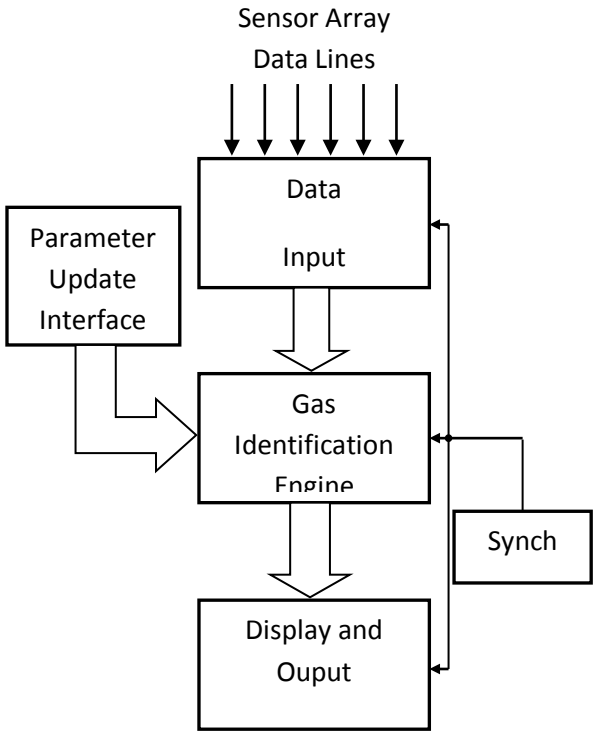

Figure 1. Gas identification computing structure.

Once variations of the sensors frequency happen it is supposed that a gas *j*, not yet identified, has been detected.

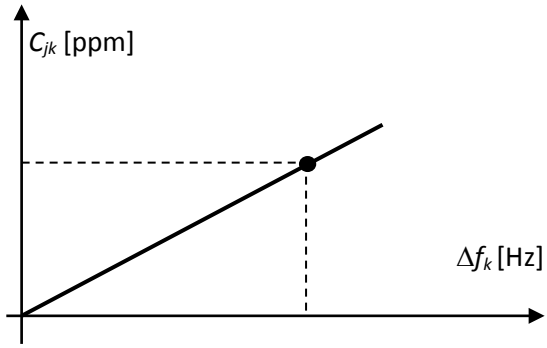

Figure 2. Sensor's linear characteristic.

Suppose that unknown gas *j* (one belonging to the set {Chloropicrin, Soman, Lewisite}) has to be detected knowing frequency variation Δf_k of each of the six sensors.

It is obvious that the gas concentration has to be the same for each sensor in the array.

Frequency variation for each sensor could be translated in different concentrations of gas depending on the sensor's characteristic.

The mean of the concentration for each considered gas at each sensor and is computed.

$$< C_j >= \frac{\sum_{k=1}^{n} C_{jk}}{n}, \quad 1 \le j \le m. \tag{2}$$

Gas type has to be decided among the six sensors frequency variation. The sample size of our statistical sample is equal to the number of independent data we are able to collect from our sensor array. It is limited to only six such data, $n = 6$.

Results are evaluated using this formula:

$$\delta_j = \frac{\sum_{k=1}^{n} \left| C_{jk} - < C_j > \right|}{n} \tag{3}$$

Estimated gas concentration satisfies this relationship for each gas:

$$C_j \in [< C_j > -\delta_j, < C_j > +\delta_j], \tag{4}$$

for $: 1 \le j \le m.$

The relative errors of our determinations are computed as follows:

$$\varepsilon_j = \frac{\delta_j}{< C_j >} \cdot 100[\%], \quad 1 \le j \le m. \tag{5}$$

The size of our statistical sample is equal to the number of independent data sources we are able to collect from our sensor array. It is limited to only six such data.

4. Experimental Results

Since gas sensors could deliver frequency variations with random ±10 [%] errors, several tests were made in order to determine the robustness of our approach targeting gas identification and concentration.

Table 2 is showing gas identification and concentration with test data derived from frequency variations of Chloropicrin, 1000ppm, but having ±5%, ±10% and ±15% errors.

Table 2. Gas detection and identification using input data.

Sensors	Δf_k Hz	Chloropicrin		Soman		Lewisite	
	Error ±5%	*P* %	ppm	%	ppm	%	ppm
S_1	95						
S_2	945						
S_3	285	95	1000	66	472	34	291
S_4	420						
S_5	190						
S_6	105						
	Error ±10%	*P* %	ppm	%	ppm	%	ppm
S_1	90						
S_2	990						
S_3	270	90	1000	69	463	33	290
S_4	440						
S_5	180						
S_6	110						
	Error ±15%	*P* %	ppm	%	ppm	%	ppm
S_1	85						
S_2	1035						
S_3	255	90	1000	69	463	33	290
S_4	460						
S_5	170						
S_6	115						

Gas having greatest probability (column denoted P %, in Table 2) is recognized as the detected gas.

From the first section of table 2 (±5% error of sensors frequency variation) a particularly robust result was obtained when Chloropicrin gas has been recognized (95% probability while Soman and Lewisite gas are recognized with 66% and, respectively, with 34% probability).

The second section of Table 2 outlines gas identification when sensors deviation frequencies are determined with ±10% accuracy.
Chloropicrin was the identified gas, having 90% probability while Soman with 69% probability and Lewisite with only 33% probability were discarded.

Third, and last section of Table 2, is showing gas identification results when for each sensor deviation frequency is within ±15 %.
Applying same screening criteria, Chloropicrin gas was detected and recognized (it has 85% probability) while the two other gases have lesser probabilities (71% and, respectively, 33%).

4. Conclusions

We have demonstrated the possibility of applications of an array of six elementary SAWS to discriminate three CWA.

Proposed and used computing procedure to identify gas and its concentration has satisfactory time performance (few milliseconds). Gas identification accuracy has linear dependency with the error of input data (detected frequency deviation).

Hardware implementation of the gas identification computing structure will use field programmable technologies. Such approach has the flexibility and the low cost features needed in order to build-up such a prototype.

Actual computing procedure could be implemented using LUT based FPGAs. Embedded processor approach is targeted for our computing procedure. Portability and low power consumption are essential features for such a device, Bucur et al. [1].

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