An Electronic Nose Prototype for the On-Field Detection of Nerve Agents

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A portable electronic nose prototype for nerve agent detection

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***Abstract*—This paper presents a cost effective electronic nose prototype for the detection of 1.6 ppm of dimethyl methylphosphonate (DMMP) in a complex background. The device comprises of seven cross-sensitive carbon nanotube mat (CNT-mat) type sensors, an impedance measurement circuit and a micro-computer for data pre-treatment and classification stages. This study focused on the detection of DMMP in a gas mixture, using the responses of the sensors before they reach a stable and repeatable behavior. Even with this major constraint, the support vector machine used for classification reached 98% precision for the recognition of the samples.**

I. Introduction

The detection of toxic vapors at low concentration is a major challenge to detect an industrial leakage or a chemical attack. Nerve gas like sarin are very potent toxins which have very low immediately dangerous to life and health (IDLH) values in the tens of parts per billion (ppb).

The currently available technologies to detect these coumpounds are bulky and expensive. As such, the need for a low-cost, light-weight portable solution for the real time detection of nerve agents has driven research in the two last decades. Several transduction techniques have been investigated to transform the chemical information into electronic signals such as ion mobility spectrometry [1], metal oxyde frameworks (MOS) [2], MEMS such as surface accoustic wave sensors [3] or capacitive ultrasonic transducers [4], metal-insulator-metal ensembles [5], liquid cristals [6], or carbon nanotubes (CNT-mat) [7]. Most of these sensors have major drawbacks such as the lack of repeatability of the responses whithout a calibration phase or a broad chemical selectivity.

A solution to deal with these issues is to use several sensors in an electronic nose (E-nose) system. Such a system includes an array of chemical sensors which react selectively to different molecules, a pre-treatment stage which extracts relevent features from the sensor signals and a classification stage which links non-specific responses from the sensors to a specific response of the system.

This work focuses on showing the first results of our portable e-nose system for the detection of DMMP, a sarin simulant, in a mixture without previously calibrating the sensors.

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In this work, CNT-mat type sensors have been used as they have high sensitivity at ambient temperature and are cost effective. Furthermore, their selectivity is tunable by adding polymers in the CNT-mat [8]–[10]

The choice of the features which are extracted from the raw responses of the sensors is crucial for E-nose systems. Transient features such as integrals and maximum derivatives have been showned to be reliable features [11].

Many algorithms have been investigated for the classification stage of E-nose systems such as Principal Component Analysis (PCA) [12], Artificial Neural Networks (ANN), Suport Vector Machines (SVM) [13]. In this study, SVM is successfully employed for the correct recognition of samples containing DMMP.

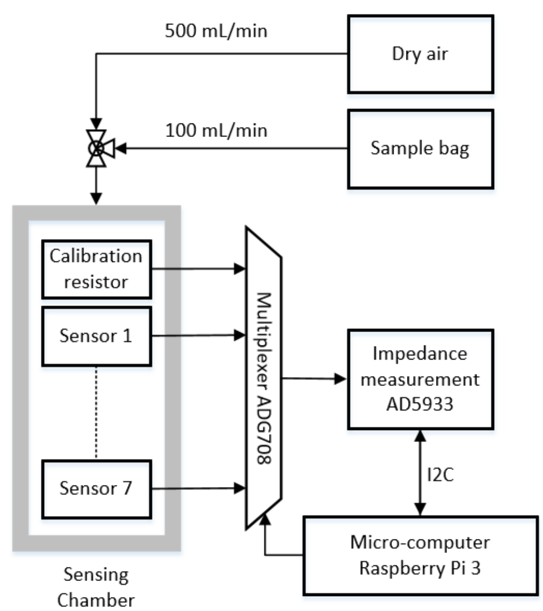

Figure 1: Schematic of the proposed electronic nose system

II. Proposed E-nose system

The developped electronic nose systems is described in Figure 1. It comprises of:

1) seven CNT-mat sensors
2) an impedance measurement circuit including a multiplexer to sample the signals from the seven sensors
3) a micro computer to preprocess and classify the data from the measurement circuit.

A. CNT-mat sensors

A CNT-mat sensor is a nanocomposite structure of conductive CNTs and non-conductive polymers to add selectivity. The nanocomposite is sprayed on interdigitated electrodes layer by layer as described in [14]. CNT intrinsec conductivity varries when molecules get adsorbed on the tubes surface. Molecules reacting with the embedded polymers change the tunnel conductivity between CNTs of the network. These phenomena cause a measureable capacitance change between the interdigitated electrodes. Seven different sensors were proposed and manufactured by our partners from the IRDL in order to have cross sensitivity:

1) Polyvinylpyrrolidone (PVP) + phosphate (PO4)
2) PVP
3) Polystyrene (PS) + PO4
4) PS + anthracene (ANT)
5) Poly(methyl methacrylate) (PMMA) + PO4
6) PMMA
7) Polycaprolactone (PCL)

B. Measurement front end

The capacitances from the sensor array are measured in a cyclic fashion thanks to an analog multiplexer (ADG708) and using an impedance converter chip (AD5933). The base resistances of the sensors are comprised between 5 and 36 kΩ. As such, a calibration resistance of 10 kΩ is used to compensate for the internal impedance of the system. The micro-computer (Raspberry Pi 3) retrieves the capacitances from the array through an I2C interface and controls the multiplexer though four digital IOs. This systems allows to sample the sensors at a rate of 2Hz. The datasheet of the AD5933 claims a 0.5% accuracy. An accuracy of 0.3% was observed during the experimentations.

C. Data pre-processing

The capacitance signals are filtered (low-pass) and the relative response is calculated before feature extraction stage. The relative capacitance responses of the sensors to 12 ppm of DMMP is presented in Figure 2, with the relative capacitance of a sensor given by equation 1:

$$\Delta C(t) = \frac{C(t) - C0}{C0} \tag{1}$$

Selecting good features from the curves is of utmost importance to improve the accuracy and decrease the complexity of the classification stage. Seven features have been extracted from the capacitance responses and are presented on Figure 3:

- the magnitude of the relative signal
- the magnitude of the adsorption phase: *Cmax - C0*
- the magnitude of the desorption phase: *Cmax - Cmin*

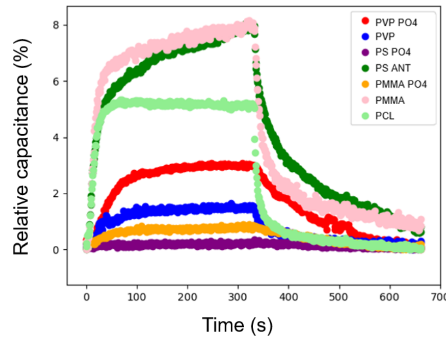

Figure 2: Relative capacitance responses of the sensors to 12 ppm of DMMP

- the integral value of the adsorption phase: $\int C\ abs$
- the integral value of the desorption phase: $\int C\ des$
- the maximum slope of the signal: $\delta C\ max$
- the minimum slope of the signal: $\delta C\ min$

D. Classification stage

The seven features from the sensor array are then forwarded to the classification stage. SVM is a supervised learning method which requires to be trained with a fraction of the database. The training dataset is used to define a hyperplan in a *N-1* dimensional space (where *N* is the number of features). This hyperplan is calculated to segregate at best the vectors from different classes. The vectors which are the closest to the interclass frontiers are called the Support Vectors and define the hyperplan. Once the SVM has been trained, test vectors can be feeded to the algorithm which will predict its corresponding class. In this study, there are two classes: samples containing DMMP and samples which do not contain DMMP. Seven features are extracted from the responses of the seven sensors, *N* is then equal to 49.

Stratified cross validation (8 folds) was used to randomly separate the training and testing datasets.

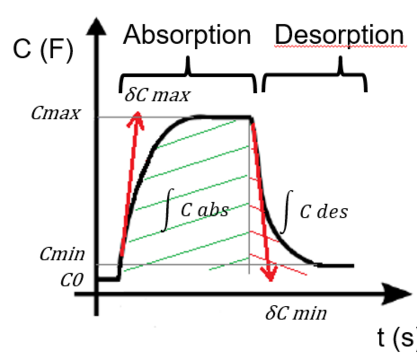

Figure 3: Description of the six features extracted from the capacitive responses of the sensors

Table I: Chemical composition of the background mixture

Coumpound	Ethanol	Water	Propanol	Toluene	Xylene	Octane	Tetramethylbenzidine
Concentrations (ppm)	1500	1200	400	300	80	40	4

III. Experimental setup

A. Samples preparation

Two tedlar bags were filled with the vapor mixture presented on Table I. A concentration of 1.6 ppm of DMMP has been added to one of the two bags.

B. Mixture expostion protocol

An exposition cycle consists of emptying the bag at a flow rate of 100 mL per minute on the sensor array for five minutes, this constitutes the absorption phase. The sensors are then cleaned with dry air at 500 mL per minute to let the sensors desorb and return to their original state.

For each bag, the three first consecutive cycles are chained. This has been repeated eight times in a randomized order and on a whole week to avoid cognitive biais for the SVM.

A database of 48 was gathered, 24 samples for each bag.

IV. Results and discussion

A. Classication results

The 48 samples were used to train and test our algorithms using a stratified 8-fold cross validation method. The SVM reached an accuracy of 98%, averaged for the 8 folds (Table II).

Other studies have shown transducing methods selective enough to recognize pure vapors of DMMP from pure vapors of potential interferants. In this study, the ability to reliably detect the presence of DMMP in a known mixture of interferants has been demonstrated. However, the experimental limit of detection (LOD) of 1.6 ppm is too high compared to the IDLH of nerve agents. Furthermore, the ability of the developped system to specifically recognize DMMP from other coumpounds has yet to be proven. Testing the system against more diverse blends of potential interferants is required to assess if the proposed system is field-ready.

B. E-nose prototype features

The proposed E-nose prototype is small enough to be embedded into an handheld device. The electrical consumption of the system is 1.35 W at rest, 1.5 W during measurement and 2.1 W during classification. This prototype works for 14 hours with a battery of 5000 mAh. The impedance measurement circuit consumption is only 0,1 W. As such, autonomy could be easily increased by scalling down the complexity of our control and data-treatment hardware.

Table II: Confusion matrix of the SVM algorithm, averaged on the 8 folds

	Prediction: no DMMP	prediction: DMMP
Background bag	98%	2%
DMMP bag	2%	98%

Table III: Result discussion

Transduction method	MOS	CNT-mat	CNT-mat
Experimental LOD	500 ppb	50 ppb	1.6 ppm
DMMP identification	yes, vs. 6 competitors	yes, vs. 6 competitors	not assessed yet
In mixture detection	no	no	yes
Reference	[2]	[7]	this study

V. Conclusion and future work

The electronic nose system presented in this paper allows to indentify the presence of DMMP in a complex mixture with a accuracy of 98%. The development of a cost-effective, portable E-nose system is described. Future work will focus on implementing the proposed feature extraction methods and SVM algorithm on a dedicated circuit. This downsizing will be an other step toward a military uniform embedded E-nose system and will drastically reduce its power requirements. Tuning the set of transducers in the sensor array will also be investigated. In order to even lower the risk of false alarms, tailoring the prototype for the specific identification of the DMMP compared to a broader range of interferants is required.

VI. Acknowledgment

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