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Trace Detection of Nerve Agent Simulant in the Fuel Vapour Environment using Metal Oxide/Surface Acoustic Wave E-Nose

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ABSTRACT

Nerve agents are often used at the military warfront, where diesel is a very common interferant. In the present work, a group of surface acoustic wave (SAW) sensors, called E-Nose with dissimilar sensing layers is developed for the recognition of the mixture of diesel and dimethyl methylphosphonate (DMMP) vapors. The exposure of DMMP and diesel vapors is kept at ppb and ppm levels respectively. Varied response patterns of DMMP and diesel vapors were obtained by SAW E-nose. Principal component analysis (PCA) has been used to extract features from the response curves of SAW sensors. Artificial Neural Network pattern recognition has been implemented to identify the precise detection of DMMP vapors in the binary mixture of DMMP and diesel. The effect of pre-processing (using PCA) the raw data before feeding it to artificial neural network is also studied.

Keywords: E-nose; Metal oxide; Sensor

1. INTRODUCTION

Today chemical attack is one of the biggest threats for us. Nerve agents (Sarin, Soman) are the deadliest and widely used class of chemical warfare agents, employed several times during a war[1]. Sensors employed for their detection must take care of the interferants also. Since the accuracy level required in the detection of warfare agents is very high, special technologies are required to minimize the possibility of false alarms. Nerve agents are mostly used at warfronts, where diesel is the major source of interferant. Diesel is used in tanks, trucks, generators, starting compressors for jet engines[2]. Therefore, sensor systems should be capable of detecting nerve agents in the presence of such interferants.

Presently, there exist various sensing techniques like IR spectroscopy, chromatography, calorimetry, conductometric, Ion mobility spectrometry, and surface acoustic wave (SAW)[3,4] for accurate detection of target vapours. Various inherent advantages like high sensitivity, low cost, small size, portability, and operation at room temperature give SAW sensors the edge over other techniques[5]. However, RF electronics and sensitive coatings remain critical issues. A careful PCB designing, components placement, and soldering are required for measuring small frequency changes of different SAW oscillators placed closely[6]. The literature emphasizes mainly on the use of polymers as sensing layers[7-8]. However, because of their inherent disadvantages like swelling, non-uniform deposition, lack of long-term stability, metal oxide sensing layers have also been tried[9-10].

The use of a single sensor is generally not sufficient to detect a particular vapour in a mixture. Hence an E-nose (an array of sensors) is essentially required. The sensing data of E-nose along with suitable pattern recognition technique (PCA, ANN etc.) allows correct recognition of target vapours[11]. In literature, SAW E-nose has been employed for the recognition of various target vapours[12-15]. Joo[13], *et al.* fabricated an array of polymer- coated SAW sensors for the recognition of simulant vapours but individual vapours were tested and the neural network algorithm was not implemented for precise prediction. Matatagui[9], *et al.* implemented Principal Component Analysis and neural network on the SAW response of few simulants, however, detection was not perfect as neural network output showed overlapping of vapours. Love wave-based SAW E-nose was also reported but neural network results were not shown[14]. Very few reports are available for the detection of a binary mixture of vapours using SAW E-nose[16-17]. Penza and Cassano, used the sensing response of polymer-coated SAW E-nose along with PCA/ANN techniques for the detection of binary mixture of alcohols (methanol/2-propanol)[16]. Penza[18] , *et al.* used polymer-coated SAW sensors for the recognition of the binary mixture of methanol and acetone using PCA and multilayer perceptron technique. Few reports are also available where a binary mixture is detected using quartz crystal microbalance (QCM). Detection of the binary mixture of TCE (Tri-chloro ethylene)/acetone and TCE/n-hexane respectively using neural network is also reported using QCM[19-20]. Other

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reports are also available related to the detection of the binary mixture of organic vapours (methanol, 1,2-dichloroethane, benzene, and cyclohexane), using polymer-coated QCM[21-22]. Binary mixtures of freons R22 and R134a by another technique (surface plasmon resonance (SPR)) along with neural network is also reported[23]. Hence reports related to the detection of binary mixture using metal oxide coated SAW sensors are very less in literature.

Pattern recognition is a very important aspect in E-nose. For analysing sensing characteristics patterns of various target vapours, principal component analysis (PCA) has been widely used[11-12]. It is a mathematical tool to orthogonally transform and converts possibly associated variables into a set of uncorrelated variables, thus helpful in identifying the patterns[12]. The new variables thus formed are called principal components. An artificial neural network (ANN), is a very powerful tool for nonlinear and multiple processing systems. ANN model learns from known patterns (called training) without the necessity of explicit functional relationships. Initially designed for, possible model of human brain activity, it has more applications now as problem-solving algorithms. ANN can be effectively applied in numerous areas as a classy non-linear computational tool for modelling. Different types of architecture of ANN are available, but the most extensively utilised is the feed forward network. It allows only the one-way movement of signals from input to output. So, the output of a particular layer cannot affect the same layer.

In the present work, an array of SAW sensors (E-nose) with different sensing layers is projected for the recognition target gas in a binary mixture. This is an extension of our previous work[12] where the ability of metal-oxide coatings being alternate to polymer coatings for detection of individual vapours was showcased with simple PCA. However, in order to realise a useful gadget in real-life situations, detection of target vapour in the presence of interfering vapours is to be studied. Thus, the present study is on binary mixtures of target gas DMMP and interfering gas Diesel. In the present manuscript, PCA and ANN are extensively used for the precise detection of target vapours in the binary mixture with minimum false alarm.

2. EXPERIMENTAL WORK

Commercially available SAW resonators (center frequency = 433.9 MHz) are used. Response of the bare SAW device is shown in the supplementary file (Fig. S1). Radio frequency (RF) magnetron sputtering technique has been employed for the growth of ZnO, TeO_2, SnO_2, and TiO_2 thin films onto SAW devices. The sensing layers have been deposited at room temperature. Other deposition parameters are optimised for the deposition of sensing layers are reported earlier[12]. The sensing layers are approximately 40 nm thick. The XRD patterns of ZnO thin film show only one reflection corresponding to (002) plane, indicating the oriented growth such that c-axis is perpendicular to the substrate surface[24]. The XRD spectra of SnO_2 thin film show the reflections at $2\theta = 33.83^o$ and 51.61^o corresponding to (1 0 1) and (2 1 1) planes, confirming polycrystallinity in the film[12]. No reflections are observed for TeO_2 and TiO_2 films indicating their amorphous nature. Surface morphology and optical properties are also reported earlier[12].

An amplifier with a metal oxide coated SAW device in the feedback loop is designed make a Colpitt oscillator[25]. The differential frequencies ($\Delta F = f_0 - f_s$) of the oscillators have been measured to reduce the effect of pressure, temperature etc. Here f_0 and f_s are the reference frequency (without coating) and the sensor frequency respectively. A frequency counter has been employed to measure the difference frequency and is also interfaced with computer.

For the testing of DMMP vapours, very low concentrations are required. Hence a special lab-made vapour delivery system has been designed. The schematic of the vapour delivery system is shown in supplementary Fig. S2. The liquid can be placed in any of the 4 flasks (F1-F4) which can be heated to generate vapours. The carrier gas (N_2) is passed through the flasks and carry the target vapours to the dilution flask (F5). The temperature of the flasks and the flow/pressure of the carrier can be varied to obtain the required concentration of target vapours. Pressure controllers and precise needle valves are used to control the flow of N_2. Carrier is passed onto the sensor surface through flask6 so that there is no temperature difference between target vapours and carrier gas. Pressure relief valves are also used at the appropriate places to avoid an accumulation of excess pressure. Before recording the sensing response, SAW devices (in differential oscillator circuit) are stabilised for about 30 mins. in the constant flow of N_2 gas. The stable baseline of SAW sensors was achieved when the noise level in the differential frequency ($\Delta f = f_0 - f_S$) is ≤10Hz. So, keeping signal to noise ratio of 2, a minimum of 20 Hz is considered as the limit of the frequency shift. The noise profile of all the 4 sensors before exposing vapours has been shown (for 1 minute) in the supplementary Fig. S3.

3. RESULTS

3.1 Sensing Characteristics of SAW E-nose

The differential frequency shift of SAW E-nose in DMMP (250 ppb) environment is displayed in an inset of Fig. 1. Differential frequency shifts for sensor arrays coated with ZnO, TeO_2, SnO_2, and TiO_2 sensing layers are 470 Hz, 68Hz, 55 Hz, and 63 Hz, respectively. The ZnO/SAW sensor is most sensitive towards DMMP vapours (Fig. 1). The sensing responses at different concentrations of DMMP vapours (90 to 450 ppb) have also been studied (Fig. 1). With increasing levels of DMMP, the value of ΔF also increased. Figure 2 shows the sensing characteristics of the prepared E-nose towards diesel vapours (5 ppm). The ZnO, TeO_2, SnO_2 and TiO_2coated SAW sensors are giving shift of 95 Hz, 40 Hz, 46 Hz, and 90 Hz respectively, for diesel. Figure 3 shows the transitory response with exposure to mixture of DMMP and Diesel (450 ppb DMMP + 5 ppm diesel). Figure 4 shows frequency shifts ΔF of SAW sensors at different binary concentrations of DMMP and diesel vapours. It is important to note that a substantial statistical variation is obtained between sensing curves of the four sensors which is vital for detecting target vapour in a binary mixture.

3.2 Principal Component Analysis

Principal component analysis (PCA) has been applied on the sensing response of E-nose (four SAW sensors). The

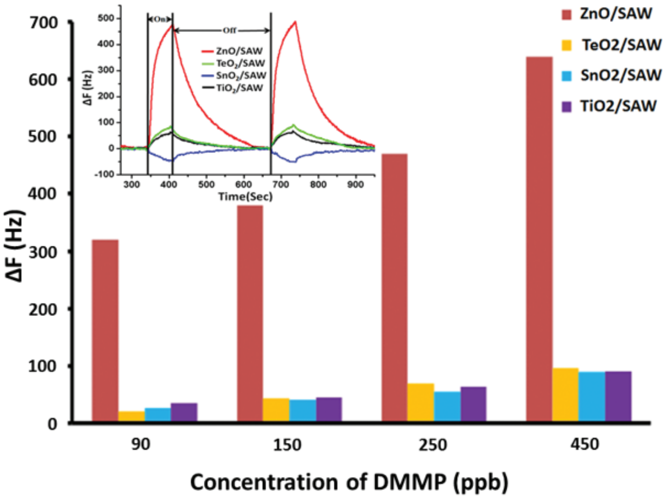

Figure 1. The differential frequency shifts (ΔF) of SAW E-nose for DMMP vapors at different concentrations. (Inset shows the Frequency response (ΔF) curve with exposure to 250 ppb of DMMP vapours).

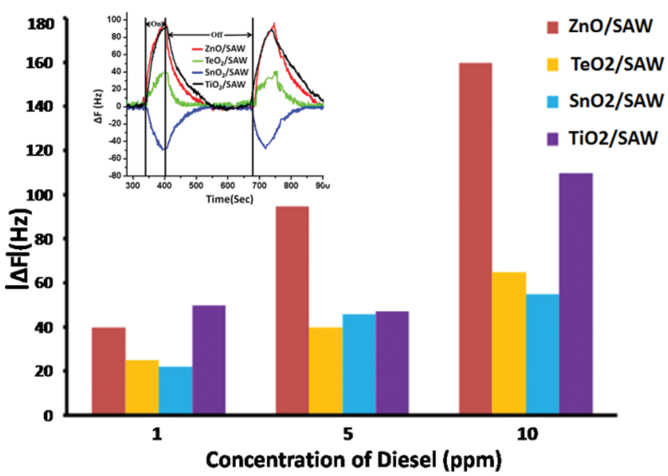

Figure 2. The differential frequency shifts (ΔF) of SAW E-nose for diesel vapors at different concentrations. (Inset shows the Frequency response curve (ΔF) with exposure to 5 ppm of diesel vapours.

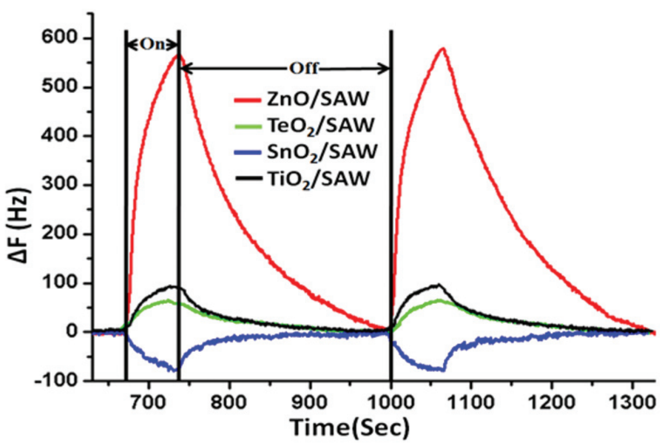

Figure 3. Variation in ΔF of SAW E-nose with exposure to a mixture of DMMP (450 ppb) and diesel vapours (5 ppm).

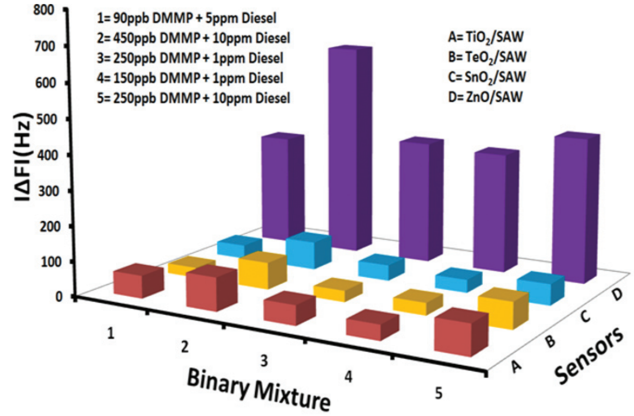

Figure 4. Variation in ΔF of SAW E-Nose for a binary mixture of DMMP and diesel vapours at different concentrations.

standard algorithm used to evaluate principal components (PC1-PC4) is written in Matlab[12]. The obtained sensing database has been normalised to reduce the effect of the wide range of concentration. Figure 5 shows the score plot of diesel and DMMP vapours individually along with their combination in the PC1-PC2 plane. The data points of diesel, DMMP vapours along with their combination comes under different ellipses (Fig. 5). Table 1 shows the variance of four principal components. It can be seen that the first two principal components contain approx. 95 % variance, thereby restoring maximum information. The load plot in the PC1–PC2 plane is shown in Fig. 6. The load plot specifies the amount of redundancy in the sensing characteristics. The points of ZnO/SAW and SnO_2/SAW sensor are in the third quadrant and hence

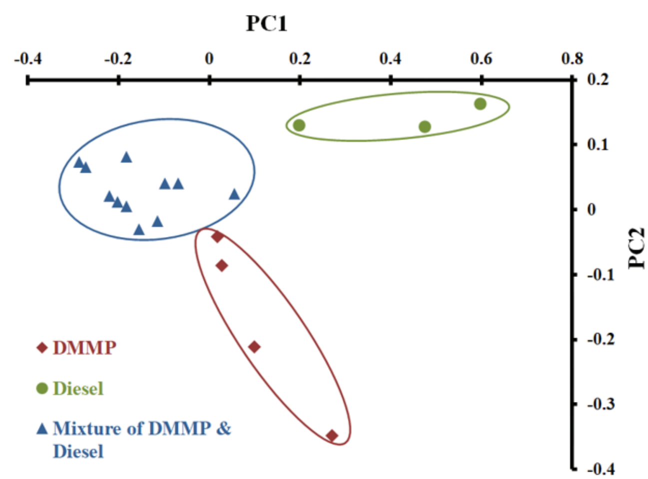

Figure 5. PCA score plot of the frequency response (ΔF) of SAW E-nose for DMMP and diesel vapours along with their binary mixture.

Table 1. Eigenvalue and % variance as evaluated by PCA analysis.

Eigenvalue	Variance (%)	Cumulative variance (%)
0.0694	79.314	79.314
0.0141	16.114	95.428
0.003	3.428	98.856
0.001	1.142	99.998

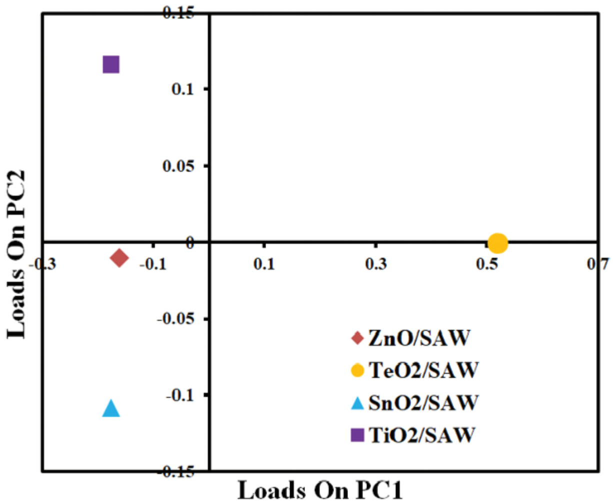

Figure 6. PCA load plot of the frequency response (ΔF) of SAW E-nose for DMMP and diesel vapors along with their binary mixture.

one of them can be considered as redundant (Fig. 6).

3.3 Artificial Neural Network

The fundamental structure of an artificial neural network is displayed in supplementary Fig. S4. Artificial neurons are organised in the input layer, hidden layers and the output layer. A neuron sums up all the inputs, multiply them by weights (w) and then bias is added. Finally, the output is evaluated using a transfer function[16-17]. There is only 1 hidden layer in the present work, hence ANN used is a 3 layered structure. The input, hidden and output layer comprises of 4, 10, and 2 neurons respectively. The two different types of input data are used to evaluate the performance of the neural network.

(i) Responses of SAW sensors
(ii) First 2 principal components

In the first case, the normalised frequency shift from the E-Nose is fed directly to the ANN. (0 1), (1 0) and (1 1) are the codes for diesel, DMMP and their mixture respectively. To implement ANN, the existing sensing database is divided into the training set and testing set[17]. The training and testing set comprises of 14 and 7 input vectors respectively. The target and output of the ANN during training with inputs directly from SAW sensors is shown in Table 2. During training, excellent success is attained (Table 2). The testing results of the network after training are shown in Table 3. Hence, the presence and absence of the DMMP in the diesel environment can be detected successfully.

Table 2. Target and output data of the ANN during training with inputs directly from SAW sensors.

Training no.	Compound	Target data		Output data	
1	DMMP	1	0	0.9968	0.0078
2	DMMP	1	0	1	0.0049
3	DMMP	1	0	1	0.0021
4	Diesel	0	1	0.0033	0.9967
5	Diesel	0	1	0.0057	1
6	Diesel	0	1	0.0003	0.9999
7	DMMP+Diesel	1	1	0.9937	0.9999
8	DMMP+Diesel	1	1	0.9937	0.9987
9	DMMP+Diesel	1	1	0.9876	0.9990
10	DMMP+Diesel	1	1	1	0.9973
11	DMMP+Diesel	1	1	1	1
12	DMMP+Diesel	1	1	0.9954	1
13	DMMP+Diesel	1	1	1	0.9873
14	DMMP+Diesel	1	1	0.9987	1

In the second case, PCA data is utilised for training and testing of the neural network. The training and testing results using inputs from PCA is shown in Table 4 and 5, respectively. The prepared sensors with the trained network are capable of identifying DMMP in the diesel environment. The classification

Table 4. Target and output data of the neural network during training with PCA data as Input

Training no.	Compound	Target data		Output data	
1	DMMP	1	0	1	0.006092
2	DMMP	1	0	1	2.45E-06
3	DMMP	1	0	1	3.21E-05
4	Diesel	0	1	2.52E-05	0.99744
5	Diesel	0	1	4.36E-04	1
6	Diesel	0	1	1.38E-06	1
7	DMMP+Diesel	1	1	0.99991	1
8	DMMP+Diesel	1	1	1	1
9	DMMP+Diesel	1	1	1	1
10	DMMP+Diesel	1	1	1	1
11	DMMP+Diesel	1	1	1	1
12	DMMP+Diesel	1	1	1	1
13	DMMP+Diesel	1	1	1	1
14	DMMP+Diesel	1	1	1	1

Table 3. Output and target data of the neural network during testing with differential frequency shift as Input

Test	True target	Predicted target	1st Target	1st Output	2nd Target	2nd Output
1	DMMP	DMMP	1	0.99999	0	6.67E-05
2	DMMP	DMMP	1	0.98723	0	5.65E-06
3	Diesel	Diesel	0	0.00012	1	0.99964
4	Diesel	Diesel	0	4.35E-05	1	1
5	DMMP+ Diesel	DMMP+ Diesel	1	0.99999	1	0.99807
6	DMMP + Diesel	DMMP+ Diesel	1	0.87632	1	1
7	DMMP + Diesel	DMMP+ Diesel	1	1	1	0.98735

Table 5. Output and target data of the neural network during testing with PCA data as input

Test	True target	Predicted target	1st Output	1st Target	2nd Output	2nd Target
1	DMMP	DMMP	1	1	0	0
2	DMMP	DMMP	1	1	3.53E-06	0
3	Diesel	Diesel	0	0	1	1
4	Diesel	Diesel	0	0	1	1
5	DMMP+ Diesel	DMMP + Diesel	1	1	1	1
6	DMMP + Diesel	DMMP + Diesel	1	1	1	1
7	DMMP + Diesel	DMMP + Diesel	1	1	1	1

threshold is set to (0.90, 0.1) for DMMP; (0.1, 0.90) for diesel and (0.90, 0.90) for the combination DMMP and diesel. Also, by comparing the testing results of Table 3 and 5, it can be concluded that the accuracy of the results improved if the output of PCA data is fed to the neural network algorithm. Hence, PCA/ANN is a better approach for the detection of DMMP vapours.

4. DISCUSSIONS

It is very vital to study several factors influencing the SAW sensing response. Presently, most of the environmental conditions like temperature, pressure etc. are kept constant, so change in mass (mass loading), resistance/capacitance (acoustoelectric interaction) and the elasticity of the thin film are responsible for change in frequency. The equation representing the above factors is as follows[26-27].

$$\frac{\Delta F}{f_0} = -C_m f_0 \Delta\left(\rho_s\right) + C_e f_0 h \Delta\left(\left(\frac{4\mu}{v_0^2}\right)\times\left(\frac{\mu+\lambda}{\mu+2\lambda}\right)\right) - \frac{K^2}{2}\times\Delta\left(\frac{1}{1+\left(\frac{v_0 c_s}{\sigma_s}\right)^2}\right)$$

where ΔF is the frequency shift with the interaction of target vapours, f_o is the reference frequency, v_o is the initial SAW velocity, μ and λ are the Lame's constants, C_m and C_e are the sensitivity coefficients of mass and elasticity respectively, h and ρ_s are the thickness and mass per unit area of the film, K^2 is the electro-mechanical coupling coefficient, σ_s, and C_s are the conductivity and capacitance per unit length. When target vapours get accumulated on the SAW surface, there are three possible mechanisms:

(i) Mass/density of the sensing film changes and hence frequency decreases or differential frequency increases[26]
(ii) Electrical properties like resistance or capacitance of the sensing film can change due to which difference frequency can either increase or decrease
(iii) Adsorbed molecules may change the elastic properties due to which differential frequency decreases[26-27].

Separately performed electrical measurements proved insignificant variation in resistance and capacitance of metal oxide thin films with adsorption of DMMP vapours, indicating the insignificant contribution of acousto-electric interaction. Hence if there is an increase in differential frequency, it is due to mass loading, whereas if elastic properties of the films are changing, then there is a decrease in differential frequency. As can be seen from Figs. (1-3), only SnO_2 coated sensor oscillator shows a decrease in the differential frequency whereas, in all other sensor oscillators, there is an increase in the value of differential frequency. Hence it may be concluded that elastic changes are dominant in SnO_2/SAW sensor whereas mass loading is dominant in other sensors.

The adsorbed molecules on the film surface can increase the stiffness due to which frequency increases, therefore differential frequency decreases[26] (Fig. 1). The elastic changes depend on the adsorption and surface properties of thin-film like porosity, roughness, grain boundaries etc. Further, the influence of mass loading and elastic changes also depends on the concentration of vapours[22]. In literature, very few reports are available where elastic changes are observed in SnO_2 thin films[29]. It is difficult to separate the contribution of the three above mentioned sensing mechanisms in a single SAW device since they affect the SAW response simultaneously. In literature, there are few reports related to it. The contributions of mass and elasticity are studied in a report by depositing the identical sensing layer on Quartz and GaAs.[27]. Similarly, the metal film was grown on different substrates (quartz, LiNbO3, etc.) and the contributions of mass and elasticity were evaluated with exposure to H_2[30]. Hence, separate contributions were studied by using same sensing layer on multiple substrates. Nonetheless, since only the magnitude of ΔF is included in PCA/ANN, the direction of differential frequency is not so important from a practical point.

Another important factor called long term stability of the prepared E-nose has also been studied. Degradation in differential frequency shift (%) is defined as $(\Delta F_2/\Delta F_1)*100$, where ΔF_2 and ΔF_1 are the current and initial differential frequency shift respectively (supplementary Fig. S5). It has been observed that variation in the frequency of all metal oxide coated SAW sensors is below 5 % after 2 years except TeO_2/SAW. Especially for ZnO/SAW sensor, the degradation in the performance is below 2 % and for TiO_2/SAW & SnO_2/SAW, it is nearly 5%. The properties of SAW sensors get degraded mostly due to harsh environments (temperature, the interaction of film surface with the target analytes). Initially, metal oxides were used at high temperature so only polymers were preferred for SAW sensors but later because of their advantages metal oxides have also been used. Hence reports related to the long-term stability of SAW sensors with metal oxide layers are not readily available. Long term stability of metal oxides for e-nose applications was reported by Romain and Nicolas[31]. They also proposed techniques to take care of the problems related to long term drift mathematically. It has also been reported that amorphous or polycrystalline metal oxides have poor long term stability, since there is a possibility of crystallisation and grain growth in thin films during sensor operation[32].

5. CONCLUSIONS

The prepared SAW-based E-nose having different sensing films is capable of distinguishing DMMP vapours in the presence and absence of diesel vapours. The four sensors showed dissimilar patterns with exposure to DMMP and diesel vapours. PCA analysis classifies the response from the sensor array for two target vapours independently along with their combination correctly. Using the load plot, it is found that the response of ZnO/SAW and SnO_2/SAW sensors are correlated, so one of them can be neglected from the sensor array. 100% identification performance has been obtained using ANN classification for the given target vapour. Pre-processing of data using PCA is a better approach for getting more accurate and precise detection using ANN.

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In the present work, he has contributed for detailed literature survey, development of experimental setup, data collection and analysis.

Dr Harpreet Singh received his MSc (Electronics) from Kurukshetra University, Haryana, in 2009 and PhD from Bharathiar University, Tamil Nadu, in 2016. His research interests include passivation of SAW device, development of RF and Digital subsystem (FPGA and PLD), development of SAW E-Nose, and GC based SAW E-Nose for the detection of CW agents.
In the present work, he is involved in the fabrication of SAW E-nose and also contributed in pattern recognition algorithms.

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Dr A.T. Nimal received MSc (Physics) from Government Arts College, Bharathiar University, Coimbatore, in 1993 and PhD from National Physical laboratory, Delhi, and University of Delhi, Delhi, in 2004. He is working as a Scientist at DRDO-Solid State Physics Laboratory, Delhi. Presently involved in

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In the present work, he has helped in the designing of vapour generation and delivery system, RF electronics, fabrication of SAW E-nose, overall methodology.

Prof. Vinay Gupta received the BSc, MSc, and PhD degrees in physics in 1987, 1989, and 1995, respectively, from University of Delhi, Delhi. Presently, he is a Professor in the Department of Physics and Astrophysics, University of Delhi. He is a recipient of BOYSCAST fellow and MRSI medal. His current research interests are in piezoelectric thin films and layered structures, semiconductor and surface acoustic wave (SAW) sensors, ferroelectric films for electro optic applications, and nano-structured oxide materials for multifunctional application.
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Prof. Vinay Kumar Singh received the PhD (Analytical chemistry) from Delhi University of Delhi, in 1990. Presently, he is a Associate Professor at Sri Aurobindo College, University of Delhi. He is involved in the development and characterisation of GC-SAW based chemical sensor for the detection of Toxic Industrial chemicals and gases.
In the present work, he provided the research inputs for selection and characterisation of metal oxides.

Supplementary Figures

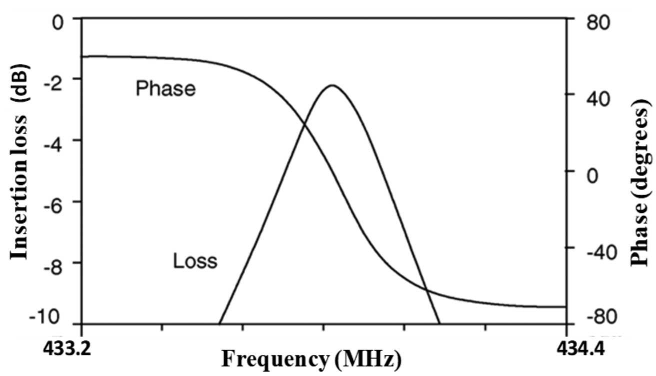

Figure S1. Frequency and Phase response of the SAW device.

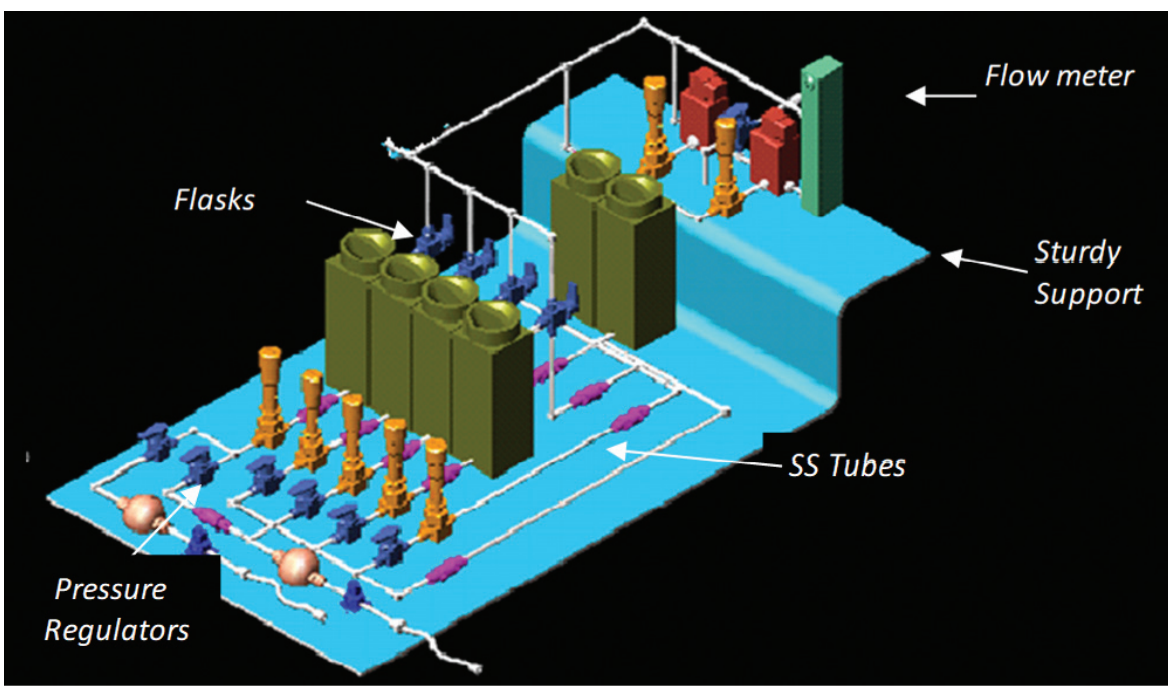

Figure S2. Design of the Multiple vapor generation and delivery system.

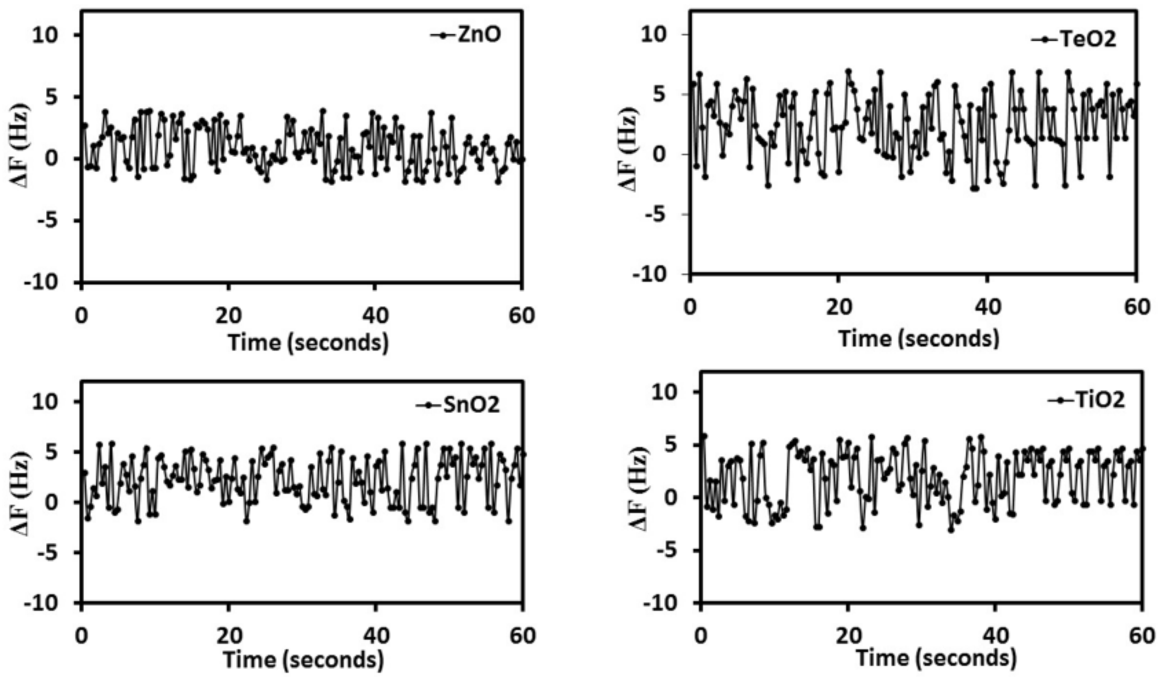

Figure S3. The noise profile of all 4 sensors.

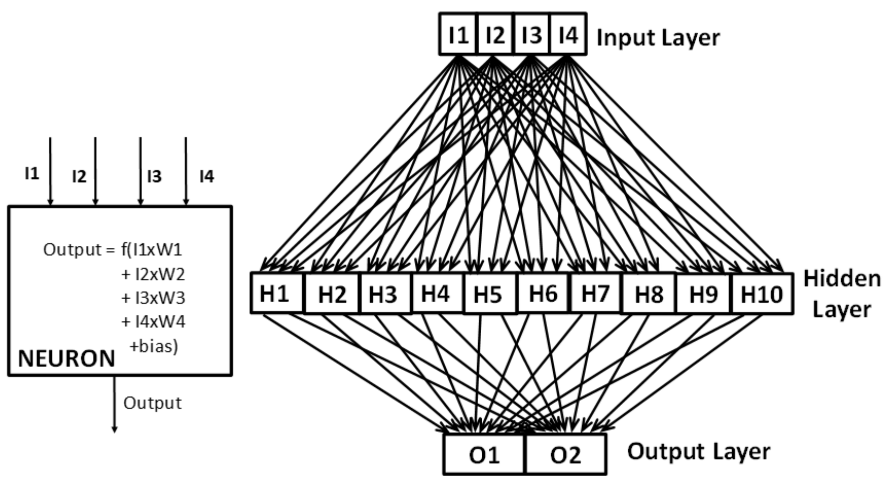

Figure S4. Schematic of artificial neural network used.

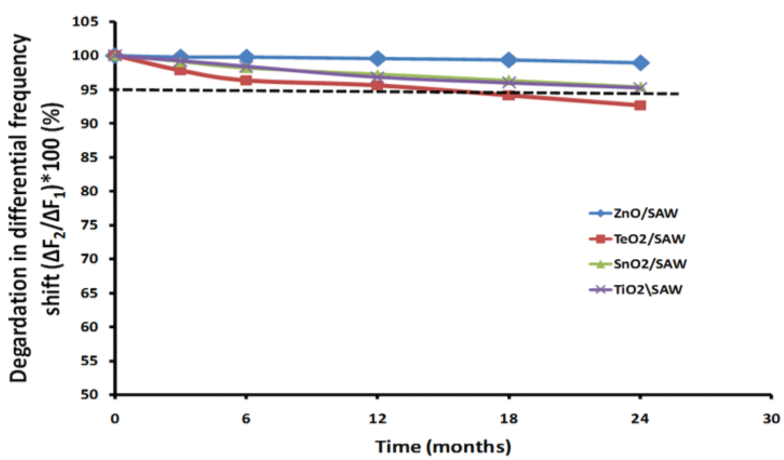

Figure S5. Long term stability of the SAW E-nose.