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on Sensor Device Technologies and Applications

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August 21-27, 2011 - French Riviera, France



### Important deadlines:

Submission deadline	March 23, 2011
Notification	April 30, 2011
Registration	May 15, 2011
Camera ready	May 22, 2011

### Tracks:

- Sensor devices
- Photonics
- Infrared
- Ultrasonic and Piezosensors
- Sensor device technologies
- Sensors signal conditioning and interfacing circuits
- Medical devices and sensors applications
- Sensors domain-oriented devices, technologies, and applications
- Sensor-based localization and tracking technologies

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Camera ready	May 22, 2011

### Tracks:

- APASN: Architectures, protocols and algorithms of sensor networks
- MECSN: Energy, management and control of sensor networks
- RASQOFT: Resource allocation, services, QoS and fault tolerance in sensor networks
- PESMOSN: Performance, simulation and modelling of sensor networks
- SEMOSN: Security and monitoring of sensor networks
- SECSN: Sensor circuits and sensor devices
- RIWISN: Radio issues in wireless sensor networks
- SAPSN: Software, applications and programming of sensor networks
- DAIPSN: Data allocation and information in sensor networks
- DISN: Deployments and implementations of sensor networks
- UNWAT: Under water sensors and systems
- ENOPT: Energy optimization in wireless sensor networks

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in Circuits, Electronics and Micro-electronics

## CENICS 2011

August 21-27, 2011 - French Riviera, France



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### Tracks:

- Semiconductors and applications
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- Arithmetic computational circuits
- Microelectronics
- Electronics technologies
- Special circuits
- Consumer electronics
- Application-oriented electronics

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## Chemical Vapor Identification by Plasma Treated Thick Film Tin Oxide Gas Sensor Array and Pattern Recognition

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**Abstract:** Present study deals the class recognition potential of a four element plasma treated thick film tin oxide gas sensor array exposed with volatile organic compounds (VOCs). Methanol, Ethanol and Acetone are selected as target VOCs and exposed on sensor array at different concentration in range from 100-1000 ppm. Sensor array consist of four tin oxide sensors doped with 1-4 % PbO concentrations were fabricated by thick film technology and then treated with oxygen plasma for 5-10 minute durations. Sensor signal is analyzed by principal component analysis (PCA) for visual classification of VOCs. Further output of PCA is used as input for classification of VOCs by four pattern classification techniques as: linear discriminant analysis (LDA), k-nearest neighbor (KNN), back propagation neural network (BPNN) and support vector machine (SVM). All the four classifier results 100 % correct classification rate of VOCs by response analysis of sensor array treated with plasma for 5 minute. *Copyright © 2011 IFSA.*

**Keywords:** Tin oxide sensor, Plasma treatment, Pattern recognition methods, Chemical vapor identification.

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### 1. Introduction

Metal Oxide sensor (MOS) is the most widely used sensing platform for different application namely food quality monitoring, emission monitoring of toxic and combustible gases for environment safety purpose and for other domestic and industrial application etc [1-2]. Based on surface morphology of metal oxide sensing layer MOS is classified into different category as: porous film, thick film, thin



film MOS etc. Interaction of chemical vapor with sensing layer results in change in conductance of sensing layer; such change in characteristics of sensing layer is transduced in form of electrical signal [3-5]. Besides, having the number of advantages such as low cost, small size, fast response, simple design, robustness, high mechanical strength and commercial availability, a number of shortcomings are also associated with these sensors like low selectivity, high operating temperature, high power consumption, low reproducibility due to ageing, high sensitivity for humidity etc. Several efforts have been made to remove these limitations, like doping the sensing layer with noble metals and catalyst nano materials, by controlling sensing film morphology and by temperature programming etc [6-7]. Plasma treatment is a very recent and successful approach that has been used to enhance the selectivity and sensitivity of MOS gas sensor [8-9]. It has been observed that not only the plasma density but also the exposure time affects the sensitivity and vapor discrimination capability of MOS gas sensor.

In the present work, same approach has been made to enhance the sensitivity and selectivity of tin oxide based thick film gas sensors by treating them with oxygen plasma for different durations (5 min., 10 min. and 15 min.). Plasma treated sensor arrays were tested for different concentrations (100-1000 ppm) of methanol, propanol and acetone. For discrimination purpose sensor array response matrix is preprocessed then analyzed with feature extraction method principal component analysis. Transformed feature vectors are further used as input of four classification approach as linear discriminant analysis (LDA), k-nearest neighbor (KNN), back propagation neural network (BPNN) and support vector machine (SVM) for classification purpose. Details of all data preprocessing, feature extraction, and classification methods are described in section 3.1-3.6. Identification results of VOCs are summarized in section 4.1-4.5.

## **2. Experimental**

Tin oxide based gas sensors were fabricated by the thick film screen printing technique. The gas sensitive tin oxide paste was developed in our laboratory. The SnO<sub>2</sub> nanoparticles were synthesized using Sol-gel method. Here, pure SnO<sub>2</sub> powder was prepared by slow reaction of SnCl<sub>4</sub>.5H<sub>2</sub>O with ammonia water (NH<sub>4</sub>OH). After some time, tin hydroxide, in the white precipitated form, was obtained. The precipitate was then washed with distilled water so as to remove excess ammonium chloride. The precipitate is then filtered and dried in an oven at about 150 °C. The powder so obtained is the tin hydroxide which when calcined at 400 °C for four hours, yields the tin oxide desired for sensor development. Doped SnO<sub>2</sub> powder was obtained by mechanically mixing the appropriate amounts of PbO. This mixture was ball milled for 15 hours to get homogeneous powder and was then sintered at 600 °C for 2 hours in a furnace. To get a proper paste, PbO-doped tin oxide powder was mixed with lead glass powder and the organic binder followed by ball milling for one hour, then  $\alpha$ -terpineol and Diethyl glycol monobutyl ether were added to the mixture and kept at 80 °C for 24 hours. Three set of sensor arrays (each consisting of four different (1 %, 2 %, 3 % and 4 %) PbO doped sensors) were prepared in our laboratory and they were exposed to oxygen plasma for three different durations of time (5 min., 10 min and 15 min.).

Oxygen plasma was generated at low pressure by using dual frequency PECVD (plasma enhanced chemical vapor deposition) system (made in National Physical Laboratory (NPL), New Delhi). The pressure in the chamber was maintained at 0.06 Torr and oxygen flow rate was kept at 99 sccm/min. The surface of the sensing layer was bombarded by oxygen plasma. The top electrode was driven by microwave power (200 W) operated at 2.45 GHz while the bottom electrode at which the substrate is kept was driven by RF power (20 W) operated at 13.56 MHz. The entire experiment was performed in an air ambient at a relative humidity around 40 %. The fabricated sensor was then exposed to varying concentration of acetone, methanol and propanol in a locally developed test chamber of volume 2047cm<sup>3</sup> having placed at the metal base. The change in resistance of sensor is measured using KEITHELY 195A multimeter.



### 3. Sensor Signal Processing

#### 3.1. Preprocessing

Collected sensor signal have drift effect, noise, nonlinearity of sensor response with concentration/vapor pressure of exposed chemical vapor, signal fluctuation. These limitations occur due to experimental conditions like temperature, humidity, reference air etc. Before processing the response matrix with pattern recognition techniques response matrix must be fresh from above mentioned limitations. Preprocessing steps helps more to avoid such limitations and improves results of latter processing steps. A number of data preprocessing strategies are mentioned in literature for tin oxide sensor response analysis [10]. In most of the cases relative resistance value  $R/R_0$  or, fractional resistance change  $(R_0-R)/R_0$  is employed as normalization method of sensor signal.  $R_0$  represents sensor resistance in reference air and  $R$  as sensor response in presence of VOC. Above mentioned normalization methods helps in reducing effect of sensor drift and dependency of vapor concentration. In present analysis we normalize the sensor response by relative resistance value. After normalization normalized variable gets different higher and lower value, to remove such problem and make the entire normalized variable in equal range a most popular data standardization method reoffered as autoscaling is employed on normalized sensor array response matrix. Autoscaling method transforms the normalized variables into zero mean and unit variance. It is implemented as follows [11].

$$R_{ij} = (R_{ij} - \bar{R}_j) / \sigma_j, \quad (1)$$

$\bar{R}_j = \frac{1}{N} \sum_{i=1}^N R_{ij}$  represents the mean and  $\sigma_j = \sqrt{\frac{1}{N} \sum_{i=1}^N (R_{ij} - \bar{R}_j)^2}$  represents the variance over samples denoted by the first subscript 'i' for the  $j^{\text{th}}$  sensor in the array.

#### 3.2. Principal Component Analysis (PCA)

After pre-processing, sensor response matrix, is processed with, linear feature extraction technique principal component analysis (PCA). It is a most widely used method introduced by Pearson, also known as Karhunen-Loeve transform [12]. Its objective is to reduce the dimensionality sensor array response vector without much loss of its coded chemical information. PCA is a transformation of correlated sensor array response vector of dimension 'm' from measurement space to a new artificial space referred as principal component (PC) space, of dimension 'n' ( $n < m$ ). PC space is formed with a set of orthogonal axes named as principal components arranged in order of amount of variance of original data. First principal components ( $PC_1$ ) locate the direction along which variance is maximum; second principal component ( $PC_2$ ) find another direction orthogonal to first with maximum residual variance and so on [13-14]. Original response matrix is projected along first few directions thus reducing the direction. New projected response vector are linear combination of original variable and uncorrelated with each other and used for further analysis. PCA is employed using 'stats' package [15] of statistical computing language 'R'.

#### 3.3. Linear Discriminant Analysis (LDA)

LDA is a widely used method in image recognition and microarray data classification [16-17]. Method is mainly used for feature extraction, dimensionality reduction and classification. LDA classification is based on Gaussian distribution of pattern vectors in data set. In present analysis LDA is used for

classification of chemical vapor. Output of PCA is used as input for LDA. Method transforms the data into a low dimensional space with maximizing the class separation at the same time minimizing the class compactness. It is implemented in following steps [18].

In first step two scatter matrix namely within class scatter matrix  $S_w$  and between class scatter matrix  $S_b$  are calculated as:

$$S_w = \sum_{j=1}^c \sum_{i=1}^{N_j} (y_i - \mu_j)(y_i - \mu_j)^T \quad (2)$$

$$S_B = \sum_{j=1}^c (\mu_j - \mu)(\mu_j - \mu)^T \quad (3)$$

$C$  is the total number of pattern classes,  $N_j$  is the number of samples and  $\mu_j$  is the mean vector of 'j' th class,  $\mu$  is the mean vector of entire data set. Second step involves transformation of Pattern vector

from high dimensional space into a low dimensional space under the condition  $\max \left[ \frac{\det(S_B)}{\det(S_W)} \right]$ ,  $S_w^{-1}$  is

related with class compactness and  $S_b$  represents separation of class. In final step after transformation Euclidian distance of unknown sample (which has to be classify) with mean of each class in transformed space is calculated, and unknown pattern is assigned to those class having minimum value of Euclidian distance. 'MASS' package [19] of statistical computing language "R" is employed for analysis purpose.

### 3.4. K-nearest Neighbor (KNN)

KNN is based on distance learning approach. Euclidian and mahalanobis are the two most widely used distance measure for method. Basic steps of method is summarized as [20-21]; (a) 'k' nearest neighbors are selected from given set of training pattern; (b) distance of unknown sample (which has to be classify) is calculated from the entire training sample by using any distance measure discussed above; (c) distances are sorted in decreasing order and (d) and finally unknown sample is assigned to that class with maximum number of nearest neighbors. Tuning the nearest neighbor parameter 'k' is used to achieve the best performance of classifier. For analysis 'class' package [19] of statistical computing language "R" is employed.

### 3.5. Back Propagation Feed Forward Neural Network (BPNN)

Artificial neural network (ANN) is arrangement of artificial neurons into different layers namely input layer, hidden layer and output layer. Feed forward neural network is one of the categories of neural network which transmit the output of neurons in forward direction through different layer. ANN is a supervised classification technique, i.e. method is trained on basis of assigned target value of each training pattern. Difference between the assigned target value and actual output of method is named as 'error'. If error is minimized by back propagation algorithm method is named as back propagation neural network (BPNN) in which error is propagated in back direction of signal. Initially a random weight is assigned to each neurons in different layers, weights of each neurons is adjusted in every iteration until error is minimized. A detail of method is described in [20-22]. In present analysis method is implemented in statistical computing language 'R', using 'nnet' package [19].

### 3.6. Support Vector Machine (SVM)

SVM is a supervised pattern classification technique. From given set of training data method construct a decision function by mapping the training vectors into a high dimensional feature space and tuning the controlling parameter. Target value (class level) for each training pattern is provided to the model. After that on basis of optimized model, SVM predicts class level for a new part of data set (test set) with the help of decision function calculated formerly. SVM employ the following optimization problem for computation of decision function [23-24]; maximization of

$$\sum_{i=1}^N \alpha_i - \frac{1}{2} \sum \sum \alpha_i \alpha_j y_i y_j x_i x_j, \quad (4)$$

under condition  $\sum \alpha_i y_i = 0$ .

Lagrange multiplier  $\alpha_i$  is computed from training data vector  $(x_1, x_2, x_3, \dots, x_m)$ , and used for design of decision function. Computational complexity of model is reduced by employing Kernel function. Kernel function maps training vectors into high dimensional feature space, in search of linear separating hyper plane with maximum margin. Margin is measured with help of closest data point to the Hyperplane named as support vector. Commonly used kernel functions are linear kernel, polynomial kernel, radial Gaussian kernel and sigmoid. SVM is implemented using statistical computing language 'R' with help of 'e1071' package [25].

## 4. Analysis and Result

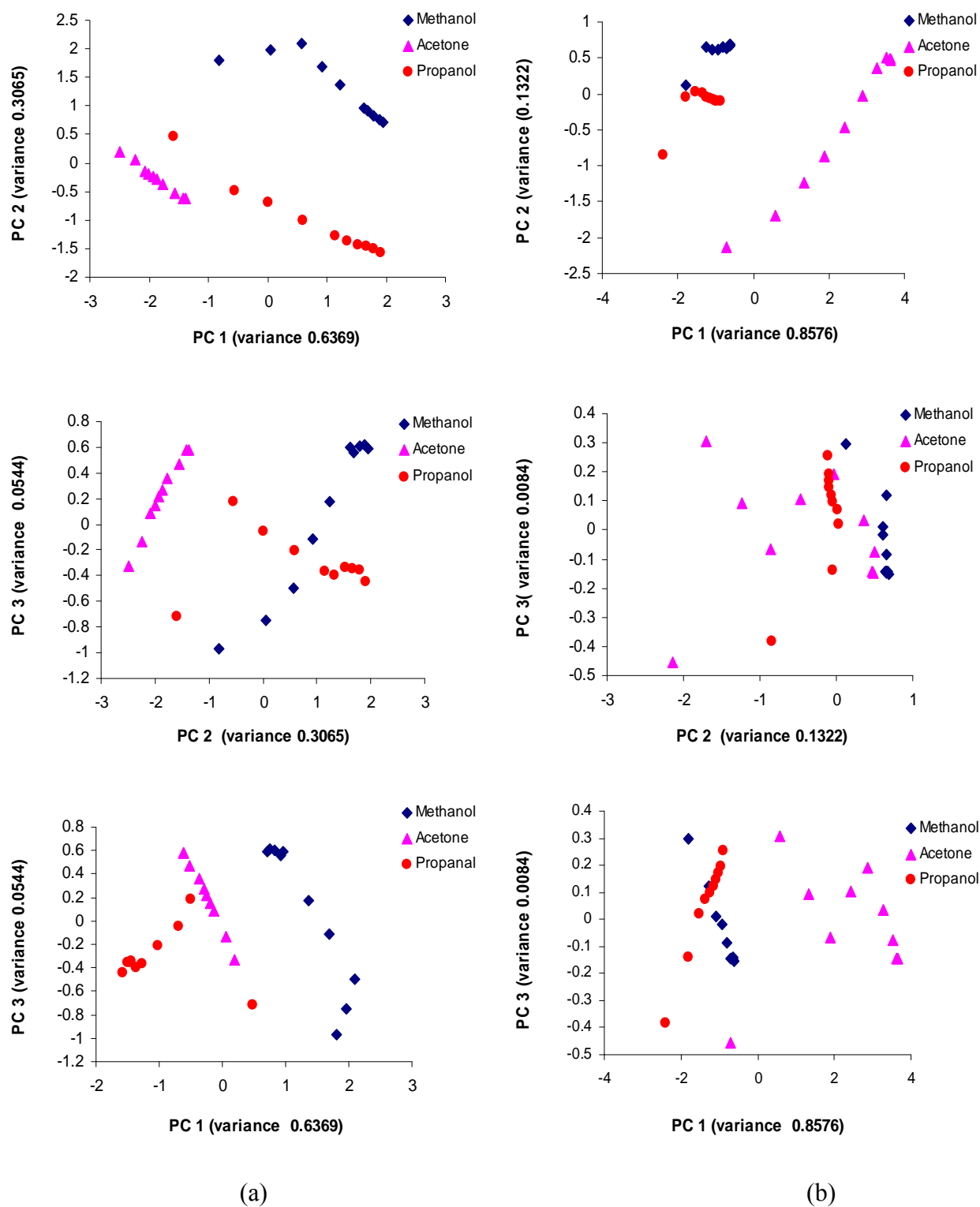
### 4.1. PCA Analysis

Fig. 1 (a) represents PC score plots for the response matrix of plasma treated tin oxide sensor array (with plasma radiation time 5 minute). Similarly Fig. 1 (b) represents PC score plot for response matrix of tin oxide sensor array (plasma radiation time 10 minute) and Fig. 2 represents PC score plot for response matrix of tin oxide sensor array (with plasma radiation time 15 minute). Table 1 shows the eigenvalues and cumulative variance for different principal components of sensor array response matrix treated with plasma radiation for 5 minute, 10 minute and 15 minute respectively. It can be seen that the first 3 PCs carry more than 90 % of the total variance for response of tin oxide sensor array with plasma treated for 5 minute. Whereas for sensor array treated with plasma radiation for 10 minutes and 5 minutes, only first two PCs carry 95% of the total variance. Comparing PC 1-PC 2 score plot, it is clear that three class of vapor are well separated in PC space for plasma radiation time 5 minute (see Fig. 3 (a)). Methanol and Propanol groups are very close to each other whereas acetone form separate cluster for sensor array treated with plasma radiation by 10 minute (see Fig. 3 (b)). For sensor array treated with plasma radiation by 15 minute within class dispersion of three vapor class increases and methanol vapors are very closer to acetone only Propanol class is well separated from remaining.

### 4.2. LDA Analysis

Output of PCA is given to input of LDA model and analysis is carried out with default parameters of model. Table 2 shows classification results for three class of chemical vapor exposed to sensor array treated with plasma radiation for three different time duration. All the three class of chemical vapor are correctly classified from response of sensor array treated with plasma radiation for 5 minute. Whereas

correct classification result of chemical vapor decreases by 7 % for sensor array response matrix treated with plasma radiation for 10 minute and by 10 % sensor array response matrix treated with plasma radiation for 15 minute. Propanol vapor is misclassified most in above mentioned cases. Fig. 3 shows visual classification performance of chemical vapors with three types of sensor array. Again three class of vapors are well separated for sensor array treated with plasma radiation by 5 minutes compare to those sensor array with plasma radiation treatment time 10 minutes and 15 minutes.



**Fig. 1.** PCA score plot for Sensor array response treated with plasma radiation for 5 minute (a); PCA score plot for Sensor array response treated with plasma radiation for 10 minute (b).



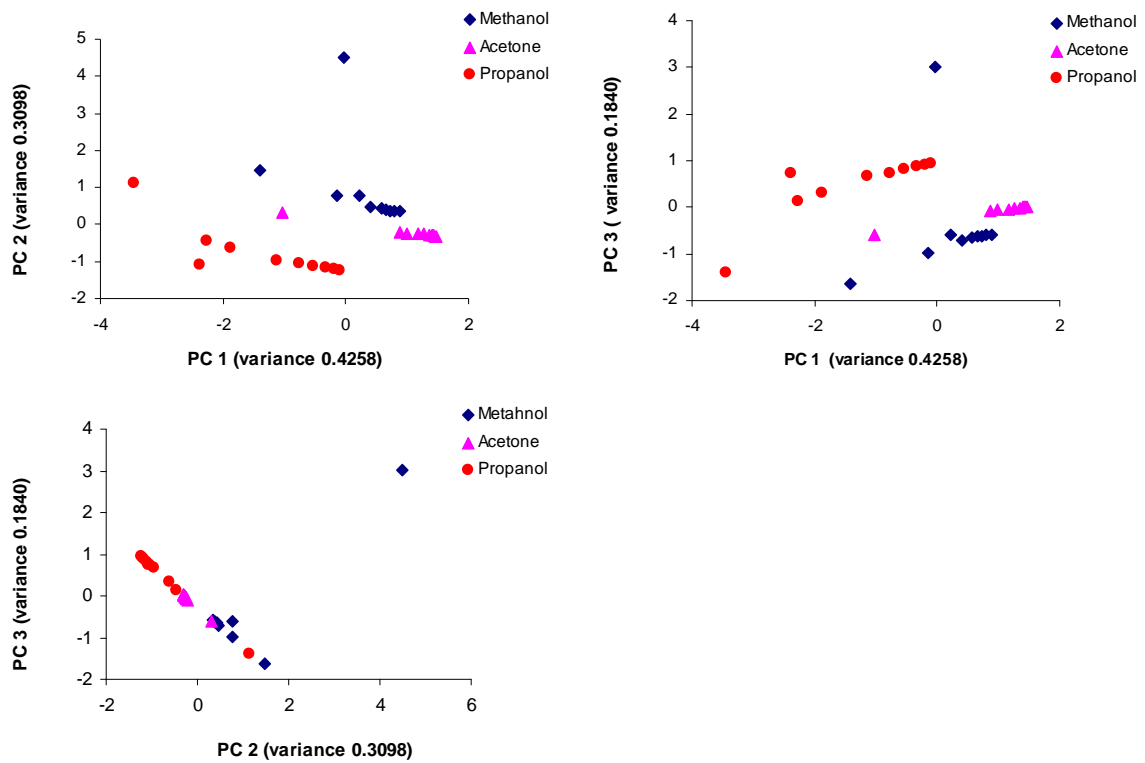


Fig. 2. PCA score plot for Sensor array response treated with plasma radiation for 15 minute.

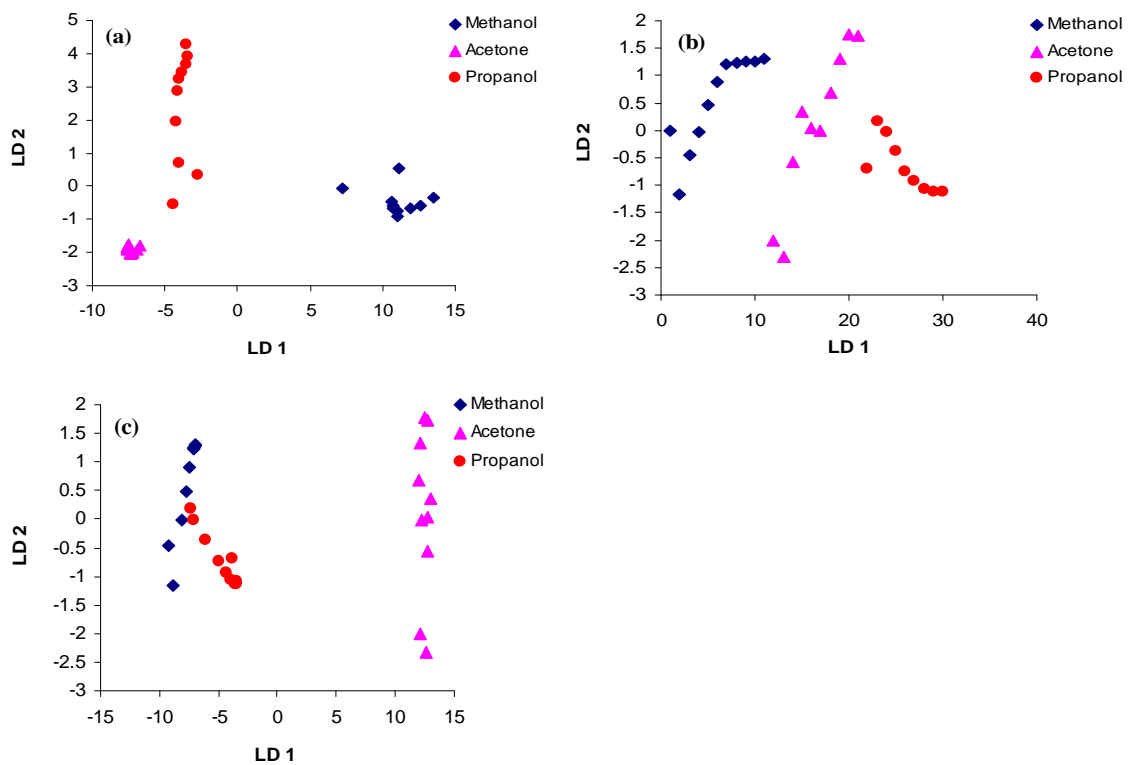


Fig. 3. LDA plot for Sensor array response (a) treated with plasma radiation for 5 minute, (b) treated with plasma radiation for 10 minutes and (c) treated with plasma radiation for 15 minute.

**Table 1.** PCA results for sensor array response matrix treated with plasma radiation for different time duration.

PC	Sensor array plasma treatment time 5 minute		Sensor array plasma treatment time 10 minute		Sensor array plasma treatment time 15 minute	
	Eigen value	Cumulative variance %	Eigen value	Cumulative variance %	Eigen value	Cumulative variance %
1.	2.5478	63.70	3.4304	85.76	1.7032	42.58
2.	1.2262	94.35	0.5289	98.98	1.2394	73.57
3.	0.2174	99.79	0.0336	99.82	0.7760	92.97
4.	0.0085	100	0.0071	100	0.2814	100

**Table 2.** Confusion matrix of LDA classification for sensor array response matrix (training plus test data) treated with plasma radiation for different time duration.

Sensor array Plasma treatment time=5 minute					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	10	0	0		100
	0	10	0		
0	0	10			
Sensor array Plasma treatment time=10 minute					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	10	0	2		93
	0	10	0		
0	0	8			
Sensor array Plasma treatment time=15 minute					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	10	0	3		90
	0	10	0		
0	0	7			

#### 4.3. KNN Analysis

Output of PCA for sensor array response in each case is divided into two parts namely training and tests data set. Total eighteen observations (six observation from each vapor class) is utilized in training data set and remaining twelve observation (four from each chemical class) is employed in test data set. After a number of experiments with neighbor parameter 'k', optimized performance of model is achieved for  $k = 3$ . 100 % correct classification rate is achieved for test data set in each type of sensor array. Details of class wise classification result is summarized in form of confusion matrix in Table 3.

**Table 3.** Confusion matrix of KNN classification for sensor array response matrix (test data only) treated with plasma radiation for different time duration.

<b>Sensor array Plasma treatment time=5 minute</b>					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	4	0	0		100
	0	4	0		
0	0	4			
<b>Sensor array Plasma treatment time=10 minute</b>					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	4	0	0		100
	0	4	0		
0	0	4			
<b>Sensor array Plasma treatment time=15 minute</b>					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	4	0	0		100
	0	4	0		
0	0	4			

#### 4.4. BPNN Analysis

Feed forward neural network with three layers (one input layer one hidden and one output layer) is build and trained with training set of each type of sensor array. Parameters of model namely number of neurons in hidden layer, activation function, and training epoch are optimized to achieve best classification performance in training data set. Optimized performance of model is achieved for 5 neurons in hidden layer, number of epoch 300, sigmoid activation function in hidden layer and linear activation function in output layer. Table 4 shows confusion matrix for classification result of training and test data set for each type of sensor array. All the vapors are identified correctly by plasma treated sensor array (treatment time minute) in training phase. However for sensor array with plasma treatment time 10 minute correct identification rate decreased by 6 % and for sensor array with plasma treatment time 15 minute correct identification rate decreased by 11 % in training phase (see Table 4). Although such decrements in classification rate in training phase don't affect classification performance of model for test data set with all three different type of sensor array. And all the vapors are 100 % correctly identified.

**Table 4.** Confusion matrix of BPNN classification for sensor array response matrix (training data and test data set both) treated with plasma radiation for different time duration.

<b>Sensor array Plasma treatment time=5 minute</b>				
Predicted class	True class			Classification Rate in %
	Methanol	Acetone	Propanol	100
	4	0	0	
	0	4	0	
0	0	4		
<b>Sensor array Plasma treatment time=10 minute</b>				
Predicted class	True class			Classification Rate in %
	Methanol	Acetone	Propanol	100
	4	0	0	
	0	4	0	
0	0	4		
<b>Sensor array Plasma treatment time=15 minute</b>				
Predicted class	True class			Classification Rate in %
	Methanol	Acetone	Propanol	100
	4	0	0	
	0	4	0	
0	0	4		

#### 4.5. SVM Analysis

A SVM model is build with the help of same training data set used for training of KNN and BPNN, for each type of sensor array. After a number of experiments on available kernel function and their tuning parameter, optimized classification performance of model is achieved with radial Gaussian kernel function with tuning parameters as: gamma equal to 0.01 and default cost value. 6 % vapors are misclassified for sensor array treated with plasma radiation with 5 minute, 17 % vapors are misclassified for sensor array treated with plasma radiation with 10 minute and 22 % vapors are misclassified for sensor array treated with plasma radiation with 15 minute in training phase. Similarly in validation phase no vapor is misclassified for first type of sensor array (sensor array treated with plasma radiation by 5 minute) and second type of sensor array (sensor array treated with plasma radiation by 10 minute), however 50 % vapors are misclassified with third type of sensor array (sensor array treated with plasma radiation by 15 minute). Classification results in each case are summarized in Table 5.



**Table 5.** Confusion matrix of SVM classification for sensor array response matrix (training data and test data set both) treated with plasma radiation for different time duration.

<b>Sensor array Plasma treatment time=5 minute</b>					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	4	0	0		100
	0	4	0		
0	0	4			
<b>Sensor array Plasma treatment time=10 minute</b>					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	4	0	0		100
	0	4	0		
0	0	4			
<b>Sensor array Plasma treatment time=15 minute</b>					
Predicted class	True class			Classification Rate in %	
	Methanol	Acetone	Propanol		
	1	0	3		50
	3	4	0		
0	0	1			

## 5. Conclusions

Present study explores the effect of plasma exposure on tin oxide sensor array and their chemical vapor identification capability and performance of pattern recognition methods like PCA and LDA for visual classification of vapors and quantitative classification performance of method like LDA, KNN, SVM and BPNN. It is observed that sensor array treated with plasma radiation with 5 minutes shows best discrimination efficiency for three classes of vapors compare to sensor array treated with plasma radiation for 10 minutes and 15 minutes. Analyzing response of sensor array (treated with plasma radiation by 5 minute results) by PCA and LDA each class of vapor is 100 % visually separated (see figure1-4). Also analyzing the response matrix of same type of sensor array with LDA, KNN, BPNN and SVM method for quantitative classification results 100 % correct classification rate except for training data set by SVM method which gives 94 % correct classification. Comparing the classification ability of used classification methods in analysis performance of KNN method is best compare to LDA, BPNN and SVM, and BPNN perform better compare to SVM and LDA. Comparing advantages of these classification methods, BPNN method has good classification speed, less computational complexity and storage complexity compare to KNN method. KNN and BPNN works well for classification with large number of training pattern, whereas SVM works well even for a data set having less number of training patterns. Some disadvantage associated with KNN and BPNN methods are searching of optimal value of k parameter in case of KNN and hidden layer neurons in case of BPNN for getting best classification performance.

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## Guide for Contributors

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### Aims and Scope

*Sensors & Transducers Journal* (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because of it is a peer reviewed international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per year by International Frequency Sensor Association (IFSA). In addition, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc. Since 2011 the journal is covered and indexed (including a Scopus, Embase, Engineering Village and Reaxys) in Elsevier products.

### Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

### Submission of papers

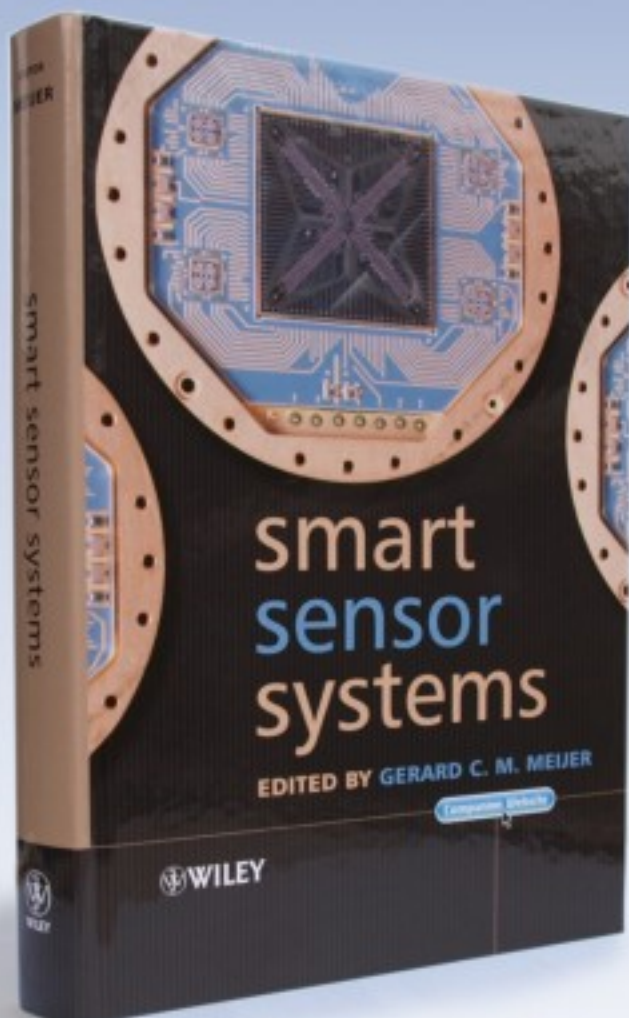
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