# Best Frequency for Temperature Modulation of Tin Oxide Gas Sensor for Chemical Vapor Identification

R Chutia [#1], M Bhuyan [*2]
[#] Research Scholar, Dept. of Electronics and Communication engineering, Tezpur University
Assam, India
[1] rikuchutia@yahoo.co.in
[*] Professor, Dept. of Electronics and Communication engineering, Tezpur University
Assam, India
[2] manab@tezu.ernet.in

*Abstract*— **In this paper, we describe a method of optimum temperature modulation of metal oxide semiconductor (MOS) based gas sensor, operated in dynamic temperature measurement for identification of gas. The volatile organic compound (VOC) sample space consists of fourteen laboratory chemicals sampled at various concentration. We have used eleven number of gas sensors, manufactured by Figaro sensors, Japan. The heater of the sensors were modulated with sawtooth heating waveform of different frequency. Features were obtained from the response waveforms using wavelet transformation. The best frequency of heating waveform were determined using classification accuracy obtained using support vector machine.**

**Keyword- Electronic nose, Gas sensor, Temperature modulation, Wavelet decomposition, Support Vector machine**

## I. INTRODUCTION

Electronic nose is a device which is able to detect and reveal the identity of odours. The system consists of an array of gas sensors, for sensing the odour. The pattern of responses of the array is analysed by a pattern recognition system to identify the odour. Metal oxide semiconductor (MOS) based gas sensor are being widely used in the array of gas sensors. These sensors have high repeatability, sensitivity and are low in cost. Therefore they are widely popular in electronic nose design. These sensors have a sensing surface whose conductance varies at high temperature when the sensing surface is exposed to oxidizing and reducing gases. In normal air oxygen is adsorbed on the surface to form a positive surface potential. In normal air oxygen is adsorbed on to the sensing surface to form a positive surface potential which serves as a potential barrier to electron flow leading to increase surface resistance. In the presence of a reducing gas, the positive surface potential decreases leading to decrease in surface resistance [1]-[3]. MOS gas sensors are commonly operated in static temperature mode. In it the sensing surface is operated at a constant temperature by applying a fixed heating voltage.

MOS gas sensors are also reported to be operated in dynamic temperature mode. In temperature modulation of gas sensor the sensing surface is periodically modulated by a heating waveform. Temperature modulation alters the kinetics of adsorption and desorption of oxygen species on the sensor surface [4]. The influence of temperature modulation on selectivity of MOS gas sensor depends in part on the optimum oxidation temperature of gas which indeed varies from gas to gas and the change in stability of different oxygen species at different temperature [1],[4]. This gives rise to a characteristic conductance-temperature profile specific to a gas. In addition to the type of gas, the response curve is also dependent on the heating waveform used as each heating waveform varies the sensor temperature in its own way resulting in the conductance-temperature profile. Figure 1 shows a typical gas sensor response to a ramp temperature profile. The figure shows the response of four different sensor in presence of voc when the heater is modulated by a ramp waveform.

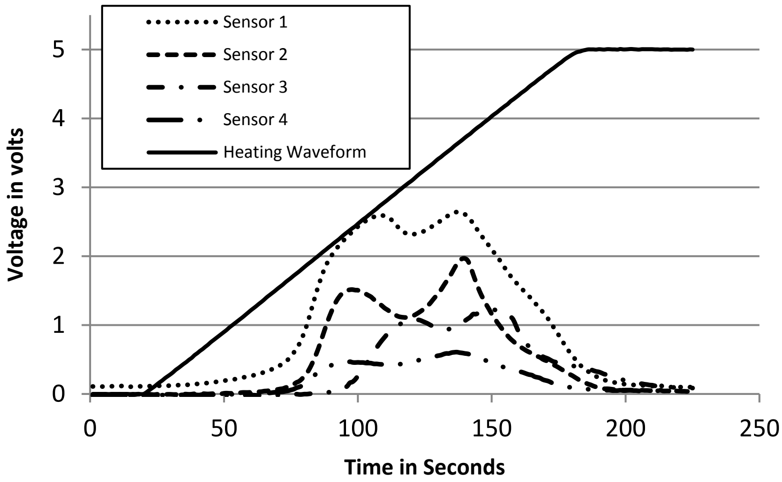


Fig. 1. Typical MOS gas sensor response at modulating heater temperature, modulated by a ramp heating waveform.

There are many reported research in gas sensor temperature modulation. In [5] Nakata et al. interrogated the MOS gas sensor by a sinusoidal temperature waveform and obtained multidimensional information. The features from the resulting response waveform was obtained using fast fourier transform. It was concluded that higher harmonics of the fft provided information about the type of VOC. In [6] Heilig et al. used a sinusoidal heating waveform of 0.05 Hz for temperature modulation on a micromachined sensor array. The resulting waveform was analysed using fast fourier transform (FFT) to obtain feature. These features were then used in neural network based classifier to identify and quantify CO and NO in binary mixtures. In [7] Cavicchi et al. also used a single sensor for temperature modulation. They used a cyclic pulsed heating waveform. The speed of cyclic waveform in these works was 20 to 25 seconds per cycle. In [8] Bukowiecki et al. used a variety of heater voltage waveforms triangular, sawtooth, asymmetric square wave to distinguish between CO, methane, ammonia and hydrogen. The time for the increase and for the decrease of the heating voltage in each of the waveform was 60 seconds.

In [9] Ngo et al. used a sensor array based on metal oxide gas sensors to identify three industrial and environmental gases. The gases are namely carbon monoxide, acetylene and hydrogen sulphide. Sensor response were obtained using temperature modulation ( triangular waveform ) with a frequency of 25 mHz. These results were compared to experiments with different constant temperatures of the sensor. Both principal component analysis (PCA) and artificial neural networks (ANN) were used to identify the target gases. In [10] Huang et al. investigated the gas sensing behavior of a single tin oxide gas sensor based on a dynamic measurement method. They experimented with various heating waveform and frequency, and the results were compared with those of static measurement. The heating waveforms studied were rectangular, sinusoidal, triangular, saw-tooth, pulse, trapezoidal etc. In [11] Ding et al. experimented with temperature modulation of semiconductor gas sensors. They used only one metal oxide gas sensor and employed wavelet decomposition to extract features from the thermally modulated sensor's response curves. They have been able to discriminate between gases studied (hydrogen, carbon monoxide and their binary mixture) over a wide concentration range, from 10 to 1000 ppm, using a single sensor.

In [12] Vergara et al. used a multi-sinusoidal temperature-modulating signal on an array of four metal oxide gas sensors. They have optimized the heating frequency based on the use of multi-level pseudo-random sequences. The best temperature modulating frequencies to discriminate and quantify gases was identified. The gases and gas mixtures were discriminated with a 100% success rate using FFT features from the sensors dynamic response and using fuzzy ARTMAP neural network as classifier. In [13] Dutta et al. presented a method to systematically determine the optimal set of temperature modulating frequency and duty cycles using system identification theory for sensor modeling. The model parameters was estimated using iterative prediction-error minimization (PEM) method. Using sensor stability, the best suited transfer function was chosen for the MOS gas sensors and the sensors were operated at the respective best frequencies and duty cycles. Data classification was performed using supervised neural network classifiers.

In [14] Tekin et al. used a sinusoidal heating profile to the heater of a micromachined gas sensor to detect binary mixtures of gas. In [15] Osuna et al. also investigated a sinusoidal heating profile. The result was analyzed for different frequency and it was concluded that at a lower frequency the response provided more discriminative features as at a lower frequency the sensors approached isothermal behavior. In [16] also Osuna et al. studied a staircase waveform temperature profile on the sensor. Each step in temperature yielded a characteristic transient shape. Transient analysis methods were used in the analysis. In [17] Huang et al. applied a pulse heating profile to identify pesticide residue in ambient atmosphere using a modulating frequency of 20mHz. In [18] Nakata et al. applied a cyclic temperature profile comprising of two sinusoid, a fundamental and its second harmonic. The response revealed characteristic shape which were analyzed using fft. In our work we are using a heating waveform consisting of a sawtooth waveform. The waveform is selected so as to smoothly increase the sensor heater from a lower temperature to a higher temperature.

The main objective of the proposed work is determination of best frequency of heater temperature modulation for dynamically heating MOS based gas sensor and extraction of distinguishable features from the sensors operated in dynamic temperature modulation. In this work we investigated to extract distinguishable features from the MOS gas sensor response for fourteen different laboratory chemicals as odor source at various concentrations. The gas were injected into the sensor chamber and their responses were acquired for different frequencies. The sawtooth heating signal starts at 0 Volt and increases upto 5 volt. We have acquired the responses using 11 different gas sensors.

## II. EXPERIMENTAL

The block diagram of the experimental setup is shown in figure 2. Figure 3 shows the photograph of the experimental setup. The gas sensors are mounted inside a sensor chamber. The voc air mixture is prepared by injecting a fixed amount of liquid chemical into a beaker placed inside the gas chamber and allowing the chemical to evaporate into the environment of the gas chamber, piping and the sensor chamber. The dashed arrow represents gas pipes and the direction of pure air flow. The solid arrow represents the direction of voc flow from gas chamber to sensor chamber. The gas is injected into the sensor chamber with the help of air pump. Air pump facilitates movement of the volatile organic compounds from the gas chamber to the piping, then to the sensor chamber and then back to the gas chamber through the return piping.

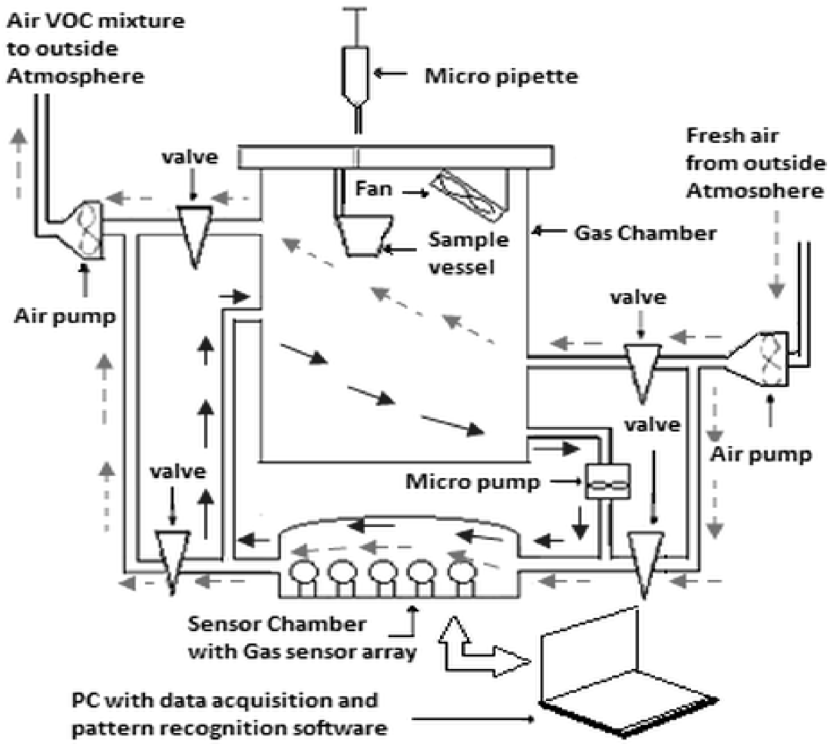


Fig. 2. Experimental setup

The sensors are modulated with heating profile with the help of PC DAQ (data acquisition card ) card, National instruments PCI 6024E and a driver circuit. The analogue output signal is acquired at 50samples / second using the same DAQ card. After the acquisition is complete, fresh air from outside atmosphere is allowed to enter the gas chamber, piping and sensor chamber and the gas to escape to the outside atmosphere in order to clean the system. The cleaning of the sensors and the chambers with fresh air is done for 30 minutes, so that the present gas does not interfere with the next gas acquisition. The separation between the inlet air piping and outlet gas piping in the outside atmosphere is kept at a distance so that exhaust gas does not enter the inlet.

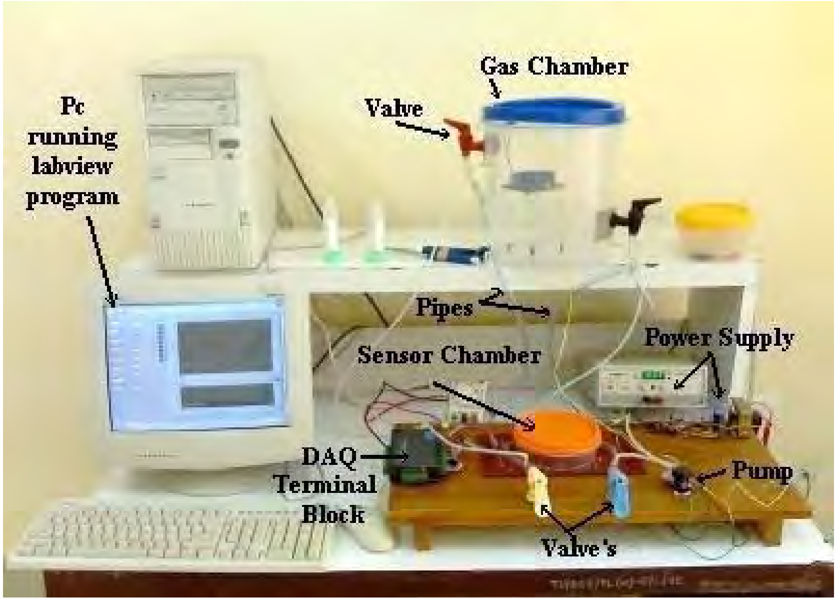


Fig. 3. Photograph of the experimental setup

## III.DATA ACQUISITION

In data acquisition, the sensors were interrogated with a sawtooth temperature modulation waveform. The sensors were heated using a sawtooth waveform that varied form 0 volts to 5 volts. The responses were acquired for ten different modulating frequency of the sawtooth waveform. We have used eleven different MOS based gas sensor namely TGS-832, TGS-826, TGS-821, TGS-816, TGS-2600, TGS-2610, TGS-2620, TGS-2611, TGS-825, TGS-822 and TGS-813. All the sensors were heated by the same sawtooth modulating waveform. We have used fourteen different laboratory chemicals as odour source and is shown in table 1.

TABLE 1
Chemicals used and their concentration

| **Chemical** | **Density (g/cm3)** | **Molecular Weight (g/mol)** | ***Vliq* and Concentration (ppm)** | | |
|---|---|---|---|---|---|
| | | | **14(µl)** | **26(µl)** | **38 (µl)** |
| Acetic acid | 1.05 | 60.05 | 554 | 1029 | 1504 |
| Acetone | 0.791 | 58.08 | 432 | 802 | 1172 |
| 1-Butanol | 0.810 | 74.1216 | 346 | 643 | 940 |
| Di methyl sulfoxide | 1.10 | 78.13 | 446 | 829 | 1212 |
| Ethanol | 0.789 | 46.06844 | 543 | 1008 | 1474 |
| Ethyl acetate | 0.897 | 88.105 | 322 | 599 | 876 |
| Formaldehyde | 0.8153 | 30.03 | 861 | 1599 | 2337 |
| Iso amyl alcohol | 0.8104 | 88.148 | 291 | 541 | 791 |
| Iso propyl alcohol | 0.786 | 60.1 | 414 | 770 | 1126 |
| Methanol | 0.7918 | 32.04 | 783 | 1455 | 2127 |
| N-propanol | 0.8034 | 60.09502 | 424 | 787 | 1151 |
| Pyridine | 0.9819 | 79.10 | 393 | 731 | 1068 |
| Toluene | 0.8669 | 92.14 | 298 | 554 | 810 |
| Xylene | 0.864 | 106.16 | 258 | 479 | 700 |

The concentration of the chemical voc is calculated in volume by volume (ppm) using the method given in [19]. A fixed amount (***Vliq***) of liquid chemical is evaporated into the gas chamber. The resulting concentration of voc in the air-voc mixture in the chamber can thus be calculated. We have taken measurements at three different concentrations of each chemical as shown in table 1. Each chemical response at a particular concentration was acquired at ten different frequencies of the sawtooth heating waveform. The frequencies used were 80mHz, 40mHz, 25mHz, 20mHz, 16.6mHz, 13.3mHz, 10mHz, 8mHz, 6mHz and 5mHz which corresponds to a period of 12.5s, 25s, 40s, 50s, 60s, 75s, 100s, 125s, 166.6s and 200s respectively of the sawtooth heating waveform.

Figure 4 shows the response of three sensors TGS-832 (solid), TGS-816 (dashed) and TGS-825 ( dotted ) to Di Methyl sulfoxide for 9 different modulating frequencies. The sample rate for data acquisition was 50 Hz. The raw data was then passed through a moving average filter to smoothen the signal and eliminate high frequency noise signals. The smoothened signal was then down sampled, so that the resultant signal from each sensor consists of 256 points. In figure 4 the response of three sensors are shown, although eleven sensors were used for measurement to avoid cluttering in the graph. It is seen that as the frequency decreases or the period of the sawtooth modulating waveform increases, the characteristic response waveform of the sensors becomes more distinct. This may be attributed to the near isothermal operation of the sensors at lower frequency and existence of equilibrium between adsorbed oxygen and chemical voc. At high frequency or lower period of modulating waveform the sensors operation is not isothermal and no equilibrium exists between adsorbed oxygen and chemical voc.

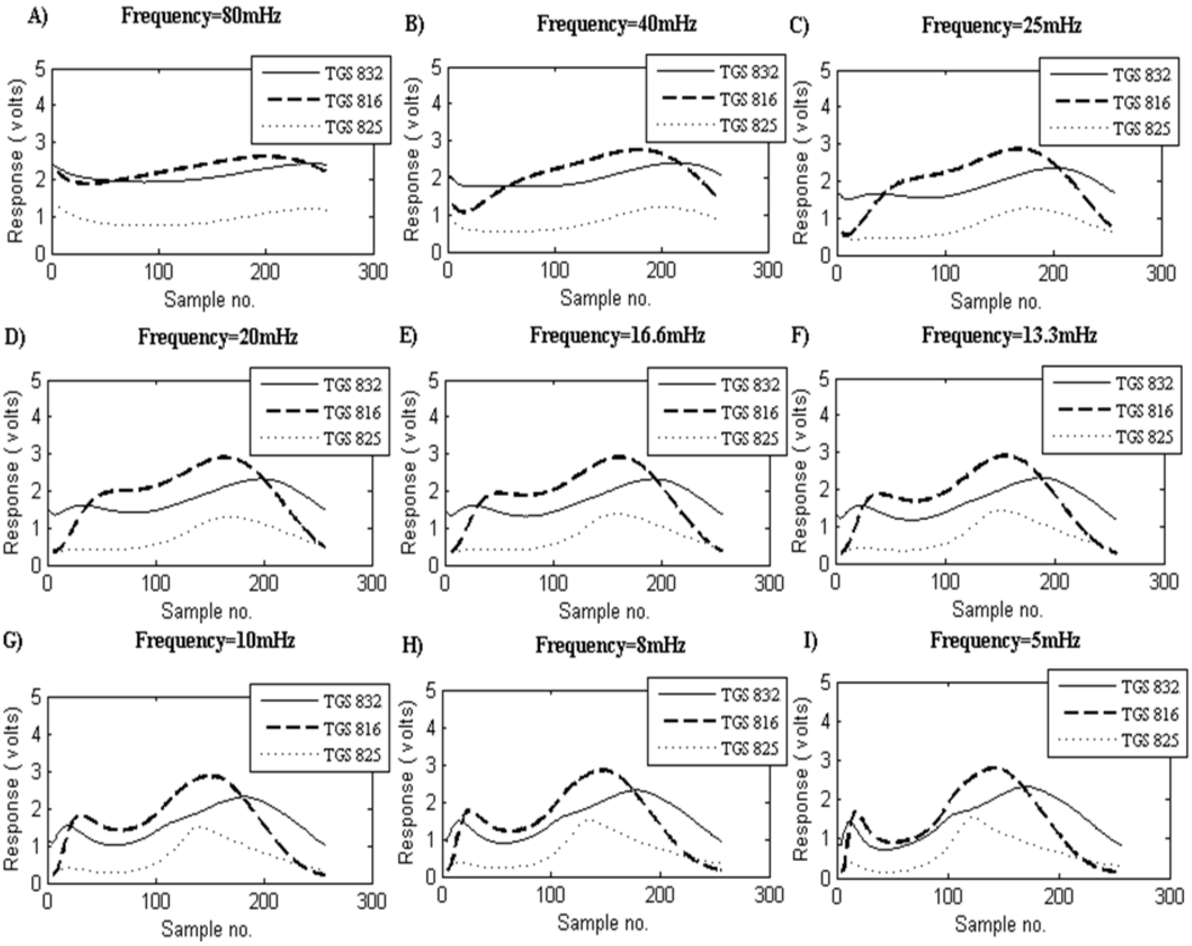


Fig. 4. Response of Three sensors to Di Methyl Sulfoxide at 9 different sawtooth heating waveform

Figure 5 shows the response of four different (1-Butanol, Acetic Acid, Acetone, Ethanol) gases at one fixed frequency ( 25 mHz) of modulation. As expected the response pattern of the four gases are found to be different at least for one of the sensor. These combined response pattern of all the sensors serves as a signature of the concerned gas. Features were derived from the characteristic signature response of the gases.

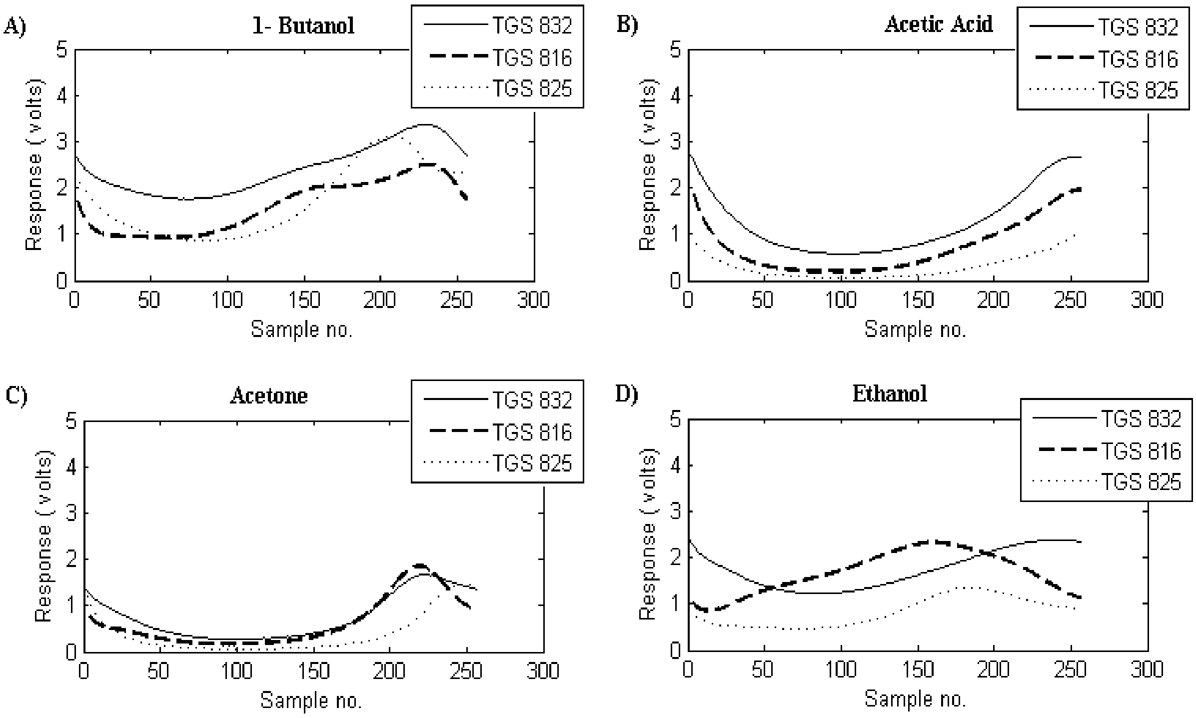


Fig. 5. Sensor response for 4 gases ( A) 1-Butanol B) Acetic acid C) Acetone and D) Ethanol ) at a sawtooth modulating frequency of 25 mHz

## IV. Data evaluation and feature extraction

### A. Wavelet transform

The wavelet transform analyses a signal by using a short duration finite energy function known as mother wavelet. It transforms the original signal into another more usable representation. A mother wavelet is denoted mathematically by equation 1. In the equation $b$ represents a location parameter and $a$ represents a scaling parameter. Using a linear combination of scaling and translation parameters of the selected mother wavelet, the signal under study is represented in wavelet domain by some coefficients mathematically denoted by equation 2.

$$\psi_{a,b}(t) = \frac{1}{\sqrt{|a|}}\psi\left(\frac{t-b}{a}\right) \quad (1)$$

$$W(a,b) = \int_{-\propto}^{\propto} f(t)\frac{1}{\sqrt{|a|}}\,\psi\left(\frac{t-b}{a}\right)dt \quad (2)$$

From equation 2 we get a wavelet transform coefficient for every scaling and translation parameter a and b respectively and it indicates the similarity of the scaled wavelet at the location b/a. If the scale and position is varied in continuous fashion then the transform is called continuous wavelet transform. But if the variation of the scale and position is done in discrete steps, then the transform is called discrete wavelet transform. Discrete wavelet analysis splits the signal into two parts using a highpass and a lowpass filter and depends upon choosing a mother wavelet. The smoothed signal after the lowpass filtering is called the “Approximation” coefficients. The signal after highpass filtering is called the “Details”. In multi level wavelet decomposition the approximation coefficients is further broken down into higher level approximation and details coefficients.

### B. Feature extraction using wavelet decomposition

The acquired responses of fourteen gases were analysed using wavelet decomposition. Each sensor response has 256 data points. We have analysed each signal upto level 7 wavelet analysis. We have used daubechies 2 wavelet as the mother wavelet. Figure 6 B,C and D shows a plot of all the coefficients of three sensor TGS-832, TGS-816 and TGS-825 for ethanol. It is seen that the coefficients below sample number 25 has some variance. All other coefficients value are zero. These characteristics is seen for all other sensors and for all other gases. These coefficients below sample number 25 mainly has the approximation coefficients of level 4 wavelet decomposition. We have therefore used the approximation co-efficient of level 4 wavelet decomposition as features for classification. At level 4 wavelet decomposition each sensor resulted 18 coefficients. Since we have 11 gas sensors, therefore we have a total of 198 coefficients which are used as features for a particular gas. Figure 7 shows the approximation coefficients of level 4 wavelet decomposition of four gases for three sensors at 25 mHz frequency.

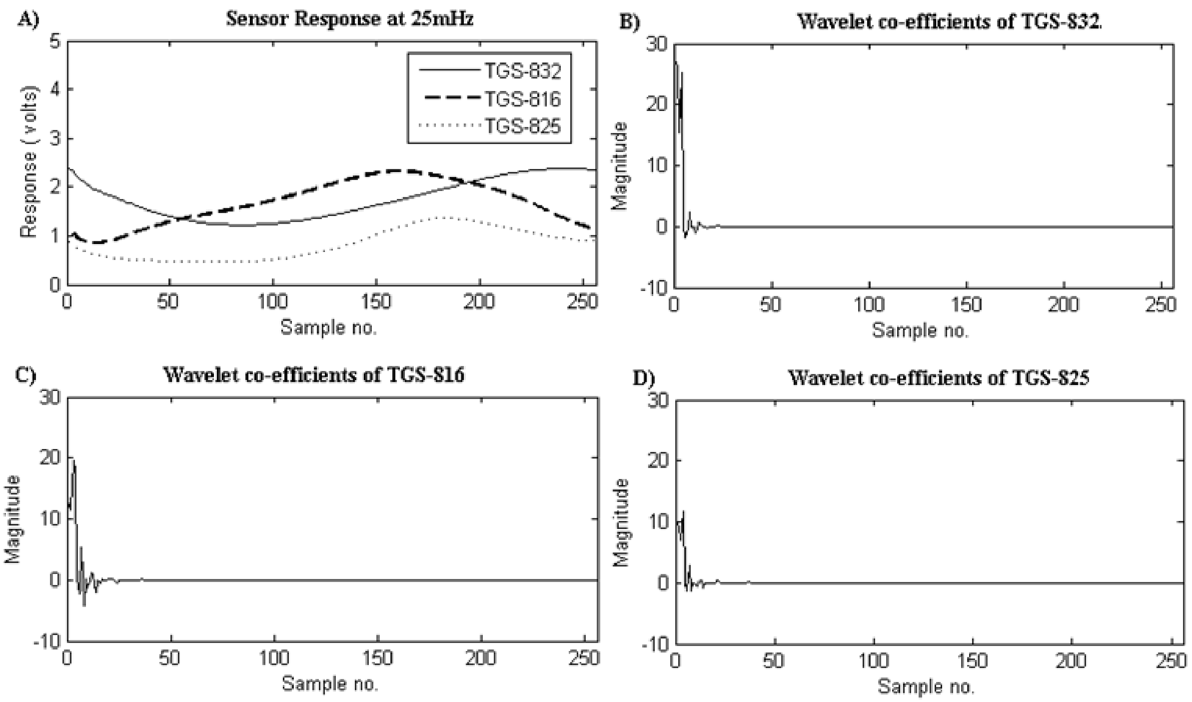


Fig. 6. Wavelet coefficients level 7 for Ethanol at a frequency of 25 mHz

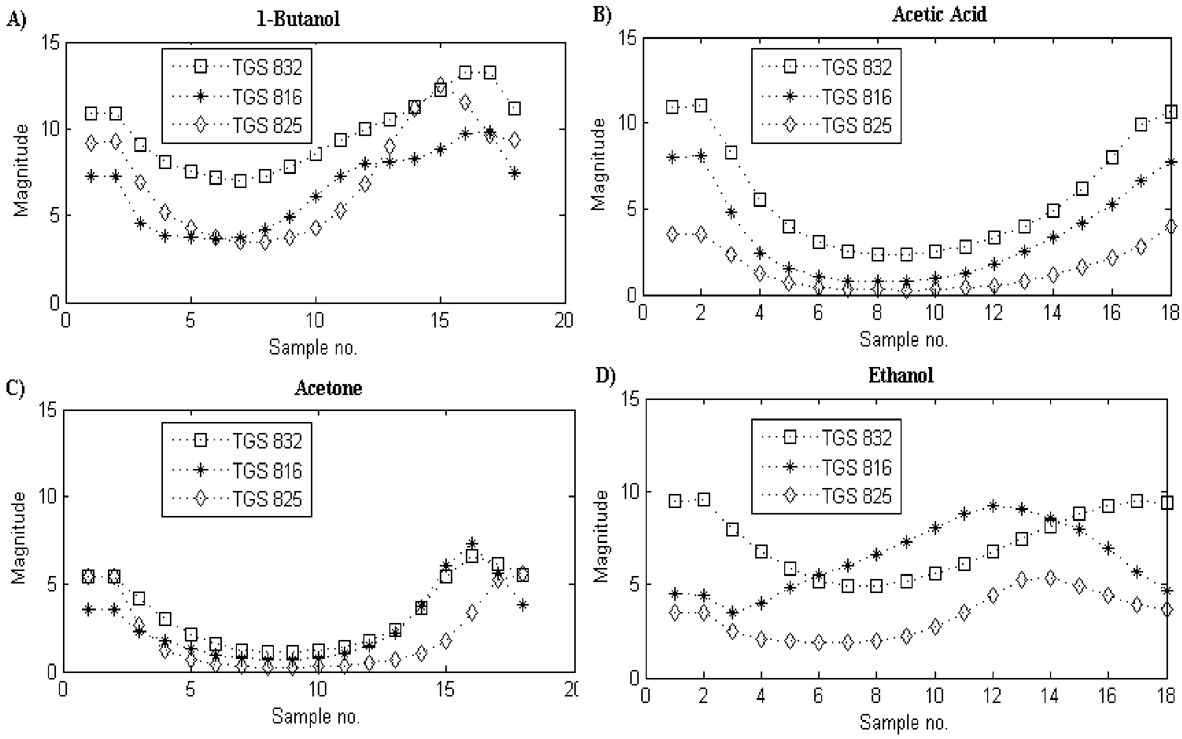


Fig. 7. Wavelet feature coefficients (level 4 approximation) for 4 gases at a frequency of 25 mHz

## V. BEST FREQUENCY DETERMINATION

After feature extraction using wavelet decomposition the classification of gases is done by support vector machines. We have used multi Support vector machine training implemented in Matlab for each of the modulating frequency. The training dataset consists of 50% of acquired data and remaining 50% were used for testing the system. The training of the SVM and classification is done for all possible combination of 11 sensors. The number of all possible combination of 11 sensors is 2047. The training of SVM and retrieving the classification accuracy for one combination took around 3 seconds in our computer with intel core i5 processor and running windows 7. Hence an exhaustive search for 2047 combination took around 102 minutes to complete. Figure 8 shows the maximum classification accuracy obtained against combination of 1, 2 … 11

number of sensors. At frequency 80mHz a minimum of eight sensors is required for 100% classification accuracy. At frequency 25mHz a minimum of three sensors is required for 100% classification accuracy. At frequency 5mHz two sensors is required for 100% classification accuracy. The signal acquisition time at 5 mHz is very high as it takes 200 seconds to acquire 1 cycle of response waveform. At 80 mHz it takes 12.5 seconds to acquire 1 cycle of response waveform. The best frequency for modulating the sensors is therefore a trade-off between detection time required and number of sensors in the system. If the number of sensors to be used is less, then the detection time will be high as the sensors has to be interrogated with lower frequency heating waveform to get characteristic features. If the number of sensors to be used is higher, then the detection time will be less as it is sufficient to interrogate the sensors with higher frequency heating waveform to get characteristic features.

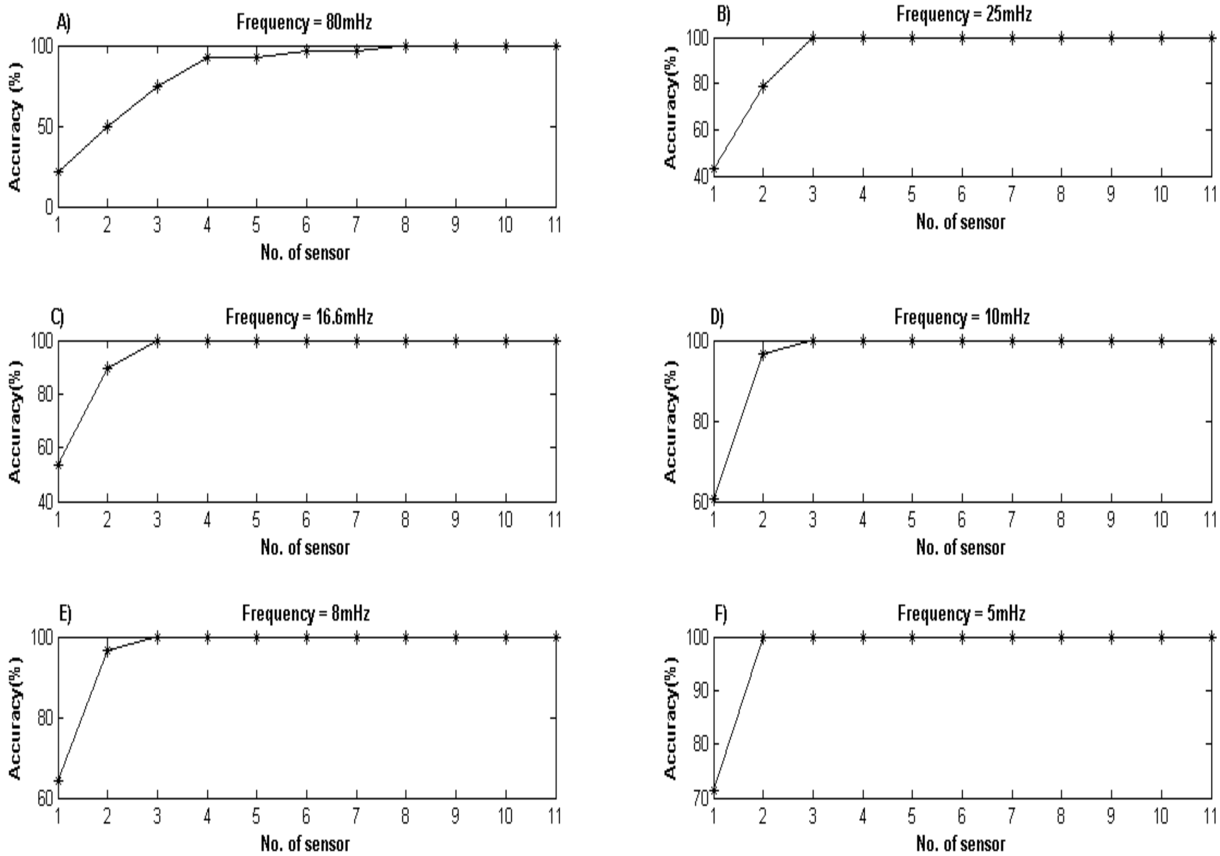


Fig. 8. Maximum classification accuracy obtained against no. of sensors at different frequency

## VI. CONCLUSION

The effect of temperature modulation is significant in the sensing behaviour of MOS based gas sensor. In dynamic temperature modulation with the application of varying heating signal, there exists no equilibrium among the adsorbed surface oxygen species. The periodic application of high temperature modulating signal results in repeated adsorption and desorption of oxygen species. Experimental results showed temperature modulated sensor response produced discriminatory information. The frequency of the interrogating temperature modulating signal has a major role in the response characteristic of the gas sensor. The near isothermal operation of the sensor at low frequency provided more distinct characteristic response of the sensor to a gas than at a high frequency. The response characteristics between 20 to 30mHz provided discriminatory information while requiring lesser time period for the modulating signal. The dynamic temperature modulation produced features resulting in 100% classification accuracy.

## REFERENCES

[1] H. Meixner and U. Lampe," Metal oxide Sensors", Sensors and Actuators B: Chemical, Vol. 33, pp. 198-202 , 1996.
[2] J. Watson, K. Ihokura and G. S. V. Coles ," The tin dioxide gas sensor", Measurement Science and Technology, Vol. 4, No. 7 , pp. 711-719, 1993.
[3] "Operation principle of Figaro Gas Sensors", Available at: http://www.figarosensor.com/products/general.pdf [Feb 10, 2014]
[4] N. Barsan, D. Koziej and U. Weimar, "Metal oxide-based gas sensor research: How to?", Sensors and Actuators B: Chemical, Volume 121, Issue 1, Pages 18-35, 30 January 2007.
[5] S. Nakata, S. Akakabe, et al., "Gas sensing based on a nonlinear response: discrimination between hydrocarbons and quantification
[6] of individual components in a gas mixture", Anal. Chem. 68 (1996) 2067–2072.

[7] A. Heilig, N. Barsan, U. Weimar, M. Schweizer-Berberich, J.W. Gardner, W. Gopel, " Gas identification by modulating temperatures of SnO2-based thick film sensors", Sensors and Actuators B: Chemical, Volume 43, Issues 1-3, September 1997, Pages 45-51
[8] R.E. Cavicchi, J.S. Suehle, K.G. Kreider, M. Gaitan and P. Chaparala, "Fast temperature programmed sensing for micro-hotplate gas sensors," Electron Device Letters, IEEE , vol.16, no.6, pp.286,288, June 1995
[9] S. Bukowiecki, G. Pfister, A. Reis, A.P. Troup, H.P. Ulli, "Gas or vapor alarm system including scanning gas sensors", US Pat. 4567475, January 28, 1986.
[10] Kieu An Ngo, Pascal Lauque, Khalifa Aguir, "High performance of a gas identification system using sensor array and temperature modulation", Sensors and Actuators B: Chemical, Volume 124, Issue 1, 10 June 2007, Pages 209-216,
[11] Xingjiu Huang, Fanli Meng, Zongxin Pi, Weihong Xu, Jinhuai Liu, "Gas sensing behavior of a single tin dioxide sensor under dynamic temperature modulation", Sensors and Actuators B: Chemical, Volume 99, Issues 2–3, 1 May 2004, Pages 444-450
[12] Hui Ding, Haifeng Ge, Junhua Liu, "High performance of gas identification by wavelet transform-based fast feature extraction from temperature modulated semiconductor gas sensors", Sensors and Actuators B: Chemical, Volume 107, Issue 2, 29 June 2005, Pages 749-755
[13] A. Vergara, E. Llobet, J. Brezmes, P. Ivanov, C. Cané, I. Gràcia, X. Vilanova, X. Correig, "Quantitative gas mixture analysis using temperature-modulated micro-hotplate gas sensors: Selection and validation of the optimal modulating frequencies", Sensors and Actuators B: Chemical, Volume 123, Issue 2, 21 May 2007, Pages 1002-1016
[14] Nimisha Dutta and Manabendra Bhuyan, "Optimal Temperature Modulation of MOS Gas Sensors by System Identification", International Journal of Signal Processing, Image Processing and Pattern Recognition, Volume 5 (No. 2) , 2012
[15] Tekin A. Kunt, Thomas J. McAvoy, Richard E. Cavicchi, Steve Semancik, "Optimization of temperature programmed sensing for gas identification using micro-hotplate sensors", Sensors and Actuators B: Chemical, Volume 53, Issues 1-2, 26 November 1998, Pages 24-43
[16] R Gutierrez-Osuna, S Korah and A Perera, "Multi-frequency temperature modulation for metal oxide gas sensors", Proceedings of the 8th Intl. Symp. On Olfaction and Electronic Nose, Washington, DC, March 25-30, 2001
[17] R. Gutierrez-Osuna, A. Gutierrez-Galvez, N. Powar, "Transient response analysis for temperature-modulated chemoresistors",
[18] Sensors and Actuators B: Chemical, Volume 93, Issues 1-3, Proceedings of the Ninth International Meeting on Chemical Sensors, 1 August 2003, Pages 57-66
[19] X. J. Huang, J. H. Liu, Z. X. Pi and Z. L. Yu, " Detecting pesticide residue by using modulating temperature over a single tin dioxide-based gas sensor", Sensors, 2003, 3(9), pages 361-370
[20] Satoshi Nakata, Hirokazu Okunishi and Yusuke Nakashima, "Distinction of gases with a semiconductor sensor depending on the scanning profile of a cyclic temperature", Analyst, 2006, 131, pages 148-154
[21] A. Uyanik and N. Tinkiliç, "Preparing Accurate Standard Gas Mixtures of Volatile Substances at Low Concentration Levels", The Chemical Educator, Volume 4, Number 4, pages 141-143