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Temperature Modulation with Specified Detection Point on Metal Oxide Semiconductor Gas Sensors for E-Nose Application

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Abstract: Temperature modulation technique, some called dynamic measurement mode, on Metal-Oxide Semiconductor (MOS/MOX) gas sensor has been widely observed and employed in many fields. We present its development, a Specified Detection Point (SDP) on modulated sensing element of MOS sensor is applied which associated to its temperature modulation, temperature modulation-SDP so-named. We configured the rectangular modulation signal for MOS gas sensors (TGSs and FISs) using PSOC CY8C28445-24PVXI (Programmable System on Chip) which also functioned as acquisition unit and interface to a computer. Initial responses and selectivity evaluations were performed using statistical tool and Principal Component Analysis (PCA) to differ sample gases (Toluene, Ethanol and Ammonia) on dynamic chamber measurement under various frequencies (0.25 Hz, 1 Hz, 4 Hz) and duty-cycles (25 %, 50 %, 75 %). We found that at lower frequency the response waveform of the sensors becomes more sloping and distinct, and selected modulations successfully increased the selectivity either on singular or array sensors rather than static temperature measurement. *Copyright © 2015 IFSA Publishing, S. L.*

Keywords: Temperature modulation, Specified detection point, MOS gas sensor, E-nose, PCA analysis.

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1. Introduction

Since many Metal Oxide Semiconductor (MOS) gas sensors and their variances are manufactured [1], the utilization of commercial MOS gas sensors has been investigated and applied extensively in many fields, like environment [2], biomedical [3] and food/agriculture [3-4]. Electronic-nose (E-nose) is the most popular term for the application in which are typically uses array of gas sensors mounted in a chamber with different selectivity and sensitivity towards the various compounds. MOS gas sensors become most favorable choice in E-nose application since they offer high sensitivity, compact, fast response and recovery times, and low cost devices with versatile applications [5].

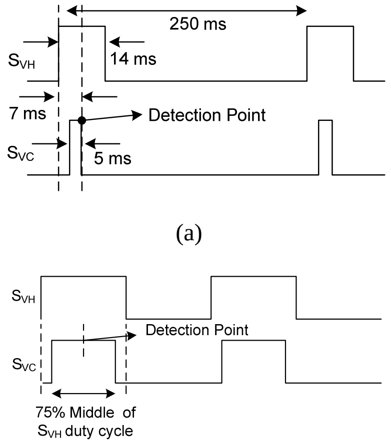
Along with those advantages of MOS sensors, they also perform a series of undesirable characteristics, such as lack of stability and cross-selectivity [5-6]. They are also prone to output drift. Drift problem and cross-sensitivity are the high considered limitation of MOS gas sensors. That is potentially caused from temperature variation which changes the baseline of the sensor signal shifts. It can affect both the baseline (additive) and the sensitivity of the sensor (multiplicative) [7]. Moreover in [8], it reviewed that besides intrinsic factors (chemical composition, surface modification by noble metal particles, as well as microstructure), the circumstance parameters, especially temperature and humidity also strongly contribute and affect the sensitivity of MOS gas sensor. On other hand, the apparent problem of MOS gas sensors are that the sensors are sensitive to variation of temperature and humidity which changes the baseline of the sensor signal shifts with time and large noise exists in sensor output which are potentially resulted from use of static temperature on gas sensor and mounting the sensor in chamber.

As report in [9], temperature modulation through oscillation of heater voltage, also some called dynamic measurement technique, has been most potential promising and established technique of temperature modulation than temperature transient or pulsed techniques to be applied on MOS gas sensors. Temperature modulation alters the kinetic of the sensor through changes in the operational temperature of device. The operating modulation voltage, also consequently the operating temperature, of the sensor changes periodically either by square (rectangular) or triangular or sine waveform [10]. Temperature modulation provides more information from a single sensor than static measurement [11], which also means that cyclic variation of temperature gives a unique signature for each gas, differ type of modulation showed a slight difference signal response and amplitude [10, 12]. By using rectangular waveform, Dutta and Bhuyan [13] has determined the optimal frequency applied for each sensor using theory of system identification based on best fit transfer function, pole-zero plot and the overshoot percentage. And, It is also reported the use of rectangular modulation to detect and distinguish the presence of two pesticide gases, a binary gas mixture (acephate and trichlorphon), in the ambient atmosphere [14-15].

This paper discusses an improved technique of temperature modulation on MOS gas sensor as an alternative attempt to overcome cross-selectivity problem or gain its sensitivity. The technique implements rectangular heating Temperature Modulation with Specified Detection Point, Temperature Modulation-SDP so-called. It means detection (acquiring) of MOS gas sensor output is put at specified point with respect to temperature modulation on its heater. The temperature modulation-SDP is regulated and configured using Timer block in PSoC (Programmable System on Chip, Cypress Semiconductor Corporation) CY8C28445-24PVXI. A single modulation circuit could be applied to drive either single or multi (array) sensors with similar type and characteristic. This technique is more addressed to be implemented in PSoC (microcontroller) since typical low rate of data transfer when used to acquire multi sensors (depended on time consuming of sequential process on multiplexing and digital conversion) and send them to outer device, such as computer. It is also easy to construct the modulation since availability of required blocks to meet the desired modulation. In addition, the PSoC is configured to acquire array sensors and transmit data to computer as well by employing Timer (signal to get data), Multiplexer, ADCs, and UART blocks.

2. Design of Rectangular Temperature Modulation-SDP

The temperature modulation-SDP design is based on required modulation which applied on TGS 2444. As shown in Fig. 1(a), TGS 2444 requires application of a 250 ms heating cycle (S_{VH}) which comprised by 4.8 Volt (high state) applied to the heater for the first 14 ms, then followed by 0 (low state) volt pulse for the remaining 236 ms. The sensing cycle S_{VC} consists of low state applied for 2 ms at first, then by high state for 5 ms and followed by low state for remaining 243 ms. For achieving optimal sensing, detection is measured after the center of S_{VH} pulse [16].



(a)

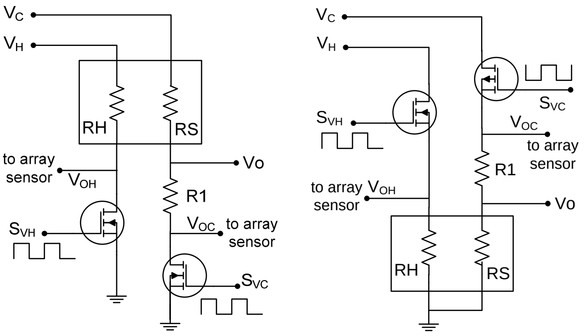
(b)

Fig. 1. Required modulation of TGS 2444 and (b) the temperature modulation-SDP.

In our design (Fig. 1(b)), compared with TGS 2444 detection time, on signal detection (S_{VC}), we put an additional time after detection point so that detection point is in center of S_{VC} to ensure the acquisition system (PSOC based) have adequate time to acquire the sensor amplitude. The S_{VC} is positioned on midpoint 75 % of "on/high" state of temperature modulation (S_{VH}) whereas the detection point is laid on center of S_{VC} pulse.

We constructed a common temperature modulation-SDP that might be applied on single or even array MOS gas sensor (Fig. 2) which has similar type and characteristic. We applied two common modulation circuits that employing FET (Field Effect Transistor) and op-amp buffer to drive array of TGS Sensors (manufactured by Figaro Engineering Inc.) and FIS sensors (manufactured by FIS Inc.)

respectively since there is slight difference pin configuration on them.



(a) (b)

Fig. 2. Schematic of temperature modulation-SDP for array (a) TGS sensor and (b) FIS sensor with V_H is heater voltage, V_C is sensing circuit voltage, S_{VH} is modulation signal for V_H, and S_{VC} is modulation signal for V_C.

We employed internal main oscillator (IMO) in PSoC CY8C28445-24PVXI which is set at 5 V/24 MHz (Vcc/SysClk) to supply 12 MHz for CPU clock. Clock signal of IMO contains the jitter around 200-300 ps [17]. However, in this research the timing error of detection point is negligible.

3. Experimental

We tested 6 commercial MOS gas sensors (TGS-2444, TGS-2602, TGS-825, FIS-12A, FIS-30SB, and FIS-AQ1) and used 3 environment sensors (KE-25, LM35 and HSM30G). We configured PSOC CY8C28445-24PVXI to construct the temperature modulation-SDP and act as acquisition system to computer in which the diagram of PSOC-based system is shown in Fig. 3. The acquisition system transmits all data wirelessly through Radio Frequency using XBee serial communication (IEEE 802.15.4) Digi International Inc. We designed two temperature modulation-SDP timing generators by Timer8 block to provide fixed modulation and adjustable modulation that is set from acquisition software in Personal Computer (PC). Fixed modulation is associated with TGS-2444 which its recommended temperature modulation is 4 Hz 5.6 % [16], while adjustable modulation is provides modulation on array of TGSs and FISs but TGS-2444.

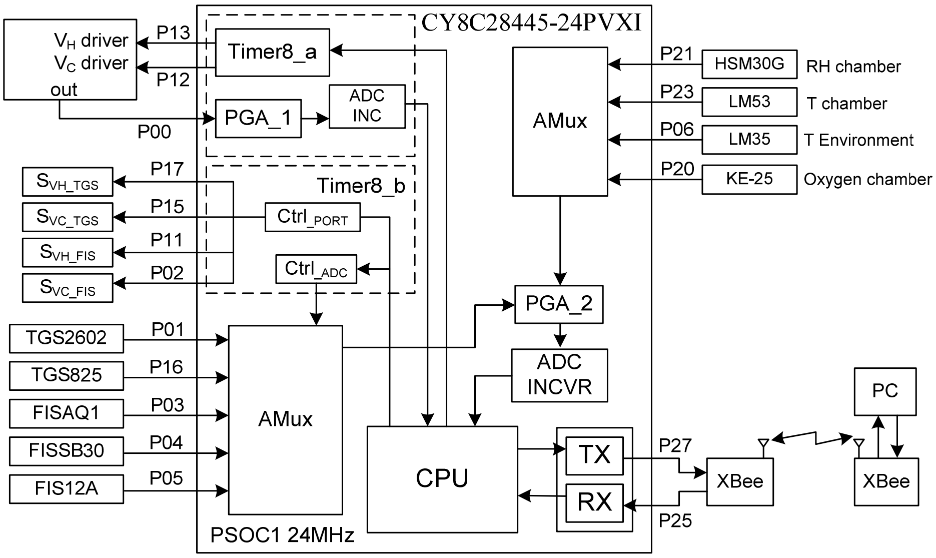


Fig. 3. Diagram block of system based on PSOC CY8C28445-24PVXI with pins configuration.

Measurement and setting were adjusted and monitored automatically through developed software which built using Visual Studio VB Net 2012 that expanded from our previous work [18]. It is functioned to monitor the initial conditioning of chamber oxygen level, to set the modulation signal, and to acquire output of all sensors. The dynamic chamber measurement of system is shown in Fig. 4. The arrow represents the gas pipes and direction of flow. For analyte gas, the flow is helped by small air pump.

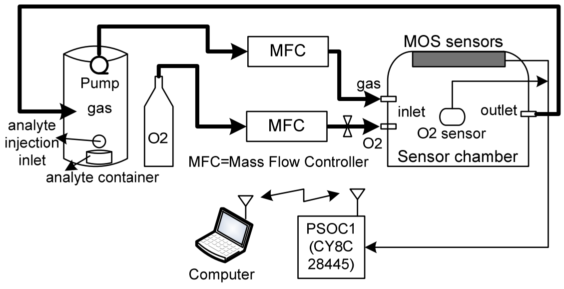


Fig. 4. Diagram of dynamic chamber measurement.

Initially, all MOS gas sensors are inactive (the voltage of heater and sensing element are on off mode). Then, oxygen concentration in chamber is measured and increased the concentration when under 21 % by flowing oxygen into chamber constantly up to minimum recommended level of 21 % [19]. Both flow controllers (Kofloc RK200/RK400) are tuned on rate of 0.4 LPM (0.67 cm^3/s). After that, the gas sensors are activated and driven by certain modulation that chosen the frequency and duty cycle which set from PC. Then, the pump is turned on and waits the initial conditioning time of MOS sensors for 2 minutes plus certain steady time (15 or 30 minutes) for selectivity performance analysis. Next step is measuring the baseline for 1 minute, continued with injecting the analyte solution, and then measuring the analyte gas for 6 minutes. We used hypodermic (Bolo-silicate hard glass) syringe 1 ml to measure and inject the volume of solution.

Finally, purging chamber is done for 10 minutes using two fans on cover of sensor and solution chamber. The (acquisition) software is connected to Microsoft Excel to store and process data, such as: (a) create file, read and write data, (b) create and show graph, and (c) determine average value of each sensor for each measurement mode (baseline and analyte sample measurement). Our acquisition software creates automatically 2 worksheets to store 2 mode measurement at once cycle measurement.

We observed on 3 frequencies (0.25 Hz, 1 Hz, 4 Hz) with 3 duty cycles (25 %, 50 %, and 75 %) of temperature modulation-SDP and no modulation as comparator. No modulation means MOSs were driven using traditional technique, or, they run on modulation of 100 % duty cycle. Hence, we generated 10 temperature modulation-SDPs from PSOC. Initial response and selectivity evaluation of array sensor was performed and visualized using statistical tool and Principal Component Analysis (PCA) to differ 3 analyte gases (Ammonia, Ethanol, and Toluene). The analyte concentration (in gas phase) was arranged in 5000 ppm that resulted from 1 ml injection of prepared solution. The method of preparing accurate analyte in gas phase for volatile solution in air is described and applied in [20-21]. By using Equation (1), we calculated the necessary amount of analyte liquid in distilled water as prepared solution for once measurement which then injected 1 ml of it into solution container to produce that gas concentration in total volume including (11×8×6) cm sensor chamber (528 ml), gas sample chamber (1800 ml), and piping (24 ml). As an example, It is calculated to be 0.344 ml of 99.5 % liquid ethanol (molecular weight 46.07 g/mol and density 0.79 g/ml) added to 12 ml distilled water at laboratory pressure (1 atm) and temperature (293 ^{o}K) to produce 5000 ppm ethanol gas in volume 2352 ml. Table 1 shows the properties of analyte liquid used and calculation result of prepared solution. MOS gas sensors are presented by its resistance (R_s) and sensitivity as defined Equation (2) [14-15].

$$V_S = \frac{M_A \times Cppm \times P \times V}{CAW \times D \times R \times T} \times V_P \times 10^{-6}, \qquad (1)$$

where C_{ppm} notes analyte gas concentration, M_A is the molecular weight (g/mol), P is the laboratory pressure (atm), which assumed = 1 atm, V is the volume of total chamber (m^3 or uL), R is the ideal gas constant (L atm/mol/ ^{o}K), T is the laboratory temperature (^{o}K), CAW is the Catalyst Altered Water (liquid concentration in %), D is the solution density (g/ml), V_P is the volume of prepared solution = 12 ml, and V_S the is volume of solution (ml).

$$S = R_0 / R_g, \qquad (2)$$

where S defines sensitivity, R_0 is the sensor resistance in air and R_g is the sensor resistance in analyte gas exposure.

Table 1. Properties of analyte liquids and their calculated portion in prepared solution.

Analyte Liquid	Density (g/ml)	Mol. weight (g/mol)	CAW (%)	$v_s^{*)}$ (ml)
Toluene $C_6H_5CH_3$	0.87	92.14	99	0.628
Ethanol C_2H_5OH	0.79	46.07	99.5	0.344
Ammonia NH_3	0.90	17.03	28	0.397

$^{*)}$ in 12 ml prepared distilled-water

4. Result and Discussion

4.1. The Modulation and Sensor Response under Modulation

All modulations applied on MOS gas sensor have been checked with oscilloscope Tektronix TDS 2024B (exemplified in Fig. 5) and meet the desired modulation as depicted in Fig. 1(b). Fig. 5 only shows responses of three modulations, although ten modulations were generated and observed in the measurement to avoid cluttering in the graph. The measured frequency of V_{OH} was 0.2510 Hz and high state of V_{OC} is laid in middle 75 % of high of V_{OH}. The acquiring of all MOS (in array) begins at middle of V_{OH} and takes 0.08 s to complete it. The high state of V_{OH} of TGS and FIS were measured about 4.98 and 0.95 Volt respectively and the V_{OC} of both TGS and FIS were 4.98 Volt.

Fig. 6 shows MOS gas sensor's original responses (amplitude (v) vs. time (s)), which taken and compiled from digital output of oscilloscope Tektronix TDS 2024B, to analyte gases under each rectangular modulation. The oscilloscope probes were pointed directly at pin of MOS's sensing elements. In Fig. 6(a), it seen that TGS2444 works on 4 Hz modulation and responses sensitively to only ammonia gas since give similar response when sensed the air, ethanol gas, or toluene gas, but ammonia gas. As typical work of MOS gas sensor, the presence of ammonia gas leads the sensing layer's resistance of TGS2444 decreases depending on its concentration in the air.

Then, shown in Fig. 6 (b)-(d), the responses of five sensors (TGS2602, TGS825, FISAQ1, FISSB30 and FIS12A) appear to differ in amplitude due to different types of gases and to differ in pattern caused the applied modulation on the sensors which serves as a signature of concerned gas. Temperature modulation leads to the generate response patterns, which may be characteristic of the species being detected. The figures show that even though the captured response was only at high state of modulated sensing element circuit as resulted from modulated heater, it remains provided significant characteristic feature to distinguish among ammonia, toluene, ethanol and clean air (no gas).

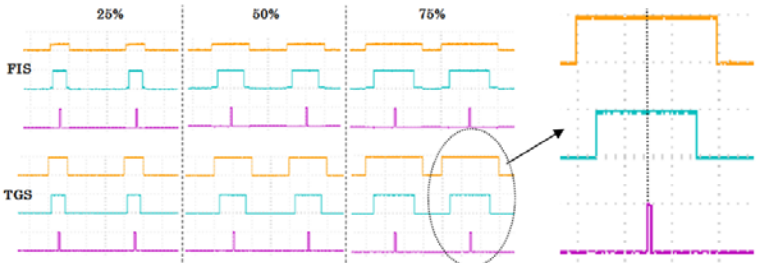
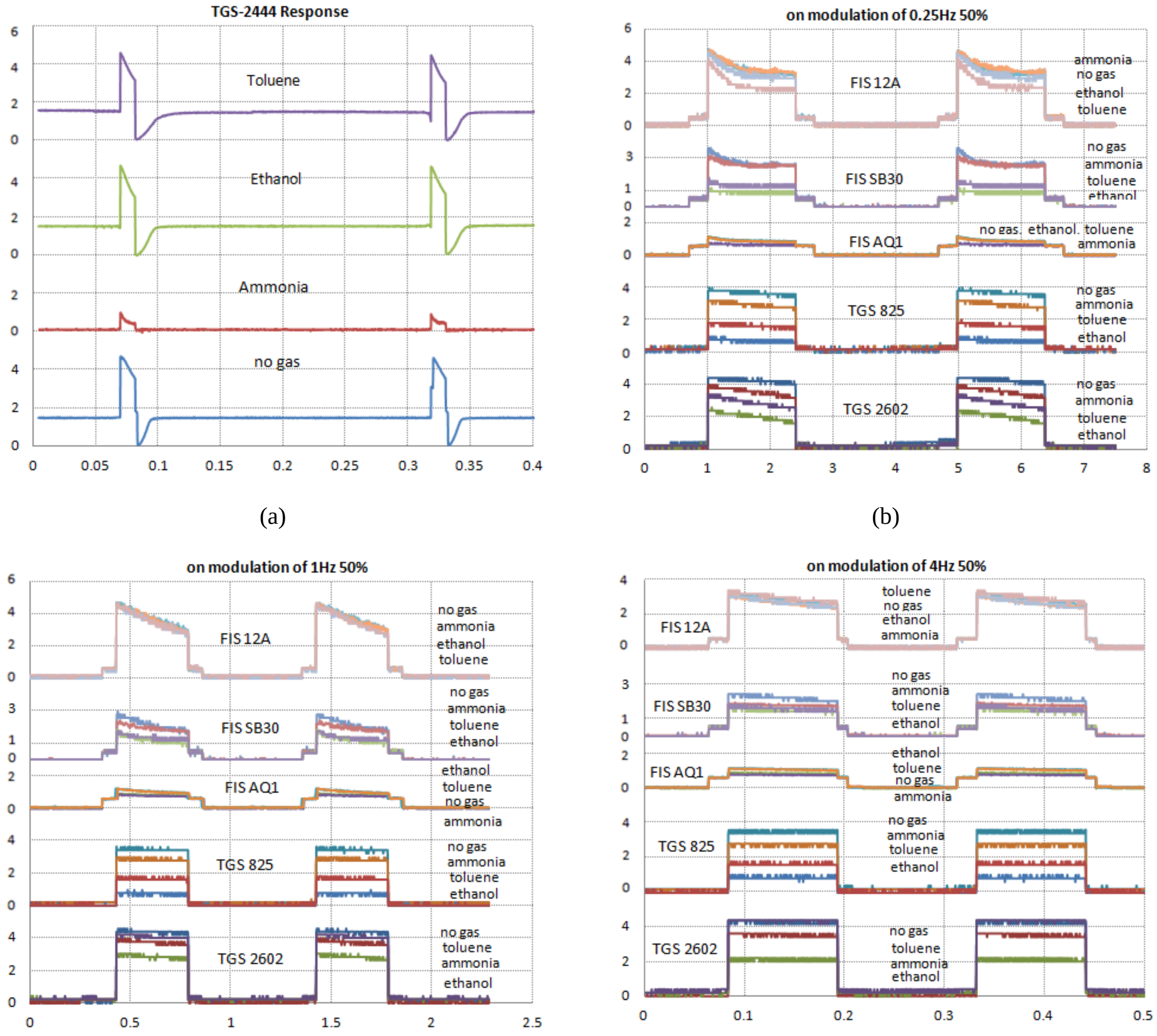


Fig. 5. Captured signal on MOS gas sensors under applied modulation of 0.25 Hz with duty cycle 25 %, 50 % and 75 %, where: V_{OH} (top) = 2 V/div of FIS; V_{OH} (top) = 2 V/div of TGS; V_{OC} (middle) = 5 V/div; Time of detection Point (below) = 5 V/div; Time-Div = 1 s.



(a)

(b)

(c)

(d)

Fig. 6. Response of (a) TGS 2444, and the others (TGS2602, TGS830, FISAQ1, FISSB30 and FIS12A) operated on (b) modulation 0.25 Hz, (c) modulation 1 Hz, and (d) modulation 4 Hz to air (no gas), ammonia, ethanol, and toluene gas.

An important information of TGS2444 published by Figaro (manufacturer of TGS series) which contributes to performance of MOS gas sensors is application of modulated voltage of sensing element (V_{OC}). Applying the V_{OC}, which is in phase with the modulation of V_H, may lead to prevent sensor from possible migration of heater materials into the sensing material which could causes long term drift of sensing material's resistance to higher values. It means that a pulsed-V_C giving less force to drive migration than a constant V_C, rendering negligible possibility of migration, particularly under high humidity and temperature operation [16].

It also seen in Fig. 6(b)-(d) that as the lower frequency, the response waveform of the sensors becomes more sloping and distinct, notably the FISs. It is apparent that all MOS gas sensors, both TGSs and FISs, are more selective to differ gases at lower frequency. It is because sensor operates near (to meet) a quasi-isothermal behavior at multiple temperatures and, therefore, existing the equilibrium condition between adsorbed oxygen and volatile chemical compound of analyte gas [22]. Contrarily, at higher frequency sensor behaves non isothermal operation and, therefore, the information content is no longer in the shape of the dynamic signal but rather closely in static (DC offset) mode, especially on TGS-825 and TGS-2602.

Primarily, the work of modulated temperature is supposed to alter the kinetics of both adsorption and reaction process at the surface of sensor while detecting reducing or oxidizing species in the presence of atmospheric oxygen. The well-known and accepted mechanism itself so-called ionosorption model. As described in [23]. The interaction between the surface of MOS and atmospheric oxygen causes the oxygen adsorption in form species of molecular (O_2^-) and atomic (O^- and O^{2-}) ions, where the atomic ions are more dominant at above 150 °C, and O^- is reckoned as the most reactive species when presence of reducing gases. The oxygen adsorption can be described by reactions as follow:

$$\mathrm{O}_2(gas) + \mathrm{e}^- \leftrightarrows \mathrm{O}_2^-(ads),$$
$$\mathrm{O}_2^-(ads) + \mathrm{e}^- \leftrightarrows \mathrm{O}_2^{2-}(ads) \leftrightarrows 2\mathrm{O}^-(ads).$$

In case of n-type semiconductor, e.g. SnO_2, the chemisorbed oxygen, which mainly as O^-, binds off electronic carriers and leads to the formation of a depletion layer at the surface. The electrons are drawn from ionized donors via the conduction band, so the charge carrier density at the interface between the oxydized layer and semiconductor is reduced and a (Schottky) potential barrier is created at grain boundaries. When the surface charge increases, the adsorption of further oxygen is hindered. The adsorption rate slows down because the charge is transferred to the adsorbate over that surface barrier, and the coverage saturates at a rather low value. At the junctions between the grains, the depletion layer and associated potential barrier cause high resistance contacts. Any presence of reducing gases will release the chemisorbed oxygen, lessen the surface oxygen concentration, thus decrease the resistance. As seen in Fig. 6, we perceive that MOS responses under a rectangular modulation mode were correlated to the different reaction kinetics of the interacting gases at its surface. In this way the reaction with the reducing and oxidizing gases was dramatically influenced, e.g. at higher temperatures (high voltage of V_S) the response to gases such as ammonia, ethanol, and toluene exhibited their characteristic wave shape due to the reaction with certain oxygen species. The equations of Schottky barrier potential and Arrhenius in [24] show that conductance of semiconductor and rate constants respectively are depended on temperature, where the temperature of gas sensor surface is controlled by varying the voltage applied to its heater [9]. In Addition, It means that all employed MOSs are intrinsically made of n-type semiconductor. Simply, n-type semiconductor responds to atmospheric oxygen and decrease its resistance while p-type is of opposite manner [25].

4.2. Environmental Circumstances and Initial Response

We employed KE-25, LM35DZ, and HSM20G to measure oxygen level in chamber, ambient temperature, and temperature and humidity in chamber respectively. The working ambient temperature during experiments was at 18 to 22°C and the oxygen concentration in the chamber was kept constant at round 21.8 % (not changed by operation of sensors, as shown in Fig. 7). As assumed, it is also seen clearly in Fig. 7 that higher frequency and duty cycle of applied modulation in 30 minutes operation lead the increment of temperature significantly and humidity inside the chamber.

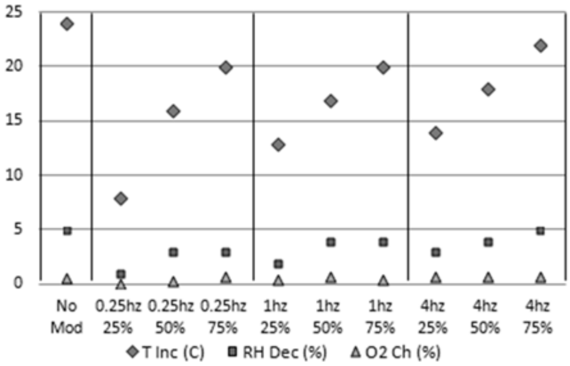


Fig. 7. Change of chamber environment (temperature, relative humidity, and oxygen concentration) after 30 minutes initial action.

The presence of minimum required ambient oxygen is essential to the sensor's operation which mean oxygen plays an important complementary role to reducing gases and its concentration effected to detection of combustible or reducing gas which mediated by reaction with adsorbed oxygen on the sensor surface [26]. The behavior of steady-state conductance of MOS with temperature is greatly influenced by ambient oxygen concentration [27] and the reduced oxygen pressure will lead the decrement of the sensor's resistance [19]. Moreover, Clifford and Tuma [27] also reported that the dynamic response of metal oxide gas sensor shows complex kinetics characterized by time constants which range, depends on ambient conditions. The long-term drift of the TGS resistance resulted from the diffusion of a native non-stoichiometric defect, an oxygen vacancy, evoked by changes in temperature or ambient oxygen pressure.

We tested initial action for 30 minutes on each temperature modulation with specified detection point by flowing natural air on measurement system in Fig. 4. At a minute of initial action, the resistance of TGSs was very high, i.e. 90 kΩ of TGS 2602 and 130 kΩ of TGS 825, then in second afterward dropped sharply which then toward its steady value in about 10 seconds. Other side, typically FISs have same responses. Yet, they have lower initial resistance, i.e. 20 kΩ of AQ1, 2.6 kΩ of SB30 and 25 kΩ of 12 A, then gradually dropped in longer time (about 30 seconds) toward their steady value in first minute.

However, after a minute, as shown in Fig. 8, the steady state of both TGSs and FISs were slightly and gradually changed (mostly increased but FISAQ1 on all modulations with duty cycle of 25 % were decreased) along with elapsed time during 30 minutes. Therefore, the baseline resistance (base-resistance) was different to each temperature modulation. We found that higher frequency and duty cycle resulted in higher base-resistance. These increasing phenomena are potentially caused by heater temperature operation on MOS gas sensor and cumulative rising temperature in chamber. Typical curve of working heater temperature vs. resistance is shown in Fig. 9, where the responses increase and reach their maximums at a certain temperature, and then decreased rapidly with increasing the temperature [28]. It is assumed that gas sensors with different compositions have similar shapes.

By using equation (3) [29] to determine working heater temperature from running voltage on heater and by calculating the effective voltage (V_{eff}, depend on its duty cycle) of modulated voltage operated on MOS gas sensors, we calculated the effective working heater temperature of TGSs resulted from duty cycle modulation 25 %, 50 %, and 75 % are 69 °C, 197 °C, and 325 °C respectively. Hence, it is clear that when a sensor is operated in the modulation mode and uses the recommended voltage Vs (e.g. 5 V of TGS and 0.9 V of FIS), the response (R_s) tends to increase in higher frequency of operating modulation. Also from Fig. 8, we noticed that it takes more than a minute to initiate the MOS to reach its steady state condition. Hence, We used minimum 10 minutes of initial action as base-resistance prior the measurement. It is a quasi-steady state at each temperature modulation-SDP.

$$T_H = 102.83 \times V_H - 58.79, \qquad (3)$$

where T_H (°C) is the working heater temperature, V_H (Volt) is the running voltage on heater.

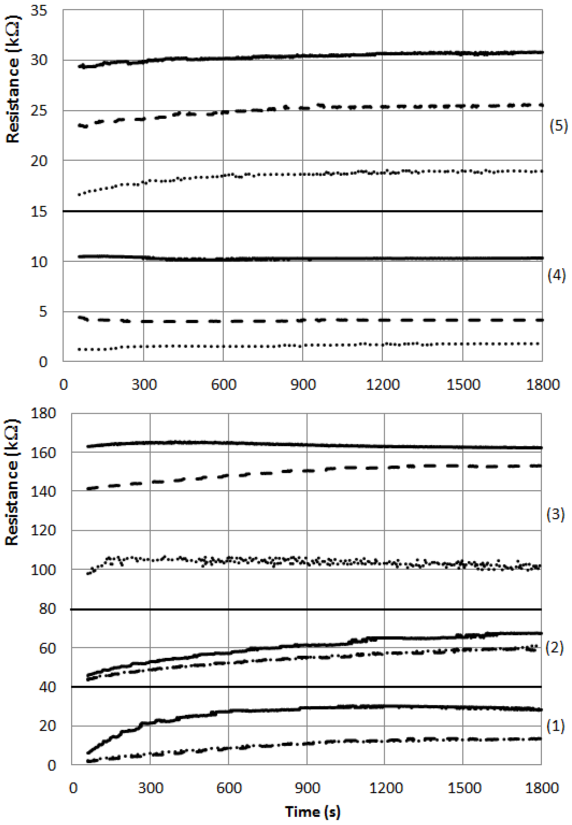


Fig. 8. Resistance of MOS sensors vs. time (s) of initial action responses during 30 minutes after ready state conditioning (1 minute) of each MOS gas sensors: (1)=TGS-2602, (2)=TGS-825, (3)=FIS-12A, (4)=FIS-AQ1, and (5)=FIS-SB30 on modulation frequency: 0.25 Hz (dotted), 1 Hz (dashed) and 4 Hz (solid). All modulation was on 50 % duty cycle.

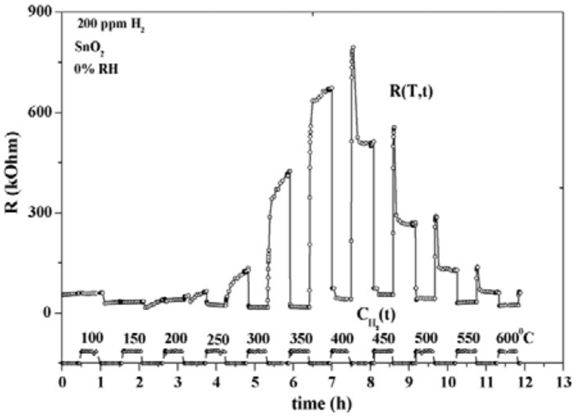
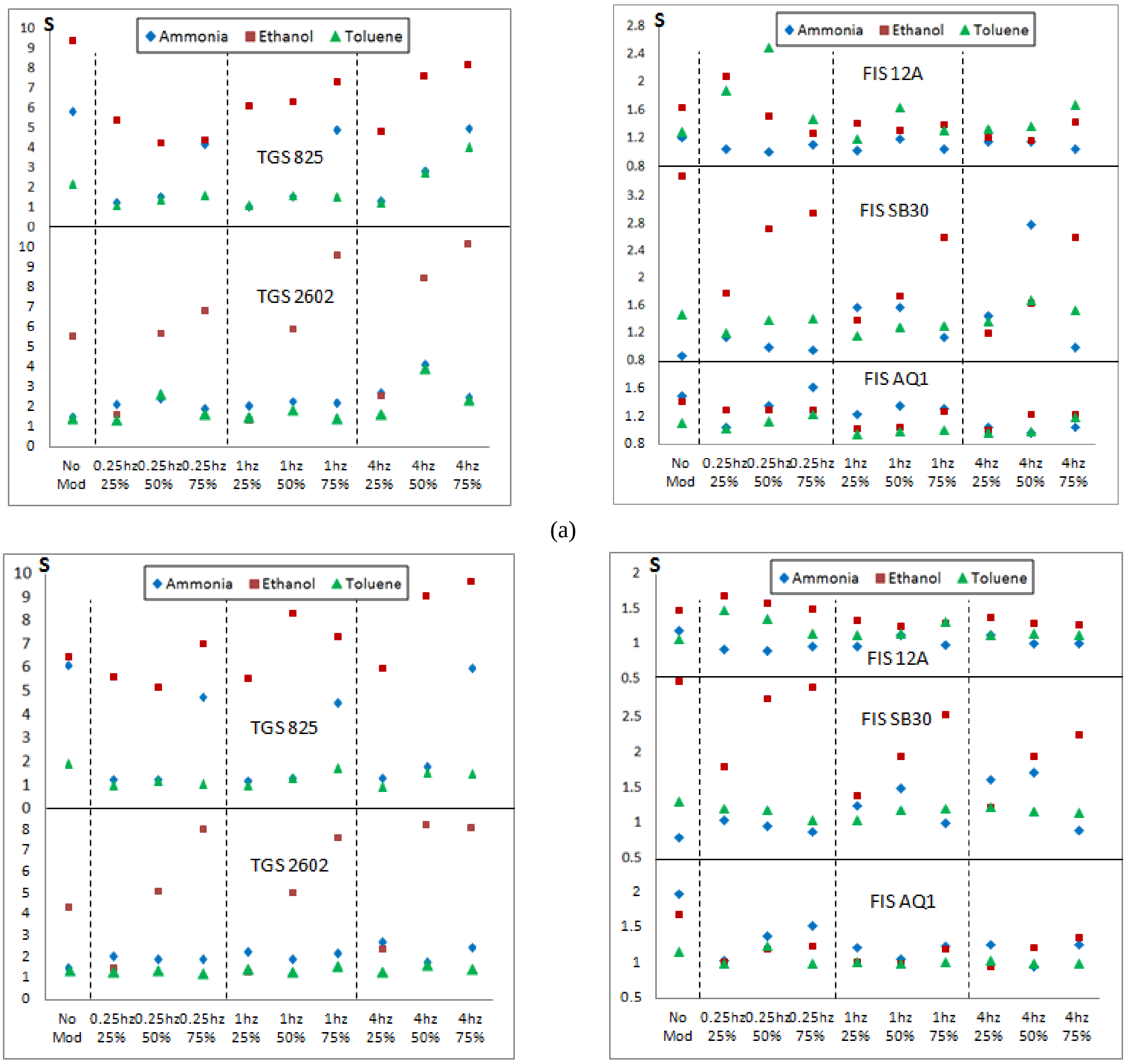


Fig. 9. The resistance responses of the SnO_2 sensor on 200 ppm H_2 pulses at various operating temperatures [28].

4.3. Selectivity Evaluation

We performed test of Principal Component Analysis (PCA) to evaluate selectivity performance in identifying the ammonia, ethanol, and toluene on each modulation. PCA is commonly used in electronic nose application as feature extraction part to test distinguish (selectivity) performance and a powerful linear classification technique that is usually employed in correlation with cluster analysis and visualization the difference in similarities or differences among the treatments [25, 30]. The large dimension of interrelated variables are reduces into few important principal components. The first two or three uncorrelated components hold most significant of variation present in all variables and widely used in various application [31-33].

We observed 2 durations of quasi-steady state (i.e. 15 minutes and 30 minutes) prior the measurement and used each sensitivity value of MOS gas sensors to represent variables in PCA. Here, we only utilized 5 MOS gas sensors but TGS2444 in order to avoid ambiguous results after seeing that it is only sensitive to ammonia. The first three Principal Components (PC1, PC2, and PC3) were used throughout our study, as at most together they usually contained over 90 % of the variance within the data sets [31]. Then, the Euclidean norm was used as gas significant features to assess the fit modulation which has highest selectivity to analytes. Selectivity refers to characteristics that determine whether a sensor can respond selectively to a group of analytes or even specifically to a single analyte [34] which can be indicated by how far the difference (distance) among responses on analytes is. Therefore, besides we tested PCA on same modulation for array sensors, we also performed a test on selected temperature modulation-SDP (shown in Table 2) of each MOS gas sensor based on the largest distance of sensitivity value among analyte gases. The variation value of sensitivity are shown in Fig. 10.



(a)

(b)

Fig. 10. Sensitivity variation of each MOS gas sensors and modulation upon exposure to various gases after (a) 15 minutes; and (b) 30 minutes quasi-steady state.

Table 2. Selected temperature modulation-SDP of MOS gas sensors based on their sensitivities for 15 minutes and 30 minutes quasi-steady state prior measurement.

Sensor	Selected Modulation	
	15 m	30 m
TGS2602	1 Hz 75 %	0.25 Hz 75 %
TGS825	1 Hz 75 %	4 Hz 75 %
FISAQ1	0.25 Hz 75 %	0.25 Hz 75 %
FISSB30	0.25 Hz 75 %	0.25 Hz 75 %
FIS12A	0.25 Hz 50 %	0.25 Hz 25 %

Table 2 implies that FISs individually performed best selectivity under temperature modulation-SDP at 0.25 Hz 75 % of both 15 minutes and 30 minutes quasi-steady state to differ ammonia, toluene and ethanol, while TGS 2602 and TGS825 tend more varied.

On array gas sensor which commonly used in e-nose application, the selected temperature modulation-SDP on each MOS gas sensor and measurement after 30 minutes quasi-steady state carried out better selectivity rather than single modulation on all gas sensors, as shown in Fig. 11. Moreover, compared to static (without modulation) mode (shown in Table 3 and Fig. 12), the selected modulation and 30 minutes quasi-steady state give highest increment of selectivity, up to 64.7 %.

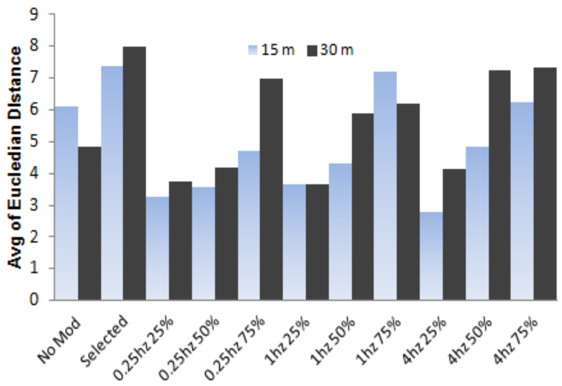


Fig. 11. Comparison of selectivity performance of array sensors among temperature modulation-SDP to differ analytes gases based on distance of Principal Component's score after 15 minutes and 30 minutes quasi-steady state.

Table 3. Euclidean distance between Principal Component score of no modulation vs. selected modulation of 15 minutes and 30 minutes quasi-steady state.

Euclidean distance	15 m		30 m	
	no Mod	Mod	no Mod	Mod
Am-Et	6.005	8.103	3.630	7.50
Et-Tol	3.730	3.822	4.777	5.118
Am-Tol	8.558	10.198	6.176	11.408
Average	**6.097**	**7.374**	**4.861**	**8.007**
Increament	20.9 %		64.7 %	

5. Conclusions

In this paper, we present a (new) technique to enhance selectivity of MOS gas sensors which is developed of common temperature modulation technique, namely temperature modulation with specified detection point (temperature modulation-SDP). The design of this modulation in principle resembles the required modulation on TGS2444 where applied a rectangular modulation type. As expected, our test on TGSs and FISs shows that their responses are in accordance with common rectangular modulation, where each modulation provides particular response and at lower frequency has more sloping and distinct characteristic. We also found that the modulation with duty cycle 75 % leads higher selectivity on each frequency modulation, and most gas sensors especially the FISs performed highest selectivity under 0.25 Hz modulation.

The results of PCA test indicated that selected temperature modulation-SDP for array sensors obtained good sensitivity and selectivity. Experimental results showed that in measurement after 30 minutes quasi-steady state, the increment of selectivity to identify among ammonia, ethanol, and toluene was up to 64.7 % compared with static temperature mode.

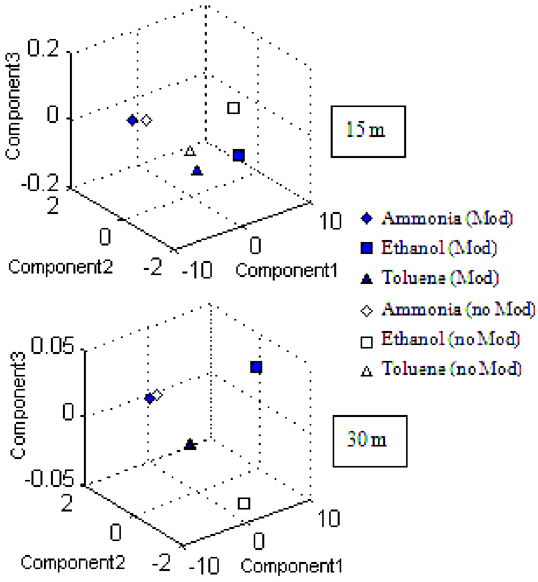


Fig. 12. Visualization of PCA plot of selected temperature modulation-SDP Vs without Modulation using 3 major PCs.

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References

[1]. M. Aleixandre, M. Gerboles, Review of Small Commercial Sensors for Indicative Monitoring of Ambient Gas, *Chemical Engineering Transactions*, Vol. 30, 2012, pp. 169-174.

[2]. W. Bourgeois, A. Romain, J. Nicolas, R. M. Stuetz, The use of sensor arrays for environmental monitoring: interests and limitations, *Journal Environment Monitoring*, Vol. 5, 2003, pp. 852–860.

[3]. A. D. Wilson, M. Baietto, Advances in Electronic-Nose Technologies Developed for Biomedical Applications: Review, *Sensors*, Vol. 11, 2011, pp. 1105-1176.

[4]. A. Berna, Metal Oxide Sensors for Electronic Noses and Their Application to Food Analysis, *Sensors*, Vol. 10, 2010, pp. 3882-3910.

[5]. A. D. Wilson, M. Baietto, Applications and Advances in Electronic-Nose Technologies (Review), *Sensors*, Vol. 9, 2009, pp. 5099-5148.

[6]. K. Arshak, E. Moore, G. M. Lyons, J. Harris, S. Clifford, A review of gas sensors employed in electronic nose applications, *Sensor Review*, Vol. 24, No. 2, 2004, pp. 181–198.

[7]. A. Bermak, S. B. Belhouari, M. Shi, D. Martinez, Pattern Recognition Techniques for Odor Discrimination in Gas Sensor Array, *Encyclopedia of Sensors*, Vol. 10, 2006, pp. 1–17.

[8]. C. Wang, L. Yin, L. Zhang, D. Xiang, R. Gao, Metal Oxide Gas Sensors: Sensitivity and Influencing Factors (Review), *Sensors*, Vol. 10, 2010, pp. 2088-2106.

[9]. A. P. Lee, B. J. Reedy, Temperature modulation in semiconductor gas sensing, *Sensors and Actuators B*, Vol. 60, 1999, pp. 35–42.

[10]. 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*, Vol. 99, 2004, pp. 444–450.

[11]. Y. Sun, X. Huang, F. Meng, J. Liu, Study of Influencing Factors of Dynamic Measurements Based on SnO_2 Gas Sensor, *Sensors*, Vol. 4, 2004, pp. 95-104.

[12]. A. Ortega, S. Marco, A. Perera, T. Sundic, A. Pardo, J. Samitier, An intelligent detector based on temperature modulation of a gas sensor with a digital signal processor, *Sensors and Actuators B*, Vol. 78, 2001, pp. 32–39.

[13]. N. Dutta, M. Bhuyan, Optimal Temperature Modulation of MOS Gas Sensors by System Identification, *International Journal of Signal Processing, Image Processing and Pattern Recognition*, Vol. 5, No. 2, 2012, pp. 17-28.

[14]. X. Huang, J. Liu, D. Shao, Z. Pi, Z. Yu, Rectangular mode of operation for detecting pesticide residue by using a single SnO_2-based gas sensor, *Sensors and Actuators B*, Vol. 96, 2003, pp. 630–635.

[15]. X. Huang, J. Liu, Zongxin, Z. Yu, Detecting Pesticide Residue by Using Modulating Temperature Over a Single SnO_2-Based Gas Sensor, *Sensors*, Vol. 3, 2003, pp. 361-370.

[16]. Figaro. Tentative Product Information: TGS 2444 - for the detection of Ammonia, *Figaro Engineering Inc.*, 2010, pp. 1-2.

[17]. PSoC® Programmable System-on-Chip™ CY8C28243/CY8C28403/CY8C28413/CY8C28433/CY8C28445/CY8C28452/CY8C28513/CY8C28533/CY8C28545/CY8C28623/CY8C28643/CY8C28645 (http://www.cypress.com/?docID=50827).

[18]. A. Sudarmaji, A. Kitagawa, J. Akita, Design of Wireless Measurement of Soil Gases and Soil Environment Based on Programmable System-on-Chip (PSOC), in *Proceedings of the International Symposium on Agricultural and Biosystem Engineering (ISABE'13)*, Yogyakarta, Indonesia, 28-29 August 2013, pp. E5-1- E5-13.

[19]. Figaro. General Information For TGS Sensors: Technical Information on Usage of TGS Sensors for Toxic and Explosive Gas Leak Detectors, *Figaro Engineering Inc.*, 2005, pp. 1-12.

[20]. A. Uyanik, N. Tinkilic, Preparing Accurate Standard Gas Mixtures of Volatile Substances at Low Concentration Levels, *Chemical Educator*, Vol. 4, 1999, pp. 141–143.

[21]. R. Chutia, M. Bhuyan, Study of temperature modulated tin oxide gas sensor and identification of chemicals, in *Proceedings of 2nd National Conference on Computational Intelligence and Signal Processing (CISP'12)*, 2-3 March 2012, Guwahati, India, pp. 181-184.

[22]. R Chutia, M Bhuyan, Best Frequency for Temperature Modulation of Tin Oxide Gas Sensor for Chemical Vapor Identification, *International Journal of Engineering and Technology (IJET)*, Vol. 6, No. 2, 2014, pp. 1158-1166.

[23]. D. Puzzovio, Surface interaction mechanisms in metal-oxide semiconductors for alkane detection, PhD Thesis, *Università Degli Studi di Ferrara*, 2008.

[24]. S. Nakata, K. Kashima, Distinguishing Among Gases with a Semiconductor Sensor Depending on the Frequency Modulation of a Cyclic Temperature, *Electroanalysis*, Vol. 22, No. 14, 2010, pp. 1573–1580.

[25]. T. C. Pearce, S. S. Schiffman, H. T. Nagle, J. W. Gardner, Handbook of Machine Olfaction: Electronic Nose Technology, *WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Book*, 2006.

[26]. P. K. Clifford, D. T. Tuma, Characteristics of Semiconductor Gas Sensors I. Steady State Gas Response, *Sensors and Actuators*, Vol. 3, 1982, pp. 233–254.

[27]. P. K. Clifford, D. T. Tuma, Characteristics of Semiconductor Gas Sensors II. Transient Response to Temperature Change, *Sensors and Actuators*, Vol. 3, 1982, pp. 255-281.

[28]. V. V. Malyshev, A. V. Pislyakov, Investigation of gas-sensitivity of sensor structures to hydrogen in a wide range of temperature, concentration and humidity of gas medium, *Sensors and Actuators B*, Vol. 134, 2008, pp. 913–921.

[29]. J. Zakrzewski, W. Domanski, P. Chaitas, Th. Laopoulos, Improving Sensitivity and Selectivity of SnO_2 Gas Sensors by Temperature Variation, in *Proceedings of the IEEE International Workshop on Intelligent Data Acquisition and Advanced Computing Systems: Technology and Applications*, Lviv, Ukraine, 8-10 September 2003, pp. 296-299.

[30]. J. W. Gardner, Detection of Vapours and Odours from a Multisensor Array Using Pattern Recognition. Part 1. Principal Component and Cluster Analysis, *Sensors and Actuators B*, Vol. 4, 1991, pp. 109-115.

[31]. H. V. Shurmer, J. W. Gardner, Odour discrimination with an electronic nose, *Sensors and Actuators B*, Vol. 8, 1992, pp. 1-11.

[32]. J. W. Gardner, H. W. Shin, E. L. Hines, C. S. Dow, An electronic nose system for monitoring the quality

of potable water, *Sensors and Actuators B*, Vol. 69, 2000, pp. 336–341.

[33]. Z. Haddi, M. Bougrini, K. Tahri, Y. Braham, M. Souiri, N. El Bari, A. Maaref, A. Othmane, N. Jaffrezic-Renault, B. Bouchikhi, A Hybrid System Based on an Electronic Nose Coupled with an Electronic Tongue for the Characterization of Moroccan Waters, *Sensors & Transducers*, Vol. 27, Special Issue, 2014, pp. 190-197.

[34]. V. E. Bochenkov, G. B. Sergeev, Sensitivity, Selectivity, and Stability of Gas-Sensitive Metal-Oxide Nanostructures, in Metal Oxide Nanostructures and Their Applications, Chapter 2, *American Scientific Publishers*, 2010.