Selectivity enhancement of target volatile organic compounds using sensor array and temperature modulation

Ali AHMAD[1]

1 Dept. of Microelectronics, Faculty of Electrical Engineering, CTU in Prague, Technicka 2, 16627 Prague, Czech Republic

ahmadali@fel.cvut.cz

Abstract. *In this paper, we report the performance of a volatile organic compounds identification system based on a commercial metal-oxide gas sensor array. Analyses of five volatile organic compounds (heptane, pentane, isooctane, isopropyl alcohol, and tetrachloroethylene) Have been performed with these unselective sensors. The device consists of three MOX commercial sensors (AS-MLN, AS-MLK, AS-MLC), The behavior of these sensors was measured at different ranges of temperature. Principal component analysis (PCA) was applied in order to identify the target gases. We obtained a high classification of the five VOCs by temperature modulation. The final aim of this research is to improve the selectivity of commercial sensors based on metal oxide to classify different VOCs.*

Keywords

Gas sensor array, metal oxides, selectivity enhancement, temperature modulation, principal component analysis.

1. Introduction

The measurements of volatile organic compounds (VOCs) are becoming more important due to stringent environmental regulations and increasing health concerns [1], also Human breath includes many volatile organic compounds (VOCs) that can be used as biomarkers for diseases. Therefore, breath-monitoring diagnostic methods are desirable as diagnostic tools because they are fast and non-invasive [5]. Consequently, many researchers have attempted to develop breath-monitoring systems [6–7]. Metal oxide (MOX) sensors are well known as multifunction materials and employing MOS in detecting VOCs is one of the most studied areas [3], [4]. The advantages of metal oxide sensors in comparison with sensors based on other materials are well known like low costs, short response time and versatility. Currently, these sensors are sufficiently sensitive for most applications [8–11]. However, the use of them is limited due to their lack of selectivity. which has stimulated researchers to look for different strategies to overcome this drawback, Recent works have shown that temperature modulation of metal oxide sensors improves selectivity [2],[13–19]. The kinetics of adsorption and desorption are modified when the temperature of the sensor is modulated, and the sensors have specific response patterns to different gases [12]. Usually, an electronic nose measures the stationary response of the sensors working at one constant temperature, but because the response of a sensor depends on its working temperature, the combination of the standard approach and a temperature stepping increases the number of signatures specific to each gas without increasing the number of sensors. The improvement of selectivity is investigated and reported in this paper by using a portable device consists of three metal oxide commercial gas sensors (AS-MLN, AS-MLK, AS-MLC) with modulation of the heating voltage to classify and identify different volatile organic compounds. We performed principal component analysis (PCA) to analyze the data extracted by exposing different VOCs during the temperature change.

2. Experimental:

The analyzed data sets were gathered from the portable gas detector Fig.1 which was made and equipped with three commercial conductivity gas sensors (Applied Sensor) with different MOX thin sensing films: AS-MLN sensitive mainly on NO_2, AS-MLC sensitive mainly on CO, and AS-MLK sensitive mainly on CH_4 [20].

Fig.1 Portable gas detector [20]

These sensors require low heating power 30 - 45 mW. Due to their low thermal capacity, these sensors react quickly to the temperature changes of the heating plate. The sensor with dimensions 2 x 2 x 0.38 mm is placed in the metallic case TO-39-4. Two pins relate to the gas sensor layer for the measurement of its resistivity changes, two other pins are for the heating element (Fig.2). The sensor AS-MLN based on the WO_3 film has the sensitivity of 0.1 ppm – 2 ppm of NO_2 at the temperature of 270°C. The sensor AS-MLK based on the SnO_2 film has the sensitivity of 0.01% to 4%. of methane at the temperature 320°C. The sensor AS-MLC based on the SnO_2 film has the sensitivity 0.5ppm to 500ppm of CO at the temperature 270°C. The detector measures the sensor resistivities and the heating elements resistivities for the temperature regulation. The measurement was made at the constant flow of prepared gas mixtures with different concentrations and temperatures during several cycles. The flow meters and regulators kept the specified gas concentrations of specific gases in the carrier gas. The purging of the sensing chamber has been realized in each cycle.

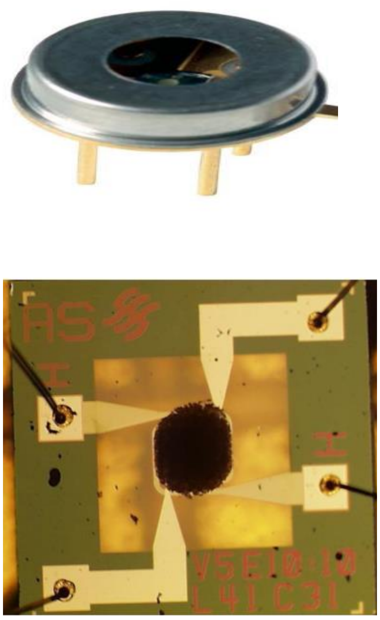
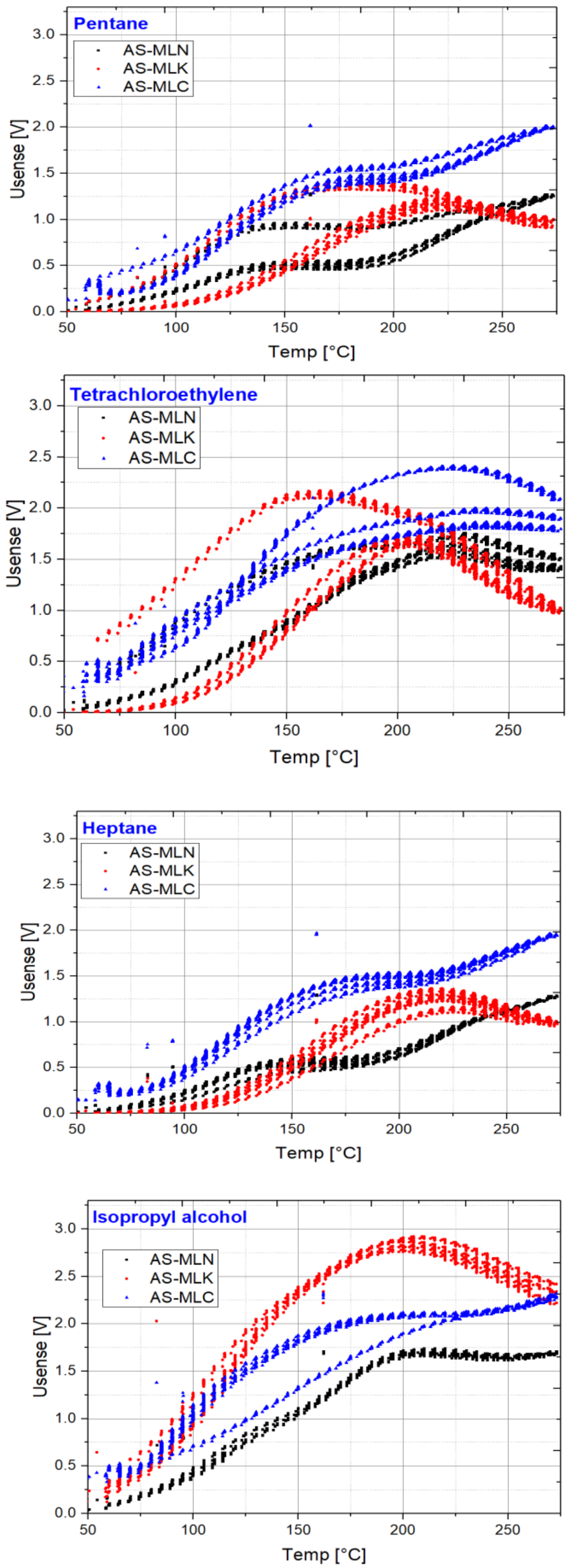


Fig. 2 Sensor AS-MLX (The case and detailed view.) [20]

3. Results and discussion:

3.1 Characterization of gas sensors:

The sensor Characterization was initially obtained by exposing five volatile organic compounds (VOCs) to an array of sensors in the temperature range of (50 –260) ° C, Fig.3 presents the response of the three commercial metal oxide sensors AS-MLN, AS-MLK, AS-MLC to five volatile organic compounds, the result showed that the sensors have very good sensitivity to the target gases, sufficiently stable and have good reproducibility which is very important for most of the applications .



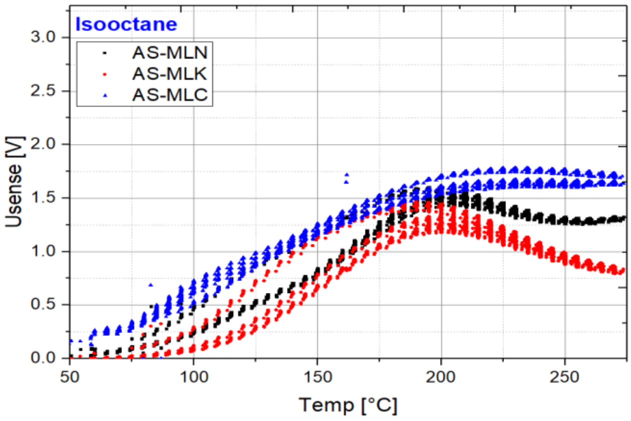


Fig. 3 the response of the three sensors AS-MLN, AS-MLK, AS-MLC to five volatile organic compounds in the temperature range of (50 –260) ° C

3.2 Discrimination of the target gases:

In order to obtain more information about the system, PCA was performed to discriminate among five compounds.

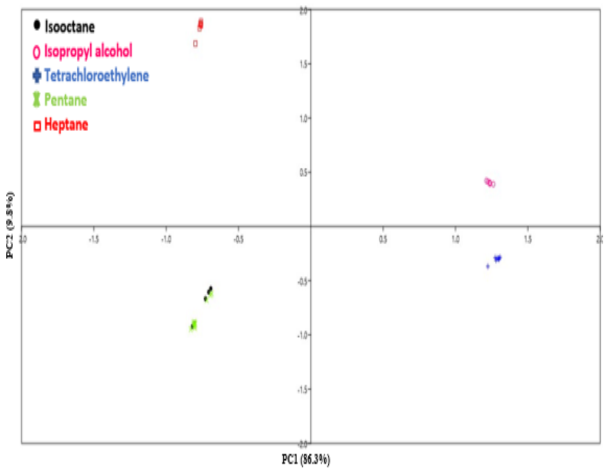


Fig.4 Discrimination of five compounds by three MOS commercial sensors in the temperature range (60 to 120) °C

Fig.4 presents the result of applying PCA on the dataset which extracted during increasing the temperature in the range of (60 to 120) °C, The first principal component describes 86.3% of data variation and PC2 describes 9.8% of data variation which is neglected in comparison with PC1,so we will focus in our comparison on the variation of PC1, Fig.4 shows an overlap between heptane, pentane, and isooctane which they have approximately the same influence on PC1 and also overlap between Isopropyl alcohol and Tetrachloroethylene. The system has poor classification with a low range of temperature. However, a high classification of the five compounds in clearly separated clusters is obtained in Fig.5 with a temperature range of (160 to 220) °C The experimental results of this work points out that the capability for gas identification is hugely improved for commercial sensors by temperature modulation.

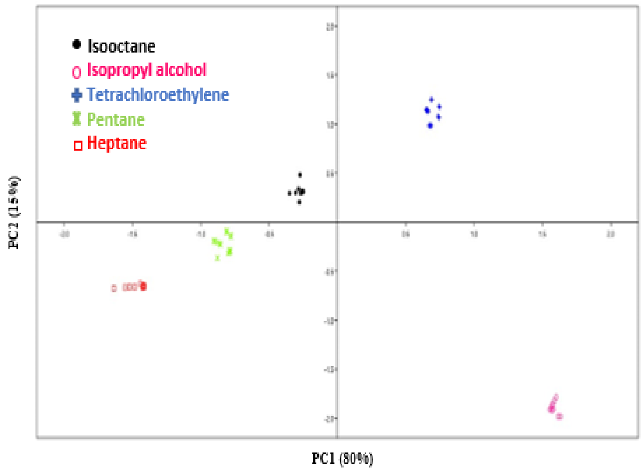


Fig.5 Discrimination of five compounds by three MOS commercial sensors In the temperature range (160 to 220) °C

4. Conclusions:

In this work, we studied the ability to carry out gas analyses with a metal-oxide sensor array, the advantages of these sensors are their high commercial availability and low cost. PCA was performed as a pattern recognition method in order to identify different compounds (heptane, pentane, isooctane, isopropyl alcohol, and tetrachloroethylene). The results pointed out that sensors have very good classification in a higher range of temperature, also pointed out to the importance of a sensor temperature programming procedure and confirm that different temperatures give more information about the chemical response.In spite of the low selectivity of MOS sensors, the improvement of gas identification is realizable with cheap sensors and a simple temperature programming method.

Acknowledgments

The research described in the paper was supervised by doc. RNDr. Jan Voves, CSc., FEL CTU in Prague.

References

[1] TOSHIO ITOH *, TAKAFUMI AKAMATSU, AKIHIRO TSURUTA,AND WOOSUCK SHIN selective Detection of Target Volatile Organic Compounds in Contaminated Humid Air Using a Sensor Array with Principal Component Analysis.

[2] A.FORT *, M.GREGORKIEWITZ , N.MACHETTI , S.ROCCHI,B.SERRANO , L.TONDI , N.ULIVIERI Selectivity

enhancement of SnO sensors by means of operating temperature modulation.

[3] J. HUANG, Q. WAN Gas sensors based on semiconducting metal oxide one-dimensional nanostructures Sensors, 12 (2009), pp. 9903-9924.

[4] N.H. AL-HARDAN, M.J. ABDULLAH, A. ABDUL azizsensing mechanism of hydrogen gas sensor based on RF sputtered ZnO thin films Int J Hydrogen Energy, 35 (2010), pp. 4428-4434.

[5] AMANN, A.; SPANEL, P.; SMITH, D. Breath analysis: The approach towards clinical applications. MiniRev. Med. Chem. 2007, 7, 115–129. [CrossRef] [PubMed].

[6] PENG, G.; TISCH, U.; ADAMS, O.; HAKIM, M.; SHEHADA, N.; BROZA, Y.Y.; BILLAN, S.; BORTNYAK, R.A.; KUTEN, A.; HAICK, H. Diagnosing lung cancer in exhaled breath using gold nanoparticles. Nat. Nanotech. 2009, 4, 669–673.

[7] MAZZONE, P.J.; HAMMEL, J.; DWEIK, R.; NA, J.; CZICH, C.; LASKOWSKI, D.; MEKHAIL, T. Diagnosis of lung cancer by the analysis of exhaled breath with a colorimetric sensor array. Thorax 2007, 62, 565–568.

[8] C. PIJOLAT, C. PUPIER, M. SAUVAN, G. TOURNIER, R. LALAUZE, Gas detection for automotive pollution control, Sens. Actuators B 59 (1999) 195 202.

[9] M. PENZA, G. CASSANO, F. TORTORELLA, G. ZACCARIA, Classification of food, beverages and perfumes by WO3 thin film sensors array and pattern recognition techniques, Sens. Actuators B 73 (2001) 76–87.

[10] K. AGUIR, C. LEMIRE, D. LOLLMAN, Electrical properties of reactively sputtered WO3 thin films as ozone gas sensor, Sens. Actuators B 84 (2002) 1–5.

[11] D.S. LEE, Y.T. KIM, J.S. HUH, D.D. LEE, Fabrication and characteristics of SnO2 gas sensor array for volatile organic compounds recognition, Thin Solid Films 416 (2002) 271–278.

[12] KIEU AN NGO, PASCAL LAUQUE ∗, KHALIFA AGUIR .High performance of a gas identification system using sensor array and temperature modulation.

[13] A.P. LEE, B.J. REEDY, Temperature modulation in semiconductor gas sensing, Sens. Actuators B 60 (1999) 35–42.

[14] 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, Sens. Actuators B 78 (2001) 32.

[15] A. FORT, M. GREGORKIEWITZ, N. MACHETTI, S. ROCCHI, B. SERRANO, L. TONDI, N. ULIVIERI, V. VIGNOLI, G. FAGLIA, E. COMINI, Selectivity enhancement of SnO2 sensors by means of operating temperature modulation, Thin Solid Films 418 (2002) 2–8.

[16] N.J. CHOI, C.H. SHIM, K.D. SONG, D.S. LEE, J.S. HUH, D.D. LEE, Classification of workplace gases using temperature modulation of two SnO2 sensing films on substrate, Sens. Actuators B 86 (2002) 251–258.

[17] R. IONESCU, E. LLOBET, WAVELET transform-based fast feature extraction from temperature modulated semiconductor gas sensors, Sens. Actuators B 81 (2002) 289–295.

[18] A. GRAMM, A. SCHUTZE, High performance solvent vapor identification with ¨ a two sensor array using temperature cycling and pattern classification, Sens. Actuators B 95 (2003) 58–65.

[19] R. IONESCU, A. HOEL, C.G. GRANQVIST, E. LLOBET, P. HESZLER, Ethanol and H2S gas detection in air and in reducing and oxidizing ambience: application of pattern recognition to analyses the output from temperature-modulated.

[20] J. NEMAZAL: Portable gas detection monitor, master thesis, CTU Prague, 2015.

About Authors...

Ali AHMAD was born in Latakia in 1993. He graduated in communication and electronic engineering at the Tishreen University in Latakia, now he is a PhD student in FEL, CTU in Prague, Dept. of Microelectronics.