

SELECTIVE SENSING OF VOLATILE ORGANIC COMPOUNDS VIA A TEMPERATURE MODULATION OF METAL OXIDE GAS SENSORS WITH PRINCIPAL COMPONENT ANALYSIS

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Abstract

The measurements of volatile organic compounds are becoming more important due to stringent environmental regulations and increasing health concerns. The human breath which includes many volatile organic compounds that can be used as biomarkers for different diseases as well. Metal oxide (MOX) sensors are well known as multifunction nanomaterials and employing MOX in detecting VOCs is one of the most studied areas. The advantages of metal oxide sensors are well known as low costs, short response time and versatility. Currently, these sensors are sufficiently sensitive for most applications. 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. Sensing mechanisms of gas sensors depend on temperature, and this is, in particular, true for metal-oxide semiconductors where the peculiar role of temperature suggested the modulation of temperature as a viable method to tune selectivity and sensitivity. In this work, a device consisted of metal oxide gas sensor array has been used to discriminate different volatile organic compounds. The device consists of three MOX commercial sensors (ASMLN, AS-MLK, AS-MLC), The behavior of these sensors was measured at different ranges of temperature. By Principal Component Analysis (PCA) as a recognition algorithm and modulated temperature, selective sensing has been accomplished.

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

1. INTRODUCTION

Volatile organic compounds (VOCs) are carbon-based chemicals that easily emit from industry productions or indoor environments (e.g. furnishings, paints, and building materials), which is due to their rather low boiling points. VOCs are believed to have short-term and long-term adverse effects on the environment and human health, including the potential cause of cancer [1-3]. Moreover, some exhaled VOCs are found as effective biomarkers that could be used for the detection of some diseases, including lung cancer. Thus, there is a large demand for the sensitive and selective detection of VOCs in the gas phase for environmental monitoring, process control, and medical diagnostics purposes [4-8]. Consequently, many researchers have attempted to develop breath-monitoring systems [9]. Metal oxide semiconductors are widely studied and exploited layers in gas-sensing devices, MOX sensors change their electrical resistance upon contact with reactive gases. The operating principle is based on the chemisorption of gases in the presence of atmospheric oxygen. The potential of chemiresistor sensors arises from their sensitivity to several gases, their reduced size, and weight, which make them suitable to develop portable instrumentation and the reduced preparation costs [10]. On the other hand, these devices have poor selectivity, which has stimulated researchers to look for different strategies to overcome this drawback. The most popular solution is to use the so-called electronic nose (EN), an array composed of different sensors, each one showing a different response spectrum to gases, handled by a pattern recognition software. Besides this, other approaches based on temperature profile protocols or the exploitation of different sensing and transduction mechanisms have been and are still being studied worldwide [11,12]. The improvement of selectivity is investigated and reported in this paper by using electronic nose based on an array of commercial sensors (AS-MLN, AS-MLK, AS-MLC) with changing the operating

temperature of these sensors. The discrimination model based on principal component analysis (PCA) was implemented.

2. EXPERIMENTAL

2.1. Structure and material characterization of MOX sensors

Metal oxide sensors (Applied Sensor) with different sensing layers were chosen to prepare the electronic nose system. The AS-MLX sensors are very convenient thanks to their miniature hot-plate design.

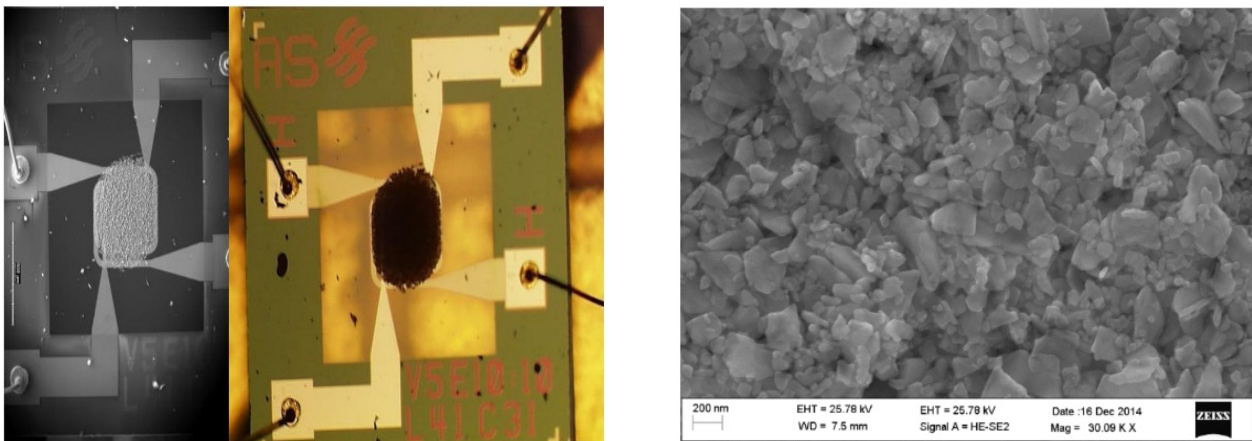


Figure 1 Scanning electron and optical microscope image

These sensors (AS-MLN, AS-MLK, AS-MLC) 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. The result of the scanning electron microscope in nanoscale and optical microscope for AS-MLN is shown in **Figure 1**.

2.2. Sensor array measurement setup

The experimental setup used for the testing of the thick-film sensor array is shown in **Figure 2**. The evaporation process took place in the test chamber by direct injection of prepared volatile organic compounds via a medical syringe, the measurements of the sensor resistivities and the heating elements resistivities for the temperature regulation were made with different temperatures during several cycles. The purging of the sensing chamber has been realized in each cycle.

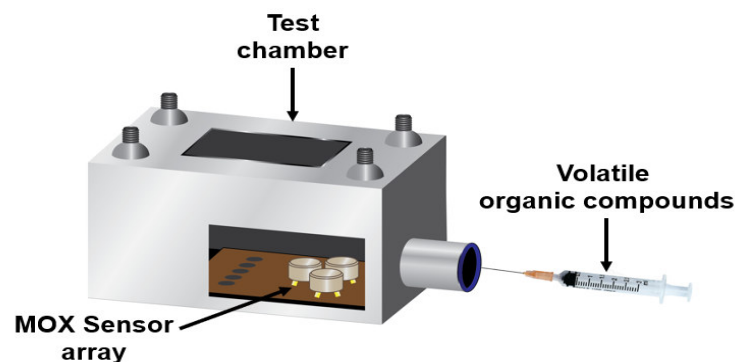


Figure 2 Description of measuring apparatus

3. RESULTS AND DISCUSSION

3.1. The gas sensing measurement

The sensor characterization was initially obtained by exposing six volatile organic compounds (VOCs) to an array of sensors in the temperature range of (60 °C - 273 °C).

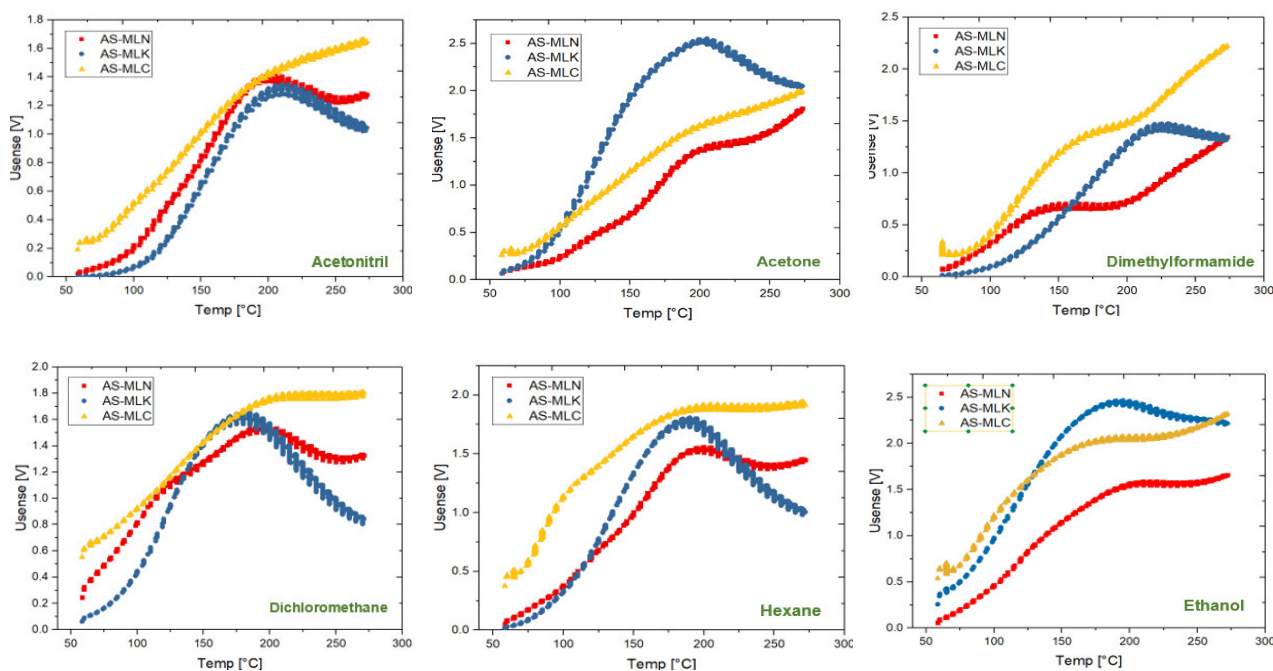


Figure 3 Response of the three sensors AS-MLN, AS-MLK, AS-MLC to six volatile organic compounds in the temperature range of (60 °C -273 °C)

Figure 3 presents the response pattern of the sensor array to six different volatile organic compounds, the results showed that the sensors have very good sensitivity to the target gases, also that the response of the sensor array was increasing during increasing the temperature range from 60 °C to 200 °C and it starts to decrease after exceeding the temperature range (200 °C - 220 °C) especially for AS-MLK sensor, we had the max response of the sensor array in temperature range (170 °C - 200 °C), which will be very helpful information to obtain the ideal gas classification.

3.2. Data analysis by pattern recognition algorithm (PCA):

Figure 4(a) presents the result of applying PCA on the dataset which was extracted during temperature modulation in the range of (60 °C - 130 °C), **Figure 4(b)** in the temperature range of (175 °C - 205 °C), **Figure 4(c)** in the temperature range of (230 °C - 270 °C), in the three experiments first principal component (PC1) describes approximately 86 % of data variation and PC2 describes 9% of data variation which is neglected in comparison with PC1. The focusing is on PC1 in our comparison to evaluate the variation difference of different compounds.

In a low-temperature range, an overlap (black circle) was detected between (Acetonitrile, Dimethylformamide) and partial overlap was detected between (Acetone, Dimethylformamide). In the intermediate-temperature range a high classification in clearly separated clusters is obtained. In the high-temperature range also an overlap was detected between (Hexane, Dimethylformamide), (Hexane, Dichloromethane) and (Hexane, Dichloromethane, Acetonitrile) which is the logical result because the response of sensors decreased.

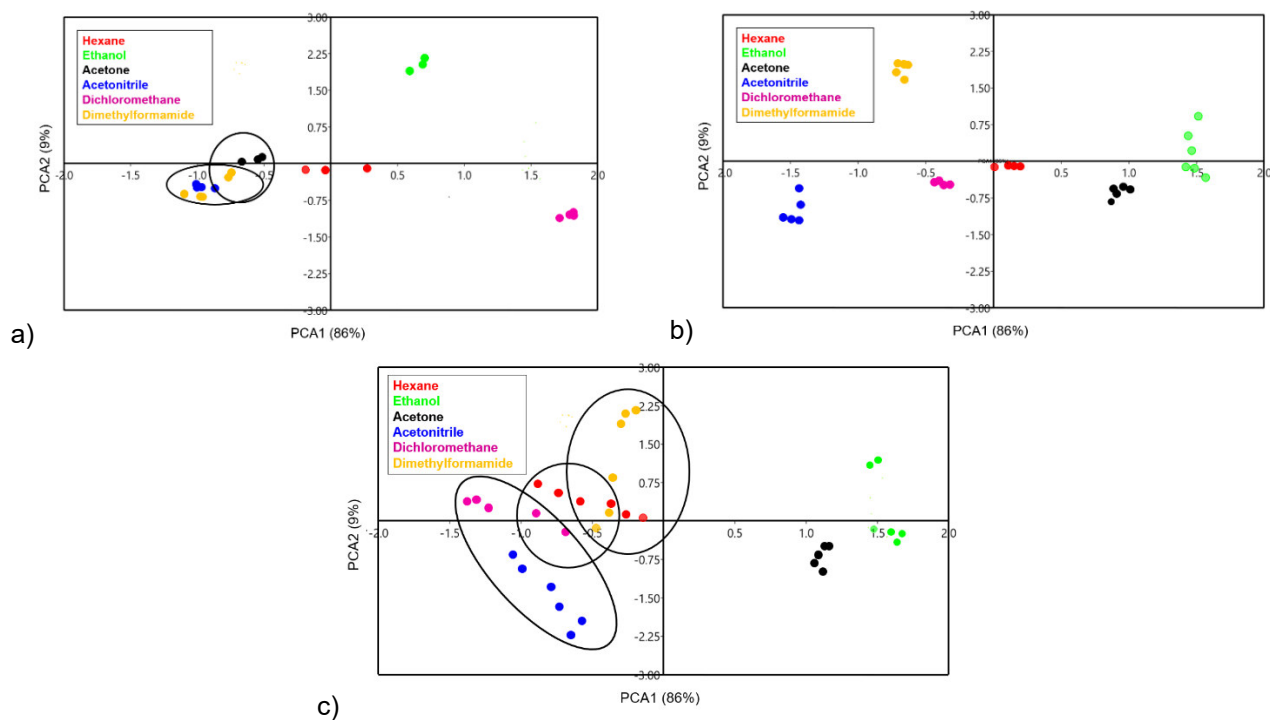


Figure 4 PCA results in the three temperature ranges (a) Low (b) Intermediate (c) High

The impact of sensors number with different sensing layer in the EN have been studied, a comparison between using two sensors and three sensors in the intermediate temperature range is presented in **Figures 5(a)** and **(b)**.

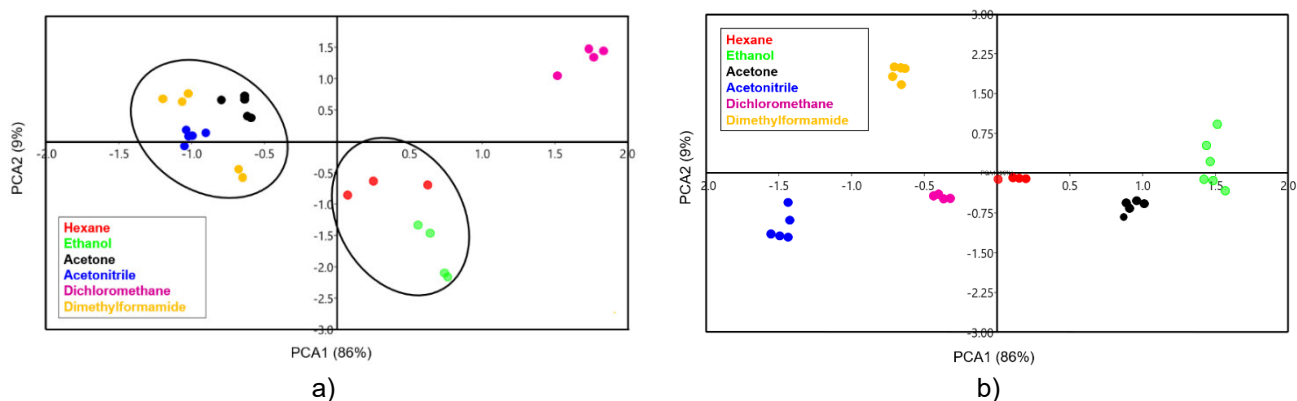


Figure 5 PCA results in the intermediate temperature range (a) two sensors (b) three sensors

The results in **Figure 5** proved that using a higher number of sensors with different sensing layers enhanced the selectivity of the electronic nose (EN).

5. CONCLUSION

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 the pattern recognition method in order to identify different compounds. The results pointed out that sensors have a very good classification in the temperature range of (175 °C - 205 °C). They also pointed out the importance of

increased sensor number in the EN. In spite of the low selectivity of the MOX sensors, the improvement of gas identification is realizable with cheap sensor array and a simple temperature programming method.

ACKNOWLEDGEMENTS

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