Discriminating among different tea leaves using an operating temperature-modulated tin oxide gas sensor

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Abstract. We report distinguishing different types of tea leaves from each other based on their aroma using a thermal shock-induced generic tin oxide gas sensor. The sensor used in this work consists of a microheater and a tin oxide pellet, both connected to outside circuitry with noble metal contacts. The heater is powered with a series of narrow high magnitude voltage impulses of predetermined thermal impacts adjusted to produce step-like temperature rises of different magnitudes on the gas sensitive pellet. The sensor is exposed to aromas collected from various types of tea leaves at different concentrations. Within 4.5 s, nine 500 ms-wide voltage pulses, each as high as 9.3 V in magnitude, are applied to the microheater. Each pulse causes a step-like temperature jump on the pellet temperature. The transient responses recorded for different tea leaves look different even after amplitude normalization. The sensor profiles are recorded, digitized, and compared with the database of previous experiences. A heuristically defined high dimensional feature vector is automatically generated for each analyte. Classifications are graphically achieved in a 3-D feature space after applying principle component analysis for dimension reduction.

Keywords: Artificial olfaction; Metal oxide gas sensor; Thermal shock; Microheater; Tea leaves.

1. Introduction

Successful classification of single component gases and complex odours with a single thermal shock-induced metal oxide gas sensor has recently been demonstrated [1, 2]. Artificial olfaction systems are seriously considered for many applications including dangerous gas identification [3, 4], fire detection [5, 6], disease recognition [7, 8] and foodstuff quality control [9, 10]. Gas identification systems such as mass spectroscopy and gas chromatography are massive, expensive and difficult to operate [11, 12]. Moreover, the sensor array-based electronic noses suffer from the drifts of the array components and require expensive array replacements and cumbersome system calibrations [13, 14]. Single sensor electronic noses are proven alternatives for sensor arrays which significantly reduce required calibration activities and maintenance costs [15-19]. A thermally modulated gas sensor can provide sufficient discriminative information for the recognition of different analytes [20-23]. It’s also been reported that thermal modulation of a gas sensor reduces aging drifts [24]. Furthermore, environmental fluctuations and gradual microstructural changes cause drift terms in the responses of a thermally modulated gas sensor, which may be eliminated by the means of mathematical compensation methods [25].
It has been shown that the response patterns obtained by an array made virtually by the thermal shock induction of a single generic tin oxide gas sensor contain analytical information on the nature of the odour enough for its discrimination from a number of other target analytes [1, 2]. Here, we are reporting fabrication of an olfaction system based on this concept. The performance of the system is evaluated by classifying 3 types of tea leaves by analyzing their odours. The presented system requires only 4.5 s for the analysis of each analyte [1, 2].

2. Experimental
A generic SnO$_2$ gas sensor comprises a microheater and a SnO$_2$ sensing pellet integrated on an insulating ceramic substrate. The structure of a typical chemoresistor is schematically presented in figure 1 [1]. Pellet temperature is elevated by applying different heating voltages to the microheater. The pellet is thermally shocked by applying heating pulses of ~0.5 s duration and different amplitudes to the sensor microheater. The thermal impulse resulting from each pulse is calculated and compared by time integration of its respective V$^2$/R, where V is the pulse amplitude and R is the resistance of the microheater (57 Ω, for the sensor used). The suitable voltage waveform for thermal shock induction was established by trial and error. In each trial different combination of pulses is applied and its effect on the systems distinguishing power between ethanol and methanol contaminations is estimated. The selected combination of pulses is given in figure 2. The maximum temperature on the pellet is 300°C, which its occurrence coincides t = 3.5 s in figure 2.

At the standby state, the microheater is warmed up by 5V for cleaning the pellet surface from the residues of the previous tests and condensed humidity. After pressing the start button for sampling, for 18 s the voltage level is zero which is followed by a 1.5 s rest at 1 V heating voltage. This initial signal adjusts the microheater temperature and prepares the system for response sampling. Then, different thermal shock pulses are applied to the microheater. Shock pulses are increased in amplitude from 6.5V to 9.3V as shown in figure 2. The duration of each step is 0.5 s.

Numerical information is collected from the transient responses of the sensor at different conditions. The information is used for establishing a database which is analyzed by principle component analysis (PCA) for classification of the data recording conditions. The electronic system designed for performing this process is schematically described in figure 3. The sensor Response voltage is transmitted to the microcontroller, where, it is read by the ADC of the microcontroller and saved. Sampling rate is 100 s$^{-1}$. Pellet resistance is mathematically calculated. Response signals transmitted to PC by a USB port. The received signal is processed, classified and identified. The system is shown in figure 4.

![Figure 1. The schematic diagram of the sensor and microheater.](image-url)
Figure 2. The selected heating voltage waveform applied to induce thermal shock.

Figure 3. The schematic diagram of the system designed for performing response recording and signal processing for analyte classification.
Figure 4. Photographs of the fabricated system: (a) the printed board of the CPU; (b) the complete system.
3. Results
The temperature modulated gas sensor was exposed to the odours collected from 3 different types of tea leaves (Earl Gray tea, Ceylon tea, and Iranian tea). The recorded response patterns at different analyte concentrations are shown in Figure 5. The ambient temperature and relative humidity in which the experiments were carried out are 25±2°C and 25±5% respectively. Owing to the negligible environmental fluctuations, there is no need to compensate their effect on the responses [1]. The obtained patterns are normalized between 0 and 1 to diminish the effect of gas concentration level on the shape of the responses. Normalized responses are depicted in Figure 6.

The normalized response patterns obtained from various tea leaves are quite different in shape, so that they can be visually distinguished. However, by the utilization of simple pattern analysis methods analyte classifications can be automated. It is clear in Figure 6 that the normalized responses in the 2.5-3.5 s time range have the most decisive discriminative information. By applying the principal component analysis (PCA) to the feature vector dataset, the number of feature space dimensions is reduced to three. The results, then, can be visualized in a 3-D feature space, as is shown in figure 7. Complete segregation of the different classes is clear in figure 7. Test patterns, obtained in a different work session, are mapped into the same feature space utilizing the same procedure. The results are depicted with filled markers in figure 7. Test data points are all successfully clustered to the correct classes validating the reproducibility of the obtained sensor responses and the efficacy of the fabricated system.

![Raw response patterns of the thermal shock-induced gas sensor recorded for different concentration levels of Earl Gray tea (black), Ceylon tea (red), Iranian tea (blue), and clean air (green).](image)

**Figure 5.** Raw response patterns of the thermal shock-induced gas sensor recorded for different concentration levels of Earl Gray tea (black), Ceylon tea (red), Iranian tea (blue), and clean air (green).
Figure 6. Normalized response patterns related to different concentration levels of Earl Gray tea (black), Ceylon tea (red), Iranian tea (blue), and clean air (green).

Figure 7. The 3-dimensional feature space obtained by applying PCA mapping to the normalized response patterns of Earl Gray tea (black), Ceylon tea (red), Iranian tea (blue), and clean air (green). Hollow markers are related to system training datasets and filled markers are used for the validation tests.
4. Conclusion
Design, fabrication and test of an electronic nose with a single thermal shock-induced sensor were reported. Accuracy, sensitivity and response time of the system was improved by using a suitable heating voltage waveform. The efficacy of the system in odor classification was demonstrated by utilizing it for the recognition of three different tea leaves. The recognition success rate was 100%. The designed system is cost effective, small and suitable for industrial applications.

References
[1] F. Hossein-Babaei, A. Amini. "A breakthrough in gas diagnosis with a temperature-modulated generic metal oxide gas sensor." *Sensors and Actuators B: Chemical* 166 (2012): 419-425.
[2] F. Hossein-Babaei, A. Amini. "Recognition of complex odors with a single generic tin oxide gas sensor." *Sensors and Actuators B: Chemical* 194 (2014): 156-163.
[3] L. Feng, J. Musto Christopher, W. Kemling Jonathan, H. Lim Sung, S. Suslick Kenneth. "A colorimetric sensor array for identification of toxic gases below permissible exposure limits." *Chem. Commun.* 46.12 (2010): 2037-2039.
[4] M. Ryan, H. Zhou, M. Buehler, K. Manatt, V. Mowrey, S. Jackson, K. Adam A. Shevade, M. Homer. "Monitoring space shuttle air quality using the jet propulsion laboratory electronic nose." *Sensors Journal, IEEE* 4.3 (2004): 337-347.
[5] E. Scorsone, A. Maria Pisanelli, C. Krishna. "Development of an electronic nose for fire detection." *Sensors and Actuators B: Chemical* 116.1 (2006): 55-61.
[6] C. Arnold, M. Harms, J. Goschnick. "Air quality monitoring and fire detection with the Karlsruhe electronic micronose KAMINA." *Sensors Journal, IEEE* 2.3 (2002): 179-188.
[7] S. Dragonieri, M. van der Schee, T. Massaro, N. Schiavulli, P. Brinkman, A. Carrat. "An electronic nose distinguishes exhaled breath of patients with Malignant Pleural Mesothelioma from controls." *Lung Cancer* 75.3 (2012): 326-331.
[8] A. PF Turner, M. Naresh. "Electronic noses and disease diagnostics." *Nature Reviews Microbiology* 2.2 (2004): 161-166.
[9] M. Peris, E. Laura. "A 21st century technique for food control: Electronic noses." *Analytica Chimica Acta* 638.1 (2009): 1-15.
[10] A. Loutfi, S. Coradeschi, G. Mani, P. Shankar, J. Rayappan. "Electronic noses for food quality: A review." *Journal of Food Engineering* 144 (2015): 103-111.
[11] F. Hossein-Babaei, V. Ghafarinia. "Gas analysis by monitoring molecular diffusion in a microfluidic channel." *Analytical chemistry* 82.19 (2010): 8349-8355.
[12] Z. Ouyang, R. Graham Cooks. "Miniature mass spectrometers." *Annual Review of Analytical Chemistry* 2 (2009): 187-214.
[13] M. Peris, E. Laura. "On-line monitoring of food fermentation processes using electronic noses and electronic tongues: a review." *Analytica chimica acta* 804 (2013): 29-36.
[14] A. Vergara, S. Vembu, T. Ayhan, M. Ryan, M. Homer, L. Huerta. "Chemical gas sensor drift compensation using classifier ensembles." *Sensors and Actuators B: Chemical* 166 (2012): 320-329.
[15] F. Hossein-Babaei, M. Paknahad, V. Ghafarinia. "A miniature gas analyzer made by integrating a chemoresistor with a microchannel." *Lab on a Chip* 12.10 (2012): 1874-1880.
[16] E. Martinelli, D. Polese, A. Catini, A. D’Amico, C. Di Natale. "Self-adapted temperature modulation in metal-oxide semiconductor gas sensors." *Sensors and Actuators B: Chemical* 161.1 (2012): 534-541.
[17] F. Hossein-Babaei, A. Hooshyar Zare, V. Ghafarinia, S. Erfantalab. "Identifying volatile organic compounds by determining their diffusion and surface adsorption parameters in microfluidic channels." *Sensors and Actuators B: Chemical* 220 (2015): 607-613.
[18] A. Szczurek, M. Maciejewska. "Virtual sensor array as a tool for classifying air pollution." *International Journal of Environmental Analytical Chemistry* ahead-of-print (2015): 1-14.
[19] F. Hossein-Babaei, M. Hemmati, M. Dehmobed. "Gas diagnosis by a quantitative assessment of the transient response of a capillary-attached gas sensor." Sensors and Actuators B: Chemical 107.1 (2005): 461-467.

[20] S. M. Hosseini-Golgoo, F. Hossein-Babaei. "Assessing the diagnostic information in the response patterns of a temperature-modulated tin oxide gas sensor." Measurement Science and Technology 22.3 (2011): 035201.

[21] F. Herrero-Carrón, D. J. Yáñez, F. de Borja Rodríguez, P. Varona. "An active, inverse temperature modulation strategy for single sensor odorant classification." Sensors and Actuators B: Chemical 206 (2015): 555-563.

[22] R. Gosangi, R. Gutierrez-Osuna. "Active temperature modulation of metal-oxide sensors for quantitative analysis of gas mixtures." Sensors and Actuators B: Chemical 185 (2013): 201-210.

[23] M. Roth, R. Hartinger, R. Faul, H-E. Endres. "Drift reduction of organic coated gas-sensors by temperature modulation." Sensors and Actuators B: Chemical 36.1 (1996): 358-362.

[24] F. Hossein-Babaei, and V. Ghafarinia. "Compensation for the drift-like terms caused by environmental fluctuations in the responses of chemoresistive gas sensors." Sensors and Actuators B: Chemical 143.2 (2010): 641-648.

[25] F. Hossein-Babaei, M. Orvatinia, "Thickness dependence of sensitivity in thin film tin oxide gas sensors deposited by vapor pyrolysis." International Journal of Engineering Transaction B: Applications 16.1 (2003): 33-40.