CHEMICAL ENGINEERING TRANSACTIONS
VOL. 54, 2016

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Selena Sironi, Laura Capelli

ISBN 978-88-95608-45-7; **ISSN** 2283-9216

DOI: 10.3303/CET1654057

Development of an Electronic Nose to Identify and Classify Odours from Spirits Beverages

Andy Blanco-Rodríguez[a], Fernando Campo[b], Orestes M. Morales[c], Rodolfo Valiente[d], Bradies Lambert[c], Liliam Becherán[c], Alejandro Garcia-Ramirez[b], Henrique de Melo Lisboa[a], Alejandro Durán*[c]

[a]Laboratory of Air Quality Control (LCQAr), Department of Sanitary and Environmental Engineering (ENS), Federal University of Santa Catarina (UFSC), 88040-900, Florianópolis-SC, Brazil.
[b]Centro em Ciências Tecnológicas da Terra e do Mar (CTTMar), Universidade do Vale do Itajaí (UNIVALI), 88302-202, Itajaí-SC, Brazil.
[c]Instituto de Ciencia y Tecnología de Materiales (IMRE), Universidad de la Habana (UH), 10400, La Habana, Cuba.
[d]Centro de Investigaciones en Microelectrónica (CIME), La Habana, Cuba.
duran@imre.oc.uh.cu

This paper presents the development of an electronic nose (e-nose) prototype for classifying odours from alcoholic beverages, as well as butanol and methanol vapours. The e-nose mainly comprises an array of commercial gas sensors based on metal oxide semiconductor (MOS) technology. Instrumental measurements were based on obtaining the voltage response from the sensor array for each odorant sample. Then, these signals were pre-processed by Principal Component Analysis (PCA) and processed to achieve qualitative results. Three classification tools were used: a Multi-Layer Perceptron (MLP), a Self-Organizing Map (SOM) and Clustering Analysis (CA). The analysis by MLP showed a suitable prediction capability of 92.5 %, while, SOM and CA, being unsupervised techniques, were applied to establish certain odour patterns among the odorants samples. The results of this study support the potential of e-noses as reliable electronic instruments for qualitative analyses of odorants from different alcoholic beverages.

1. Introduction

A large volume of alcoholic beverages is produced and consumed every year. For instance, Cuban rum enjoys a high international reputation and it is one of the top exports for this country. Other spirits drinks like vodka, tequila and whiskey are also popular in many regions. Usually, during the quality control process of distilled beverages, professional tasters are used to evaluate the aroma compounds associated to these products. However, this method presents some drawbacks such as slow response, poor reproducibility and subjective interpretation. Moreover, it is frequent that these specialists only analyse certain families of compounds. Gas chromatography coupled to mass spectrometry (GC-MS) is another technique that can be used for gases assessment. This analytical technique allows the identification and quantification of chemical compounds in vapour samples and provides accuracy and repeatability of measurements. However, odours analysis is not performed, samples preparation is complex and it is time-consuming. Therefore, besides these methods, it would be interesting to use a tool for classifying beverages according to their origin, identifying contaminants and distinguishing other qualitative characteristics. Thereby, an e-nose could be applied as a feasible, low cost and non-destructive instrument, to evaluate different kinds of drinks. In addition, electronic noses are less time-consuming during analysis and the measurement process can be automated. As it is known, the e-nose is an instrument which mainly contains an array of sensors with cross sensitivities, and an appropriate patterns recognition system capable of recognising simple or complex odours (Gardner and Bartlett, 1994).
Electronic noses have several applications (Alam and Saeed, 2013; Bootsma et al., 2014; Sironi et al., 2014), including alcoholic beverage qualitative tests. There are reported studies related to the analysis of Chinese spirits flavours (Zhang et al., 2005; Liu et al., 2012), aromas of wines and wine grapes (Santonico et al., 2010;

Please cite this article as: Blanco-Rodriguez A., Campo F., Morales O., Valiente R., Lambert B., Becherán L., Garcia-Ramirez A., De Melo Lisboa H., Durán A., 2016, Development an electronic nose to identify and classify odours from beverages, Chemical Engineering Transactions, 54, 337-342 DOI: 10.3303/CET1654057

Kumar, 2012), the detection of methanol contamination in whiskeys (Wongchoosuk et al., 2010), as well as the evaluation of agricultural distillates (Dymerski et al., 2013). The comparative analysis of different types of alcoholic liquids by using electronic noses has also been performed (Ragazzo-Sanchez et al., 2009; Śliwińska et al., 2016). These kinds of assessments can be helpful to notice illegal substitution, mixtures or adulteration among spirits beverages, especially when it involves expensive drinks. In terms of healthcare, for instance, a proper classification between distilled beverages and liquid pollutants is relevant because some mixtures may be inadequate or even poisonous. This aspect is more critical taking into account that some dangerous substances, such as methanol, have similar characteristics to beverages, so, their distinction is a difficult task through the conventional methods. Unfortunately, illegal sales of spirits contaminated with methanol have caused injuries and deaths in several countries (BBCNews, 2002; BBCNews, 2011; Cubadebate, 2013).
Although electronic noses have been widely used to investigate alcoholic beverages (Berna, 2010), the analysis usually involves a sample pre-treatment stage for removing some volatile compounds non-responsible of the beverage's aroma, which implicates a higher cost of analysis and an increased complexity of the measuring system. Thus, the use of a simple e-nose to establish patterns of odours associated with different popular alcoholic drinks like rum, tequila, vodka and whiskey could be an appropriate tool for this purpose. In addition, the analysis can be significant to recognize effective relationships between these compounds and other liquid pollutants, highlighting similarities and differences.
This study presents an e-nose prototype and its application for identifying and classifying odours from beverages, as well as butanol and methanol vapours. The system comprises five MOS gas sensors, a stainless steel chamber, three electro-valves, a vacuum pump, and a PCI data acquisition card, commanded by a LabVIEW routine (Virtual Instrument) which is executed in a Personal Computer. Electrical signals corresponding to odorant profiles were obtained and stored. Then, the acquired data were pre-processed to extract the main odorant parameters without losing useful information and to reduce data dimensions. Afterward, three different classification algorithms for qualitative analysis were performed. The experimental set-up, procedures and results of this investigation are presented in this paper.

2. Materials and methods

This section presents the set-up features as well as the experimental procedure to prepare and measure odorants samples. It also describes the data pre-processing, the feature extraction and the pattern recognition algorithms developed to obtain a qualitative response with the prototype.

2.1 Experimental set-up

Figure 1a shows the e-nose prototype schematic diagram. It includes: (1, 2, 3) three solenoid valves; (4, 5) Teflon and silicone tubes; (6) sampling chamber; (7) sensor chamber; (8) sensor array; (9) zeolite and charcoal filter to obtain the baseline from ambient air; (10) vacuum pump; (11) control card for handling the valves and the pump; (12) 5 and 12 VDC power supply; (13) electronic conditioning board with a voltage divider circuit for each gas sensor; and (14) PCI-6221 Data Acquisition (DAQ) Card, plugged in a Personal Computer and controlled by a Virtual Instrument (VI) application software.
Nalophan ® bags, with capacity of 50 L under standard conditions, were used as sampling chamber and for preparing vapour samples of the beverages. This kind of bag preserves the sample gas composition during a certain time due to its adsorption properties. In addition, a stainless steel sensor chamber with 0.8 L of volume was designed. This material ensures low interaction with volatile compounds. The chamber provides input and output electrical connectors, as well as an inlet and an outlet to allow the flow of gases. The gas sensor array comprised five MOS sensors: TGS26xx (xx = 00, 02, 10, 11 and 20) from Figaro manufacturer (Figaro Inc., Japan) was located inside this chamber.

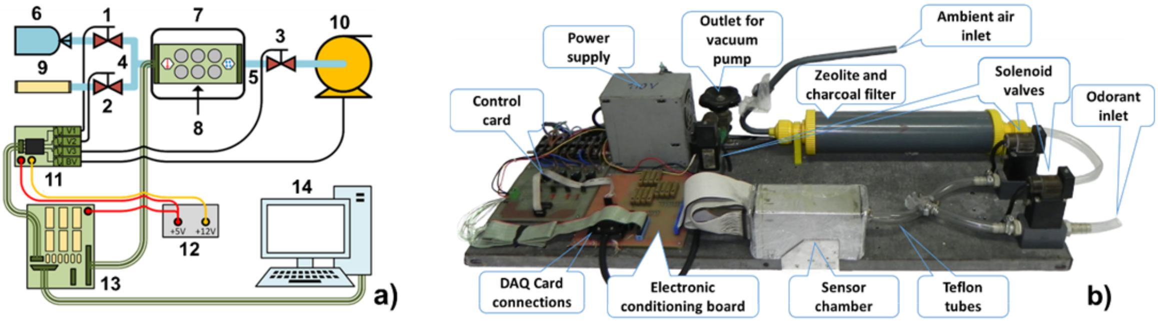

Figure 1: E-nose laboratory prototype: a) Schematic diagram; b) Photograph.

Additionally, a temperature sensor LM-335 and a relative humidity sensor Honeywell HIH-4030 (National Semiconductor, USA) were used. A conditioning board was also developed to this specific application, which adjusts the sensor outputs to the next stage. Then, the signals are acquired through a PCI-6221 DAQ (National Instruments, USA) coupled with a VI developed in LabVIEW platform (National Instruments, USA). This VI commands the acquisition process, stores data from sensors, shows graphical information about odorant profiles and manages the e-nose control card.

2.2 Experimental procedure

For collecting the samples, 11 different vapours were generated from liquid compounds, corresponding to: Aguardiente hard liquor, Havana Club Añejo 5 Años Rum, Havana Club Añejo Especial Rum, Dorado Rum, Blanco's Tequila, Calero's Tequila, Poliakov's Vodka, Svedka's Vodka, Johnnie Walker Whiskey, and butanol and methanol vapours. In the dilution process, a 50 µL volume of each liquid sample was injected inside a Nalophan ® bag containing 50 L of clean air. Every experiment was made under the assumption that liquid samples were completely evaporated inside the sampling chamber after a certain time. In order to check the repeatability and minimize the measurements errors, four odorants profiles were performed by the e-nose for each vapour sample. Time intervals for each pulse sequence were experimentally determined: baseline 15 s, rising transient 5 s, steady state 10 s and recovery transient 430 s. Both, sample preparation and measurement were developed under laboratory conditions at 25 ˚C.

2.3 Data pre-processing and feature extraction

In order to perform qualitative analyses, some tools for data pre-processing and processing were applied. The first stage was use to adequate the output signals of the sensors and to select the most representative parameters from odorants profiles. These pulses at constant concentration level were initially measured. A filter was applied to each voltage data profile in order to remove random errors. Then, a baseline manipulation fractional method given by V_R was computed, Eq (1), thus reducing noise and sensor drifts.

$$V_R = \frac{V_S - V_0}{V_0} \qquad (1)$$

Afterward, Euclidian norm to data scaling for fitting to non-dimensional values was applied, because it is necessary for the following pattern recognition stage. During feature extraction, different parameters from odorant profiles were computed. Then, the Principal Component Analyses (PCA) technique was performed, to estimate the parameters with higher discrimination capability. PCA allows to evaluate each feature and select those parameters with the highest scores.

2.4 Assessment of odorants samples

To process the information, three different pattern recognition algorithms were computed: Multi-Layer Perceptron (MLP), Self-Organizing Map (SOM) and Clustering Analysis (CA). MLP is a powerful and relative simple method for data pattern analysis, with high capacity to interpolation and also it allows to establish complex and non-linear patterns. On the other hand, SOM, also called Kohonen's Map, is another kind of Artificial Neural Network (ANN) which transforms multiple data into a one or two-dimensional discrete map, useful for visualising patterns. Finally, to check and improve the results obtained by the SOM, a CA was also applied to establish similarity or dissimilarity associated with each odorant sample by generating different clusters.

3. Results and discussion

An example of the sensor array response to the above-mentioned odorants, in terms of mean and standard deviation, is shown synthetically in Figure 2.

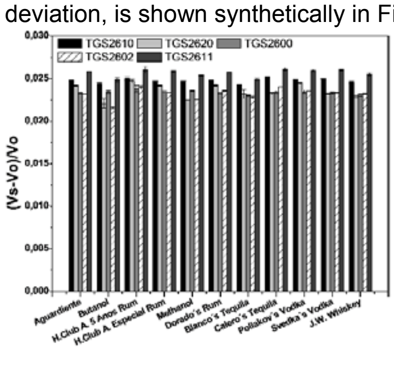

Figure 2: Response of the sensor array to odorants from alcoholic beverages, butanol and methanol vapours.

As can be seen from the previous figure, all sensors presented a suitable response and low dispersion values for all odorants.
Figure 3 shows the PCA transform resulting from two of the parameters computed: recovery transient slope and rising transient slope.

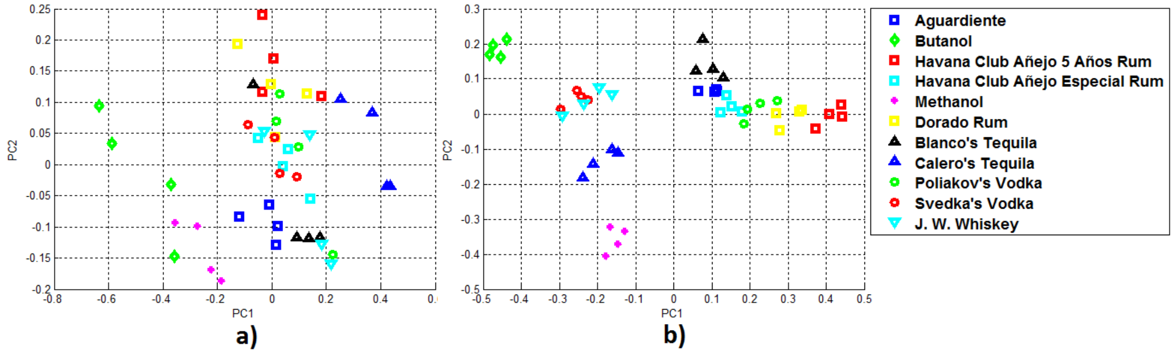

Figure 3: PCA data analysis to select the main features of odorants profiles: a) PCA computed from recovery transient slope; b) PCA computed from rising transient slope.

In the first case, Figure 3a, no distinction among odorants is observed because the plots are very close in these two components. This graph reveals that the recovery transient slope is not an appropriate parameter for classifying odorants in this e-nose prototype. However, the rising transient slope parameter, Figure 3b, allows to distinguish some clusters, corresponding to each kind of odorant. For this parameter, only the odorant plots corresponding to Svedka's Vodka and Whiskey were very close in the PCA graph.
In addition to the rising transient slope factor, other parameters with proficient discrimination capability were also identified by PCA analysis: the maximum voltage value of recovery transient in the odorant profile and the Fourier Fast Transformation (FFT) computed with six coefficients per odorant with 98 % of correlation. These parameters will be used as input models at the next qualitative analysis stage to assess the response capability of the proposed approach.

3.1 Odours classification by Multi-layer Perceptron (MLP)

The architecture of this ANN was defined with 35 input nodes in the input layer, 30 hidden nodes in each of the two hidden layers, and 11 nodes in the output layer. Input layer neurons were connected to first hidden-layer neurons via *tansig* function. Neurons between hidden layers were coupled through *logsig* function, and second hidden-layer neurons were connected to output-layer neurons by using *purelin* function.
Forty-four samples, four replicates per each of the 11 odorants, were analysed through the MLP. This data were randomly divided into two groups, 36 samples (80%) were used for training dataset and 8 samples (20%) for testing dataset. The training group was used to compute the MLP weights and the test group was employed to infer the MLP performance.
Four experiments using different input data were developed by MPL. Therefore, each dataset corresponding with the best parameters extracted in the earlier pre-processing stage were introduced to the ANN. Since the samples selected for training and testing groups were shaped randomly, each experiment was repeated 10 times. This procedure also increases the results' confidence. The combinations of parameters used and their accuracy calculated by MPL are shown in Table 1. From these analyses it is possible to evaluate the performance of MLP for classifying 11 odorant samples. It can be seen that the FFT+ Rising transient slope feature and the FFT+ Maximum of recovery transient feature, with 92.5 % and 91.25 % accuracy respectively, were the parameters that provided better results. This suggests that MLP is a suitable algorithm to identify odorants from different alcoholic beverages, as well as butanol and methanol vapours.

Table 1: Accuracy of odour classification by MLP.

Parameters extracted from odorants profiles	Confusion matrix. Means of 10 tests
FFT	85,00 %
FFT+ Rising transient slope	92,50 %
FFT+ Maximum of recovery transient	91,25 %
FFT+ Rising transient slope +Maximum of recovery transient	87,50 %

3.2 Odours classification by Self-Organizing Map (SOM)

A SOM with hexagonal lattice in competition layer with 100 neurons (10x10) was configured and the training process was performed over 2000 epochs. Data input to the network was the combination of parameters FFT and Rising transient slope (so-called above as FFT+ Rising transient slope feature). The response of the SOM was evaluated on the basics of the distance of weights in the competitive layer, Figure 4a, and analysing how many times the neurons won the competition, Figure 4b.

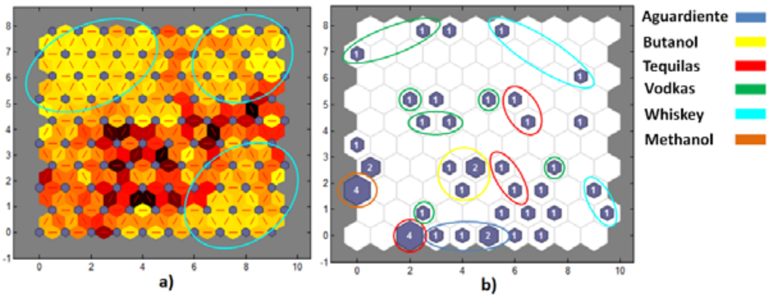

Figure 4: Two-dimensional lattice of SOM: a) neighbour connections and the odour patterns; b) sample hits.

The map of Figure 4a does not provide a visual information with high accuracy about groups of odours. However, the lighter colours help to identify clusters, which allows to establish three odour patterns, marked with blue lines. These clusters formed by the SOM could be associated with odorant classes.

Figure 4b shows that the more defined clusters were for butanol and methanol samples, probably due to their differences regarding the alcoholic beverages aroma. The odorants samples of Aguardiente were placed close. On the other hand, the neurons that represent the samples of Johnnie Walker Whiskey were spread in the map but even so, they were disjointed from the other neurons. The relative long distance between this cluster and the others could be useful to differentiate the whiskey odour regarding the rest of the samples. Four tequilas samples were close and their corresponding neurons won the competition. Nevertheless, the other samples were located separately, which may indicate differences between Blanco's Tequila and Calero's Tequila. The most spread samples are the neurons corresponding to rums. Probably, it is due to the similarities of these samples regarding the other alcoholic beverages.

SOM network was able to depict odour patterns from the substances measured with the e-nose prototype. Also, through this unsupervised technique it was possible to recognize some qualitative relationships among the samples.

3.3 Odours classification by Clustering Analysis (CA)

The results by CA are presented as a dendrogram in Figure 5, where the horizontal axis ("X") represents the Euclidian distance among groups and the vertical axis ("Y") indicates the odorants similarity. Then, the most similar samples were joined to form clusters. Similarly to the SOM procedure, the data input to CA was the FFT+ Rising transient slope feature. From the analysis of the dendrogram of Figure 5 it is possible to establish some clusters hypotheses. It was considered that the most appropriate groups could be defined in X=5 or in X=7. According to the first hypothesis, four clusters were formed: methanol; butanol; Calero's Tequila and Havana Club Añejo 5 Años Rum; and the others alcoholic beverages. In the second option, similarly to the findings in the SOM analysis, there are three clusters: methanol; butanol; and all the drinks.

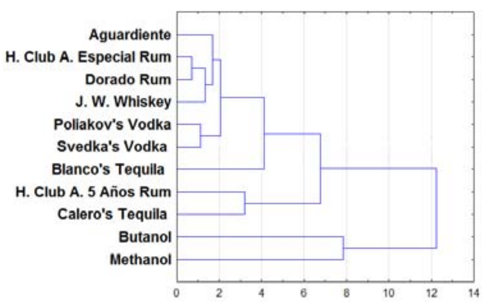

Figure 5: Cluster analysis dendrogram from different odorants.

The difference between beverages and the rest of the samples was more evident by CA than by SOM analysis. At the same time, through the graph information it was also possible to recognize that the more similar odorants are the two groups formed by: Havana Club Añejo Especial Rum and Dorado Rum; and the vodkas.

4. Conclusions

In the present study, odorants from beverages, butanol and methanol vapours were analysed using a developed e-nose laboratory prototype. The beverages evaluated are some of the more popular alcoholic drinks which are produced and consumed every year. MLP was applied to assess 11 kinds of odorants generated from their corresponding liquid substances. The model output can predict each compound measured with an accuracy of 92.5 %. Also other qualitative analyses by SOM and CA were performed. These classification algorithms allowed to identify odour patterns and establish relationships among the samples. The use of different techniques to evaluate the target odorants was useful to achieve more effective results, since, the discriminative ability of the developed e-nose was successful in identifying odorant patterns. This e-nose prototype could be a feasible and suitable choice to evaluate the substances studied regarding to classical techniques and professional tasters.

Acknowledgments

The authors thank Project CAPES-MES 139/11 “Desenvolvimento de narizes eletrônicos para a detecção de substâncias gasosas no meio ambiente: contribuição para a avaliação do impacto de odorantes”, and Programa de Estudantes-Convênio de Pós-Graduação (PEC-PG) de CAPES/CNPq–Brasil.

References

Alam H., Saeed S., 2013, Modern Applications of Electronic Nose: A Review, International Journal of Electrical and Computer Engineering (IJECE) 3, 52-63.

BBCNews, 2002, Deadly brew hits Madagascar, <www.news.bbc.co.uk/2/hi/africa/1900624.stm> accessed 17.06.2016.

BBCNews, 2011, Who, What, Why: Why are Indians dying from alcohol poisoning, <www.bbc.com/news/magazine-16197280> accessed 17.06.2016.

Berna A., 2010, Metal Oxide Sensors for Electronic Noses and Their Application to Food Analysis, Sensors 10, 3882-3910.

Bootsma S., Leuwerink T., Bilsen I., 2014, Online Air Monitoring with eNoses at the TATA Steel Plant in the Netherlands, Chemical Engineering Transactions 40, 79-84.

Cubadebate, 2013, Suman 11 los fallecidos por intoxicación con alcohol metílico <www.cubadebate.cu/noticias/2013/08/03/suman-11-los-fallecidos-por-intoxicacion-con-alcohol-metilico/#.V2g28PnhDIU> accessed 15.05.2016.

Dymerski T., Gębicki J., Wardencki W., Namieśnik J., 2013, Quality Evaluation of Agricultural Distillates Using an Electronic Nose, Sensors 13, 15954-15967.

Gardner J., Bartlett P., 1994, A brief history of electronic noses, Sensors and Actuators B: Chemical 18-19, 211-220.

Kumar R., 2012, An Intelligent E-Nose System For Discrimination Of Alcoholic Odorants, International Journal of Computing & Business Research, 1-11.

Liu M., Han X., Tu K., Pan L., Tu J., Tang L., Liu P., Zhan G., Zhong Q., Xiong Z., 2012, Application of electronic nose in Chinese spirits quality control and flavour assessment, Food Control 26, 564-570.

Ragazzo-Sanchez J. A., Chalier P., Chevalier-Lucia D., Calderon-Santoyo M., Ghommidh, C., 2009, Off-flavours detection in alcoholic beverages by electronic nose coupled to GC, Sensors and Actuators B: Chemical 140, 29-34.

Santonico M., Bellincontro A., De Santis D., Di Natale C., Mencarelli F., 2010, Electronic nose to study postharvest dehydration of wine grapes, Food Chemistry 121, 789-796.

Sironi S., Eusebio L., Capelli L., Remondini M., Del Rosso R., 2014, Use of an Electronic Nose for Indoor Air Quality Monitoring, Chemical Engineering Transactions 40, 73-78.

Śliwińska M., Wiśniewska P., Dymerski T., Wardencki W., Namieśnik J., 2016, Evaluation of the suitability of electronic nose based on fast GC for distinguishing between the plum spirits of different geographical origins, European Food Research and Technology, 1-7.

Wongchoosuk C., Wisitsoraat A., Tuantranont A., Kerdcharoen T., 2010, Portable electronic nose based on carbon nanotube-SnO_2 gas sensors and its application for detection of methanol contamination in whiskeys, Sensors and Actuators B: Chemical 147, 392-399.

Zhang Q., Xie C., Zhang S., Wang A., Zhu B., Wang L., Yang Z., 2005, Identification and pattern recognition analysis of Chinese liquors by doped nano ZnO gas sensor array, Sensors and Actuators B: Chemical 110, 370-376.