Electronic Nose Based on Temperature Modulation of MOS Sensors for Recognition of Excessive Methanol in Liquors

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ABSTRACT: An electronic nose based on metal oxide semiconductor (MOS) sensors has been used to identify liquors with excessive methanol. The technique for a square wave temperature modulated MOS sensor was applied to generate the response patterns and a back-propagation neural network was used for pattern recognition. The parameters of temperature modulation were optimized according to the difference in response features of target gases (methanol and ethanol). Liquors with excessive methanol were qualitatively and quantitatively identified by the neural network. The results showed that our electronic nose system could well identify the liquors with excessive methanol with more than 92% accuracy. This electronic nose based on temperature modulation is a promising portable adjunct to other available techniques for quality assurance of liquors and other alcoholic beverages.

1. INTRODUCTION

Chinese liquors have a long cultural history in China and are praised by countries all over the world. However, liquors are often intentionally adulterated with cheap industrial alcohols to increase beverage profit (up to 50 vol %) and the content of methanol in liquors may exceed the limit (<400 mg/L). Also, there may be a lot of methanol in a liquor that is produced by irregular operations during fermentation (1.25 vol %). Methanol is toxic to humans and acute intoxication of methanol usually causes headache, vertigo, fatigue, nausea, vomiting, blurred vision, blindness, and even death. The most important ingredients in fake liquors are methanol and ethanol. Both of them are colorless and transparent liquids, and they cannot be distinguished easily by human olfaction or vision. Therefore, methanol detectors are urgently needed by consumers and authorities to reduce the occurrence of methanol poisoning incidents.

Traditionally, many analytical techniques could be used to detect methanol in liquors, such as Fourier near-infrared spectroscopy (NIR), ultraviolet and visible spectrophotometry (UV–VIS), nuclear magnetic resonance (NMR), and gas chromatography–mass spectrometry (GC–MS). Nowadays, attention to the portable e-nose device has greatly increased because it is a promising alternative for quality inspection of food at a low cost. There are three parts in the e-nose system, including an array of gas sensors with cross-sensitivity and selectivity toward various gases, an analogue to the digital converter, and pattern recognition software. The useful information could be obtained after feature extraction to the response signals of the sensors. Therefore, one could obtain the composition and concentration information of the gas mixture through the pattern recognition system. An e-nose is generally not capable of detecting specific compounds of liquors as the MS system. It seems to be able to distinguish between mixtures of volatile compounds, thus allowing fast discrimination of volatile organic compound (VOC)-releasing samples.

The common electronic nose is based on a metal oxide semiconductor (MOS) sensor array, which is generally operated at a constant temperature to extract its static response parameters as the features of pattern recognition. Wozniak et al. proposed that changing (modulating) the operating temperature of the MOS sensor affects the desorption and adsorption reactions of VOCs. That could provide more detailed information from sensor response characteristics about the gas species. Furthermore, it has been shown that the transient response is less sensitive to the changes in ambient temperatures and humidity than the steady-state sensor response. For example, Ngo et al. have successfully used an electronic nose to classify and identify the target gases (carbon monoxide, acetylene, and hydrogen sulfide) by heating each sensor between 200 and 450 °C.
Gwizdż et al.\textsuperscript{18} prepared an array of MOS sensors to work on an induced sinusoidal temperature profile and realized reliable hydrogen detection in spite of interference of humidity and residual gases (methane and propane). Therefore, an e-nose could be a promising portable adjunct for the traditional analysis techniques in terms of fast screening.

In this work, an electronic nose system based on a temperature modulation model is designed for the identification of liquors, which contain excessive methanol. Four kinds of MOS sensors were operated in dynamic mode by the square voltage applied to their heating elements.\textsuperscript{19} Our investigations indicated that the e-nose could well identify the liquor which contains excessive methanol in temperature modulation mode.

2. RESULTS AND DISCUSSION

2.1. Liquor Sample Characterization. A liquor is a complex mixture that contains water, alcohols, acids, sugars, and aromatic compounds.\textsuperscript{20} The example of the GC–MS chromatogram for one of the measured liquor samples (Fenjiu) is presented in Figure 1. It turned out that there were about 10 volatile compositions, which showed good coordination with Chinese liquor characteristics.\textsuperscript{20} As shown in Figure 1a, some volatile compounds (including ethyl acetate) were well separated from ethanol under these conditions, reflecting the chemical complexity of liquors. Clearly, ethanol was the dominant species in the vapor phase due to its high content in the sample. In addition, there was no methanol peak in the chromatogram. It is demonstrated that the sample of Fenjiu did not contain methanol (or below the resolution of the chromatogram). Figure 1b shows the GC–MS chromatogram of the Fenjiu sample with added methanol (10 vol %). The volatile compositions were well separated and the peak of methanol was observed. Concentrations and compositions of volatile compounds or congeners, are one of the most important parameters responsible for the quality of the produced alcoholic products. Generally, in various aroma-type liquors, the content of esters was significantly different and they were important aroma components in Chinese liquors.\textsuperscript{21} Ethyl acetate, as the major and characteristic contributor to the aroma, was the second-largest component (except methanol) in VOCs (Figure 1). Meanwhile, the flavor components such as 2-methyl-1-propanol and 3-methyl-1-butanol existed in less amounts. The results of GC–MS suggested that the contents of methanol in liquor samples were well controlled.

2.2. Response of MOS Sensors to Temperature Modulation. It is well accepted that the selective performance of MOS gas sensors is modulated by a balance of gas adsorption and reaction on the surface, which is temperature dependent.\textsuperscript{16,22} However, the sensing process is a very complex process of surface chemical reactions and electron conduction.\textsuperscript{23} Thus, there were no mature models for the temperature-dependent selective characteristics. Generally, sensor conductance could be well described by eq 1, which is also known as the Morrison equation for MOS gas sensors\textsuperscript{24}

\[
G(T) = G_0 \exp\left(-eV_i/kT\right)
\]  

where \(G_0\) denotes the sensor conductance free of depletion, \(e\) the elementary charge, \(k\) the Boltzmann’s constant, and \(T\) the absolute temperature (K). The surface Schottky barrier height is given by the surface concentration of ionosorbed oxygen, as in eq 2

\[
V_i = eN_s^2/2\epsilon\kappa_0N_d
\]

where \(N_s\) denotes the surface density of ionosorbed oxygen such as O\textsuperscript{-} on the surface of MOS, \(\epsilon\kappa_0\) the semiconductor permittivity, and \(N_d\) the volumetric density of an electron donor. Equations 1 and 2 imply that the electron density of the semiconductor surface and the conductance of the sensor could increase when the reducing gas is oxidized by ionosorbed oxygens. Similarly, the conductance of the semiconductor increases with temperatures.\textsuperscript{25}

To enhance the discrimination ability of the sensors, a series of experiments were conducted by optimizing the working temperature of the sensors. Using a rectangular voltage to heat the sensors, the transient response could be useful because the difference in the gas response is mainly reflected in the process of heating or cooling of the sensor according to eqs 1 and 2. When the temperature is constant, the resistance or conductance of the gas sensor does not change much over time. In this case, the sensor reaches its response in an equilibrium state. Therefore, the heating period of the sensors was controlled to make them work in a nonequilibrium state. If the frequency of the heater voltage is too high, the surface temperature of the sensor could not keep up with the variation of the heater voltage. Because the thermal response time of the sensors, which is the time taken to heat the thick film sensor to a set temperature, is estimated to be about 10 s from 25 to 300 °C.\textsuperscript{17,25} Thus, the sensor does not reach the maximum temperature for the first period and its average temperature evolves slowly on several tens of periods. However, if the
frequency is too low, the sensor changes slowly and tends to reach its equilibrium response, similar to a constant temperature mode. In this case, the nonlinear features of sensors could not be extracted and the feature dimension extracted at this constant temperature mode is unstable. Therefore, the frequency of the heater voltage should adapt to the chemical reaction rate of the sensors. The infrared camera showed that it took about 15 s when it was working normally (200–400 °C) from the beginning of heating to a constant temperature (Figure S5). Thus, the period of the temperature cycle was set to 30 s.

With temperature modulation, the sensor with dynamic responses presents unique “shape” characters with different gases. Figure 2 shows that the transient resistive response of Pd-SnO2 depends on time for methanol (29 ppm) and ethanol (30 ppm) at 200–400 °C. From Figure 2, one can clearly observe the differences in the “shape” profile of different gas species. The sensor response as a function of methanol concentrations shows one peak of resistance in a period (30 s), while ethanol has two. Differentiation of the waveform could be enhanced by adjusting the range of temperatures. The profiles of resistive response at different temperature ranges are given in Figure S6.

When the temperature of the MOS sensor changes, the kinetic processes of the gas–solid reaction, i.e., the adsorption/desorption are altered. According to the depletion theory, the surface concentration of isonionsorbed oxygen and the bulk resistance are the two factors that could change the macroscopic resistance of a SnO2 film. It is widely accepted that the chemical reaction between surface oxygen and the reducing gas is the primary mechanism of tin oxide. When the temperature of the MOS sensor is constant, an equilibrium state among the chemisorbed species exists on the surface of the sensor

$$\text{O}_2 + 2\text{e}^- \rightarrow 2\text{O}^-$$

The sensing mechanism of ethanol can be explained by the charge transfer process represented by the following reaction

$$\text{CH}_3\text{CH}_2\text{OH} + 6\text{O}^- \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 6\text{e}^-$$

For simplicity, the oxidation of ethanol is assumed to be completed in one step. However, this is a somewhat rough assumption because ethanol oxidation is rather complex. The resistance of the sensor significantly reduced during the interaction of the sensing material with gas molecules (ethanol). During temperature modulation, the equilibrium state no longer exists for oxygen species on the surface of SnO2. In this case, complicated response transient characteristics are due to the reactions between reducing and oxidizing gases. When the temperature cooled down from 400 to 200 °C, the resistance in methanol increased. However, the resistance in the presence of ethanol increased and then decreased (Figure 2). Obviously, it was caused by the underlying surface reaction mechanisms between ethanol and chemisorbed oxygens on the surface. The basic sensing mechanism for ethanol and methanol is the same one as that for MOS gas sensors. That is, a chemical reaction, more specifically oxidation of the reducing gas such as ethanol and methanol induce a charge transfer between adsorbed oxygens on the surface and the conduction band of MOS semiconductors. Nevertheless, the sensing response in terms of resistance variations and patterns is not identical for ethanol and methanol even for the same sensor. Because the reactivity and the molecular structure of ethanol and methanol are different, which show different properties in diffusion and reaction characteristics when reacting with gas molecules. Consequently, the sensing response exhibits different and unique patterns in resistive variation, which could be used for pattern recognition. When a sensor array is based on several different MOS gas sensors, pattern recognition of odors could be achieved with neural networks. Furthermore, the response to target gases showed good repeatability in temperature modulation. Therefore, the shape of the response curve was used as the basis for temperature optimization. The temperature range with the largest gas response difference was selected as the working temperature of the sensors. Finally, the modulation range of temperature for the Pd-SnO2 sensor was set at about 200–400 °C.

In addition, the response waveform of the sensor exhibits an asymmetrical shape in the heating and cooling process, as shown in Figure 2. It is believed that this is caused by the hysteresis of sensor temperature. Nakata has demonstrated that the degree of hysteresis corresponds to the rate of the reaction of the gas species on the sensor surface and the rate at which the temperature is changed. If the diffusion rate of the gas at the scanning temperature is significantly higher than the reaction rate of the gas, the amplitude of hysteresis is almost independent of the temperature modulation rate. When MOS sensors are exposed to the liquor samples, the humidity is 87% RH (20 °C). The humidity dependence of the response of MOS sensors could be found in the Supporting Information (Figure S9).

### 2.3. Pattern Recognition

In the application of gas identification, the efficiency of the classifier significantly depends upon the input dataset due to partial cross responses. This demands suitable data preprocessing of the sensor array response patterns before they are fed into a classifier. One can clearly observe that the dynamic response curves (the shape of the profile) depend on the kind of gas being analyzed, and the waveforms are repeatable, suggesting that the separation of methanol and ethanol is possible. Thus, the sensor resistance in the time domain was selected directly as the characteristic parameter for pattern recognition.

It was considered that the amplitude of the waveform is a function of gas concentration in a period and it is not conducive to classification. Thus, the method of data normalization was used. It is described as eq 5

![Figure 2. Resistance curves of Pd-SnO2 to methanol and ethanol at 200–400 °C.](https://doi.org/10.1021/acsomega.1c04350)
where $R_i$ is the sensor resistance under temperature modulation and $R_{\text{min}}$ and $R_{\text{max}}$ are the minimum and maximum values of $R_i$, respectively. $S_i$ denotes the data of the sensor response after preprocessing by eq 5. In this work, the period of temperature modulation is 30 s and the sampling frequency is 1 Hz, so there are 30 data points in a single modulation period for one sensor. The data acquired by each sensor was preprocessed by eq 5. Finally, 120 features (30 features × 4 sensors) were extracted to represent the “fingerprint” information of one sample.

For unsupervised clustering algorithms, once the clustering regions emerged overlap, incorrect classification would happen.\textsuperscript{35} In the process of supervised learning, the data vectors are tagged with a descriptor, and the classes are learned according to their description. Then an unknown vector may be classified using the relationships found from the known vectors.\textsuperscript{36} As a typical supervised classification algorithm, back-propagation neural network (BPNN) has the ability to deal with nonlinearities and has been widely used in the field of pattern recognition. The mapping relations between the input and output can be learned and stored by the network, while there is no need to define the mathematical equation between them. Therefore, the BPNN models in this paper were implemented with Python 3.7 and Pytorch module. Sigmoid activation function and cross-entropy loss function were used in the neural network.

Three groups of network models were trained to classify methanol and ethanol gases under well-controlled conditions, eight different liquors mixed with methanol and a kind of liquor with different methanol contents. They were composed of three layers. The input layer had 120 nodes, corresponding to 120 dimensional features of the sensors (30 × 4). The number of nodes in the hidden layer was 70. For the three models, the numbers of neurons for the output layer were 3, 2, and 6, respectively. The training number was 20,000 and learning rate was 0.01. The weights were continuously updated in the training process. The procedures of the parameter tuning could be found in the Supporting Information.

Under the well-controlled conditions of the verification experiment, features of all samples formed a feature space of 300 × 120 dimensions (300 samples × 120 features). The dataset was randomly divided into two parts: 80% for training and 20% for validation. Actually, for each kind of gas 80 sets of samples were used for training and 20 sets of samples for validation. Each set of data was labeled “A” (methanol, 29 ppm), “B” (mixture of methanol and ethanol, 1:1 vol), or “C” (ethanol, 30 ppm). After multiple trainings, the test dataset was verified. The confusion matrix of the classification is shown in Figure 3. The diagonal elements represent the number of data for which the predicted results are the same as those of the true category. Higher diagonal values of the confusion matrix indicate a higher number of correct predictions. As one can observe, the classification accuracy is 100%. The three categories of gas samples were classified successfully, indicating that the e-nose can be used to distinguish methanol and ethanol gas under lab conditions.

For the first group of liquor samples, we aimed to verify the ability of the electronic nose to qualitatively detect the liquor with excessive methanol content. It is a typical binary classification problem. Thus each kind of liquor was formulated into a volume fraction of 0 and 10% methanol, a total of 16 groups (2 × 8). For each liquor sample, 36 replicates were collected. 30 sets of samples were randomly selected as the training dataset, and the remaining 6 sets of samples were used as the test dataset in each kind of sample. Each set of data was labeled “A” (not containing methanol) or “B” (containing methanol). Then, the BPNN model was trained by the training dataset and verified by the test dataset. Finally, 480 sets of samples (30 training datasets × 16 groups) for training and 96 sets of samples (6 test dataset × 16 groups) for validation were used. Unlike the lab-controlled gas sample, the liquor sample contains a variety of interfering gases (unknown) and the relative humidity in the VOCs can be as high as 90%. These interference gases are VOCs and water vapor, which can also react with the sensor surface. In this case, the selective gas detection of the e-nose may not be accomplished well. The confusion matrix of the classification on the first group of samples is shown in Figure 4. It can be seen from the confusion matrix that the classification accuracy is about 94%. Though classification accuracy is lower than that
of the experiment under well-controlled conditions, the e-nose can be used to identify whether methanol is present in the liquor.

For the second group of liquor samples, the e-nose was investigated to realize a multi-label classification problem for a quantitative rating of the methanol content level in the liquor. A kind of liquor was selected and a set of mixed samples were prepared by adding different amounts of methanol (Table 2). The contents of methanol mixed in the liquor were 0, 10, 20, 30, 40, and 50%. The presence of methanol in liquors distinguishes liquor samples from each other. Thirty-six replicates were collected for each liquor sample. Finally, 216 sets of data (36 replicates × 6 liquor samples) were randomly divided into 180 sets for the training dataset and 36 sets for test dataset. The confusion matrix of the classification on the second group of samples is shown in Figure 5. It can be seen from the confusion matrix that the classification accuracy is 92%, which means that this electronic nose can well distinguish liquors with different degrees of methanol exceeding the standard.

3. CONCLUSIONS

In this study, an e-nose based on temperature modulation of MOS sensors has been developed as the tool for the recognition of odors. Four kinds of MOS sensors were operated in the dynamic mode (temperature modulation) to reduce the recognition time and to expand the dimensionality of the feature space associated with the sensor signal being recorded. The range and period of temperature variations were optimized to enhance the differentiation of the sensor response to different target gases. The performance of the e-nose was verified by the identification of adulterated liquors. The results of GC−MS reveal whether the liquor samples contain methanol. The resistances of the sensors in a period were normalized as the input feature of the artificial neural network. The e-nose system could not only qualitatively identify whether the liquor contains methanol but could also quantitatively identify the methanol content in the liquor. Our study shows that temperature modulation of gas sensors is a simple and powerful strategy to achieve selective gas detection. Additionally, with only a few changes, such as adjusting the combination of sensors, the e-nose can be applied to the food and beverage industry for quality control and assurance. In the near future, more work on temperature modulation of the e-nose will be taken for a lower methanol detection limit.

4. EXPERIMENTAL SECTION

4.1. Design and Fabrication of the Temperature Modulation System. A set of gas sensors based on MOS, namely SnO2, Pd-loaded SnO2, WO3, and Ru-loaded WO3, have been made by the screen-printing technique by the same process as in our previous reports.30,37,38 The reagents used in the experiment were provided by Shanghai Aladdin Biochemical Technology Co., Ltd. The processes of sensor fabrication and characterization could be found in the Supporting Information. The main framework and experimental setup of the temperature modulation system are presented in Figure 6. The MCU chip (STM32H70VBT6, ST), as the core of the system, has three 16-bit A/D converters. The analogous voltage signals from sensors were converted to digital signals employing the MCU chip. A rectangular voltage with a period T = 30 s was generated using a D/A converter module (MCP4725, MICROCHIP) and the driving capability of the signal was enhanced by the power amplifier (TDA2030, UTC). Then it was applied to the heater of the gas sensors. The amplitude (0–10 V) and period of the voltage can be programmed. The voltage, current, and power of the heater were monitored using a current/power monitor module (INA219, TI). The temperature profile of sensor surfaces was analyzed by an infrared camera (PI200, Optrics, Germany). All of the data obtained by the MCU chip were sent to the PC through the wireless communication module (2.4 GHz, SEEKFREE, Sichuan, China) based on a single chip microcomputer (cortex-M3). The chamber of the sensor array was designed by Auto CAD (Autodesk 2019) and fabricated by 3D printing with an HP Jet Fusion 4200 machine (Nylon, 0.2%, WeNext, Shenzhen, China).

4.2. Feasibility Verification of the e-Nose for Gas Recognition. To verify the ability of the e-nose, measurements with the response to target gases (methanol and ethanol) were carried out under well-controlled conditions such that the relative humidity of gas was about zero (less than 40 ppm in volume). Target gases including methanol (29 ppm) and ethanol (30 ppm) were supplied from gas cylinders (100 scm). Synthesized air was used to clean the remaining gas in the tube. Figure 7 shows the schematic drawing of the setup for gas sensor characterizations. The target gases fed through a Teflon tube into the sensor chamber were precisely controlled with the mass flow controllers (MFCs) to provide a well-defined total flow value of 100 scm. The sensor chamber was cleaned by air (79% nitrogen, 21% oxygen).

A rectangular voltage was applied to the heater of the sensor by controlling the duty ratio as 15 s/(15 s + 15 s). The waveform of multiple cycles of the experiment was used as the training sample. Finally, 100 cycles of sensor response to gas were acquired for each kind of analyte gas. The sampling rate was set at one sample per second, and the details of the experimental procedures could be found in the Supporting Information.

4.3. Recognition of Methanol in Liquor. Eight common liquors were obtained from local suppliers and are listed in Table 1. They were divided into two groups to verify the ability of the e-nose to recognize methanol in liquor. The first group...
was eight liquors from different brands. The eight liquors which were not mixed with methanol were marked as “A”. The other eight liquors were mixed with methanol (purity ≥99.9%, Shanghai Aladdin Biochemical Technology Co., Ltd.) and marked as “B”. However, the content of methanol was kept the same, 10 vol %. The other group was selected, a kind of wine from “A” randomly, which was mixed with different contents of methanol, as shown in Table 2. Details of the sample preparation could be found in the Supporting Information.

Figure 6. (a) Diagram of the temperature modulation system. (b) Top view of the temperature modulation system based on STM32H750VBT6.

Figure 7. Schematic view of the e-nose system operated under lab conditions.
The compositions of the samples were characterized qualitatively using a GC−MS equipment (ISQ 7000, Thermo), which matched with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). Briefly, helium was used as the carrier gas at the flow rate of 1 mL/min (splitless mode). Electronic impact (EI) mode was used for the MS fragmentation and full-scan mode (35−550 m/z) was used for acquisition. The liquor samples (0.5 μL) were injected into the GC inlet in a splitless mode at 250 °C. The oven temperature program was as follows: 60 °C for 4 min; 10 °C/min ramp to 300 °C, and holding for 30 min. Aroma compounds were identified by aligning their recorded mass spectra with the NIST library according to the retention indices (RI) and those with similarity greater than 85% were selected. All GC−MS measurements were carried out in triplicate under repeatability conditions.39

Figure 8 shows the schematic drawing of the e-nose system. Different from the system above (Figure 7), the odor of the liquor was pumped into the sensor chamber by a vacuum pump with a flow rate of around 300 mL/min. To keep a constant gas concentration, the odor was continuously circulated in the chamber. One drop of the sample liquor (about 50 μL) was placed in a headspace sample vial (20 mL) using a micropipette. The VOCs could leave the liquid phase and enter the headspace. Procedures for the recognition of methanol in the liquor could be found in the Supporting Information.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04350.

Experimental details: sensor fabrication, procedures of the sample preparation, sensor response graphs, and parameter tuning and humidity dependence of the response of the MOS sensors (PDF).

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**Notes**
The authors declare no competing financial interest.

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