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Can Electronic Nose Replace Human Nose?—An Investigation of E-Nose Sensor Responses to Volatile Compounds in Alcoholic Beverages

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Cite This: *ACS Omega* 2023, 8, 16356−16363

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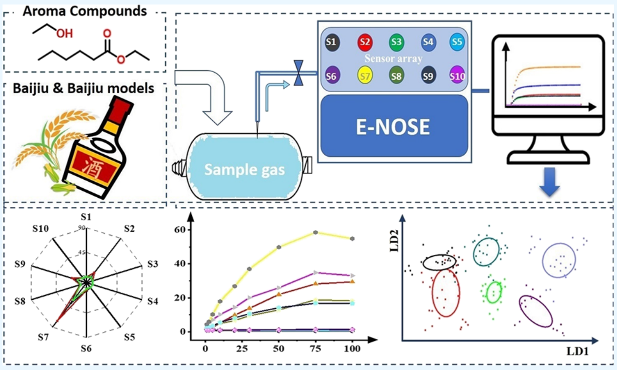
ABSTRACT: Electronic nose (E-nose) technology is frequently attempted to simulate the human olfactory system to recognize complex odors. Metal oxide semiconductors (MOSs) are E-noses' most popular sensor materials. However, these sensor responses to different scents were poorly understood. This study investigated the characteristic responses of sensors to volatile compounds in a MOS-based E-nose platform, using baijiu as an evaluation system. The results showed that the sensor array had distinctive responses for different volatile compounds, and the response intensities varied depending on the sensors and the volatile compounds. Some sensors had dose−response relationships in a specific concentration range. Among all the volatiles investigated in this study, fatty acid esters had the greatest contribution to the overall sensor response of baijiu. Different aroma types of Chinese baijiu and different brands of strong aroma-type baijiu were successfully classified using the E-nose. This study provided an understanding of detailed MOS sensor response with volatile compounds, which could be further applied to improve the E-nose technology and its practical application in food and beverages.



INTRODUCTION

An electronic nose (E-nose), also known as the artificial olfactory system, is a device that imitates human olfactory perception to recognize odors.[1] This platform consists of a sampling system, an array of heterogeneous electrochemical gas sensors with partial specificity, a signal collection unit, and pattern recognition software.[2] The sampling system takes volatile compounds from the headspace of a sample and carries them to the sensor arrays. Then, the sensing materials on the sensor surface interact with the compounds (such as adsorption, desorption, or reversible reaction), converting the volatile profile into electrical signals. Finally, the pattern recognition software processes the signals and identifies and classifies samples based on the information learned previously.[3]

The core element of the E-nose is the gas sensor. Different principles can be applied to develop the gas sensor. Metal oxide semiconductor field effect transistor (MOSFET), metal oxide semiconductor (MOS), electrochemical sensor (EC), quartz crystal microbalance (QCM), conducting polymer (CP), and surface acoustic wave (SAW) sensors have been used in the E-nose.[4] Among all these gas sensors, the MOS sensor is the most common commercial sensor for aroma classification. The working principle of this type of sensor is based on the change in conductivity and resistance value caused by the reaction between the measured odor and the sensor.[5] MOSs have unique advantages, such as low cost, small size, reliable sensitivity, high stability, and long usage life.[6] Thus, MOS sensor-based E-nose has been used in many different fields, such as disease diagnosis,[7] environmental monitoring,[8] and food quality control.[9] However, most studies have focused on the application and response analysis of the systems. No study has been published on the mechanism of MOS sensors responding to specific volatile compounds, especially those responsible for the aroma and flavor of alcoholic beverages.

Chinese baijiu is one of the six most famous distilled spirits globally.[10,11] The unique production process gives the baijiu very diverse aroma compounds, including esters, acids, alcohols, aldehydes, ketones, phenols, nitrogen heterocycles, and sulfur compounds.[12] Baijiu can be generally classified into

Received: February 20, 2023
Accepted: April 11, 2023
Published: April 25, 2023

https://doi.org/10.1021/acsomega.3c01140
ACS Omega 2023, 8, 16356−16363

twelve categories based on their aroma types; however, strong, light, and sauce aroma-type baijiu are the three major aroma types.[13] Although sensory evaluation[14] and gas chromatography−mass spectrometry (GC−MS)[15] are the most common methods for baijiu analysis and classification, these techniques are time-consuming and labor-intensive.

Various E-nose technologies have been used for Chinese baijiu analysis for detecting baijiu authenticity, brand, origin, and age. GC-based E-nose has successfully distinguished baijiu of different aroma types and origins with correct classification rates for aroma and region of 91.5 and 93.9%, respectively.[16] MOS-based E-nose was successful in discriminating different ages of baijiu by principal component analysis (PCA) and linear discriminant analysis (LDA).[17] A QCM-based E-nose with multidimensional scaling and support vector machine algorithms can classify ten baijiu brands.[18] However, the interaction mechanisms of the sensor with the volatile compounds in the baijiu matrix have never been reported.

This study aimed to understand the dynamic responses of MOS sensors on different classes of volatile compounds and further study the potential application of the MOS-based E-nose system in the discrimination of different Chinese baijiu samples.

■ MATERIALS AND METHODS

Reagents and Chemicals. Ethanol of HPLC grade (≥99.8%) was purchased from Supelco (Darmstadt, Germany). All chemical solvents used in this study were of GC grade. Ethyl acetate (99.5%), ethyl butanoate (99.0%), ethyl hexanoate (99.0%), butanal (>98.0%), 1,1-diethoxybutane (97.0%), and 1-butanol (≥99.0%) were purchased from J&K Chemical Corporation (Beijing, China). Methanol (≥99.9%), benzyl alcohol (analytical standard), *m*-cresol (analytical standard), *o*-cresol (≥99.0%), (−)-terpinen-4-ol (≥95.0%), *β*-damascenone (≥90.0%), butanoic acid (≥99.0%), hexanoic acid (≥99.5%), lactic acid (≥98.0%), and acetaldehyde (≥99.5%) were purchased from Sigma−Aldrich (Shanghai, China). Benzeneacetaldehyde (≥90.0%) was purchased from Alfa Aesar (Tewksbury, MA, USA). Ethyl propanoate (98.0%), ethyl pentanoate (98.0%), ethyl heptanoate (>97.0%), ethyl octanoate (>98.0%), ethyl 2-methylpropanate (>99.0%), ethyl 3-methylbutanoate (>99.0%), 1-propanol (>99.5%), 2-butanol (>99.0%), 2-methylpropanol (>99.0%), 1-pentanol (>99.0%), 3-methylbutanol (>99.0%), 1-hexanol (>98.0%), butanal (>98.0%), 2-methylpropanal (>98.0%), 3-methylbutanal (>98.0%), hexanal (>95.0%), heptanal (>95.0%), 1,1-diethoxyethane (>98.0%), phenol (>99.5%), *p*-cresol (>99.0%), guaiacol (>98.0%), phenethyl alcohol (>98.0%), ethyl benzoate (>99.0%), 4-ethylguaiacol (>97.0%), ethyl phenylacetate (>99.0%), ethyl 3-phenylpropanoate (>98.0%), *β*-caryophyllene (>90.0%), (+)-limonene (>95.0%), linalool (>96.0%), *β*-ionone (>95.0%), (+)-menthol (>99.0%), 2,6-dimethylpyrazine (>98.0%), 2,3,5-trimethylpyrazine (>98.0%), 2,3,5,6-tetramethylpyrazine (>98.0%), and furfuryl (98%) were purchased from TCI Chemical Co., Ltd. (Shanghai, China). Acetic acid (99.5%) and (−)-*α*-pinene (≥99.0%) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Purified water was prepared with a Milli-Q water purification system (Millipore, USA).

Samples. A total of six aroma types of Chinese baijiu were collected, including strong, light, sauce, rice, laobaigan, and feng aroma types. All baijiu samples were purchased from a local market and were stored at room temperature in the dark before analysis. The detailed sample information is listed in Table S1.

Instrument and Operation. A PEN3 portable E-nose (Airsense Analytics GmbH, Schwerin, Germany) was employed to analyze volatile compounds and baijiu samples. The system contains an array of 10 metal oxide thick film gas sensors labeled as S1 (W1C), S2 (W5S), S3 (W3C), S4 (W6S), S5 (W5S), S6 (W1S), S7 (W1W), S8 (W2S), S9 (W2W), and S10 (W3S).

The E-nose operation parameters were set as follows: presampling time, 5 s; measurement time, 60 s; flushing time, 90 s; chamber flow rate, 200 mL/min; injection flow rate, 200 mL/min; and non-dilution mode. The data collection time ranged from 46 s to 50 s for each detection, and the response value of each sensor was G/G_0, while G and G_0 being the resistance value of the sensor when exposed to sample volatiles and clean air, respectively. Each sample was analyzed at least three times.

Headspace Sampling Optimization. The container volume of headspace sampling was optimized first to obtain an ideal headspace condition and achieve a steady sensor response. Different volumes of containers (50, 100, 250, 500 mL, and 5 L glass bottles and 10 L airtight PTFE gas sampling bags) were selected, filled with pure nitrogen (99.99%), and 15 μL of ethanol was added and tested immediately. The sample container with the longest stable response curve was chosen for further experiment.

Response of Sensors for a Single Aroma Compound. A total of 52 volatile compounds were selected to study the responses of different sensors. An aliquot of 15 μL of individual pure aroma compound was injected into a 10 L gas sampling bag, and then the bag was filled with pure nitrogen (99.99%). The sample was equilibrated at 25 °C for 5 min, and subjected to testing.

The headspace concentration of aroma compounds is defined as the mass-volume concentration of 15 μL compounds after being completely volatilized in the 10 L sampling bag (eq 1).

$$C_A = (10^3 \times V_A \times \rho)/V_B \tag{1}$$

where V_A (15 μL) and V_B (10 L) are the volumes of the added sample and the volume of the sampling bag, respectively; ρ is the density of the compound (g/cm^3); and C_A (μg/L) is the headspace concentration after the compound was completely volatilized.

Effect of Volatile Concentration on Sensor Responses. *Effect of Ethanol Concentration on Sensor Responses.* Various amounts of 52% ethanol (v/v) (1, 2.5, 5, 10, 20, 30, 50, 75, and 100 μL) were added into 10 L sampling bags, which were then filled with pure nitrogen (99.99%). The sample was equilibrated at 25 °C for 5 min and subjected to analysis.

Effect of Ethyl Hexanoate Concentration on Sensor Response. Different amounts of ethyl hexanoate (1, 2.5, 5, 10, 20, 30, 50, 75, and 100 μL) were added to 10 L sampling bags and analyzed the same way as described previously.

Sensor Responses of a Binary Mixture of Ethanol and Ethyl Hexanoate. Ethyl hexanoate solutions (1, 2, and 5% v/v) were prepared in 52% ethanol (v/v), then 15 μL mixture was injected into the sampling bag, and sensor responses were obtained following the above operation steps. Blank ethanol (52%, v/v) was used as the control.

Chinese Baijiu Model. Three different aroma types of the baijiu model systems (strong aroma, light aroma, and sauce aroma) and the corresponding components of Strong aroma model (acids, esters, and alcohols) were prepared in 52% ethanol with standard compounds (v/v) (Table S2). The model systems were analyzed with the same protocol as described previously.

Commercial Chinese Baijiu Analysis. Twenty-six different aroma types of baijiu samples (listed in Table S1) were analyzed using the E-nose according to the protocol described previously.

Data Analysis. The raw data from the E-nose detection were subjected to statistical analyses, including PCA, LDA, and loading analysis. The WinMuster software program (version 1.6.2) bundled with the PEN3 E-nose instrument was used for data analysis.

■ RESULTS AND DISCUSSION

Headspace Sampling Size Selection. Earlier studies using PEN3 E-nose were conducted in a small glass vial,[19] and different headspace methods were employed according to the volatility of aroma compounds in the food matrices.[20] For Chinese baijiu, a 250 mL glass jar[21] and a 500 mL glass beaker[17] were employed in previous studies. However, the basis for the sampling has not been explored.

It is well known that the signal of a MOS sensor reflects the interactions of the volatile compounds with the sensors. Steady signal output is necessary for achieving the representative and reproducible sensor signal profile. However, the signals of the sensors were not steady during headspace sampling. Figure 1 illustrates the sensor response during typical sampling time. At a small sample size (Figure 1A−C), the sensor signals rose quickly and then decreased due to the depletion of the volatile in the headspace, and a steady response could not be achieved at small sample headspace. However, the responses became more stable with increasing headspace volume, and a steady response curve could be obtained using a 10 L sampling bag. This is because a larger container can provide a sufficient volume of headspace for sampling, the gas−liquid phase equilibrium can be maintained during the period of sampling time, and the concentration of the collected gas is consistent. Thus, for subsequent studies, volatile compounds were added into a 10 L PTFE headspace bag filled with pure nitrogen (99.99%) and sealed. The temperature was kept at 25 °C for 5 min to equilibrate the sample in the headspace.

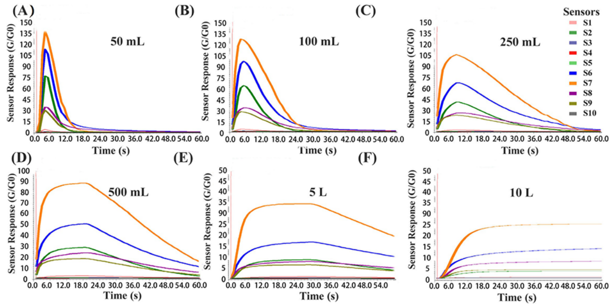


Figure 1. Response curves to data from different headspace sampling containers (each response curve represents the G/G_0 value variation of each sensor with time when the sample's volatiles entered in the measurement chamber): (A) 50 mL; (B) 100 mL; (C) 250 mL;(D) 500 mL; (E) 5 L; (F) 10 L.

Sensor Response for Individual Volatile Compounds. More than 2000 volatile compounds have been identified in Chinese baijiu, mainly esters, alcohols, and acids.[22] Esters are the most abundant compounds, contributing to fruity and floral aromas, and they present a dominant role in odor contribution in Chinese baijiu, especially the strong aroma-type baijiu. While alcohols contribute to alcoholic odors, acids contribute to sweaty and cheesy notes. In addition, many other volatile compounds, some at low concentrations, can also be important because of their unique aroma contribution. For example, pyrazine is a group of nitrogen-containing compounds contributing to toasting, nutty, and baked odors in Chinese baijiu.[12] Thus, it is vital to understand how the E-nose would respond to these compounds.

It has been reported that S2 (W5S), S6 (W1S), S7 (W1W), S8 (W2S), and S9 (W2W) sensors have high responses for nitrogen oxides, methane, sulfide, alcohols—aldehydes—ketones, and aromatic-organic sulfide, respectively.[23] However, it is not known how these MOS sensors respond to volatile compounds in alcoholic beverages. Thus, various classes of volatile compounds, including fatty acid esters, short-chain fatty acids, alcohols, aldehydes, acetals, aromatics, terpenes, and pyrazines, were investigated. The results revealed that different sensors responded to the group of compounds differently. In general, S2, S7, and S9 were more responsive than other sensors for these compounds (Figure 2). The response profile was similar for the same class of compounds.

Different classes of volatile compounds had different response orders. The response orders were S2 > S7 > S6 ≥ S9 for alcohols, but for aldehydes and esters, the sensor response order was S7 > S2 ≥ S9. Similarly, the sensor response order for fatty acids was S7 > S9 ≥ S2. Acetals, aromatics, terpenes, and pyrazines all had the same order S7 > S9 ≥ S2. It is worth noting that lactic acid and β-damascenone had no sensor response in this study (Figure S1). These results did not agree with the supplier's recommendation.

Difference classes of compounds had different response intensities on the sensors (Figure 2), and the main sensor responses (S2, S6, S7, S8, and S9) of esters and aldehydes were higher than those of other classes of compounds, and alcohols had the lowest responses. Furthermore, each sensor has different response values to individual compounds; with increasing carbon chain number, the S2 response intensities of alcohols increased; the S6 and S8 response intensities of esters decreased; and the S7, S9, S6, and S8 response intensities of aldehydes decreased. The response value of each sensor varied with the class of the volatile compound.

Each characteristic sensor response was further compared with the highest sensor (S7) (Table 1). The results suggested that the characteristic sensor response for a single chemical compound was a combination of sensitive sensors of S2 (W5S), S6 (W1S), S7 (W1W), S8 (W2S), and S9 (W2W) with different response intensities.

Effect of Volatile Concentration on Sensor Responses. *Ethanol.* Ethanol is the most abundant volatile compound in baijiu, as well as other alcoholic beverages, and the alcohol strength of commercial Chinese baijiu is mostly set as 52% ethanol (v/v). Thus, 52% ethanol (v/v) was used to investigate the effect of ethanol concentration on sensor responses.

The sensor responses to ethanol quantity (volumes of 52% ethanol (v/v)) are illustrated in Figure 3A. The results revealed that S7, S6, S2, S8, and S9 were the characteristic sensors for

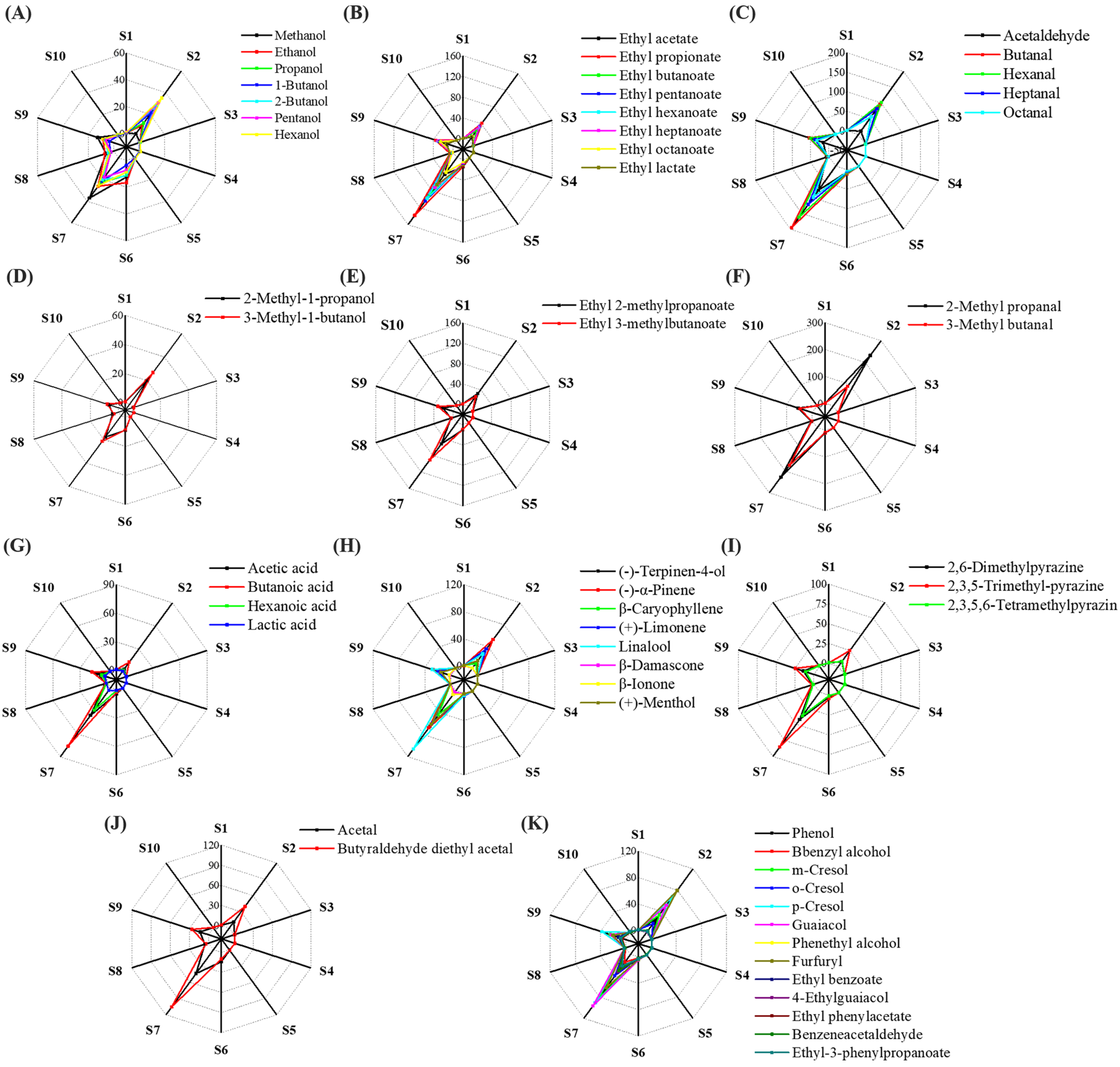


Figure 2. Radar maps of the sensor response of (A) straight-chain alcohols, (B) straight-chain esters, (C) straight-chain aldehydes, (D) branched-chain alcohols, (E) branched-chain esters, (F) branched-chain aldehydes, (G) acids, (H) terpenes, (I) pyrazines, (J) acetal, and (K) aromatics.

ethanol. In addition, S1, S3, S4, S5, and S10 did not change at different ethanol concentrations. As shown in Figure 3A, the response intensity for S7 increased rapidly with ethanol quantity and peaked at 75 μL. Interestingly, the response of some sensors showed good linearity within a specific range of the ethanol (v/v). For example, the coefficient of determination (R^2) for sensor S7 was higher than 0.98, which indicated that the concentration of ethanol could potentially be measured by the electronic nose when the amount of 52% ethanol (v/v) was under 75 μL.

Ethyl Hexanoate. Ethyl hexanoate, which contributes to an important fruity aroma, is the predominant volatile compound in strong aroma-type baijiu and is considered one of the grade indicators to quantify the quality of strong aroma-type baijiu by the Chinese national standard GB/T10781.1 <Quality requirement for Baijiu, Part I: Nongxiangxing baijiu>.[24] The concentration of ethyl hexanoate varied in different aroma types of baijiu, ranging from 10^1 to 10^3 mg/L,[25,26] so it was necessary to study the sensor responses of ethyl hexanoate at different concentrations to better understand the effect of ethyl hexanoate on the overall response of Chinese baijiu.

The characteristic response sensors for ethyl hexanoate were S7, S2, and S9 (Figure 3B). Similar to ethanol, the responses of the characteristic sensors increased linearly with ethyl hexanoate and reached the peak values. The response of S7 increased rapidly with the amount of ethyl hexanoate and showed good linearity in the range of 1 to 30 μL (R^2 of the linear relationship >0.99). Different sensors had different linear response ranges. For example, the response of S6 continued to increase even S7, and S9 reached a plateau. The results further suggested that the E-nose could differentiate concentration differences in a specific range.

Table 1. Characteristic Sensors of Each Aroma Compound and Their Relative Abundances to S7[a]

	S2 (W5S)	S6 (W1S)	S7 (W1W)	S8 (W2S)	S9 (W2W)
compound	S2/S7	S6/S7	G_0/G	S8/S7	S9/S7
esters					
ethyl acetate	23%	36%	1	17%	33%
ethyl propanoate	30%	10%	1	5%	26%
ethyl butanoate	26%	11%	1	4%	32%
ethyl pentanoate	30%	9%	1	3%	29%
ethyl hexanoate	33%	9%	1	3%	34%
ethyl heptanoate	39%	15%	1	5%	58%
ethyl octanoate	31%	18%	1	6%	74%
ethyl lactate	16%	16%	1	10%	22%
ethyl 2-methylpropanoate	58%	21%	1	9%	42%
ethyl 3-methylbutanoate	26%	11%	1	4%	35%
alcohols					
methanol	5%	34%	1	16%	34%
ethanol	36%	63%	1	27%	32%
1-propanol	52%	49%	1	17%	32%
1-butanol	96%	16%	1	12%	16%
2-butanol	136%	58%	1	21%	34%
1-pentanol	159%	40%	1	13%	37%
1-hexanol	139%	34%	1	12%	34%
2-methylpropanol	111%	50%	1	22%	37%
3-methylbutanol	122%	41%	1	15%	36%
aldehydes					
acetaldehyde	14%	8%	1	8%	20%
butanal	49%	5%	1	2%	27%
hexanal	62%	5%	1	1%	32%
heptanal	67%	5%	1	1%	32%
octanal	56%	5%	1	2%	33%
2-methylpropanal	101%	5%	1	2%	24%
3-methylbutanal	52%	5%	1	2%	28%
acetals					
1,1-diethoxyethane	25%	33%	1	14%	30%
1,1-diethoxybutane	38%	10%	1	4%	25%
aromatic					
furfuryl	109%	8%	1	4%	37%
phenol	28%	3%	1	1%	25%
benzyl alcohol	40%	26%	1	13%	59%
m-cresol	35%	3%	1	1%	25%
p-cresol	18%	2%	1	1%	12%
o-cresol	70%	4%	1	1%	39%
guaiacol	53%	5%	1	2%	24%
phenethyl alcohol	10%	9%	1	4%	27%
ethyl benzoate	10%	9%	1	5%	37%
ethyl phenylacetate	13%	10%	1	5%	26%
4-ethylguaiacol	2%	2%	1	1%	9%
benzeneacetaldehyde	13%	7%	1	3%	26%
ethyl 3-phenylpropanoate	8%	4%	1	4%	23%
terpenes					
(−)-terpinen-4-ol	16%	3%	1	2%	24%
(−)-*α*-pinene	78%	6%	1	2%	41%
(+)-limonene	63%	7%	1	3%	35%
linalool	25%	3%	1	1%	27%
(+)-menthol	24%	1%	1	1%	25%
β-ionone	18%	16%	1	13%	39%
β-caryophyllene	22%	4%	1	2%	35%
pyrazines					
2,6-dimethylpyrazine	18%	6%	1	5%	33%
2,3,5-trimethylpyrazine	29%	5%	1	3%	29%
2,3,5,6-tetramethylpyrazine	22%	2%	1	3%	30%
acids					
acetic acid	11%	13%	1	6%	28%
butanoic acid	17%	4%	1	2%	22%
hexanoic acid	8%	4%	1	3%	21%

[a] Note: *β*-damascenone and lactic acid did not respond and are not listed here.

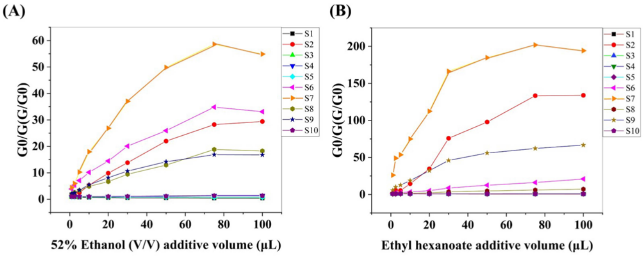


Figure 3. (A) Scatter plot of different volumes of 52% ethanol (v/v); (B) scatter plot of different concentrations of ethyl hexanoate.

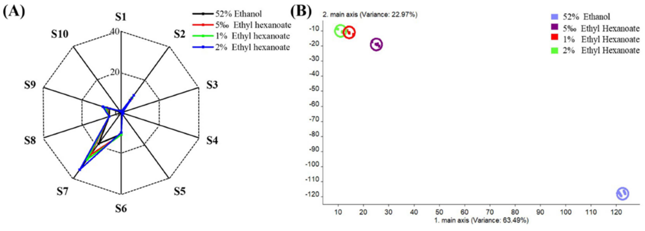


Figure 4. (A) Radar maps and (B) PCA diagram of different concentrations of ethyl hexanoate in 52% ethanol (v/v).

Mixtures of Ethanol and Ethyl Hexanoate. Due to its high concentration, ethanol might produce a strong signal background, which would interfere with the signals generated by other volatile compounds and weaken the ability to distinguish odors.[27] Different concentrations of ethyl hexanoate (0.05, 1, and 2%) in 52% ethanol (v/v) were studied to better understand the interaction of ethanol with ethyl hexanoate. In Figure 4A, the lowest response intensity value was detected in 52% ethanol (v/v). S7, S2, S6, S9, and S8 were characteristic sensors of the mixed samples, and the response intensities of S2, S7, and S9 increased with the proportion of ethyl hexanoate (from 0.05 to 2%), while no changes were seen in S6 and S8. PCA showed that three clusters were clearly separated according to the PC1 loading values (Figure 4B). This result suggested that although ethanol has a high response background, the E-nose, coupled with statistical analysis, could tentatively distinguish slight differences in the content of aroma compounds.

Sensor Response to Different Chinese Baijiu Model Systems. *Response of the Baijiu Model System.* Chinese baijiu can be classified into twelve categories based on its aroma characteristics, including strong, light, and sauce aromas. The sensory properties are significantly different among these aroma types of baijiu because the volatile compositions vary in different baijiu. Three main baijiu model systems, including strong, sauce, and light aroma-type baijiu models, were designed to discuss the response of the E-nose to the multiplex baijiu system in depth.

Aroma compounds with concentrations greater than 100 mg/L were selected to mix baijiu models at concentrations typically in actual baijiu samples. WLY, MT, and FJ are the representatives of the strong, sauce, and light aroma-type baijiu, respectively. LDA analyzed the sensor response relationship between these baijiu and their corresponding baijiu models, and the results showed that all of the samples were ideally classified, and that each model was closely clustered with the type of baijiu it represented. There was a blatant discrimination among the various clusters representing different aroma types of baijiu and their models (Figure 5A). This result suggested that their characteristic sensor responses had specific differences. However, the projections of the three groups of baijiu partially overlapped with their corresponding baijiu models on the LD1 axis, indicating that they have some similar sensor responses. It is speculated that those skeleton compounds in baijiu could significantly contribute to the overall sensor response of baijiu.

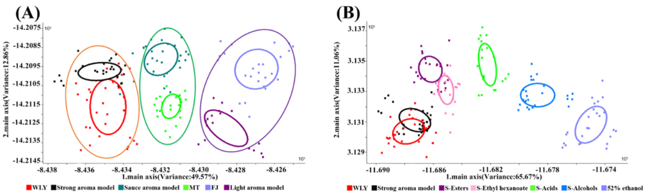


Figure 5. (A) LDA of three different aroma types of baijiu and their baijiu models; (B) LDA of Wuliangye and its corresponding model components.

Volatile Compounds Contribution to Strong Aroma-Type Baijiu and Model. Strong aroma-type baijiu was set as an example to explore which type of aroma compound contributes to the overall sensor response in recognizing Chinese baijiu. In addition, the sensor responses from different classes of volatile compounds were investigated.

In Figure 5B, the order of the LD1 axis from left to right was WLY, strong aroma model, S-ester mixture, S-ethyl hexanoate, S-acid mixture, S-alcohol mixture, and 52% ethanol. Among them, the data points of the WLY and strong aroma model clustered closely and partially overlapped, which suggested that the strong aroma model can reflect the main response characteristics of WLY. Compared with S-alcohols and S-acids, the distances between S-esters and WLY were shorter, indicating that esters could have a dominant contribution to the overall response of WLY.

Application of E-Nose in Chinese Baijiu Classification. *Different Aroma Types of Baijiu.* Six aroma types of baijiu were studied to investigate whether the E-nose can distinguish different baijiu. LDA was used to distinguish six aroma types of baijiu (strong, light, sauce, rice, laobaigan, and feng aroma-type baijiu). The results of the two-axis analysis showed that LD1 accounted for 89.75% of the data variance and LD2 accounted for 3.40%, and the cumulative contribution was higher than 90%, indicating that these two principal components could reflect the overall information of the volatile compounds of different aroma types of Chinese baijiu.

An obvious separation of different aroma types of baijiu was achieved, and all samples were ideally classified (Figure 6A). It is worth noting the WLY sample (representative brand of strong aroma-type baijiu) was located on the right side of Axis 1. MT samples (sauce aroma-type baijiu) were found on the upper side of Axis 2 and the middle of Axis 1. The XF sample was a Feng aroma-type baijiu derived from light aroma-type but combined the production process of light and strong aroma-type.[28] Its aroma and taste were characterized by both light and strong aroma-type baijiu. The sensory attributes agreed with LDA that XF was located between WLY and FJ (light aroma-type baijiu), and closer to FJ. LBG and GLSH are representatives of Laobaigan and rice aroma-type baijiu, and they were close to each other in LDA.

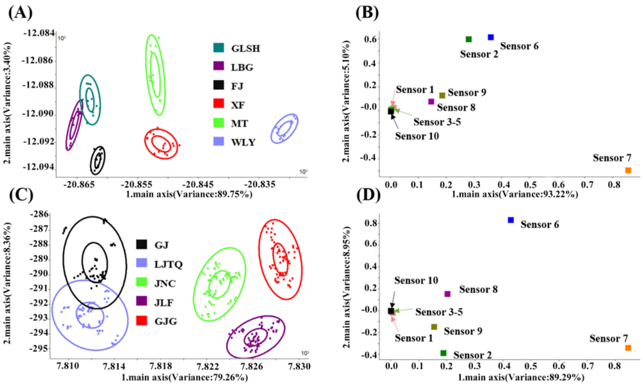


Figure 6. (A) LDA and (B) loading analysis diagram of six aroma types of baijiu, (C) LDA and (D) loading analysis of five brands of strong aroma-type baijiu.

In the loading analysis, the sensor response near the center (0, 0) of the loading diagram contributed less to the total response of the array. The loading diagram (Figure 6B) showed the relative importance of the sensors in the array. S2, S6, and S7 had high loading values, with LD1 > 0.3 and LD2 > 0.5. This result suggested that these sensors were the main response sensors classifying the aroma type of Chinese baijiu, while sensors S1, S3−S5, and S10 had loading values of 0, indicating that these sensors cannot effectively identify the aroma type of Chinese baijiu.

Differentiating Different Brands within the Strong Aroma-Type Baijiu. Five different brands of strong aroma-type baijiu (Jinliufu, Jiannanchun, Gujinggong, Laojiaotequ, and Guojiao 1573) were analyzed in this study. In general, this sensor array in the E-nose was able to classify the different brands of strong aroma-type baijiu (Figure 6C). As demonstrated in Figure 6C, the total contribution of LD1 and LD2 was 87.62%, and most of the samples could be well discriminated except for a few overlaps. The characteristic values of the five brands of strong aroma-type baijiu on LD1 can be clearly divided into two regions. Samples produced from pure sorghum (GJ and LJTQ) were located on the left side of the LD1 axis, while samples produced from multiple grains (JNC, JLF, and GJG) were located on the right side of the LD1 axis. In addition, there was a small overlap between the GJ and LJTQ samples. Indeed, these two samples came from the same manufacturer and had similar flavor characteristics.

On the other hand, the GJG sample was located on the right-most side of Axis 1 and clearly separated from the other brands of strong aroma-type baijiu, which may be because it was produced in Anhui Province, China, and the other four strong-aroma baijiu were all produced in Sichuan Province, China.

The loading analysis showed that S7 and S6 were the main sensors for brand differentiation within the strong aroma type of baijiu (Figure 6D). Sensors S1, S3, S4, S5, and S10 had very small contributions. Removing sensors with low contributions could improve the experimental performance.[29] These results could facilitate further optimization of the sensors and improve the ability of the E-nose to recognize different aroma types of baijiu and brand differentiation.

CONCLUSIONS

In this study, the responses of MOS sensors in the E-nose to different volatile compounds in alcoholic beverages were investigated for the first time. The MOS E-nose presented different characteristic sensor profiles for different classes of volatile compounds but similar characteristic sensor profiles within the same class of compounds. The relationships of sensor response with the concentration were also studied. The dose−response relation was found for some sensors within a specific concentration range. Different aroma types of Chinese baijiu and different brands of strong aroma-type baijiu were successfully classified using the E-nose. This study provided an understanding of detailed MOS sensor response with volatile compounds, which could be further applied to improve E-nose technology and practical application in the classification of different Chinese baijiu and other alcoholic beverages using the MOS E-nose.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c01140.

> List of Baijiu samples used in this study; composition of the three aroma types of baijiu models; and sensor response curves of lactic acid, β-damascenone and blank sample (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This study was sponsored by Yibin High-tech Program, grant number 2021GH001.

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https://doi.org/10.1021/acsomega.3c01140
ACS Omega 2023, 8, 16356−16363