Rapid Quantification Analysis of Alcohol During the Green Jujube Wine Fermentation by Electronic Nose

Guifeng Li¹, Lu Yuan¹, Xiaonan Wang¹, Yaxu Meng¹, Jing Li¹, Yunsong Zhao¹, Yankun Peng²
¹ Department of Food Science, Shanxi Normal University, Linfen 041000, China
² College of Engineering, China Agricultural University, Beijing 100083, China
*Corresponding author’s e-mail: liguifeng99@163.com

Abstract. In order to explore the applicability of electronic nose technique for alcohol dynamic change, electronic nose was used to predict the alcohol content of the green jujube wine fermentation. The principal component regression (PCR) and multiple linear regression (MLR) were applied to establish the forecast model of the alcohol content. The results showed that the response values of sensors S1, S8, S3, S5 and S4 were the largest among the 10 sensors and changed significantly during 7 days of fermentation. The linear simulation equation was established by using the MLR to predict the alcohol content and the R² value was 0.949, and the RMSEC was 0.974. The model shows the better predict alcohol content correlation (R²=0.946) and RMSEP (1.016). The results show that it is feasible to use the electronic nose system to analyses alcohol content dynamic chance of the green jujube wine fermentation, and electronic nose technique provides a method for rapid quantification analysis of alcohol of wine fermentation.

1. Introduction
In recent years, with the development of economy and the improvement of people's living quality, the requirement of food nutrition value and health efficacy is becoming higher and higher, the wine industry is turning a corner gradually. Fruit wine has the advantage of high nutritional value, strong health care effect and unique flavor, which is trusted and liked by consumers. The fruit wine is developing rapidly in the wine market, and it’s future trend is pretty good. At present, it is necessary to focus on promoting innovative products such as new fruit wine, and solve the core production technology and rapid detection technology of fruit wine.

Jujube is cultivated all over our country, rich in protein, minerals and vitamins. It is a health product integrating medicine, food and tonic. However, due to the high output of Jujube in China, the products are seriously unsalable, the benefits are reduced, the losses of jujube farmers are serious, which greatly affects the sustainable development of jujube industry. In order to solve the problem of the development of jujube industry, to change the current situation of the depressed jujube industry, it is urgent to develop new products of jujube and solve the production technology of products. Popular both at home and abroad under the situation of high nutrition health food, this research focuses on the development of new elaborated wine products and to solve wine alcohol during the fermentation process of continuous change information rapid detection. The research adjusts production process conditions and ensures the high-quality product. Due to the time-consuming, cumbersome and low accuracy of traditional detection methods, it is difficult to meet the requirements of producing rapidly...
and timely. However, the Electronic nose is a new instrument that integrates the functions provides for analysis, identification and detection of complex volatile components, featuring fast detection speed, simple operation, high sensitivity and good reproducibility [1].

Electronic nose simulates human’s sense of smell and uses pattern recognition technology to identify and process sensor array response information for detection, which meets the requirements of modern detection such as fast, real-time, accurate and non-destructive [2]. Now, the rapid detection of electronic nose technology is used in alcohol detection of exploration and research. Buratti’s team used electronic nose and electronic tongue to monitor the aroma and taste of the wine phase change [3]. XU Wan-xiu’s team used electronic nose technology to detect Chinese liquor wine age [4]. ZHANG Shu-ming’s team used the combination of near infrared reflectance spectrum (NIRS) and electronic nose to analyze the alcohol content in grape wine process of fermentation [5]. ZHOU Hui-min’s team used electronic nose system to predict Shao Xing rice wine total sugar content [6]. The existing using electronic nose technology research mainly set in wine identification, wine age detection, aroma components and sugar analysis. There are few studies on the on-line policy analysis of alcohol content of the fermentation process of fruit wine (especially jujube wine). This study elaborates electronic nose technology in the process of wine fermentation policy analysis the changes of alcohol and using linear discriminant analysis (LDA) to distinguish the company’s fermentation times elaborated wine. The established model could predict the alcohol content of wine fermentation stage. The methods provide a set of efficient, accurate and rapid analytical methods for alcohol quantitative online monitoring in fruit wine fermentation process.

2. Materials and methods

2.1. Sample preparation and reagents
The brewing process of jujube wine:

Ju jube → cleaning → nucleating → heating and softening → killing enzyme → adding sugar to adjust the sugar concentration → adding yeast → fermentation → filtration → aging → canning → sterilization → finished product.

Taking 9 fermenting glass pots, then put the jujube juice with the sugar concentration of 20%, 24% and 26% into the fermentation tank marked with numbers 1-3, 4-6 and 7-9. Jujube juice from add yeast to the fruit wine fermentation, a total of 7 days, 26 ℃ fermentation temperature. Samples are taken at a fixed time every day from the first day to the seventh day of fermentation, and the alcohol content is measured with alcohol meter and electronic nose respectively. The yeast is active dry wine yeast of Angel, and the sugar used in the experiment was commercially available sugar.

2.2. Instruments and equipment
Alcohol meter, will instrument factory of Wuqiang City in Hebei Province; PEN3 portable electronic nose, German company Airsense. PEN3 electronic nose contains 10 metal oxide sensor arrays: S1 (W1C aromatic benzene), S2 (W5S nitrogen oxide), S3 (W3C ammonia), S4 (W6S hydrogen), S5 (W5C alkanes), S6 (W1 S methane), S7 (W1W hydrogen sulphide), S8 (W2S ethanol), S9 (W2W organic sulphide) and S10 (W3S aromatic alkanes). S1-S 10 is expressed as response signal strength of 10 sensors.

2.3. Methods

2.3.1. Determination of alcohol content. The alcohol content was determined by alcohol meter (GB 5009.225-2016) [7], the measurement result was the volume percentage of alcohol, namely the alcohol content (%) Each sample was repeated for 3 times, and the difference between the measurement results was within 0.5%.
2.3.2. **Electronic nose data collection.** The alcohol content of jujube wine was determined by electronic nose. Before the test, 10mL of the removed sample was placed in a 20ml test tube sealed with plastic wrap and placed for 10 mins to allow volatile substances to accumulate and reach an equilibrium state before the electronic nose test. To start the test, click the "clean" icon to start cleaning, and keeping it stables for a period of time until the baseline recombination to obtain the base value of the measurement, and then carrying out the sample measurement. The volatile gas was passed through the electronic nose sensor at a flow rate of 600 mL/min, and the sampling time of the electronic nose was 80s. After each sample was measured, the recovery time of the electronic nose was 300 s, so as to ensure that the electronic nose was fully restored to the base valued state, and then carry out the measurement of the next sample [8]. A total of 63 samples were taken at a fixed time every day from the first day to the seventh day of fermentation, and 3 parallel tests were conducted for each sample.

2.4. **Data analysis**

Experimental results using PEN3 electronic nose system data processing software Win Muster, sorting and principal component analysis (PCA) on the test data and linear discriminant analysis (LDA); SPSS 19.0 and excel software are used to extract the characteristic values of the signal response values obtained by electronic nose measurement, analyze and process them, and establish and verify the model. The determination coefficient (R²), root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) of the model are selected as evaluation indexes for the quantitative results of the model. The higher the R² is, and the smaller the RMSEC and RMSEP are, the better the prediction effect of the model is [9].

3. **Results and analysis**

3.1. **Sample alcohol content analysis**

Alcohol content is an important index in the process of fruit wine brewing. The accurate detection of alcohol is an important guarantee for the production of qualified fruit wine. It is an important method for many wineries in China to monitor the alcoholic fermentation stage and also a method for determining the national standard alcoholic content. Table 1 shows the measured and predicted results of alcohol content in the fermentation of jujube wine.

The quality of the established model depends largely on the detection accuracy of sample standard values and the coverage of sample evaluation parameters. The alcohol content of 189 samples in this experiment covers high, medium and low levels, and presents normal distribution basically, indicating that the samples have good representativeness, and the quality of the model established on this basis is reliable.

| Parameter          | Sample type | Sample number | Maximum | Minimum | AVG  | SD   |
|--------------------|-------------|---------------|---------|---------|------|------|
| Alcoholic strength | Measured    | 189           | 14.8    | 2.0     | 11.19| 4.85 |
|                    | Predicted   | 21            | 15.34   | 2.85    | 11.28| 4.19 |

3.2. **Signal response of electronic nose to sample alcohol precision**

The response curve of 10 metal oxide semiconductor type chemical sensor elements in the PEN3 electronic nose sensor for the detection of jujube wine samples is shown in figure 1. Each curve in the figure represents a sensor. The response signals of each sensor show a trend of increasing first and then decreasing with the change of time, and the electronic nose response signals of each sensor tend to be stable after 60s. At the beginning of injection, the signal was strengthened with the increase of injection quantity. With the completion of sampling, the signal begins to decrease until reaching a stable state, so the maximum value of the response signal is selected for date analysis. As can be seen
from figure1, the response values of electronic nose sensors S1, S3, S8, S5 and S4 are relatively large, and the response signals of each sensor gradually strengthen with time and then tend to be stable. It can be seen that the electronic nose has an obvious response to alcohol and other volatile components in the fermentation of jujube wine, and the response values of each sensor are different, indicating that it is feasible to use the PEN3 electronic nose system to determine the change of alcohol content in the fermentation of jujube wine.

Figure 1. E-nose sensors signal intensity of jujube wine.

3.3. Principal component analysis of jujube wine during fermentation
Principal component analysis (PCA) is a statistical method of dimension reduction, multiple correlation indicators into several comprehensive index, the strong correlation of main components of general cumulative variance greater than 85% of the total variance can represent the characteristics of the original data basically [10]. PCA is a multivariate statistical analysis method, through orthogonal transformation to multiple variables through linear transformation to choose fewer important variables. The electronic nose sensor S1, S3, S8, S5 and S4 with large response values were selected for LDA analysis, Figure 2 PCA analysis of the electronic nose sensor signal of the green jujube fermentation broth after continuous fermentation for 7 days. The circles in different areas in the figure respectively represent the collection of points of samples with different days of fermentation, and the numbers besides the circles are the days of fermentation. The distance between circles in the two-dimensional diagram indicates the level of the discrimination. With the increase of distance, the degree of differentiation between different fermentation times became better. As can be seen from figure 2, the data collection points in the figure don’t overlap with different fermentation times, so the degree of differentiation of different fermentation times is relatively good. In the 40s analysis results, the first principal component (LD1) is 65.2%, the second principal component (LD2) is 21.8%, and the third principal component (LD3) is 6.8%. The cumulative contribution rate is up to 93.8%, higher than 85%. The results show that the three principal components have basically represented the main information characteristics of the samples.

3.4. Establishment of multiple linear regression model for electronic nose detection of alcohol content
The response signals of 10 sensors to the 60s of green jujube wine were taken as independent variables, while the alcohol content of green jujube wine was taken as dependent variables. Forty-two groups were randomly selected from the 63 groups of data measured by the samples for the establishment of the regression model, and the remaining 21 groups were used for the test of the established model. The prediction model was established by multiple linear regression method (MLR), and the regression model between the response value and the alcohol content of jujube wine was established as follows:
Alcohol content = 59.8642 + 135.6709S_1 + 0.0026S_2 - 141.4525S_3 + 1.8502S_4 - 56.2497S_5 - 0.1156S_6 + 0.0221S_7 + 89.9235S_8 - 0.1183S_9 + 0.4825S_10

R^2 = 0.949, RMSEC = 0.974

3.5. Test of multiple linear regression model for electronic nose detection of alcohol content
In order to test the reliability of the MLR model, the quality of the model was tested with 21 groups of samples in the test set. As can be seen from the scatter plot of the predicted and measured alcohol values (Figure 3), there was a high correlation between the predicted and measured values of the MLR model, with a high R^2 (0.946) and a low RMSEP (1.016). Thus, the MLR model can be used to predict the alcohol content of jujube wine during fermentation.

Figure 3. Correlation between measured and predicted values from MLR model for alcohol content.

4. Conclusion
The electronic nose technology is used to analyze the change of alcohol content during the fermentation of jujube wine rapidly and quantitatively, and the relationship between the response value of electronic nose gas sensor and the alcohol content during the fermentation of jujube wine is
determined by principal component analysis and multiple linear regression analysis, and establish an electronic nose detection model for alcohol.

The green jujube fermentation broth is fermented continuously for seven days. Response valued larger electronic nose sensors is the S1 (aromatic benzene class), respectively the S8 (alcohol), S3 (ammonia), S5 (alkane) and S4 (hydrogen), electronic nose. PCA of sensor signal, the contribution rate of LD1, LD2 and LD3 is respectively 65.2%, 21.8% and 6.8%. The cumulative contribution rate is 93.8%. It suggests the 3 principal components can represent the main characteristics of information of the sample.

The alcohol precision electronic nose detection model established by MLR is used, with R2 of 0.949 and RMSEC of 0.974. The determination coefficient of the predicted and measured alcohol precision of the model is high (R2=0.946) and the predicted standard deviation is low (RMSEP=1.016). The results show that the proposed model can be used to analyse the alcohol content in the fermentation process of jujube wine rapidly and quantitatively, and it is feasible to measure the alcohol content in real time in the fermentation process of jujube wine.

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