Application of Electronic Tongue in Detecting the Component of Yellow Water from Solid-state Fermentation Process

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Abstract: Yellow water is a brown-yellow, viscous, hazy liquid that is produced during the solid-state fermentation of liquor. Yellow water contains a large number of acids, esters, aldehydes, alcohols and other substances as well as the beneficial fermentation of micro-organisms, and it is a highly productive by-product. In this paper we analyzed the yellow water by using the sensor relaxation characteristics of the electronic tongue, established fisher functions to describe the basic features of yellow water, and used GRNN to model the sensor data to obtain a method for detecting alcohol, acidity, reducing sugar and residual starch in yellow water.

Keywords: yellow water; electronic tongue; general regression neural network; measurement technology; discrimination function analysis.

1. INTRODUCTION

Yellow water is the most valuable by-product from the fermentation process of Luzhou-flavor liquor. It is a brown-yellow, viscous, hazy liquid and is rich in alcohols, aldehydes, acids, esters and other aroma substances[1]. Furthermore, it contains many beneficial microorganisms domesticated for a long time[2]. At present, the main purpose of yellow water in the wine industry is mainly the following: (1) evaluating the quality of the fermentation through yellow water; (2) being esterification liquid for fermentation after particular treatments; (3) used for cultivating new cellars; (4) poured yellow water into the bottom pot for distillation to obtain base wine. The composition of yellow water can be used to evaluate the quality of the fermentation in the cellar and the condition of fermented grains[3]. At the same time, due to the extremely high utilization value of yellow water, the analysis of its components can make...
better use to carry out a series of production activities to increase the quality and efficiency of production and reduce environmental pollution.

There is extremely high utility value of yellow water in fermentation process, but the current detection method for yellow water is basically focused on liquid chromatography, gas chromatography, GC-MS, or physi-chemical method analysis\[4\]. Low efficiency makes the use of yellow water extremely cumbersome.

Electronic tongue is a rapid method for analyzing and identifying liquids. It mainly consists of sensors array, signal conditioning analysis and pattern recognition. The sensor responds to the liquid sample and outputs a signal. The signal conditioning system conditions and processes the signal, and after pattern recognition, the characteristics of the liquid can be analyzed\[5\]. Compared with instruments or physico-chemical method analysis, it has the characteristics of rapid measurement, simple operation and low sample consumption. Some researchers have used electronic tongues to identify and classify beverages, quality of wine, and vinegar fermentation process monitoring. At present, the classification and identification of electronic tongues have been widely used in the food industry, especially liquids, but detection of yellow water has been rarely studied\[6\]-\[9\].

### 2. MATERIALS AND METHODS

#### 2.1 Raw materials

Samples of yellow water were collected from different batches of a certain Luzhou-based winery in Yibin District.

#### 2.2 Detection Methods

2.2.1 Physico-chemical method analysis

The alcoholicity of yellow water was read with alcohol meter after evaporation and condensation, and converted to a standard reading at 20°C; The acidity was detected by acid-base titration with acetic acid; the reducing sugar was measured by Fihling reagent titration method; residual starch was transferred to glucose, and detected by Fihling reagent titration method.

2.2.2 Electronic Tongue Measurement

The sensors array of electronic tongue system consists of six inert noble metal electrodes. The six inert noble metal electrodes are a gold electrode, a palladium electrode, a silver electrode, a platinum electrode, a titanium electrode, and a tungsten electrode. The auxiliary electrode is a platinum electrode with a diameter of 2 mm, and silver/silver chloride (Ag/ACl) is used as the Reference electrode. Using the relaxation characteristics of the amplitude-frequency pulse detection material, the corresponding signals of the voltammetric characteristics of the respective substances are obtained.

Four times samples were taken for each sample, and 30 ml portions were measured. Set the initial voltage to start from +1V, the step down voltage is 0.2V, and the termination voltage is -1V. The sensor accuracy was set to 10-3. Each sample is measured in parallel at the frequency
of 1Hz, 10Hz and 100Hz for 4 times. the corresponding characteristic data of yellow water in different frequency bands was recorded and saved.

2.2.3 Analysis methods
The General Regression Neural Network (GRNN) is a variant of radial basis functions. GRNN is based on non-parametric regression, using the sample data as a posterior condition, and calculating the network output based on the principle of maximum probability. The generalized regression neural network is based on a radial basis network and is established on the basis of nonlinear regression. Therefore, it has good nonlinear approximation performance and is fast in training, especially in small sample learning. At present, it is mainly used in function approximation problems, signal processes, structural analysis, and control decisions. The generalized regression neural network has added a summation layer compared to the radial basis neural network. The basic mechanism network is shown in Figure 1.

![Basic model network of general regression neural network](Fig.1)

GRNN has strong advantages in approximating ability, classification ability and learning speed. The network finally converges to the optimized regression surface with the largest number of sample clusters, and the effect is better when the data is lacking. Therefore, when the sample size is small and the noise is high, the regression prediction effect is generally also ideal.

### 3. Results and Analysis

#### 3.1 Discriminant function analysis

Discriminant function analysis (DFA) is a statistical method for discriminating the type of a sample. First, according to known class of things, a technique is used to establish a function, then the identification of new things of an unknown class is classified into a known class\[^{[10]}\]. It is one of the common pattern recognition methods for electronic nose and electronic tongue. However, detection and analysis are relatively time-consuming and are generally used for short-term quality control\[^{[11]}\].
3.1.1 discrimination of different kinds of yellow water

Fig.2 Scatter plot based on discriminant function analysis by Fisher function

Figure 2 shows the linear discriminant analysis scatter plots based on the Fisher discriminant function analysis. It can be seen that the sample clusters have a clear clustering trend on the discriminant classification map, and the overall characteristics are far apart, and the same samples are closer together. Sample groups 9 and 10, sample groups 2 and 7 have very few overlaps, which proves that the discriminant function is not ideal in the discrimination of these sample groups, but the group center of each sample can be effectively distinguished, proving that the discriminant function analysis can effectively distinguish different groups of samples. Table 1 is a coefficients matrix based on Fisher discriminant function for yellow water. The significant is removed when the function whose feature value is too small. Each Fisher discriminant function consists of three coefficients and a constant whose basic form is:

\[ F(x) = u_1X_1 + u_2X_2 + u_3X_3 + \delta \]  

(1)

Tab.1 Fisher discriminant analysis classification function coefficients

<table>
<thead>
<tr>
<th></th>
<th>Coefficient 1</th>
<th>Coefficient 2</th>
<th>Coefficient 3</th>
<th>constant $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-39957075.7</td>
<td>36225159.15</td>
<td>-18721391.9</td>
<td>-4260.762</td>
</tr>
<tr>
<td>2</td>
<td>-42022122.4</td>
<td>38842839.21</td>
<td>-14950819.9</td>
<td>-4483.428</td>
</tr>
<tr>
<td>3</td>
<td>-4015857.2</td>
<td>3048598.84</td>
<td>-16122328.9</td>
<td>-3360.213</td>
</tr>
<tr>
<td>4</td>
<td>-41031578.4</td>
<td>3433200.95</td>
<td>-13522062.8</td>
<td>-4263.652</td>
</tr>
<tr>
<td>5</td>
<td>-45112185.9</td>
<td>562540.71</td>
<td>-8919531.592</td>
<td>-5788.879</td>
</tr>
<tr>
<td>6</td>
<td>-46214025.0</td>
<td>45487261.68</td>
<td>-1345852.0</td>
<td>-4855.925</td>
</tr>
<tr>
<td>7</td>
<td>-41225751.4</td>
<td>39838362.44</td>
<td>-14622148.8</td>
<td>-4087.325</td>
</tr>
<tr>
<td>8</td>
<td>-37968950.7</td>
<td>31510657.85</td>
<td>-19147920.2</td>
<td>-3534.607</td>
</tr>
<tr>
<td>9</td>
<td>-4419247.9</td>
<td>43498327.70</td>
<td>-12523896.7</td>
<td>-5516.671</td>
</tr>
</tbody>
</table>
Based on the above, DFA can be used to effectively distinguish the yellow water from the fermentation byproducts of different fermentation qualities of Luzhou-flavor liquor with the composition changes.

3.1.2 Rating Yellow Water Based on Yellow Water Components

According to the analysis of 3.1.1, based on Fisher's discriminant function analysis, the yellow water samples with different yellow water components can be classified and identified. In order to analyze the significance of sensor array, Fisher functions were established to classify different yellow water. The classification method is shown in Table 2. In Table 2, 1 corresponds to a low content, 3 indicates a high content of the substance, and 2 indicates a middle content of the substance.

<table>
<thead>
<tr>
<th>fraction</th>
<th>alcohol(%)</th>
<th>acidity(g/100g)</th>
<th>Reducing sugar(g/100g)</th>
<th>Residual starch(g/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(low)</td>
<td>3.3&lt;</td>
<td>4.5&lt;</td>
<td>2.6&lt;</td>
<td>2.6&lt;</td>
</tr>
<tr>
<td>2(middle)</td>
<td>3.3~4.5</td>
<td>4.5~6.0</td>
<td>2.6~4.5</td>
<td>2.6~4.0</td>
</tr>
<tr>
<td>3(high)</td>
<td>&gt;4.5</td>
<td>&gt;6.0</td>
<td>&gt;4.5</td>
<td>&gt;4.0</td>
</tr>
</tbody>
</table>

Figure 3 shows the results of discriminating the alcohol content, acidity, reducing sugar, and residual starch content.
From this figure, it can be seen that the composition ratios of the four substances in the training sample can be distinguished based on the established three Fisher functions, and the group centers in each group are more closely spaced. Far, and the group members rarely overlap or overlap, indicating that the level of the four substances can be better distinguished by discriminant analysis. In the analysis of the predicted samples, it can be seen from the figure that the sample features with close predictions of alcohol, acidity, and residual starch have a better aggregation of sample features, and that sample scatters of reducing sugar are not concentrated enough.

Table 3 shows the evaluation results for different components. From Table 3, it can be seen that when judging the four parameters of yellow water, the misjudgment number of residual starch is a little more. It is presumed that the possible reason is that the selected interval critical value is closer than the critical value of the interval, resulting in a poorly differentiated effect. The remaining three items have better discrimination results. The correct rate of four substances are all above 87.5%, and alcohol, acidity, reducing sugar are above 90%.

### Tab. 3 Results of discriminant analysis for different components of yellow water

<table>
<thead>
<tr>
<th>Preference</th>
<th>Alcohol</th>
<th>Acidity</th>
<th>Reducing sugar</th>
<th>Residual Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Actual number</td>
<td>Result of analysis</td>
<td>Actual number</td>
<td>Result of analysis</td>
</tr>
<tr>
<td>1(low)</td>
<td>4</td>
<td>4</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>2(middle)</td>
<td>12</td>
<td>12</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>3(high)</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Misjudged number</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Correct rate</td>
<td>100%</td>
<td>93.75%</td>
<td>100%</td>
<td>87.5%</td>
</tr>
</tbody>
</table>

### 3.2 Component detection of yellow water by electronic tongue and GRNN

In this experiment, 16 batches of yellow water samples were selected, all from Luzhou-flavor liquor company in Yibin District. In training, the data measured in the training set of 12
samples (number of sample sets) × 4 (repeat number) for a total of 48 samples were used as the training input, with their measured acidity, alcoholicity, reducing sugars, and Residual starch serves as the output. After several trainings, the number of hidden layers and the training step length of the neural network model are repeatedly modified to reconstruct four GENN models[12].

Using the coefficient of determination as an index of the evaluation model reflects the degree of fit of the regression model, and the value is between 0 and 1. The closer the value is to 1, the more significant the correlation is, and the more suitable the regression model is. For the established model, the regression model's coefficient of determination should be greater than 0.85. Only in this way can the data be well-fitted. If it is less than 0.85, the degree of fit is not high and the model is not applicable.

\[
R = \frac{\sum (\hat{y}_i - y_i)^2}{\sum (y_i - \bar{y})^2}
\] (5)

The sample standard deviation \( S \) was used to compare the prediction results of each parameter. The formula for calculating the standard deviation of the sample \( S \) is:

\[
S = \sqrt{\frac{\sum (\hat{y}_i - y_i)^2}{df}}
\] (6)

Where: \( \hat{y}_i \) - fitted or predicted value; \( n/m \) - number of fitted samples; \( y_i \) - actual measured value of the sample; \( \bar{y} \) - mean value of true value; \( df \) - degree of freedom of the selected sample, \( df = n-1 \).

Here, the correlation coefficients of the final four components obtained from the calculations and the actual values are 0.9588 for alcohol, 0.9662 for acidity, 0.9772 for reducing sugar, and 0.9536 for residual starch. Fit the renderings. It can be seen in Fig. 4 that the prediction sample fitting degree of the four models is as high as 95% or more, which proves that the observed model has a high degree of fit to the sample, and the model is used for fitting the sample. Among them, the sample standard deviation of the training set for each index was 0.1684, 0.2010, 0.1523, and 0.1521, respectively.

Table 2 compares the predicted and predicted values of the predicted sample. The standard deviations of the prediction index of each parameter index are alcoholicity 0.1794, 0.4332, 0.2663, 0.3041 respectively.

First of all, the forecasting models established for four components respond good prediction results. It is speculated that the possible reason is that those four component in yellow water have certain redox and ionization properties, and their strong electrochemical properties produce a strong pulse relaxation phenomenon. Therefore, the electronic tongue can obtain sufficient and complete information. However, the detection method is not accurate enough, but it can basically judge the characteristics of yellow water.
(Fig.4 Training and prediction of four substance in yellow water by GRNN)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$R$</th>
<th>$S_{training}$</th>
<th>$S_{prediction}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td>0.9588</td>
<td>0.1684</td>
<td>0.1794</td>
</tr>
<tr>
<td>Acidity</td>
<td>0.9662</td>
<td>0.2010</td>
<td>0.4332</td>
</tr>
<tr>
<td>Reducing sugar</td>
<td>0.9772</td>
<td>0.1523</td>
<td>0.2663</td>
</tr>
<tr>
<td>Residual starch</td>
<td>0.9536</td>
<td>0.1521</td>
<td>0.3041</td>
</tr>
</tbody>
</table>

4. **SUMMARY**

Based on the experiments and analysis results presented in this paper, it can be speculated that the electronic tongue technique can be applied to the rapid detection of yellow water. This method can rapidly achieve the quantitative analysis of various components in yellow water. The prediction results of acidity, reducing sugar and residual starch can basically reach the actual production. Compared with physicochemical methods or instruments analysis, this method is less time-consuming to measure and calculate, and easy to operate. On the other hand, it costs much less sample consumption.
Based on this method, it can be applied to other aspects of yellow water or other related liquids, especially for acids such as acetic acid and propionic acid in yellow water, which can quickly analyze the substances in the liquid.

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REFERENCES