Application of Electronic Nose in Detection of Fresh Vegetables Freezing Time Considering Odor Identification Technology

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In this paper, the application of electronic nose (e-nose) technology in the detection of fresh vegetables freezing time is taken as the research goal. This paper uses the literature analysis method, test detection method and comparative analysis method, basing on a brief introduction of e-nose technology, it takes fresh beans stored for different days (1-6 days) at room temperature and -18°C freezing condition as the research object. According to the response of the sensor array to the volatile components and three model analysis methods, the freezing time of fresh vegetables is determined, among which, both PCA and LDA can accurately detect the freezing time of fresh vegetables. Loadings analysis shows that hydrogen sulfide and nitrogen oxides play a major role in detecting the freezing time of fresh vegetables. The results show that the e-nose can quickly and accurately detect the freezing time of fresh vegetables.

1. Introduction

Fresh vegetables are an integral part of people's dining tables, they provide people with a wealth of vitamins and minerals. Since fresh vegetables are still performing respiratory movement after being picked, improper storage would easily lead to spoilage (Amalia, 2010), and as the harvest time increases, the new nutritional value may gradually decrease. From being picked until the consumer's home, fresh vegetables must be transported and stored, therefore, how to ensure the nutritional value of fresh vegetables has gradually become the focus of attention. In recent years, frozen vegetables have become more and more popular. Some studies have shown that (Martínez et al., 2011) frozen vegetables have no difference with fresh vegetables in the nutritional value, but too long storage time will affect their quality.

The chemical analysis method (Favell, 1998) is a widely used method for detecting the freshness of vegetables. Although it has the advantage of high detection accuracy, as it is a destructive testing method, and the sample processing is complicated and the detection efficiency is low, it's difficult to meet the needs of the market. With the continuous development of science and technology, near-infrared detection method, high-performance liquid chromatography and other instrumentation measuring methods have gradually been applied to the detection of fresh vegetables. Although these methods have improved the detection accuracy and efficiency to some extent, the instrument parameters and detection conditions still have some influence on the test results (Prasad and Chetty, 2008). Unlike ordinary chemical instruments, the e-nose (Amalia, 2010) can be used to identify and detect the overall information of the volatile components of the sample. Because of its fast, accurate and reproducible advantages, it has been widely used. Since 1992-1993, e-nose technology has been applied in the food field abroad, with the continuous maturity and development of technology (Goñi et al., 2008), commercial e-nose products have been available since 2000, until now it has been widely used in various fields of production and life (Beghi et al., 2017). Compared with foreign countries, China's research on e-nose technology started late. The research on e-nose began to be active in 2005, although it has certain applications in the food field, it still has great limitations (Maul et al., 2000).

Based on the above analysis, this paper applies the e-nose nondestructive testing technology to the detection of fresh vegetables freezing time. The fresh beans of different storage days (1-6 days) under room temperature and -18°C freezing condition are studied, and e-nose detection models are constructed...
respectively. Using linear discriminant analysis (LDA), principal component analysis (PCA) and load loading analysis (Loadings) method, this paper determines the storage time of fresh vegetables, the results show that e-nose technology can achieve fast and accurate detection of the freezing time of fresh vegetables.

2. Overview of e-nose analysis method

2.1 E-nose working principle

The e-nose is a high-tech product developed by simulating animal organs. It consists of three parts of gas sensor array (Li and Shi, 2018), signal processing and pattern recognition (Xu and Dai, 2016). The gas sensor array is equivalent to the olfactory receptor cells in the animal's olfactory system. The cells can adsorb the volatile components of headspace gas, and the signal processing system is equivalent to the olfactory vesicle, which converts the chemical signals into electrical signals that can be recognized by the system, after being processed, the signals are sent to the pattern recognition system (Sun, 2018), which is equivalent to the olfactory center in the olfactory system of the animal, then by using an appropriate identification method we can achieve qualitative or quantitative detection of the gases (Mokheimer et al., 2010). Figure 1 shows the structural comparison of the e-nose and animal olfactory system. The sensor array is the core of the e-nose system. Acoustic sensors, mass sensors, metal oxide sensors, etc. are currently commonly used sensors (Cleland and Earle, 2010). This paper selects PEN3 portable e-nose system with 10 metal oxide sensors.

![Figure 1: Structural comparison of e-nose and animal olfactory system](image)

2.2 Overview of e-nose analysis method

2.2.1 Principal Component Analysis (PCA)

PCA (Trihaas and Nielsen, 2005) is based on the principle of dimensionality reduction, it converts multiple variables into several comprehensive indicators (i.e., principal components) that can characterize data information. The specific steps can be described as (Siddiq et al., 2014): 1) Normalize the original data; 2) Calculate and establish the correlation coefficient matrix of the variable; 3) Solve the eigenvalue and the eigen variable; 4) Determine the principal component by the cumulative variance contribution rate.

2.2.2 Linear Discriminant Analysis (LDA)

LDA is a generalization of Fisher's linear discriminant method, it tries to find a linear combination of the characteristics of two types of objects or events, using the linear discriminant function in each analysis to analyze which classification the sample belongs to, so as to characterize or distinguish them (Saba and Lockhart, 2016). LDA is a common pattern recognition method for the classification of all kinds of samples.

2.2.3 Load loading analysis (Loadings)

The relative importance of each sensor to the sample and its contribution to the PCA can be determined by load-loading analysis, specifically, it is to determine according to the sensor's score factor on the principal component with the highest contribution rate (Osvald and Stirn, 2008), load loading analysis and PCA are based on the same data analysis algorithm.

3. Freezing time detection of fresh vegetables determined by e-nose

3.1 Extraction of e-nose detection data

3.1.1 Sample collection and preparation

For the sample, 50 grams of freshly picked beans are provided daily by the local vegetable garden. They are placed in a peeling container and stored at room temperature and -8 °C freezing condition for 1-6 days. Six replicate samples are taken every day for detection by e-nose of different temperature and different storage times.

The selected e-nose is a PEN3 portable e-nose with 10 metal oxide sensors. Table 1 shows the names and performance of each sensor.
Table 1: Standard sensor array for e-nose PEN3

<table>
<thead>
<tr>
<th>Array serial number</th>
<th>Sensor name</th>
<th>Performance description</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W1C</td>
<td>Aromatic ingredients</td>
<td>Toluene, 10ml/m³</td>
</tr>
<tr>
<td>2</td>
<td>W5S</td>
<td>Nitrogen oxides</td>
<td>NO₂, 1ml/m³</td>
</tr>
<tr>
<td>3</td>
<td>W3C</td>
<td>Ammonia, Aromatic ingredients</td>
<td>Benzene, 10ml/m³</td>
</tr>
<tr>
<td>4</td>
<td>W6S</td>
<td>Hydrogen</td>
<td>H₂, 100ml/m³</td>
</tr>
<tr>
<td>5</td>
<td>W5C</td>
<td>Alkane, Aromatic ingredients</td>
<td>Methane, 1ml/m³</td>
</tr>
<tr>
<td>6</td>
<td>W1S</td>
<td>Methane</td>
<td>CH₄, 100ml/m³</td>
</tr>
<tr>
<td>7</td>
<td>W1W</td>
<td>Sulfide, organic sulfide</td>
<td>H₂S, 1ml/m³</td>
</tr>
<tr>
<td>8</td>
<td>W2S</td>
<td>Ethanol</td>
<td>CO, 10ml/m³</td>
</tr>
<tr>
<td>9</td>
<td>W2W</td>
<td>Aromatic ingredients, organic sulfide</td>
<td>H₂S, 1ml/m³</td>
</tr>
<tr>
<td>10</td>
<td>W3S</td>
<td>Alkane high concentration detection</td>
<td>CH₃, 10ml/m³</td>
</tr>
</tbody>
</table>

3.2 Freezing time detection of fresh vegetables determined by e-nose

3.2.1 PCA analysis of fresh vegetables

Figure 2 shows the PCA analysis of fresh vegetables during storage at room temperature. It can be seen from the figure that the e-nose system can completely separate the samples stored for 1-6 days, and the contribution rates of the primary component and the secondary component of the volatile substances during storage are 88.64% and 8.02%, respectively.

Figure 2: PCA diagram of fresh vegetables during storage at room temperature

Figure 3: PCA diagram of freezing time of fresh vegetables
Figure 3 shows the PCA diagram of the freezing time of fresh vegetables. It can be seen from the figure that although the e-nose can completely separate the samples of 1-6 days, the change trend of the volatile components of fresh vegetables at different freezing times is not obvious. The contribution rates of the primary component and secondary component are 75.78% and 13.68%, respectively.

3.2.2 LDA analysis of fresh vegetables
Figure 4 shows the LDA analysis of fresh vegetables during storage at room temperature. This method focuses on the change rate of odor of the fresh vegetables. It can be seen from the figure that the samples of 2nd, 3rd, and 4th day overlap partially and cannot be completely distinguished. The reason is that the contribution rates of the discriminant LD1 and LD2 are 92.45% and 5.66%, respectively, due to their similar volatile components.

Figure 4: LDA diagram of fresh vegetables during storage at room temperature

Figure 5 shows the LDA analysis diagram during the freezing of fresh vegetables. It can be seen from the figure that the samples of the 2nd and 3rd day overlap partially and cannot be completely distinguished. The main reason is that the volatile components are similar, and the contribution rates of the discriminant LD1 and LD2 are 53.69% and 35.56%, respectively.

Figure 5: LDA diagram during freezing of fresh vegetables

3.2.3 Loadings analysis of fresh vegetables
The relative importance of each sensor and its contribution rate in PCA can be distinguished by Loadings analysis. The more important a sensor is in pattern recognition, the farther its horizontal and vertical
coordinate values are from zero, and the less the horizontal value of the response value is, it indicates less importance of it in the pattern recognition, and the role of the sensor can be ignored.

Figure 6 shows the Loadings analysis diagram of the room temperature of fresh vegetables. It can be seen from the figure that the proportions of sensor 7 and sensor 2 on the primary principal component and the secondary principal component are the largest, indicating that the two play a greater role. Since sensor 7 and sensor 2 are most sensitive to sulfides and nitrogen oxides, respectively, it is indicated that sulfides and nitrogen oxides play a major role in distinguishing fresh vegetables stored at room temperature.

Figure 6: Loadings analysis diagram of fresh vegetables at room temperature

Figure 7 shows the Loadings analysis diagram of fresh vegetables during freezing. It can be seen from the figure that the sensor 7 and the sensor 2 account for the largest proportion of the primary principal component and the secondary principal component, respectively, during the room temperature storage period of fresh vegetables. It is indicated that sulfides and nitrogen oxides play a major role in distinguishing fresh vegetables during freezing.

Figure 7: Loadings analysis diagram of fresh vegetables during freezing

4. Conclusion

In this paper, the e-nose PEN3 system combined with stoichiometry was used as the research method. Fresh beans stored for different days (1-6 days) at room temperature and -18°C freezing condition were taken as research objects to study the detection methods of freezing time of fresh vegetables, the results showed that,
by using e-nose technology, we can achieve fast detection of the freezing time of fresh vegetables. The specific conclusions are as follows:

(1) PCA showed that it can completely separate vegetables stored under room temperature and freezing conditions.

(2) LDA showed that the LDA analysis results partially overlap due to similar volatile components, and the vegetables under room temperature and freezing conditions could not be completely distinguished.

(3) Loadings analysis results show that sensor 7 and sensor 2 have a large contribution rate to the test, indicating that sulfides and nitrogen oxides play a major role in distinguishing fresh vegetables during freezing.

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