Development of food electronic nose for prawn (Macrobrachium rosenbergii) quality rapid assessment and their relationship with the physicochemical index

Chenhao Jiang, Jingyuan Ning, Zhenghao Mei, Jiaqi Chen, Yuanyuan Gao, Xiaomei Yi, and Peng Wu

Zhejiang A&F University, Key Laboratory of Forestry Sensing Technology and Intelligent Equipment of China Ministry of Forestry, Key Laboratory of Forestry Intelligent Monitoring of Zhejiang Province, Hangzhou

ABSTRACT

Construction of food electronic nose (FEN) for prawn (Macrobrachium rosenbergii) quality rapid assessment assisted with physicochemical parameters was explored in this paper. Sensory analysis, weight, GC/MS, and K value, and microbial were examined to provide the assisting basis for FEN system design. Results indicated that sensory acceptance decreased with the increase in time. The decline of prawn physicochemical parameters was associated with microbiological propagation. The volatile gases emitted by prawn could be utilized for sample quality characterization. FEN successfully discriminated all samples, and presented good detecting accuracy. The method proposed in this work is promising in aquatic products quality rapid analysis.

INTRODUCTION

The consumption of aquatic products in China has been reported to increase in the last 5 years. The people living in the cities of Eastern China consumed a large amount of aquatic products due to the perfect nutrition provided by these foods. The quality of aquatic products sold on the market is not unique. Prawn (Macrobrachium rosenbergii) is the globally most widely cultured and highest-yielding prawn species due to its unique advantages including disease resistance, rapid growth, and high-density cultivation properties.[1–3] In eastern China, it is popularly cultured and consumed. After harvest, prawn is easy to get deteriorated due to environmental and microbial factors, such as temperature, microbial, moisture, etc.[4,5] So accurate and rapid characterization of the prawn quality is an important topic for farmers, inspectors, and consumers. During storage, poisonous substances, such as tyramine, aromatic amines, aliphatic amines, cadaverine, and putrescine, are produced within prawn due to the microbial growth and the decarboxylation of certain amino acids due to the catalysis function of some active enzymes.[6,7] During this procedure, the feature volatile organic compounds (VOCs), such as aldehydes, ketones, alcohols, esters, are also produced. These substances lead to corresponding olfactory senses to alert the freshness level to people.[8–10] Currently, there are standard protocols for aquatic product quality examination, such as physicochemical indexes, microbial, instrumentation, and sensory analysis, which provides reliable references for this kind of food.[11,12] However, the disadvantages of these methods, such as expensive, time-consuming, and fuzzy operations, seriously limit the applications in field detection.

CONTACT Peng Wu alphawu@yeah.net Zhejiang A&F University, Key Laboratory of Forestry Sensing Technology and Intelligent Equipment of China Ministry of Forestry, Key Laboratory of Forestry Intelligent Monitoring of Zhejiang Province, Hangzhou 311300.

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In the past two decades, electronic nose technique develops very quickly.\textsuperscript{[13]} Its structure generally contains an array of a certain number of gas sensors with good selectivity. It also has a suitable pattern recognition model built by exercises on known odors to construct a pattern database so that the unknown ones can be classified and identified based on a trained pattern database.\textsuperscript{[14]} In the past decade, the electronic nose has been applied in food quality rapid analysis. It has presented good measurement abilities in vegetables, fruits, meat, fishes, juice, wine, etc.

The aim of this work was to develop an FEN system, and build a prawn quality rapid assessment method using the FEN system by the assistant of physiochemical indexes and microbial parameters. Sensory analysis, weight, GC/MS, and K value, and microbial were examined to provide the assisting basis for FEN system design. The FEN system was designed according to these parameters. The quality assessment model of the prawn was developed by FEN measurement.

**MATERIALS AND METHODS**

**Materials**

Fresh prawns (\textit{Macrobrachium rosenbergii}) in the same weight (20.0 ± 5.0 g) were purchased from the aquatic market. Prawns were taken to the laboratory with an ice package. All samples were packaged with PE bags and stored at 4°C. The samples were randomly taken every day for physical/chemical, microbial, sensory analysis, and electronic nose experiments from day 0 to day 10. Another 80 samples were stored at 4°C and utilized for validating testing.

**Physicochemical examination**

\textit{Weight:} Weight loss percentage was decided by weighing samples before and after storage. The results were presented as loss percentage with respect to the initial weight.\textsuperscript{[14]}

\textit{GC/MS:} Gas chromatography (7890A, Agilent Technologies Inc., Santa Clara, USA) with mass spectrum (5975 C, Agilent Technologies Inc., Santa Clara, USA) was coupled by headspace sampler (7694E, Agilent Technologies Inc., Santa Clara, USA). The data processing tool was MSD ChemStation. The sample was minced as the percentage of 1:1 (g/mL) with water. Three samples were examined every two days. The minced sample was distilled, and the fraction was kept as an analyte. The fraction was put into a 15 mL headspace sample bottle. The sample was heated and stirred on a mixing platform at 360 rpm/min for about 26 min. SPME needle tubing was put into the headspace sample bottle. The extraction time was 35 min. When extraction finished, the emitted gas was injected into GC/MS system for 3 min for desorption. Chromatographic column: DB-1701 (30 m × 320 μm × 0.25 μm). Carrier gas was high-purity helium (≥ 99.999%). In a typical analysis, the oven was kept for 0.25 min at 40°C, and then programmed at 120°C and 5°C/min speed. The injector temperature was 280°C and the split ratio was fixed at 1:1.

\textit{K value:} K value was tested by nucleotides and derived compounds extraction and deproteinisation, standards preparation, and HPLC analysis.\textsuperscript{[13]} About 5 g minced prawn without skin was extracted with 25 mL 0.6 M perchloric acid for 1 min with a 0°C water bath. The extraction was centrifuged for 10 min. 10 mL supernatant was rapidly neutralized to pH 6.5–6.8 with 1 M KOH using a digital pH meter (Mettler Toledo, Zurich, Switzerland). The neutralized supernatant lasted for 30 min in an ice bath to precipitate the majority of potassium per chloride, which was got ridden of by 10 min of centrifuging. The identification of nucleotides, nucleosides, and bases was conducted by comparing their retention times with those of commercially obtained standards and by adding or spiking of standards. K value was calculated as the percent rate of HXR and Hx to the sum of ATP and degradation products as follows:

\[
K \text{value} (\%) = \frac{HxR + Hx}{ATP + ADP + AMP + IMP + HXR + Hx} \times 100
\]
Table 1. Sensory score attribution.

| Attributes  | 5      | 4      | 3      | 2      | 1      |
|-------------|--------|--------|--------|--------|--------|
| Touch       | Very hard | Hard   | Slight soft | Soft   | Very soft |
| Color       | Very white | White  | Slight white | Dull white | Dark white |
| Appearance  | Very bright | Bright | Slight dull | Dull   | Very dull |
| Viscosity   | Smooth     | General smooth | Slight viscous | Viscous | Very viscous |
| Odor        | Neutral    | Slight fishy | Fishy    | Slight odorous | Spoiled |

where ATP is adenosine triphosphate, ADP is adenosine diphosphate, AMP is adenosine monophosphate, IMP is inosine monophosphate, HxR is inosine, and Hx is hypoxanthine.

Microbial: Microbial index was examined according to AOAC standard protocol.[15–17] Total viable count value was defined in plate count agar by the spread plate method.

Sensory analysis
Sensory analysis is conducted according to Table 1. The prawn samples are evaluated from the following aspects: (a) Touch estimation on prawn firmness and resilience by hand. (b) Color estimation on prawn sample by eyes of panelists. (c) Appearance observation on prawn color, and skin wetness. (d) Viscosity estimation on prawn sample. (e) Odor estimation on sample smell by the human nose.

FEN design
FEN schematic structure was displayed in Figure 1 (a). The gas sensor utilized in the experiments was shown in Figure 1(b), and the working principal was shown in Figure 1(c). The arrangement of the sensor array was displayed in Figure 1(d). The gas sensor array has 8 MOS gas sensors. The selectivity toward volatile compound classes is indicated by the manufacturer: S1 (MQ-2: propane), S2 (MQ-3: ethanol), S3 (MQ-4: methane), S4 (MQ-5: propane, butane), S5 (MQ-6: butane), S6 (MQ-7: carbon monoxide), S7 (MQ-8: hydrogen), S8 (MQ-9: methane, carbon monoxide). The sensor responses are recorded as voltage (V). The gas sensors monitor the changes in conductivity induced by the adsorption of molecules on subsequent surface reactions. They consist of a ceramic substrate coated by MOS film, and heated by a wire resistor. Due to the high temperature (250–500°C), the volatiles near the sensor surface are completely combusted to carbon dioxide and water, inducing the changes in electrical resistance. High temperature avoids water interference and provides sensors with fast response and recovery properties. Polytetrafluorethylene (PTFE) is used to fabricate the sensor chamber. Each sensor room is separated to avoid the cross-influence of gas flow.

Each sample was placed into a 50 mL air-tight vial, and sealed with a sealing membrane. The vials are equilibrated for 30 min at room temperature. Turn on the power, and start valve 2 and washing pump. Valve 1 and sampling pump remain off. Zero gas is got by filtering gas with active carbon. The sensor array is recovered by zero gas. Then shut off valve 2 and washing pump, and turn on valve 1 and sampling pump. The gas in the sample’s headspace is inhaled into the sensor chamber at a flux speed of 400 mL/min. When the measurement is over, gas sensors are recovered by zero gas at a flux speed of 1000 mL/min for 600 s.

Statistical analysis
One-way analysis of variance (ANOVA) was applied on the physicochemical parameters, microbial, and sensory analysis. Pearson’s correlation analysis, and was performed to determine the influence. All statistical procedures were carried out using software SPSS.
RESULTS AND DISCUSSION

Physiochemical parameters

Weight loss increased with the increase of time (see Figure 2(a)). This index was less than 5% between day 0 and day 2. In this procedure, prawn samples lost a little moisture and nutrition. It exceeded 10% in day 5, and increased rapidly after this day. Finally, this index exceeded 25% in day 9.

As Figure 2(b) displayed, some feature spoilage-induced compounds were captured in prawn samples by GC/MS examination. At the beginning, the concentration of the chemicals was relatively low. The representative content, such as trimethylamine, increased dramatically in the experiments. Prawn quality decreased rapidly according to GC/MS results.

Figure 2(c) displays the K value examination results. It was about 7% at the beginning, and rapidly climbed. K value mainly characterized meat quality acceptable level. The prawns with K values of more than 30% were considered as nonfresh and not suitable to eat. When prawns were captured, some feature chemicals were produced with help of inner enzymes. K value increased when prawn meat was functioned by IMP decomposition. AMP and IMP were produced when ATP was functioned by microbiological activities. As a result, K value is an important index, characterizing aquatic product quality accurately. According to K value examination results, it exceeded 30% in day 5. So the freshness of samples after day 5 was regarded as nonfresh.
Figure 2. Physiochemical indexes: (a) weight loss; (b) GC/MS; (c) K value; (d) microbial; (e) sensory analysis.
**Microbial**
Microbial examination results were displayed in Figure 2(d). At the beginning, it was about 2.2 log CFU/g. Microbial increased with the increase of time. During experiments, spoilage microbes, including *Photobacterium phosphoreum*, and Lactic acid bacteria, propagated fast with the help of nutrients within prawn meat and environmental factors, such as temperature, humidity, etc. Compared with examination results in section 3.1, the microbial index had a positive correlation with K value, indicating that K value was mainly influenced by microbial.

**Sensory analysis**
Sensory analysis results were displayed in Figure 2(e). In day 0, the score of all samples was 5. With the increase of time, sensory score declined continuously. In day 4, the preference score was about 3.8, and it decreased to about 1.8 in day 9. Results demonstrated that the sensory score given by panelists actually reflected the prawn quality changes.

**FEN measurement results**
FEN responses to prawns were displayed in Figure 3(a). Sensor 4 had the largest signals than other sensors and sensor 2 had the smallest responses. According to examination results in section 3.1, different chemical components were produced when the prawn was functioned by microbial propagation promoted by environmental factors and nutrients. The produced chemicals released feature gases, which was captured by FEN gas sensors. The responding signals were generated during the capture procedure. Different sensors presented different responses, providing feature prawn sample fingerprint information toward prawn quality fast characterization.

![Figure 3](image-url)

Figure 3. Quality determination model: (a) FEN responses; (b) signal/noise curves; (c) determination model.
Figure 3(b) displayed FEN discrimination results. First, the signal/noise ratio increased, and reached their peak values at the noise intensity of 220. After the peaks, signal/noise started to decrease, and reached the valley at a noise intensity of 360. Finally, the signal/noise ratio slowly decreased, and got to a stable state. Here, peak values of samples in different time was utilized for prawn quality determination.

Prawn quality determination model was constructed by linear fitting between signal/noise ratio peak values and time. Regression results were displayed in Figure 3(c) and Eq. (5). The regression coefficient $R^2 = 0.98$ indicated that the constructed equation was suitable for prawn quality determination.

$$\text{Time} = 77.15 + 0.8 \times \text{MAXIMAL} \quad (R^2 = 0.98) (5)$$

According to K value examination results, it exceeded 30% in day 5. So the freshness of samples after day 5 was regarded as nonfresh. Based on Eq. (5), the MAXIMAL value regarding to day 5 was $-90.18$. Results indicated that the sample was nonfresh if the FEN responses exceed $-90.18$.

**Validation**

Validating experiments on the quality determination model of prawn were held. Another 80 samples were selected and measured by FEN. Results displayed that the accuracy of the proposed model was 93.75%, indicating that this model was capable of prawn quality rapid determined.

**CONCLUSION**

FEN was designed and developed for prawn (*Macrobrachium rosenbergii*) quality rapid assessment based on physicochemical and microbial parameters in this paper. FEN system was designed for prawn quality rapid detection. Meanwhile, sensory analysis, weight, GC/MS, and K value, and microbial were also examined to provide quality references for FEN. Results demonstrated that sensory acceptance decreased with the increase in time. The decline of prawn physiochemical parameters was associated with microbial propagation. The volatile gases emitted by prawn could be utilized for sample quality characterization. The prawn quality determination model was $\text{Time} = 77.15 + 0.8 \times \text{MAXIMAL}$ with $R^2 = 0.98$. FEN discriminated all samples successfully. The proposed method is promising in aquatic products quality rapid analysis.

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**ORCID**

Peng Wu [http://orcid.org/0000-0003-1980-8352](http://orcid.org/0000-0003-1980-8352)

**Compliance with Ethics Requirements**

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