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Study of grass carp (*Ctenopharyngodon idellus*) quality predictive model based on electronic nose

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ABSTRACT

An electronic nose based quality predictive model of grass carp (*Ctenopharyngodon idellus*) stored at 277 K temperature was proposed in this paper. The changes of sensor array response to samples were caused by the new-generated gas species released by microbial propagations. Principal component analysis method discriminated fresh grass carp samples from medium samples and aged samples. Stochastic resonance signal-to-noise ratio maximums distinguished fresh, medium, and aged grass carp samples successfully. The quality predicting model was developed based on signal-to-noise ratio maximums non-linear fitting regression. Validating experiments demonstrated that the predicting accuracy of this model was 87.5%. This method presented some advantages including easy operation, quick response, high accuracy, good repeatability, etc. This method is promising in aquatic food products quality evaluating applications.

1. Introduction

Since aquatic food products deteriorate rapidly after post-mortem as a consequence of biochemical and microbial breakdown mechanisms [1], freshness becomes an important factor to evaluate the quality of aquatic products from any given species. Many studies had reported useful methods to reduce the rate of the deterioration of fish and to extend their shelf life, such as high hydrostatic pressure [2], irradiation process [3], ozonized slurry ice [4], super chilled vacuum packed [5], edible films and coatings [6]. However, low temperature treatment remains one of the primary methods to maintain fish freshness based on the reduction in the rates of microbiological, chemical and biochemical changes [7].

Grass carp (*Ctenopharyngodon idellus*) is a popular freshwater fish in China because of its rapid growth, high yield, and low cost. As a result of the rapid deterioration and compositional variations, difficult processing problems exist in the utilization of fish as a basic raw material [8]. Therefore, investigations on the freshness changes and shelf life extending in cold chain circulation are of considerable interest. The prediction of freshness allows companies to optimize their storage management and thus to reduce of economic losses, which is one of the most important issues in company planning these days [9]. Recently, some studies have applied models to predict the quality changes of food during storage. Baudrit et al. proposed a representation/modeling and an explicit overview of the whole ripening process of a soft mold cheese (Camembert type) by means of dynamic Bayesian networks [10]. Zanoni et al. built a mathematical model to predict microbial stability and sensory quality of cut, ready-to-use, fresh carrots during shelf life under both isothermal and non-isothermal conditions [11]. Emborg et al. proposed a mathematical model that allowed growth and histamine formation by *Mycobacterium psychrotolerans* to be predicted in growth band histamine [12]. The predictive model of microbiology growing has been also used to successfully predict the effect of various time-temperature storage conditions on the shelf life of meat. PCR-DGGE technique was developed to characterize the dominant spoilage bacteria in cooked meat product and to monitor the community dynamics of predominant spoilage bacteria of sliced vacuum-packed cooked ham during refrigerated storage [13]. A predictive model was proposed to determine the shelf life of modified atmosphere-packed (MAP) cooked sliced ham in each step of the cold chain based on the growth of LAB under different temperature conditions [14]. While the above-mentioned methods have some drawbacks for practical or in situ determinations, the detecting procedure is time-consuming and easy to be affected by environmental factors. Furthermore, these techniques usually bring damage to samples. So a fast, lossless, and robust technique is badly needed in food quality prediction.

Nowadays, there is an increasing interest in developing Electronic nose (E-nose) system for food quality analysis. The sensor array in an E-nose system consists of some sensors. The gases emitted by detecting samples generate a characteristic signal pattern from the sensor array. Patterns from the known samples are employed to construct a database and train a pattern recognition

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system. Later, under certain circumstances, the unknown pattern of new sample measurements can be classified and identified by the pattern recognition system [15–17]. An important advantage of this approach is that the technique is non-destructive, since it only analyzes the gases emitted by samples [18]. The E-nose technology has been successfully employed in diverse fields such as agriculture [19], pharmaceutical [20], environmental control [21–23], and clinical diagnostics [24,25]. In the past decade, E-nose technique, most notably, has been employed in food and agro-products quality analysis, such as beverages [26,27], milk [28], edible oil [29,30], meat [31,32], fish [33], vegetables [34,35], and fruits [36,37].

In this paper, a grass carp quality predicting method was proposed. The grass carp samples were stored at 277 K temperature. E-nose sensor array responses to samples were measured for eight days. Principal component analysis (PCA) method could not class medium samples from aged samples. Signal-to-noise ratio (SNR) spectrum was calculated by stochastic resonance (SR). The maximum SNR successfully distinguished fresh, medium, and aged grass carp samples. The quality predicting model was built using SNR maximums. The predicting accuracy of the developed model was 87.5%. This method provided a novel way for aquatic food products quality analysis.

2. Materials and methods

2.1. Raw materials

The fresh grass carps weighted 2500.0 g (±100.0 g), purchasing from Wen'er Road market in Hangzhou, China, and were transported to our laboratory alive.

Five fishes were selected each day and killed by blow in head, decapitated, eviscerated, and washed with cold water. Forty-three samples were taken per fish, and each sample weighed 25 g. The samples were stored at 277 K and packaged with sealing membrane.

Three samples per fish were used for TVC measurement each day. The rest forty samples per fish were used for PCA analysis and predicting model development. Each sample was put into a vial and sealed with sealing membrane. Four experimental groups were conducted: the same samples from the same fish; different samples from the same fish; the same samples from different fishes; different samples from different fishes.

In validating experiments, two new fishes were killed every day. Forty samples were taken per fish. Each sample weighed 25 g. Thirty-two samples were taken randomly to validate the robustness of the developed predicting model. The samples were taken randomly.

2.2. E-nose system

The grass carp samples were monitored by a self-developed portable E-nose. Its structure is shown in Fig. 1. It includes three main parts: data acquisition, modulating and transmitting unit (U1); sensor array and the chamber unit (U2); power and gas supply unit (U3). The sensor array system is composed of 8 metal oxide semiconductors (MOS) of different chemical compositions and thickness to provide selectivity toward different gases. The selectivity toward volatile compound classes of MOS sensors is indicated by the supplier: 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 response is expressed as sampling voltage (V). The MOS sensors rely on changes in conductivity induced by the adsorption of molecules in the gas phase and on subsequent surface reactions. They consist of ceramic substrate coated by metal oxide semiconducting film, and heated by wire resistor. Due to the high temperature (250–500 °C), the volatiles transferred to the surface of the sensors are totally combusted to carbon dioxide and water, leading to a change in the resistance. The high temperature avoids water interference and provides MOS fast response and rapid recovery time. Polytetrafluorethylene (PTFE) material is utilized to fabricate the chamber. Each sensor room is separated, which helps to avoid the cross-influence of the gas flow.

In E-nose measurement, 25 g of grass carp samples were placed into 50 mL glass air-tight vials, and sealed with sealing membrane. The vials were stored at 277 K until analysis. The vials were equilibrated at room temperature for 45 min and analyzed in standardized conditions. After the power is turned on, washing pump and valve 2 are started, and sampling pump and valve 1 are close. The air is filtered by active carbon to obtain zero gas. Sensor S1–S8 are washed by zero gas. When the sensor' response reach the baseline, the washing pump and valve 2 are closed. Then the sampling pump and valve 1 are started. The E-nose sucked the headspace gases of samples through the sensor array at 400 mL/min for 40 s. The measurement interval of E-nose was 0.05 s. When measurement is finished, the sensors are washed by zero gas for 600 s at a flow rate of 1000 mL/min prior to the next sample measurement.

2.3. Methods

2.3.1. E-nose analysis

25 g of grass carp was put into a 50 mL glass air-tight vial at 277 K temperature. After 1 h, we placed the sampling pinhead into

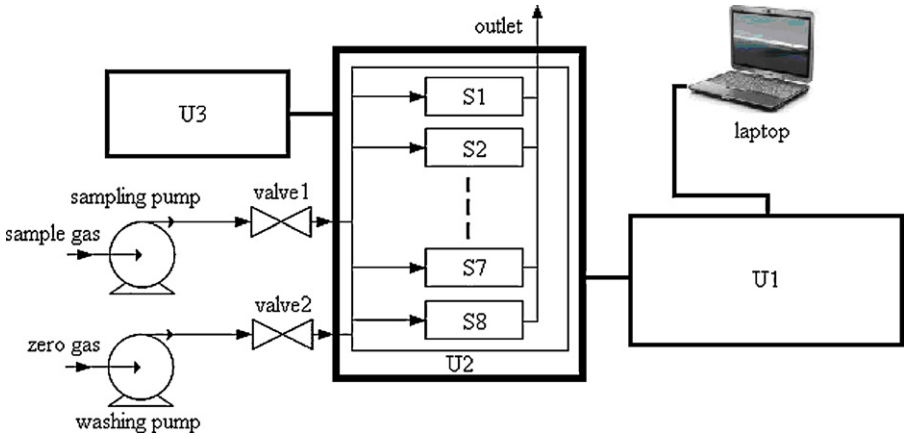

Fig. 1. Schematic diagram of E-nose system.