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Discrimination and prediction of multiple beef freshness indexes based on electronic nose

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ABSTRACT

An electronic nose (e-nose) instrument combined with chemometrics was used to predict the physical–chemical indexes (sensory scores, total volatile basic nitrogen (TVBN) and microbial population) for beef. The e-nose data generated were analyzed by chemometrics methods and pattern recognition. Mahalanobis Distance (MD) analysis, Principle Component Analysis (PCA) and Linear Discriminant Analysis (LDA) confirmed the difference in volatile profiles of beef samples of 7 different storage times (ST). The Back Propagation Neural Network (BPNN) and Generalized Regression Neural Network (GRNN) were used to build prediction models for ST, TVBN content, microbial population and sensory scores. The result of GRNN was better than that of BPNN, and the standard error (SE) of GRNN prediction model for ST, TVBN, microbial population, sensory scores were 1.36 days, 4.64×10^{-2} mg g^{-1}, 1.612×10^{6} cfu g^{-1} and 1.31 respectively. This research indicates that it is of feasibility to use e-nose to predict multiple freshness indexes for beef.

1. Introduction

Due to its high nutritional value and tasty taste, the consumer demand for beef increases dramatically during the last decades. In USA alone the beef industry has a retail value equals to $73 billion in 2009 alone with about 26.9 billion pounds of beef being consumed in that year [1]. However, beef is highly susceptible to spoilage and contamination. The freshness of beef degrades because microbial spoilage and biochemical reactions occur during storage. The main ingredients like protein, fat and carbohydrates will be decomposed by enzymes and bacteria, producing odor: the protein will be decomposed into ammonia, hydrogen sulfide, ethyl mercaptan, etc.; the fat will be decomposed into aldehydes and aldehyde acids; the carbohydrates will be decomposed into alcohols, ketones, aldehydes, and carboxylic acid gases [2]. Metabolites such as trimethylamine, aldehydes, ketones and esters, as well as other low molecular weight compounds responsible for off-flavors and sensory product rejection are produced. During storage, these substances and other basic nitrogenous compounds together make up total volatile basic nitrogen (TVBN). The odor gets more and more intense with the decrease of beef freshness. Consumption of spoilage beef could cause serious health hazards [3].

A number of techniques have been used to assess beef freshness. Traditionally, sensory evaluation, chemical experiments including TVBN evaluation and microbial population evaluation are three key techniques [4]. The sensory evaluation attributes usually cover color, flavor and texture including viscosity and elasticity [5]. This method provides immediate quality information but suffers from some disadvantages, for example, the subjective nature of the assessment. Errors may arise from fatigue of panelists, and low threshold concentrations of stale odor compounds may not be perceived [6]. The TVBN evaluation and the microbial population evaluation methods are objective and precise. However, these two methods are destructive and time-consuming.

The developments of electronics and sensor technologies show promises for developing rapid and nondestructive sensors for meat quality/safety [7]. Electronic nose (e-nose), also known as artificial olfactory, is a simulation of biological functions to identify some simple or complex odor [8,9]. A typical e-nose system contains a selective chemical sensor array, a signal processing subsystem and a pattern recognition subsystem. The sensors in the sensor array are sensitive to different substances, for example, some sensors can discern ammonia and some can discern aldehydes. So instead of detecting one or two components of the substances, the e-nose extracts the whole information for identification.

Since the last decades, some researchers have been studying the potential of using the e-nose as a non-destructive method for food detection [10–14]. Zhang et al. [15] reported using a nine nano ZnO thick film gas sensors based e-nose to analyze 17 kinds of commercial Chinese vinegars, and the Principle Component Analysis (PCA) and Cluster Analysis (CA) results showed that characterizing the Chinese vinegars by the e-nose was highly related to their type,

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Table 1
Sampling protocol employed for beef strip loins (*M. Longissimus lumborum*).

Procedures	Storage temperature (°C)	Storage time (days)	Numbers of replications per day	Total samples for one experiment
Pre-experiment	8	1, 2, 3, 4	12 for direct e-nose test, 12 for e-nose with EDU	96
E-nose detection	2	0, 3, 5, 7, 10, 12, 14	30	210
Sensory evaluation	2	0, 3, 5, 7, 10, 12, 14	30	210
TVBN evaluation	2	0, 3, 5, 7, 10, 12, 14	30	210
Microbial population evaluation	2	0, 3, 5, 7, 10, 12, 14	30	210

raw materials, total acidity, fermentation method and production area. After performing the Learning Vector Quantization (LVQ) neural network, the accuracy in terms of predicting tested vinegar measurements was 72.1%, 76.5%, 77.9%, 94.1% and 82.4% according to their type, raw materials, total acidity, fermentation method and production area, respectively; Pang et al. [16] investigated the capacity of using an e-nose to classify wheat samples of five storage ages. The PCA and Linear Discriminant Analysis (LDA) results showed that all the five wheat groups could be discriminated. Artificial Neural Network (ANN) was also performed, and 85% of the testing set was classified correctly by a Back Propagation Neural Network (BPNN); Yu et al. [17] reported using an e-nose to classify Longjing tea grade based on dry tea leaf, tea beverages and tea remains volatiles. PCA was applied to decrease the data dimension and optimize the feature vector. LDA and BPNN were employed for the classification, and the result showed that both of the LDA and the BPNN methods achieved better discrimination for the tea grades based on the tea beverages. However, most of the previous research just focused on the discrimination without building multiple prediction models. In many cases, only an e-nose was used, with no other experiments combined. So even if we can predict the storage time (ST) of the food, we still do not know its microbial population or other indexes to precisely identify their freshness degree.

In this research, four experiments were conducted: e-nose detection, sensory evaluation, TVBN and microbial population evaluation. As for the e-nose detection, a pre-experiment was conducted to observe if an Enrichment and Desorption Unit (EDU) had significant effect on the performance of the e-nose. The main objective of this research is to evaluate the capacity of using an e-nose to classify beef strip loins (*M. Longissimus lumborum*) of seven ST (0, 3, 5, 7, 10, 12 and 14 days), as well as to predict the ST, TVBN content, microbial population and sensory scores of the samples. Mahalanobis Distance (MD), PCA, LDA and Stepwise Linear Discriminant Analysis (Stepwise LDA) were applied to distinguish beef samples with different ST, and BPNN and Generalized Regression Neural Network (GRNN) were applied to build prediction models for the physical–chemical indexes. The accuracy of these two methods was compared.

2. Materials and method

2.1. Sample preparation

Fresh beef strip loins (*M. Longissimus lumborum*) from different carcasses (at Hangzhou Farmers' Market, Zhejiang province, China, 30.26 N, 120.19 E) were obtained right after being killed. From each carcass, 100 g of strip loin was obtained and manually packed and sealed in commercial food grade polymer wraps with ice surrounded before being transported to the lab, where it was further divided into four equal parts. As all the four samples were taken from the same strip loin, and the sample size was small (only 25 g); it was assumed that the meat conditions and the spoilage characteristics of all the samples were same. Out of these four samples from the original 100 g of beef samples, one sample was used for sensory evaluation, one was used for TVBN evaluation, one was used for microbial population estimate and the last one was used for e-nose headspace analysis. In the pre-experiment, storage temperature of 8 °C was chosen to expedite the spoilage of meat, while in the further experiments, all the samples were stored at 2 °C. The number of samples for each experiment and the ST are shown in Table 1.

2.2. Electronic nose system and Enrichment and Desorption Unit (EDU)

The headspace analysis was performed with an electronic nose (e-nose, PEN2, Airsense Analytics, GmBH, Schwerin, Germany) (Fig. 1a). This analytical instrument consists of an auto-sampling apparatus that is exposed to the volatiles, an array of sensors, and a pattern recognition software that is run on a connected computer. The sensor array is composed of ten different metal–oxide semiconductors (MOS) positioned in a small chamber. A description of the ten metal–oxide semiconductors is given in Table 2.

A pre-experiment was conducted to observe if an EDU would improve the performance of the e-nose. EDU (Fig. 1b) is an automatic sampling and desorption device that could be connected to e-nose to lower the detection limit, as well as to increase the selectivity of the e-nose. With this technique compounds of interest can

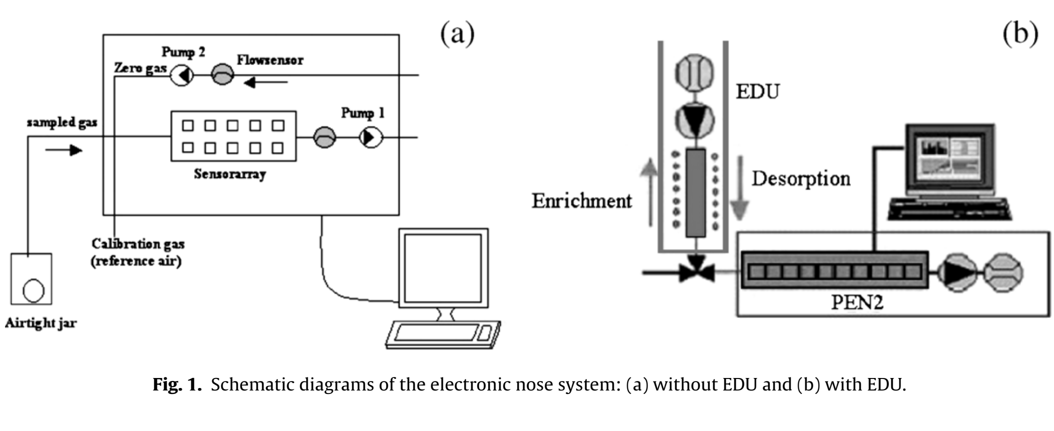

Fig. 1. Schematic diagrams of the electronic nose system: (a) without EDU and (b) with EDU.