Computers and Electronics in Agriculture 108 (2014) 112–122

Contents lists available at ScienceDirect

Computers and Electronics in Agriculture

journal homepage: www.elsevier.com/locate/compag

Tracing floral and geographical origins of honeys by potentiometric and voltammetric electronic tongue

Zhenbo Wei, Jun Wang *

Department of Biosystems Engineering, Zhejiang University, 886 Yuhangtang Road, Hangzhou 310058, PR China

ARTICLE INFO

Article history:
Received 17 February 2014
Received in revised form 27 June 2014
Accepted 28 July 2014

Keywords:
Potentiometric electronic tongue
Voltammetric electronic tongue
Honey
Classification
Regression

ABSTRACT

A potentiometric electronic tongue (PE-tongue) and a voltammetric electronic tongue (VE-tongue) were used as rapid techniques to classify and predict the honey samples from different floral and geographical origins. The PE-tongue, which was named α-ASTREE, was developed by Alpha M.O.S. (Toulouse, France), and it comprises seven potentiometric chemical sensors. The VE-tongue was self-developed at Zhejiang University and comprises six metallic working sensors. Four types of honey of different floral origins (acacia, buckwheat, data, and motherwort) and four types of acacia honey of different geographical origins were classified by both multisensor systems. Multivariate statistical data analysis techniques such as principal component analysis (PCA) and discriminant function analysis (DFA) were used to classify the honey samples. Both types of electronic tongue have good potential to classify the honey samples, and the positions of the data point for the samples in the PCA score plots based on the VE-tongue were much more closely grouped. Three regression modes, principal component regression (PCR), partial least squares regression (PLSR), and least squared-support vector machines (LS-SVM), were applied for category forecasting. These regression models exhibited a clear indication of the prediction ability of the two types of electronic tongue, and a positive trend in the prediction of the floral and geographical origin of honey was found. Moreover, the performance of these regression models for predicting the four types of honey of different geographical origins by the VE-tongue is very stable.

1. Introduction

Traditionally, sensory and instrumental techniques are used to determine the taste of food products (Beullens et al., 2008). The interest in the concept of electronic tongues or taste sensors has grown considerably during the past years (Gil et al., 2008; Ghasemi-Varnamkhasti et al., 2010; Lvova et al., 2009; Tiwari et al., 2013). Basically, electronic tongues comprise an information collecting unit for use in aqueous solutions and pattern recognition for multivariate data processing (Legin et al., 1999). The information obtained by the sensors, which could be taken as the "digital chemical fingerprint" of an unknown chemical ambient in a liquid, is non-specific, i.e., in a multi-component solution, they do not respond to a particular constituent of the aqueous solution; however, they respond on the whole to different constituents in the solution (Abdul Rahman et al., 2004). It could be understood that valuable information can be obtained through "soft" measurement techniques, where the quality (e.g., taste or a state of a process) can be measured instead of the traditional measurement techniques with which a single parameter (e.g. temperature or conductivity) is measured (Ivarsson et al., 2001).

Three major types of electronic tongue, which are based on potentiometric, voltammetric, and impedance spectroscopy electrodes, have been developed in recent years. The potentiometric electronic tongue (PE-tongue), which comprises several types of lipid/polymer membranes, is now widely used for the analysis of beers (Polshin et al., 2010; Rudnitskaya et al., 2009; Ciosek and Wŕoblewski, 2006), red wines (Di Natale et al., 2004; Apetrei et al., 2007; Legin et al., 2003) and others (Wei and Wang, 2013; Escriche et al., 2012; Ghosh et al., 2012); The voltammetric electronic tongue (VE-tongue) is based on voltammetry, and comprises different working electrodes in a standard three-electrode configuration. The working electrodes of the VE-tongue are composed of metal (Banerjee(Roy) et al., 2012; Alcaniz et al., 2012), carbon (Apetrei et al., 2010; Shamsipur et al., 2004), and conducting polymers (Pigani et al., 2000). This concept has already proven valuable in many applications such as to monitor the quality changes in milk (Winquist et al., 2005), to recognize different microbial species (Olsson et al., 2008), and to supervise of rinses in a washing machine (Söderström et al., 2003). The electronic tongue based on impedance spectroscopy electrodes, which are modified by pure

* Corresponding author. Tel.: +86 571 88982178; fax: +86 571 88982191.
E-mail address: jwang@zju.edu.cn (J. Wang).

http://dx.doi.org/10.1016/j.compag.2014.07.014
0168-1699/

and composite nanostructured films of conducting polymers, is used to classify several commercial beverages (Riul et al., 2003). Among these different types of electronic tongues, there is little comparative knowledge of their performance.

In this study, the PE-tongue developed by Alpha M.O.S. (Toulouse, France) and the VE-tongue self-developed at Zhejiang University were used to classify and predict the honey samples of different floral and geographical origins. The PE-tongue system developed by Alpha M.O.S., which was evaluated for applications in horticulture, comprises seven potentiometric chemical sensors, and the sensitivity of the seven chemical sensors is different from that of the five tastes (bitterness, savoury, saltiness, sourness, and sweetness). The PE-tongue system is able to classify food and beverages (Kantor et al., 2008; Chen et al., 2008), determine bitterness in coffee (Alpha, 2006), and predict the sensory characteristics of apple juice (Bleibaum et al., 2002).

The VE-tongue self-developed at Zhejiang University comprises six metallic electrodes (gold, silver, platinum, palladium, tungsten, and titanium), and measurements were conducted on the basis of multi-frequency large-amplitude pulse voltammetry (MLAPV). Different metallic electrodes have different sensitivities to the samples, and the signals obtained by different electrodes presented different information regarding the samples. Therefore, the composition of the sensor array is very important, and each of them is indispensable.

The objective of this experiment is to evaluate the potential of both electronic tongues for fast qualitative determination of monofloral honeys of different floral and geographical origins. Therefore, the ability of the electronic tongues to classify and predict the four types of honey of different floral origins and four types of acacia honey of different geographical origins is investigated using multivariate statistical techniques.

2. Materials and methods

2.1. Samples

All samples were produced in March 2008. Four types of honey of different floral origins were derived from the same geographical origin (27.47 N, 114.23 E, Jangxi province, China) and were produced by the Wang Shi Company. The following four certified monofloral honey categories were included: acacia (*Acacia Mill*), buckwheat (*Fagopyrum esculentum Moench*), data (*Ziziphus jujuba Mill*), and motherwort (*Leonurus artemisia* (*Laur.*) *S. Y. Hu F*). The four types of acacia honey, which derived from the same spaces but of different geographical origins, were produced by the Fengzhiyu (FY), Runlu (RL), Wangshi (WS), and Tianchu (TC) companies, respectively (Table 1). Those honey samples were processed with the same processing procedures, and the details were as follows: uncapping is the first real step of honey processing thin wax layer that seals the honey cells were removed by the completely automated uncapping machines, than centrifugal extractors was applied for separating wax and honey. Because the combs will become softer and might break at higher temperatures, therefore the extraction temperatures should not exceed 30 °C. The next step is the removal of any impurities such as wax particles, other debris and air bubbles incorporated during extraction by settling and straining. For preventing fermentation by reducing moisture content, the purity honey supers were left in warm rooms at 30–35 °C and were blown by circulating warm air for few days. At the same time, pasteurization is also employed for the purpose through destructing the osmophilic yeasts. At last, the finished honey products were stored at −4 °C. In the study, a total of 168 samples were detected by the e-tongues, and 24 samples of each type of honey of different floral and geographical origins were randomly selected for the detection.

2.2. Potentiometric electronic tongue

The PE-tongue (Alpha MOS company, France) comprises seven potentiometric chemical sensors (ZZ, BA, BB, CA, GA, HA, and JB) based on chemically modified field effect transistor technology (ChemFET), which is similar to ion-selective FET technology. However, the sensors are coated with specific materials that have different sensitivities to the five basic tastes (bitterness, savoury, saltiness, sourness, and sweetness). The PE-tongue is equipped with a 16-position autosampler and a swing head for sampling. These sensors and their attributes are summarized in Table 2. Each sensor is composed of an organic coating sensitive to chemicals inducing basic tastes in the samples and a transducer that can convert the response of the membrane into signals to be analyzed. The principle of the method is to detect the changes in the voltage (mv) intensity between the chemical sensor and the Ag/AgCl reference electrode. Therefore, an integral signal of each sample comprises a vector with seven individual sensor measurements.

The mass for each honey sample is 60 g, which was dissolved in 400-ml deionized water. Further, the mixture was poured into an airtight glass jar with a volume of 150 ml (concentration chamber), and each sample had a volume of 80 ml. The measurement time was set to 120 s for each sample, and the sensors were rinsed for 10 s using deionized water before detecting the next sample. During the PE-tongue experiment, the response values at 110th second were extracted for analysis. Twenty-four samples of each type of honey were tested, and all samples were tested at room temperature.

The typical responses of the seven sensors for detecting the sample "data" and "buckwheat" are shown in Fig. 1. Each curve represents the corresponding voltage (mv) intensity of each sensor vs. time (s). During the initial period, the voltage (mv) intensity of each sensor was low, then increased continuously, and finally stabilized after approximately 75 s. In this research, the response values of each sensor at 110th second were extracted and analyzed.

2.3. Voltammetric electronic tongue

The VE-tongue self-developed at Zhejiang University comprises six working electrodes (gold, silver, platinum, palladium, tungsten, and titanium, all the working electrodes had a diameter of 2 mm

Table 1
Samples of the test sets.

Botanical origin	Geographical origin	Number	Company	Geographical origin	Number
Acacia	Yichun, Jiangxi province, China (27.47 N 114.23 E)	24	Fengzhiyu (FY)	Tonglu, Zhejiang province (119:49 E, 29:10 N)	24
Buckwheat	Yichun, Jiangxi province	24	Runlu (RL)	Hangzhou, Zhejiang province (120:10 E, 30:15 N)	24
Data	Yichun, Jiangxi province	24	[a]Wangshi (WS)	Yichun, Jiangxi province, China (114.23 E, 27.47 N)	24
Motherwort	Yichun, Jiangxi province	24	Tianchu (TC)	Hongkong (114.10 E, N22.18′)	24
	Total number	96		Total number	96

[a] One type of the acacia honey samples of different geographical origins was produced by Wangshi Company, the acacia honey samples was also taken as one type of the honey samples of different floral origins. Therefore, the total number of the honey sample applied in the study was 168.