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Research Article

Detection of Edible Oils Based on Voltammetric Electronic Tongue

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Abstract: A voltammetric electronic tongue to classify five different types of edible oil samples is described in this study. The standard three-electrode configuration composes the sensor array: gold electrode, platinum electrode and saturated calomel electrode. Using cyclic voltammetric measurement, respectively, on five different types of edible oil samples (peanut oil, corn oil, soybean oil, sesame oil and sunflower oil) collected data. The data extracted from the cyclic voltammetry are processed by three algorithms: Principal Component Analysis (PCA), Factor Analysis (FA) and Hierarchical Cluster Analysis (HCA). The result shows that the voltammetric electronic tongue could discriminate all of the five edible oil samples very well.

Keywords: Edible oils, electronic tongue, hierarchical cluster analysis, hierarchical factor analysis, principal component analysis

INTRODUCTION

Electronic tongue is composed of sensor array, signal processing module and pattern recognition module. The samples are classified by the response signal from the sensor array. Electronic tongue has found increasing interest for recognizing and differentiating foodstuffs on the basis, for instance, of their geographical origin or manufacturing processes (Ciosek *et al*., 2007; Toko, 1998; Parra *et al*., 2006; Martina *et al*., 2007). A variety of chemical sensors has been employed in the design of electronic tongues, embracing mass, optical and electrochemical systems. Different types of electronic tongues are developed, such as the voltammetric electronic tongue (Fredrik *et al*., 1997), the potentiometric electronic tongue (Jordi *et al*., 2005), the impedance-based electronic tongue, the hybrid electronic tongue and so on.

Electronic tongue could recognize the various samples such as fruit juices, still drinks, milk and could follow the aging processes of milk and orange juice. Michele Forina and others described an electronic tongue which was able to classify different types of edible oil. For the past few years, there has been a growing interest among consumers in the safety and trace ability of food products. In particular, there has been an increasing focus on the geographical origin of raw materials and finished products, for several reasons including specific sensory properties, perceived health values, confidence in locally produced products and media attention. In order to assure quality and to safeguard consumers from commercial frauds, there is an increasing need for analytical tools able to verify whether a product, sold with a specific label, is actually compatible with that claim or not. Physico-chemical techniques (GC, GC-MS, HPLC), chemical analysis and sensorial analysis (panel test) are the classical methods used for this purpose. Each of these analyses only gives partial information about the extent of oxidation. They are expensive and time consuming. In recent years, considerable efforts have been devoted to the development of innovative analytical instrumentation such as the electronic tongue, which can mimic the human sense of olfaction and of taste and provide low-cost and rapid sensory information for monitoring food quality and state of a process.

In this study, we propose a new strategy to perform voltammetric measurements in the oil samples. All plant oils contain some redox active compounds such as tocopherols, polyphenols, carotenoids, etc. Therefore, the presence of such compounds in vegetable oils could be analysed by means of electrochemical methods. In this study the measurement characteristics curve were obtained with cyclic voltammetry, as for the chemometrics strategies, classification and, foremost, class-modelling techniques represent appropriate tools for verifying authenticity of a product. Classification methods-such as the Principal Component Analysis (PCA), Factor Analysis (FA) and Hierarchical Cluster Analysis (HCA) were used to classify five different types of edible oil. There are three samples of each kind of edible oil. The result shows that the voltammetric electronic tongue could discriminate all of the samples very well.

METHODOLOGY

Structure of electronic tongue: The electronic tongue system is composed of the sensor array, electrochemical

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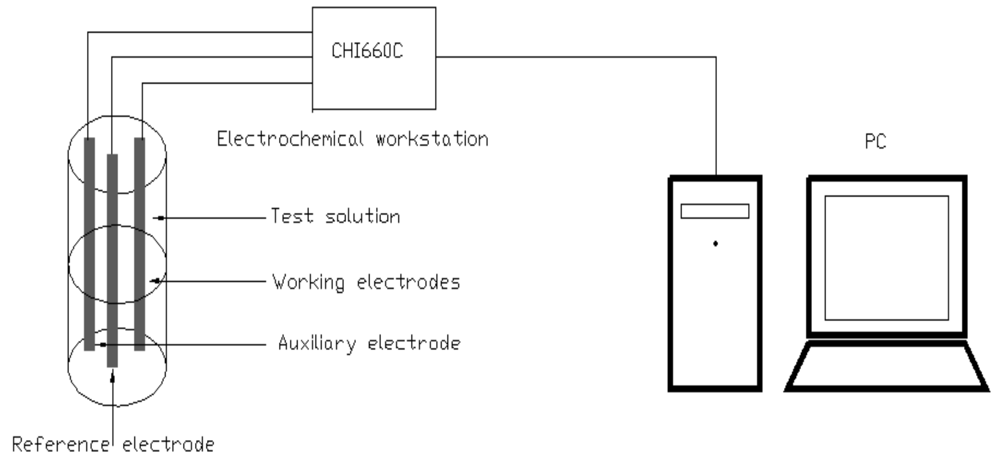

Fig. 1: Electronic tongue system

workstation, Personal Computer (PC), which is shown in Fig. 1.

The proposed method has three stages viz. skin segmentation to detect the hand, edge tracking for feature extraction and particle filter for hand tracking. The overall diagram of our method is given in Fig. 1.

The sensor array is formed by the standard three-electrode configuration: a gold disk working electrode, a saturated calomel reference electrode and a platinum wire auxiliary electrode. The gold disk electrode and platinum wire electrode are purchased from Shanghai Chenhua Instrument limited Company. The reference electrode is made in Ltd Rex Instrument Factory belonging to Shanghai Precision Scientific Instrument Company. The electrochemical workstation is also bought from Shanghai Chenhua Instrument limited Company. The cyclic voltammetry is applied as the measurement principle in the electronic tongue and the parameters are set as follows: initial potential = 1.0 V; low potential = -1.0 V; high potential = +1.0 V; final potential = 1.0 V; initial scan polarity: negative; scan rate = 100 mVs-1; T = 30ºC.

Sample source: The edible oil samples under study are shown in Table 1. They include samples of five varieties of edible oil, samples from different geographic areas. The edible oil samples were stored at 20ºC under dark and unfrozen just before use.

Sample pretreatment: The oil samples heat to 30ºC and shake, measure 30 mL and pour it 100 mL separatory funnel, add an equal volume of 30ºC deionized water, turbulent 5 min, still stratification will lower water phase into a 50 mL beaker, take the beaker into the 30ºC water bath, extract until the water temperature stable at 30ºC, Electronic tongue measure it. Each sample take twice, extract the average. All samples were measured at 30ºC. Attention to determination of next sample, the electrode head with a large number of ethanol rinse, in order to avoid contamination of a sample of the electrode under the influence of determination.

Table 1: Samples of olive oils from different origins and varieties

Sample	Origin	Brand
Oil_1	Guangdong (China)	Jinlongyu
Oil_2	Guangdong (China)	Jinlongyu
Oil_3	Guangdong (China)	Jinlongyu
Oil_4	Tianjin (China)	Fulinmen
Oil_5	Tianjin (China)	Fulinmen
Oil_6	Tianjin (China)	Fulinmen
Oil_7	Liaoning (China)	Jinlongyu
Oil_8	Liaoning (China)	Jinlongyu
Oil_9	Liaoning (China)	Jinlongyu
Oil_10	Tianjin(China)	Fulinmen
Oil_11	Tianjin (China)	Fulinmen
Oil_12	Tianjin (China)	Fulinmen
Oil_13	Heilongjiang (China)	Jialiang
Oil_14	Heilongjiang (China)	Jialiang
Oil_15	Heilongjiang (China)	Jialiang

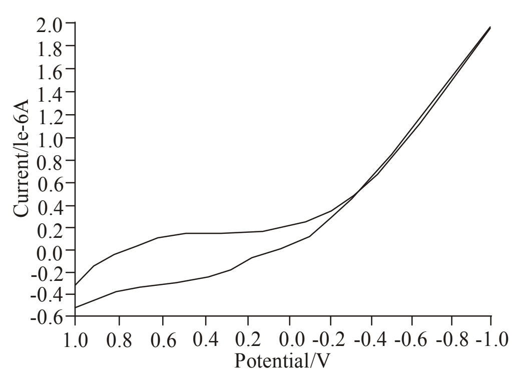

Fig. 2: Voltammogram obtained from peanut oil

Data acquisition: The experimental subjects in this experiment are five types of edible oil, including soybean oil, corn oil, peanut oil, sunflower oil, sesame oil. They are purchased from Darunfa supermarket in Jilin of China. The experiment is conducted at room temperature. The representative voltammograms corresponding to each kind of tea are shown in Fig. 2 to 6, which will be processed as the raw data.

Data processing: The data of cylic voltammetry curve were very large. In order to reduce the data redundancy and the burden of data processing, the data were needed feature extraction. For the characteristics of cyclic voltammetry curves, the eigenvalue extraction was the peak current, the second peak current. These points could reflect the characteristics of each substance and greatly reduce the amount of data to be processed.

Principal component analysis: The principal component analysis is a dimension reduction statistical method, it is by means of an orthogonal transformation, its component related to the original random vector into its components is not related to the new random vector performance in the algebra of the original random vector covariance matrix of transform pairs of angular array performance to transform the original coordinate system into a new orthogonal coordinate system so that the point of sample points spread most open p orthogonal directions geometry, then the multi-dimensional variable system down dimension, so that it can convert to a high precision, low-dimensional variable system, by constructing a suitable value function and further low-dimensional systems into one-dimensional system. Principal component analysis was applied to the set of CV responses obtained from these five different vegetable oils as indicated in the "Experimental" section. The best results, with regard to oil differentiation, were obtained after column autoscaling. R principal components were selected and counted the scores:

$$F_k = a_{1k}X_1 + a_{2k}X_2 + \cdots\cdots + a_{pk}X_p, \ \mathrm{k} = 1, 2, \ldots, \mathrm{r}$$

The new data were selected (F_1, F_2, …, F_r) as new matrix for cluster. Then the new matrixes were counted by the mean score of all types in the samples to determine the ranking. Finally, the types of the sample order were determined according to the first the principal component scores within the class. Principal component analysis of the specific calculation process is as follows:

- In order to prevent the impact of each dimension is different to the original data must be standardized original variable coordinate translation and scale transformation. Set the input sample data matrix $X_{n\times p}$, the sample data normalized to:

$$\tilde{x}_{ij} = (x_{ij} - \bar{x}_j)/S_j, (i = 1,2,...n, j = 1,2,...p)$$

- Find the covariance matrix Z
- Characteristics of decomposition $Z = U\Lambda U^t$, is about to axis rotation to new axes U: eigenvalues

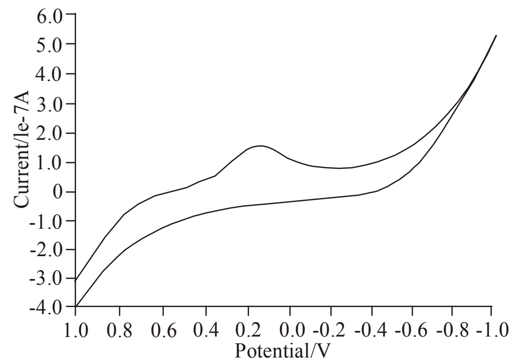

Fig. 3: Voltammogram obtained from corn oil

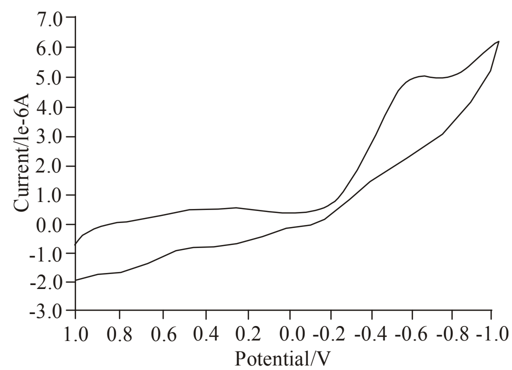

Fig. 4: Voltammogram obtained from soybean oil

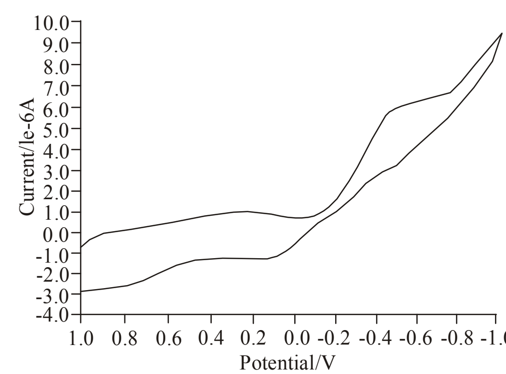

Fig. 5: Voltammogram obtained from sunflower oil

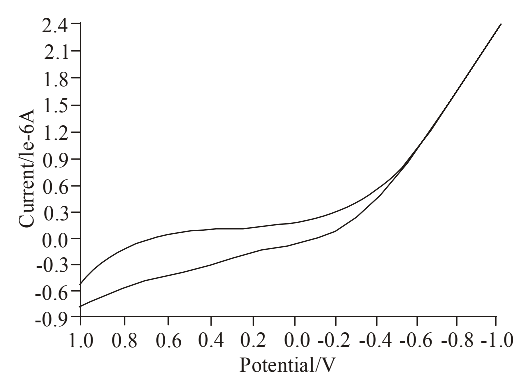

Fig. 6: Voltammogram obtained from sesame oil

for the covariance matrix Z consisting of diagonal matrices $\wedge$; U characteristic vectors by column orthogonal matrix Z, it constitutes a new vector space, also known as the load axis as the axis of the main ingredients, the characteristic value indicates the size of the principal component of variance to determine the number of principal components according to their size.

- According to the cumulative contribution rate η_m is greater than the threshold, can be considered the principal component number m.
- Find the value of the principal components, each line of the F matrix is equivalent to the projection of the vector of the original data matrix in the principal component axes, the principal component score vector.

Factor analysis: Factor analysis of each original variable into two parts: part of the few factors common to all variables and the so-called public factors were partially, another part of the factors of each variable alone, the so-called unique factor parts. Factor analysis is a data reduction technology. Internal dependencies between the number of variables of the study and explore the basic structure of the observational data and a few hypothetical variables to represent the basic data structure. These hypothetical variables that reflect the main message of the original number of variables. The original variables can be observed in the variable the imaginary variable is the potential unobserved variables called factors. Its mathematical model is:

Set variables as $X_i(i = 1, 2,\ldots, p)$, expressed as:

$$X_i = \mu_i + a_{i1}F_1 + \ldots.. + a_{im}F_m + \varepsilon_i \ \ (m \le p)$$

$F_1, F_2, \ldots.., F_m$ as the common factor is an unobservable variable, their coefficients are called factor loadings ε_i is a special factor, the first m common factor cannot be included in part, and satisfy:

$$\operatorname{cov}(F, \varepsilon) = 0$$

So $F_1, F_2,\ldots, F_m$ are unrelated, variance is 1.

Hierarchical cluster analysis: Hierarchical Cluster Analysis is a statistical method which can be described as "birds of a feather flock together". It looks for statistics that can objectively reflect the similarity and dissimilarity among the researching objects ignorant of how m any classifications they will be and then classify these objects into several categorizations in line with geographic distance or attribute similarity based on the statistics. Cluster analysis theory especially applies to solve the problem of classifying massive samples and diversified pavement condition indicators. Hierarchical Cluster Analysis theory includes three major application methods, namely, Hierarchical Cluster Analysis, Dynamic Cluster Analysis and Optimal Partition Analysis, each of which has its own application conditions. Hierarchical Cluster Analysis application steps are demonstrated as follows:

Step 1: To calculate the distance d_{ij} between two samples:

$$d_{ij} = \sum_{k}^{m} \left| \overset{*}{x}_k - \overset{*}{x}_{jk} \right|$$

Step 2: To merge two nearest samples into a new class at a time and then the total number o f segments l will decrease by one segment namely l = n – i + l.

Step 3: To calculate the distance between the new class and other classes and then combine two nearest classes.

Referring to the following equation:

$$D_{pq}^2 = \frac{1}{n_p n_q} \sum_{i \in G_p, j \in G_q} d_{ij}^2$$

Note that,

D_{pq} : The distance between class D_p and class D_q

n_p : The number of samples of class G_p and n_q for class G_q

Step 4: To repeat step three and step four to obtain a new distance matrix. If the number of classes after combination is still larger than 1, then to repeat step three and step four until the number of classes remains 1.

When class G_p and class G_q are combined into G_r ($G_r = \{G_p, G_q\}$ and $n_r = n_p + n_q$, n_r is the number of samples of G_r), the recursion formula of the distance between class G_r and other classes G_s is:

$$D_{rs}^2 = \frac{n_p}{n_q} D_{ps}^2 + \frac{n_q}{n_r} D_{qs}^2 \ \ (s \ne p, q)$$

In the formula, D_{rs} is the distance between class D_{ps} and class D_{qs}.

Step 5: To draw a clustering figure and decide the number of classification and its membership.

RESULTS AND DISCUSSION

A sensor array generates data of high dimensionality, hard to handle and visualize. First, the original data were extracted for the Eigenvalues and then use multivariate statistical analysis software

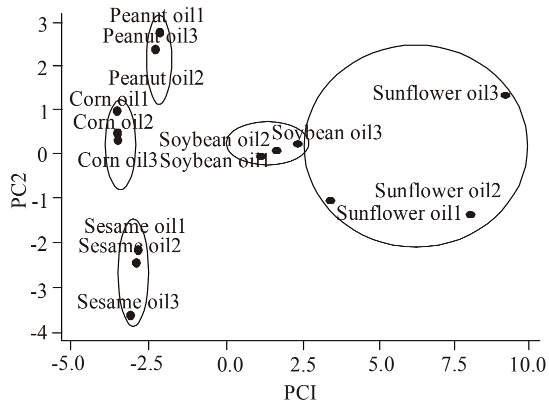

Fig. 7: The PCA score plot

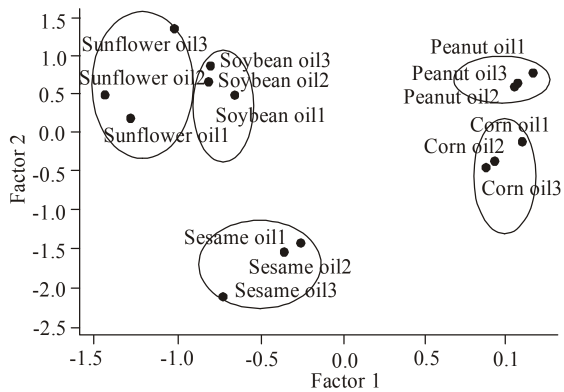

Fig. 8: The FA score plot

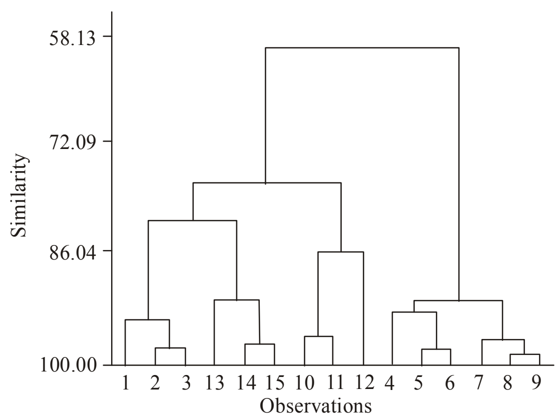

Fig. 9: Dendrogram of five oils (from 1 to 3 are soybean oils, from 4 to 6 are corn oils, from 7 to 9 are peanut oils, from 10 to 12 are sesame oils, from 13 to 15 are sunflower oils)

MINITAB16 to linear discriminant analysis and principal component analysis.

Figure 7 present the PCA result. This different information is well distinguishable on the two first principal components, respectively. In fact, PC1, which explains 58.14% of the variance contained in the original data, is the variable that permits a good separation Instead, PC2, which explains a lower variance percentage (19.96%). which is shown in Fig. 7.

The results show that PCA can distinguish between various types of edible oil, the classification is obvious and the operation speed is fast, high accuracy, it can be used for classification and identification of other products.

As is shown in Fig. 8 present the Factor analysis result, the samples are clustered at five independent zones and the samples belonging to the same kind of edible oil together. The distance between different types of edible oil is large.

The result shows that the factor analysis algorithm can discriminate edible oil very well. And a sample in which the region is easier to distinguish between classification and recognition.

The data extracted from the voltammograms are also processed by the cluster analysis algorithm. The clustering result is shown in Fig. 9.

Results can show the degree of similarity between each kind of edible oil. However, this method is applicable to distinguish between the different kind of oils are relatively large, the same kind of oil is quite similar. And through human screening data for the large amounts of data, there is the possibility of misclassification, so this method is applicable to certain limitations.

The identification of different types of edible oil with above three types of pattern recognition algorithms demonstrates that the correct rate of discrimination with PCA and FA is better than that with HCA.

CONCLUSION

Edible oil was tested by the three-electrode voltammetric electronic tongue system, the data were processed by feature extraction. Based on cyclic voltammetry electronic tongue can be a better classification of five kinds of edible oil with the higher recognition rate. The results showed that PCA, FA and HCA can identify the edible oil, Principal Component Analysis (PCA), Factor Analysis (FA) can be better applied to the edible oil detection than Hierarchical Cluster Analysis (HCA), but the effect of the PCA was better than the FA. In this study, we introduce a new method for the detection of the edible oil.

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