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ROUND UP

Development and application of electronic noses in freshness assessment of fishery product

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Abstract: Quality control of fishery product is of utmost importance to fishery product processing industry. Traditionally, the freshness of fishery product has been evaluated either by sensory organs or by gas chromatography that are expensive, time consuming and not suitable for real-time application. Development of an efficient and objective technique to monitor the quality of fish is therefore of increasing interest. Electronic nose has proven to be a rapid, automatic and non-destructive technique for measuring volatile compounds that exhibit spoilage odors in fish. The principle of electronic noses and the development of chemical sensor technology were described in this paper. The application of electronic noses in freshness assessment of fishery product and future prospect were discussed as well.

Key words: electronic nose; fishery product; freshness assessment

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1 Introduction

Odor is one of the most important indicators for fish freshness. During the storage of fish the odor changes from fresh through flat, sweet and stale and ends as spoilage or putrid odor[1]. Research has shown that during each phase of storage different volatile compounds are present and characterize the odors. Fresh fish odor is mainly contributed by compounds that are oxidatively derived from such long chain polyunsaturated fatty acids as eicosapentaenoic acid 20∶5ω_3[2]. These compounds have low odor thresholds and are present at low concentrations (ppb). Compounds that contribute to microbial spoilage odors of fish are well known. TMA, ethanol and hydrogen sulphide that result from microbial degradation of amino and fatty acids exhibit odor such as fishy, stale, rotten and putrid and are present in high concentrations in the fish during storage[3].

A number of techniques have been used to assess fish freshness. Traditionally, the sensory test is the key technique to subjectively evaluate fish freshness. This provides immediate quality information but suffers from some disadvantages, including 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[4]. Gas chromatography (GC) and mass spectrometry (MS) have been applied to determine the aroma products of fish. GC and GC/MS provide much accurate data and are able to define the chemical nature of aroma compounds. However, GC and GC/MS

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systems are complicate, destructive, and unsuitable for real-time and on-line application in the modern fishery and food industries[4,5]. Some chemical measurements could also be classified as freshness monitoring methods when they are used to determine one specific compound or a class of compounds that are important indicators of fish freshness. Examples are TVN (total volatile nitrogen) and TMA (trimethylamine) measurements[6]. Unfortunately, these methods are still laboratory techniques that are complicate, destructive and time consuming, and sometimes give no information about the quality changes during the early storage of fish[7,8]. In recent years, electronic noses have been introduced as a rapid, and portable method to perform objective, un-destructive and reproducible tests of volatile compounds and odors in food and fishery products[9].

2 Principle of electronic noses

2.1 The concept of electronic noses

Electronic noses are used to "sniff" the volatile components in the headspace of a product in a sealed sampling system by transferring them to the sensor array. An electronic nose comprises an array of chemical sensors and matched with a suitable data processing system[10]. The concept of electronic nose dates back to 1982, and the first commercial instrument was introduced to the market in 1993[11]. The response from a chemical sensor is usually measured as the change of some physical parameters, e. g. conductivity or current. The responses from all sensors form a response pattern. The response pattern from different odors can be learnt by a computer in order to recognize them when the sensors again are exposed to one of the initially learnt odors. The learning can be made using a number of different techniques, e. g. statistical methods and artificial neural networks.

2.2 Sampling methods

Sampling is a crucial step in electronic nose measurements. The goal of sampling is to collect the volatile components that represent the real condition of an analytical problem and to provide an adequate concentration/ amount of compounds to the sensors for detection. There are two main sampling methods: static headspace analysis (SHA) and flow injection analysis (FIA). The SHA is commonly used i. e. the sample to be 'sniffed' is placed in a container where the volatile components in headspace then diffused into the chamber with the sensor array installed. It is simple and low-cost and able to measure volatile compounds of low molecular weight such as hydrogen sulphide, dimethysulphide and amines[5,12]. The FIA is usually computerized and automated and employs clean air as background gas which is constantly pumped into the sensor chamber. The gas containing volatile compounds is injected into the background gas before it reaches the sensor chamber. The mixture ratio of background gas to volatile compounds can be precisely controlled. The FIA is complex and expensive and usually used for collecting and concentrating less-volatile compounds such as those contributing to 'fresh fish' and 'oxidized' odors[12].

2.3 Data analysis

Data analysis is an important issue in electronic nose measurements. Its role is to determine the relation between sensor output patterns and the properties of the samples being analyzed. Artificial neural networks (ANNs) and chemo-metrics analysis such as principal component analysis (PCA) and partial least squares regression (PLS - R) are frequently used.

The ANNs that are based on a non-linear approach are powerful pattern-recognition techniques. Many ANN configurations and training algorithms have been used in electronic noses including back propagation-trained feedforward networks and self-organizing maps (SOMs). Back propagation is a supervised algorithm that must be trained with labeled odors. It learns the relationship between the sensor values and the given odor labels. A SOM is an unsupervised algorithm that does not require predetermined odor classes for training. It essentially performs clustering of the data into similar groups based on the measured attributes or features that serve as inputs to the algorithm. It can be thought of as way of projecting multiple dimensions (usually each dimension represents a different sensor output or a feature extracted from the sensor array) onto a two-dimension output allowing the user to visualize the grouping and relationships of the odors or volatile compounds. One of the main problem of an ANN approach is that the training typically becomes more difficult, and the class prediction is less satisfactory when the data sets are smaller[10,13].

In addition to the ANNs used in a majority of the electronic noses, more traditional pattern recognition and clustering techniques, such as principle components analysis (PCA), partial least squares (PLS), discriminate factorial analysis (DFA), and cluster analysis (CA), are also used. The PCA breaks apart data into linear combinations of orthogonal vectors based on axes that maximized variance. The application of the PCA to a data set provides two quantities, namely the score and the loading. The score plots, limited to the most significant PCs, give a visual image of the data set of an electronic nose. The loading is used to evaluate the contribution that each sensor carries to the total information of the data set[14]. The PCA can simplify complex and diverse relationships of observed variables by contracting information into a smaller number of principle compounds. The PLS which is based on known probability of variable distribution, is used as a prediction model. The DFA is a multivariate technique which best discriminates one group of objects from another by determining a set of variables.

3 Development of chemical sensors

Even though the broad selectivity of the sensors in an electronic nose is compensated by advanced information processing, the sensors must still meet key design parameters for the system. These include selectivity, sensitivity, stability, speed of operation, cost, size, manufacturability, ability to operate in diverse environments, and the ability to be automatically and quickly cleaned. Many types of chemical sensors are now available for use in electronic nose instruments. The most frequently used sensors are metal oxide semiconductor sensors (MOS), metal oxide field effect transistors (MOSFET), conducting polymer sensors (CP), surface acoustic wave sensors (SAW), quartz microbalance (QMB), and electrochemical sensors.

MOS sensors are made from a metal-oxide film (e.g. tin oxide). The odorant molecules undergo a reaction on the film surface producing a conductivity change in the sensor. The heaters in the sensors aid the reaction process. The advantages of MOS sensors include low cost, longevity and electronic simplicity, and the disadvantages are the necessity to operate at high temperatures (200 - 500 ℃), limited selectivity, high power requirements and modest sensitivity[10,15].

MOSFET sensors consist of a doped semiconductor and an insulator (oxide) covered by a catalytic metal. The output signal is based on a change of potential in the sensor due to electrical polarisation when molecules react on the catalytic surface. The sensors operate at temperatures between 100 - 200 ℃. The selectivity and sensitivity of this type of sensors are dependent on temperature and choice of metal[10].

CP sensor is a semi conducting polymer film coated to adsorb specific species of molecules. When the odorant molecules interact with the coating, the conductivity of the sensor changes. CP sensors have wide selectivity, high sensitivity, stability, and operate at ambient temperature. The drawback of CP sensors is a strong sensitivity to humidity[15].

SAW sensors are piezoelectric quartz crystals coated with selective coatings that adsorb species of molecules.

The adsorbed molecules increase the mass of the sensor changing its resonance frequency. By measuring this change, the concentration of odorant can be derived. The advantages of SAWS include high selectivity, high sensibility, stability over wide temperature ranges, low response to humidity, and good reproducibility. The disadvantage is the complexity in the interface electronics[15].

QMB sensors are similar to SAM sensors in the use of mass change on a piezoelectric crystal coated to indicate presence and concentration of the odorant molecules. However, a QMB sensor consists of a quartz disk sandwich between two electrodes. The functions of QMB sensors are similar to SAM sensors, but the latter operate at much higher frequencies (50 - 100MHz) than the former (5 - 30MHz)[10].

An electrochemical sensor consists of several electrodes and an electrolyte. The odorant molecules are either oxidized or reduced at the working electrode, while the opposite reaction takes place at the counter electrode. The reaction between the electrodes generates a voltage between the electrodes, which is measured as the output signal. The electrochemical sensors are very sensitive to short chain alcohols that are produced during the spoilage of fish and not sensitive to humidity[1,11].

4 Applications of electronic noses in freshness assessment of fishery product

The advent of the electronic nose has opened a variety of applications and new possibilities in many fields where the presence of odors is the relevant phenomenon. Currently, the biggest market for electronic nose is the food industry. Application of the electronic nose include: checking the quality, taints and off-flavors of the raw material; quality monitoring of foods during processing; quality control of finished food products[15,16,17].

The research focusing on fish has also been done by means of electronic noses for freshness monitoring and odor evaluation. Ólafsson et al.[7] have reported the application of an array of MOS sensors for monitoring the freshness of haddock and cod stored in ice. They found a linear response to increasing concentration of these volatile compounds at levels that occur naturally in fish, and were able to detect early spoilage of the fish in real time. It is desirable, however, to distinguish between the different aroma molecules, something that is not easily achieved with tin oxide sensors. Schweizer-Berberich et al.[18] used an array of eight amperometric sensors to monitor changes in odor of cold stored trout. The responses of the sensors changed with storage time. After calibration of the array with well-defined gases, these results correlated well with the concentrations of amines and sulfides in the complex odor of fish. The concentrations of long chain alcohols and carbonyls, however, could only be monitored with relatively large errors. An array of metalloporhyrins-coated QMB sensors was used to recognize the storage time of cod fillets by Di Natale et al.[19]. Small compounds such as alcohol, sulphur compounds, and trimethylamine in fish were detected successfully. Deng et al.[20] used eight CP films as sensitive coatings for acoustic wave sensors to determine the aroma molecules nona-2,6-dien-1-en-3-ol, oct-1-en-3-ol and nona-2,6-dienal. These vapors are all related to fish quality and are important determinants of early fish spoilage. The result showed that most of the polymer coatings exhibited a quick, reversible response to the target analyses. The response of the sensors was generally found to be linearly dependent on vapor concentration. Unfortunately, the effect of humidity was not addressed because this was an important factor in the practical measurement of fish freshness using an array of PC sensors. Hurst[11] demonstrated that an array of twelve CP sensors could correlate the odor of salmon fillets with storage time when the moisture of the samples was the same.

An electronic nose with electrochemical gas sensors has been developed in recent years for rapid detection of volatile compounds in fishery product. Ólafsdóttir et al.[5,21] used this kind of instrument and a static headspace sampling technique to monitor the volatile compounds such as alcohols, amines, and sulphur compounds in the headspace of capelin during spoilage. The instrument showed good sensitivity, selectivity and reproducibility, and correlated also well with classical TVB - N measurements. Another positive attribute was that the electronic nose did not respond to water. Similar results were obtained when measuring herring, whole or peeled shrimp and fresh roe[6,22,23].

5 Future prospects

As a new technology, electronic nose is certainly the most promising among new analytical methodologies for objective evaluation. However, many problems have been encountered in nowadays applications such as poor sensitivity and selectivity to odorant molecules measured, sensor drift, and sensitive to environmental humidity and temperature. Possible improvements in electronic nose technology will concern on new odor sensing materials, new transducers, multi-type or hybrid noses, smarter pattern recognition techniques and micro noses.

There is obviously a great need for an objective, automated and real-time analyzing system for food quality evaluation. So electronic noses will find wider applications in food industry in future. The use in food industry could grow to include fish inspection, fermentation processes, container examinations etc. Another futuristic application of electronic noses is environmental problems such as analyzing hazardous waste, fuel mixtures, ground water, air quality, or factory emissions. The future for electronic noses also looks very promising in medical diagnostics, biotechnology, and even in domestic applications.

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电子鼻技术的研究进展及其在水产品鲜度评价中的应用

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摘要: 水产品的质量管理是水产加工企业的重要环节。传统上, 水产品的鲜度主要是采用感官评价或气相色谱分析的方法进行的。这些方法费时昂贵, 而且不便于对产品质量的适时监测。因此, 高效、快捷的水产品质量监测技术的研究受到了很大关注。利用电子鼻监测水产品的鲜度, 被公认是一种快速、可靠、可实现自动检测、而且对水产品无任何伤害的新型技术。本文阐述了电子鼻的工作原理和化学传感器技术的研究进展, 并且讨论了电子鼻技术在水产品鲜度评价中的应用和未来发展前景。

关键词: 电子鼻; 水产品; 鲜度评价

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