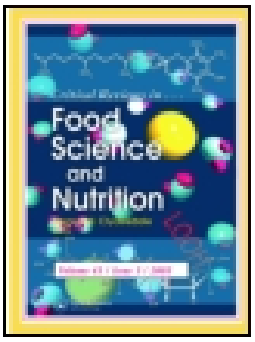

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Advances of Electronic Nose and Its Application in Fresh Foods：A review

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**ABSTRACT**

The science and technology aspects of electronic nose (E-nose) has been developed rapidly in last decade (2006-2016). This paper reviews of the publications that that cover the developments in science and technological aspects of electronic nose together with its application in fresh foods. The first part of this review covers the sensing and pattern recognition system of E-nose. The second part covers the application of E-nose in classification, flavor detection, and evaluation of spoilage in fresh foods area. With more new sensor materials to be found and more combination between E-nose and other analysis technologies, the usages of E-nose in fresh foods will have wider prospects.



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**Keywords**

Electronic nose, sensors, pattern recognition, flavor research, quality monitoring

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## 1. *Introduction*

The electronic nose (E-nose) is an instrument which mainly contains three parts, a sample handing system, number of chemical sensor arrays and a pattern recognition system, it is usually used for detecting simple or complex volatile organic compounds (VOCs) (Amalia, 2010), it eventually became on of the most useful instrument in food industry. Before 1990s, human nose was normally used to detect different olfactory factors, it is convenient but not precise, reproducible neither objective. What’s more,human noses are more easily influenced by many ambient factors or inner condition like physical and mental health (Pearce et al., 2003). Instrument analysis has been widely used in the food industry, including nondestructive testing, chromatography, scanning electron microscopy, texture analysis and so on (Jirovetz et al., 2005). Chromatographic analysis, scanning electron microscopy and texture analysis has high sensitivity, but often requires pretreatment of the sample, and the pre-treatment is complex and time-consuming, so it is difficult to meet the needs of modern food industry for the rapid detection of the quality of the products.

As a kind of nondestructive testing technology for odor of volatile substances in food, at the same time, the electronic nose technology has been widely used in the food industry, but also gradually extended to the chemical, textile (Thomas et al., 2012) biomedical diagnostic disease (Scarlata et al., 2015; Schnabel et al., 2015; Wilson and Baietto, 2011), microbial fermentation (Jiang et al., 2015) environmental monitoring (Capelli et al., 2014-a; Capelli et al., 2014-b), agricultural and forestry (Dymerski et al., 2013; Wilson, 2013), customs security (Haddi et al., 2011) and military fields (Brudzewski et al., 2012),with the objective of efficient, real-time, low training cost, a confident recognition power of various product decay conditions and easy

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adjustment to changing conditions (Musatov et al., 2010) and other advantages, it truly has a very broad prospects for the development and application of electronic nose in food area.

Compared with traditional olfactory sensing technology, E-nose has a wider application range, higher accuracy and better quality. This article is aimed at reviewing the recent developments in the application of electronic nose in fresh food area, such as classification, flavor research, freshness and spoilage evaluation and quality monitoring. Some trends of the application of electronic nose have been summarized too in this paper.

## 2. *Electronic nose*

In 1994, the term of “electronic nose” was formally defined as “an instrument, which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system, capable of recognizing simple or complex odors” (Gardner and Bartlett, 1994). In recent years, electronic nose has a more extensive meaning, based on the change of enviromental atmosphere which leads the change of odor sensor in a special way and change the general principle to detect smell around, which associated with the gas sensors (Loutfi et al., 2015). Compared with other instruments, E-nose tends to be more effective, easy to implement and not computationally expensive. Discrimination of Pecorino cheeses using electronic nose combined with artificial neural network may get a higher classification capability, compared with GC--MS analysis of volatile compounds (Cevoli et al., 2011).

The electronic nose is a kind of instrument to detect and identify the complex smells with gas sensor array, the sensor array is composed of wide coordination (low specificity) sensors, these sensors can deal with all kinds of smell sensitive biological or chemical materials (Pearce

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et al., 2003). An odor sensor array creates a specific fingerprint (or scent fingerprint) (Choi and Jeong, 2014). Patterns or fingerprints of known gases can be used to establish and train a pattern recognition system that can be used to detect and analyze unknown smells. When use a E-nose for discriminating or detecting, inject the sample to the headspace, then the odorants will be absorbed by the sensing system, the signal generated before will be sent to the signal handling system for processing, the product will be taken to the pattern recognition system (PR) for a judgment, a terminator will put out the final result of the analysis.

### 2.1 Sensing system employed in electronic nose

The sensing system can be an array of several different sensing elements or a single device or a combination of both. The films of sensors elements chemically react with sampling adour molecules and these chemical reactions always accompany the transformation of electrons, which is detected by sensors device as electrical signal (Arshak et al., 2004). At present, the commercial gas sensor technologies comprise metal oxide semiconductors (MOS), metal oxide semiconductor field effect transistors (FET), organic conducting polymers, and piezoelectric crystal sensors (Ghasemi-Varnamkhasti et al., 2009). The metal oxide sensor has the most widely used range and history (Mikosch and Starica, 2000; Zohora et al., 2013). In addition to these conductive sensors, there are optical sensors (Zhao et al., 2016), chemiresistor sensors (Alizadeh, 2010), Surface Acoustic Wave (SAW) sensors (Verma and Yadava, 2015) and Quartz Crystal Microbalance (QCM) (Ali et al., 2003; Papadopoulou et al., 2013) sensors for gas detection. The detection result is not only affected by the type of sensor but also the number of sensors.

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### 2.2 Pattern recognition system

Pattern recognition system is used for data processing of signals generated by each sensor. Data processing techniques used in post processing of pattern recognition. All of the pattern recognition methods can be devided by the terms of parametric or nonparametric and supervised or nonsupervised. If the sensor data can be described by a probability density function (PDF), it is classified as a parametric technique, otherwise is nonparametric technique. As a supervised pattern recognition method, the odors sent to the E-nose will be classified by known descriptors and if the odors are out of primary knowledge base, they will be tested again. Other pattern recognition methods will automatically learn to classify from the responses (Hines et al., 1999). Routines include principal component analysis (PCA), which is most often used(B. Zhang et al., 2012), linear discriminate analysis (LDA) (Musatov et al., 2010), partial least squares (PLS) (Pallottino et al., 2012), functional discriminate analysis (FDA), hierarchical cluster analysis (HCA) (Alizadeh, 2010), Learning Vector Quantization (LVQ) (Nimsuk, 2014), fuzzy c-means (FCM) (Verma and Yadava, 2015), artificial neural network (ANN) (Cevoli et al., 2011) such as probabilistic neural net-work (PNN). Among these techniques, PCA, PLS, LDA, FDA and CA are based on a linear approach while fuzzy c-means (FCM), ANN and PNN are regarded as nonlinear methods (Scott et al., 2006).

The experimental results are usually different with application of diverse pattern recognition algorithm, Hasan et al. (2012) detected the meat and fish freshness with the electronic nose based on three pattern recognition algorithms (artificial neural network, support vector machine and k-nearest neighbor), and compared them based on accuracy, sensitivity, and specificity. The results demonstrate that the k-nearest neighbor algorithm has the highest accuracy.


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Different recognition methods have different applicability, And a variety of pattern recognition algorithms are often used in a study. Tian et al. (2013) applied an E-nose in analysis of pork adulteration in minced mutton. In their experiment, Feature extraction methods, Principle component analysis (PCA), loading analysis and stepwise linear discriminant analysis (step-LDA) were employed to optimize the data matrix, finding that step-LDA was the most effective method. Then Canonical discriminant analysis (CDA) was used as pattern recognition techniques for the authentication of meat. Partial least square analysis (PLS), Multiple Linear Regression (MLR) and Back propagation neural network (BPNN) were used to build a predictive model for the pork content in minced mutton. Results showed that the model built by BPNN could predict the adulteration more precisely than PLS and MLR do. Hong and Wang (2014) build feature construction of fusion datasets with Principle Component Analysis (PCA), factor F and stepwise selection, apply Canonical Discriminant Analysis (CDA) and Library Support Vector Machines (Lib-SVM) on the Qualitative recognition of adulteration levels. All the approaches presented well classification performances on detection of adulteration in cherry tomato juices.

Recent experimental findings in the field of neuroscience suggest the human brain to be an optimal Bayesian brain, with the argument that sensory information can be represented in the form of probability distribution (Rich et al., 2015), so the Bayesian parametric method maybe a novel promising pattern recognition algorithm in the feature, and some studies has proved it’s advantages (Banerjee et al., 2014; Hassan and Bermak, 2016).


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## 3. *Application in fresh food*

The application of electronic nose is expanding rapidly, mainly reflected in the expansion of its application areas, such as: food industry, health care, pharmaceutical industry, environmental testing, security and military fields. In addition, the depth of application of electronic nose is also increasing, which is reflected in its application in the same field but different sectors of the food industry, such as the process monitoring, E- nose can be used to achieve real-time monitoring for raw material management, harvesting, processing, storage and other processes; the investigation of the shelf life, it can be used for the identification of fruit and vegetable maturity, determination of the grain's shelf life; the evaluation of freshness degree, we can use the E-nose to detect the fresh level on the consideration of microbial content and spoilage odor of aquatic fishes, also we can identify the usage of anti-corrosion materials of food by detecting the VOC; in terms of the evaluation of the reliability, E-nose can be used to discriminate all kinds of alcoholic beverages, dairy product and food on the species, authenticity and so on (Peris and Escuder-Gilabert, 2009). We provide this article to introduce the recent applications of intelligent olfactory, E-nose, on main areas about classification, flavor research, freshness evaluation, shelf life appraisal and so on associated with fresh food.

### *3.1 Classification*

Smell is an important olfactory parameter in sensory evaluation of food quality. Through the detection of some VOCs with specific odor characteristics, the types, origin and processing modes of fresh food can be determined. The application of he electronic nose system in the food classification is very extensive due to its fast and stable detection and analysis ability on VOCs.

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Among applications to fresh food authenticity assessment, successful applications to differentiation of meat, fish, cheese, grains, spices on the basis of geographical origin, genotype and individual containment have been reported in many literatures (Table 1).

Zheng et al. (2009) successfully identified four rice samples of long grain type using an electronic nose (CRYnose-320) consisting of 32 polymer sensors. They had investigated the composition of the rice odors, considered the optimum parameter setting and concluded that the CRYnose-320 has the potential to differentiate between types of rice.

Liu et al. (2013) studied on the chemical and flavor qualities of white pepper (*Piper nigrum L.*) derived from five new genotypes. They analyzed major volatile compounds with headspace solid-phase micro-extraction gas-chromatography mass spectrometry (HS-SPME-GC-MS), for volatiles of unknown nature with electronic nose (E-nose), and flavor quality was assessed by sensory testing. The five genotypes of white pepper got distinguished well, and the results came from the electronic nose and HS-SPME-GC-MS were in high consistency.

Nurjuliana et al. (2011) used an electronic nose and gas chromatography mass spectrometer with headspace analyzer (GCMS-HS) analyzed the volatile compounds of pork, other meats and meat products. By using a visual odor pattern called VaporPrint™, the zNose™ was successfully employed to identify and differentiate the pork and pork sausages from beef, mutton and chicken meats and sausages, the information handled by the odor pattern was derived from the frequency of the surface acoustic wave (SAW) detector. Principal component analysis (PCA) was applied for data interpretation and was able to cluster and discriminate pork from other types of meats and sausages. It was shown that the meat samples were separated along the first PC which

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described 67% of the peak variations and the result provided the rapid, accurate, low cost advantages about the E-nose's performance on halal verification.

An Electronic Nose Based on Coated Piezoelectric Quartz Crystals was used to Certify Ewes' Cheese and to Discriminate between Cheese Varieties (Pais et al., 2012). In their experiment, Two sensors coated with Nafion and Carbowax could certify half the ewes' cheese samples, exclude 32 cheeses made from cow's milk and to classify half of the ewes' cheese samples as possibly authentic. Two other sensors, coated with polyvinylpyrrolidone and triethanolamine clearly distinguished between Flamengo, Brie, Gruyère and Mozzarella cheeses. As a result, Brie cheeses were further separated according to their origin, and Mozzarella grated cheese also appeared clearly separated from non-grated Mozzarella.

In the application of fish classification, Guney and Atasoy (2015) distinguished between three different species of fish--horse mackerel, anchovy and whiting -- by using an electronic nose composed of 8 different metal oxide gas sensors. A whole new method, which is not applied to this kind of data previously, is used in three parts such as signal pre-processing, feature extraction and classification and proposed for use in the pattern recognition unit. The overall accuracy of the identification of fish species achieved with the proposed methods is 96.18%, compared to conventional methods such as Naïve Bayes, k-Nearest Neighbor and Linear Discriminant Analysis, whose accuracy of the classification are 84.73%, 80% and 82.4%, respectively.

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### *3.2 Flavor research and quantification*

Fruits produce a wide range of volatile organic compounds that impart their characteristically distinct aromas and contribute to unique flavor characteristics. Fruit aroma and flavor characteristics are of key importance in determining consumer acceptance in commercial fruit markets based on individual preference (Baietto and Wilson, 2015). Fruit aromas consist of a complex mixture of VOCs whose composition is specific to plant species and fruit variety, the most important aroma compounds include amino acid-derived compounds, lipid-derived compounds, phenolic derivatives, and mono- and sesquiterpenes (Schwab et al., 2008). There is the same principle in other fresh food with unique flavor just like dairy, aquatic product, spices and so on (Ampuero and Bosset, 2003; Ghasemi-Varnamkhasti et al., 2009; Table 2**)**.

Zhang et al. (2012) studied the changes in the physicochemical and volatile flavor characteristics of scomberomorus niphonius during chilled and frozen storage. Correlation and multivariate analysis showed a significant time-dependent relationship between total volatile base nitrogen (TVBN)/ trimethylamine (TMA) (Y) and storage time (X) for fish stored in cold rooms, and there was a good linear relationship between TVBN and TMA. The electronic nose analysis revealed that the variation of muscle volatile flavor compounds was found out along the PC1 to the right, and then along the PC2 to the upward and further to the downward based on the principal component analysis (PCA). Furthermore, the linear discriminant analysis (LDA) had better distinction effect for the changes of fish flavor than PCA. Results from this study suggested that the texture analysis in combination with electronic nose techniques might be

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utilized as a rapid expeditious process for predicting quality and shelf life of the fresh fish or other aquatic products.

Li et al. (2013) identified the aroma compounds in Stinky Mandarin fish (*Siniperca chuatsi*) and compared of volatiles during fermentation (with spices and salt) and storage by using electronic nose (e-nose) combining with gas chromatography--mass spectrometry (GC-MS). Among the 61 detected volatiles, 13 aroma-active compounds, especially linalool, were identified in stinky mandarin fish according to thresholds and concentrations. Totally, 24 aroma compounds correlated well with the periods of fermentation and storage. Trimethylamine, indole, sulphur-containing compounds, acetic acid, esters and phenols increased continually, while aldehydes decreased. According to these quality indicators, E-nose data using principal component analysis showed a clear discrimination of the fermented fish and were in good agreement with the results of GC-MS. In conclusion, fermentation favoured to retard spoilage and provided new aroma compounds. The technique employing an e-nose in combination with GC-MS could compare and identify the aroma and quality of stinky mandarin fish.

Ravi et al. (2013) characterized the aroma active compounds of cumin (*Cuminum cyminum L.*), from eight samples (S1-S8), GC-MS analysis showed that the major compounds present in cumin were cuminal (8--17%), β-pinene (22--27%), β-myrcene (1.3--1.75%), ρ-cymene (23--39%), γ-terpinene (11--27%), and ρ-mentha-1,4-dien-7-ol (1.0--5.5%). γ-Terpinene content was 26.36 and 27.73% in S7 and S8 samples by GC-MS, E-nose, and sensory techniques. Sensory odour profiling indicated that samples S7 and S8 had significantly ($p \leq 0.05$) higher intensity of floral, cumin-like, and citrussy aroma notes. Principal component analysis revealed these two samples were associated more with floral, citrussy, and cumin-like aroma notes. An electronic

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nose was found useful to differentiate odor pattern. This study revealed the differences in odour profile of cumin samples of different regions. Thus, these results are useful in the development of designer flavours foods containing spice essential oil.

Song et al. (2013) investigated whether an electronic nose, comprising 18 metal oxide semiconductor gas sensors, could be used for measuring and modelling flavour quality changes of refined chicken fat during controlled oxidation. Partial least squares regression (PLSR) was applied to determine the predictive relationships between the chemical parameters, GC--MS data, free fatty acid profiles and electronic nose responses for controlled oxidation of refined chicken fat. The results showed that peroxide value (PV) and acid value (AV) were significantly well predicted by the electronic nose responses, whereas p-anisidine value (p-AV) was found to be fairly well predicted especially for deeply oxidised chicken fat. Thus, this study gave evidence of the electronic nose system to be a promising device for future at- or on-line implementation in oxidation control of chicken fat for producing meat flavorings.

Wilson et al. (2013) evaluated the capability of detecting the presence of off-flavor malodorous compounds in catfish meat fillets to assess meat quality for potential merchantability with the Aromascan A32S conducting polymer electronic nose. Sensor array outputs indicated that the aroma profiles of good-flavor (on-flavor) and off-flavor fillets were strongly different as confirmed by a Principal Component Analysis (PCA) and a Quality Factor value ($QF > 7.9$) indicating a significant difference at ($P < 0.05$). The A32S e-nose effectively discriminated between good-flavor and off-flavor catfish at high levels of accuracy (>90%) and with relatively low rates (≤5%) of unknown or indecisive determinations in three trials. This A32S e-nose


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instrument also was capable of detecting the incidence of mild off-flavor in fillets at levels lower than the threshold of human olfactory detection.

Tian et al. (2014) examined the feasibility of electronic nose as a method to discriminate chicken and beef seasonings and to predict sensory attributes. Sensory evaluation showed that 8 chicken seasonings and 4 beef seasonings could be well discriminated and classified based on 8 sensory attributes. The sensory attributes including chicken/beef, gamey, garlic, spicy, onion, soy sauce, retention, and overall aroma intensity were generated by a trained evaluation panel. Principal component analysis (PCA), discriminant factor analysis (DFA), and cluster analysis (CA) combined with E-nose were used to discriminate seasoning samples based on the difference of the sensor response signals of chicken and beef seasonings. The correlation between sensory attributes and electronic nose sensors signal was established using partial least squares regression (PLSR) method. The results showed that the seasoning samples were all correctly classified by the electronic nose combined with PCA, DFA, and CA. The electronic nose gave good prediction results for all the sensory attributes with correlation coefficient (r) higher than 0.8. The work indicated that electronic nose is an effective method for discriminating different seasonings and predicting sensory attributes.

Vallone et al. (2012) used an electronic nose system to analyse fruit volatile compounds. The electronic nose used in our work (zNose, EST, Newbury Park, CA, USA), consists of ultra-fast gas chromatography coupled with a surface acoustic wave sensor (UFGC-SAW). This system can perform the three major steps of aroma analysis: headspace sampling, separation and detection of volatile compounds. In about one minute, the output, a chromatogram, is produced and, after a purging cycle, the instrument is ready for further analysis. The results obtained with

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the zNose can be compared to those of other gas-chromatographic systems by calculation of Kovats Indices (KI). A series of programs and graphical interfaces were therefore developed to compare calculated KIs among samples in a semi-automated fashion. These programs reduce the time required for chromatogram analysis of large data sets and minimize the potential for misinterpretation of the data when chromatograms are not perfectly aligned.

Russo et al. (2013) reported preliminary results on the potential of a metal oxide sensor (MOS)-based electronic nose, as a non-destructive method to discriminate three '‘Tropea Red Onion'’ PGI ecotypes (TrT, TrMC and TrA) from each other and the common red onion (RO), which is usually used to counterfeit. The signals from the sensor array were processed using a canonical discriminant function analysis (DFA) pattern recognition technique. The DFA on onion samples showed a clear separation among the four onion groups with an overall correct classification rate (CR) of 97.5%. In addition, this work demonstrated that artificial olfactory systems have potential for use as an innovative, rapid and specific non-destructive technique, and may provide a method to protect food products against counterfeiting.

### *3.3 Freshness and spoilage evaluation*

Freshness is an important quality property in the food industry. Since a number of different VOCs are generated during storage or process of foods, the electronic noses have shown their potential in predicting freshness or spoilage of different food raw material and products. Microbial infection is a major factor in the spoilage of meat, aquatic products, fruit and vegetable. The traditional method of microbial detection includes plate pouring method, plate coating method and spiral inoculation method, but these methods are inappropriate for the

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complexity, time-consuming operations and professional knowledge requirements. Now many rapid determination methods have been developed,such as PCR, ELISA and DNA probe (Botes et al., 2013). Electronic nose is a nondestructive testing instrument, with a variety of pattern recognition algorithms, it can detect the species and content of microorganisms in food quickly and precisely. In particular, foods where significant release of volatiles occur during storage due to procedure of cellular metabolism and degradation bacterial processes, such as fishes, meats, eggs, milk, fruit and vegetable(Table 3).

Tian et al. (2012) reported a method for building a simple and reproducible electronic nose based on commercially available metal oxide sensors (MOS) to monitor the freshness of hairtail fish and pork stored at 15, 10, and 5°C. Sample delivery was based on the dynamic headspace method, and two features were extracted from the transient response of each sensor using an unsupervised principal component analysis (PCA) method. Total volatile basic nitrogen (TVBN) and aerobic bacterial counts of the samples were measured simultaneously with the standard indicators of hairtail fish and pork freshness. Good correlation coefficients between the responses of the electronic nose and the TVBN and aerobic bacterial counts of the samples were obtained. For hairtail fish, correlation coefficients were 0.97 and 0.91, and for pork, correlation coefficients were 0.81 and 0.88, respectively. The results also showed that the electronic nose could analyze the process and level of spoilage for hairtail fish and pork.

Total volatile basic nitrogen (TVB-N) content is an important freshness index of egg. An electronic nose was used to distinguish room-temperature storage periods of eggs by means of principal component analysis (PCA; Liu and Tu, 2012). The loadings plot analysis was used to identify the sensor responses as input parameters of support vector regression (SVR) model.

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Responses of sensor array in electronic nose were employed to establish TVB-N content model able to describe egg storage periods. Results showed that the E-nose could distinguish the fresh of eggs under different storage periods by PCA.

Ying et al. (2015) developed a new non-destructive evaluating method about litchi freshness using electronic nose (e-nose). Principal component analysis (PCA) and non-linear stochastic resonance (SR) methods were utilized to analyze EN detection data. They found that PCA method could not totally discriminate litchi samples while SR signal-to-noise ratio (SNR) eigen spectrum successfully discriminated all litchi samples.

An electronic nose (E-nose) technique was used to predict the freshness of peach (Guohua et al., 2012). Peaches are measured by a self-developed E-nose system with eight metal oxide semiconductors gas sensor array. Principal component analysis (PCA) and stochastic resonance (SR) are used for measurement data analysis. Results show that the E-nose can distinguish peaches between fresh and stale conditions.

Ye et al. (2014) investigated a beef strip loins (*Musculus longissimus lumborum*) freshness determination method utilizing E-nose. They measured the total viable count (TVC) index, total volatile basic nitrogen (TVB-N) index, and e-nose responses to beef strip loins samples every day. Principal component analysis (PCA) and Stochastic resonance (SR) signal-to-noise ratio (SNR) spectrum were implied to discriminated all the beef samples. The result showed high accuracy on the determination of the meat freshness.

A method using electronic nose (e-nose) and non-linear data processing technique is studied for the determination of freshness of penaeus orientolis prawn stored at 4°C (Wei et al., 2015).E-

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nose measurement data is analyzed by principal component analysis (PCA), stochastic resonance (SR), and double-layered cascaded serial stochastic resonance (DCSSR). Meanwhile, physical/chemical indexes (firmness, pH, total volatile basic nitrogen (TVB-N), total viable count (TVC), and human sensory evaluation) are examined to provide freshness references for e-nose analysis. Validating experiments demonstrate that forecasting accuracy of this model is 94.29%.

### *3.4 Quality Monitoring*

With the continuous improvement of people's life standards, the general requirements for desirable nutritional value, flavor and sensory of fresh food has been improved rapidly. Modern food industry has also developed a series of food preservation and processing technology like controlled atmosphere storage, frozen storage, vacuum preservation to meet consumer's needs. So we need to understand what has changed in the fresh food, in many papers mentioned of monitoring of food by using the E-nose. The specific application about E-nose includes real time operation system, air-condition control, food adulteration, effect of processing and shell life identification (Table 4).

Rajamäki et al. (2006) evaluated the applicability of an electronic nose for the quality control of modified atmosphere (MA) packaged broiler chicken cuts in different temperature regimes. The electronic nose results were compared with those obtained by microbiological, sensory and headspace GC analyses. The electronic nose could clearly distinguish broiler chicken packages with deteriorated quality from fresh packages either earlier than or at the same time as the sensory quality deteriorated. Concerning the microbiological quality, the counts of

Enterobacteriaceae and hydrogen sulphide-producing bacteria were most consistent with the electronic nose results. The results indicated that the electronic nose was capable of detecting even early signals of spoilage in MA packed poultry meat.

Miyasaki et al. (2011) investigated The change of volatile compounds in fresh fish meat during 3-4 days ice storage for several fishes using an electronic nose system and a gas chromatography-mass spectrometer (GC/MS) with headspace solid-phase micro-extraction (SPME).Principal component analyses for samples using the electronic nose system revealed that the increase of some volatile compounds during storage was rapid in sardine, jack mackerel, and chub mackerel; moderate in yellowtail, skipjack, and young oriental blue fin tuna. In contrast to these fishes, the changewas little in “whitemeat” fishes such as red seabream, Japanese seabass, flatfish, puffer, and bartail flathead. SPME-GC/MS analysis showed that some aldehydes and alcohols such as 1-heptanol, (E)-2-octenal, (E)-2-hexenal, 1-pentanol, (E,E)-2,4-heptadienal,2,4-hexadienal, 1-hexanol, 4-heptenal, and so forth increased rapidly in jack mackerel and chub mackerel, slowly in skipjack, and a little in red seabream and puffer during the storage. The increase of these compounds was considered to have an effect on the change of electronic nose response. Hexanal was a dominant compound increased from the beginning of the storage in jack mackerel. The increase of volatile compounds was little in red seabream and puffer. The increase of these aldehydes and alcohols was thought to be an appropriate marker for monitoring the freshness of “fresh” fish except for white meat fish.

Sivalingam and Rayappan (2012) developed a real time operating system (RTOS) based electronic nose (e-nose) with an array of commercial metal oxide semiconductor based sensors and a homemade nanostructured zinc oxide (ZnO) based sensor element for real time quality

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analysis of raw milk. The sensors were empanelled and calibrated towards various concentrations of volatile organic compounds (VOCs) which are responsible for off-flavors (ethanol, trimethylamine, acetaldehyde, dimethylsulfide, acetic acid, etc.) in milk produced due to microbial contamination, chemical reactions and genetic effects in cow. With the calibrated data, a look-up table was formed and threshold limits were fixed with reference to the response of the sensor array towards real milk samples for final decision making. The selectivity and discrimination efficiency of the developed e-nose was confirmed with principal component analysis and gas chromatography. Also, the prototype model was validated in a local dairy with their experts committee and certified for real time raw milk quality discrimination.

Kang et al. (2013) investigated the effects of high pressure processing (HPP) on fatty acid composition and volatile compounds in Korean native black goat (KNBG) meat. Fatty acid content in KNBG meat was not significantly ($p > 0.05$) different among the control goats and those subjected HPP. The 9,12-octadecadienoic acid and octadecanoic acid, well-known causes of off-flavors, were detected from meat of some KNBG. Adifference between the control and HPP treatment was observed in the discriminated function analysis using an electronic nose. The results suggest that the volatile compounds in KNBG meat were affected by HPP.

Papadopoulou et al. (2013) assessed the sensory and microbiological quality of beef fillets at different storage temperatures (0, 4, 8, 12, and 16°C) using a portable electronic nose in tandem with support vector machine analysis. Electronic nose data were collected from the headspace of meat samples in parallel with data from microbiological analysis for the enumeration of the population dynamics of total viable counts, *Pseudomonas spp*, *Brochothrix*

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*thermosphacta*, lactic acid bacteria and Enterobacteriaceae. The obtained results demonstrated good performance in discriminating meat samples in one of the three pre-defined quality classes.

Brodowska et al. (2016) evaluated the effect of dietary antioxidants (complex of 100 mg·kg-1 vitamin E and 1 mg·kg$^{-1}$ of organic selenium added to fodder) on lipid oxidation and flavour of pork after freezing storage. Meat was derived from animals fed with control fodder, fodder containing linseed oil (rich in polyunsaturated fatty acids) or fodder containing linseed oil and antioxidants. The oxidation process was assessed by analysis of thiobarbituric acid reactive substances (TBARS) and volatile organic compounds, which were analysed using the electronic nose based on the technique of gas chromatography. The level of TBARS was in range from (2.16 ± 0.89) mg·kg$^{-1}$ to (2.94 ± 1.41) mg·kg$^{-1}$ and was associated with the stage of oxidation in all experimental groups. There was no effect of dietary supplementation of antioxidants on lipid oxidation of pork meat after 9 months of freezing storage. In all samples, organic volatile compounds characteristic for oxidation process were identified, but there were differences in the volatile profile between experimental groups and the control group. After a prolonged period of freezing storage, the process of lipid oxidation occurred, regardless from the diet, but the volatile compounds profile varied.

A commercial electronic nose was used to evaluate the shelf life of fresh-cut pineapple during storage (Torri et al., 2010), at three different temperatures (4--5, 7--8, and 15--16°C) for 6--10 days. The results showed that the electronic nose was able to discriminate between several samples and to monitor the changes in volatile compounds correlated with quality decay. And the fruit freshness was maintained for about 5 days at 4°C, 2 days at 7.6°C and 1 day at 16°C by the analysis of PCA.

Fruit during storage often infected by a variety of bacteria and lead to poor quality, affecting food and sales. The quality of fruits usually decreases with the infection by a variety of bacteria during storage, which influences the tasting and saling of them. So it is necessary to carry out detection of bacteria earlier and take actions to prevent. A method combined with E-nose and GC-MS was applied to detect and classify the pathogenic fungal disease in post-harvest strawberry fruit (Pan et al., 2014). And the result showed E-nose was able to realise the early diagnosis of fungal disease, in addition to an accurate classification of the pathogenic fungal types.

## 4. *The trend of application with E-nose on fresh food*

### *4.1 Development of new sensors and pattern recognition algorithm*

The electronic nose systems based on sensor arrays composed of a set of microelectronic chemical sensors rely on the abilities of individual sensors to generate output by combining in some way contributions from latent variables of odors and the efficiency of data processing methods to build a parametric representation of the measured array responses in such a way that individual odor types (or classes) are associated with distinctly different sets of values of these parameters. Many types of E-nose systems, which constitute with the sensors including Piezoelectric (also called gravimetric or acoustic) sensors, Electrochemical sensors, Optical and Calorimetric or thermal sensors, and with the data processing methods containing PCA, LDA, CDA, PLS, MLR, BPNN have been developed. There are still some deficiencies in these two important parts of the E-nose, just like the drift of sensors and the fitting between the sensory response and the analysis result. In order to improve the performance of electronic nose, we can develop new type of sensors, improve data processing methods existed before or the develop new pattern recognition algorithm.

Yang et al. (2015) developed a novel electronic nose consisting of only one type of semiconductor metal oxide (SMO) material based on porous $In_2O_3$ microtubes sensor array for the discrimination of VOCs. The representative SMO material, porous $In_2O_3$ microtubes in this work, offered great surface area and large gas penetration channels. By using a solvent casting process, different amounts of porous $In_2O_3$ microtubes were coated on $Al_2O_3$ substrate, forming a resistometric SMO sensor array-based electronic nose. They have successfully applied this electronic nose to distinguish four alcohols at the same concentrations (100 ppm), and also utilized the electronic nose for the discrimination of 14 volatile organic compounds (VOCs).

Jha and Yadava (2011) analyzed the role of singular value decomposition (SVD) in denoising sensor array data of electronic nose systems. They found that the SVD decomposition of raw data matrix distributes additive noise over orthogonal singular directions representing both the sensor and the odor variables. The noise removal is done by truncating the SVD matrices up to a few largest singular value components, and then reconstructing a denoised data matrix by using the remaining singular vectors. In electronic nose systems this method seems to be very effective in reducing noise components arising from both the odor sampling and delivery system and the sensors electronics.

Chemical sensor drift shows a chaotic behavior and unpredictability in long-term observation which makes it difficult to construct an appropriate sensor drift treatment. Zhang et al. (2012) studied a new methodology for chaotic time series modeling of chemical sensor observations in embedded phase space. This method realizes a long-term prediction of sensor baseline and drift based on phase space reconstruction (PSR) and radial basis function (RBF) neural network. PSR can memory all of the properties of a chaotic attractor and clearly show the motion trace of a time series, thus PSR makes the long-term drift prediction using RBF neural network possible. Experimental observation data of three metal oxide semiconductor sensors in a year demonstrate the obvious chaotic behavior through the Lyapunov exponents. Results demonstrate that the proposed model can make long-term and accurate prediction of E-nose sensor drift.

When we apply an electronic nose on detection, the data generates by human experts is used to train the instruments, sometimes these data are conflecting and in accurate and thus the performance of an electronic nose is degraded. Bag et al. (2014) found that some of the sensors may not be required, While deploying an electronic nose for a specific application, and only a subset of the sensor array contributes to the decision. So they applied a rough-set based algorithm to remove the conflicting training patterns and optimize the sensor array in an electronic nose instrument.

Zhang et al. (2014) proposed a novel sensor selection using pattern recognition technique in electronic nose. They studied the portable E-Nose based on metal oxide semiconductor (MOS) gas sensors for detection of multiple kinds of indoor air contaminants. A potential and full contribution analysis of the small sized sensor array, in detection of indoor air contaminants

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coupled with a kernel principal component analysis (KPCA) based linear discriminant analysis (LDA) pattern recognition technique was applied and the recognition results clearly demonstrate the contribution of each sensor to gas detection which helps the sensor selection in E-nose design.

### *4.2 Combination with other analytical tools*

The electronic nose is not usually used alone, we can carry out the experiments using E-nose combined with any other instruments or methods to improve the accuracy, objectivity and predictability of the results of the tests. According to the literatures consulted before, it concludes that, in modern food industry the electronic nose is mainly used with three methods including the sensory evaluation of human, other instruments (Near infrared spectroscopy, mass spectrometry, nuclear magnetic resonance, gas chromatography) and artificial sensory systems (electronic tongue, electronic mucosa (Ghasemi-Varnamkhasti and Aghbashlo, 2014)). With the development of Instrumentation Science, electronic nose can be used in combination with more and more instruments to complement the advantages of their own.

Masoero et al. (2010) compared four rapid methods, which are complementary to the usual MIR-based analyses, in order to characterize local milk products. A set of 278 fresh samples from four separately reared Jersey, Piemontese and Valdostana cattle and Saanen goat herds was analyzed by: Fluorescence Spectroscopy, Electronic Nose, UV-Vis-NIRS and FT-NIRS (total 5851 digits by record). The average $R^2$ cross-validated values of the six discriminant contrasts were lower for the Gross Composition (0.47), very high for the FT-NIRS scans (0.97), for the Fatty Acids (0.96), and also high for the Fluorescence (0.90) and the UV-Vis-NIRS evaluation (0.89), while

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the Electronic Nose gave lower distinction between the groups (0.64). The patterns based on the distance matrix showed a remarkable complementarity between the Gross Composition evaluation and the rapid methods, which were close to the Fatty Acids evaluation. The FT-NIRS and Fluorescence analyses converged together, clustering the Jersey & Piemontese, the Valdostana and then the Goat milk. The Jersey-Piemontese cluster was also confirmed by EN. The UV-Vis-NIRS appraisal, distinguished the Piemontese milk more clearly, while it paired the Jersey and Valdostana milk. These rapid methods could be of great interest in the milk research.

Cole et al. (2011) present a novel, smart sensing system developed for the flavour analysis of liquids. The system comprises both a “electronic tongue” based on shear horizontal surface acoustic wave (SH-SAW) sensors analysing the liquid phase and a “electronic nose” based on chemFET sensors analysing the gaseous phase. Flavour is generally understood to be the overall experience from the combination of oral and nasal stimulation and is principally derived from a combination of the human senses of taste (gustation) and smell (olfaction). Thus, by combining two types of microsensors, an artificial flavour sensing system has been developed. Initial tests conducted with different liquid samples, i.e. water, orange juice and milk (of different fat content), resulted in 100% discrimination using principal components analysis; although it was found that there was little contribution from the electronic nose. Only the combined flavour analysis system could achieve 100% discrimination between all the different liquids. It maybe the first report of a SAW-based analysis system that determines flavour through the combination of both liquid and headspace analysis. Qiu et al. (2015) also used An electronic nose (E-nose) and an electronic tongue (E-tongue) to characterize strawberry juices based on different processes (i.e. Microwave Pasteurisation, Steam Blanching, High Temperature Short Time

Pasteurisation, Frozen-Thawed, and Freshly Squeezed). They found that this combination method have high performance on strawberry juice classification but not on the prediction of the values of quality parameters (vitamin C, pH, total soluble solid, total acid, and sugar/acid ratio).

Wang et al. (2012) predict the total viable counts (TVC) in chilled pork using an E-nose together with support vector machine (SVM). EN and bacteriological measurements were performed on pork samples stored at 4°C for up to 10 days. Bacterial numbers on pork were determined by plate counts on agar. Principal component analysis (PCA) was used to cluster EN measurements. The model for the correlation between EN signal responses and bacterial numbers was constructed by using the SVM, combined with partial least squares (PLS). Correlation coefficients for training and validation were 0.94 and 0.88, respectively, which suggested that the EN system could be used as a simple and rapid technique for the prediction of bacteria numbers in pork.

A mass spectrometry based electronic nose and chemometrics was used to analyse the volatile compounds (Gupta et al., 2015). Single peak obtained was integrated to obtain total mass spectrum of the volatile fraction of samples. A data matrix having relative abundance of all mass-to-charge ratios was subjected to principal component analysis (PCA) and linear discriminant analysis (LDA) to identify radiation treatment. PCA results suggested that there is sufficient variability between control and irradiated samples, LDA successfully aided in segregating control from irradiated samples at all doses (0.1, 0.25, 0.5, 1.0, 1.5, 2.0 kGy). This method was successfully demonstrated as simple screening method for radiation treatment.

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### *4.3 Miniaturization*

Electronic noses have potential applications in fresh food, but are restricted by their bulky size and high price. Compared to traditional gas analysis methods, such as gas chromatography mass spectrometry (GC-MS) and Fourier transform infrared (FT-IR) spectrometry, the electronic nose has the potential to be small, fast, and inexpensive, which are great benefits for a gas identification mechanism. Furthermore, the electronic nose is suitable for non-expert users and easily applicable to daily life in terms of various fresh food. The electronic noses of most manufacturers are realized by fixing gas collectors and detecting devices to personal or notebook computers (Chiu and Tang, 2013). However, the electronic nose has not achieved its full potential as a commercial device; the bulky size and high price restrict its applications in daily life. Fortunately, the appearance of new sensing materials, development of fabrication technologies, and evolution of data processing methods offer the possibility of creating the next generation of electronic noses.

## 5. *Concluding remarks*

In this paper, we have introduced the main application of intelligent olfactory based on E-nose in terms of classification, flavor research, freshness and spoilage evaluation and quality monitoring in fresh food area. The application of electronic nose in the food industry can be seen is so widespread, in meat, aquatic products, fruits and vegetables, dairy products and even spices. With the combination of E-nose and other detection methods or instruments, an application with high performance, rapidly speed and high accuracy maybe employed to the detection of food, as long as the quality discriminated is associated with volatile flavor in food. In food industry,

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especially in fresh foods aspect, it is extremely prospective that applying the intelligent odor detection system based on electronic nose to monitor the shelf life of those more corruptible foods, then it can contribute to providing consumers with fresh and safe food.

While there are still limitations on the performance of E-nose, including drift, enviromental atmosphere influence, redundancy of sensors, selectivity and signal to noise ratio and the choice of appropriate mathematical relationship between the response and flavor. These problems maybe solved by the combination with E-nose and other methods of detection, while the more thorough way on improving the stability of performance and the range of applicability about E-nose is to upgrade the odor detecting system and the pattern recognition system of itself. In addition to expand the scope of application of intelligent olfactory system, the solution about how to reduce the volume, cost, and the complexity of the operating process of electronic nose instrument should be considered. In a word, with the continuous development of Instrument Science and Computer Science, the applications of intelligent olfactory system based on electronic nose will be more extensive in the future.

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**Table 1** The application of electronic nose on classification of fresh food

| Sample | Authors | Type of study | Sensing system | Pattern recognition system | Method |
|---|---|---|---|---|---|
| Four rice samples | Zheng et al. (2009) | Differentiate between varities of rice | Crynose-320, 32 polymer sensors | PCA, CDA | E-nose only |
| Pork | Nurjuliana et al. (2011) | Identification of pork from other meat | VaporPrint™, SAW | PCA | Combined with GC-MS-HS |
| Cheese | Pais et al. (2012) | Discriminate between cheese varieties | Coated with piezoelectric quartz crystals, 5 sensors | PCA | Combined with SPME fiber |
| White pepper | Liu et al. (2013) | Classification by genotypes | Alpha M.O.S. SA, 6 MOS sensors | PCA | Combined with HS-SPME-GC-MS |
| Cumin | Ravi et al. (2013) | Discriminate the types from different regions | Alpha Fox 3000, MOS | PCA | Combined with GC-MS, E-Nose, and Sensory Techniques |
| Chicken and beef | Tian et al. (2014) | Discriminate chicken and beef seasonings | Alpha MOS Toulouse, 18 MOS sensors | PCA,FDA,CA | E-nose only |
| Fish | Güney and Atasoy (2015) | Discriminate between fish species | DBT, 8 MOS sensors | Naïve--Bayes classify, k-NN, LDA | E-nose only |
| Red meat | Haddi et al. (2015) | Distinguishing among meat species and identifying the degree of spoilage | Figaro TGS, 6 heated MOS sensors | PCA, SVM | Combined with E-tongue |
| Garlic | Trirongjitmoa-h et al. (2015) | Classification of garlic cultivars | Figaro E-nose, 8 semiconductor sensors | PCA | Combined with AFLP and GC-MS |

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**Table 2** The application of electronic nose for detection and quantification of flavor in fresh food

| Sample | Authors | Type of study | Sensing system | Pattern recognition system | Method |
|---|---|---|---|---|---|
| Fruit | Vallone et al. (2012) | Volatile analysis | Z-Nose, EST, SAW sensors | KI value | Combined with UF-GC |
| Fish | Li et al. (2013) | Identification of the aroma compounds | e-nose, PEN3,10 MOS sensors | PCA | Combined with GC-MS |
| Red onion | Russo et al. (2013) | Non-destructive flavor evaluation | ISENose 2000, 12 MOS sensors | DFA | Combined with HPLC |
| Chicken | Song et al. (2013) | Measuring and modeling flavor quality changes | FOX 4000, 18 MOS sensors | PLSR | Combined with GC-MS |
| Catfish | Wilson et al. (2013) | Detection of Off-Flavor | Aromascan A32S, polymer-type 32-sensor array | PCA,QF | E-nose only |

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**Table 3** The application of electronic nose for detection of freshness or spoilage evaluation

| Sample | Authors | Type of study | Sensing system | Pattern recognition system | Method |
|---|---|---|---|---|---|
| Peach | Guohua et al. (2012) | Freshness prediction | DBT, 8 MOS sensors | PCA, SR | Combined with GC-MS |
| Egg | P. Liu and Tu (2012) | Distinguish storage periods by freshness | PEN3, 10 MOS sensors | PCA, SVR, BPNN | E-nose only |
| Fish and pork | Tian et al. (2012) | Rapid classification of freshness | 8 tin oxide based MOS sensors | PCA | Combined with sensory evaluation |
| Beef strip loins | Xiao et al. (2014) | Determination of the freshness | 8 MOS sensors | PCA, SR | E-nose only |
| Penaeus | Wei et al. (2015) | Rapid freshness determination | DBT, 8 MOS sensors | PCA, SR, DCSSR | Combined with micro kjeldahl apparatus and sensory evaluation |
| Litchi | Ying et al. (2015) | Rapid non-destructive evaluation of freshness | DBT, 8 MOS sensors | PCA, SR | E-nose only |

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**Table 4** The application of electronic nose on quality monitoring of fresh food

| Sample | Authors | Type of study | Sensing system | Pattern recognition system | Method |
|---|---|---|---|---|---|
| Poultry meat | Rajamäki et al. (2006) | Quality assessment of MA packaged chicken | NST 3320, 10 MOS-FET, 12 MOS and 1 infra-red absorption sensors | PCA, PLS | Combined with GC and sensory evaluation |
| Pineapple | Torri et al. (2010) | Shelf life evaluation | PEN 2, 10 MOS sensors | PCA, CA | E-nose only |
| Fish | Miyasaki et al. (2011) | Change of volatile compounds during ice storage | α-Fox2000, 6 sensors | PCA | Combined with SPME-GC-MS |
| Raw milk | Sivalingam and Rayappan (2012) | Real time operation | TGS, 6 MOS sensors | PCA | E-nose only |
| Goat meat | Kang et al. (2013) | Effect of high pressure processing on fat and VOC | Smart Nose300, MOS | PCA | Combined with GC-MS |
| Strawberry | Pan et al. (2014) | Detection and classification of pathogenic fungal disease | PEN 3, 10 MOS sensors | PCA, MCT | Combined with GC-MS |
| Pork | Brodowska et al. (2016) | Effect of dietary antioxidants after freezing storage | Alpha M.O.S., 8 MOS sensors | PCA | Combined with UF-GC |

All abbreviation mentioned in these tables includes: AFLP = amplified fragment length polymorphism, BPNN = back propagation neural network, CA = cluster analysis, CDA = canonical discriminant analysis, DBT = designed by themselves, DCSSR = double-layered cascaded serial stochastic resonance, FDA = functional discriminate analysis, GC = gas chromatography, HS = headspace analyzer, KI = Kovats indices, LDA = linear discriminate analysis, MCT = multiple comparison test, MOS = metal oxide sensor, MS = mass spectrometer, NN = neural net-work, PCA = principal component analysis, PLSR = Partial least squares regression, QF = quality factor, SAW = surface acoustic wave, SPME = solid-phase micro-extraction, SR = stochastic resonance, SVM = support vector machines, SVR = support vector regression, UF = ultra fast.


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