

# Chapter 2

## Electronic Nose and Electronic Tongue

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### 2.1 Introduction

The sensations of smell and taste resulting from a series of specific and nonspecific molecular recognition can be used as an analytical tool in many industries to measure the quality of food, drinks, and chemical products. In a few cases, there are olfactory receptors or gustatory receptors which are specific for individual chemical molecules. However, most tastes and odorants are identified through a synthesis of the global chemical information from nonspecific interactions. Taking mammalian gustation as an example, the combination of “gustatory buds” which respond to five taste categories: sour, sweet, bitter, salty and umami creates a distinct pattern for each taste.

To mimics the nonspecific recognition, traditional electronic nose and electronic tongues that are composed of solid-state sensors array were developed. The sense of smell and taste are linked to a variety of different transduction schemes.

Herein, we review the research effort that has been carried out over the past years or so to create an electronic nose or electronic tongue, and then discuss some of the technologies that have been explored in what is essentially an intelligent chemical array sensor system. Finally, we summarize the applications of electronic noses to date and suggest where future applications may lie.

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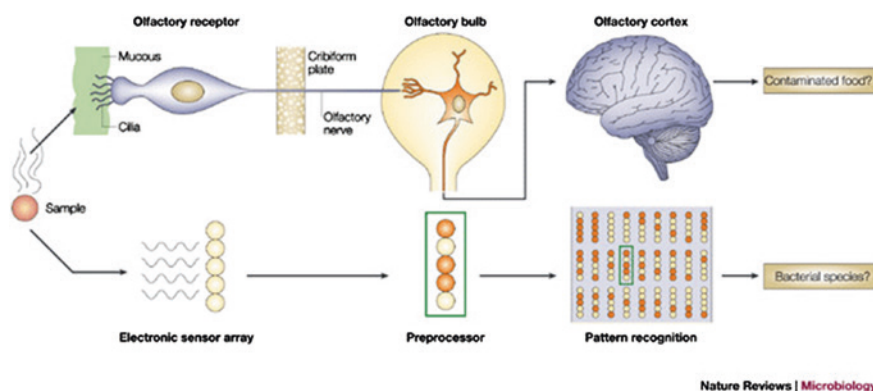
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## 2.2 Traditional Electronic Nose

An accepted definition of an electronic nose is “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 odor” [1] and tries to characterize different gas mixtures. Comparing with any other analysis techniques, such as gas chromatography and electronic nose systems are easy to build and could provide sensitive and selective analysis in real time. The present section focuses mostly on sensing techniques used in traditional electronic noses.

### 2.2.1 Principle and Structure

One cannot discuss electronic nose without comparisons to the biological nose. Upper panel of Fig. 2.1 shows a biological nose and illustrates the important features of this “instrument,” while lower panel of Fig. 2.1 shows the artificial electronic nose. It is instructive for us to make comparisons between biological nose and electronic nose. For biological nose, mucous and vibrissae in nasal cavity implement filtering and concentration of odorant molecules. Odorant molecules are brought to the olfactory epithelium due to the passive pressure provided by the lung. Olfactory epithelium contains millions of sensing cells and olfactory receptors are located on the membranes of these cells. Receptors convert chemical signals into electroneurographic signals. The unique pattern of these Electroneurographic signals is interpreted by olfactory cortex neural network. Considering the general design of electronic nose, pump acts as the lung; inlet sampling system acts as the mucous and vibrissae in nasal; array of sensors acts as the olfactory receptors; and the signal processing system, e.g., computers, acts as the olfactory cortex neural network.



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**Fig. 2.1** Electronic nose devices mimic the human olfactory system [2]. (Reproduced with permission from Ref. [2]. Copyright 2004 Nature Publishing Group)

**Table 2.1** Comparing electronic nose with human nose

Bio-nose	Electronic nose
It uses the lungs to bring the odor to epithelium layer	It employs a pump to smell the odor
It has mucus, membrane, and hair to act as filter	It has an inlet sampling system that provides filtration
The human nose contains the olfactory epithelium, which contains millions of sensing cells that interact with odorants in unique	Electronic nose has a variety of sensors that interact differently with a group of odorous molecules
The human receptors convert the chemical response to electronic nerve impulses whose unique patterns are propagated by neurons through a complex network before reaching the higher brain for interpretation	Similarly, the chemical sensors in the electronic nose react with the sample and produce electrical signals. A computer reads the unique pattern of signals and interprets them with some form of intelligent pattern classification algorithms

Electronic nose are used to characterize different gas mixtures as well as biological nose. However, there still exist some fundamental differences in both hardware and software. Details of comparisons between these two “noses” are listed below (Table 2.1).

In summary, an electronic nose is composed of two main components: sensing system and signal processing system. They are discussed in the following sections, respectively.

### 2.2.2 Sensing System

The sensing system consists of a sensor array is the “reactive part” of the instrument. The non-selectivity of some solid-state sensors (e.g., metal oxide sensors) was considered as a severe drawback. However, the idea of assembling arrays of such sensors with different sensitivities and selectivities was performed in the early 1980s. Although both the qualitative and quantitative information obtained from each sensor was highly ambiguous, their combination resulted in some sorts of “fingerprint” of the sample. With the help of statistical programs, the classification of samples into groups could be achieved [3].

Sensor technology has developed rapidly over the past decade, and this has resulted in a range of different sensor formats and the development of complex microarray sensor devices. The most commonly used sensors include metal oxide semiconductor (MOS) sensors, conducting polymer (CP) sensors, optical sensors, and piezoelectric sensors.

### 2.2.2.1 MOS Sensors

MOS sensors are one of the most commonly utilized sensor systems for the development of electronic noses to detect gaseous molecules. It has been known that adsorption or desorption of gaseous molecules on the surface of a metal oxide changes the conductivity of this material since 1962. When oxides are exposed to volatile organic compounds (VOCs), they are involved in a redox reaction on the surface of the MOS or act as oxidizing agents and, thereby, cause a shift in the resistance of the MOS. In detail, oxygen adsorbed from the air trap-free electrons from the conduction band of the semiconductor and builds up the potential barrier on the surface. The chemical reaction that results from adsorbed  $O_2$  reacting with VOCs decreases the density of  $O_2$  on the surface, thereby reducing the electron trapping effect. The change in resistance depends on the VOC interacting with the adsorbed  $O_2$  on the semiconductor as well as the metal oxide. This phenomenon was first demonstrated using zinc oxide thin-film layers. Based on the results from ZnO, further metal oxides were examined as regards their properties of varying their conductivities with the composition of the gas atmosphere surrounding them, including ZnO [4, 5],  $WO_3$  [6, 7],  $SiO_2$  [8, 9], and  $TiO_2$  [10, 11]. A schematic diagram of a MOS sensor is shown in Fig. 2.2a.

### 2.2.2.2 CP Sensors

CPs are widely used as sensor elements in electronic noses thanks to their ability to adjust their conductivity in response to organic compounds. CP sensor arrays

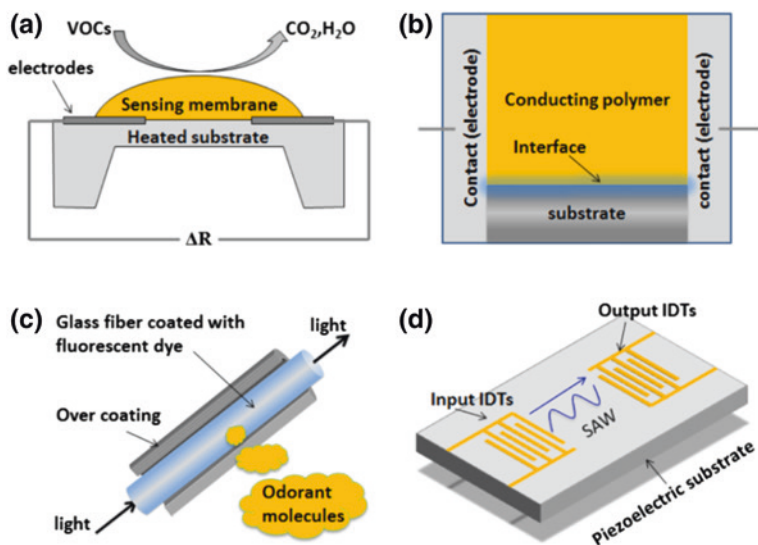


Fig. 2.2 Schematic diagrams of **a** MOS sensor, **b** CP sensor, **c** optical fiber and **d** SAW sensor

often consist of unique polymers with different reversible physicochemical properties and sensitivity to groups of volatile compounds to provide a broad specificity that overlaps with that of organic vapors. These organic vapors attach to and interact with the polymer surface, changing the resistance under ambient temperature conditions [12, 13]. Different polymers response to stimulated vapors with different physicochemical properties, and chemical modification of polymers also alters the properties of materials. Successful applications of conducting polymers to electronic noses as sensor elements have been conducted in several articles [14, 15].

Signals could be monitored for each sensor type, enabling an array to be constructed that has overlapping detection ranges for different groups of volatile compounds. However, sample presentation is crucial for CP sensor to avoid humidity and drift problems.

Figure 2.2b shows a schematic diagram of a chemiresistor which is the most common group of CP sensors. It consists of a pair of electrodes forming contacts to the CP, deposited on an insulating substrate. When a constant current is applied, the resulting potential difference at the electrode becomes the response signal.

### 2.2.2.3 Optical Sensors

Optical sensors have been widely used as gas sensors in many applications due to their response which could be measured precisely [16–18]. These sensors are based on a light source that excites the volatile molecules, and the signal can be measured in the resulting absorbance, reflectance, fluorescence, or chemiluminescence. Such output signals are detected using various detectors, including photodiodes, CCD, and CMOS cameras [19, 20].

The most classical optical sensors are optical fiber and surface plasmon resonance (SPR) sensor. Optical fiber sensors (Fig. 2.2c) utilize glass fibers coated with thin chemically active materials on their sides or ends that contain immobilized fluorescent dyes in an organic polymer matrix. The changes in dye polarity cause a shift in the emission spectrum due to interaction of VOCs with a light source. SPR technique is based on the fact that the field of surface plasma wave is extremely sensitive to changes in the refractive index of the dielectric when very close to the surface. The electrons in a piece of metal continuously and freely move like a charged cloud and are excited by light; this has been named surface plasmon resonance. When light is focused onto the surface, electrons become excited, and at a critical angle, called the resonance angle, reflectance falls to zero. Changes in the surface caused by chemical adsorption and molecular interactions alter the reflectance of the surface. This technique is a highly efficient method for detecting odorants [21, 22].

In summary, optical sensors are excessively sensitive and are able to identify individual compounds in mixtures. However, their connected electronics and software are complex and expensive. These sensors have a relatively short lifetime, which would also result in increasing the cost of detection.

#### 2.2.2.4 Piezoelectric Sensors

Piezoelectric sensors have a radio frequency resonance under such electric potential and are highly sensitive to the mass change applied to the surfaces of piezoelectric sensors. Quartz crystal microbalance (QCM) and surface acoustic wave (SAW) sensors are two of the most useful piezoelectric sensors applied in electronic noses.

QCM is an advanced type of microbalance mass sensor. Its transducer based on the piezoelectric properties of quartz material has been implemented in sensors. QCM is made of a polymer-coated resonating quartz disk, vibrating at a characteristic frequency (10–30 MHz). Its oscillation frequency decreases, while the bounding-mass increases on the crystal surface. In detail, adsorption of gas molecules onto the sensing films deposited on the crystal surface would result in the shift in the quartz crystal (QC) resonant frequency. As the gas molecules adsorbed to the polymer surface, it reduces the resonance frequency and the decrease is proportional to mass of odorant adsorbed. QC which is equipped with metal electrodes (e.g., gold) is the basic material of the QCM sensor. The selectivity of QCM sensor is based on sensitive materials coated on sensor surface. The thickness of coatings affects the sensitivity of QCM sensors. In addition, temperature, humidity, and some other environmental conditions also have influences on sensitivity of QCM sensors. SAW and QCM are both mass-sensitive sensors. However, SAW uses a surface acoustic wave sensor, while QCM uses a BAW sensor. SAW sensors require waves to travel over the surface of the device. SAW sensors operate at higher frequencies (100–1,000 MHz) and thus generate a larger change in frequency. The structure of SAW is shown in Fig. 2.2d. The output transducer and input transducer are both interdigital transducers (IDTs) which are core components of SAW. When the environment of the transducer changes, e.g., gas molecules absorbed, the vibration frequency will change. Hence, the weight information of gas molecules can be obtained through comparing signals of output IDTs with input IDTs.

### 2.2.3 Pattern Recognition System

The use of multivariate analysis methods together with sensor arrays has shown to be very powerful. Two main issues are dealt with, to search for a structure and correlation in the data, or to make a model from a training set of data, which is then used to make predictions from test data.

#### 2.2.3.1 Dimension Reduction

Principal component analysis (PCA) is a mathematical transform which is used to explain variance in experimental data [23]. The data matrix  $X$  consists of  $m$

experiments, each consisting of  $n$  variables. In PCA, a transformation in the variable space is made. Let  $Y$  be another data matrix related by a linear transformation  $P$  [24].

$$PX = Y \quad (2.1)$$

$X$  is the original recorded dataset and  $Y$  is a re-representation of that set.  $P$  is a rotation and a stretch which transforms  $X$  into  $Y$ . This transformation aims at having a minimum redundancy and a maximum signal. Considering the definition of covariance matrix, the goal of PCA is finding some orthonormal matrix  $P$  which results in a diagonalized matrix, where

$$C_Y = \frac{1}{n-1}YY^T. \quad (2.2)$$

Substituting (2.1) into (2.2), we rewrite in terms of linear transformation  $P$ .

$$C_Y = \frac{1}{n-1}(PX)(PX)^T = \frac{1}{n-1}PXX^TP^T = \frac{1}{n-1}P(XX^T)P^T \quad (2.3)$$

$$C_Y = \frac{1}{n-1}PAP^T \quad (2.4)$$

We defined a new matrix here. It is obvious that  $A$  is symmetric. A symmetric matrix can be diagonalized by an orthogonal matrix of its eigenvectors.

$$A = EDE^T, \quad (2.5)$$

where  $D$  is a diagonal matrix and  $E$  is a matrix of eigenvectors of  $A$  arranged as columns.

Now comes the trick. We select the matrix  $P$  to be a matrix where each row vector  $p_i$  is an eigenvector of  $XX^T$ . It means. Substituting into (2.5), we find. Note that  $E$  is a matrix of eigenvectors of  $A$ . That means:

$$C_Y = \frac{1}{n-1}PAP^T = \frac{1}{n-1}P(P^TDP)P^T = \frac{1}{n-1}(PP^T)D(PP^T) = \frac{1}{n-1}(PP^{-1})D(PP^{-1}), \quad (2.6)$$

$$C_Y = \frac{1}{n-1}D. \quad (2.7)$$

That is to say is a diagonalized matrix. For PCA, the real goal is to obtain eigenvectors of  $XX^T$ .

For PCA, there is no requirement to have any prior knowledge about classification of samples. It is a simple, effective, and stable multivariate analysis. But the most significant drawback of PCA is the uncertainty of the meaning of the principal components. On the contrast of PCA, other methods we introduce here are all supervising methods.

### 2.2.3.2 Classification and Prediction

Data often divided into two parts: training set and test set. Training sets of data are used to build classification models, while test sets of data are used to evaluate the classification model. The most useful methods for modeling are linear discriminant analysis (LDA), partial least squares (PLS) regression, and artificial neural nets (ANN).

LDA is method used in statistics, pattern recognition, and machine learning to find a linear combination of features which characterizes or separates two or more classes of objects or events. The resulting combination may be used as a linear classifier, or, more commonly, for dimensionality reduction before later classification. LDA is closely related to PCA for the reason that they both look for linear combinations of variables which best explain the data [25]. However, LDA explicitly attempts to model the difference among the classes of data. PCA on the other hand does not take into account any difference in class.

PLS regression finds a linear regression model by projecting the predicted variables and the observable variables to a new space. PLS is used to find the fundamental relations between two matrices (X and Y), i.e., a latent variable approach to modeling the covariance structures in these two spaces. A PLS model will try to find the multidimensional direction in the X space that explains the maximum multidimensional variance direction in the Y space. PLS regression is particularly suited when the matrix of predictors has more variables than observations, and when there is multicollinearity among X values. By contrast, standard regression will fail in these cases (unless it is regularized). In electronic nose system, PLS is often performed with each principal component obtained in PCA.

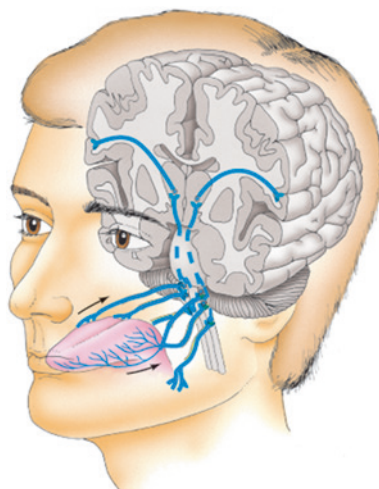
ANNs are computational models inspired by the way biological nervous systems. The key element of ANN is the novel structure of its information processing system. It is composed of a large number of highly interconnected processing elements (neurons in biological systems) working in unison to solve specific problems. ANNs can compute values from inputs and are capable of machine learning as well as pattern recognition thanks to their adaptive nature. ANN models are non-linear, thus being able to adapt to non-linear processes. An ANN can be divided in different layers, an input layer consisting of input signals, one or more hidden layers and an output layer. The hidden and the output layers consist of signal processing nodes, each connected to each other in a net, with the strength of the connections being set by a coupling weight. During learning, output values from the ANN are compared to true values and the coupling weights are adjusted to give a minimum sum of square errors.

## 2.3 Traditional Electronic Tongue

The human tongue mainly detects five tastes, salty, sour, sweet, bitter, and umami using gustatory receptor cells located in clusters called gustatory buds. After perception by gustatory cells, the taste information is transmitted via cranial nerves

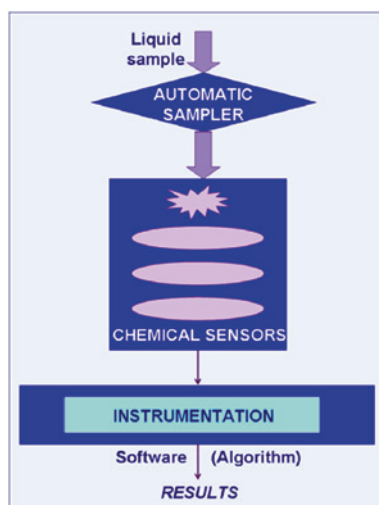


**Fig. 2.3** The gustatory system of human ([mindsmachine.com](http://mindsmachine.com))



to brainstem nuclei. Eventually, all information is analyzed in cerebral cortex and different tastes are perceived. The whole gustatory system of human is shown in Fig. 2.3. The theory of electronic tongue originates from mechanisms of the gustatory system of human. Electronic tongues (e-tongues) can be considered as analytical instruments that artificially reproduce the taste sensation. These devices are typically array of sensors coupled to chemo-metric processing used to characterize complex liquid samples [26]. The schematic representation of the components of an electronic tongue is shown in Fig. 2.4. If properly configured and trained (calibrated), the e-tongue is capable of recognizing the qualitative and quantitative composition of multi-species solutions of different natures. The IUPAC technical report on the topic defines it as “a multisensor system, which consists of a number of low-selective sensors and uses advanced mathematical procedures for signal processing based on the pattern recognition(PARC) and/or multivariate data analysis” [27].

**Fig. 2.4** Schematic representation of the components of an electronic tongue [26] (Reproduced with permission from Ref. [26]. Copyright 2010 Elsevier)



Regarding the sensor array used in the design of e-tongues, a wide variety of chemical sensors have been employed: electrochemical (potentiometric, voltammetric, amperometric, impedimetric, and conductimetric), optical, mass, and enzymatic sensors (biosensors) [28].

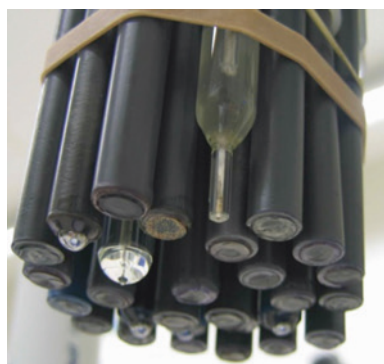
### 2.3.1 Potentiometric Sensors

In potentiometry, a potential is measured between two electrodes under the conditions of no current flow. The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component of the solution. The potential that develops in the electrochemical cell is the result of the free energy change that would occur if the chemical phenomena were to proceed until the equilibrium condition has been satisfied.

The largest group among potentiometric sensors is represented by ion-selective electrodes (ISEs), the oldest and most widely used among them being a pH-sensitive glass electrode. Different approaches of potentiometric electronic tongues and taste sensors have been demonstrated. They have in common that they all measure the potential over a charged membrane. These membranes can be of different materials, which provide enough selectivity to different classes of chemical substances. Electronic tongues have, thus, been described based on an array of chalcogenide glass sensors, including conventional electrodes such as chloride-, sodium- and potassium-selective sensors, combined with a pattern recognition routine. The photograph of ISEs array and the measuring system in the group of Andrey Legin, St. Petersburg University (Russia), is shown in Fig. 2.5. The chalcogenide sensors show cross-sensitivity which has been preferably used for measurement of metal ions in river water and suggested or environmental and process-monitoring purposes [29–33]. This type of electronic tongues has also been combined with PVC membranes for testing of beverages [34].

Potentiometric ion and chemical sensors based on field-effect devices form another group of transducers that can be easily miniaturized and are fabricated by means of microelectronic technology.

**Fig. 2.5** ISEs and the measuring system (Andrey Legin, St. Petersburg University, Russia)



Among them most studies are ion-sensitive field-effect transistors (ISFETs) [35] with different ion-selective membranes (often also called chemically sensitive field-effect transistors or Chem-FETs). ISFETs with bare gate insulator (silicon oxide, silicon nitride, aluminum oxide, etc.) show intrinsic pH-sensitivity due to electrochemical equilibrium between protonated oxide surface and protons in the solution. To obtain sensitivity to other ions, a polymeric membrane containing some ionophore may be deposited.

The LAPS [36, 37] is a semiconductor-based device with an electrolyte-insulator-semiconductor (EIS) structure, which is similar to ISFET in function. A dc bias voltage is applied to LAPS, so that a depletion layer appears at the insulator-semiconductor interface. When a modulated light irradiates LAPS from front or back side, an AC photocurrent inside the depletion layer could be induced as a measured signal. Amplitude of photocurrent is sensitive to the surface potential, and thus LAPS is able to detect the potential variation caused by an electrochemical event. Therefore, in principle, any electrochemical reaction that results in the change of surface potential can be detected by LAPS, including the ionic change [38] and redox effect [39]. By modifying the individual sensitive region with the polymer membrane or chalcogenide glass membrane which contains specific receptor molecules [40], relevant cations could be detected simultaneously. Most of the solid-state-based thin-film sensors suffer from an insufficient selectivity. Compared to the inorganic membrane, the organic one can overcome the problem with reasonable good selectivity [41] (Fig. 2.6).

### 2.3.2 Voltammetric Sensors

Voltammetry, in which a current is measured at a fixed potential, is a very powerful and often used technique in analytical chemistry. Depending on the potential applied and type of working electrode, redox active compounds are either oxidized or reduced at the working electrode, giving rise to a current. The sensitivity of voltammetric methods is often very high. The selectivity is, however, in many cases poor, since all compounds in a measured solution that is electrochemically active

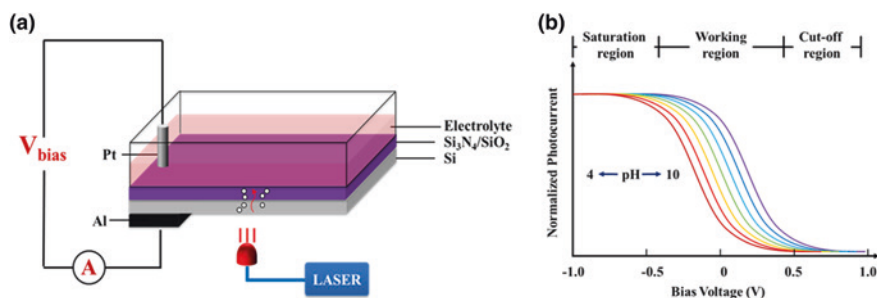
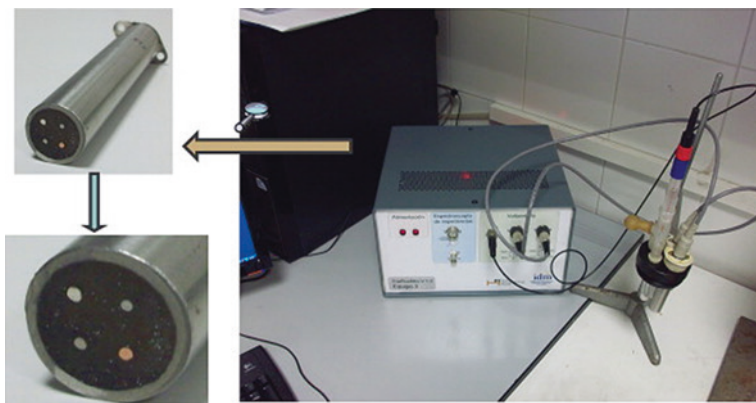


Fig. 2.6 a Working principle of the LAPS. b Characteristics I-V curve of n-type LAPS



**Fig. 2.7** A developed voltammetric electronic tongue for water quality monitoring (Reproduced with permission from Ref. [43]. Copyright 2012 Elsevier)

below the applied potential, will contribute to the measured current. Different ways to surmount this is, e.g., to cover the working electrode with a gas permeable membrane, only letting gases pass through, or to use pulse voltammetry. Voltammetry appears to have several advantages; the technique has been extensively used in analytical chemistry due to features such as its very high sensitivity, versatility, simplicity, and robustness. Besides, voltammetry offers a widespread number of different analytical possibilities, including cyclic, stripping, and pulse voltammetry. Depending on the technique, various kinds or aspects of information can be obtained from the measured solution. Normally, redox active species are being measured at a fixed potential, but using, e.g., pulse voltammetry, studies of transient responses when Helmholtz layers are formed, also give information concerning diffusion coefficients of charged species. Further information is also obtainable by use of different type of metals for the working electrodes. Different metal electrodes can be used together with voltammetric measurements to classify different liquids [42, 43]. Still, the voltammograms contain a large amount of information and to extract this information, multivariate calibration methods have been shown to be rather efficient [44, 45] (Fig. 2.7).

## 2.4 Application of Electronic Nose

### 2.4.1 Food Evaluation

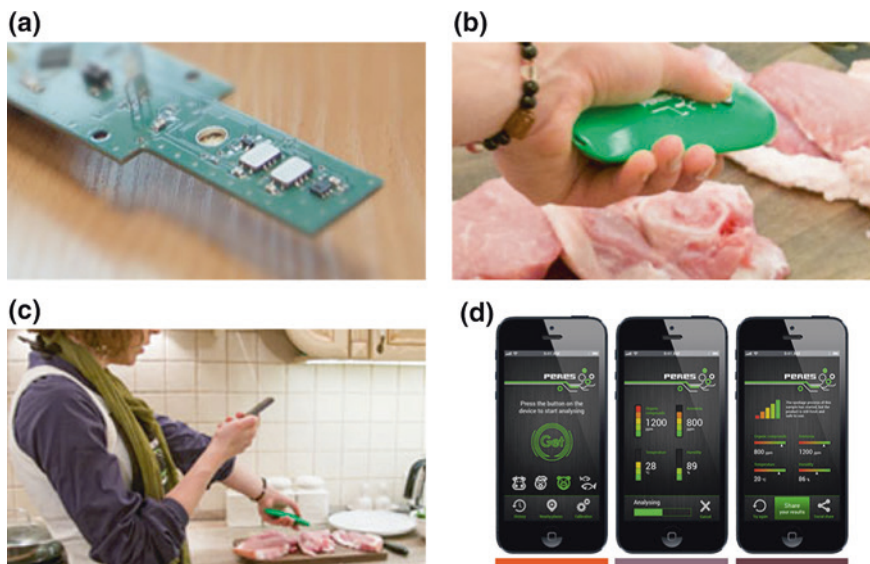
In the past, electronic noses have been developed for the classification and recognition of a large variety of foods, including meat [46, 47], fish [48, 49], grains [50, 51], fruits [52, 53], coffee [54, 55], beer [56, 57], beverage [58, 59], cheese [60], sugar [61], and vegetables [61], especially for the determination of the categories and freshness of food.

Yu and Wang [62] conducted an investigation about application of electronic nose in distinction of tea. Four tea groups (A120, A280, A380 and A600) with a different quality grade were employed. They sealed these teas (5 g) separately in vials of different volumes (50, 150, 250, and 500 ml), respectively. Then, they collected headspace compounds of these vials. The headspace generating time was 0.75, 1, and 2 h.

A portable electronic nose (PEN2) is used to detect these headspace samples. PEN2 is a commercial electronic nose system produced by WMA (Win Muster Airsense) Analytics Inc. (Germany). It consists of a sampling apparatus, a chamber containing an array of sensors, and pattern recognition software for data recording. The sensor array was composed of 10 MOSs, and its response was expressed as the ratio of conductance ( $G/G_0$ ). The headspace gas was pumped into the sensor chamber with a constant rate of 400 ml/min via a Teflon-tubing connected to a needle during the measurements process. When the gas accumulated in the headspace of vials was pumped into the sensor chamber, the ratio of conductance of each sensor changed. A computer recorded the response of the E-nose every second. When the measurement was completed, the acquired data was properly stored for later use. The temperature of the laboratory was kept  $25 \pm 1$  °C.

In this research, response values of each sensor at 15, 30, 45, and 60 s were extracted and analyzed individually. PCA, LDA, and ANN were employed for data processing. One side, the optimum experiment conditions are decided in this research. On the other hand, four groups of tea were measured under the decided conditions, and authors evaluated the ability of PEN2 to distinct these four groups of tea. Only A120, A380, and A600 could be discriminated by PCA. However, the four tea groups were discriminated completely by LDA. The response value of the E-nose at 60 s was optimum to be used for discrimination. The method of ANN (network topology 20-12-4) was performed, and 90 % of the total tea samples were classified correctly using the back-propagation neural network.

PERES is the world's first portable "electronic nose"—a unique and innovative device and mobile application which enables users to determine the quality and freshness of pork, beef, chicken, and fish (<http://www.getperes.com>). It is designed to detect: whether a product is fresh, whether it is hazardous to health, whether there is a risk of food poisoning, and whether it has been left unrefrigerated for some time. The device has four types of sensors: temperature, humidity, ammonia, and volatile organic compounds sensors (Fig. 2.8a). To operate the device, the user simply directs it toward the food product and clicks a button (Fig. 2.8b). The device uses Bluetooth technology to transmit data to the user's smartphone or tablet, which displays detailed results with recommendations regarding the safety of the product (Fig. 2.8c). Users control PERES, start the sampling process, analyze the results of readings, and share their experiences with friends just by interfacing with a user-friendly environment on their phone or tablet (Fig. 2.8d).



**Fig. 2.8** A portable commercial electronic nose named PERES. **a** Structure. **b** User simply directs PERES toward the meat and clicks a button to complete detection. **c** A detailed result with recommendations regarding the safety of the detected meat would be provided on a mobile phone. **d** The user interface of PERES (<http://www.getperes.com>)

### 2.4.2 Public Security

One important application for the electronic nose is for use in detection of explosives. An electronic nose capable of detecting explosive substances may be used for the detection of landmines and for homeland security purposes [63]. Homeland security applications include screening people packages, luggage, and vehicles at key locations such as airports or government buildings, for the prevention of terrorist attacks.

Brudzewski et al. [64] designed a differential electronic nose which consists of two chemo-sensor arrays working in parallel to measure typical explosive materials including trinitrotoluene (TNT), pentaerythritolte-tranitrate (PETN), and cyclotrimethylenetrinitramine (RDX). The experimental system contains two sensor arrays instead of one. One of them forms the “measurement array” and the other forms the “reference array.” The streams of air are delivered to both chambers of gas sensor arrays from the odor acquisition place through the socket outlet. The measurement channel contains inside the vapor of explosive material, while the reference one only the outside air, free of explosive odor. For either sensor array, 12 heated MOS sensors of Figaro series were used. The corresponding signals registered by the appropriate sensors of both arrays are subtracted from each other using the differential amplifier, then converted by A/D converter to the digital form and finally delivered to the computer interface for further processing,





**Fig. 2.9** An example of a suitable effluence detection device—the Quantum Sniffer QS-H150 Portable Hand-held Explosives Trace Detector ([anjian110.com](http://anjian110.com))

which leads to the recognition of odor. PCA was employed to perform model recognition. 12 sensor signals corresponding to RDX, PETN, and TNT were mapped on two most significant principal components: PCA1 and PCA2. Results showed that these three kinds of typical explosive materials could be discriminated by the present electronic nose (Fig. 2.9).

### 2.4.3 Medical Applications

It has been reported that some volatile organic compounds (VOCs) in human exhaled breath can be potential biomarkers for lung cancer [65, 66]. Wang et al. designed an electronic nose based on surface acoustic wave (SAW) sensor combined with capillary column for early detection of lung cancer [67, 68].

The electronic nose consists of thermal desorption system, capillary column, SAW sensor, and data processing system on PC. VOCs in exhaled breath was enriched by an adsorption tube, desorption happened in the inlet of the capillary with high temperature, then VOCs were carried into the capillary to be separated by the carry gas. When VOCs come out from the capillary, there would be a frequency change because VOCs can attach to the surface of the SAW sensor independently owing to condensation. Comparing with general electronic nose, it contains one SAW sensor instead of a sensor array. Owing to capillary column, VOCs can be separated and would be detected one by one. That made the single sensor could work as a virtual gas sensor array. Authors extracted response of SAW sensor at 5 specific time points according to retention time of 5 kinds of potential biomarkers. PCA and ANN were applied for multivariate data processing.

Researchers at the University of Pennsylvania School of Medicine have demonstrated the effectiveness of an electronic nose device for diagnosing common respiratory infections, specifically pneumonia [69]. Doctors hope that the device—called the Cyranose 320, or e-nose—will provide a faster, more cost-effective, and easier-to-use method for accurately diagnosing pneumonia and, as a result, help

**Fig. 2.10** Electronic Nose is used for Diagnosing Pneumonia ([spectrum.ieee.org](http://spectrum.ieee.org))



reduce over-prescription of antibiotics. Pneumonia is a serious bacterial infection that can cause serious injury or even death; indeed, it remains a leading cause of death in intensive care units (ICUs). All bacteria, as living organisms, produce unique arrays or mixtures of exhaled gases. The e-nose works by comparing “smellprints” from a patient’s breath sample to standardized, or known, readings stored on a computer chip. These “smellprints” are created from both electrochemical and mathematical analysis of exhaled gases contained in a breath sample. Figure 2.4 shows the situation that diagnosis of infection by electronic nose (Fig. 2.10).

## 2.5 Application of Electronic Tongue

Electronic tongue was first proposed by Toko et al. [70–72] in 1990s for the intention of mimicking the functions of human gustatory receptors. The objective of electronic tongue is to study five basic taste substances: salty (NaCl, KCl, and KBr), sour (HCl, citric and acetic acids), bitter (quinine), sweet (sucrose), and umami (monosodium glutamate). Afterward, other tastes like astringent and pungent substances were investigated, and many expansive applications of electronic tongue have been explored including food evaluation, drink discrimination, and even hazards detection, etc.

### 2.5.1 Food Evaluation and Discrimination

Traditional food analysis is carried out using a wide range of methodologies based on chemical, biochemical, physico-chemical, and microbial principles aiming to determine the concentration or the presence of different compounds that directly participate in the characteristics of food. These traditional approaches are always destructive, time-consuming, and require laboratories equipped with complex and



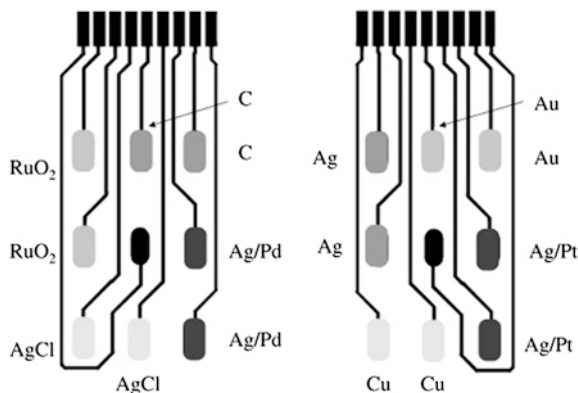
expensive equipments. Additionally, the analysis should be carried out by specialized personnel which is not suitable for in situ or at site monitoring. As a comparison, electronic tongue indicates a promising technique in food analysis due to its capability of rapid and simple procedures for qualitative and quantitative analysis. Many applications have been investigated in food evaluation and discrimination.

Beullens et al. [73] presented an electronic tongue consisting of 27 potentiometric sensors for determining the sugar and acid profile of four tomato cultivars. Based on all these information, different multivariate data analysis techniques such as principle components analysis (PCA) and canonical discriminant analysis (CDA) were applied to detect differences in sugar and acid profiles between the four tomato cultivars. The potential of both the electronic tongue and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) was used to predict the chemical composition of the sample using partial least squares (PLS). The electronic tongue is proved to be able to classify different tomato cultivars based on CDA.

Kaneki et al. [74] introduced an electronic tongue with potentiometric solid-state electrodes for pork freshness evaluation. Pt, CuS, and Ag<sub>2</sub>S electrodes were selected as solid-state electrodes to detect the organic compounds such as putrescine and dimethyl sulfide which were produced during the initial stage of putrefaction in meat. PCA was performed in the study by datasets from electric potential on each electrode for qualitative evaluation of pork freshness. And measurements were proved to be useful for qualitatively showing the degree of the pork freshness by analysis of the potential on electrodes. On the other hand, MRA was performed for quantitative evaluation of pork freshness by potential on electrodes and viable bacteria counts. Relationship between experimental values and predicted values of viable bacterial counts was analyzed by MRA. Results showed that the coefficient of determination ( $R^2$ ) was 0.762, suggesting a good linear correlation relationship.

In another study by Gil et al. [75], an electronic tongue consisting of 16 potentiometric electrodes was applied for fish freshness analysis. The potentiometric electrodes were the type metal, metal oxide, insoluble metal salts, and graphite as well. All electrodes were screened on to a surface substrate with different inks to manufacture the electronic tongue electrode array. Figure 2.11a shows the fabricated electrode array with 16 electrodes. Fish freshness indicators such as texture, pH, color, microbial analysis, total volatile basic nitrogen, and biogenic amines were determined versus time. The effectivity of the electronic tongue in the assessment of the evolution with time of fish fillets was evaluated. The electronic tongue was used to classify samples according to different time with PCA and artificial neural network (ANN). Figure 2.11b shows the PCA results for different metallic electrode response. Satisfactory cluster results were obtained in which fish fillets were distinguished with different days. Besides, the electronic tongue was used to predict the results obtained from chemical and biochemical analyses by building quantitative partial least square (PLS) models. A remarkable correlation was found between the electronic tongue formed by the 16 simple electrodes and parameters such as total biogenic amines, pH, TVB-N, and microbial analysis with correlation coefficients larger than 0.98.

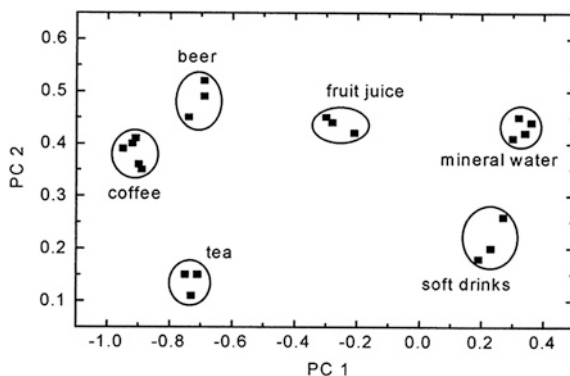
**Fig. 2.11** **a** Electronic tongue design containing and array of 16 electrodes in thick-film technology; **b** PCA results for the metallic electrode response. Ellipses cluster together measurements carried out the same day (from Day1 to Day14) [75] (Reproduced with permission from Ref. [75]. Copyright 2008 Springer-Verlag)



Beverages recognition and discrimination are other fields which are widely applied with electronic tongue. Beverages industry, such as beer, wine, tea, mineral water, coffee, is in great demand for qualitative analysis [34]. Compared to conventional analytical tools such as various chromatographs, spectrometers, and electronic tongue show outstanding superiority in flexibility, simplicity, and costing for beverages analysis.

Vlasov et al. [76] introduced an electronic tongue based on the sensor array of nonspecific solution sensors to reliably discriminate various sorts of beverages. The electronic tongue sensor array includes two parts of potentiometric sensors: (1) conventional chloride-, sodium-, potassium-selective, and pH sensor, (2) specially designed nonspecific sensors with enhanced cross-sensitivities based on chalcogenide vitreous materials. Based on those electrodes, electronic tongue was used for qualitative and quantitative analysis of beverages. Figure 2.12 presents the discriminating abilities of the electronic tongue for beverages and different beverages can be distinguished apparently. Besides, quantitative performance of the electronic tongue for some ions (Cu, Fe, Mn, Zn, Ca, Mg, Na, Cl, and  $\text{SO}_4$ ) were also evaluated, in which satisfactory results were obtained in quantitative analysis with acceptable errors.

**Fig. 2.12** Discriminating abilities of electronic tongue in different types of beverages by PCA [76] (Reproduced with permission from Ref. [76]. Copyright 2000 Elsevier)

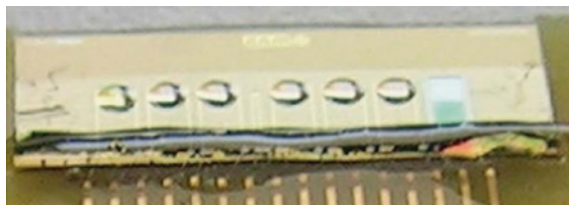


Evgeny Polshin et al. introduced an electronic tongue comprising 18 potentiometric chemical sensors for quantitative analysis of beer. Fifty Belgian and Dutch beers were measured using electronic tongue and conventional analytical techniques with different physicochemical parameters including real extract, real fermentation degree, alcohol content, pH, bitterness, color, polyphenol, and CO<sub>2</sub> content. Canonical correlation analysis (CCA) was used to study the correlations between electronic tongue data and physicochemical data. PLS calibration model was constructed based on electronic tongue data for physicochemical parameters prediction. The results showed that the electronic tongue was capable of predicting parameters including real extract, alcohol and polyphenol content and bitterness, which could be used for the evaluation of beer quality.

### ***2.5.2 Water Environment Monitoring***

Water environmental pollution has received extensive attentions worldwide due to its severe toxicity to humans. However, environmental monitoring requires onsite measurements simultaneously of a wide range of different chemical compounds and species [23]. The robustness, sensitivity, and broad selectivity are the main obstacles for on-sit monitoring. Electronic tongue with global selectivity, good stability, and high sensitivity turns to be a promising approach for environmental monitoring. Using electronic tongue with cross-selectivity, it is plausible to realize real-time multicomponent measurement in samples with a convenient and simple instrument. Various data processing methodologies such as PCA and ANN are used in electronic tongue to analyze the data of sensors, from which effective information are extracted for quantitative analysis. In fact, many studies have been investigated for water environment monitoring based on different electronic tongues.

Di Natale et al. [77] introduced a sensor array of ion-selective electrodes to simultaneously detect concentrations of a number of chemical species in solutions. In the electronic tongue system, 22 electrodes, which are mainly based on chalcogenide glasses variously doped and conventional electrodes, were used for cross-selective measurements of eight cations and anions (Cu, Cd, Fe, Cr, Zn, Cl, SO<sub>4</sub>, and H). Different data analysis approaches were utilized to ensure the best performance of the electronic tongue, including multiple linear regression (MLR), partial least squares (PLS), non-linear least squares (NLLS), and back-propagation neural network (BP-NN). About 150 chemical solutions were measured in order to construct robust calibration models of different analysis approaches. The results showed that modular models could significantly reduce the errors for concentration prediction of different ions with multiple approaches coupled. And very good concentration prediction results (mean relative absolute error <6 %) were obtained to validate the feasibility of the electronic tongue for environmental monitoring.



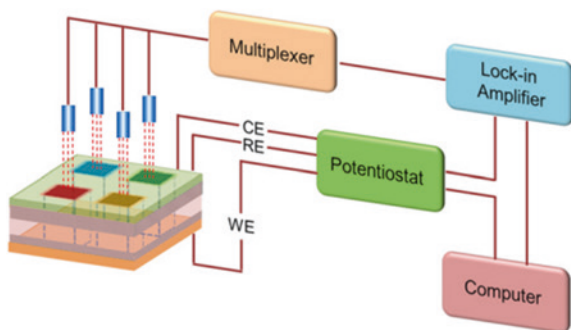
**Fig. 2.13** **a** The photograph of the chemical multi-sensor array; **b** Error analysis table of the PLS prediction of the concentration of  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Cl^-$  in water samples [78] (Reproduced with permission from Ref. [78]. Copyright 2006 Elsevier)

Moreno et al. [78] presented an electronic tongue based on a monolithically integrated array of chemical sensors. The electronic tongue was composed of six independent ion-selective field-effect transistors (ISFETs), an interdigitated platinum electrode (IDS), and a silicon diode used as a temperature sensor. The photograph of the chemical multi-sensor array is Fig. 2.13a.  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Cl^-$  ISFET-based sensors were obtained by depositing different photocurable membranes onto their gates. IDS was used to measure conductivity and redox potential. Partial least square (PLS) model was calibrated and used for concentration prediction. The concentration prediction results are shown in Fig. 2.13b, in which SEP means the standard error of prediction and  $r$  is the regression coefficient. From the results, the slope of the regression for all ions is quite close to 1.0 and the intercept to zero, which indicates very good quality of the prediction. The electronic tongue demonstrated very good performance for quantitative determination of  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ , and  $Cl^-$  in samples, which could be further used for water quality assessment and discrimination.

In spite of the cross-selectivity of traditional electronic tongues, some studies have also been investigated for cross-talk rejection and increasing the selectivity of sensors. Ha et al. [79] introduced a multi-sensor array based on light addressable potentiometric sensor (LAPS) with polyvinyl chloride (PVC) membrane modification for determination of heavy metal cations. Cross-talk was decreased by heavily doping part of the silicon substrate with boron and fabrication thick oxide formation on its surface. The schematic diagram of the multi-sensor array measurement setup is shown in Fig. 2.14. Three electrodes system was used for electrochemical characterization, and a potentiostat was utilized for potential control. The results showed that different light addressable potentiometric sensors demonstrated very high sensitivity and rapid response time to zinc, cadmium, and lead. And long-term stability was also investigated that the standard deviation was less than 0.12 mV in continuous tests for 4 h.

Besides traditional analytical methodologies used for environmental analysis such as spectroscopy and analytical chemistry, electronic tongue also plays a very important role in water environment monitoring. Compared to other approaches, electronic tongue presents significant advantages in terms of detection time, instrumentation cost, on site measurement, and multielement analysis.

**Fig. 2.14** Schematic diagram of the multi-sensor array measurement setup (Reproduced with permission from Ref. [79]. Copyright 2012 Elsevier)

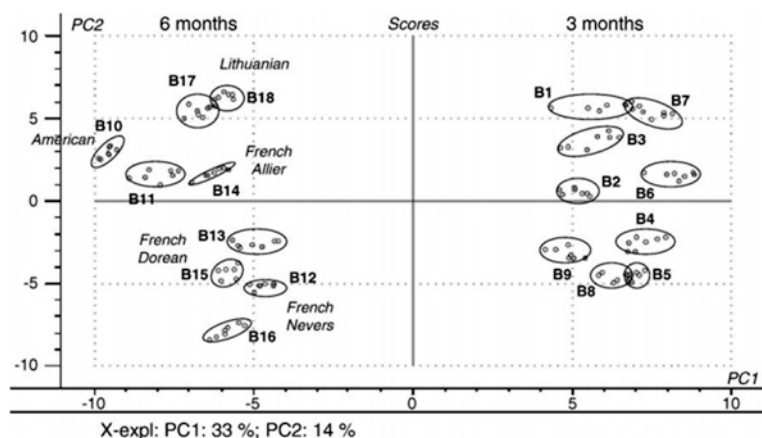


### 2.5.3 Process Monitoring

The electronic tongue has developed rapidly in recent years due to its potential application in various fields. Besides the applications mentioned above, the electronic tongue is also used for process monitoring in industry. In some industries such as dairy industry, brewery industry, and fermentation industry, it is very important to monitor the quality parameters in the process. Normally, control of the process in these industries is achieved by controlling the time for different events, while no real-time information could be obtained in the process. Analytical tools for process monitoring should withstand complicated environments in the process, and no extra substance is allowed to be introduced in the background environment in case of pollution. Thus, some approaches such as electrochemistry are very hard to realize in the process monitoring due to the reference electrode. Electronic tongue with good ruggedness and simplicity is developed as a promising tool for industrial applications.

Winquist et al. [80] presented a specially designed voltammetric electronic tongue for application in the dairy industry. Two different electronic tongues were used, one consisted of three working electrodes of gold, platinum, and rhodium embedded in a dental material; the other consisted of four working electrodes of gold, platinum, rhodium, and stainless steel embedded in PEEKTM. In case of pollution from the reference electrode, two-electrode configuration was used to measure the current with large amplitude pulse voltammetry. All electrodes were directly immersed in the process line to monitor the conductivity, turbidity, and temperature in real time. The study showed that milk from different sources with different qualities could be identified. The information provided guidance for off-flavors monitoring, which is very concerned in dairy industry.

Parra et al. [81] introduced a novel hybrid sensor array based on voltammetric electrodes to monitor the aging of red wines and to discriminate wine samples aged in oak barrels of different characteristics (wood origin and the toasting level). The hybrid sensor array was formed by three families of chemically modified electrodes, including polypyrrole sensors doped with a range of counterions, carbon paste electrodes modified with metallophthalocyanine complexes, and carbon



**Fig. 2.15** PCA score plot obtained from the electronic tongue data of the wine aged during 3 and 6 months [81] (Reproduced with permission from Ref. [81]. Copyright 2005 Elsevier)

paste electrodes modified with perylene imide derivatives. The diversity of the sensing materials has allowed obtaining a high cross-selectivity in the responses of the sensors forming the array. All information acquired by the electronic tongue was used for principal component analysis and soft-independent modeling of class analogy to confirm the high capability of discrimination and classification of the electronic tongue. Figure 2.15 presented the PCA score plot for the wine aged in the nine oak barrels during 3 months (B1–B9) and during 6 months (B10–B18). Wine samples were discriminated into two groups: red wines aged during 3 months were situated on the left side and wines aged during 6 months were located on the right side. The results indicated that the electronic tongue was able to monitor the process of aging in oak barrels.

## 2.6 Summary

Various electronic noses and electronic tongues have been developed by the combination of nonspecific sensors array. A significant feature of traditional electronic nose and electronic tongue is the global selectivity which is important in recognition of odorants and tastes. It results from the nonspecific characteristics of solid-state sensor array. Comparing with the other artificial olfactory and gustatory techniques that discussed in the following chapters, traditional electronic nose and electronic tongue have absolute superiorities in some aspects, e.g., low cost, rapid detection, and convenient operation. Those features made them widely used in food industry, environment evaluation, and public security.

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