Innovative Application Electronic Nose and Electronic Tongue Techniques for Food Quality Estimation

Himanshu K. Patel, Prutha H. Patel, Harsh Patel

Abstract: Smell and Taste are the two very imperative senses which enable us in detection and discrimination of several volatile organic compounds, which in turn may be identified as indicators for specific desirable or undesirable conditions in various industries. Electronic nose and electronic tongue are recent technologies which have attracted many researchers to work in order to provide effective solutions for various industrial applications. This paper overviews the functionality of the electronic nose and electronic tongue and presents a summary of different sensors used for the said technologies. Also, a comparison between an E-nose and E-tongue is presented on the basis of relative figure of merits. A case study is presented wherein application of artificial nose and artificial tongue is discussed for the quality analysis of the fruits. The paper is aimed to emphasis on the possibilities of combining e-nose and e-tongue techniques to enhance the overall performance of the system used for food quality analysis. An E-nose combined with an E-tongue can be a highly efficient, non-invasive, fast and low cost method of quality analysis that can serve the industry and society for the betterment of the mankind.

Index Terms: E-Nose, E-Tongue, Food Quality, Sensors, Analysis

I. INTRODUCTION

Generally, quality of fruits is arbitrated by the consumers by visible appearance (size, colour and absence of stains), maturity, fragrance and flavour. The quality of the fruits constantly changes through the various developing stages from pre-harvest to post-harvest [4]. Due to differences in the composition, the fruit varieties vary widely in aroma characteristics and taste characteristics [5]. Earlier, trained human professionals were hired to check the quality of the fruits based on aroma and visual characteristic [6]. In the domain of quality analysis of food, electronic-noses are relatively modern electronic instruments for ascertaining and classifying fruit odours from diverse fruits and its diversities. Electronic nose is capable of recurrently estimating intricate volatile gaseous combinations without separately identifying all the chemical ingredients existing in the mixture of fruit odours [7]. Each fruit has a unique odour depending upon the specific combination of Volatile Organic Compounds (VOCs)[3].

MOS sensors comprise of a ceramic substrate, which could be flat or round in shape, heated by wire and coated with a film of metal-oxide semiconductor material. The metal-oxide coating could be either of two types: n-type coating is usually made up of zinc oxide, iron oxide, titanium dioxide or tin dioxide, whereas the p-type coating is generally made up of nickel oxide or cobalt oxide [1]. Each sensor type is further classified as either thin film (6 to 1000 nm) or thick film (10 to 300 µm) types based on the film deposition technique. Redox reactions results on the surface of the MOS sensors when volatile organic compounds (VOCs) are exposed to oxides. Due to this reduction – oxidation process, resistance of the MOS sensor changes. The variation in resistance of the sensor depends on the interaction between VOC and adsorbed oxygen on the semiconductor and the metal oxide coating. This phenomena was firstly revealed with the help of zinc oxide thin-film layers [2].

Electronic tongue is an instrumental device to roughly mimic the gustatory system [2]. It is a multisensory system which consists of specific sensors to sense the markers and a pattern recognition system, which is capable of recognizing soluble non-volatile molecules and multivariate calibration for the data-processing. The human tongue is able to detect five distinctive tastes like sweet (sucrose), bitter (quinine), sour (acids), salty (Sodium and Potassium Chlorides) and umami (monosodium glutamate) and this vital information are transmitted to brainstem nuclei using cranial nerves.

II. TYPES OF ELECTRONIC NOSE SENSORS

A. MOS (Metal Oxide Semiconductor)

Electronic nose is capable of estimating the composition, the fruit varieties vary widely in aroma characteristics and taste characteristics. It is a non-invasive, fast and low cost method of quality analysis that can serve the industry and society for the betterment of the mankind.

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B. Conducting organic Polymer (CP)

Like MOS sensors, CP sensors also exhibit change in resistance in response of the surface assimilation of gas. CP sensors contain a fibre-glass or silicon substrate, a conducting organic polymer as a sensing element and a pair of gold-plated electrodes. The polymer film is deposited between both electrodes, previously fixed to the substrate, by electrochemical deposition. The arrays of CP sensor usually consist of unique polymer having different physicochemical properties and sensitivity towards group of volatile compounds. These arrangement is aimed to provide extensive specificity that overlaps with that of organic vapours. The organic vapours interact with the polymer surface resulting in to the change in resistance. Good selectivity of the CP sensor should be achieved as different polymers react to stimulated vapours with different physicochemical properties [2]. In general, CP sensors offer good sensitivities, especially for polar compounds. However, they are more sensitive to moisture due to their low operating temperature (≤50 °C) [1]. CP sensors are resistant to poisoning, like MOS sensors. Nevertheless, the lifetime of MOS sensors is only about 9–18 months because of corrosion effects. Furthermore, difficulty in achieving good reproducibility and a prominent drift in the response are the main drawbacks for this sensors.

C. Piezoelectric Crystal Sensors

QCM-Quartz Crystal Microbalance and SAW-Surface Acoustic Wave are the two piezoelectric sensors, most commonly used. QCM is advanced microbalance mass sensor, which uses bulk acoustic wave (BAW) [1], whereas QCM is made up of a polymer-coated resonating quartz disk, which is vibrating at a characteristic frequency (10 to 30 MHz). Its oscillation frequency is inversely proportional to the bounding-mass adsorption on the crystal surface. As the gas molecules gets adsorbed to the polymer surface, the oscillating frequency decreases and this diminution is proportional to the mass of aroma compound adsorbed. The thickness of coating has an influence on the sensitivity. Furthermore, humidity, temperature and some other environmental conditions also affect the sensitivity [20].

SAW sensors are operated at relatively high frequency (100–1000 MHz) and that is the reason behind the generation of a larger change in the frequency. SAW has two core components, input transducer and output transducer and both are integrated transducers (IDTs). Like QCM, in case of SAW also, vibration frequency varies with the change in adsorption of gas molecules. Hence, the information about the gas concentration can be easily obtained through the comparison of the signals from output transducer and input transducer [21] [22].

D. Mosfet

MOSFET sensors incorporate three distinct layers: a silicon semiconductor, a SiO2 insulator and a catalytic metal (like Pt, Rh, Pd, or Ir) termed the gate. In the MOSFET, source and drain terminals allow the current while the gate controls the current through the transistor. Conductivity of the transistor is influenced by the electric field generated due to the voltage applied between the gate and drain contacts. Interaction of the polar compounds with the gate causes a corresponding change in the current flowing through the sensor which in turn modifies the conductance. The gate structure affects the interaction between gaseous vapour and gate. Thick structure prepared from dense metal film having thickness of 100-200 nm is advantageous over a thin structure of porous metal film of 6-20 nm size. The operating temperature, the composition of the metal gate, and the microstructure of the catalytic metal affect the sensitivity and selectivity of MOSFET sensors. Relatively low sensitivity to moisture makes the MOSFET sensors very robust. For MOSFET sensors, good reproducibility and quality can be accomplished through high level of manufacturing expertise [1]. Table-1 summarizes the important features of all E-Nose sensors [7].
Table 1 – Performance comparison of E-Nose Sensors

| E-nose sensors | Sensor sensitivity | Response time (s) | Sensitive Component | Detection mechanism | Advantages | Disadvantages |
|----------------|--------------------|------------------|--------------------|---------------------|------------|---------------|
| MOS            | 5-500 ppm          | 5-35             | Inorganic metal oxide | Electric resistance change | Low cost, rapid sensor recovery, longer sensor life, moderate sensitivity | Higher operating temperature, sensitive to humidity, higher power consumption |
| CP             | 0.1-100 ppm        | 10-90            | Doped aromatic polymer | Electric resistance change | Low cost, ambient temperature | Limited sensor life because of oxidation, sensitive to humidity |
| QCM            | 1 ng               | ~10              | Organic or inorganic films | Frequency change | Excellent sensitivity, good precision, wide sensor range | Intricate circuitry, poor signal strength, sensitive to humidity and temperature |
| SAW            | 1 ng               | ~10              | Organic or inorganic films | Frequency change | Ultrahigh sensitivity, wide range of gases can be detected | Intricate circuitry, sensitive to humidity and temperature |
| MOSFET         | 5-500 ppm          | 5-35             | Inorganic metal oxide | Conductivity change | Low cost, quick sensor recovery, longer sensor life | Low sensitivity to moisture, high level of manufacturing expertise is necessary |

III. METHODS OF E-TONGUE

A wide variety of processing methods including electrochemical (potentiometry and voltammetry), optical, mass change detection, amperometry, and conductometry are being used to distinguish tastes from liquid samples.

A. Potentiometry Method

Ion-selective electrodes, reference electrodes, and voltage measuring devices are mainly used in the potentiometric method. Silver chloride (Ag/AgCl) is used as reference material. The ion-selective membrane should be non-porous, insoluble in water and mechanically stable. Two electrodes are used in a potentiometric sensor to measure a potential of the solution under no current condition [17]. Charged membrane or voltmeter is used to measure the value of potential which determines concentration level of some component in the particular solution. It is most widely used method for taste sensing system. The membrane is the most vital component in the sensor because critical characteristics like reproducibility and stability depend on it.

B. Voltammetry Method

In this method, a voltage is applied on the working electrode and resulting current is calculated in the working electrode with respect to the reference electrode. Oxidation or reduction of redox compounds at the electrodes causes a rise in the value of current. The voltammetry method has excellent sensitivity but the selectivity is inferior in most of the cases when several redox-active compounds and various ions are a very high amount in solution. It is very useful because of its robustness and high sensitivity [17]. Analytical principles like cyclic, stripping or pulses can be applied in voltammetry method. Pulse voltammetry offers good sensitivity and resolution.

C. Impedance Spectroscopy based Electronic Tongue

Electrochemical impedance spectroscopy (EIS) is very efficient in qualitative applications. This method has shorter response times compared to Potentiometry and Voltammetry methods. Pure and composite nanostructured films of conducting polymers are used to make sensors [17].

D. Optical Technique

This technique is based on absorbability of light by chemical compounds at a specific wavelength over a wide range from ultraviolet (UV) to near-infrared (NIR) and infrared (IR) band. Different compounds have distinct absorption wavelength, so it can be useful to identify the concentration of a compound in solution [17]. Optical technique offers very good stability.

E. Conductometry Method

Jenish Shah has presented an electronic tongue which works on Conductometry method to discriminate tastes such as salty, sweet, sour and bitter. NaCl, sugar, and lemon are used to make salty, sour and sweet taste respectively. Some food juice is used to generate a bitter solution. The polarization of ions at electrodes can be determined in terms of current flow, which describes a function of distinct chemical compositions.
The presence of ions is measured by the conductivity of the solution. Two copper electrodes were used to form an electrochemical cell. A potentiostat is used to measure a voltage difference between two electrodes [18]. The voltage applied to one of the electrodes which lead to the rise of current in the solution. Pulses with some amplitude are given as input waveform. Sensitivity can be controlled by changing the magnitude of pulses. Electronic tongue based on the conductometric method can identify different taste based on the value of current. Value of current is depended solely on the concentration of ions in solution like the highest current is found in salty solution whereas sweet sample has the lowest value of current. Table-2 presents the summary of E-Tongue methods.

Table 2: Advantages of E-tongue Methods

| E-tongue methods     | Advantages                                           |
|----------------------|------------------------------------------------------|
| Potentiometry        | High reproducibility, long term stability            |
| Voltammetry          | Excellent sensitivity and resolution, robustness, versatility, simplicity |
| Impedance Spectroscopy | Shorter response time, good for qualitative applications |
| Optical              | Good stability                                       |
| Conductometry        | Very precise to discriminate salty and sweet solutions |

IV. E-NOSE APPLICATION IN FRUITS’ QUALITY ANALYSIS

In case of apple, a large number of volatile organic compounds are generated from the epidermal tissue (peel) as compared to the internal fleshy (pericarp) tissues of the apple [10,11]. The reason behind this greater capacity for odour generation by peel tissue of the fruit is either higher metabolic activity or the profusion of fatty acid substrates [12]. More than 100 volatile compounds are found in the Peach aromas. Among these numerous compounds, alcohols and C6 aldehydes are responsible for green-note odor whereas esters and lactones provide fruity smells [10]. The flavor characteristics of peach fruit is largely influenced by the odorants like esters, such as hexyl acetate and (Z)-3-hexenyl acetate. During post-harvest ripening and fruit development stages of peach fruit, changes are observed in these volatiles [11]. During the development, esters increase, while aldehydes tend to decrease. During postharvest treatments, peach odor quality is influenced by the low temperature and controlled atmosphere [13]. Apricot fruit odors consist of more than 200 different VOCs [11] among them aldehydes, primarily hexanal and (E)-2-hexenal are the most abundant volatile compounds by concentration. The concentration of these compounds decreases during ripening [10]. Banana fruit odor includes nearly 250 volatile compounds. However, the typical banana fruity aromas are from volatile esters, like isobutyl acetate and isovalyl acetate, whose concentration increases through ripening and developing [11]. Few more odorants like isovalyl acetate, butyl acetate, isovalyl alcohol, elemicinc etc. are also spotted through olfactometric analysis of variety of banana odours. Extensive studies have been carried out on citrus volatile compounds accumulated in the oil glands of the coloured outer peel layer of citrus fruits as well as in the oil bodies of the juice sacs. These studies reveal that, the variances observed in the volatile profile of citrus juices are primarily quantifiable, and only a limited combinations are variety-specific [10]. Different varieties of melon fruit have aromas constituted from more than 240 VOCs however quantitative data is still lacking [11]. Melon fruits release various compounds with different volatility. Among them, C9 aliphatic compounds are the most important elements considered by the consumers while fruit quality is determined. Variety and physiological characteristics of the fruit largely affect the concentration of these compounds. For example, cantaloupes (one type of climacteric melon) have shorter shelf life and greater aroma intensity as compared to honeydew melons (less climacteric melons) [10]. Grape fruit aromas contain plethora number of VOCs, including monoterpenes, alcohols, C13 norisoprenoids, carbonyl compounds and esters. Variety of Grapes may be broadly classified into aromatic and nonaromatic categories. Both red and white grapes contains terpenoids as major volatiles [11]. (E)-2-hexenal is the compound which increases significantly in concentration in both Riesling and Cabernet Sauvignon varieties especially post-veraison. More than 270 Volatile compounds are found in variety of Mango fruit odours [11]. Monoterpenes are the major components responsible for mango flavour [14], whereas terpenes are the abundant composites in New World and Colombian mangoes, having concentration of the compounds ranging from 16% to 90%. On the contrary, the characteristic aroma of Old World mangoes are characterized by the existence of alcohols, ketones, and esters [11]. Important chemical changes occur just before ripening. Prior to ripening, volatile compounds like terpenic alcohol and aromatic alcohols are glycosidically bound and are part of the volatile profile as part of the ripening process [10]. More than 280 VOCs have been found in pineapple fruit aromas [10], in which major constituents of fruit aromas are Esters and hydrocarbons, whereas minor aromatic components include methyl ester, hexanoic acid, octenioic acid, octanoic acid and ethyl ester. Aroma profile of Pineapple fruit development is characterised by the significant variation in the relative content of different volatiles [11].

V. E-TONGUE IN FRUIT JUICE ANALYSIS

Zoltán Kovács et al. has experimented and compared the results of sensory panel evaluation and electronic tongue to determine an intensity of taste attributes in apple juice samples especially sweet and sour taste. In this experiment total, five different samples from top brand were used. They discriminate them by using "A, B, C, D, E" alphabets. 1-liter juice was made by only water and apple juice so it was 100% pure. For electronic tongue modified apple juice was prepared by adding either citric acid or glucose. The sensory panel takes 3 major procedure to evaluate the apple juice [19]. Potentiometric electronic tongue and the auto-sampler unit used to perform this experiment. It is able to identify all dissolved organic and inorganic compounds in juice. Seven potentiometric chemical sensors with each
have different organic membrane coatings are used in this electronic tongue. Coating helps sensors to cross sensitive and cross selective. To evaluate electronic tongue data various multivariate techniques are used. Test panel found sweet taste attributes different in sample “B” compared to other samples. Whereas sour taste was found the most intensive in the samples “D” and “E”. It concluded that apple taste is most important taste attribute in apple juice.Electronic tongue consisting 36 cross-sensibility sensors was used to identify different commercial fruit juice like orange, mango, pineapple etc. from various brands [10]. A typical electronic tongue can be constructed using ion-sensitive microelectrodes for the testing of orange juices. It was possible to classify orange juice from fruit picked from healthy trees and injected trees using e-tongue. A research paper presented by Smita Raithore et.al. discusses the usage of Alpha MOS – ASTREE electronic tongue to discriminate orange juice prepared from healthy fruit and infected fruit which are affected by the citrus greening or Huanglongbing (HLB) disease. The major constituents of the orange juice are citric acid (0.1 to 3.0 % g/100 mL), sucrose (0.2 to 5.0 g/100 mL) and KCl (0.1 to 3.0 g/100 mL). Additionally, it includes the secondary metabolites nomilin (1 to 30 µg/mL), hesperidin (30 to 400 µg/mL), limoninglucose (30 to 200 µg/mL) and limonin (1 to 30 µg/mL). Juice from infected oranges has higher concentration of bitter compounds like limonin and nomilin. Level of sugar is also very low in the HLB juice. Due to the HLB disease orange juice can result bitterer, more salty and less sweet. It is very tedious and time consuming for sensory panel. In HLB infected orange juice balance of flavour is disturbed because the concentration of citric acid, limonin, and nomilin increases and sucrose concentrations decreases which result into salty or umami taste [19].

VI. CONCLUSION
A variety of E-Nose sensors are available to enhance the quality assurance and testing of fruits and juices. For a specific application, a suitable sensor or a combination of multiple sensors can be used to measure critical parameters, in order to optimize the desired quality requirements. The electronic tongue is very useful in the food industry to maintain a standard quality of products. Still, development of E-tongue is at the early stage because of absorbability or catalysis of materials which contain ions highly affect the ability of sensors. In near future, a multisensory system like electronic tongue would be portable so it can be used for different food samples easily. The electronic tongue will be a great alternative to traditional time-consuming methods. Incorporating the advances in the sensor developments and methodologies, one can combine E-Nose and E-Tongue to cumulate their respective merits and offer a highly sensitive and accurate system for food industry. Authors of this paper foresee huge potential of the combination of electronic nose and electronic tongue technologies in terms of food quality measurement, analysis, improvement and optimization.

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