CHAPTER 1

INTRODUCTION

From the last decades, the non-natural (artificial) sense of smelling systems have generated a notable importance for its possible ways solving a wide variety of problems from many fields, initializing with important pharmaceutical industry area, like chemical engineering manufacturing, atmosphere monitoring, foodstuff industry and getting to regions which are still having only theoretical concepts like tele surgery, recognition of predicament situations, noninvasive medical analysis and at least recognition of people on biometric base. In the last 10 years electronic noses, imitate the biological olfactory system and have been developed fast. In the last 10 years electronic noses, imitate the biological olfactory system and have been developed fast.

To create the sense of odors electronics uses machine olfaction. The envisioned realization of this technology is the electronic nose, or e-nose, which is an electronic device that can sense and identify different vapors. Gardner and Bartlett in 1994 [1] formally define electronic nose as: “An electronic nose is an instrument which comprises a series of electronic chemical sensors by means of limited sensitivity and a suitable pattern recognition system competent of recognizing easy or complex odors.”

Since the eighties, the electronic nose had many implementations, with a lot of societal impact e-nose has yet to be realized as a well-known technology. In fact, the assurance of a widespread e-nose technology includes uses ranging from explosives detection to product safety monitoring to
environmental and spoilage detection. To penetrate these exciting areas unfortunately, most electronic noses today are too expensive

In the late 90s, the price of commercial artificial noses began to decrease with the arrival of micro manufacture techniques that directed to low-cost integrated sensors [2], but since then cost have been stable and remained at the similar level as in 1998 [7]. Current fabrication techniques enabled cheaper sensor elements to be integrated into a single array but still it is a complicated proposition for these sensors.

The technologies which substantially raise the price tag of the sensor array rely on subtractive processes, which usually contain metal oxide sensors that are costly to add onto a general substrate. The key to opening the gate to a lot of attractive uses is to decrease the price and specifically, to get a way to make the sensor array much more cheaply. This key may recline in the meeting of two upcoming areas of research: additive processing and organic electronics.

Additive giving out is the most excellent substitute to manufacture the sensor array since it really is the key issue of materials integration. The prototypical case of additive processing is key giving out in which the materials of attention are dissolved into solution and then onto the substrate it is deposited as an ‘ink’. This allows the material to be located on the substrate where preferred and avoids the question of materials integration since deposited materials have no result on what materials are then deposited. Additionally, additive dispensation is inherently cheaper than subtractive processing as the material is placed in one processing step rather than the numerous steps that are necessary in a subtractive approach like photolithography.
Obviously additive processing via solution has a major condition, which is that all the materials should be soluble. This brings in another field of importance, namely organic electronics. Organic electronics refers to carbon-based materials that possess semiconducting and conducting properties depending on the collection of bonds inside the organic molecules. One of the main attractive features of these materials is that they can be processed by means of printing techniques such as ink-jet or gravure [3-5]. Ink-jet printing of transistors and circuits is even under commercial development by some companies and has been demonstrated by several research groups [4,6].

To characterize off flavors, sensory assessment has been the customary approach. The call for smell sensing devices becomes larger when volatile and semi-volatile organic compounds are there in the product in parts per billion or even in the parts per trillion concentrations series that cause off flavors. Today, sophisticated, responsive instrumental tests such as e-nose technology coupled with gas chromatography are able of identifying, detecting and quantifying the specific chemical agents responsible for off flavors. The ability to meet specific customer requirements in its most general sense is quality. In production and food quality control, safety is of extreme importance, that is, insurance of the health and life of customers by taking suitable action at each phase of production and food distribution.

Among the several sensory quality components such as colour, rheological properties and packaging, the taste and flavour profile plays a particularly important aspect to the consumer, i.e. the odor and taste sensations received while eating. Thus the presence, contents and composition of volatile substances (viz. flavour and aroma) in food have a substantial influence on its quality. What is more, each product has a characteristic and
unique composition of volatile components that make up the aroma. The aroma of nearly all food products consists of complex mixtures, sometimes consisting of quite a few hundred compounds. An examination of odor, its recognition and quantitative evaluation, can comprise a valuable source of information on the value of food, which includes together the sensory value and the consumer’s health and safety.

To process digital information great advances have been made with the advent of gradually more powerful electronics technology. To match these gains in processing power, transduction technologies have also advanced, enabling these digital systems to interrelate with real-world signals in the surroundings. Speech recognition, image processing, touch-screens and pressure sensors, are just a few examples. These technologies have enlarged the scope and benefit of electronics. Fascinatingly, most of these are centered on the basic senses of sound, touch and sight, while taste and smell are usually overlooked. The latter two are closely related and, in fact, the realm of smell is a warehouse of useful information. Odors and smells are ubiquitous and biological olfaction is used every day from basic functions like survival to evaluating the quality of foodstuffs, beverages, perfumes, and others.

If one doubts the importance of olfaction in society, consider that grain spoilage is still inspected by a human expert who sniffs the grain and rates it with four classifications: Good, Sour, Musty, or COFO (commercially objectionable foreign odor) [1] that canines maintain to be the most reliable and accurate way to detect explosives and narcotics [2] that air quality, while important to health and comfort, is often poorly assessed or that odor and aroma, which cannot be assessed in-line during processing or shipping, can completely invalidate consumer products such as foodstuffs, perfumes, sunscreens, carpet, wines, and more [1,3,7]. Odors are repository of useful
and important information and besides all these applications there are still untapped areas in early detection of cancer, product spoilage detection and environmental monitoring.

1.1 Motivation for this Research work

Industrial revolution have made human living standard grown remarkably. The negative aspects of industrialization on human health are the emission of different gases that pollute environment and create risk to public health. To protect unwanted incidence of explosion or fire, flammable gases are made to be monitored. The demand for gas sensors in recent years have increased due to its applications that ensures human health and safety, protect the environment, monitor manufacturing process and optimize the performance of control system. The requirements of these applications demand immediate and continuous analysis to detect target gases. Assuring safety at work place and to have quality control in industrial production online analysis of gas mixtures is required. In many technological fields sensing of various gases is important, like in oil and petrochemical industry, water treatment plant and biogas applications. Traditional detecting method and identification of drunken drivers have been replaced by the modern alcohol breath analyzers based on ethanol sensors. Poor indoor quality due to emission of toxic gases, volatile organic compounds and microbial contaminants can reduce the health and comfort of occupants of a building. Hence monitoring of toxic and hazardous gases is a subject of growing importance of both industrial and domestic built environment.

When considering the applications for machine olfaction, the specific benefits of an electronic nose should be taken into account. While electronic noses are more sophisticated than single sensor elements, the
tradeoff with complexity means that single sensors still make sense for a number of applications such as oxygen sensors in automobiles. However, there are a number of exciting applications that are waiting to benefit from electronic noses that have discriminatory powers akin to mammalian olfaction. The best of these applications are those in which single element sensors offer little to no value, yet a functionally superior electronic nose would offer an unprecedented advantage over any existing technology. Examples of these include food spoilage detection, environmental monitoring and explosives detection. The first of these, spoilage detection, will be discussed as a motivation for electronic noses since it provides a good framework for discussing the challenges and requirements of a good electronic nose technology.

Food spoilage detection presents a very exciting opportunity for electronic nose technology because, currently, there are no satisfactory methods of detection that can be employed at critical points in the food supply chain. Food spoilage continues to pose an enormous societal burden both in financial terms as a loss of resources, as well as the time and energy invested in producing the foodstuffs and the loss in productivity associated with food borne illnesses. It is estimated that 25% of the world’s food supply is lost through microbial activity alone [8] (For non-grain staples, such as vegetables and fruits, the World Health Organization believes the loss to be as high as 50% [9].) Food loss occurs throughout the entire supply chain, beginning on the farm and continuing throughout post-harvest storage, distribution, processing, wholesaling, retailing and use in the home and in catering [10]. Approximately 76 million illnesses are caused by food borne diseases, 5,000 deaths in the US each year and 325,000 hospitalizations have been estimated by the Centers for Disease Control and Infections. [11]
While the food industry made great gains in modernization and automation during the latter half of the 20th century, the conventional methods of microbiological testing, on the whole, saw little progress [12]. Though there are over 40 methods to classify and enumerate bacterial spoilage in meats [13,14], their effectiveness in detecting food spoilage is negligible because they are alert on identifying pathogens of interest using microbiological methods. These laboratory techniques are not as suitable for detection since they are often time intense, intractable and display. For instance, holding times of eight hours are occasionally required for certain sterilized foods while pending the outcome of microbial assessment [15].

Presently the most robust identification methods are these microbiological techniques which involve obtaining a food sample and isolating the pathogen of interest. These methods are based on two different approaches, the first involves immunological techniques and the second is concerned with nucleic acid detections. The most widespread immunological method is the enzyme-linked immune sorbent assay (ELISA) and is based on using an enzyme label to find surface antigens of specific microorganisms responsible for spoilage or contamination [13]. Of the nucleic acid discovery schemes, polymerase chain reaction (PCR) is the most popular route [14]. PCR amplifies specific gene fragments and then identifies them using gel electrophoresis [15, 16]. PCR has the advantages of being relatively rapid and discriminating but it can also introduce false positives since any whole nucleic acid sequences are amplified during the reaction. In addition to identification, quantification is approved by measuring ATP bioluminescence, impedance or using microscopy to count cell colonies [12].

Clearly, none of these techniques are sufficient to notice food spoilage at the processing or consumer level. There is still the need for quick,
in-line detection methods in food method control as well as instruments that could be used by food retailers or consumers. Current in-line methods monitor several parameters including color, using reflectance, or temperature, via infrared thermometry [15]. The most relevant parameters to spoilage might be by pH and humidity, but this is still a rather indirect quantity at best. Gas chromatography has been used for stink analysis and in some processes, gas chromatography olfactometry (GCO) has been tried, which consists of a gas chromatography (GC) tool with an added sniffing port for the human worker (Fig.1.1) [15].

![Figure 1.1 Gas chromatography olfactometry (GCO) configuration. The gas chromatographer accommodates a sniffing port for the human operator. Figure taken from ref [7].](image)

Since GC can only give the substance analysis of the odor but cannot determine the olfactory impact of the molecules. The sniffing port allows the human operator to determine the quality of the odor. At the sell or consumer level, there is no method except through human olfaction or illustration clues such as staining or changes in feel.
1.2 Problem Statement

Smell has traditionally been the most hard to define moreover impartially or accurately, of all the human senses. Unlike light (lumen) or sound (decibels), there is no level for measuring the intensity or excellence of aromas other than by subjective clarification or similarity to a more recognizable one. The human sense of smell to charge the quality of food or the instantaneous environment is the natural function of being sense. It is easy to distinguish between the smell of a perfume and the putrid odor of decomposing meat, and our reactions towards these smells vary accordingly. However it is not so easy to portray or explain the difference in sensitivity [20].

Odor sensing devises are required because, the chemical mixture to be sensed are different and the difficulty of measurement becomes larger when it is noticed that the headspace of foods, odours or beverages in the normal human surroundings may contain many hundreds of compounds all interacting with the chemical sense to let sharpness of a countless number of odor nuances. Assessment of the organoleptic character of ripe foods, or contaminants or off-odours is major concern of many food product manufacturers and involves panels of humans trained in distinctive subtle variations in odours [20]. At times the most highly trained human testers are slanted, illness and other factors can affect their action [21].

1.3 The Electronic Nose

An electronic nose is made of a chemical sensing system (such as a sensor array) and a pattern detection system. The sensing system can be a compilation of some different sensing elements (chemical sensors), where
every constituent measures an extraordinary property of the sensed chemical, or it can be a sole sensing devise (spectrometer), that produces a collection of capacity for each chemical, or it can be a merger [21]. A series of sensors that responds to unstable components of headspace above a sample are simply the electronic nose sensors. Gas chromatography or sensory analysis is supposed not to be confused with current electronic nose technology which could perhaps be most exactly defined as odor sensors. These electronic odor discovery systems integrate sensors (which are conceptually similar to human olfactory receptors), and a data-processing system (which theoretically simulates the brain) just like the human sensory system [22]. Just as humans does not need to distinguish deliberately each different constituent of an odor in order to recognize it, electronic noses operate by recognizing the model of components. [23] defined an electronic nose as “an device which comprises an group of electronic chemical sensors with limited specificity and a appropriate model recognition system, able of recognizing simple or complex odours”.

The feeler or detector is the main constituent in an analytical system. The choice of sensors is quite large; however it can be confidential into two broad categories: viz 1. Hot sensors‘ mainly the semiconducting metal oxide gas sensors’ and 2.Cold sensors ‘conducting polymers, bulk acoustic wave (BAW) and surface acoustic wave (SAW) radio frequency sensors.

1.3.1 Semiconductors – metal oxide gas sensors

The hot semi-conducting gas sensors are the most generally used because they currently offer the best portion of drift and lifetime to compassion. These sensors have a logarithmic transfer function: The log of
the strength of the incentive is related to the electrical response. This creates a lively compression difficulty when using a elevated value baseline (e.g. in the existence of high levels of water vapour, ethanol or CO₂) or a high attentiveness of the analyze [22]. Poor selectivity is the main problem with semi-conducting metal oxide gas sensors. Although to a different extents the sensors react to all of the stimuli. Because of the bad selectivity, the sensors are used in series of 4-32 sensors, all with a faintly dissimilar selectivity [24], to obtain an inimitable overall prototype or fingerprint that corresponds to the overlapping responses of the dissimilar sensors to the range of compounds within the sample. As well as giving improved selectivity the use of such arrays leads to a convinced amount of redundant information, which is very useful if one of the sensors fail. Conducting organic polymer sensors are obtained by electro-polymerization of a thin film of polymer across the gap flanked by gold plated electrodes. The electrical conductance will alter according to the molecules adsorbed onto its surface. Many polymers with different useful groups are now obtainable, the main one being poly pyrroles.

The main benefit is that they operate at room warmth. However the response time is long (20 –40 sec), which is a disadvantage for rapid analysis. The inherent drift over time or with changes in temperature is very high [25]. The main confines of cold sensors for use in the food industry are their high compassion to compounds such as ethanol, CO₂, or humidity [26], which masks preferred responses to aroma compounds. The use of such sensors is thus very restricted in the field of alcoholic or luminous beverages, as it can be very luxurious and time consuming to remove CO₂ or ethanol from the unstable flavour component.
1.4 Aroma Scan (A32S)

The Aroma scan detector arrangement is an array of 32 organic conducting polymers. These are based on heterocyclic molecules such as derivatives of polypyrrole and polythiophene. These polymers have sole adsorptive surfaces that interact with adsorbed volatile chemicals based on their form and size. The polymers display reversible changes in electrical resistance when polar volatiles adsorb and desorb. Each polymer in the array has a variety of selectivity to different substance class. Thus the collection exhibits a broadband answer to many thousands of chemical species [27]. The advantage of the electronic nose sensors comprise rapid, real-time finding of volatiles, less research time, greater safety and lower costs [21]. Many studies have been approved out using the electronic nose. In a study carried out by [28], the electronic nose was used as a rapid method to monitor changes in the headspace gas higher than capelin (fish found mainly in Alaska) during storage. Results obtained point to that the electronic nose can be used as a rapid revealing technique to predict the total unstable base value of the raw fabric stored under different conditions. In using the electronic nose for dairy products, Ampuero and co-workers found that this new knowledge can potentially be applied to process control and monitoring, acceptance or rejection of raw material, middle and final products, as well as appraisal of synergistic effects of individual odorants.
1.4.1 Data acquisition

The software provided for the unstable sensing system (electronic nose) consists of three modules: data gaining and instrument manage, data treatment for removal of patterns and prototype recognition. The gaining software samples the sensor array confrontation at regular intervals, storing the ensuing data in the computer. As the resistances of the conducting polymers are inversely proportional to temperature, the temperature of the array is forbidden and monitored (typically to 35 ±0.1°C). The sample temperature and sample moisture are also monitored. Individual sensors on the array may be deactivated or activated as required. The responses of the sensors are shown in real time in a strip chart show on screen, as can be seen in Fig. 1.2.

![Figure 1.2: Response of a 32 sensor conducting polymer array to ethyl acetate vapour. The percentage change in resistance (dR/R) in response to the vapour is shown [27].](image)

The signal is articulated as the proportion resistance alters of each sensor compared to the original sensor resistance. The reaction to the vapour is then normalized by expressing the partial change of the individual
feeler as a fraction of the fractional changes summed over the whole array. As denoted by the equation below, for an array of n sensors:

$$N_X = \frac{100 \Delta r_x / r_x}{\sum_{i=1}^{n} \Delta r_i / r_i}$$

Where, $1 \leq x \leq n$, $N_X$ is the normalized response of sensor $x$, $\Delta r_x$ is the confrontation change of the sensor $x$, $r_x$ is the base (initial) resistance of sensor $x$, and $\Delta r_i / r_i$ is the partial change in resistance of the $i^{th}$ component of the array.

### 1.4.2 Data treatment

Any application will rely heavily on the data processing and pattern recognition software associated with it. The response to a volatile odor of each sensor is proportional to the attentiveness and is sole for each type of single or complex odor. With each sensor in an array having a certain answer character, an array of sensors with broad but different chemical specificities provides an extent pattern of broad overlapping selectivity. These response or signals, are processed to produce a set of descriptors for the input, which can be identified as a ‘fingerprint’ for the odor and then saved into the database for further manipulation within statistical pattern gratitude methods, cluster analysis and synthetic neural networks [27].

Here exists linear multivariate analysis such as principal component analysis (PCA), discriminate function analysis (DFA), non linear methods such as artificial neural networks [29,30]. A parametric categorization is very rarely possible. Usually the addition into a given group is determined by the Euclidian distance or the Mahalanobis distance. The
latter takes into explanation the definite shape of the group whereas the previous assumes that the data points belonging to the group are evenly dispersed in a sphere in the region of the centre of the group.

1.4.2.1 Principle Component Analysis (PCA)

Principle component analysis (PCA) is a linear combinatorial method which reduces the convolution of the facts set, from the initial \( n \)-dimensional break (\( n \) sensors) to a few dimensions. The intrinsic structure of the data set is conserved while its resulting variation is maximized. Data points will be scaled beside new dimensions, linear combinations of the preliminary dimensions. The magnitude of the coefficients in the resulting linear combinations, give a suggestion of the relative importance of the initial dimensions in the data structure. Principle component analysis is performed with no information on the classification of samples. It is based exclusively on the discrepancy of the data set.

1.4.2.2 Discriminant Function Analysis (DFA)

Discriminant function analysis (DFA) is based on previous data organization. The linear combinations maximized the involvement of those proportions that generate the largest difference between predestined groups. With this method, different classifications on the same data set are probable following different properties (e.g. freshness, fruitiness, etc.). Fastidious care should be taken conversely to avoid over fitting of errors, i.e. classification based on noise slightly than real differences. The resulting DFA classification is extremely reliant on the data set used for preparation.
1.5 Objectives of the Thesis

1. To study various parameters of electronic noses: There are diverse parameters in electronic noses like voltage developed due to gas absorption, type of sensors, the number of sensors etc. For different applications, different parameters give the best results [32, 33]. In this thesis various parameters have been studied that can give best possible detection of stink for different applications.

2. The comparative study of different classifiers on electronic nose datasets: Various types of classifiers are used for the categorization work. Decision trees, Neural networks, PCA, PLS and Support vector equipment are some of the popular classifiers. Each has got strengths and weaknesses. In this thesis relative study of specially PCA and PLS techniques as classifiers for a certain domains have been carried out.

3. To study algorithms used for uncertain data for electronic nose datasets: As there are fluctuations in feeler values, a range of values instead of a single value have been obtained. In this thesis those classifiers has been studied that can switch these uncertain data. This may recover the performance of the systems.

4. To identify different domains for electronic nose: Electronic noses have been active study areas, however, in India, its uses are not prevalent. Food processing, surroundings control, cosmetic area is some of the areas where electronic noses can be very beneficial. In this thesis various domains in Indian perspective have been studied where these can be easily employed to benefit the large population.
5. Explore the application of electronic nose for food processing: After checking the classifier algorithm the work is to analyze its application in the agricultural group and an oil refinery industry. For first purpose of the work the database of samples of three different value of medicinal plant *Glycyrrhiza glabra* known as *Liquorice* have been used. For testing the classifier algorithm in the sphere of organic gases which are mostly found in oil and natural gas industry the samples of ethanol, acetone and propane gas have been measured.

1.6 Contribution of the Thesis

Agriculture products that are used in biomedicines requires very sophisticated processing and storage, hence it is a very important research area. The present day high cost of biomedical plants also shows the importance of proper storage of such kind of agriculture products. In pharma industry there is a large amount of use of *Glycyrrhiza glabra* products which are get destroyed because of lack of proper storage. To avoid this wastage it is important to have a continuous monitoring of conditions of such products so that necessary actions can be taken to protect the products quality. For example, cold storages are used to store *Glycyrrhiza Glabra* roots after drying. During the storage time, it is very difficult to assess the conditions of these roots, therefore sometimes rotten roots are received after the storage time. To reduce these wastage electronic noses inside the bags can be placed. Through a wire-less system, one may receive the output of the electronic nose. Hence, one can know the condition of roots, without opening the packing bags. Therefore, one may take the action to prevent the further detoriate of the roots.
1.7 Organization of Thesis

The thesis is organized as follows. Chapter two presents the overview of Biological olfaction and the basic principle of electronic nose and its different types. In this chapter the applications of electronic nose and literature review of electronic nose is also discussed. In chapter three discussion about various data processing and transmission techniques that are used in this research for evaluating the quality assessment or odor classification of electronic nose sensor applications have been done. In chapter four investigations about the performance of various nose sensors in classifying two different types of sample used in pharmaceutical and in petroleum industry has been done. The analysis in this thesis has been performed in three steps that can be broadly defined to classify the implementation of work. The thesis is finally concluded in chapter five.