CHAPTER 1

Introduction and Literature Review

1.1 Introduction

Let's start with some latest stories worldwide:

"Human Nose Can Detect a Trillion Smells"- Thursday, March 20, 2014 [Internet Resource (IR1)].

"In future we will be sniffing out disease. Technology is being developed to create electronic devices that will be able to 'smell' the presence of diseases such as TB"- Science News, 2 April 2014 [Internet Resource (IR2)].

"Electronic Nose Sniffs Out Prostate Cancer Using Urine Samples" New York, NY, May 1, 2014 [Internet Resource (IR3)].

The above news are just few latest examples to indicate the growing interest of researchers in developing the highly efficient olfactory machines and electronic-nose (e-nose) systems. The advancements in medical science, industrialization, war weapons and environmental pollution etc. have driven the need of classification and quantification of odorants in highly efficient manner. It is very necessary to monitor and precisely measure the leakages of combustible/explosive and/or hazardous gases/odors and volatile organic compounds (VOCs) to prevent the accidents both in public and private spaces [Persuade *et al.* (2005); Natale *et al.* (2014)].

The conventional monitoring methods for most chemical contaminants are costly, time intensive, bulky and involve limited sampling and analytical techniques. Thus, there is a natural requirement of cheap, improved and reliable methods which can rapidly and reliably detect/quantify the environmental chemical pollutants and harmful explosive gases/odorants before crossing the safe limit and prevent the occurrence of any fatal accident. The advancements in e-nose technologies in the past decades have explored better quality control capabilities to monitor chemical pollution in various environments by providing relatively cheap, portable odorant detection devices with a wide range of organic, inorganic, gaseous and chemical pollutants [Wilson (2012)]. Table 1.1 summarizes some applications of gas sensors and the devices used for detecting various harmful gases/odorants in different environments/areas.

Modern gas sensing devices are mostly driven by the principle of mammalian olfaction system. The complexity of mammalian olfaction system is very high which is still in the understanding phase. To understand the olfaction phenomenon and realizing them in the artificial world is a big challenge for the researchers. Moreover, the mammalian olfactory system is very efficient in terms of power, memory and speed which are still a challenge for the researchers to achieve in the future e-nose systems.

1.2 Human Olfaction System

Three sensory systems in humans viz. olfaction (the sense of smell), gustation (the sense of taste) and the trigeminal sense (responsive to irritant chemical species) contribute to the sensation of flavor. Among these, smell is the dominant factor in our sensation of flavor. Almost all living things, from plants to human, are adapted to sense the molecules in the environment [Gardner (1994); Chiu *et al.* (2013)].

Olfaction, called the sense of smell, has been an inherent source of information of visible/invisible objects/odors for human as well as other mammalian/vertebrates since their evolution. The skill of identifying the objects/odors by smell is a result of chemo-sensitive phenomenon in higher organisms.

In the past decades, there had been great interests for researchers to understand and realize the real phenomenon of olfaction system. In mammalian/vertebrates there are wide range of multiple and integrative functions such as physical regulation, emotional responses, reproductive functions and social behaviors which are regulated by their olfactory system [Karlosen *et al.* (1959); Luo *et al.* (2003); Rajput (2011)].

Human olfaction system can be understood as depicted in Fig. 1.1. The main constituents of this system are:

a) Olfactory receptors
b) Olfactory bulb
c) Brain
d) Neurnal processing (Memory)

Table 1.1 Classification of gas sensors (Pearce *et. al* (2002), Arshak et. al (2004). Wilson et. al (2009), Xiao Liu (2012))MOS= Metal oxide semiconductor, MOSFET=MOS field effect transistor, QCM= quartz crystal microbalance, SAW =surface acoustic wave, SPR=surface Plasmon resonanc

Sensor Type		Sensitive Material	Detection Principal	Commercial Availability (Sensitivity	Fabrication method	Measurand	Advantages	Disadvantages
Chemoresistor	MOS	Gate material	Conductometric	Commercial, 5-500 ppm	Microfabricated Sputtering, thermal eveporation	Conductance	Ambient temperature operation, sensitive to many VOCs, short response time, diverse sensor coating, inexpensive, resistance to sensor poisoning	Sensitive to humidity and temperature, sensors can be overloaded by certain analytes
	Conducting Polymers	Modified Conducting Polymers	Resistance Change	Commercial, many type, 0.1-100 ppm	Microfabricated electroplating		Ambient temperature operation, micofabricated	Very sensitive to humidity
Chemocapacitor	Polymers capacitor	Polymers	Capacitance change	Research	Microfabricaed, spin coating	Capacitance	Applicable to CMOS based chemosensors	Very sensitive to humidity
Chemidiode	Schottky diode		potentiometric	Research	Microfabricated	Threshold voltage change	Intergrated, Applicable to CMOS based chemosensors	Needs Pd, Pt, Au (expensive)
Chemotransistor	MOSFET	Catalytic metals	potentiometric	Commercial	Microfabricated , thermal evaporation	I-V/C-V	Intergrated, Applicable to CMOS based chemosensors	Odorant reaction product must penetrate gate, baseline drift
Thermal chemosensor	Thermister (pyroelectric)	Organic dyes	calorimetric	Research	Microfabricated Ceramic fab	Temperature	Low Cost	Slow response
	Pellistor			Research	Microfabricated		Low Cost	Slow response
	Themocouple			Research	Microfabricated		Low Cost	Slow response
Mass Sensitive Chemosensor	QCM	Organic or inorganic film layer	Mass change (frequency shift), Gravimetric	Commercial	Microfabricated, screen printing, dip-coating, spin coating	Piezoelectricity	Well understood technology	MEMS fabrication, temperature and humidity sensitivity interface electronics?
	SAW			Commercial			Differential devices can be quit sensitive	Interface electronics, temperature sensitivity, specificity to analyte groups
Resonant type chemosensor	SPR	Light sensitive, Photodiode, fluorescent sensitive	Light modulation, optical changes, fluorescent light emission	Research	Microfabricated, screen printing, spin coating, dip-coating	Refractive index	High electrical noise immunity, high sensitivity, multiparameter detection capability	Complex sensor array system, expensive, low poertability
Fiber-optic chemosesnor	Fluorescence, chemoluminescence					Intensity/spectrum		Restricted availability of light sources
Toxic gas sensor	Electrocatalyst	Solid or liquid electrolytes	Current or voltage change (Amperometry)	Commercial	Composite electrodes	Current	Low cost, Rh interference , ambient temperature operation, low power	Size,portability

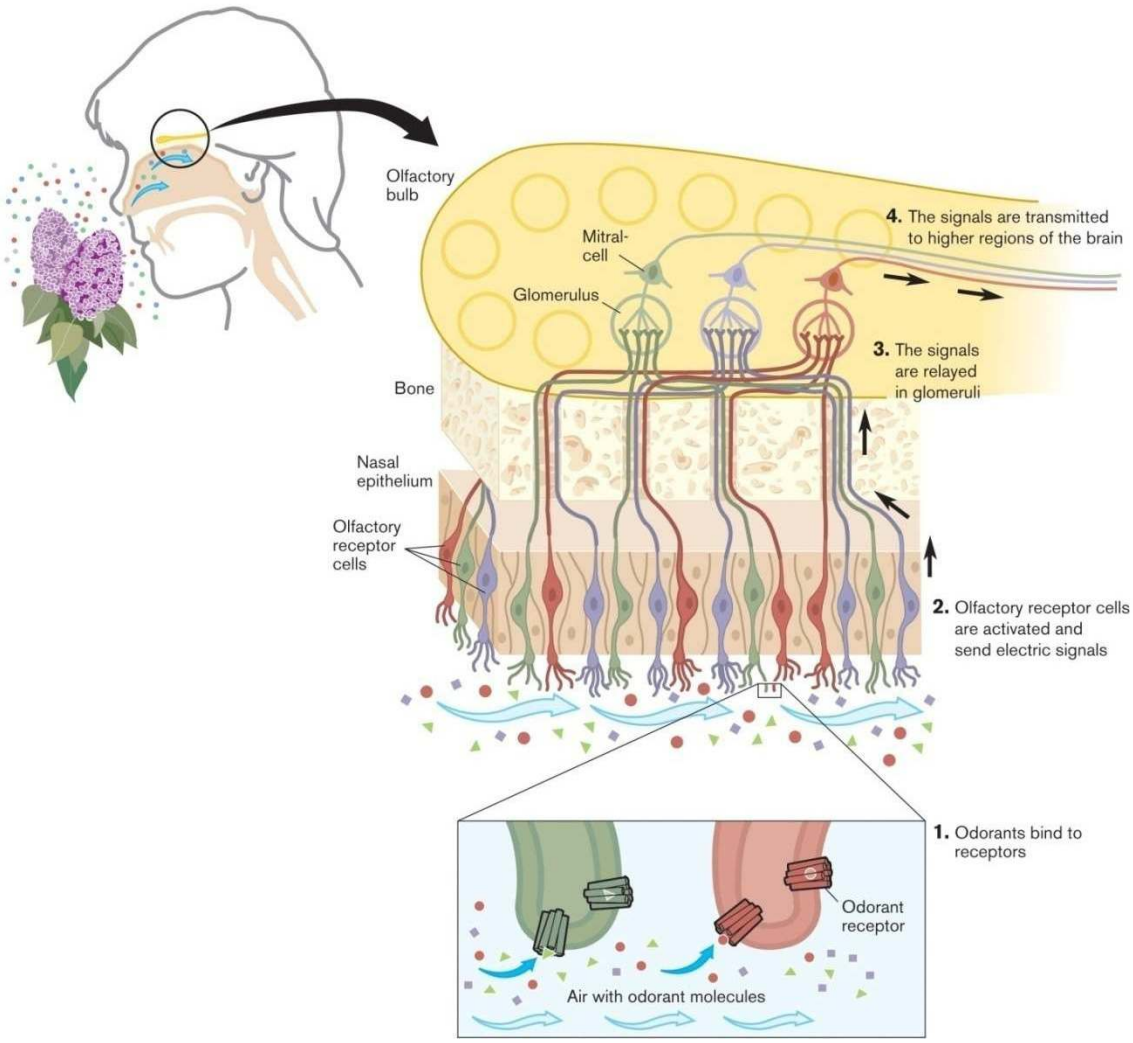

Fig. 1.1 Odorant receptors and organization of the olfactory system [Internet Resource (IR4)]

The odorant molecule is inhaled by the nose and moves to past curved bony structure called turbinates which create turbulent flow that carry odorant molecule to the thin mucus coating of olfactory epithelium. The ends of the nerve cells show up in the olfactory epithelium which senses the odorants [Nagle and Osuna (1998)].

The neuroepithelium is located in the posterior of recesses of the nasal cavity and contains mainly the three types of cells viz. olfactory sensory neurons, sustentacular or supporting cells and the basal cells. Olfactory neurons are generated in the basel cell are replaced in approximately every 30 days interval and are generated throughout the life. The sensory neurons in the epithelium are bipolar such that a dendritic process extends to the mucosal surface and are covered with cilia

which are hair like structure with receptors located on the outer membrane of the cell [Buck and Axel (1991)].

The odorant binds to a specific surface receptor protein called *G* proteins, [Jones and Reed (1989)] which initiate a cascade enzyme reaction which results in depolarization of the cell membrane. These reactions result in generation of action potential which propagates along the olfactory sensory neural wires called axons. These axons wend to the brain olfactory bulb and terminate in a cluster of neural network called glomeruli. Each glomerulus is also the terminus for dendrites from about 25 large *mitral cells* and about 60 smaller *tufted cells*. There are more than 2000 such glomeruli in the olfactory bulb which represent the first tier of the central odor information processing.

Olfactory sensory neurons in the epithelium can respond to more than one odorant which create pattern of response across multiple glomeruli that codes the quality of the olfactory system. This olfactory information ultimately reaches to the higher level of the brain for processing [Buck and Axel (1991)]. Olfactory neurons in the epithelium can respond to more than one odorant. Hence, the qualitative parameters of olfaction are determined by the pattern of response across multiple glomeruli [Kauer (1991)]. The subsequent neural processing through the use of its parallel architecture with distributed memory enhances sensitivity and provides discrimination between several odors [Gardner & Bartlette (1994); Kumar (2011(a))]

1.3 Machine Olfaction and Electronic Nose

Inspired by the theory developed for the mammalian olfactory system, it has been a topic of keen interest for researchers for decade to mimic the olfactory system artificially. Human nose was primary instrument in early stage of history to identity and quantify the odorant. Before the advancement in the artificial olfactory system, human panel were used to evaluate the smell of flavor such as perfume (cosmetics, soap etc.), food stuff (like fish, meat and cheese) and beverages (like bear, whiskey, coffee) [Gardner (1994)]. But the problems with human expert were of individual variability, adaptation (become less sensitive during prolong exposure), fatigue, infection, mental state, subjectivity and exposure to hazardous compounds. Also, using human panel is a costly process as they can work for very small time.

Initially, some conventional analytical methods were developed such as gas chromatography (GC) and mass spectrometry (MS). The conventional methods are not only time consuming but also the results produced by them are inadequate sometimes. Moreover, the conventional methods rely on bulky instruments which are hardly portable plus rarely useful for real time and online monitoring [Bodenhofer *et al.* (1997)].

In order to resolve the previously mentioned problems in conventional methods and to achieve the goal of continuous real time monitoring of odorants with portability and low cost issues in mind, researchers have tried to develop the artificial model of the natural olfactory systems. To develop such olfactory system, Dodd and Persuade in 1982, proposed a model of nose. This developed the term electronic nose (e-nose), though the term electronic nose appeared around late 1980 [Gardner (1987)]. The standard definition of e-nose is *"an electronic nose is an instrument, which comprises an array of electronic chemical sensors with partial specificity and appropriate pattern recognition technique"* [Gardner (1994)]. The odorants produce change in electrical/chemical properties of sensor array devices which convert the chemical inputs into the electrical signals which are further utilized by pattern recognition (PARC) techniques. The PARC techniques are getting importance with development of artificial intelligence in the modern era, which provides a hope for the great future in the field of e-nose.

The e-nose thus, is a system consisting of three basic functional blocks that operate serially. First is an odorant handler, second is an array of sensors and third is signal processing system as show in Fig. 1.2.

The fundamental principal of operation of electronic nose lies in the fact that each sensor in the sensor array has different sensitivity to different odorants. This is to mimic the mammalian olfactory system where sensory neurons in the epithelium can respond to different odorants with different sensitivity. The pattern of response of sensor array is different for different odorants. This pattern of response of sensor array basically acts as *signature pattern* for a particular gas. Thus, each sensor in the array has a unique profile to the spectrum of odorants under test [Nagle and Osuna (1998)]. Fig. 1.3 is a photo image of compact hand-held device developed by NASA for detection of hazardous compounds in spacecrafts. This e-nose device employs an

array of chemical sensors to achieve appreciable selectivity to different gases/odors to be detected.

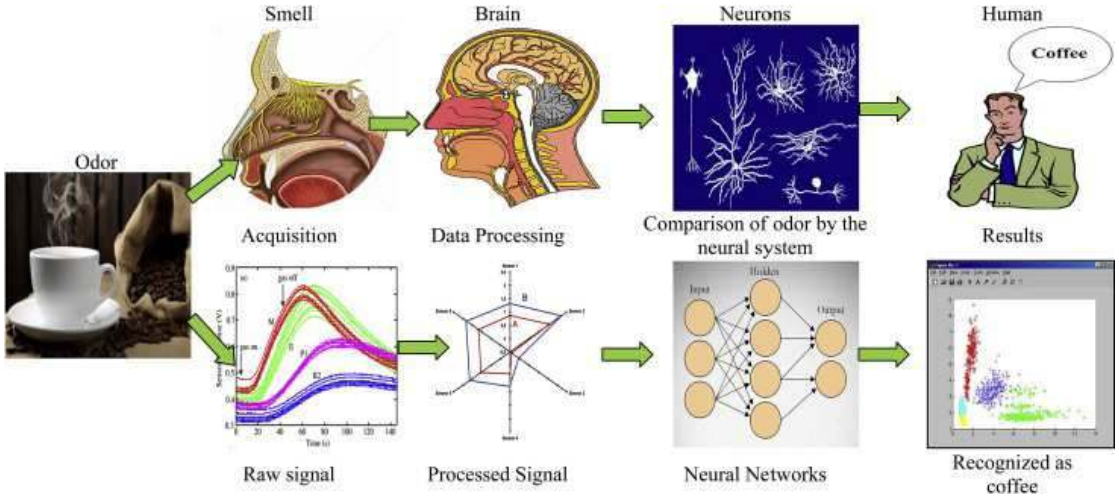

Fig. 1.2 A comparison of the biological and artificial olfactory systems [Mahdi Ghasemi *et al.* (2014)]

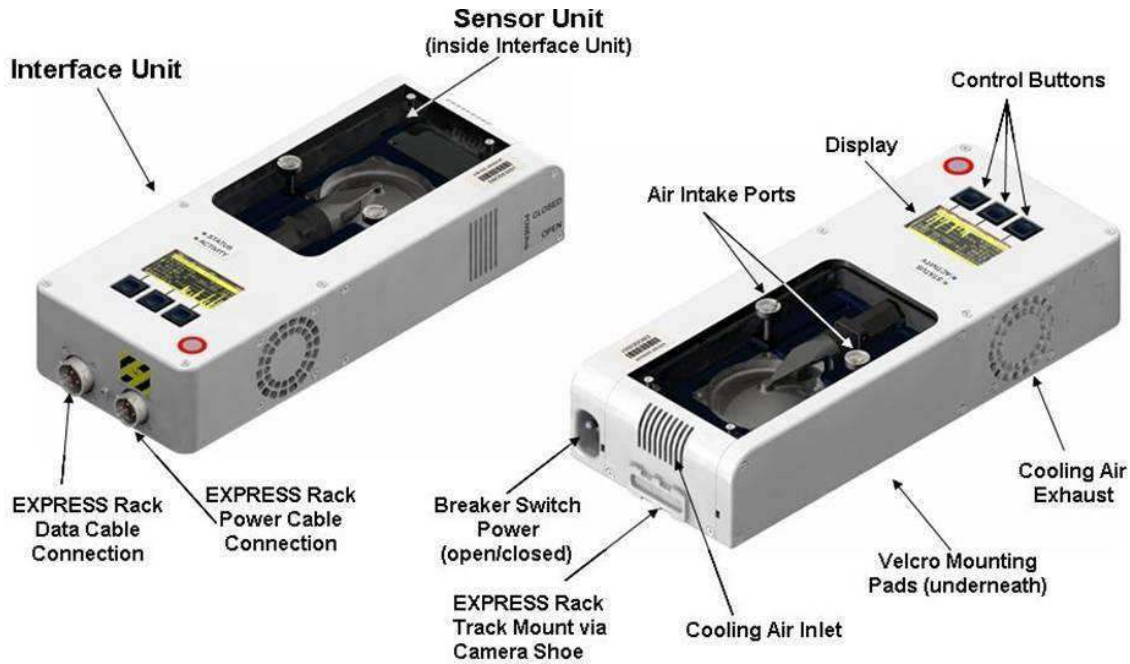

Fig. 1.3 Photo image of compact hand-held device developed by NASA for space application [Internet Resource (IR5)]

1.4 Advancement in Artificial Olfaction

For the past few decades, the artificial olfaction which basically is an electronic nose system is gaining much attention to mimic the way information is processed in mammalian olfaction system. In the view of consequences of toxic, hazardous and explosive gases, it is required that the artificial olfaction be rapid and reliable enough to detect and quantify these odorants before they cross the safe limit and occurrence of any fatal accident could be avoided. The advancement is being done in various sub-modules of electronic nose which includes [Gutierrez and Horrillo (2014)]:

1. Array of gas sensor
2. Signal-processing techniques
3. Pattern recognition methods

However, there is much scope for the researchers to develop new materials, sensor technologies, data processing, interpretation and validation of the results.

The conventional gas detecting instruments like Gas Chromatographs (GC), Mass spectrometers (MS) etc. are selective analyzers [Camman (2001); Wilson (2009)] which are accurate but their in situ operations are very cumbersome. They are relatively very bulky and expensive too. Also, other classical analytical instruments such as electron capture detectors (ECD), flame ionization detectors (FID), flame photometry detectors (FPD), infrared spectrometers (IRS), ion mobility spectrometers (IMS), nuclear resonance spectrometers (NMRS), photo-ionization detectors (PID) and quadruple fingerprint mass spectrometers (QFMS) are not considered e-noses in the strictest case because they do not provide a collective data from a multi-sensor array and are designed to identify individual component of a gas mixture [Wilson (2009); Rajput (2011(a))].

Table 1.2 shows various commercial and available electronic nose instruments and Table 1.3 provides some industry based applications of gas sensors, gas involved and the gas sensors used.

1.4.1 Solid State Sensor Technology

Solid state sensors are very attractive for artificial olfaction applications due to their simplicity, low cost, compactness, simple fabrication, easy handling and low maintenance. These sensors thus overcome various disadvantages of traditional methods mentioned in previous section.

Table 1.2 Commercial and available electronic nose instruments [Chiu *et al.* (2013)]

Manufacturer	**Model**	**Sensor Array Type/Technology**	**Size**
Agilent, http://www.chem.agilent.com/	4440A	Fingerprint of MS	Desktop
AIRSENSE Analytics, http://www.airsense.com/	i-PEN/MOD PEN3	MOX MOX	Laptop Laptop
Alpha MOS, http://www.alpha-mos.com/	FOX 2000, 3000, 4000 Gemini Heracles AIRSENSE	MOX MOX Ultra Fast GC with two column Soft IMS	Desktop Desktop Desktop Desktop
AltraSens, http://www.altrasens.de/	OdourVector	QCM	Desktop
AppliedSensor, http://www.appliedsensor.com/	Air Quality Module	MOX	Laptop
Aromascan PLC, http://www.aromascan.com/	A32S	CP	Desktop
Dr. Foedisch AG, http://www.foedisch.de/	OMD 98	MOX	Laptop
Draeger, http://www.draeger-safety.com/	Multi-IMS MSI 150 Pro2i	IMS MOX	Palmtop Laptop
Electronic Sensor Technology, http://www.estcal.com/	ZNose 4200, 4300, 4600 ZNose 7100	GC and SAW GC and SAW	Laptop Laptop
Environics, http://www.environics.fi/	M90-D1-C ChemPro100	IMS IMS	Laptop Palmtop
Forschungszentrum Karlsruhe, http://www.fzk.de/	SAGAS	SAW	Laptop
GSG Mess- und Analysengeräte, http://www.gsg-analytical.com/	MOSES II	Modular Gas Sensor Array: QCM, MOX	Laptop
Owlstone Nanotech, Inc., http://www.owlstonenanotech.com/	Lonestar	IMS	Laptop
Rae Systems, http://www.raesystems.com/	ChemRAE	IMS	Palmtop
RST-Rostock, http://www.rst-rostock.de/	FF2, FF2D GFD1	MOX MOX	Desktop Desktop
Sacmi, http://www.sacmi.eu/	EOS Ambiente	MOX	Desktop
SMart Nose, http://smartnose.com/	SMart Nose 2000	Fingerprint of MS	Desktop
Smith Group, http://www.smithsdetection.com/	Cyranose 320 GID-2A, 3 SABRE 4000 ADP 2000	CP IMS IMS IMS	Palmtop Desktop Desktop Palmtop
Sysca AG, http://www.sysca-ag.de/	Artinose	MOX	N/A

CP-Conductive polymer; MOX-Metal-oxide semiconductor; IR-Infra red; SAW-Surface acoustic wave; QCM-Quartz crystal microbalance; QMS-Quadrupole mass spectrometry; GC-Gas chromatography; IMS-Ion mobility spectrometry

Table 1.3 Some industry based applications of gas sensors, gas involved and the gas sensors used [Wilson (2009); Bemark (2006)]

Industry sector /Application area	**Smells/gases involved**	**Specific use types and examples**	**Examples of gas sensors**
Environmental air & water quality monitoring indoor air quality control pollution abatement regulations	CO, NO_x, SO_2, CH_4 C_6H_6, C_4H_{10}, C_3H_8	pollution detection, effluents, toxic spills malodor emissions, toxic/hazardous gases control of point-source pollution	gradient sensor microarray TGS, MOS, MOSFET tin oxide doped Pd/Al/Pt, and different film thickness
Food & beverage consumer fraud prevention quality control assessments ripeness, food contamination taste, smell characteristics	coffee, vinegar, perfume, aroma, dairy products wine, etc...	ingredient confirmation, content standards brand recognition, product consistency marketable condition, spoilage, shelf life off-flavors, product variety assessments	TGS-109-203-311-800-812 , TGS-813-815-823-832-842 , TGS-2600-2610-2611-2620 ,ZnO=Al_2O_3, SnO_2=P d, ZnO , SnO_2-/ZnO-/CdS-Pt-/La_2O_3 , WO_3=Au, MOS, MOSFET,
Manufacturing processing controls product uniformity safety, security, work conditions	H_2;CO;NO_2;NH_3 CH_4;$CHCl_3$;H_2S; CH_3C_3N;OC_2H_5OH;C_4H_{10}; C_2H_6O;C_3H_8;C_6H_6 CF_3CH_2F;CH_4CH_3SH;	product characteristics & consistency aroma and flavor characteristics fire alarms, toxic gas leak detection	TGS-109-203-311-800-812 , TGS-813-815-823-832-842 , TGS-2600-2610-2611-2620 ,ZnO=Al_2O_3, SnO_2=P d, ZnO , SnO_2-/ZnO-/CdS-Pt-/La_2O_3 , WO_3=Au, MOS, MOSFET,
Medical & clinical pathogen identification pathogen or disease detection physiological conditions	NA	patient treatment selection, prognoses disease diagnoses, metabolic disorders nutritional status, organ failures	Quartz microbalance (QMB), metal oxide semiconductor electrochemical sensors
Military & Space personnel & population security	CO;NO_x; SO_2;CH_4	biological & chemical weapons explosive materials detection	TGS-2600, 2610, 2611, 2181, polymers and Quartz
Scientific research botany, ecological studies engineering, material properties microbiology, pathology	NA	chemotaxonomy, ecosystem functions machine design, chemical processes microbe and metabolite identifications	TGS-2600, 2610, 2611, 2181, polymers and Quartz
Cosmetics personal application products fragrance additives	NA	perfume & cologne development product enhancement, consumer appeal	TGS-813-880-822-825-812 SnO_2-/Sb_2O_3-/ZnO-/NiO Polymer,MOSFET,Quartz Thin-film WO_3/Pd-/-/Bi-/Sb

They are also highly reliable and compatible with the microelectronic circuitry [Fogila *et al.* (1999); Srivastava (2011)]. Also, as discussed section 1.2, many receptor sites are needed for mammalian olfaction to detect odorant. So, to mimic such system there is a requirement of large array with multiple sensor elements along with the associated signal processing and pattern recognition techniques. For such sensor array, the solid state sensors are ubiquitous choice due to previously mentioned advantages. To achieve the portability and easy in situ operations, these sensors are fabricated and miniaturized to micron ranges.

1.4.2 Micro Gas Sensors

The micro gas sensor is a miniature device which transduces a chemical parameter into an electrical signal [Nylander (1985); Srivastava (2011)]. Depending on the various microelectronic technologies used for the development of gas sensors, there are basically three types of solid state sensors.

(i) MOS Gas Sensor

Metal-oxide semiconductor (MOS) based gas sensors have been studied for many years. The first MOS based gas sensor was palladium gate Metal Oxide Semiconductor Field Effect Transistor (MOSFET) for sensing hydrogen gas [Lunderstrom *et al.* (1975)]. Since then the MOS devices with various transition-metal gate electrodes have been studied primarily for hydrogen containing gases and some for CO gas. Since these sensors are based on standard microelectronic fabrication technique, they are suitable for mass production which ultimately results in relatively very low cost per unit.

In MOS gas sensors, the surface of the gate electrode catalytically decomposes the gas atoms, say the hydrogen gas, into the hydrogen atoms. These atoms diffuse through electrode into the electrode/insulator interface. Most common metals for sensing hydrogen and hydrogen containing gases are therefore palladium, platinum and certain noble metals. Dwivedi *et al.* (2000) have studied the sensing properties of Pd-gate MOS hydrogen sensor fabricated utilizing plasma technology (dry plasma of Si wafer and growth of oxide layer on Si by using oxygen plasma).

For MOS sensor to be sensitive towards other gases like CO, alcohols, ammonia and wide range of hydrocarbons, the porosity of gate is imperative. This means that the morphology of metal gate should consist of appreciable amount of cracks. Recently, Influence of gridded gate structure on gas sensing behavior for

hydrogen and hydrogen sulphide sensing have been reported [Kumar *et al.* (2014)], where gridded gate structure showed improved sensitivity and response behavior. Further research is going on in the area of MOS gas sensors to improve their sensitivity, selectivity and stability. Several commercial available e-noses based on this technology are now available as PEN-3 for Airsense Analytics and Fox 4000 from Alpha MOS [Wilson (2009)]

(ii) Thin Film Gas Sensor

Thin film (thickness vary from about 50 angstroms to several thousands of angstroms) is deposited on an insulating substrate generally by vacuum deposition, and finer structures are made either by an additive method through masks or by a subtractive method by means of photolithography [Gupta (2003)]. In another definition, a thin film is defined as low-dimensional material created by condensing, one by one, atomic/molecular/ionic species of matter whose thickness is less than several microns [Wasa *et al.* (2004)].

Any thin film process involves three main steps:

a) Production of appropriate atomic, molecular or ionic species
b) Transport of these species to the substrate through a medium, and
c) Condensation on the substrate, either directly or via chemical and/or electrochemical reaction.

A post deposition annealing at the temperature higher than the deposition temperature may vary the grain size [Chaudhary (2013)]. The thin resistive films of SnO_2 or ZnO on glass, alumina or silicon substrate are generally used for gas sensors. The first thin film semiconducting gas sensor was reported by Seiyama *et al.* (1962). Different techniques such as spray pyrolysis [Paraguay *et al.* (2005); Rhaleb *et al.* (2002)], sputtering [Kim *et al.* (2006); Bhattacharya *et al.* (1985)], chemical vapor deposition (CVD) [Huang *et al.* (2006)] and electron beam evaporation [Sugiyama *et al.* (1994)] have been used to fabricate thin films. Also, a very low percentage of noble metals such as Pd and Pt are added in such thin film sensors for enhancing the reaction between gas and the semiconductor surface and hence improving the sensitivity and selectivity to specific gases [Srivastava (1994); Srivastava (2011)].

(iii) Thick Film Gas Sensor

The features and potential of thick-film technology has made it one of the leading solid-state sensor technologies. The history of thick-film technology dates back to the

1950s. The result of fabricating components simultaneously with different technologies could open up a whole new field in electronics. In the mid 1960s, thick-film processing was capable of producing fine-line conductor geometries, thereby allowing a high component packing density on a single substrate. The essence of today's modern thick-film process is almost identical to that used thirty years ago [Prudenziati (1994)]. The versatility of semi-conducting materials and the miniaturization of VLSI pattering techniques promise new sensors with better capabilities and performance-to-cost ratio than those of conventionally machined devices. Integrated circuit technology allows thousands of electronic circuits to be batch-fabricated simultaneously in a single processing sequence. By optically repeating the patterns on the substrate, many units are fabricated with just one application of the process. For most metal oxides, Al_2O_3 is the most suitable substrate material, but in recent years other substrates such Si and micro-hotplates have also been investigated. These devices have several advantages. They are small and perform well because of the precise dimensional control during fabrication and are cheap. Their thermal inertia and power consumption is very low [Ivanov (2004)].

Thick films are indeed usually *thicker* than thin films, the terms no longer relate primarily to thickness but also to the processes used to deposit them. The term thick-film is derived from the fact that the fired film is fairly thick (5 to 50 μm) compared to thin- film (0.02 to 1μm) [Burdet *et al.* (2006)]. In most recent, generic term is associated with their respective methods of film deposition which states that the thick film uses screen-printing technology for laying out circuits, whereas thin film generally uses vacuum deposition or sputtering technology [Gupta (2003)].

Thick film technology can be preferred as it offers several advantages such as high sensitivity, fast response and flexibility in the choice of materials, high reliability, design ruggedness, hybridization of signal processing circuit along with sensory elements and cost effectiveness. Also, the use of thick film hybrid circuit modules in fabrication of a sensor reduces susceptibility to the external noise sources. Moreover, the complete instrumentation is possible with thick film hybrid circuits with high level of integration and miniaturization which results in compact, rugged and portable e-nose devices. Thick film processing also lends to mass production for large production runs and providing more cost effective solution [Srivastava (2011)]. There are some limitations too for thick film sensors such as lack of selectivity which

result in a large amount of cross sensitivities. Sensitivity of the base tin oxide material is generally low. So, depending on the requirements, dopants are always added to the base material to enhance the sensitivity and selectivity of the sensors towards certain species of gases.

Nayoshi Taguchi was first to report the work in the areas of gas sensors by utilizing the concept of change in conductance due to adsorption of gas on the surface of semiconductor which was earlier demonstrated by W. H. Braittain [Braittain *et al.* (1953)].Taguchi sensor used zinc oxide as base material but later the tin oxide based gas sensors became popular due to its sensitivity to large number of reducing as well as oxidizing gases [Watson (1984)].

The Taguchi gas sensor abbreviated as TGS [Watson and Yates (1985)] was manufactured by Figaro Engineering Company, Osaka. The basic sensor configuration is shown in Fig. 1.4. The sensor consists of ceramic (alumina) tube provided with gold electrode pattern on which a gas sensing layer is deposited. A coiled heating element (chrome alloy) is also threaded inside the tube to provide an adequate operating temperature (generally between 200 ºC to 400 ºC) suitable for the sensor to respond.

As mentioned earlier, due to non-selective behavior of gas basic sensitive layer (tin oxide), different dopants depending on the need of the catalysts are always added to the tin-oxide base material to improve the selectivity and the sensitivity of the sensors. The substrate is usually mounted on a TO-socket provide with some other necessary arrangements. The power consumption of the Figaro type sensors have ranges from 0.6 to 1.2 W and such type of sensors are still on market. However, most of the commercially available sensors are nowadays manufactured by screen printing technology on small and thin ceramic substrates.

The basic thick film sensor is generally comprised of a gas sensitive layer which is deposited on a substrate (generally alumina) provided with electrodes for electrical characterization. Normally, the device is heated at high temperature (above 300 ºC) by the heater provided at the back surface of the sensor element(s). The sensor is either as a single element for sensing individual gas or in array form constituting the basic building block of e-nose system for discriminating mixture of gases.

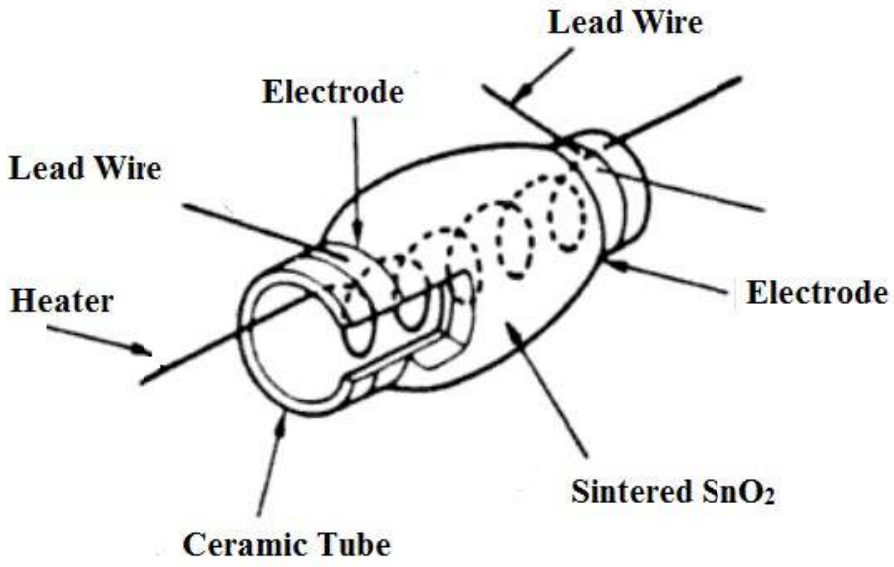

Fig. 1.4 Basic configuration of Taguchi (Figaro products) gas sensor

1.4.3 Advancements in Sensor's Signal Preprocessing

It is generally helpful to preprocess the input data generated from the sensor array before it is fed to the pattern analysis module to improve the overall performance of the classifier/quantifier. Data preprocessing can play an important role in classification and in better cluster separation. Raw data obtained from the sensors initially may be susceptible to noise, missing values or inconsistency. Preprocessing the raw data with suitable preprocessing technique may lead to better classification results, reducing in system complexity and response time of the gases/odors identification system [Osuna *et al.* 2002].

So, the data preprocessing step is considered as the backbone for most of the successful PARC analysis. Applying an appropriate data preprocessing technique may lead to drastic improvement in the accuracy of the classifier as well as quantifier. The main purpose of a preprocessing stage is to carefully select a number of parameters that are descriptive of the sensor array response, as this choice can significantly affect the performance of the subsequent modules in the pattern analysis system [Gardener *et al.* (1999), Rajput (2011(a))].

Although, the preprocessing is somewhat tied to the underlying sensor technology, three general steps can be identified [Osuna and Nagle (1999); Osuna *et al.* (2002)]:

a) Baseline manipulation,

b) Compression, and

c) Normalization.

Baseline manipulation is to transform the sensor response relative to its baseline (e.g., response to a reference analyte) to enhance the contrast and drift compensation. The drift compensation requires additional processing. There are three commonly used baseline manipulation methods viz. difference, relative, and fractional. The difference method directly subtracts the baseline and can be used to eliminate additive drift from the sensor response. Relative manipulation divides by the baseline, removing multiplicative drift, and generating a dimensionless response. Finally, the fractional manipulation subtracted and divided by the baseline, generates dimensionless and normalized responses.

Different compression algorithms can be used to generate descriptive parameters from the sensors' transient response. The standard procedure is to select the steady-state responses of the sensors. Besides, a number of compression algorithms have been proposed to extract more helpful information from the transient response which results in improved selectivity, reduced acquisition time, and increased sensor lifetime.

Finally, in the normalization procedures, the feature vector is prepared for the subsequent pattern analysis modules. Table 1.4 provides brief summary of signal preprocessing techniques employed to the sensors' signal [Llobet *et al.* (1997); Osuna *et al.* (1999); Osuna (2002)].

(i) Dimensionality Reduction

Even after the preprocessing stage, sometimes the feature vectors are not suitable for processing by the subsequent pattern analysis module. This may be due to high-dimensionality and redundancy in the preprocessed dataset. If the dataset is very high dimensional, it is presumed that *curse of dimensionality* has occurred in statistical pattern recognition. The problem states that the number of training examples must grow exponentially with the number of features in order to learn an accurate model. But in real world a limited number of examples are generally available. Also, there are an optimal number of feature dimensions beyond which the performance of the

pattern analysis model starts degrading. The problem of redundancy is particularly significant in e-nose devices due to the cross-sensitivity of chemical gas sensors. The problem of the redundancy is also called the collinearity in chemometrics and statistics. When two or more feature dimensions are collinear, the covariance matrix of the whole dataset becomes singular and, therefore, noninvertible, which leads to numerical problems in various statistical techniques. Due to these two reasons, a dimensionality reduction stage is required in most cases. The dimensionality reduction can either be feature extraction and/or feature selection process.

Table 1.4 Brief summary of signal preprocessing techniques employed to the sensors' signals [Osuna *et al.* (1999); Osuna *et al.* (2002); Rajput (2011(a))]

	Technique	**Sensor Type**[#]
Baseline manipulation	Difference	QMB, MISFET
	Relative	MOS
	Fractional	MOS, CP
Transient compression	Sub-sampling	MOS
	Parameter extraction	MISFET
	Model fitting	MOS, CP, QMB
Normalization	Sensor, vector, autoscale	MOS, CP
[#]QMB: Quartz Crystal Microbalance, MISFET: Metal Insulator-Semiconductor Feield-Effect Transistor, MOS: Metal-Oxide Semiconductor, CP: Conducting Polymer		

In the feature extraction process a low-dimensional mapping is established in such a way that most of the information in the original feature vector is retained. Most feature extraction techniques which are used in e-nose applications are based on linear techniques. Two of the important techniques are principal components analysis (PCA) and Fisher's linear discriminant analysis (LDA). PCA is a signal representation technique that generates projections along the directions of maximum variance and is unsupervised and non-parametric in nature. LDA is a supervised signal classification technique that directly maximizes class separability to generate projections in such a way that the examples of each class form compact clusters and the different clusters are well separated from each other. Feature subset selection (FSS) is a dimensionality

reduction technique that can be used to configure small sensor arrays for specific odor-measurement applications. In the FSS, the goal is to find an *optimal* subset of *M* sensors (or features) that maximizes information content or predictive accuracy. The simplest FSS approach evaluates each feature individually and selects those *M* features with the highest scores [Sammon (1969); Byun *et al.* (1997); Duda *et al.* (2000); Osuna (2002)].

1.5 Advancements in Pattern Recognition

Pattern recognition (PARC) is the science of making inferences from perceptual data, using tools from statistics, probability, computational geometry, machine learning, signal processing, and algorithm design [Internet Resource (IR6)]. *Pattern Recognition is formally defined as the process whereby a received pattern/signal is assigned to one of a prescribed number of classes (categories*) [Haykin (2008)]. Thus, the PARC methods basically perform classification task using machine (computer). The classification problems have been extensively studied in the field of vision and speech. The responses generated by an array of odor sensors may be processed using a variety of techniques. However, in the field of gas and odor sensing also the classification techniques have shown promising applications [Dalby and Shrumer (1988); Shrumer and Gardner (1992); Wilson (2009); Varnamkhasti (2014)].

In the context of e-nose system, the term pattern recognition or pattern analysis applies to both qualitative and quantitative analysis of odors. Better PARC technique results in improved e-nose performance. But the choice of an appropriate technique is highly dependent on the problem in hand. There are several issues which require careful consideration for successful design of pattern analysis system. The signal processing technique, feature extraction, feature selection, clustering and cross-validation play a critical role for the successful implementation of pattern analysis methods for e-nose systems [Dickinson *et al.* (1998); Guang *et al.* (2009); Kumar (2011(a))].

The nature of a PARC engine is usually classified in terms of being parametric or nonparametric, and supervised or unsupervised [Pearce (2003); Gupta (2003)]

a) Parametric techniques: Parametric techniques are also known as statistical approaches. These methods are based on the assumption that the spread of the sensor data can be described by a probability density function (PDF). In most cases, the

assumption made is that the data follow a normal distribution with a constant mean and variance. These techniques try to find an underlying mathematically formulated relationship between system inputs, odor vectors and its outputs, classes or descriptors.

b) Non-parametric. The non-parametric methods apply more generally than assuming any specific PDF for the sensor data. This approach to multivariate data analysis has led the fields of artificial neural networks (ANNs) and expert systems.

c) Supervised. This is also known as *learning with a teacher.* A supervised learning PARC system is first trained with a set of known odors training samples which are systematically introduced to the e-nose. When the PARC system is learned in sufficient manner then the unseen examples are fed to the learned system which predicts the class membership against the knowledge base to test the efficacy of the system. Since the learning process requires a teacher (supervisor), this kind of training is named supervised learning. Unknown odor vectors are analyzed using relationships found a priori from a set of known odor vectors used in an initial calibration, learning, or training stage. The idea of testing a method using unseen response vectors is well established and is often referred to as cross-validation.

d) Unsupervised: This is also known as learning without a teacher. In this type of learning, PARC methods learn to separate the different classes from the response vectors routinely, discriminating between unknown odor vectors without being presented with the corresponding descriptors. These methods are closer to the way that the human olfactory system works using intuitive associations with no, or little, prior knowledge. Fig. 1.5 shows the classification scheme of the multivariate pattern analysis techniques applied to e-nose data.

Recently, a new paradigm has also been introduced which is known as *semi-supervised learning*. In this scheme, training utilizes both labeled as well as unlabelled data. Generally, a small amount of labeled data with a large amount of unlabeled data is used. Thus, this method falls between unsupervised and supervised learning. Researchers have found semi-supervised learning more promising for many applications.

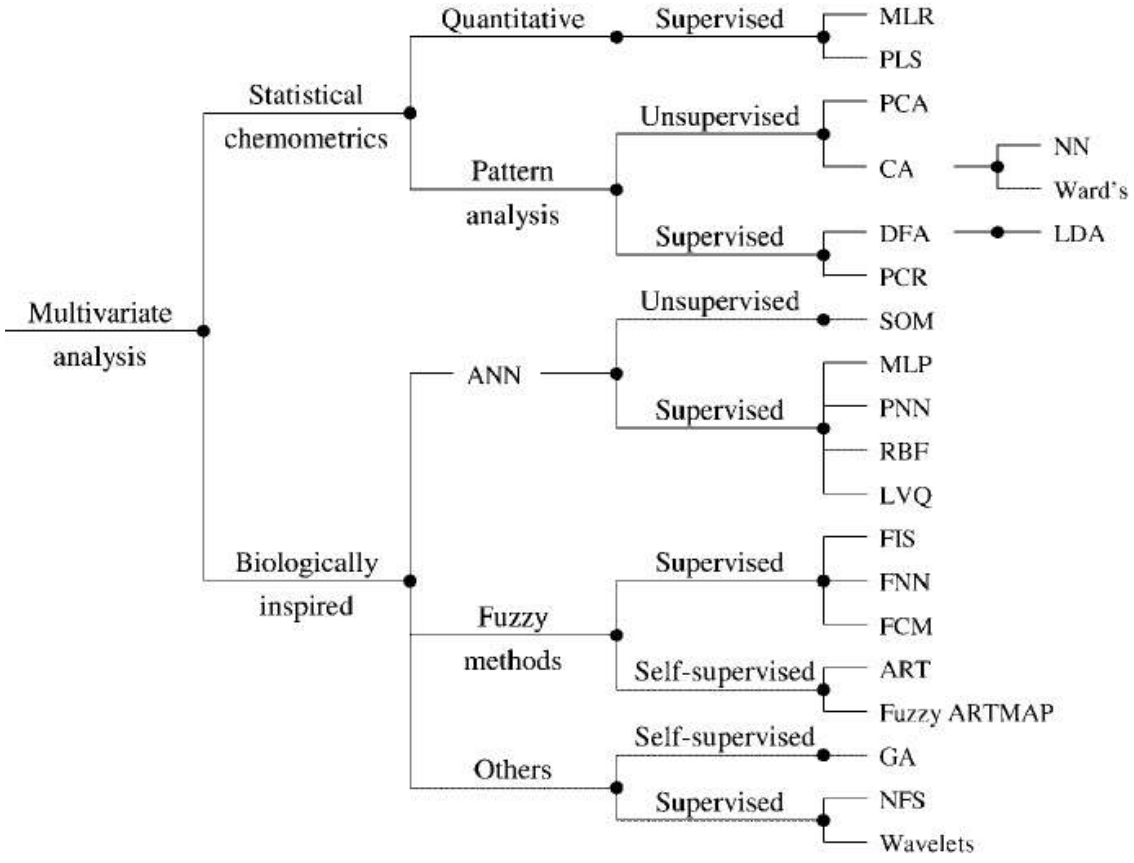

Fig.1.5 Classification scheme of the multivariate pattern analysis techniques applied to e-nose data [Pearce (2003)]

1.5.1 Traditional Statistical Discrimination Methods

A large number of e-nose prototype devices have been reported in literature to discriminate the complex gases/odors/VOCs and their mixture which employ different technologies. The use of sensor array and pattern recognition technique to discriminate odorant was first reported by Persuad *et al.* in 1982. Different researchers in the field of odorant discrimination throughout the world have reported various aroma detection technologies such as quartz resonators [Carey *et al.* (1986); Nakamoto and Moriizumi (1988); Ema *et al.*(1989), Nakamoto *et al.* (1990)], semiconducting polymers [Meyerhoff (1980); Meyerhoff *et al.* (1983); Yim *et al.* (1993)], electrochemical gas sensors [Miller (1987); W. Weppner (1987); Bartlet (1989); Gardner *et al.* (1999)], metal-oxide [Shrumer *et al.* (1989); Egashira *et al.*(1993)], conductive electro-active polymers [Hatfield *et al.* (2004)], field effect transistor [Lundstrom *et al.* (1986); Miyahara *et al.* (1988); Sundern *et al.* (1990)], optical sensors [Tiefenthaler and Lukosz (1984); Zhu and Petty (1990)],

electrochemical cells [Stetter *et al.* (1986)] and acoustic wave based technologies [Ballantine *et al.* (1996); Staple *et al.* (2000)] etc. have been employed to discriminate various gases.

Statistical pattern analysis techniques like principal component analysis (PCA), cluster analysis (CA), principal component regression (PCR), discriminant factor analysis (DFA), analysis of variance (ANOVA) between groups, partial least square (PLS) regression are few popular non-parametric techniques which have potential to be utilized for e-nose application [Jain *et al.* (2000); Rajput (2011(a))].

1.5.2 Biological Inspired Discrimination Methods

It has been reported in literature that biologically inspired computational methods result in improved odorant discrimination with the gas sensor array responses. The multi-sensor array responses are analyzed by biological inspired mathematical rules such as artificial neural network (ANN), probabilistic neural network (PNN), adaptive resonance theory (ART), genetic algorithm, fuzzy rule based algorithms, self organizing map (SOM), learning vector quantization (LVQ) etc. A new paradigm called artificial immune recognition system (AIRS) have been utilized for gases/odor recognition which provided promising results [Scott *et al.* (2007); Kumar *et al.* (2009(a)); Kumar *et al.* (2010); Rajput *et al.* (2011(a)); Sharma *et. al* (2013)]. These biological inspired methods have opened a window for the new techniques which could be used for better results in the odorant sensing area.

1.6 Literature Review

To develop an electronic model of olfactory system, two fundamental characteristics of mammalian olfactory system *i.e.* the odorant detectors, the primary neurons which respond to a wide range of chemical types and outputs form the detectors to be processed in a convergent feature detection system and perform parallel feature detection [Persuad and Dodd (1982)], are realize in artificial manner. It is evident from the previous discussion that the pattern analysis techniques play a very important role in the processing of e-nose data to identify and quantify the gases/odors/VOCs. Depending on the application and the types of data being used for the analysis different types of preprocessing, feature extraction and/or pattern analysis techniques are employed for processing the sensor array data [Shrumer (1992); Osuna (2002)].

A lot of work has been reported in the past which provides necessary information in the field of gas sensing area. Sundgren *et al.* (1991) have reported analysis of individual components in a gas mixture using artificial neural network and gas sensor array with six metal-oxide-semiconductor field-effect transistors (MOSFETs) operating at elevated temperature. The sensor array was exposed to multicomponent gas mixture and the signals from the sensor array were analyzed with conventional methods like multivariate analysis, partial least square analysis, partial least squares (PLS) and artificial neural network (ANN).

Moore *et al.* (1993) have reported a modified multilayer perceptron based model for gas mixture analysis using a sensor array with fully and partially connected multilayer perceptron neural network and found better performance with the latter in terms of identification and concentration estimation.

Nayak *et al.* (1994) have used conventional iteration technique in association with multiple regression method for identification of mixture of gases using integrated thick film gas sensor array. The method was successfully tested on the mixture of carbon tetrachloride and ethyl- methyl ketone.

Wilson and Dewerth (1995) have reported odor discrimination using both, the steady state and transient characteristics of tin oxide sensors by converting their outputs into binary representation by thresholding technique. By evaluating both steady-state and transient characteristics of tin-oxide chemical sensors at various operating temperature, the authors were able to discriminate the chemicals containing one or two components. They reported their technique to be suitable for VLSI implementation.

Nakata *et al.* (1996) have reported sensing approach based on multidimensional information contained in a dynamic non-linear response using fast Fourier transformation (FFT) to analyze the sensor data and found it possible to distinguish different gases in gaseous mixture with single detector using the non-linear dynamic responses.

Heiling *et al.* (1997) have reported gas identification by modulating the temperatures of tin-oxide based thick film sensors. They successfully classified and quantified the binary gas mixture (CO/NO_2) in the ambient atmosphere by using only one sensor in modulated temperature mode. The method was reported to be compatible with hybrid technology.

Llobet *et al.*(1997) have also used both, transient and steady-state of a thick film tin-oxide gas sensor array for qualitative and quantitative analysis of volatile organic compounds. The steady state and transient conductance of sensor array were processed with artificial neural networks (ANN). In the first stage, a feedforward backpropagation trained ANN discriminates among studied compounds. Afterward, three separate ANN (one for each vapour) are used to quantify the previously identified compounds.

Fagila *et al.* (1997) have reported identification and quantification of methane and ethyl alcohol in an environment at variable humidity by a hybrid array of five tin oxide thin films. They used humidity values with a two layered perceptron network to identify individual component in a gas mixture.

Marco *et al.* (1997) have presented gas identification with tin oxide sensor array and self-organizing maps with adaptive correction of sensor drifts. They showed that the combination of a gas sensor array together with self-organizing maps (SOMs) permit success in the gas classification problems. The system was found to be able to determine the gas present in an atmosphere with error rates lower than 3%. Correction of the sensor's drift with an adaptive SOM has also been investigated.

Shukla *et al.* (1998) have presented as identification approach for individual gases/odors based on adaptive resonance theory (ART) artificial neural network (ANN). They utilized published steady state responses of four sensors with four gases and processed them with ANN and ART NN method. They reported the proposed method to be suitable for hardware implementation as well.

Singh *et al.* (1999) have proposed minimum difference method for discrimination of individual gases/odors using integrated sensor array. In their approach the decision of unknown gas/odor was made by finding the value of the sum of square of the difference between the relative minimum difference value between the training and sniffing mode parameters. The method was successfully applied to the linear characteristics of the sensor array.

Lee *et al.* (2000) have reported explosive gas recognition system using thick film sensor array and neural network. They have used sensor array with nine discrete sensors integrated on a substrate, developed for recognizing the species and quantity of explosive gases such as methane, propane and butane. The principal component analysis (PCA) technique and a gas pattern recognizer was implemented using a

multi-layer neural network with an error back propagation learning algorithm. The simulation and experimental results demonstrated that the proposed gas recognition system was effective in identifying explosive gases.

Capone *et al.* (2001) have reported qualitative and quantitative analysis of CO and CH_4 gas mixtures by using a micromachined sensor array using PCA and multiple linear regression (MLR) and principal component regression (PCR). They developed an array of highly sensitive and mechanically stable gas sensors based on different sol-gel fabricated Pd-doped SnO_2 nanocrystalline thick films for the analysis of ternary mixtures.

Penza *et al.* (2002) have reported successful identification and quantification of individual volatile organic compounds in a binary mixture by SAW multisensor array and pattern recognition analysis. They developed a surface acoustic wave (SAW) multisensory array with five acoustic sensing elements configured as two-port resonator and a recognition system was realized by using the relative frequency change as the output signal of the SAW multisensor array with an artificial neural network (ANN), for the identification and quantification of tested VOCs. They concluded that the combination of PCA as a preprocessing technique and ANNs as a pattern classifier constitutes a powerful tool for classification and prediction and an increasingly accessible technology for the simultaneous, precise, fast and quantitative analysis of the concentrations of single components in a binary mixture.

Jervis *et al.* (2003) have reported concentration estimation of gas in mixtures of known gases using an array of different tin-oxide sensors by using two multilayer-perceptron (MLP) artificial-neural-network (ANN) committee methods and a mathematical-macromodeling method. For determining the concentrations of gases in a known gas mixture, the outputs of an array of tin-oxide gas sensors placed in the mixtures were used. Bayesian-trained committees were used to obtain accurate predictions of the gas concentrations in the gas mixtures (2-11%). The macromodeling method was less accurate (19.7- 33%), but much faster and easier.
Srivastava (2003) has reported detection of volatile organic compounds (VOCs) using SnO_2 gas-sensor array and artificial neural network. The effect of transformation on the raw data with the transformed cluster analysis (TCA) on the classification ability of neural network was also studied by varying the size of array and corrupting the

data with synthetic noise. The simulation results demonstrated that the developed system was capable to identify target vapors successfully even in the noisy conditions. Distante *et al.* (2003) have reported olfactory signals recognition using support vector machines (SVM). They showed that SVM performance was better as compared to radial basis network and the error backpropagation training method for identifying the gases/odors. The leave-one-out procedure was used for all classifiers to find the near-optimal SVM parameter and to reduce the generalization error avoiding outliers.

Taurino *et al.* (2003) have reported use of an array of sol-gel based gas sensors to perform qualitative and quantitative analysis of VOCs viz. Acetone, Hexanal and 2-pentanone mixtures by means of a microsensors array and different evaluation methods like PCA, radial basis function and multilayer perceptron. The modified version of MLP showed better capabilities in solving regression problems with respect to RBF network.

Pardo and Sberveglieri (2005) have also reported classification of electronic nose data with support vector machines. They analyzed the test error of SVM as a function of the number of principal components (on which the data are projected), the kernel parameter value for both the polynomial and the RBF kernel, and the regularization parameter to explore the insurgence of under fitting and over fitting effects limitations of non-parametric learning techniques. It was found that the regularization parameter often set a priori to C=1 to strongly influence the SVM performance.

Ozmen *et al.* (2006) have reported identification of composition of gas mixtures by a phthalocyanine-coated QCM sensor array with eight sensor elements and an artificial neural network. The digital data collected from the sensor responses were preprocessed by a sliding window algorithm, and then used to train a three layer ANN to determine the gas compositions. The system was tested with different gas mixtures viz. Ethanol–Acetone, Ethanol-Trichloroethylene and Acetone-Trichloroethylene. The success rate of the system in identifying the constituent component amounts was reported 84.5% and 94.3%. Similarly, overall average prediction error was 10.6%.

Sobanski *et al.* (2006) have used sensor dynamic response analysis to improve the accuracy of odour-measuring systems. A system consisting of a matrix of three semiconductor gas sensors was used for classification of different orange juices. The

dynamic responses were processed by discrete wavelet transform (DWT) together with the k-nearest neighbour (kNN) classification algorithm or by the probabilistic neural network (PNN). The obtained results showed that both types of signal processing (DWT with kNN and PNN) applied provided very good class separation for time response analysis, while in the case of the static response analysis the correct classification coefficients are much lower. For both processing methods, the results obtained with the dynamic response of a single sensor were better than those obtained with the three-sensor array measured in static conditions.

Gulbag and Temurtas (2006) have reported a study on quantitative classification of binary gas mixture using neural networks and adaptive neuro-fuzzy inference systems (ANFISs). The quartz crystal microbalance (QCM) type sensors were used as gas sensors. The components in the binary mixture were quantified by applying the steady state sensor responses from the QCM sensor array as inputs to the FFNNs and ANFISs. A hybrid training method consisting of combination of least-squares and back propagation algorithms was used as the training method of the ANFISs. Quantitative analysis of Trichloroethylene and Acetone was evaluated in terms of training algorithms and methods.

Gulbag *et al.* (2007) have reported study on radial basis function neural network size reduction for quantitative identification of individual gas concentrations in their gas mixtures. They used the multilayer neural networks (MLNNs) with sigmoid hidden layers and radial basis function neural networks (RBFNNs) to compare the quantitative identification of individual gas concentrations in their gas mixtures (Trichloroethylene and n-hexane). A method to reduce the RBFNN size for quantitative analysis of gas mixtures was also proposed.

Daqi and Wei (2007) performed simultaneous estimation of odor classes and concentrations using an electronic nose with function approximation model ensembles. They reported simultaneous estimation problems as multi-input/multi-output (MIMO) function approximation problems. The predicted results for four kinds of fragrant materials, ethanol, ethyl acetate, ethyl caproate, and ethyl lactate, 21 concentrations in total, showed that the proposed approximation model ensembles and combination strategies with the electronic nose were effective for simultaneously estimating many kinds of odor classes and concentrations.

Gulbag and Temurtas (2007) have reported a study for transient and steady state sensor data for identification of individual gas concentrations in their gas mixtures. A comparative study was performed for the quantitative identification of individual gas concentrations (Trichloroethylene and Acetone) in their gas mixtures using transient and steady state sensor responses. Three neural network (NN) structures were used. The quartz crystal microbalance (QCM) type sensors were selected as gas sensors. One of the neural networks was used for quantitative identification using only steady state response while the other two neural networks were used for quantitative identification using both transient and steady state responses. One of them was a neural network with tapped time delays, which used sensor frequency responses and past values of these responses. The other NN structure used sensor frequency responses and slope values of these sensors frequency responses to quantify the components in the binary mixture.

Vito *et al.* (2007) have reported gas concentration estimation in ternary mixtures with room temperature operating sensor array using tapped delay architectures. A hybrid multisensor system equipped with sensor fusion architectures for continuous gas concentration estimation was presented. They used ad-hoc sensor fusion algorithms based on neural networks and support vector machines, together with an array of heterogeneous, room temperature operating sensors to enhance array performances. Results obtained by different architectures for individual analyte quantification in NO_2-NH_3-humid air mixtures were presented. Overall system responsiveness was also found to be very good with respect to the original sensor dynamics.

Gulbag *et al.* (2008) have showed quantitative discrimination of the binary gas mixtures using a combinational structure of the probabilistic and multilayer neural networks. The quantitative discrimination of seven different types of binary volatile organic gas mixtures were realized by using a proposed structure which was combination of probabilistic neural networks (PNNs) and multilayer neural networks (MLNNs). In the first phase of the discrimination, the binary gas mixtures were classified using PNNs and the MLNNs were processed for the quantitative identification of individual gas concentrations in their gas mixtures in second phase. They reported the overall results of quantitative discrimination performance of the proposed structure were quit promising.

Zhang *et al.* (2008) have evaluated peach quality indices using an electronic nose by multivariate linear regression (MLR), quadratic polynomial step regression (QPST) and backpropagation (BP) network. The electronic nose consisted of a sensor array and a data acquisition card was used for analysis. The superior performance for the analysis carried out with the QPST method has been demonstrated when comparing the correlation coefficients (R^2) and average percent errors with those found by using the ANN and MLR methods.

Mumyakmaz *et al.* (2008) have presented a system to predict concentration ratios of ternary gas mixtures using QCM sensor array responses for a predefined 3D sample space. The data processing was divided into pre- and post-processing sections to increase the performance. The pre-processing section filters redundant data out, and extracts meaningful data. A quadratic polynomial curve fitting was applied to the data. The post-processing section included two feed-forward multi-layer artificial neural networks (ANNs); one for classification of species, and the other for quantification of the concentration ratios. The average success rate of finding the concentration amounts in the testing phase was 93.87%, and identifying the species (classification) was 100% using this method.

Ni and Chan (2009) have reported identification and measurement of gas mixture by using the support vector regression technique. They proposed a support vector regression (SVR) system used for recognizing and measuring the gas compounds characterized by near infrared molecular absorption spectrometry (NIR-MAS). The experimental results demonstrated that the SVR system showed high feasibility and reliability to be used in the trace gas detection field.

Kumar *et al.* (2009(a)) have reported a radial basis function neural network classifier for the discrimination of individual odor using responses of thick-film tin-oxide sensors. They performed 100% discrimination of alcohols and alcoholic beverages using published data obtained from the responses of thick film tin oxide sensor array and employing a combination of transformed cluster analysis and radial basis function neural network.

Szczurek *et al.* (2009) have adopted profiling method for sensor array data for gas identification. They utilized dynamic response of sensor array with the emphasis on the processing of discrete measurement data. The information needed for identification of test samples was obtained in course of profiling the data from

calibration measurements. This operation consists of classification of data sets, selection of representative data sets, parameterization of classifiers associated with representative data sets and determination of data records. Discriminant function analysis (DFA) was used for data classification. The identification of unknown gas was performed on the base of data records and measurement data obtained for the gas. Kumar *et al.* (2009(b)) have reported a fuzzy logic based neural network classifier for qualitative classification of odors/gases. Fuzzy membership values were used as target vectors to the proposed neural classifier. Three different versions of backpropagation algorithm were used to train the network and their performances have been compared.

Khalaf (2009) has reported sensor array system for gases identification and quantification of individual gases using support vector machine (SVM) and support vector regression (SVR). The author utilized a system consisting of five different types of gas sensors supplied with different heater voltages to improve the selectivity and sensitivity of the sensors which were from the TGS class. The results of identification were 100 % accurate while the quantification results were also very promising even without using any preproceesing or feature extraction technique.

Rajput *et al.* (2010) have reported a neural net implementation of standardized principal component analysis (SPCA) pre-processor for gas/odor classification using the responses of thick film gas sensor array. The authors claimed that the proposed method is suitable for development of an e-nose using feature enhancement technique like SPCA.

Kumar *et al.* (2010(a)) have reported fuzzy entropy based neural network classifier for odor identification of alcoholic beverages using tin oxide based thick film sensor array. A neural classifier was trained by incorporating the class information in the training data set in the form of fuzzy entropies of the respective classes. The use of fuzzy entropy measure resulted in better identification of the alcoholic beverages as compared to those which are based on fuzzy membership representation. They also reported that the fuzzy entropy representation resulted in precise identification of the alcoholic beverages with reduced number of sensors in the array.

Kumar *et al.* (2010(b)) have reported a neuro-fuzzy classifier-cum-quantifier for analysis of alcohols and alcoholic beverages using responses of thick-film tin oxide gas sensor array. The proposed classifier retrieved both qualitative and

quantitative information simultaneously from the steady-state responses of thick-film tin oxide gas sensor array when it was exposed to seven different kinds of alcohols and alcoholic beverages. The individual concentration bands were represented in the output feature space by fuzzy subsethood measure. The qualitative and quantitative classifications were done by training an artificial neural network (ANN) with backpropagation algorithm.

Rajput *et al.* (2011(b)) have reported a fully neural implementation of unitary response model (URM) for classification of gases/odors using the responses of thick film gas sensor array. Thick-film tin-oxide sensor array responses for four gases/odors (viz. Acetone, Carbon Tetra-chloride, Ethyl Methyl Ketone and Xylene) were first transformed into equivalent unitary responses. This transformation was carried out using a pre-trained neural 'unitary response model pre-processor (URMP) and pre-trained neural response model pre-processor (Net IURMP). The classification of these responses in the unitary analysis space ware then carried out more accurately using a pre-trained neural classifier.

Kumar *et al.* (2011(b)) have reported fuzzy entropy based neuro-wavelet identifier-cum-quantifier for discrimination of gases/odors using thick film tin-oxide based gas sensor array. They used dynamic response curves of an oxygen-plasma treated thick-film tin oxide sensor array exposed to four different gases. These responses were subjected to continuous wavelet transform (CWT). Then suitable wavelet coefficients were selected using multiscale principal component analysis (MSPCA). Fuzzy entropy and fuzzy subsethood values were calculated for the individual odor/gas and for the particular concentration band of each odor/gas, respectively. The quantitative information was encoded in the fuzzy subsethood values of the particular concentration bands in the output feature space, whereas the fuzzy entropy values were used to normalize the training data set consisting of MSPCA selected wavelet coefficients. A feedforward neural network was trained with a backpropagation algorithm with the training data containing the wavelet coefficients normalized with fuzzy entropies of individual odors/gases.

Vembu *et al.* (2012) have used time series method to solve the machine olfaction problems. They applied time series kernels for two pattern recognition problems in machine olfaction, namely, odor classification and odor localization in an open sampling system along with use of time series feature extraction methods. The

study was focused on autoregressive models and linear dynamical systems to model time series. SVMs were trained with features extracted from these models.

Kumar (2013) has reported game theoretic pattern analysis approach for identification of odors/gases using response of a poorly selective sensor array. The sensor data was modeled as a coalitional game in which each sensor of the array acted like a player forming coalitions with other players. A pay-off function was associated with each possible coalition of players with higher pay-offs being given to coalitions that maximize class separability of the data. Shapley value was used to quantify the contribution of each player yielding a standard pattern for each odor class. Each test vector was then matched with the standard pattern with minimum Euclidean distance. A weighting scheme for relative scaling of the test samples was also proposed. More than 89% of the samples were identified correctly using the proposed technique.

Ceto *et al.* (2013) have reported beer classification by means of a potentiometric electronic tongue (ET) system based on an array of potentiometric ion-selective electrodes (ISEs). The array was formed by 21 ISEs combining both cationic and anionic sensors with others with generic response. The obtained responses were evaluated using two different pattern recognition methods, principal component analysis (PCA), which allowed identifying some initial patterns, and linear discriminant analysis (LDA) in order to achieve the correct recognition of sample varieties (81.9% accuracy). The results showed that the use of supervised pattern recognition methods such as LDA is a good alternative for the resolution of complex identification situations.

Pati *et al.* (2014) have presented qualitative and quantitative differentiation of gases using ZnO thin film gas sensors and pattern recognition analysis. They have grown highly textured, ultra-thin, nano-crystalline zinc oxide thin films using a metal organic chemical vapor deposition technique and addressed their selectivity towards hydrogen, carbon dioxide and methane gas sensing. The data matrices extracted from first Fourier transform analyses (FFT) of the conductance transients were used as input parameters in a linear unsupervised principal component analysis (PCA) pattern recognition technique.

From the above discussion and the literature survey, it is obvious that choosing the type of sensors, data preprocessing and feature extraction techniques and pattern analysis methods are highly problem dependent. Different types of sensors

generate different statistical properties which require proper selection of data preprocessing and/or feature extraction techniques. Selection of appropriate pattern analysis technique is also problem dependent. Further, from the literature it can be revealed that researchers have worked mostly on preprocessing and feature extraction/selection techniques to improve the results obtained with the employed pattern analysis methods. Moreover, it is very necessary to put emphasis on selection of proper classification and regression tool to achieve the best accuracy in terms of identification as well as quantification of test gases/odors.

1.7 Scope of the Present Thesis

In the light of the literature survey and the work of different researchers, the present work is oriented to develop some simple and effective techniques for the identification and quantification of gases/odors in individual as well as in binary mixture form. For this purpose different types of responses (steady state as well as dynamic responses) of tin oxide based thick film sensor array have been used. The different types of responses used are:

(a) The first dataset has been prepared from the published steady state responses of gas sensor array fabricated using thick film screen printing technology where one sensor was pure SnO_2 paste and other three were made up of Pd, Pt, and Au. The sensor array was exposed to four different types of gases viz. H_2, CO, CH_4, and LPG and the steady state responses were collected at varying concentration [Mishra and Agarwal (1998)]

(b) The second dataset has been prepared by generating the steady state responses with a sensor array fabricated by the author (Sensor Array-2, as discussed in Chapter 2) for LPG, N_2O, Acetone and 2-propanol.

(c) The third dataset prepared from the published dynamic responses of six SnO_2 based sensors which were treated in oxygen plasma. In this sensor array, one sensor was made up of pure SnO_2 and other five were doped with Pd, Pt, CuO, ZnO and Cd. This particular sensor array was exposed to four different gases/odors viz. LPG, CCl_4, CO, and C_3H_7OH and the time varying responses were observed at four different concentration viz. 25 ppm, 50 ppm, 75 ppm and 100 ppm respectively [Chaturvedi *et al.* (1999)].

(d) The fourth dataset used has been prepared from the steady state responses of SnO_2 based sensors for binary mixture of volatile organic compounds (VOCs), viz. Acetone

and 2- propanol in gaseous form. The sensor array fabricated by the author (Sensor Array-2, as discussed in Chapter 2) was used for collecting these responses. The responses were collected by keeping the concentration of one VOC fixed while varying the concentration of the other.

During the study, it was found that the reported sensor arrays as well as developed sensor array suffered from one or more of the following limitations:

(i) Overlapping sensitivity to different gases/odors leading to poor selectivity.

(ii) Saturating tendency of the sensor responses at higher concentration of the test gases leading to the difficulties in classification/quantification.

To overcome the above mentioned problems, which are hindrance to proper identification and quantification of gases/odors, computational techniques seems to be relatively preferred solutions as compared to traditional methods. Computational methods are also privileged since path breaking innovations in fabrication technology requires a large amount of time and efforts. So, development of better computational methods is a relatively easy and preferred solution.

Identification and quantification of gases/odors are more complicated when simultaneous quantification and concentration estimation of individual component in a mixture is required. In the former case, the dataset is used to extract both qualitative and quantitative information employing one classifier architecture only while in the latter case multi-output regressor is required along with suitable classifier. Depending on the nature of the problem and the dataset, suitable preprocessing techniques are employed before the data is finally fed to the classifier/regressor.

1.8 Specific Aspects of the Present Work

Followings are the main aspects of the present work:

(i) Finding and simple and effective data preprocessing (among supervised and unsupervised) technique for identification/quantification of gases/odors.

Principal Component Analysis (PCA) is a simple and effective technique used for data preprocessing and dimensionality reduction. PCA is non-parametric and unsupervised method. Linear Discriminant Analyis (LDA) another popular technique which is supervised in nature and can also be used for data preprocessing and dimensionality reduction but it requires class information to handle the data. In the present work, it has been established through various experiments that PCA preprocessing improves the classifier/regressor performance for both, backpropgation

neural network (BPNN) and support vector machines (SVMs) as discussed in Chapter-3, Chapter-4 and Chapter-5.

(ii) Simultaneous identification and quantification of gases/odors using dynamic responses of thick film gas sensor array.

In the present work, classification and simultaneous quantification of gases/odors using dynamic responses have been performed successfully. This integrated approach not only detects the class of the test gas/odor but also predicts its concentration.

(iii) Classification and quantification of individual gas/odor in the binary mixture using classification and regression model.

Classification of individual gas/odor in a mixture is a relatively complex task. In the present work this problem has been tackled with the use of classification and regression model serially. The steady state responses of the sensor array have been collected for the mentioned VOCs (Acetone and 2-propanol) in the individual as well as in mixture form. A hierarchical system consisting of gating network and three quantification networks has been designed to classify and then quantify and individual and mixture of VOCs.

(iv) Preprocessing of time varying (dynamic) raw data with newly proposed feature technique called Average Slope Multiplication (ASM).

In the present work, a relatively simple technique has been proposed for preprocessing of raw dynamic data. The raw dataset has been extracted from the published dynamic responses which were further preprocessed using proposed ASM method as discussed in Chapter-4.

(v) Use of Multi-output Support Vector Regression (M-SVR) for quantification of individual component in binary mixture of gases/odors.

In the present work, an advanced method called multi-output support vector regression (*M*-SVR) has been used for simultaneous quantification of individual component in a binary mixture of gases/odors which is explained in detail in Chapter-5.

1.9 Thesis Organization

In the present thesis, the entire work has been organized and presented in six chapters:

Chapter-1 introduces the concept of artificial olfaction and electronic nose. It gives brief introduction of the history of artificial olfaction and especially focuses on the mammalian olfactory system, its working principal and related proposed models

followed by the brief introduction to various techniques developed for artificial olfaction. This chapter also briefly introduces thick film based tin oxide sensor array. A review of the relevant literature on the various computational techniques employed for classification/quantification of individual as well as mixture of gases has been presented.

Chapter-2 illustrates the basic properties of SnO_2, giving special attention to gas sensing mechanism of SnO_2 based gas sensors and covers the possibilities to enhance the performance of SnO_2 based thick film sensors. This chapter also provides the fabrication and characterization details of thick film gas sensor array followed by the validation of sensor array responses with the proposed tin oxide based thick film sensor array model.

Chapter-3 presents the performance comparison of linear discriminant analysis (LDA) versus principal component analysis (PCA) as preprocessing and feature extraction tools for classification of gases/odors using their responses obtained from the thick film sensor arrays. The PCA and the LDA have been used for feature extraction and dimensionality reduction. The results of experiment performed for gases/odors classification show that PCA can be preferred for data preprocessing and dimensionality reduction due to its unsupervised nature and promising results obtained.

Chapter-4 proposes a new method called average slope multiplication (ASM) for classification and quantification of gases/odors using published dynamic characteristics of thick film gas sensor array. The instantaneous values of the dynamic response/recovery plots were extracted for various test gases viz., LPG, CCl_4, CO, and C_3H_7OH and correlated to its neighboring response plots by the use of proposed ASM technique. It has been demonstrated that the proposed method offers excellent results for classification and simultaneous quantification of individual gases/odors using the dynamic responses of thick film gas sensor array. Principal component analysis (PCA) has been further used for data preprocessing, dimensionality reduction and for performance comparison purpose. Backpropagation neural network (BPNN) has been used as a classifier.

Chapter-5 presents the classification and quantification of two volatile organic compounds (VOCs) viz. Acetone (CH_3COCH_3) and 2-propanol ($CH_3CHOHCH_3$) in their single as well as in mixture forms. A sensor array consisting

of four sensor elements was fabricated by the author using thick film fabrication technology. The steady state responses of the sensor array were collected for the mentioned VOCs in their individual as well as mixture form. A hierarchical system consisting of gating network and three quantification networks was designed to classify and then quantify individual and mixture of VOCs. The classification results of gating network have been insured using back-propagation neural network (BPNN) and support vector machine (SVM). For quantification multioutput support vector regression (*M*-SVR) method was used in quantification networks for individual as well as binary mixture data. *k*-fold cross validation scheme was adopted for all the experiments.

Chapter-6 summarizes the work carried out in this thesis and discusses major conclusion. Scope for future studies has also been discussed in this chapter.