



Comprehensive Review of Latest e-Nose Sensor Technologies

P. Gowdhaman¹, T. Venkatesan¹, R. Banupriya², A. T. Nimal³, Haresh M. Pandya^{1*}

¹Department of Physics, Chikkanna Government Arts College, Tiruppur, TN, India

²Department of Physics, Gobi Arts and Science College, Erode, TN, India

³Solid State Physics Laboratory, DRDO, New Delhi, India

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*haresh.pandya@rediffmail.com

ABSTRACT

ISO 14001 environmental management system standard was developed by an internationally selected standards committee to help all types of organizations develop plans to minimize their brunt on the environment aspects specially to minimize air pollution. ISO 14001:2015 helps an organization to achieve the planned outcomes of its environmental management system, which provide value for the environment and the organization. The main aim of this paper is to identify whether ISO 14001 certificate is need for an educational institution and to identify the environmental issues and finding the significant improvement in the organizational performance due to the certification. An Environmental Management System (EMS) is a part of an organization's overall management system. It is a systematic approach dealing with environmental aspects of an organization. A structural framework issued to help us to manage, evaluate and improve its environmental performance in a verifiable way. As part of its EMS, the university implemented a 'plan-do-check-act' (PDCA) cycle for controlling and continuously (Constantly) improving its environmental performance.

Keywords: Environmental Management System; Organization; Environmental performance.

1. INTRODUCTION

Over a decade, sensors have been predominantly used to detect and respond to physical environment changes such as light, heat, moisture, pressure, motion, or any other environmental phenomena. Specific physical inputs any of nature are converted to machine readable electrical signals at the sensor location or digitally transferred over a network for reading or further processing (Xu and He, 2017; Abel *et al.* 2018; Sayago *et al.* 2019). As such, present day advancements in sensing technology have been receiving increasing attention in both academic and industrial applications. Among the available sensing technologies, gas sensing technology has become progressively significant because of its widespread applications (Cheeke and Wang, 1999; Nimal *et al.* 2009; Liu *et al.* 2012; Cochrane *et al.* 2016; Xu and He, 2017; Gowdhaman *et al.* 2018) in the areas not limited to:

- industrial production (e.g., food quality testing, methane detection in mines);
- automotive industry (e.g., detection of polluting gases from vehicles);

- medical applications (e.g., electronic noses simulating the human olfactory system);
- indoor air quality supervision (e.g., detection of carbon monoxide);
- environmental studies (e.g., greenhouse gas monitoring, air quality measurements);
- defence security (e.g., detection and identification of chemical warfare agents).

Till date, the human nose or a mammalian nose has been recognized as the primary instrument to sense smell or flavor of various industrial products. Olfactory receptor cells in them have high sensitivity of the order of ppm level and that is believed to be responsible for sensing. However, these olfactory receptor cells are not reliable completely for sensing as toxic compounds as they damage these organic cells beyond repair. Thus, mimicking the remarkable performance of a human/mammalian olfactory system is highly challenging. (Gardner and Bartlett, 1994; Keller, 1995; Arshak *et al.* 2004; Scott *et al.* 2006; Burian *et al.* 2010; Gongora *et al.* 2018). Thus, in recent times, significant attempts have

been made to develop an electronic instrument capable of imitating the human nose remarkable ability.

Performance of such sensors in a dynamic environment and their subsequent calibration and analysis brings to the fore many of its latent inherent limitations which needs to be effectively addressed before such a sensor is to perform as an e-Nose, detecting and distinguishing multiple vapors at the same time (Keller, 1995; Schaller *et al.* 1998; Gole and Lewis, 2007; Liu *et al.* 2012; Laquintinie *et al.* 2019). Combined process of analyzing and subsequent neutralization of gas sensors improves sensitivity by about three orders of magnitude, removes drift and provides discrimination between several thousand odors from a mixture of toxins in the environment.

The detection and quantification of chemical species are the key objectives of a chemical e-Nose sensor. There are many conventional analytical techniques, such as gas chromatography-mass spectrometry or ion mobility spectrometry developed for these purposes. These techniques have many pros and cons, the former related with their selectiveness and sensitiveness and the latter with their high price, environment and maintenance requirements, bulkiness, as well as the requirement of highly trained personnel (Cosio *et al.* 2012; Hosseini and Hamdy Makhoulouf, 2016; Xu and He, 2017). Moreover, these conventional methods are not only time-consuming but the results are often inadequate and not total. Consequently, there is enormous demand for an electronic instrument that can mimic the human sense of smell and provide prompt low-cost sensory information (Keller, 1995; Cheeke and Wang, 1999; Arshak *et al.* 2004; Gowdhaman *et al.* 2018).

The sensing ability of a chemical sensor relies on the sensing material. Metal oxides, supramolecular structures, carbon nanotubes, molecularly imprinted polymers, self-assembled monolayers and a variety of other polymers have been widely exploited as a sensing material for chemical sensors (Nimal *et al.* 2009; Raj *et al.* 2010; Hosseini and Hamdy Makhoulouf, 2016; Gowdhaman *et al.* 2018). Development of suitable nanomaterials with enhanced sensitivity and selectivity will help improve the performance of such a chemical vapour sensor.

In a fast-paced, globally interconnected world, chemical sensors that detect explosives and chemical warfare agents are of particular interest. Chemical warfare agents and explosives pose significant societal dangers (Nimal *et al.* 2009; Raj *et al.* 2013; Hosseini and Hamdy Makhoulouf, 2016; Devkota *et al.* 2017). Their detection in real time is a significant challenge that is being addressed

from both an instrumental and chemical standpoint for homeland and civil security applications, as well as environmental and humanitarian efforts (Raj, 2012; Hosseini and Hamdy Makhoulouf, 2016; Singh *et al.* 2016; Gowdhaman *et al.* 2018).

Therefore, development of smart, cheap and portable sensory devices, is ushering a new era in the sensing of a target chemical species. A device designed for this purpose is therefore termed as an electronic nose or a e-Nose device in the current parlance. This research article focusses on giving an overview of chemical warfare agents, their importance and detection as well as the design, development and testing of such e-Nose devices.

2. CHEMICAL WARFARE AGENTS (CWAS) – AN OVERVIEW

Chemical Warfare Agents (CWAs) are hazardous chemical substances prepared to incapacitate, or be lethal (War and War, 1918; Raj, 2012; Venkatesan and Hareesh 2013; Raj *et al.* 2013; Devkota *et al.* 2017; Tripathi *et al.* 2018). Living organisms are killed, injured, or incapacitated by the toxic properties of these CWAs. Chemical warfare agents are made up of more than 70 different chemicals that can be found in solid, liquid or gaseous forms. These are classified as follows based on their toxic level and effect on living organisms:

- blistering or vesicating agents (e.g., mustards, lewisite),
- nerve agents (e.g., sarin, soman, cyclohexylsarin, tabun),
- vomiting agents (e.g., adamsite),
- tear agents (e.g., benzyl chloride, capsaicin, ethyl iodoacetate),
- blood agents (e.g., cyanogen chloride, Arsine),
- choking agents or lung toxicants (e.g., chlorine, phosgene, diphosgene),
- incapacitating agents (e.g., anti-cholinergic compounds),
- lacrimation riot control agents (e.g., pepper gas, chloroacetophenone),
- cyanides, or binary and non-traditional agents

Research on the detection of chemical vapor agents have been underway by many (Gardner and Bartlett, 1994; Keller, 1995; Schaller *et al.* 1998; Arshak *et al.* 2004;

Hosseini and Hamdy Makhlof, 2016; Benetti *et al.* 2019). Since these chemical compounds are present in vapour and solution form, their lethality, as well as their ease of synthesis, colourlessness and odourlessness highlight the need for detection. (Liu *et al.* 2012; Singh *et al.* 2016; Devkota *et al.* 2017; Gongora *et al.* 2018; Benetti *et al.* 2019). In fact, every year the anthropic activities produce billions of tons of chemical contaminants that are released in air, water and soil. Further, there is always an apprehension that rogue element in a country can effectively manipulate these chemicals for massive large scale terrorist attacks on a nation. Thus, chemical sensors to detect CWAs and volatile organic compounds (VOCs) are to be highly sensitive, selective, quickly responsive, reversible as well as being compact (Liu *et al.* 2012; Singh *et al.* 2016; Devkota *et al.* 2017; Gongora *et al.* 2018; Benetti *et al.* 2019).

Fig. 1 presents quick outlook of different gas sensing techniques available today. Different detection techniques and methodologies have been used to achieve the goal of detection of CWAs in a real-time manner, while also meeting the affordability and portability criteria. For instance, remote or standoff monitoring has

been carried out by Infrared - Raman spectroscopy, on-the-spot detection by calorimetric and surface acoustic wave sensors, ion mobility spectrometry, flame photometry, photo ionization, electrochemical detection, and carbon nanotube gas ionization sensors (Arshak *et al.* 2004; Alizadeh and Hamedsoltani, 2016; Hosseini and Hamdy Makhlof, 2016; Xu and He, 2017; Gowdhaman *et al.* 2018).

Detection and recognition of an analyte in a harsh environment is a challenging task (Gowdhaman *et al.* 2018) which cannot be achieved with the help of a single sensor. For sensing of different gases in a mixture, one will need highly selective sensors. Even if this is achieved, the number of sensors should be equal to the number of target gases, which is a difficult task. Therefore, some of these techniques use an array of sensors either based on a set of metal oxides, polymers, carbon nanotubes or porous silicon (PS) interfaces as sensing material for the development of a chemical sensor (Gole and Lewis, 2007). These sensor responses are analysed using an algorithm called pattern recognition system.

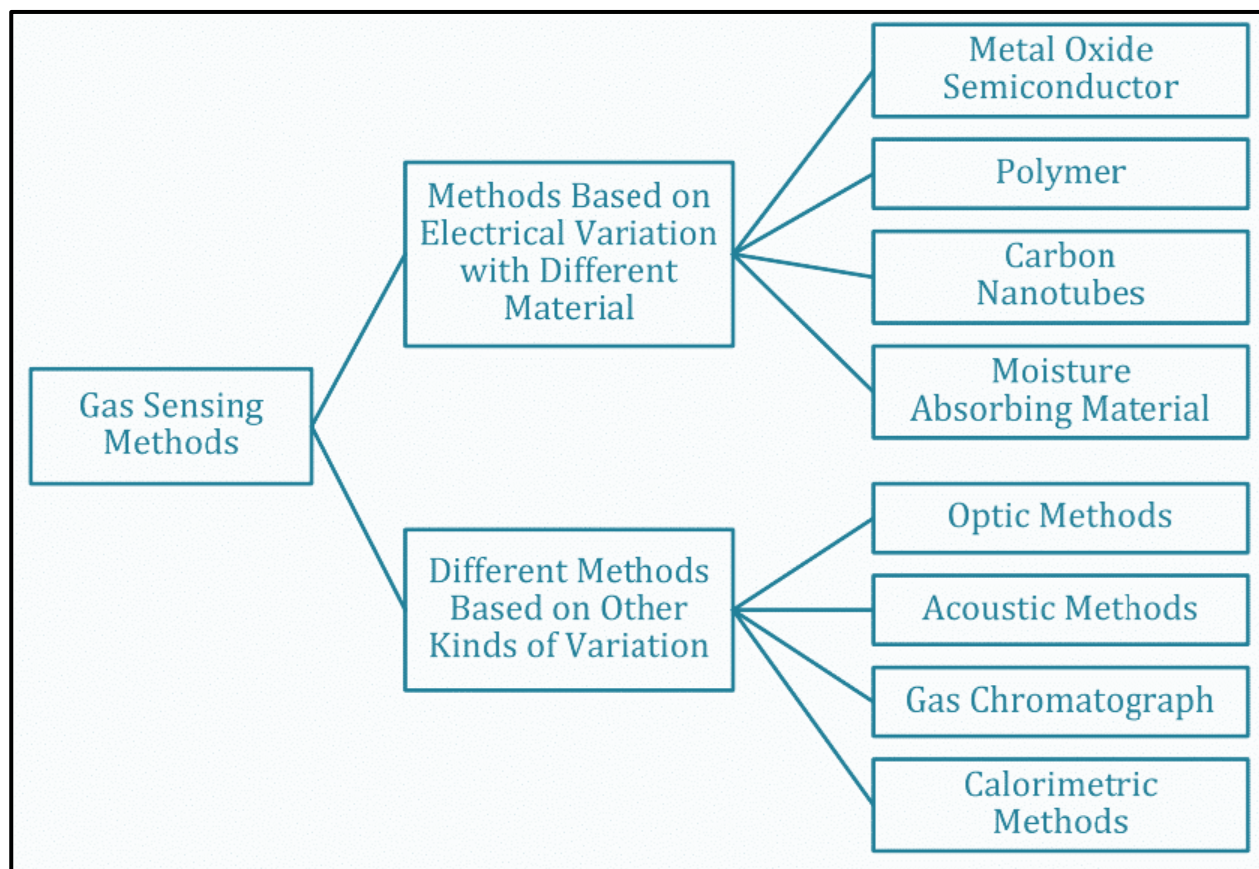


Fig. 1: Classification of chemical vapor sensing methods.

3. ELECTRONIC NOSE OR E-NOSE

An electronic nose is a device that is designed and developed as a system for detecting and classifying odors, vapors, and gases automatically. Since the 1990s, electronic noses have been commercially available and have primarily been used for the detection, discrimination, and recognition of simple and complex gaseous mixtures (Raj, 2012; Bhasker Raj *et al.* 2013; Binions and Naik, 2013). The concept of an electronic nose as an intelligent chemical array sensor system, on the other hand, has only been around for a decade (Scott *et al.* 2006; Cosio *et al.* 2012; Gongora *et al.* 2018; Benetti *et al.* 2019). Fig. 2 illustrates a generic architecture of such a device. It generally consists of three main elements namely:

- A system (pre-concentrator) for delivery, sampling, filtering and preconditioning of the vapor gas;
- A sensor array which converts the chemical interaction of the analyte into an electrical signal; and
- An automated pattern recognition system - a computing system which is able to evaluate the data and transform it into a human intelligible format (Keller, 1995; Bhasker Raj *et al.* 2012; Raj *et al.* 2013).

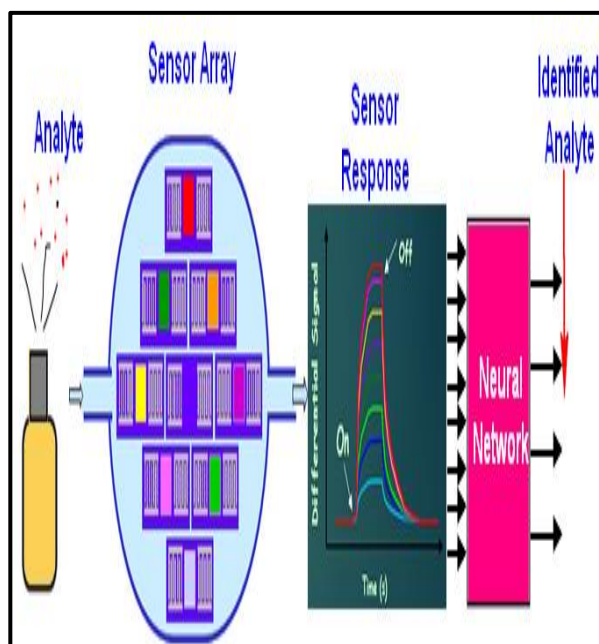


Fig. 2: The generic architecture of an Electronic nose

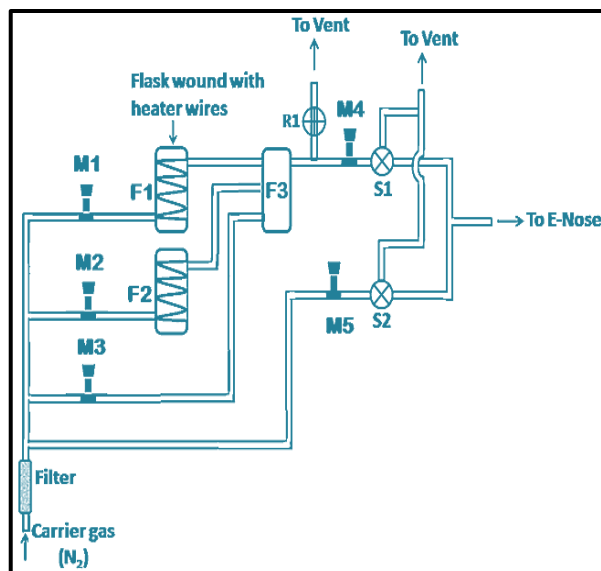


Fig. 3: A typical Block diagram of a Multi-vapor generator system (Gowdhaman *et al.* 2018)

3.1 e-Nose Input Signal Generation and Delivery System

The e-Nose devices are initially optimized in the laboratory itself before they are taken out for any field applications. This is done to train the device to behave meaningfully and to avoid false alarms and response. Therefore, in the lab e-Nose devices are initially exposed to different vapors of interest under controlled conditions (temperature, concentration, humidity, etc.) and subsequently, the type of response is recorded and saved for future use (Keller, 1995; Nimal *et al.* 2009; Raj *et al.* 2010; Bhasker Raj *et al.* 2012; Raj *et al.* 2013; Gowdhaman *et al.* 2018). Analyte vapor that needs to be tested can be generated from chemical compounds that are either available in solid or liquid phases. The analyte vapor can be either a single gas or a mixture of gases that needs to be efficiently detected by the e-nose device. Hence, initial optimization of e-Nose device is considered very crucial and the multi vapor generator (MVG) system with its design, generation and delivery system needs to be highly efficient. Fig. 3 shows a typical block diagram of a multi-vapor generator system. F1 and F2 are thermal flasks wound with heater wire for the generation of vapor from solids/liquids. The e-Nose device is exposed to generate gas vapors for sensing and detection. The concentration of the generated chemical vapors can be altered by MVG system by controlling the flow rate of carrier gas (preferably nitrogen) through thermal flasks and the corresponding sensing of the e-Nose device results are analyzed with respect to the

detection limit of e-Nose device (say Parts Per Million or Parts Per Trillion level). M1-M5 are accurate flow controllers that controls the flow rate of carrier gas. Solenoid valves (S1 and S2) control rapid switching between carrier and target gas.

The concentration of an analyte to be tested is calculated by the weight loss method by evaluating the evaporation rate of the analyte over different time intervals (Bunte *et al.* 2007; Devkota *et al.* 2017; Xu and He, 2017; Gowdhaman *et al.* 2018).

Individual sensors within the e-Nose device produce a time-dependent electrical signal (V) in response to an analyte adsorbed by the sensing layer in the e-Nose sensor array. Adsorption and subsequent desorption by the sensors in the array give rise to a signal that rises and decays. This depends on one or more of the following parameters: (Gardner and Bartlett 1994; Liu *et al.* 2012; Xu and He, 2017).

- the flow profile and type of carrier gas;
- the nature of the analyte (either toxic chemical, simulant or VOCs);
- the reaction kinetics of the analyte and the sensing layer;
- the diffusion of the analyte within the sensing layer;

- the nature of the sensing layer, e.g., porosity, physical structure, thermal time-constant;
- the nature of the substrate supporting the sensing layer, e.g., thermal conductivity, acoustic impedance;
- ambient conditions, e.g., temperature of sensing layer, humidity, carrier gas, pressure.

Thus, the critical component in the e-Nose device is the multi-sensor array with its unique sensitive layer that determines the type of vapors that can be detected by the sensor system.

3.2 Sensors and sensing materials for vapor classification

Any ideal e-Nose device needs to avoid false responses and efficiently discriminate and detect vapours in real time. Multiple arrays of sensors help in the above discrimination process. Analyte molecules undergo adsorption/absorption when they pass through the sensitive layer producing a physical/chemical change which are subsequently transduced as output electrical signal (Arshak *et al.* 2004). Fig. 4 illustrates a schematic representation of frequency response due to interaction of an analyte (test gas) with the sensing layer of a SAW sensor.

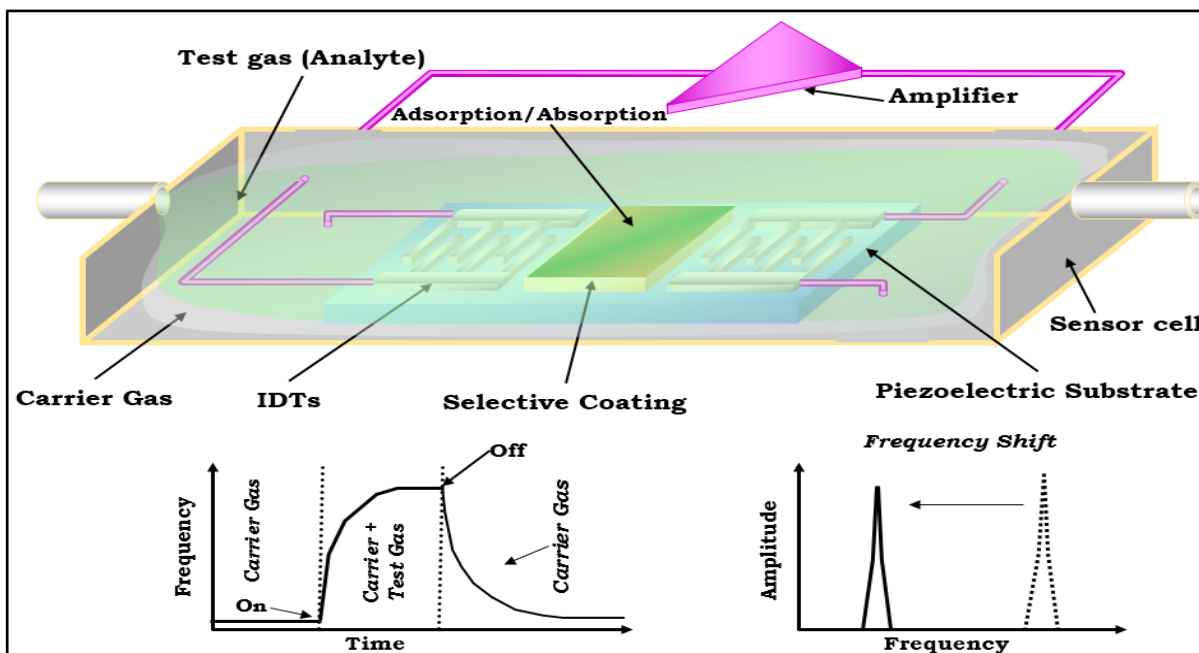


Fig. 4: A schematic architecture of a SAW sensor and its frequency response to test gas

An overview of various sensing methods have been exhaustively discussed by many researchers through further classification according to sensing materials (Arshak *et al.* 2004; Bhasker Raj *et al.* 2012; Binions and Naik, 2013; Raj *et al.* 2013; Hosseini and Hamdy Makhoulouf, 2016; Tripathi *et al.* 2018; Sayago *et al.* 2019). Intrinsically conducting polymer and metal oxide, optical gas sensors, conducting polymer composite, conductivity gas sensors, surface acoustic wave (SAW) and QCM piezoelectric gas sensors, carbon nanotubes, MOSFET gas sensors and moisture absorbing materials (Arshak *et al.* 2004; Anderson *et al.* 2009; Cosio *et al.* 2012; Raj 2012) have been effectively used for sensing. These systems offer excellent discrimination and lead the way for a new generation of “smart sensors” which have the capability to mould future commercial markets for e-Nose devices (Gardner and Bartlett 1994; Schaller *et al.* 1998; Gongora *et al.* 2018).

SAW sensors with specific sensitive layers of one-dimensional(1D) metal oxide or polymer nanostructures have shown superior performance than bulk sensors due to their large surface to volume ratio and their dimensions being comparable to the extent of the surface charge region (Raj *et al.* 2010; Raj, 2012; Raj *et al.* 2013; Tripathi *et al.* 2018).

3.2.1 SAW Sensors in e-Nose Devices

Surface Acoustic Wave (SAW) technology is a fluidic platform for sensing chemicals in gaseous and liquid states with the inherent benefits of ultra-high sensitivity, selectivity, quick response time, small size, linearity, reversibility, and the ability to work in both wired and wireless mode. Furthermore, the technology is low-cost, compatible with modern mass-production fabrication techniques and durable (Nimal *et al.* 2006; Raj *et al.* 2010; Bhasker Raj *et al.* 2012; Raj 2012; Venkatesan and Haresh M 2013; Haresh M *et al.* 2013; Raj *et al.* 2013; Banu Priya *et al.* 2014; Singh *et al.* 2016; Devkota *et al.* 2017). Proper selection of sensing layers, piezoelectric substrates and inter-digital transducers (IDTs) turn these sensors to offer excellent stability. These sensors are expected to fulfill the increasing demand with potential applications as chemical sensors in industries, pollution and emissions control, military, combustion exhausts, and other disciplines for detecting and monitoring various volatile organic chemicals (VOCs), inorganic gases, and chemical warfare agents (CWAs) amongst others (Raj *et al.* 2010; Raj 2012; Bhasker Raj *et al.* 2013; Raj *et al.* 2013; Hosseini and Hamdy Makhoulouf 2016; Singh *et al.* 2016; Gowdhaman *et al.* 2018). Therefore, chemical sensors based on this technology have continuously received increasing attention and focus since 1970's.

The sensing ability of these sensors rely on changes in the propagation characteristics of SAW during interaction with surface layers or the nearby environment. These sensors have wide range of operational frequency (MHz–GHz) which helps tuning the sensitivity and opens the possibility of operating these devices in wireless mode. SAW sensors have already been used for sensing several physical quantities (e.g., pressure, temperature, and stress) and many chemicals and biological entities (Cheeke and Wang, 1999; Raj 2012; Liu *et al.* 2012; Binions and Naik, 2013; Banu Priya *et al.* 2014; Devkota *et al.* 2017). However, e-Noses based on SAW sensors are used only for some very specific applications like detection of chemical/biological warfare agents and explosives. Lack of precession deposition techniques for the sensitive layers is the main reason for the delayed commercial development of SAW e-Noses. This is because, SAW sensors require a uniform thickness, continuous and defect-free sensitive layer along the propagation path to prevent loss due to attenuation (Cosio *et al.* 2012; Liu *et al.* 2012; Gowdhaman *et al.* 2018).

For chemical and biological sensing, SAW devices are coated with a layer of suitable material such as polymers, metal oxides and metals. A detailed study of diverse polymer and metal oxide sensing layer and the applicability of these for detection of biological and chemical threats have been reported by Gowdhaman *et al.* 2018). Any change in the mass, mechanical, or electric properties of this layer upon exposure to the foreign molecules disturbs the surface waves enabling the devices to use as sensors. A study on design, modelling, development and operation of a SAW sensor and its application to e-Nose devices had been reported in some of the authors' earlier works (Haresh, 2010; Venkatesan and Pandya, 2013; Haresh *et al.* 2013; Banu Priya *et al.* 2014; Sharma *et al.* 2014; Priya *et al.* 2016).

3.3 Pattern Recognition Tools

E-nose devices do not provide information on the nature of the compounds under investigation, but only give a digital fingerprint of an analyte. Each chemical vapor presented to the sensor array produces a signature or pattern characteristic of the vapor. By presenting many different chemicals to the sensor array, a database of signatures is built up. This database of labeled signatures is used to train and configure an automated recognition system for unique classifications of each chemical (Keller, 1995; Burian *et al.* 2010; Cosio *et al.* 2012; Gongora *et al.* 2018).

The data generated by each sensor is processed systematically and the results are analyzed by algorithm known as pattern recognition (PR). Though this type of data analysis isn't used to infer the presence or absence of

a specific chemical compound, it does aid in the development of a multivariate description of analyte. In fact, e-Nose devices' sensing techniques can provide nonspecific information about an analyte, which means they can group complex signals or combine measurements with similar properties (Raj, 2012; Bhasker Raj *et al.* 2013; Binions and Naik, 2013; Raj *et al.* 2013; Bui *et al.* 2016; Singh *et al.* 2016). As a result, increasing the use of multivariate statistical analysis improves the evaluation and interpretation of the analyte's data. As a result, analytes are distinguished, and pattern recognition is used to classify unknown patterns using artificial intelligence (Raj, 2012; Singh *et al.* 2016; Gowdhaman *et al.* 2018).

Pattern recognition reduces complexity in selection of the sensor coatings as well as it enhances the ability to characterize complex mixtures without the need to identify and quantify individual components. It can be extrapolated and exploited to search for a pattern to correlate data, or to generate a model from a set of calibration data to predict test data (Arshak *et al.* 2004; Scott *et al.* 2006; Singh *et al.* 2016). There are many parametric (statistical), non-parametric (intelligent techniques), supervised and unsupervised tools used in pattern recognition systems for reducing multi-dimensional, partly correlated data into two or three dimensions. Principal component analysis (PCA), Cluster analysis (CA), Artificial neural network (ANN),

Linear discriminant analysis (LDA) and Radar plots are some of the pattern recognition techniques being predominantly used by many researchers around the globe. Among these techniques Artificial Neural Networks (ANNs) are widely applied for classification purposes in e-Nose devices (Scott *et al.* 2006; Cosio *et al.* 2012; Raj *et al.* 2013; Singh *et al.* 2016).

Fig. 5 illustrates the structure of a sample ANN used to classify household chemicals. Harpreet *et al.* 2016, have reported a detailed study on pattern recognition systems and developed an algorithm to train e-Nose device for the detection of some of volatile organic compounds and stimulants (Singh *et al.* 2016).

3.4 Commercial Electronic Odour Detection Instruments

Many electronic gas sensors have been produced commercially for a number of years for environmental monitoring and are capable of detecting specific compound. Nimal *et al.* 2009 and Kannan *et al.* 2004; have developed handheld SAW based gas sensors for the detection of explosives and chemical warfare agents (Kannan *et al.* 2004; Nimal *et al.* 2009). Fig. 6 shows one of the e-Nose devices useful for different sensing applications which includes medical and food safety industries.

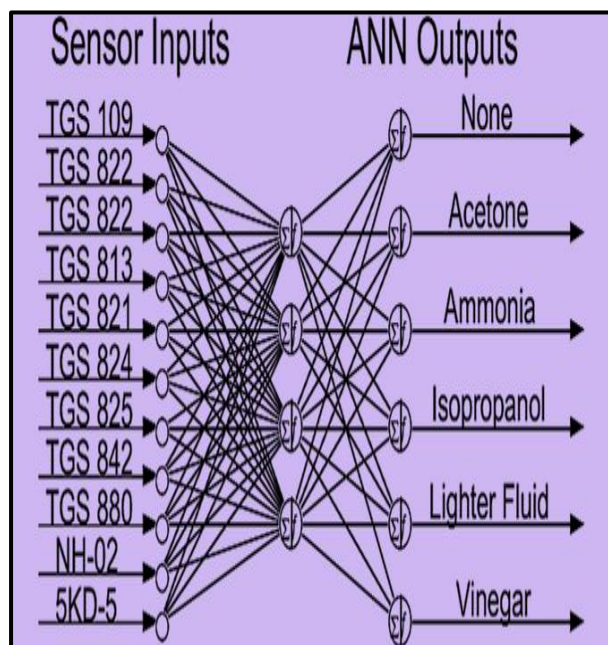


Fig. 5: Structure of a sample ANN used to classify household chemicals (Keller *et al.* 1995)



Fig. 6: Pyranose Electronic Nose

Table 1. List of commercially available electric gas sensors and electronic nose devices for environmental monitoring

Product description	Manufacturer	Comments
Portable odour monitor	Sensodyne Inc., USA	Hand-held monitor with pellistor element
Portable odour level indicator (XP-329)	New Cosmos Electric Co., Japan	Hand-held monitor with pellistor element
Pyranose 320	Sensient Intelligent Sensing Solutions, California	E-nose device for different sensing applications
Alabaster-UV	Europol Instruments, France	Desktop monitor with metal oxide element
Oral checker	National, Japan	Palm-held monitor of breath freshness with metal oxide (TGS 550) element
Rhino	USA	Desktop electronic nose with four metal oxide sensing elements
The Nose	Neutronics Ltd., UK	Prototype electronic nose using 10 polymer elements to monitor beer
Intelligent Nose (Fox 2000)	Alpha MOS, France	Desktop electronic nose with equivalent of 12 metal oxide elements
eNose Aqua and eNose QA	Sensient Intelligent Sensing Solutions, California	Portable sensor designed specifically to sense contamination in refillable water bottles
Odour Mapper	UMIST Ventures, UK	Desktop electronic nose with 20 polymer Elements
SAW DNT Sensor	SSPL-DRDO, India	Handheld device for detection of DNT - an explosive. (Non-commercial)

4. E-NOSE DEVICE - PRESENT AND FUTURE PERSPECTIVES

Present-day conventional gas sensing technologies have severe performance limitations since they suffer from problems in sensitivity under varying ambient conditions in temperature, humidity, etc. Such a scenario has forced the development of e-Nose devices as single application-specific devices. These constraints and challenges need to be circumvented by researchers today to transform such devices into multi-application e-Nose devices.

Besides this, present e-Nose devices suffer from problems like: sensor drift, moderate sensitivity, need for statistical analysis of the response signal, being not suitable for screening of indoor air and high-cost. These challenges limit their widespread applications which need to be tackled in the future. Thus, it is expected that

functionalization of these devices for chemical sensing will continue to be a highly active area of research in the future.

5. CONCLUDING REMARKS

Electronic nose (E-Nose) devices are undoubtedly reliable sensor device for the detection of chemical and biological toxins present even in harsh environments. However, these e-Nose devices need to be optimized for their effectiveness. Among various e-Nose devices, Surface Acoustic Wave (SAW) sensor-based devices show promising results. However, development of a sensitive coating material which is sensitive to chemical and biological toxins is highly recommended in such devices. The sensitive coating materials can be either an alloy of metals, metal oxide semiconductors, polymers, derivative of carbon (e.g., carbon nanotube), or any other moisture absorbing material. Further, identification of

chemical or biological toxins requires efficient pattern recognition techniques. Therefore, integrated development of sensitive coating and the pattern recognition tools will ensure high efficiency of hand-held e-Nose devices which can be then called smart e-Nose devices.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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