Chemical Sensors Employed In Electronic Noses: A Review

Syeda Erfana Zohora, A.M.Khan, A.K.Srivastava, Nisar Hundewale

Abstract*— Electronic noses utilizes an array of chemical sensors of different specificities which responds to the volatile organic compounds present in the gases. The use of electronic chemical sensors in an array design with coupled signal conditioning and appropriate pattern recognition system is capable of identifying complex odours.Such an artificial gas sensing system is called 'electronic nose'. The requirement for the sensors in a electronic nose is that they have a partial sensitivity, i.e. that they can respond broadly to a range or class of gases rather than to a specific one. However, The electronic nose will categorize many odours that contain many chemical components. Different types of gas sensors in the sensor array includes metal oxide semiconductors,optical and amperometric gas sensor, surface acoustic sensors,piezoelectric gas sensors. In this review paper,we discuss the operating principle of each chemical sensor type and its use in electronic nose system.

Index Terms*—Chemical sensors, Electronic noses, E-nose, Volatile Organic Compounds(VOC).

I. INTRODUCTION

The development of the electronic nose was encouraged by the desire for an reasonably priced, quick, and portable device capable of calculating complex mixtures of volatile compounds[1]. The techniques applied to the sensory evaluation of food materials are based on either the traditional team of skilled individuals or the analysis of some chemical substances by gas chromatography-mass spectrometry or the overall assessment of the odor strength of volatile compounds by the emerging sensor technologies[2]. The human olfactory system includes sensory tissue, which is an area of slim epithelium that is situated in the higher part of the nose[3]. The olfactory bulb and brain validate patterns in the partially overlapping signals and recognize the odor class or odor substance[4]. Sensory evaluation using the human sense is subjective, careful design and meticulous training of assessors[5] allows it to become a more objective, but still expensive option. However, it has a great disadvantage of being a lengthy and expensive methodology whose final result depends on many factors such as, for example, the panelist's training and the specific terminology used in the sensory analysis[6]. This resulted to establish a device for speedy cost-effective analysis of volatile organic compounds(VOCs) which does not need expert technicians.
These technique are used in the classification and quantification of the chemical compounds accountable for the sensory sensitivity[7]. Persaud and Dodd[8] original detailed the design of an electronic nose (e-nose) using chemical sensors and pattern recognition in 1982.

Manuscript received on May, 2013.

S. E. Zohora, N. Hundewale is with College of Computers & Information Technology, Taif University, Taif, and KSA.
A. M. Khan is with Mangalore University, Mangalore, India.
A. K. Srivastava is with LightField Corporation Philadelphia, PA, USA.

An electronic nose is a machine that is designed to detect and discriminate among complex odors using a sensor array which consists of generally refrained(non-specific) sensors that are treated with a range of odor-sensitive biological or chemical substances[9]. Chemical sensors have been widely used, but they also experience from limited amount of accuracy and problems of long-time stability. The best gas sensor would demonstrate reliability, robustness, sensitivity, selectivity and reversibility. As high selectivity with high reversibility is difficult to attain. Persaud and Dodd[8] advanced this problem using an array of reversible but only semi-selective identification layers with different chemical properties. Selectivity was achieved through the application of pattern recognition techniques to responses obtained from the sensor array. E-noses are therefore defined as devices composed of an array of independently semi-selective and reversible gas sensors, the output of which is analysed by some form of pattern recognition software[10]. Chemical sensors have become an crucial part of our technology and can be found in chemical process, pharmaceutical, food, biomedical, industrial safety, clinical, chemical sensors have gained from the growing power of computers, integrated electronics, novel designs, and processing tools[11]. The demonstration of such technical changes can be seen in the growth of miniaturized, low-priced, portable,and collection of manufacturable chemical sensors competent of static and permanent measurement. Many principles of identification can be used for chemical sensing. This review paper refers to the sensor technology used within the sensor array and the uses to which these have been implemented.

II. SENSOR TECHNOLOGY

A number of different sensors have been developed for multi-sensor arrays.These types of sensors demonstrates physical and chemical interactions with the chemical compounds when they flow over or are in contact with the sensors[11,12]. The choice of sensors is hence quite large and we have classified them into broader classes. The odor sensors, tasting sensors and biosensors, constitutes the piezoelectric crystal sensors (bulk acoustic wave sensors, surface acoustic wave sensors) and the conducting organic polymer sensors[13]. The other groups are the result of a very recent research.

A. Conducting Polymers

Conducting polymer sensors are normally used in electronic nose systems. Conducting polymers, such as polypyrrole (PPy), polythiophene (PTh) and their derivative have been used as the active layers of gas sensors from 1980s[14]. The modication in the conductivity of these substances occur as they are revealed to different types of chemicals, which link with the polymers.Conducting polymers such as polypyrrole, polythiophene [15] are typically used for e-nose sensing.

The interaction affects the transfer of electrons along the polymer chain, that is to say, its conductivity. A given compound's affinity for a polymer and its effects on the polymer's conductivity are strongly influenced by the counterions and functional groups attached to the polymer backbone and have been utilized in sensor array research[16]. The mechanism of the fundamental conducting polymer response is unknown but many theories have been suggested [10]. The major drawbacks are the effect of humidity and sensor drift due to oxidation of the polymers over time. The most common gas sensing application of conducting polymer is as chemiresistors[16] but uses of conducting polymer for Field Effect Transistors (FETs)[17] and as semi-selective coatings for piezoelectric crystals[18] have also been investigated. They have high sensitivities and short response time; especially, these features are ensured at room temperature.

Conducting polymers are easy to be produced through chemical or electrochemical development, and their molecular sequence structure can be changed suitably by copolymerization or structural derivations. In order to use these polymers in a sensor device, micro-fabrication techniques are employed to form two electrodes separated by a gap of 10 to 20 μm. Then the conducting polymer is electropolymerized between the electrodes by cycling the voltage between them. For example, layers of polypyrroles can be formed by cycling between -0.7 and +1.4 V. Varying the voltage sweep rate and applying a series of polymer precursors yields a wide variety of active materials. Response time is inversely proportional to the polymer's thickness. In order to increase the response times, micrometer-size conducting-polymer bridges are formed between the contact electrodes.The sensors can identify odors at sensitivities of 0.1 parts per million (ppm), but 10 to 100 ppm is more normal.

The main drawback of existing conducting-polymer sensors is that it is difficult and timeconsuming to electropolymerize the active material, so they exhibit undesirable variations from one batch to another. Their responses also drift over time, and their usually greater sensitivity than metal oxides to water vapor renders them susceptible to humidity. This susceptibility can mask the responses to odorous volatile organic compounds. In addition, some odorants can penetrate the polymer bulk, dragging out the sensor recovery time by slowing the removal of the VOC from the polymer. This extends the cycle time for sequentially processing odorant samples.Luo et al.[19] used a commercial preconcentrator system in conjunction with a portable Cyranose 320, consisting of 32 conducting composite polymers, to identify different cigarette brands with 88% overall identification between four brands. The use of a preconcentrator, requires a complex sampling regime. Dutta et al.[20] also used a cyranose 320 for the classification of bacteria responsible for eye infections.The best classification for six bacterial classes tested was 98%. Hopkins and Lewis [21] used an array of composite polymer sensors for the detection of nerve gas analogues di-methyl-methylphosphonate (DMMP),di-isopropyl-methyl-phosphonate(DIMP) in the presence of background VOCs such as benzene, methanol, toluene, lighter fluid, diesel fuel and tetrahydrafuran. Each sensor was 0.7 cm by 2.5 cm and consisted of 1mm separated gold electrodes, spin coated with 1 of 10 different composite polymer solutions.

B. Metal Oxide Semiconductor

The principle operation of metal oxide sensors is based on the change in conductance of the oxide on interaction with a gas and the change is usually proportional to the concentration of the gas. There are two types of metal oxide sensors; n-type (zinc oxide, tin dioxide, titanium dioxide or iron (III) oxide) which respond to reducing gases and p-type (nickel oxide, cobalt oxide) which respond to oxidising gases[22]. The n-type sensor operates as follows: oxygen in the air reacts with the surface of the sensor and traps any free electrons on the surface or at the grain boundaries of the oxide grains.

The MOSFET sensor is a metal-insulator-semiconductor (MIS) device.This particular sensor works on the principle that the threshold voltage of the MOSFET sensor changes on interaction of the gate material, usually a catalytic metal, with certain gases, such as hydrogen, due to corresponding changes in the work functions of the metal and the oxide layers [22].

The thick and thin film fabrication methods have been used to produce metal oxide gas sensors. The metal oxide films are deposited using screenprinting[24], spincoating[25], RF sputtering [26] onto a flat or tube type substrate made of alumina, glass, silicon or some other ceramic. There are various electrode designs but the interdigitated structure appears to be the most common approach. A heating element is printed onto the back of the substrate to provide the high temperatures required for metal oxides to operate as gas sensors, typically 200-5008C.Film thickness ranges from 10 to 300mm for thick film and 6-1,000nm for thin film[27]. The same preparative methods are used to apply the catalytic metal [28,29]. The general response times for tin oxide sensors with gas concentrations between 0 and 400 ppm and at temperatures between 250 and 5008C are 5 to 35s and the recovery times vary from 15 to 70s[28]. The main advantages of metal oxide sensors are fast response and recovery times, which mainly depend on the temperature and the level of interaction between the sensor and gas [29]. Thin film metal oxide sensors are small and relatively inexpensive to fabricate and have lower power consumption than thick film sensors and can be integrated directly into the measurement circuitry[30]. However, they have many disadvantages due to their high operating temperatures, which results in increased power consumption over sensors fabricated from materials other than metal oxides. As a result, no handheld e-nose system has been fabricated utilising sensors prepared from metal oxides[22].

C. Optical sensors

Optical fibre sensor arrays are another approach to odour identification in e-nose systems. The sides or tips of the optic fibres (thickness, 2mm) are coated with a fluorescent dye encapsulated in a polymer. The use of optical sensors for chemical sensing is widespread in many areas[31]. Much of the early work on the use of optical sensors for gas sensing was carried out[32]. Optical sensing is very versatile as it can allow simultaneous collection of intensity and wavelength information, and encompasses a range of techniques (absorbance, reflectance, fluorescence, refractive index and colorimetry). The most popular work on fluorescence[33, 34] was carried out on absorption and colorimetric measurements. The sensitivity depends on the type of fluorescent dye or mixture of dyes and the type of polymer used to support the dye [22].

The nature of the polymer controls the response and the most important factors are polarity, hydrophobicity, porosity and swelling tendency [34, 22]. Adsorbants, such as alumina, can be added to the polymer to improve the response by lowering the detection limits of the sensor[35]. Polyanaline-coated optical sensors have been used to identify ammonia at absorptions as small as 1 ppm and the linear active range was between 180 and 18,000 ppm,[36]. Optical gas sensors have very fast response times, less than 10 s for sampling and analysis[35]. There are several disadvantages of these types of sensors. The associated electronics and software are very complex, leading to increased cost, and the sensors have quite a short lifetime due to photobleaching [34].

D. Piezoelectric Sensor

In 1880, the Curie brothers[37] predicted and demonstrated piezoelectricity, the phenomena by which certain anisotropic crystals, when subjected to mechanical stress, generate electric dipoles.There are two types of piezoelectric sensors used in gas sensing, the surface acoustic wave(SAW) device and the quartz crystal microbalance(BAW). Both types of devices work on the principle that a change in the mass of the piezoelectric sensor coating due to gas absorption results in a change in the resonant frequency on exposure to a vapour[28].

The SAW device is composed of a piezoelectric substrate with an input (transmitting) and output (receiving) interdigital transducer deposited on top of the substrate[38]. The sensitive membrane is placed between the transducers and an ac signal is applied across the input transducer creating an acoustic two dimensional wave that propagates along the surface of the crystal at a depth of one wavelength at operating frequencies between 100 and 400MHz[22]. The mass of the gas sensitive membrane of the SAW device is changed on interaction with a compatible analyte and causes the frequency of the wave to be altered. The substrates are normally prepared from ZnO, lithium niobate or quartz, which are piezoelectric in nature[22].

A BAW sensor is a piezoelectric resonator, often made of quartz with one or both surfaces covered with a sensitive coating (membrane) of a few mm (1mm-10nm) thickness[39], whose chemical and physical (thermal) characteristics are similar to the gas-chromatography stationary phases. The structure is connected to an amplifier to form an oscillator whose three-dimensional waves travel through the crystal[27] at a frequency of 10-30MHz. In the presence of volatile compounds there is a process of adsorption or absorption of the chemical species that alter the physical properties of the membrane and hence affects the resonant frequency of the structure. Because of the response is proportional to the mass adsorbed, this device (a quartz disk sandwiched between two electrodes) is also called quartz crystal microbalance (QMB or QCM)[40] and it was already proposed as a promising sensor for gas detection .

Acoustic sensors have various advantages over other sensors, as high sensitivity and short response time, low power consumption and size and robustness. The sensitivity of the acoustic sensor is related to the operating frequency (SAW: 100MHz-1GHz; BAW:10-30 MHz), and it increases as the square of the fundamental frequency[41]. Disadvantages of acoustic sensors are the temperature and humidity dependence, the difficulty of replacing sensors, the poor reproducibility in the deposition of the coating material [42].

The acoustic sensor applications can be divided between physical and chemical applications[41]. Some physical properties can be measured by acoustic sensors, as temperature, pressure, electric field . The work carried out in the paper[43] used an array of BAW sensors for monitoring composting procedures. The BAWs were coated with 5 imprinted polymers (chosen to be representative of compound groups found in different stages of composting, namely alcohols and terpenes) and a functional polymer for water detection.The array was connected to a composter for continuous on-line measurements. It was found that the results from the array compared favourably with those obtained by gas chromatography-mass spectrometry.

III. CONCLUSIONS

Conducting polymer composite, intrinsically conducting polymer and metal oxide conductivity gas sensors, SAW and BAW piezoelectric gas sensors, optical gas sensors and MOSFET gas sensors have been reviewed in this paper. These systems offer excellent discrimination and lead the way for a new generation of “smart sensors” which will mould the future commercial markets for gas sensors. The theory of operation, fabrication methods, merits, demerits and applications of each sensor type in e-nose systems have been discussed.

REFERENCES

[1] H. Ulmer, J. Mitrovics, G. Noetzel, U. Weimar, and W. Gopel, "Odours and vapours identified with hybrid modular sensor systems," *Sensors and Actuators B*, vol. 43, pp. 24-33, 1997.

[2] Niessen, W. M. A (2001) "Current Practices of GC/Mass spectrometry," New York:Marcel Dikker, ISBN 0-8-247-0473-8.

[3] J.S. Kauer, Contributions of topography and parallel processing to odour coding in the veterbrate olfactory pathway, Trends Neuroscience, 14 (1991) 79-85.

[4] J.W. Gardner, P.N. Bartlett, "A brief history of electronic noses ," *Sens. & Actuators B* 18–19 (1994) 211–220.

[5] Vu licevic, I.R, E-S. M Abdel-AAl, G.S Mittal, X Lu "Quality and storage life of par-baked frozen breads", *LWT-Food Science and Technology*, vol 37, Issue 2 (2004), pp 205-213.

[6] Pecore, S, Kellen, L (2002) "A consumer- focused QC/sensory program in the food industry," *Food Quality and Preferences*, 13(6), 369-74.

[7] Morales, M.T., & Tsimidou, M. (2000) "The role of volatile compounds and polyphenols in olive oil sensory quality," In: J. Harwood & R. Aparicio-Ruiz (Eds.) *Handbook on olive oil: Analysis and properties* (pp. 393–458).

[8] Persaud, K. C., & Dodd, G. H. (1982), "Analysis of discrimination mechanisms of the mammalian olfactory system using a model nose," *Nature*, 299, 352-355.

[9] J.W.Gardner, E.L.Hines, C. Pang, "Detection of vapours and odors from a multisensory array using pattern recognition:self organizing adaptive resonance techniques," *Measurement and control* 29 (1996) 172-177.

[10] J. Janata, Principles of Chemical Sensors, Kluwer Academic Publishing Plenum, Dordrecht, 1989.

[11] A.Ikegami and M. Kaneyasu , "Olfactory detection using integrated sensors", *Proc. 3rd Int. Conf. Solid-State Sensors and Actuators (Tranducers'85), Philadelphia, PA, USA, June 7-11, 1985*, pp. 136-139.

[12] M. Kaneyasu , A.Ikegami, H.Arima and S. Iwanga, "Smell identification using a thick-film hybrid gas sensor", *IEEE Trans. Components,Hybrids Manufact.Technol., CHMT-10* (1987) 267-273.

[13] J. Hesse, J. W. Gardner, and W. Göpel, Sensors in Manufacturing, Sensors Applications, Vol. 1, Wiley-VCH, Dordrecht, 2001 - ISBN 3-527-29558-5.

[14] P.N. Bartlett, S.K. Ling-Chung, "Conducting polymer gas sensors Part II. Response of polypyrole to methanol vapours," *Sens. & Actuators, B, Chem.* 20 (1989) 287-292.

[15] A. G. MacDiarmid, Polyaniline and polypyrrole: where are we headed? Synth. Met. 84 (1997) 27-34.

[16] *De Wit, E. Vanneste, H.J. Geise, L.J. Nagels*, “Chemiresistive sensors of responses to nine organic vapours,” *Sensors and Actuators B*, vol. *50, 1998*, pp. *164-172.*

[17] J. A. Covington, J. W. Gardner, D. Briand and N. F. de Rooij, " A polymer gate FET sensor array for detecting organic vapours," *Sensors and Actuators B*, 77, pp. 155-162, 2001.
[18] "Selective Detection of Aroma Components by Acoustic Wave Sensors Coated with Conducting Polymer Films", Z. Deng, D. C. Stone and M. Thompson, *Analyst*, 1996, 121, 671-679.
[19] Luo D, Hosseini H.G, Stewart J.R " Application of ANN with extracted parameters from an electronic nose in cigarette brand identification," *Sensors and Actuators B-Chemical* 2004 Volume: 99 Issue: 2-3 pp 253-257.
[20] Dutta **R,** Evor L Hines**,** J. W Gardner **,** P. Boilot " Bacteria classification using Cyranose 320 electronic nose," BioMedical Engineering OnLine, 1:4.
[21] Hopkins A.R, Lewis N.S " Detection and classification characteristics of arrays of carbon black/organic polymer composite chemiresistive vapor detectors for the nerve agent stimulants, dimethylmethylphosphonate and diisopropylmethyl -phosponate," *Anal.Chem* 2001 73:884-892.
[22] T. C. Pearce, S. S. Schiffman, H. T. Nagle, J. W. Gardner, Handbook of Machine Olfaction, Wiley-VCH, Dordrecht, 2003 - ISBN 3-527-30358-8.
[23] Eisele I. ,Doll, T. and Burgmair, M. (2001), : Low power gas detection with fet sensors", *Sensors and Actuators B:Chemical* ,vol 78 No.1-3, pp. 19-25.
[24] Schmid, W., Barsan, N. and Weimar, U. (2003), "Sensing of hydrocarbons with tin oxide sensors:possible reaction path as revealed by consumption measurement", *Sensors and Actuators B: Chemical*, vol 89 No. 3, pp. 232-6.
[25] Hamakawa, S., Li, L. , Li, A. and Iglesia,E.(2002) "Synthesis and hydrogen permeation properties of membranes based on dense scre0.95yb0.0503-[alpha]thin films," *So;id State Ionics*,vol.148 No. 1-2, pp.71-81.
[26] Tao, W.H. and Tsai, C-H.(2002) "H2s sensing properties of noble metal doped wo3 thin film sensor fabricated by micromaching," *Sensors and Actuators B: Chemical*, vol 81, No. 2-3, pp.237-47.
[27] Schaller, E., Bosset, J.O and Escher, F. (1998), "Electronic noses and their application to food," *Lebensmitted Wissenschaft und-Technologie*, vol. 31 No. 4, pp. 305-16.
[28] Albert, K.J and Lewis, N.S (2000), "Cross reactive chemical sensor arrays," *Chem. Rev.*, vol 100, pp. 2595-626.
[29] Penza, M. , Cassano, G.and Tortorella, F. (2001 b), "Gas recognition by activated thin film sensors array," *Sensors and Actuators B: Chemical*, vol. 81 No.1, pp. 115-21.
[30] Dai, G.(1998), "A Study of the sensing properties of thin film sensor to trimethylamine," *Sensors and Actuators B: Chemical*, vol.53 Nos. 1-2, pp. 8-12.
[31] Wolfbeis, O.S, Schaferling M, Durkop, A.(2003) *Microchim.Acta.* 143:221.
[32] Dickenson T.A,White J.Kauer J.S, Watt D.R (1996) , *Nature* 382:697.
[33] Di Natali C, Salimbeni D, Paolesse R, Macagnano A, D'Amico A (2002) *Sensors and Actuators B: Chemical*, 65:220
[34] Rakow N.A, Suslick K.S (2000) *Nature* 406:710.
[35] Walt, D.R. , Dikenson, T. , White , J. Kauer, J., Johnson, S., Engelhardt, H., Suller, J. Jurs, P. (1998), "Optical sensor arrays for odor recognition," *Biosensors and Bioelectronics*, vol. 13 No.6, pp. 697-9.
[36] Jin Z., Su, Y. and Duan, Y. (2001) "Development of a polyaniline-based optical ammonia sensor," *Sensors and Actuators B:Chemical*, vol. 72 No. 1, pp. 75-9.
[37] Curie , J., Curie, P. (1980) Bull Soc. *Min Paris* 3:90.
[38] Khlebarov, Z.P. , Stoyanova, A. I. and Topalova, D.I., (1992), "Surface acoustic wave gas sensors", *Sensors and Actuators B:Chemical*, vol. 8 No. 1, pp. 33-40.
[39] D'Amico A.V , Cooper, M.S,Cooper, M.S., "Spatially distinct domains of cell behavior in the Zebrafish organizer region," *Biochem.cell Biol.* 75:563-577.
[40] Ferrari, V.Marioli,D., Taroni, A., Ranucci, E. (2000) "Multisensor array of mass microbalances for detection based on resonant piezolayers of screen printed P2T," *Sensors and Actuators B:Chemical*, vol.68, 81-87.
[41] Ballantine,D.S.,Wohltjen, H.(1989) "Surface acoustic wave,Devices for chemical for chemical analysis," *Anal.Chem.*, 61, 11, 704-715.
[42] Mielle, P. (1996) " Electronic noses: Towards the objective instrumental characterization of food aroma," *Food Sci. Technology*, vol. 7, 432-438.
[43] Dickert, F.L., Hayden, O., Zenkel, M.E. (1999) "Detection of volatile compounds with mass sensitive sensor arrays in the presence of variable ambient humidity," *Anal. Chem.* 71, 1338-1341.

Syeda Erfana Zohora received her B.E. Degree in Computer Science & Engineering from Mysore University, Karnataka, India & M.S. in Software Systems from BITS, Pilani, Rajasthan. She is pursuing her Ph.D Degree from Mangalore University, Mangalore and currently working in the College of Computers and Information Technology, Taif University, Taif, KSA. Her research interest are Artificial Neural Networks, Support Vector Machine and Genetic Algorithms.

A.M.Khan received his Ph.D degree in Electronics from Mangalore University, Mangalore, Karnataka, India. He is presently working as a Professor in the Electronics Dept., Mangalore University, Mangalore.. His research interest are Artificial Neural Networks , Machine Learning and Digital Image Processing.

A.K.Srivastava received his Ph.D degree in 1999 from Banaras Hindu University, India. He is presently working as Chief Technology Officer, LightField Corporation Philadelphia, PA, USA. His research interest are Artificial Neural Networks, Genetic Algorithms, Nano Sensors.

Nisar Hundewale received his Ph.D degree in 2007 from Georgia State University, USA. He is presently working as Assistant Professor in the College of Computers and Information Technology, Taif University Taif, SA. His research interest are Machine Learning, Bioinformatics and Algorithms.