ELECTRONIC NOSE BASED ON METAL OXIDE SEMICONDUCTOR SENSORS AS AN ALTERNATIVE TECHNIQUE FOR PERCEPTION OF ODOURS

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ABSTRACT
This world is divided into natural and man-made objects. The natural sensors, like those found in living organisms, usually respond with signals, having an electrochemical character; that is, their physical nature is based on ion transport, like in the nerve fibres. In man-made devices, information is also transmitted and processed in electrical form—however, through the transport of electrons. Sensors that are used in artificial systems must speak the same language as the devices with which they are interfaced. This language is electrical in its nature and a man-made sensor should be capable of responding with signals where information is carried by displacement of electrons, rather than ions. Thus, it should be possible to connect a sensor to an electronic system through electrical wires, rather than through an electrochemical solution or a nerve fibre. Chemical sensors respond to stimuli produced by various chemicals or chemical reactions. These sensors are intended for the identification and quantification of chemical species (including both liquid and gaseous phases; solid chemical sensors are not common. In this paper an effort has been made to study the "Electronic Noses" that will combine advanced sensors and sensor array.

KEY WORDS: *e-noses, sensors, ANN, microcontroller, LabVIEW.*

I. INTRODUCTION

Electronic noses or *e-noses* are less a sensor or instrument and more a *measurement strategy*. Electronic noses have become popular and combine advanced sensors and sensor array strategies with chemometrics techniques to produce a broad range of intermediate instruments and analyzers. Early e-noses tried to duplicate the behaviour and capability of human odour sensing. They combined different sensor types to represent the different cell tissues in the nasal cavity and they took the approach of detecting an odour as a collection of individual chemicals. The name "odour sensor" is used instead of "gas sensor" whenever its sensitivity approaches that of a human.

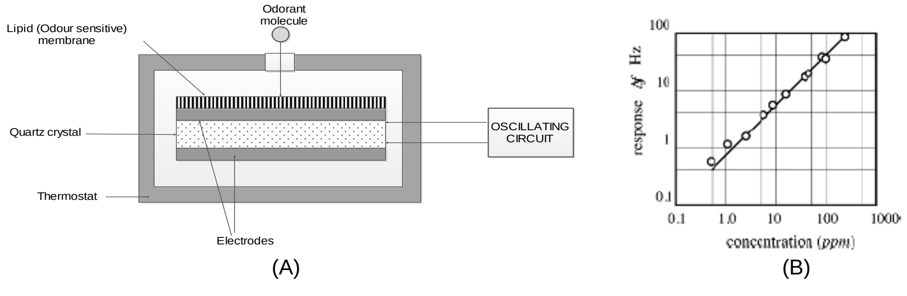

Fig. 1. Microbalance odour sensor (A) and its transfer function (B) for amyl acetate gas.

Odour and fragrance sensors find applications in forensic science, quality assurance in the cosmetic and food industry, environmental control, and so forth. All methods of odour measurements can be divided into four groups: *instrumentational analysis, semiconductor gas sensors, membrane potential type odour sensors*[1] and the *quartz microbalance method*. In general, it is based on a shift in natural frequency of a quartz crystal coated with an odour-sensitive membrane and the subsequent measurement of the shift (Fig. 1). This can be measured by electronic means and correlated with the odourant concentration. Potentially, this method has the possibility of performing with human like characteristics and sensitivity because the same membrane as the human olfactory (lipid membrane) can be used as the odourant-absorptive media of the sensor.

Olfactory cells or odour receptors of humans are covered with a phospholipid bilayer membrane, which is a kind of lipid membrane. It is believed that odourant molecule adsorption into the membrane induces nerve pulses. Using this as an analogy, a man-made odour sensor uses a composite membrane consisting of PVC, a plasticizer, and synthetic lipid[2]. The synthetic lipid molecules are randomly oriented in the polymer matrix. To produce a sensor, a quartz crystal was cut to 14 mm in diameter. Then, the lipid composite was prepared as a solution of organic solvent (tetrahydrofuran), PVC, plasticizer (dioctyl phenyl phosphonate), and synthetic lipid(dioctil phosphate, decyl alcohol, and other lipids can be employed). The membranes formed with a thickness of 200 µm on one side of the resonator by using the spin coating method. The membrane blend is selected to maintain the quality factor of the resonator *(Q)* on the level of at least $5x10^4$.

The experimental curve of the transfer function indicates that the response was detectable starting from 1 ppm concentration, which is approximately equal to the human threshold, and was linear up to a concentration of about 3000 ppm. Such a sensor has a quite fast response time—within 1sec. Newer approaches to e-nose development involve more flexible combinations of sensor designs and signal processing. The performance of these e-noses is measured more by how many compounds they can distinguish at nominal low ppm levels and less by their sensitivity and detection limit for a specific compound. Because most chemical sensors are affected by both humidity and temperature, sensors for such conditions are often included in the e-nose array[3]. One example of an experimental Chemical Sensors e-nose employed a set of nine simple, but specialized, commercial tin-dioxide gas sensors. Each metal-oxide device was doped, making the metal oxide more specific to a particular gas species. The simple time-based conductivity change responses from the devices were collected into an array response, as shown in Fig. 2.

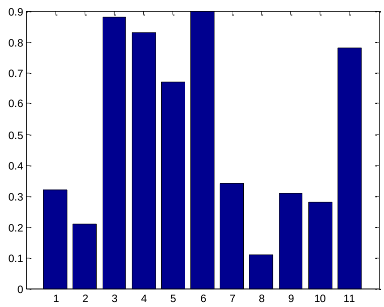

Fig. 2. Metal-oxide e-nose response array.

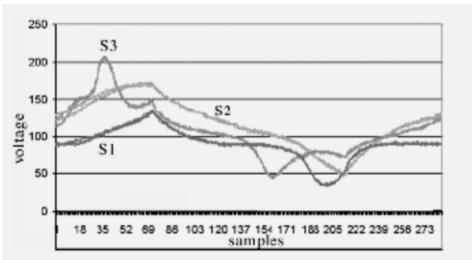

Fig. 3. Background air readings from each of the three sensors.

The combination of devices could differentiate common office chemicals such as contact cement, paint thinner, glass cleaner, and alcohol. Using these collections of sensors experiments achieved up to a 98% accuracy identification rate.

Another example electronic nose developed for fire detection employed a complementary strategy: combining fewer but more complex sensors in a smaller array[4]. The signatures from three electrochemical sensors were very different, as shown in Fig. 3, and were fused to produce a complex temporal array signature. These solid electrochemical sensor arrays were used to characterize various combustible materials commonly found on naval ships such as wood, wallboard, cleaning fluid, plastics, food, bedding materials, and fabrication shop operations such as welding. The approach employed a time-offset signature series, where the change in signatures was monitored over time as opposed to the *static* signature. Using this approach, the miniature-array e-nose was able to correctly identify 14 different types of fire with a confidence of between 70% and 100%. The combination of different types of chemical sensor (from only a couple to tens of devices) allows overlaps in their respective detection ranges to complement each other, producing higher-quality detection from simpler, less selective sensors than any individual sensor could achieve on its own. A generalized but also complete and functional model for an e-nose can be constructed that includes both simple and complex chemical sensors, along with ancillary sensors such as temperature, humidity, and barometric pressure to measure the effects of these variables on the chemistry.
For most problems, the output will be mapped to specific categories, including an "unknown" category for samples which are detected, but do not fall into existing categories within some predetermined level of confidence. Such a model is shown in Fig. 3.

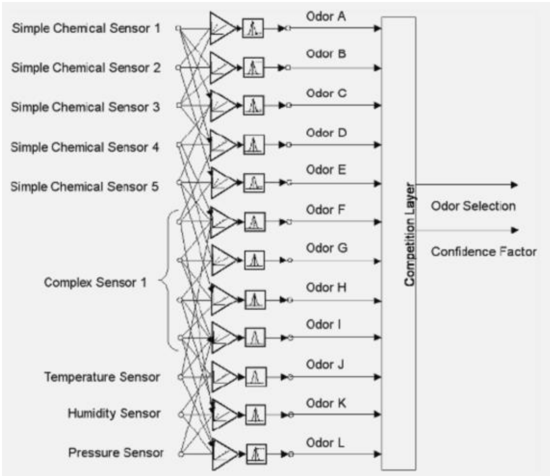

Fig. 4. Generalized e-nose model (for simplicity, only a portion of the sensor connections are represented; the full model would include connections from *all* sensors to *all* categories).

This detection/sensing model is particularly appropriate for identifying complex mixtures and ratios of chemical constituents as a group, rather than isolating and quantifying any particular single-gas species. Because of this fundamental underlying strategy, e-noses are particularly popular in food industry and process control, where they are used to categorize beverages, grade the quality of extracts, and even determine the age and expiration dates of produce. These are tasks that historically are very subjective and qualitative when performed by a human expert, but become far more reproducible when performed by an e-nose.

II. Neural Network Signal (Signature) Processing For Electronic Noses

Active array devices like an e-nose produce complex signals or "signatures," which have to be processed to extract the desired chemical species component information. It is natural and effective to pair e-nose signals with neural network classification and analysis methods that similarly mimic biological systems [4].

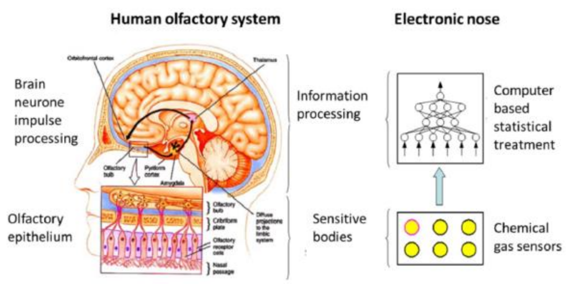

Fig. 5. Human olfactory and Electronics Nose

Neural network algorithms can duplicate the more preferred chemometrics pattern recognition methods, such as Bayesian classifiers, providing provable and statistically measurable confidence in their results. Neural methods execute simple mathematical operations in a highly parallel fashion and lend themselves to scalable execution from low-cost microcontrollers.

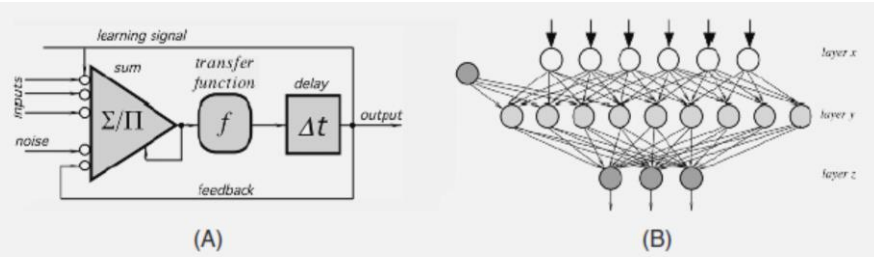

Fig.6. Generalized neuron model (A) and layers combined into a network (B).

A neural network is inspired by and loosely models the architecture and information processing capability of the biological brain[5]. An A*rtificial Neural Network*(ANN) accomplishes this by simulating each biological neuron with an integrated circuits a collection of gates and transistors, whereas a *Computational Neural Network*(CNN) accomplishes this through execution of a series of computer instructions. *Neural Networks*(NN) can be structured to perform classification[6], to approximate equations[7], and to predict values[8,9]. Several different models for neurons are available; each supports a different range of network architectures and artificial learning methods. A generalized neuron model (Fig. 6.A) includes some input stage with variable weighted interconnections to the outputs of other neurons, a summation/comparison stage for combining the weighted inputs, a transfer function that reduces the information passed along through the neuron, an output stage that connects to the inputs of other neurons, and some feedback/training method to adjust the weights so that a desired output is produced when exposed to known inputs. Some network architectures require an optional delay stage to support adaptive learning.
A generalized network architecture (Fig. 6.B) includes an input layer *x* that interfaces directly to the sensor signals, a hidden layer *y* that reduces information, makes intermediate choices, and performs feature extraction, and an output layer *z* that selects intermediate answers and provides the classification or component analysis information. In a generic architecture, neurons are referred to as nodes, and inter node connections are only made between adjacent layers.
Electronic noses generally pursue composite odour classification, with component analysis representing a more difficult secondary goal. *Probabilistic Neural Network* (PNN) classifiers are the most popular CNNs used with electronic noses. They duplicate the functionality of K-nearest neighbour or Bayesian statistical classifiers, though the NN versions often outperform both[10]. The PNN uses a radial basis function neuron and competitive hidden layer network architecture. PNNs require supervised training where a set of inputs is constructed that has predetermined desired outputs(categories). During training, a new neuron is constructed for each sample in the training set. The weights between the inputs and the competitive neuron are copies of the input values themselves. The output of each neuron goes to a matching category in the final competitive output layer. Multiple examples of a given input/output pairing create additional copies of a neuron and strengthen the

possibility of selection for that category, reflecting statistical probabilities of that category's occurrence in a population-hence, the name "probabilistic" neural network[6].

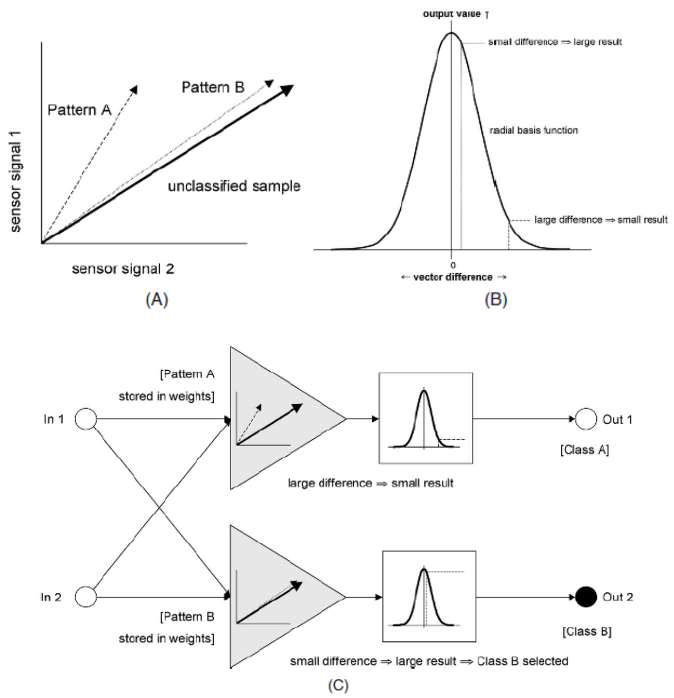

Fig. 7. Vector comparison (A), radial basis function (B), and PNN layers (C).

During the operation of a PNN, a vector containing the input values is presented to each neuron in the input layer. Each neuron compares the input vector and the vector formed from its own local set of weights by computing a Cartesian distance between the vectors (Fig. 6A). Internal to each neuron, the distance is then passed through the local radial basis transfer function (a Gaussian bell curve centred on input = 0 to produce an output = 1) that outputs a high value for small distances (differences) and very small values for larger distances (Fig. 6B). The result is that the neuron whose weights most closely match the input vector produces the highest final output value, and the output layer assigns the input to that category (Fig. 7C). The options for training PNNs vary with trade-offs among flexibility, memory resource use, and speed of training.

III. "SMART" CHEMICAL SENSORS

Many other chemical sensors, both commercial and experimental, employ a growing variety of phenomena and strategies. Trends in microelectronics and programmable controllers will lead to the production of "*smart*" chemical sensors. The future of chemical sensors lies in these smart devices. A smart sensor incorporates some level of the data processing into the sensor directly, distributing some of the intelligence of the instrument and allowing functional and useful systems to be designed with lower intelligence required in the instrument[11-13]. A smart *chemical* sensor should include inter device communication and local drift and recalibration capabilities so that remote polling control systems would only receive measurements. A smart chemical sensor may also perform routine unit conversion (i.e., from % to ppm) and report different units to different requests. In this way, the same (smart) sensor can provide a measurement to different hosts without requiring any of them to introduce any additional scaling of their own; they work with whatever local units they chose.

IV. ELECTRONIC NOSES AND SENSORS

The technique, so called electronic nose, allows continuous monitoring of volatile compounds. These electronic devices incorporate three elements: *the odour sensor array*, the *data pre-processor*, and the *data interpretation engine*. The detection system of the electronic noses, which consists of a sensor set, is the "reactive" part of the instrument. When in contact with volatile compounds, the sensors react by changing electrical properties. A range of gas sensor technologies can be used in electronic noses. Each sensor possesses some form of chemically active material. These include metal-oxide semiconductors, metal-oxide-silicon field effect transistors (MOSFETs), conducting polymers, surface-acoustic-wave devices, quartz resonators and fibre-optic chemical sensors [14].

Fig. 8. Metal-oxide semiconductors (MOS) sensors

Volatile compounds interact with the sensor array, producing a unique time-dependent electrical signal. In fact, the molecules interacting with the sensor's surface modify its resistance, which can be measured and used as representative information of the odourous sample. The responses generated by the sensor array are analysed using complex statistical analysis techniques. Electronic noses have been applied in numerous fields. The electronic nose has been extensively used in laboratories and research programs of many types. Most applications have been in the food industry but, recently, other activities, such as environmental monitoring and medical diagnosis, have been studied. Examples of applications using an electronic nose conducted in environmental monitoring are: the assessment of odours from livestock wastes, the monitoring of waste water quality or the identification of malodorous sources, the monitoring of odour emissions from wastewater treatment plants, composting and landfill sites.

V. The Proposed E-Nose System

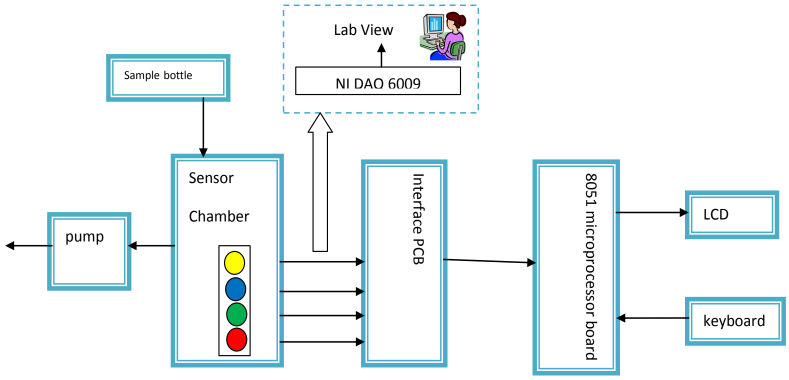

Fig. 9. Block diagram of the proposed E-Nose system.

Figure.9 shows a block diagram of the proposed E-Nose system, comprising a sensor array, an interface printed circuit board (PCB), and an 8051 microcontroller board embedded with a pattern recognition algorithm, as well as a verification program. Sensor responses pass through a data acquisition card (DAQ) to a PC with a self-developed LabVIEW program for the purpose of verifying the function of the portable E-Nose system.

5.1 Sensors

One approach to developing a chemical sensing system is to mimic mammalian olfaction. Over 1,000 different receptor genes have been identified in the olfactory system of mammals. Learning from the mammalian system, an array of different sensors is used for odour identification, with each sensor designated to respond to a number of different chemicals. In such an array, no individual sensor responds solely to a specific odour. Rather, the collective response of the entire array produces a unique pattern for the odour of interest. Ideally, to respond to the largest cross-section of analytes, the elements of the sensor array have to possess as much chemical diversity as possible. Within the range of this diversity, the sensor array produces a distinct pattern, taken as an odour signature (odour fingerprint), that can be utilized for odour classification and identification[14].

This operational principle has the advantage of being able to identify and classify a complex mixture of odours, such as those of fruits, over a one-to-one sensing mode (each sensor responds to a specific odour). In practical applications, odours of interest are usually complex mixtures, rather than pure gases. The fragrance of a fruit, for example, is a complex combination of dozens of individual scents. This complexity makes it almost impossible to find sensors corresponding to every individual component of gas mixture. For instance, banana aroma comprises several ester groups, and litchi contains higher amounts of monoterpene hydrocarbons in its scent. The odour thresholds of the human nose to these gaseous constituents generally fall in the range of Parts Per Billion(ppb). However, a number of researchers have shown that an electronic nose could classify fruit very nearly as well as a panel of tasters. In this manner, an E-Nose could be useful for the classification of the odour of fruits.

Table-I lists the eight commercial FIGARO®sensors that form the sensor array. The typical sensing material of the FIGARO® TGS gas sensors is tin oxide (SnO_2). When SnO_2 is heated to a specific temperature in the air, oxygen is adsorbed and electrons accumulate on the crystalline surface. These electrons are transferred to the absorbed oxygen, resulting in a positive charge remaining within a space charged layer. As a result, surface potential is created, which serves as a potential barrier to the free exchange of electrons, which would result in a change in resistance. In the presence of deoxidizing gas, the density of the negatively-charged oxygen at the surface would decrease, thus lowering the barrier height and resistance. Three sets of identical sensors were incorporated (TGS822, TGS825, and TGS826) in the sensor array for the following reasons:

(1) To increase the effectiveness of the sensor: For example, if TGS822 responds to a specific odour, two responses could be recorded, due to the presence of two of the same kind of sensors.

(2) To investigate the behaviour of identical sensors: Sensors of the same kind may not necessarily behave in exactly the same way. This behaviour was investigated during the experiment.

(3) In the future, algorithms will be incorporated to average the signals among identical sensors to tune out background noise and interference from temperature or humidity.

Table 1. The eight FIGARO® **sensors to form sensor array**

Sensor number	Sensor Type	Target gas (according to FIGARO ® datasheet)
1	TGS2620	Alcohol, Solvent vapours
2, 5	TGS826	Ammonia
3, 6	TGS822	Alcohol, solvent vapours
4, 8	TGS825	Hydrogen sulfide
7	TGS2602	General air contaminants

5.2 Interface PCB

Because the array consists of eight sensors, the interface PCB includes eight *Interface Processing Circuits* (IPC), an eight to one multiplexer (MUX), and an 8-bit analog-to-digital converter (ADC). The eight interface processing circuits are connected to the eight sensors, which actively adapt the circuit to a preset baseline voltage. The multiplexer reduces the need for multiple ADCs by scanning the eight channels and choosing one channel at a time. The ADC converts sensor data into a digital form for data processing. Figure 10(a) shows a block diagram of the interface PCB. Figure 10(b) shows the basic architecture of the interface processing circuit (IPC), which operates in one of the two following modes:

(1) *Adaptation mode*: in this mode, the circuit adjusts its operating point to a preset base line voltage. The multiplexer chooses path “1” in Figure 10(b), to equalize the output voltage with the reference voltage V_{ref}, which is set as the baseline value prior to sensing odours. In this mode, the NMOS transistor operates as a variable current source. At the end of the adaptation mode, the circuit enters the sensing mode, the gate voltage of the transistor becomes stable, and the transistor operates as a

constant current source. After completing the adaptation mode, the E-Nose system is ready to accept input gas.

(2) *Sensing mode*: in this mode, the circuit is ready for sensing. The multiplexer chooses path “0” in Figure 10(b), to form a negative feedback loop, which establishes the gate voltage of the NMOS. Due to a large time constant $R_{fb}C_{fb}$, the gate voltage of the NMOS can be maintained a long enough time, comparing with the sensor response time. As a result, the IPC responds to the sensor while tuning out background signals; which is similar to the process performed by biological noses. In this mode, variations in the sensor resistance are translated to a change in output voltage, which is fed into an ADC through an eight to one MUX, where upon, the ADC output is send to the 8051 microprocessor.

5.3 8051 Microcontroller

The 8051 microprocessor was chosen from the many available, for two reasons:

(1) The ability to perform mathematical calculations, *i.e.*, it can perform algorithms to a certain extent, provided the algorithms are not too complicated.

(2) The availability of open source software tools and 8051 microcontroller is available as an open source module. It is capable of handling necessary signal processing and process classification algorithms; it can also be integrated in a future system-on-chip (SoC) design.

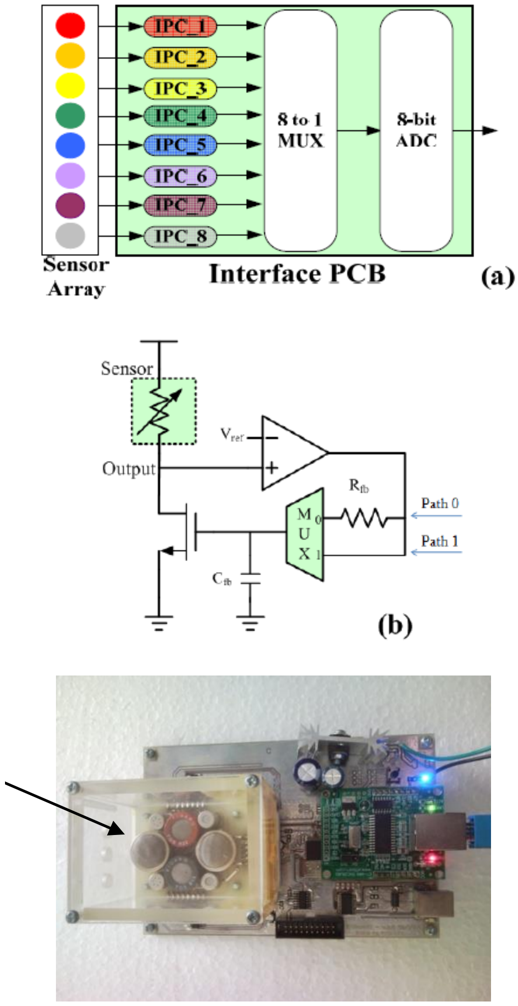

Fig. 10. (a) Block diagram of the interface PCB; **(b)** Basic architecture of the IPC; **(c)** Photograph of e-nose with interface.

After receiving the signal from the ADC, the 8051 microprocessor processes the sensor data. Before gas enters the system, the 8051 microprocessor reads the sensor resistance as its baseline resistance R_b. When the gas flows into the chamber, the 8051 determines the steady-state value of the sensor resistance R_{sense}, and calculates the percentage ratio of resistance change $(R_{sense} - R_b)/R_b$. The collective resistance change ratios of the eight sensors form a pattern according to the input odour, and the 8051 takes this odour pattern into one of its two operational modes, namely, training mode or testing mode. A K-Nearest Neighbour (KNN) algorithm is embedded in the 8051 to perform odour classification.

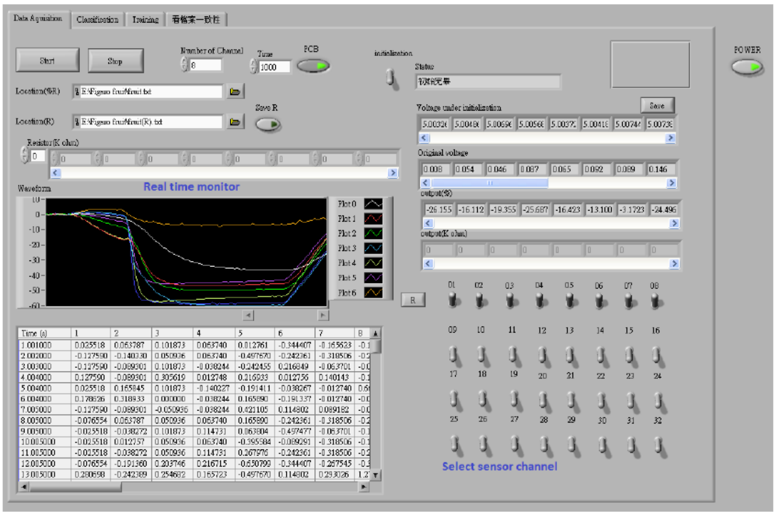

Fig. 11. Operating window

5.4 Sensor Data Acquisition and Odour Classification Interface

Running parallel to the 8051 microprocessor, sensor data enters a laptop computer through a National Instrument Data Acquisition card (interface card: NI DAQ 6009), with a LabVIEW program developed for this study, to characterize sensor and odour data and verify possible classification algorithms. Three data processing interfaces were developed to operate the E-Nose system. These include a data acquisition interface, a training interface, and a classification interface. Fig.11 shows a screenshot of the operating window of the program.
The data acquisition interface records changes in sensor resistance, and plots the change ratio of sensor resistance $\Delta R/R$ ($\Delta R = R_{sense} - R_b$) in real-time. The recorded data builds pattern recognition models for performing classification in the other two interfaces. The training interface uses data stored by the data acquisition interface, to build a classification model, which is used to recognize odours in the classification interface. A radar plot of the odour is shown by the interface for the user to observe.

VI. APPLICATIONS

Electronic nose instruments are used by research and development laboratories, quality control laboratories and process and production departments for various purposes:
In quality control laboratories for at line quality control such as:

- Conformity of raw materials, intermediate and final products
- Batch to batch consistency
- Detection of contamination, spoilage, adulteration
- Origin or vendor selection
- Monitoring of storage conditions.

In process and production departments

- Managing raw material variability
- Comparison with a reference product
- Measurement and comparison of the effects of manufacturing process on products
- Following-up cleaning in place process efficiency
- Scale-up monitoring
- Cleaning in place monitoring.

Possible and future applications in the fields of health and security:

- The detection of dangerous and harmful bacteria, such as software that has been specifically developed to recognise the smell of the MRSA (Methicillin-resistant Staphyl-ococcus Aureus). It is also able to recognise methicillin susceptible S. aureus (MSSA) among many other substances. It has been theorised that if carefully placed in hospital ventilation systems, it could detect and therefore prevent contamination of other patients or equipment by many highly contagious pathogens.
- The detection of lung cancer or other medical conditions by detecting the VOC's (volatile organic compounds) that indicate the medical condition.
- The quality control of food products as it could be conveniently placed in food packaging to clearly indicate when food has started to rot or used in the field to detect bacterial or insect contamination.
- Nasal implants could warn of the presence of natural gas, for those who had anosmia or a weak sense of smell.
- The Brain Mapping Foundation used the electronic nose to detect brain cancer cells.

Possible and future applications in the field of crime prevention and security

- The ability of the electronic nose to detect odourless chemicals makes it ideal for use in the police force, such as the ability to detect drug odours despite other airborne odours capable of confusing police dogs. However this is unlikely in the meantime as the cost of the electronic nose is too great and until its price drops significantly it is unlikely to happen.
- It may also be used as a bomb detection method in airports. Through careful placement of several or more electronic noses and effective computer systems you could triangulate the location of bombs to within a few metres of their location in less than a few seconds.

In environmental monitoring

- For identification of volatile organic compounds in air, water and soil samples.
- For environmental protection.

Various application notes describe analysis in areas such as flavor and fragrance, food and beverage, packaging, pharmaceutical, cosmetic and perfumes, and chemical companies. More recently they can also address public concerns in terms of olfactive nuisance monitoring with networks of on-field devices. Since emission rates on a site can be extremely variable for some sources, the electronic nose can provide a tool to track fluctuations and trends and assess the situation in real time. It improves understanding of critical sources, leading to pro-active odour management. Real time modeling will present the current situation, allowing the operator to understand which periods and conditions are putting the facility at risk. Also, existing commercial systems can be programmed to have active alerts based on set points (odour concentration modeled at receptors/alert points or odour concentration at a nose/source) to initiate appropriate actions.

VII. CONCLUSION

Measurements of various fruit odours show that the electrochemical gas sensors have different selectivity, sensitivity, and repeatability and can discriminate various odours. The intensity of the responses of the sensors is highly correlated with the vapour pressure and the concentration of individual analyte. The higher the concentration of the analyte, the higher the responses of sensors, and response curves are linear for the various analytes. E-Nose systems that rely on array-based sensing require some type of training set and data-processing algorithm in order to classify an analyte upon presentation to the sensor array. In this respect, the performance and range of applicability of such sensor arrays are intimately coupled to the data reduction algorithms and the computational capabilities required to achieve the sensing task of concern. The linear concentration dependence of the detection response is ideal for the minimum possible training set and the minimum requirements on computational capabilities to classify a particular analyte. The prototype has been tested with three complex odours viz. Apple, Banana and Litchi and achieved classification accuracy in excess of 90%.

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