Review

Chemical Sensors for Electronic Nose Systems

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Abstract. Chemical sensors have been widely used for the analysis of volatile organic compounds. Employing chemical sensors in an array format with pattern recognition provides a higher degree of selectivity and reversibility leading to an extensive range of applications. When such systems are used for odour analysis they are termed 'electronic noses'. Application of electronic noses ranges from the food industry, medical industry to environmental monitoring and process control. Many types of different gas sensors have been employed in the array. These include conducting polymers, metal oxide semiconductors, piezoelectric, optical fluorescence and amperometric gas sensors The transducer principle of these sensors is varied and is discussed in detail within this review. Examples of the current trends in sensor array technology as well as the applications to which the sensor-based noses have been applied are also discussed.

Key words: Electronic noses; chemical sensors.

Sensory evaluation using the human sense of smell is subjective; careful design and rigorous training of assessors [1, 2] allows it to become a more objective, but still expensive option. Instrumental methods of determining odours, such as gas chromatography/mass spectrometry (GC/MS), are also expensive and re-

quire trained personnel. As a result there has been a drive to establish a device for rapid inexpensive analysis of volatile organic compounds (VOCs), which does not require specialist technicians. Ideally the device should be portable, allowing direct on-line or offsite measurements. The device should be less prone to drift, and more consistent than sensory assessment, but the responses must be correlated with sensory techniques [3–6].

Persaud and Dodd [7] first reported the design of an electronic nose (E-nose) using chemical sensors and pattern recognition in 1982. Chemical sensors are transducers that incorporate a chemical detection layer and transform a chemical interaction into an electrical signal. They are also usually capable of continuous measurements and are generally inexpensive. Gas sensors operate by binding molecules to the device surface through one or more mechanisms including adsorption, absorption, chemisorption and co-ordination chemistry. The choice of binding mechanism has important implications for the selectivity and reversibility of the sensing system. Chemisorption is preferred when a highly selective system is required. The high binding strength will, however, result in poor reversibility. Weaker adsorptive interactions are preferred for good reversibility but as a consequence the selectivity is poor. The ideal gas sensor would exhibit reliability, robustness, sensitivity, selectivity and reversibility. As high selectivity with high reversibility is difficult to

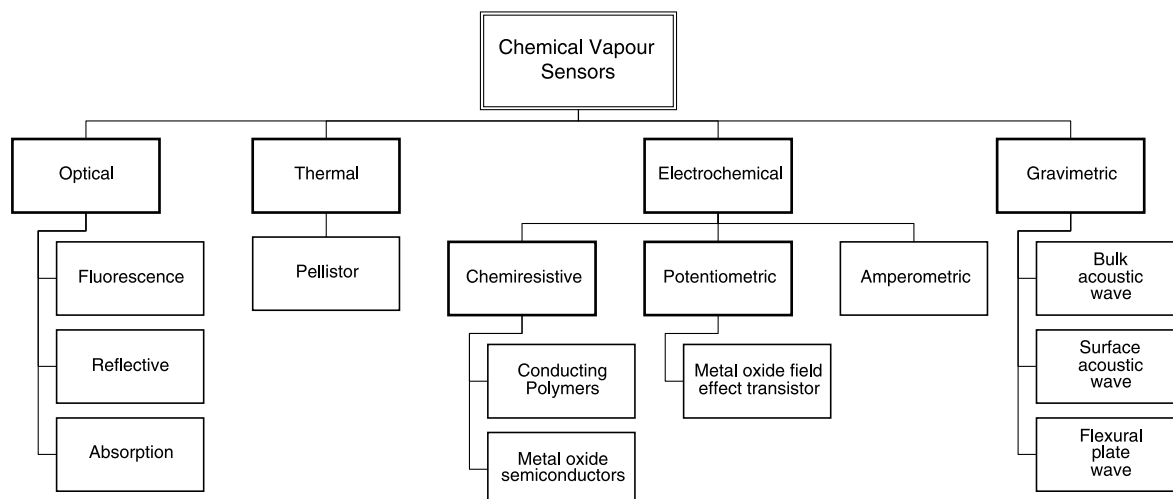* Author for correspondence. E-mail: z.ali@tees.ac.uk

Fig. 1. Principle of sensors utilised in E-nose sensing

attain, either a compromise is necessary or the sensor's detection layer must be regenerated. Persaud and Dodd [7] approached this problem using an array of reversible but only semi-selective detection 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 (for example metal oxide semiconductors (MOS), conducting polymers (CP) or piezoelectric sensors) the output of which is analysed by some form of pattern recognition software. This review focuses on the sensor technology used within the sensor array and the applications to which these have been applied.

Since the concept was first suggested over 650 papers have been published on E-noses. The book by Gardner and Bartlett [8] thoroughly covers the developments up to 1999. The "Handbook of Machine Olfaction" published in 2003 is the most recent review to date of the electronic nose field, covering all aspects from sensor technology to pre-processing and pattern recognition [9]. There have also been reviews of food applications [10–13] and potential medical applications [14]. Computational data analysis methods applied to E-noses have been reviewed by Jurs et al. [15], while signal processing techniques have been reviewed by Hines et al. [16]. Albert et al. [17] provide a detailed review of sensor technology and application. Janata and colleagues have provided critical assessment of new trends and features in chemical sensors [18–20]. There are

many proposed uses for E-noses; however most research in the field has focused on four major areas; food, medical diagnosis, environmental monitoring and bioprocess control. The design of the sensor chamber has been shown to be important; optimising the design for flow, sensor response and positioning has been undertaken by Falcitelli et al. [21] and Scott et al. [22]. Briglin et al. [23] investigated dissimilar geometric sensor form factors and spatially non-equivalent sensors to gain information to optimise performance.

Numerous commercial E-nose systems have been developed, a broad list of which can be found at the 2nd network on artificial olfactory sensing web page [24]. Many principles of detection can be used for chemical sensing. For E-nose applications, gas sensing technologies are utilised. Figure 1 summarises the principles of detection and the sensor types most widely applied.

Sensor Technologies Utilised in Electronic Noses Electrochemical Sensors (ECS) Amperometric Gas Sensors (AGS)

AGS involve the measurement of current across a working and counter electrode as a function of analyte concentration in an electrochemical cell. The working electrode is usually gold or platinum with a porous coating on the sensing side allowing analyte gas to diffuse through to the electrode surface, which acts as a catalyst for electrochemical redox reactions [8]. They are sensitive to a small range of redox active compounds, and, unlike some other sensors,

are not sensitive to water over a wide humidity range. Changing the electrode catalyst and/or potential can alter the selectivity. AGS have been found to have good selectivity and sensitivity [25], sensitivity can be in the range of ppb–ppm. Despite the selectivity, AGS have been used in array systems. Stetter et al. [26] employed four amperometric sensors for the detection of 22 hazardous gases. Each sensor could be operated in four different modes depending on the filament and temperature used, therefore effectively representing sixteen sensors. This study was extended to the quality classification of grain [27]. Knake and Hauser [28] produced a portable gas-sensing array using amperometric and voltametric measurements in series or parallel for the detection SO_2 and NO. Commercially available AGS are relatively large in size (20 mm ø electrode). Zhou et al. [29] have fabricated a solid-electrolyte microamperometric sensor (30 μm ø electrode) for CO_2 gas sensing. This was inspired by the successful use of solid-state electrolytes for some potentiometric gas sensors [30, 31] which led to micromachining of thin film gas sensors [32]. The reduction in the size of sensor makes the technology more applicable for E-nose systems.

Conducting Polymers (CP)

The first commercial E-nose system used CP based sensors and they have been utilised in much subsequent sensor array research [33]. CP can be used as sensors as the polymer conductivity is altered in response to organic vapours. The mechanism of the intrinsic CP response is unknown but many theories have been suggested [34, 35]. CP have been found to respond to a wide range of organic vapours and operate at ambient temperatures with sensitivities of 0.1–100 ppm. 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 CPs is as chemiresistors [33, 36] but uses of CPs for Field Effect Transistors (PolFETs) [37, 38]

and as semi-selective coatings for piezoelectric crystals [39–41] have also been investigated.

Intrinsic or Doped Conducting Polymers

In 1977 Shirakawa et al. showed that the conductivity of polyacetylene could be enhanced by doping [42]. CP (*p* doped) are easily prepared by chemical or electrochemical oxidation of starting monomers, in particular heterocyclic compounds [43]. A number of different monomers can be used to produce different conducting polymers, but all of the polymers have conjugated π-electron systems along their backbone [15]. Figure 2 shows four commonly utilised starting monomers.

As the CP prepared by oxidation are generally insoluble, polymerisation must be carried out directly on the sensor substrate, electropolymerisation is normally employed as it can be reproducibly and spatially managed by control of the applied potential or current at the electrodes. CP sensors are most commonly formed by polymerisation across two inert electrodes separated by a narrow gap; different gap distances have been used for sensing applications including 300 μm [44], 50 μm [45] and 10 μm [46]. While electropolymerisation involves the generation of radical cations the charge of the polymer is unbiased owing to the inclusion of anions from the solution as the film grows. The properties of the CP are dependent on the anion (counter ion) as well as the monomer. Studies of CP morphology using optical microscopy [47] scanning tunnelling microscopy (STM) [48], scanning electron microscopy (SEM) [49] and atomic force microscopy (AFM) [50, 51] have shown that the physical structure of the CP are radically different between different monomer starting groups with the same counter ion, or between the same monomer starting groups with different counter ions [52]. These physical changes are useful in chemical sensing as small changes in the polymer synthesis can lead to differing sensor responses and selectivity. Microfabrication of large arrays of CPs
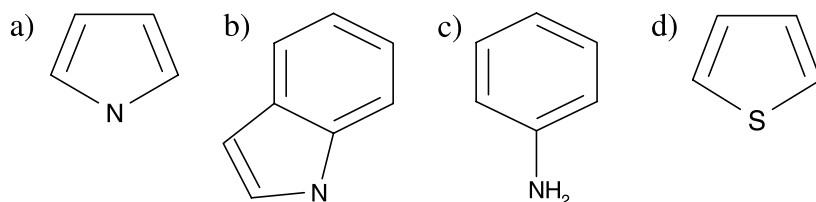

Fig. 2. Structures of common CP monomers; a) Pyrrole, b) Indole, c) Aniline, d) Thiophene

with micro-scale dimensions are possible using inter-digitated microelectrodes [53, 54] created by photo-lithography (10 µm gap widths are not uncommon). Significant work on CP E-nose systems using application specific integrated circuit design (ASIC) has been carried out by Hatfield and co-workers [55, 56] and Cole and co-workers [57, 58].

Extrinsic or Composite Conducting Polymers

The conductivity of conventional, insulating, polymers can be increased by combining them with conductive polymers or with fillers (metal powders, carbon black or graphite) to create a composite or extrinsic CP [59]. Sorption of analyte gases leads to swelling of the polymer, affecting the percolation network of the conductive particles in the composite, leading to a change in the DC electrical resistance [60].

A number of methods have been used for fabrication of composite CP including hot pressing (compression moulding) [61], simple dissolution followed by sonnication and evaporation [62], polymer grafting by γ-radiation [63, 64] as well as by reactive polymers [65]. The dissolution method with carbon black filler is commonly applied to fabrication of gas sensors. Coating of the electrodes is relatively easy; soluble composite CP can be applied using masks and spray coating. Partridge [66] demonstrated that chemiresistor gas sensors from conductive polymer composites gave higher sensitivity and reproducibility and were more easily processed than intrinsic or doped CP in their preliminary experiments.

Applications of Conducting Polymers to E-Nose Sensing

Ridgway et al. [67] used a Bloodhound E-nose incorporating 14 different conducting polymer sensors to detect *Acarus siro* L (flour mite) infestation in wheat with 83% discrimination between infected (0.001% by weight) and non-infected samples held in a controlled environment (75% RH, 20 °C). Stuetz et al. [68] used a Neotronics E-nose consisting of twelve polypyrrole sensors to collect extensive data covering a period of 8 months and successfully discriminated between raw sewage, settled sewage and final effluent samples from three unrelated sewage works, while data from single sewage works over periods of approximately 1 month were shown to have a high degree of correlation with 5-day Biochemical Oxygen

Demand (BOD5) when using static sampling. Luo et al. [69] 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, however, requires a complex sampling regime, but the technique was deemed important as the Chinese cigarette industry suffers substantial lost revenue due to counterfeit cigarettes. Dutta et al. [70] 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 [71] used an array of composite polymer sensors for the detection of nerve gas analogues dimethylmethylphosphonate (DMMP, an analogue of sarin) and diisopropylmethylphosphonate (DIMP, an analogue of soman) 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 1 mm separated gold electrodes, spin coated with 1 of 10 different composite polymer solutions. The sensor array could successfully detect the nerve agent analogues, even at high background levels of VOCs, and detection limits obtained were below the EC_{50} value of the respective nerve agents.

Metal Oxide Semiconductor Sensing Technology

Metal oxide semiconductors (MOS) and metal oxide semiconductor field effect transistors (MOSFET) have been used as gas sensing elements since some of the earliest E-noses. Employment of MOS and MOSFET sensors in the same sensor array as a hybrid E-nose is not uncommon.

Metal Oxide Semiconductor (MOS) Gas Sensor

MOS were shown to be gas sensitive by Seiyama et al. [72] in 1962, but unrelated concurrent work carried out by Taguchi led to the first commercially available MOS gas sensor in 1968 [73]. MOS are one of the most commonly used E-nose sensing technologies. Commercial Taguchi sensors consist of a ceramic cylinder (9.5 mm in length, ø 3 mm approximately) containing a heating coil mounted onto a holder. The outside of the pellet is coated with metal oxide, usually SnO_2 doped with a small amount of Pd or Pt
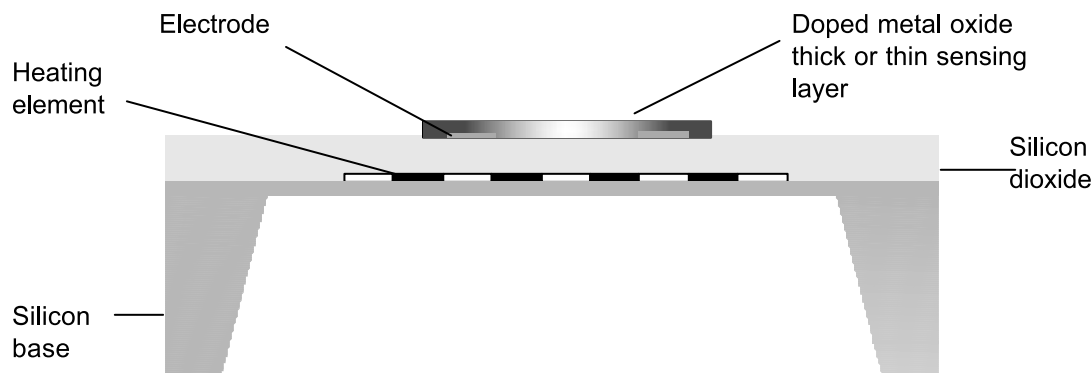
Fig. 3. Silicon planar MOS with vertical heater

catalyst [74], though many other oxides, including ZnO [75], WO_3 [76], and TiO_2 [77], have all been applied. There is a change in resistance on exposure to VOCs, which take part in redox reactions on the surface of the MOS, or to gases such as NO, which act as oxidizing agents at MOS operating temperatures. The process can be described by oxidising and reducing stages. In the oxidising stage O_2 from air is adsorbed, trapping free electrons from the conduction band of the semiconductor and increasing the resistance of the sensor. The adsorbed oxygen forms a potential barrier between grain boundaries in the metal oxide. In the reducing stage the absorbed oxygen reacts with the VOC, which results in a decrease in the surface density of the oxygen, reducing the electron trapping effect and thus allowing electrons back to the conduction band. The change in resistance is dependent upon the VOC that reacts with the adsorbed oxygen on the sensing surface, as well as the metal oxide grain size [78]. Selectivity can be gained by changing either the catalyst or the operating conditions for the sensor [79–81]. MOS generally function at 300–500 °C [78, 82, 83], allowing rapid and reversible reactions at the sensor surface and avoiding formation of a layer of chemisorbed water that would inhibit the reaction with VOCs [8]. Sensitivity is dependent upon the operating temperature, and careful temperature modulation has been shown to improve discrimination and quantification. Commercial sensors have typical sensitivities of 5–500 ppm. Heilig et al. [84] used temperature modulation to allow for quantitative measurements of a binary gas mixture. A review of this topic has been carried out by Lee and Reedy [85].

As typical Taguchi based sensors have high power consumption, around 800 mW due to the high tem-

peratures required for the sensing surface and heat loss from the ceramics, there has been much research on fabrication of smaller, more energy efficient systems, such as microfabricated silicon planar MOS sensors. Figure 3 shows the schematics of this type of sensor [8].

The metal oxide-sensing layer can be thick or thin. Thin films can be deposited by various techniques including evaporation [86], spray pyrolysis [87] and physical vapour deposition (PVD) [88]. PVD is the most widespread of these techniques [89] and 10 nm to 5 μm films have been obtained. Thick films (10–300 μm) are coated by screen printing [89–91]. Thin films are commonly believed to have many advantageous properties including faster response and greater sensitivity to strongly oxidising species [92], while thick films are more easily and reproducibly fabricated [93, 94]. Microfabrication of MOS also allows several sensors to be placed on a single chip. Gardner et al. [95] produced a 16.2 mm by 4.25 mm integrated array of six inter-digitated sensors using micromachining. Much of the work on MOS sensors has concentrated on the use of microfabrication for the production of microhotplates used as heating elements of the MOS sensors [96–99]. An interesting account of microhotplates for chemical sensors has been undertaken by Semancik et al. [100]. Heule and Gauckler [101] focused on miniaturisation of arrays of tin oxide gas sensors on a single microhotplate. Soft lithography has been used to fabricate 10 μm wide SnO_2 lines directly on the microhotplate substrate. A recent development is the work of Wollenstein et al. [102] who developed a micromachined four-sensor metal oxide array with low power dissipation by suspending the heated membranes from glass posts modelled using finite element matrices. The system was

found to perform as a sensor array to trace amounts of VOCs. These authors propose the fabrication of an integrated gas-sensor device and complementary metal oxide semiconductors CMOS driving analysis circuits on one chip as the glass posts allow thermal decoupling. This is generally impractical with MOS arrays as they operate at temperatures well above the CMOS limit of 160 °C.

Metal Oxide Semiconductor Field Effect Transistors (MOSFET)

The first reported use of a palladium gate MOSFET for H_2 sensing was by Lundstrom et al. [103] in 1975. Much subsequent work has investigated different gate metals for detection of hydrogen containing gases [104, 105] but other work has allowed detection of non-hydrogen containing gases such as CO [106]. MOSFET gas sensors have the structure of a Metal Insulator Semiconductor (MISFET) and have been shown to have sensitivity in the ppm region. The sensor is a MOSFET if the insulator is an oxide; SiO_2 is commonly used for MOSFETs. Variants of the MOSFET exist, including ISFET (Ion Sensitive), OGFET (Open Gate), and SGFET (Suspended Gate). However the standard MOSFET configuration is more commonly utilised for E-nose applications. The common source configuration (*n*-type) transistor operates with three contacts; the source, the drain and the gate.

The potential applied at the metal gate (typically Pt or Pd, though other "noble" metals can be used) determines the current. An inversion at the semiconductor-insulator boundary creates a channel (depletion region) that allows electrical current to flow from the source to the drain. The drain current of the transistor is controlled by the surface potential of the semiconductor as this determines the size of the depletion region as well as the concentration of charge carriers at the surface. The gate voltage and the differences in work functions between the insulator and semiconductor in turn affect the surface potential. Any gas reaction that causes a change in the metal gate or insulator properties will result in a change in the MOSFET sensors electrical properties and thus a change in the drain current, though the sensor response for MOSFETs is generally measured by the change in gate voltage required to keep the drain current constant at a pre-selected value. For example the metal gate is known to act as a catalyst for the decomposition of H_2 to hydrogen atoms which diffuse through the gate and are absorbed at the metal-insulator boundary resulting in a change in the MOSFET threshold voltage. It has been shown that operating at different temperatures, changing the gate metal and the thickness and porosity of the metal gate are important for the operation of MOSFETs [107]. Both *n* and *p* channel MOSFETSs are used for gas sensing. Figure 4 shows a schematic of an *n*-channel MOSFET [108].

MOSFETs can be fabricated using standard microelectronic techniques, producing die sizes of 1.5 mm by 1.5 mm that can operate at much lower temperatures (around 150 °C) than standard MOS sensors [109]. Recently work has focused on the use of silicon carbide based MOSFET devices also known as metal oxide silicon carbide field effect transistors (MISiCFET)
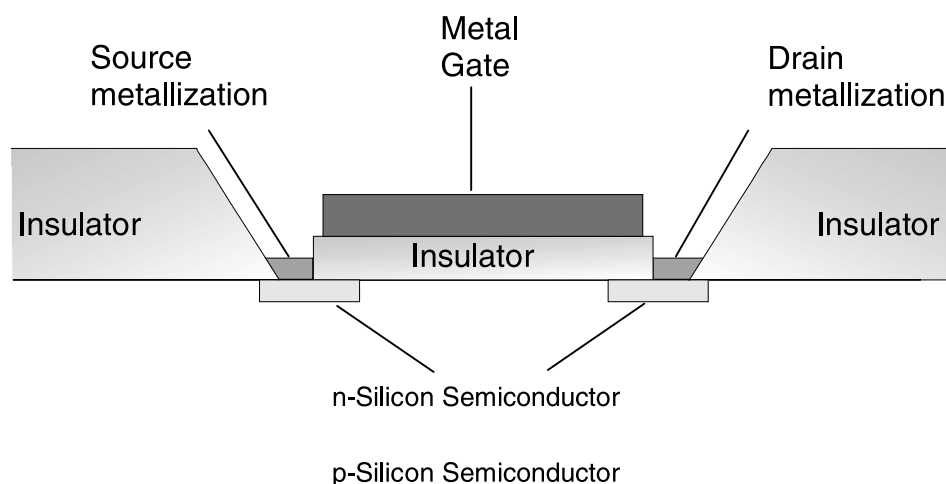

Fig. 4. Schematic of MOSFET gas sensor

[110, 111]; these devices are able to work at much higher temperatures than those based on silicon substrate. The high temperature allows reactions of previously hard to detect compounds, such as hydrocarbons, to occur at a productive rate at the metal gate [112]. Briand et al. [113] have investigated temperature modulation and have shown that cycling of the temperature can lead to discrimination between different gas mixtures and also reduce the recovery time of the sensor for hydrogen detection. This would appear to be a sensible route for development, especially with the advantages already shown for other semiconductor gas sensing technologies [84, 85].

Lundstrom et al. [114] implemented a novel alternative MOSFET chemical sensor utilising a scanning light pulse technique (SLPT). A large FET with a number of different catalytic metals with a temperature gradient across the surface was used as the detector. Scanning a pulsed light source across the detector surface generated a photocapacitive current in the semiconductor. The gate voltage was then varied to maintain a constant current. It was shown that scanning the surface with or without the gas molecules to be detected present resulted in different required gate voltages. Using this information image maps (called artificial 'olfactory' images) of the differences in voltage (ΔV) for the light beam position (x, y) were obtained. The image maps in conjunction with pattern recognition can be used for the identification of different gas samples [115, 116].

Applications of Metal Oxide Semiconductor Technology to E-Nose Sensing

Kohl et al. [76] carried out a substantial and systematic study of the responses of MOS surfaces. The group investigated different sensor materials (SnO_2, ZnO, ZnO/SnO_2, WO_3 and CuO), the addition of alloys to the sensor material, the effect of operating temperature, and the effects of the functional groups and chain length of the test sample. The sampling followed the selective odorant measurement by multisensor array procedure described in detail by Hofmann [117]. The information gained from these studies could be deemed useful for determining which sensor material and alloy to use for a specific application.

Readings were taken directly from a bioreactor exhaust gas stream during *Sacchoromyces cerevisiae* cultivation using an array of ten MOSFET sensors (operated between 140–170 °C with catalytic metal gates of Pd, Ir or Pt) and four MOS sensors (operated at 400 °C), along with a CO_2 sensor [118]. Although the constituents were not detectable in the gas phase, they were found to be predictable from the array output with relative errors of 1.7 to 20%. Concentrations of glucose, ethanol, acetaldehyde, glycerol and acetate in the reactor were monitored during the process using High Performance Liquid Chromatography.

Wang et al. [119] employed a SnO_2 thin film sensor array, optimised for the detection of acetone, to monitor the gases exhaled from the nose of 32 volunteers (18 idiopathic diabetics and 14 non-diabetics). Readings were taken before a meal and at intervals up to 2 hrs after the meal. The results allowed 100% discrimination between diabetic and non-diabetic volunteers 1 hr after eating, but at other sampling times much lower discrimination percentages, including false positives, were found.

An array of sol–gel SnO_2 sensors (pure SnO_2 or doped with Ni, Pd, Pt or Os) was used to discriminate between various commercial olive oil brands, different qualities (extra virgin, virgin and husk), and non-commercial oils [120]. The sols of the sensing layer were deposited on an alumina substrate, cut to give 9 mm^2 pieces and mounted onto commercial TO-8 sockets for use in the E-nose. The sensors were operated at three different temperatures, 200, 250 and 300 °C, with best discrimination obtained at 250 °C.

Carrasco et al. [121] used a commercial Fox 4000 E-nose, comprising 18 MOS sensors, for the discrimination of perfumes with 100% correct classifications.

A multisensor array, composed of 10 MOSFET sensors (operated at temperatures between 140 and 170 °C) and one IR-based CO_2 detector, was developed by Paulsson and Winquist [109]. Alcohol was analysed in breath samples taken after the Haldane-Priestly procedure [122] from five test subjects before and at set times after consuming alcohol. When calibrated against GC analysis, the best performance obtained had a root mean square error of 16.8 ppm ethanol in breath, but the system is not currently acceptable for forensic applications as issues involving stability and sensor drift need to be addressed.

Optical Sensors

The use of optical sensors for chemical sensing is widespread in many areas [123–127]. Much of the early work on the use of optical sensors for gas sensing was carried out by the Wolfbeis group [128–130].

There is however in comparison to other sensor types little information on the use of optical sensors in E-nose applications, but following the development of an optical E-nose system by the Walt group [131, 132] in 1996, there has been a significant increase in utilization [133–135]. 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 is fluorescence although there has been some work by Di Natale et al. [136] and Rakow and Suslick [137] on absorption and colorimetric measurements.

Fluorescence Techniques

Fluorescence techniques generally utilise optical fibres; although these can be used directly, most chemical sensor applications use them to direct the light source to the sensing element, which can be fabricated on the fibre or coated onto an inert substrate. Most commonly the distal face or tip of the fibre is coated [138]. Total internal reflection fluorescence (TIRF) and fibre optic evanescent wave (FOEW) sensors rely on evanescent field excitation [139, 140], this takes place on an unclad but coated circumference wall of the fibre. The distal tip conveys the resultant light to a detector. The first optical E-nose [131] used individual fibre optic strands coated with fluorescent polymer dyes. Different polymer/dye gradients led to differences in the sensing properties. An alternative method would be to use different dyes or polymers. Walt et al. [141] discussed two other forms of optical array sen-

sing. The first method coherently fused many fibres together and photo polymerized sensor regions onto the surface [142]. The second method involved chemically etching microwells, into which sensing beads could be placed on the distal face of the fibre [143]. The beads were 3–5 μm porous silica with differing surface chemistry containing a fluorescent dye. The system enabled numerous sensing elements on the micro-scale to be used.

Non-Fluorescence Techniques

The major work surrounding optical sensor arrays without the use of fluorescence involves absorption although other methods have been used. Leipert et al. [144] and Kraus and Gauglitz [145] used reflecto-metric interference spectroscopy for gas sensing. This system uses white light interferometry to measure thickness changes in a polymer sensing layer that swells on exposure to VOC. Different sensing layers, with a fibre bundle of 1:2 couplers attached to an optical multiplexer and photodiode array, allows for this system to be used as a sensor array. Christie et al. [146] developed a near infrared optical sensor, based on the electrochromic properties of polyaniline, for detection of gaseous ammonia. This system can be operated remotely as the 1300 nm wavelength used gives attenuation in multimode fibres of only 0.3 dB per km [147]. Although this has not been developed as an array the potential to use other electrochromic polymers or dopants for the polymer is appealing.

Porphyrin based sensor arrays have attracted attention in recent years. Porphyrin ring systems can form
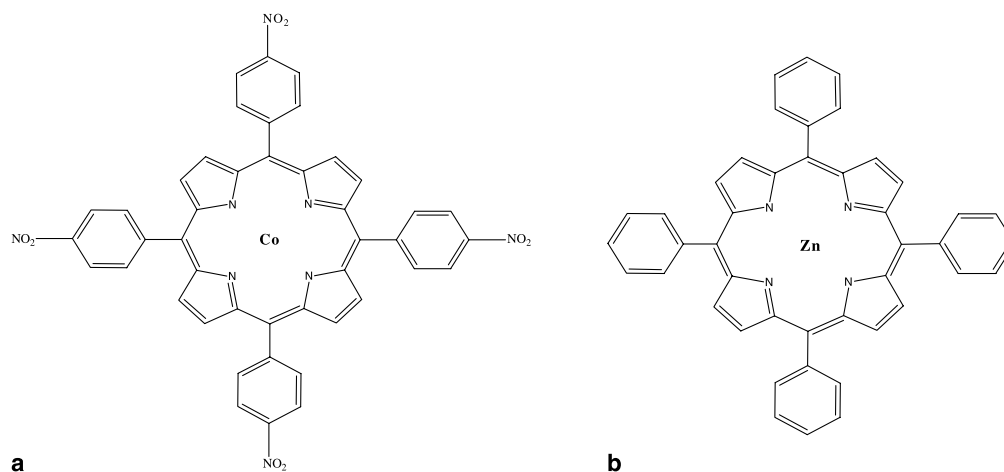

Fig. 5. Chemical structure of two metalloporphyrins; a) 5,10,15,20-tetrakis-(4-nitro-phenyl)porphyrinato cobalt(II), b) 5,10,15,20-tetrakis-(phenyl)porphyrinato zinc(II)

highly stable complexes with transition metal ions and show highly chromogenic behaviour, with absorption in the Soret band [148]. The chemical structure of two commonly used metalloporphyrins can be seen in Fig. 5, exposure to VOCs lead to changes in the absorption spectra [136].

Akrajas et al. [149] used different coloured LEDs with Langmuir-Blodgett films of metallo-octaethyl porphyrins as an optical E-nose. Light was transferred to and away from the system using optical fibres. Di Natale et al. [136] used the absorption properties of different metalloporphyrins for E-nose sensing. A blue LED was operated as a light source, chosen for the high absorption in the Soret band. Different porphyrins were deposited over 50 μm areas of a transparent Plexiglas chamber internal wall. Photodiodes were then used to detect light from each porphyrin sensing layer. A reference for fluctuations in the LED intensity was detected from an uncoated area of the chamber. When VOC were passed through the chamber the resultant changes in absorbance for each sensor were measured. A third type of porphyrin array was employed by Rakow and Suslick [137, 150]. The array was created by spotting solutions of different metalloporphyrins onto C2 reverse phase silica gel thin-layer-chromatography (TLC) plate. When VOCs were passed over the array the porphyrins changed colour, the changes were recorded using a flatbed scanner and measured by RGB value changes using computer software. Using this technique, there is the possibility to microfabricate sensing systems by inkjet deposition of the films, and to interface the array to a charged couple device for detection of colour changes. Depending upon the analysed VOC, limits of detection below 1 ppm have already been realised [151].

E-Nose Applications of Optical Sensors

Optical nose applications are currently at a preliminary stage. Most researchers are involved with optimising the current sensor systems for the detection and quantification of pure compounds or binary mixtures of the compounds. Di Natale et al. [136] used an optoelectronic nose consisting of 4 porphyrin sensors and 1 reference for detection of different concentrations of hexane, ethanol, methanol, propanal, acetone, acetic acid and triethylamine. Johnson et al. [135] used an array of 19 optical fibres, with the fluorescent dye 'Nile Red' immobilised on the distal tips in various polymer matrices for the detection 17 pure compounds and 3 complex mixtures and achieved 90% classification. Bakken et al. [133] investigated the detection of 'explosives-like' nitroaromatic compound (NAC) vapours. The aim was to optimise the system so that it could be used for the detection of buried 2,4,6-trinitrotoluene plastic land mines. The sensor array substrate consisted of 4 optical imaging fibres; the distal faces of these were etched to allow for an array of 4 different types of sensing beads containing 'Nile Red'. This resulted in 50 copies of each of the four sensor types. The 50 readings were averaged before data analysis. Test samples consisted of four VOCs (benzene, toluene, ethanol and methanol) and three NACs (ρ-nitrotoluene, 2,4-dinitrotoluene and 1,3-dinitrobenzene) at 9 different concentrations. Binary mixtures of these compounds were also collected at 9 different concentrations. Exposure time of the sensor array to sample vapours was 2.52 s and the total sampling time 7.57 s including exposure. Classification of samples as containing or not containing a NAC was possible with 100% accuracy.

Piezoelectric Sensors

In 1880, the Curie brothers [152] predicted and demonstrated piezoelectricity, the phenomena by which certain anisotropic crystals, when subjected to mechanical stress, generate electric dipoles. The converse effect, that an electrical potential would create mechanical stress within the crystal, was mathematically construed by Lippmann [153] and confirmed by the Curie brothers [154]. Piezoelectric crystals have a varied use including optoelectronics, electronics, RF filters and liquid and gas sensing devices. Quartz and $LiNbO_3$ are the most commonly utilised crystals for gas sensing. Many different forms of piezoelectric sensor exist, including bulk acoustic wave (BAW) [155], surface acoustic wave (SAW) [156], flexural plate wave (FPW) [157] and shear horizontal acoustic plate mode (SH-APM) [158]. The two major types of piezoelectric sensors used in electronic nose sensing are BAW and SAW, however in recent years FPW have been used.

Bulk Acoustic Wave (BAW) Sensor

BAW sensors are also commonly referred to as Thickness Shear Mode (TSM) sensors or Quartz Crystal Microbalances (QCM or QMB). They are generally made of AT cut (35°15′ inclination in the y-z plane)
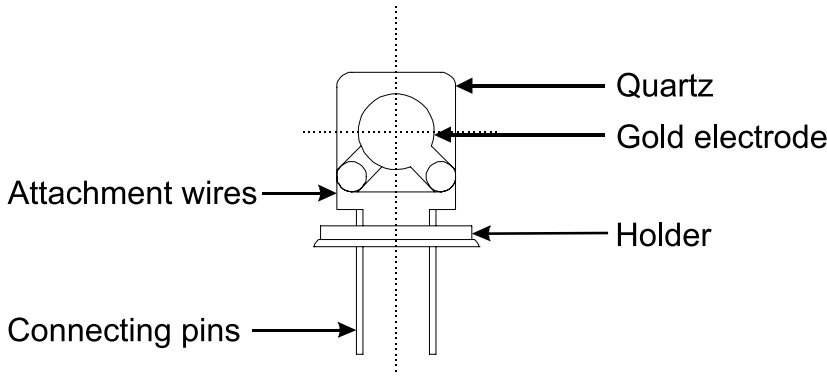
α-Quartz. A schematic of a BAW sensor in a commercial HC-49U holder is shown in Fig. 6.

Gold electrodes attached to the quartz exert an alternating current which forces the crystal to oscillate with a fundamental frequency. As the electrodes are attached to either side of the crystal the wave produced travels though the bulk of the material as illustrated in Fig. 7.

Typical BAW sensors are 6–8 mm ø quartz wafers with a 3.5–5.5 mm ø gold electrodes and having fundamental frequencies between 10 and 30 MHz. The 'T' in AT-cut refers to the temperature compensation qualities of the cut. Figure 8 shows the typical frequency change due to temperature for different basic cut angles [159].

Any layer added to the crystal, which does not dampen the oscillation, can be treated as added thickness, causing a change in frequency. In E-nose applications the crystals are generally coated with a chemical or biochemical layer that allows extraction of an analyte from a test sample. The coatings are semi-selective thus allowing for reversibility of the sensors. The principle of sensing is that the change in device frequency (frequency shift) is proportional to the mass of material deposited upon the crystal.
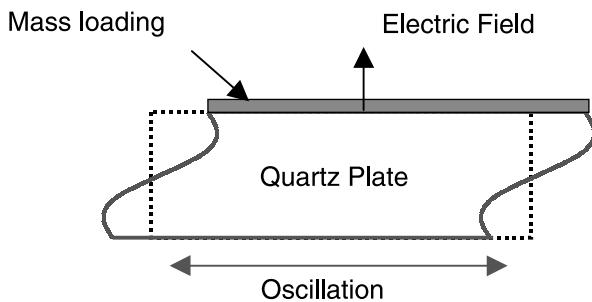

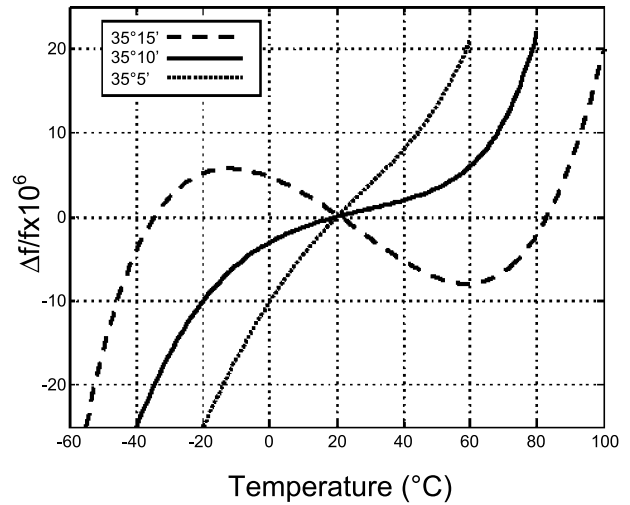**Fig. 7.** BAW sensor oscillation

Fig. 8. Temperature dependence of quartz crystal cuts

The relationship was derived by Sauerbrey [160] and is shown in Eq. (1). Any coating that can form a uniform rigid film on the electrode surface is compatible with the sensing technology.

$$\Delta f = -2.3 \times 10^6 \cdot f_o^2 \cdot \frac{\Delta M_s}{A} \qquad (1)$$

where

Δf is the change in frequency of the quartz crystal in Hz.
f_o is the fundamental frequency of the quartz crystal in MHz.
ΔM_s is the mass of material deposited or sorbed onto the crystal in g.
A is the area coated in cm^2.

For a standard sensor a 1 Hz change can relate to a 1 ng mass change. If soft polymers are used to coat the electrode it is possible for them to have viscoelastic coupling to the acoustic wave, in these circumstances the frequency shift cannot be entirely due to mass change.

The first demonstration of a piezoelectric sorption detector was by King [161]. Since then many coatings have been used including gas liquid chromatography (GLC) stationary phases [162], conducting polymers [48, 49], self assembled monolayers [163], molecular imprinted polymers [164], metalloporphyrins [165] and plasma polymerised films [166]. This allows for an almost limitless range of different coating properties to be utilised, leading to a wide range of different sensing applications and quantitative measurements at approximately parts per billion (ppb) detection. Due to the diversity of the coatings a large assortment of coating techniques are exploited. Solvent evaporation, spray and spin coating have all been used [167–169]. Gomes et al. [170] have shown that spray coating resulted in more reproducible coating layers than spin coating alone. This is an important factor if the sensors in an E-nose system need to be replaced. As with conducting polymers these sensors can be used at room temperature. However, the polymer coatings can be influenced by humidity, and changes in room temperature can have an effect on both the crystal and its polymer coating. Miniaturisation of the BAW sensors and arrays is the subject of much research. Tatsuma et al. [171] carried out work on the fabrication of multichannel quartz crystal microbalances (MQCM) using photolithography and chemical etching. This allows an array of microbalances, including a reference, to be fabricated together on one wafer. The microbalances were found to act independently.

Further work on MQCM by micromachining has been carried out by Abe and co-workers [172–174]. Deep reactive ion etching (DRIE) was utilised to create the array. It was demonstrated that the multichannel system could operate as a gas sensor array [172]. It has been shown that MQCM fabricated by DRIE could allow for very high resonant frequencies by allowing careful control of the quartz channel thickness [173, 174]. Resonators with a quartz thickness of approximately 18 μm allowed for a fundamental frequency of 94 MHz. Lower frequency, 30 MHz, etched crystals were used for liquid based applications.

Roth et al. [175] manufactured inter-digitated capacitors (IDC) and heater elements directly onto a single BAW. This system allowed for two different physical properties to be measured; dielectric and mass loading. The heating element not only allows control of the sensor operating temperature but can also allow for temperature modulation to be used with BAW measurements. Although the BAW were manually fabricated, a combination of multichannel QCM wafer processing with integrated IDC and heating element is an attractive proposition.

Surface Acoustic Wave (SAW) Sensor

The stress-free boundary at the surface of a crystal allows an acoustic mode, whose propagation is confined to the surface, known as a surface acoustic wave (SAW) [176]. Wohltjen and Dessy [177] demonstrated the first SAW gas sensor in 1979. SAWs can be excited on a piezoelectric crystal by the use of an inter-digitated transducer (IDT). The most common substrates for SAWs are ST-cut (stress temperature compensated) quartz or $LiNbO_3$. Two forms of SAW sensor exist, delay-line and resonator. In delay-line sensors the wave is propagated from the IDT, along the crystal, until it reaches a receiving oscillator. The area in which the wave travels is known as the delay line and it is here that the interaction with the sample takes place; the delay line can have a semi-selective coating. The change in frequency of the wave can be related to the added mass of the selective coating providing the mechanical properties of the coating are unaffected by the interaction with the test sample.

$$\Delta f = (k_1 + k_2)f_o^2 t_f \rho \tag{2}$$

where

$k_1 + k_2$ are material constants of the substrate.
$t_f =$ film thickness.
$\rho =$ film density.
$f_o =$ resonant frequency.

Very similar coatings and coating methods have been used for SAW sensors as those for BAWs [178, 179]. Grate et al. [180] carried out a series of experiments correlating Log K of coatings of SAWs with those from GLC methods. It was found that GLC measurements of K for a specific coating were a good indicator of relative performance and sensitivity of that coating on a SAW device, although some differences were found. Figure 9 indicates the progression of SAW on a delay-line substrate [35].

In resonator sensors the wave is reflected by ridges in the substrate back to the IDT for detection. In this system the IDT can be coated for selectivity.

SAWs generally operate at frequencies between 150 and 400 MHz, though 1 GHz SAW devices have been fabricated [181, 182]. Standard materials used have only moderate SAW velocities which make it
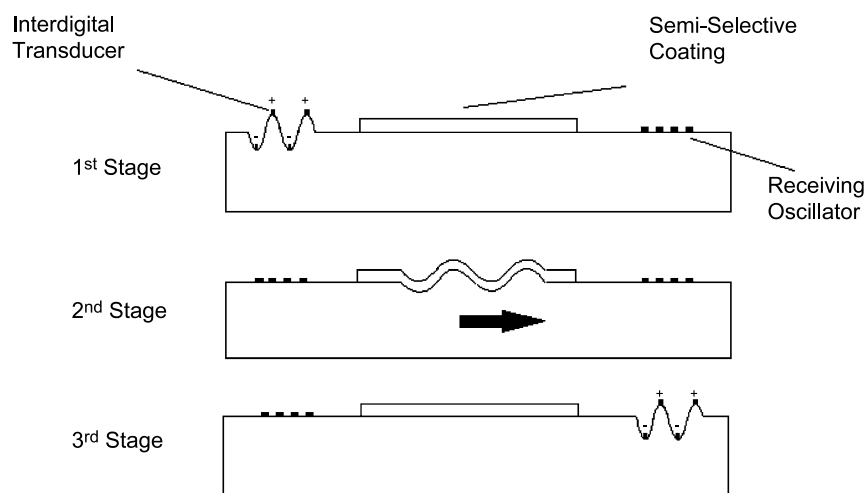
Fig. 9. Surface Acoustic Wave propagation

difficult to obtain frequencies above 1 GHz [183]. Investigations of both AlN and ZnO for SAW have taken place [184, 185]. Although at this time these systems have not been used for gas sensing, the higher frequencies obtained are attractive for sensing applications, allowing for greater sensitivity (see Eq. (2)).

An added advantage of SAW sensors is that dual delay-lines can be fabricated on the same chip. This allows one delay-line to be used as a reference line to correct for effects such as temperature drift. The array sizes are much smaller than those of BAW sensor arrays; typically 8 mm by 2 mm [186]. SAW wafers and sensors are now inexpensive and are commercially available [187]. Although greater responses are gained from SAWs the noise levels are higher than those of BAW sensors due to the electronics required for higher frequencies. Recent work in SAW gas sensing has concentrated on coatings and applications [186, 188, 189]. Pique et al. [190] utilised matrix-assisted pulsed laser evaporation (MAPLE) for depositing polymer thin films onto SAW sensors and found the performance to be comparable to that of SAW sensors coated by standard spray coating methods. MAPLE allows for deposition of solvent-free polymers onto a range of substrates.

Flexural Plate Wave (FPW) Sensor

The flexural plate wave (FPW) or Lamb wave [191] device was developed by Wenzel and White [192] in 1988. It has been utilised for both micropump [193] and sensor based applications [194, 195]. The device uses antisymmetric Lamb waves which exhibit flexural character [196]. Like SAWs, FPWs use IDTs which are separated by a polymer coated delay line. However in a FPW, Lamb waves are propagated on an acoustic plate whose thickness is smaller than the Lamb wavelength. The material is generally silicon sputtered with a piezoelectric layer such as ZnO. Decreasing the plate thickness has been shown to increase mass sensitivity as well as decreasing the oscillating frequency if the transducer dimensions remain the same [176]. The calculated sensitivity of an FPW is approximately an order of magnitude higher than an equivalent SAW, this permits the use of lower frequencies with less complicated electronics, and so lower noise levels and lower limits of detection [197]. Another advantage is that the sensing layer can be deposited on the backside of the wafer, therefore avoiding chemical exposure of the on-chip-circuitry [198]. A sensor array of six polymer coated FPW fabricated onto a single chip (9.5 × 12 mm) was utilised by Cai et al. [199]. The array was combined with an adsorbent preconcentrator and was shown to be capable of effective multi-vapour analysis, with detection limits of sub-ppm. Cunningham et al. [200] successfully used micro-electromechanical (MEM) FPW for a micro-chemical analysis array (μCANARY). It was demonstrated that the μCANARY was capable of making both qualitative and quantitative measurements of chemical vapour analytes. Liquid phase work has been applied to the detection of proteins and micro-organisms [201].

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Grate et al. [180] used a SAW array made up of four vapour sensors to detect and discriminate between

trace amounts of nerve and blister agents at trace levels. The sensors were coated with fluorpolyol, poly(-ethylenimine), ethyl cellulose and poly(epichlorohydrin) by spray coating a dilute solution of these polymers in a volatile organic solvent. The temperature of the array was controlled using a Peltier device in contact with the sensors and a thermocouple. Sampling involved the use of a preconcentration tube, which could be used not only to increase the concentration of the analyte, but to minimise the affect of humidity. Yang et al. [202] used a SAW based electronic nose consisting of eight sensors to perform discrimination for three different applications; organic reagents, liquors, and perfume. The coatings of the crystals were optimised for each application.

Dickert et al. [203] 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 GC-MS.

Di Natale et al. [204] used an eight sensor BAW array for the identification of lung cancer by breath analysis. Breath samples were taken in sterile, disposable, 4 L bags from 35 volunteers with a form of lung cancer, 9 individuals after surgical therapy and 18 healthy volunteers. Correct classification of lung cancer patients was reported to be 100%, with 94% and 44% correct classification of non-cancer and post-surgical categories respectively. Although these results are very encouraging, this was a preliminary study. Improvements by an increase in the number of test subjects allowing for neural networks data processing and coverage of different stages of cancer development in the hope of possible early diagnosis were proposed.

Bargon et al. [205] studied the ripening stages of Emmental cheese using an array of 11 BAWs coated (by means of an electrostatic spray technique) with macrocyclic oligolactums, and one uncoated BAW which served as a reference.

Other Sensors

Each chemical sensor type has its own advantages for sensor array technologies and its own intrinsic problems. One solution to this problem is the use of more than one type of sensor into the array system, these systems are known as a hybrid E-nose [206]. The data from the separate chemical sensors are combined in one data set, which should give more information for classification and separation. The major advantage with this type of E-nose is that it incorporates the advantages inherent to the different transducer technologies, also giving a choice for which chemical sensors should be used. The choice of chemical sensor will be dependent upon the sample to be tested. The most common utilisation of this system involves MOS and MOSFET sensors, however commercial systems are available that can use MOS, MOSFET, QCM and AGS in various combinations. Paper quality discrimination [207] and food applications [208, 209] have both been carried out utilising hybrid nose systems.

The thermal sensor subtype of pellistors or calorimetric sensors have not been widely employed for E-nose systems, but some examples have been demonstrated [210, 211]. They operate on the principle of detection of heat produced by catalytic oxidation of combustible gases [212]. The basic design of these sensors is a catalytic surface, platinum and palladium are most common, with a heater to maintain the sensors operating temperature as well as a temperature probe. The temperature changes detected during sensing are related to the type of gas and gas concentration of the combustible analyte. Humidity has been found to have little significant effect on the performance of pellistors. For the catalytic reaction to take place these sensors must be operated at high temperatures, with therefore high power consumption. Another problem is that they are found to be susceptible to surface poisoning from sulphur compounds [213]. Current work, as with MOS sensors, has focused on micromachining [211, 214, 215] to reduce power consumption, optimisation modelling [216] and sample pre-treatments to avoid poisoning [217].

Discussion

A wide range of transducer technologies, varied in their principle of detection, have been utilised for E-noses and each type has been applied to an equally wide range of problems. However they do share certain characteristics; they are small, inexpensive, robust and semi-selective.

The selection of chemical sensor types to be utilised is of utmost importance if E-nose classifications are to be useful for a wide range of applications.

Some studies have focused on the rational selection of chemical sensors for specific compound groups [218–221]. Of note, is a novel paper that uses molecular modelling to predict analyte interactions [222]. Improvement of sensor response and recovery has also been actively researched. Analysis times of E-nose systems are however generally influenced more by the sampling method utilised than the sensor response time. For example, some static sampling techniques require over 1 hr for a sample reading while some dynamic systems using similar sensors require less than 20 s. An average of around 5–10 min is common. The rationale for choice of sampling regime, transducer type and the sensor coatings is not always clear. Sampling procedures, coatings and data reduction algorithms are enthusiastically investigated by many different research groups who incorporate very different techniques. There are, however, relatively few comparative studies. Some reports of effective discrimination do not fully investigate the basis or robustness of the results.

E-noses are so called as they are often aimed at detection of odorous compounds, it is not always clear that discriminations are based on odorous rather than non-odorous, and possibly incidental, components of the headspace. Humidity is a known problem, especially with polymer-based sensors and care needs to be taken in their use. Some research has focused on measurement and control of humidity [223–226]. When humidity levels are not compensated for or controlled, it is possible that the humidity is responsible for some successful discriminations.

The current research trend in all of the transducer areas discussed here has focused on microfabrication to allow for reduced power, larger integrated arrays and small portable systems. This would appear to be a sensible route for future developments. It is expected that in the future numerous portable systems will become available and be used for increased offsite, on-line and at-line measurements.

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