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Review

Advances in artificial olfaction: Sensors and applications

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ABSTRACT

The artificial olfaction, based on electronic systems (electronic noses), includes three basic functions that operate on an odorant: a sample handler, an array of gas sensors, and a signal-processing method. The response of these artificial systems can be the identity of the odorant, an estimate concentration of the odorant, or characteristic properties of the odour as might be perceived by a human. These electronic noses are bio inspired instruments that mimic the sense of smell.

The complexity of most odorants makes characterisation difficult with conventional analysis techniques, such as gas chromatography. Sensory analysis by a panel of experts is a costly process since it requires trained people who can work for only relatively short periods of time. The electronic noses are easy to build, provide short analysis times, in real time and on-line, and show high sensitivity and selectivity to the tested odorants. These systems are non-destructive techniques used to characterise odorants in diverse applications linked with the quality of life such as: control of foods, environmental quality, citizen security or clinical diagnostics.

However, there is much research still to be done especially with regard to new materials and sensors technology, data processing, interpretation and validation of results.

This work examines the main features of modern electronic noses and their most important applications in the environmental, and security fields. The above mentioned main components of an electronic nose (sample handling system, more advanced materials and methods for sensing, and data processing system) are described. Finally, some interesting remarks concerning the strengths and weaknesses of electronic noses in the different applications are also mentioned.

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1. Introduction

The human nose is much more complicated than other human senses like the ear and the eye, at least regarding the mechanisms responsible for the primary reaction to an external stimulus. Therefore it has been much simpler to mimic the auditory and the visual senses. In olfaction hundreds of different classes of biological receptors are involved. Although several interesting developments have been made regarding so-called electronic noses, their performance is far from that of our olfactory sense. They are not as sensitive as our nose to many odorous compounds. The human nose contains approximately 50 million cells in the olfactory epithelium that act as primary receptors to odorous molecules. There are about 10,000 primary neurons associated with these primary receptors that link into a single secondary neuron which in turn feeds the olfactory cortex of the brain [1]. This parallel architecture suggests an arrangement that could lead to an analogous instrument capable of mimicking the biological system. Despite this difference, chemical sensor arrays combined with pattern recognition methods are very useful in many practical applications such as monotonous tasks in environment and food quality control and security. Electronic noses are thus emerging as a new type of instrumentation, which can be used to measure the quality or identify an aroma of a compound [2]. They work in a similar way and have, in that respect, a large similarity with the human nose [3,4].

The electronic nose is an electronic system that tries to imitate the structure of the human nose, so the first step is the interaction between volatile compounds (usually a complex mixture) with the appropriate receptors: olfactory receptors in the biological nose and a sensor array in the case of the electronic nose fulfilling the rule. “One odorant receptor is sensitive to multiple smells and one smell is detected by multiple odorant receptors”. The next step is the storage of the signal generated by the receptors in the brain or in a pattern recognition database (learning stage) and later the identification of one odour stored (classification stage).

Vertebrate olfactory systems can identify and distinguish volatile compounds (odorants) of diverse molecular structures with high accuracy. The mammalian nose can detect certain compounds in concentrations as low as a few parts per trillion [5]. Such performances are due to numerous olfactory receptors (ORs) expressed by olfactory sensory neurons and their subsequent neuronal processing.

Each of the ORs can bind to numerous odorants with specific affinities, although some receptors are relatively restricted to a set of few chemically related compounds in the process of sensing the smell, the binding of specific odorants to the OR proteins is the initiation step in odour recognition and the triggering of signal transduction in a cell. In [6] it is stated that “Given the fantastic odour space detected by the olfactory receptors, it is tempting to harness them to some generic electronic devices that could be endowed with some of the most prominent properties of animal olfaction: discrimination, specificity and sensitivity.” Recent studies have led to a more refined understanding of olfactory neurons and the mechanisms involving odorant detection [7].

The joint efforts of biologists and biochemists have revealed that olfactory receptor achieve odorant identification and signal transduction by employing molecular elements. An olfactory system plays an important role in identifying food and recognising environmental conditions. Olfactory sensing can be used for detecting human diseases [8–11], food contamination or hazardous agents [12–18]. Currently, olfactory research is focused on the discovery of potential commercial applications. Biomimetic design of an electronic nose on the principle of the mammalian olfactory system can aid in increased sensitivity and selectivity [19] for various trace level odorant detection applications. Different components of the biological olfactory system are being used for fabricating sensors.

This paper describes the state of the art of the use of electronic noses in: environmental quality monitoring, and citizen safety and security.

An electronic nose is a machine that is designed to detect and discriminate among complex odours using a sensor array. The sensor array consists of broadly-tuned (non-specific) sensors that are treated with a variety of odour-sensitive biological or chemical materials.

An odour stimulus generates a characteristic fingerprint (or “smellprint”) from the sensor array. Patterns or fingerprints from known odours are used to construct a database and train a pattern recognition system so that unknown odours can subsequently be classified and identified [2]. This is the classical concept of an e-nose; however, in recent years, as discussed below, the classical sensor types used for e-noses have been enhanced and complemented by other technologies introduced in this field.

An accepted definition of an electronic nose is: “an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours and tries to characterise different gas mixtures [3]. This definition restricts the term electronic nose to those types of sensor array systems that are specifically used to sense odorous molecules in an analogous manner to the human nose. However, the architecture of an electronic nose has much in common with the multisensor systems, designed for the detection and quantification of individual components in a simple gas or vapour mixture. A simple flow chart of the typical structure of an electronic nose consists of an aroma extraction technique or air flow system which switches the reference air and the tested air; an array of chemical sensors which transform the aroma into electrical signals; an instrumentation and control system to measure the sensors signal and a pattern recognition system to identify and classify the aroma of the measured samples in the classes previously learned when using supervised learning or perform by itself the classification in unknown classes. It uses currently a number of individual sensors (typically 5–100) whose selectivity towards different molecules overlaps. The response from a chemical sensor is usually measured as the change of some physical parameter, e.g. conductivity, frequency or current. The response times for these devices range from seconds up to a few minutes. By teaching a computer (or hardware) to recognise different patterns, it should now be able to classify the compounds belonging to the different classes of learned patterns. A very important part of the electronic nose is thus an efficient technique for pattern recognition.

Nevertheless and in a broader sense, electronic nose instruments are composed of three elements, namely: (i) a sample handling system, (ii) a detection system, and (iii) a data processing system, which will be described hereafter.

2. Sample handling system

Although a considerable amount of attention is normally given to the selection of the most suitable type of analyser to perform the desired analytical task, a similar amount of attention is all frequently not extended to the sample conditioning system. This may be due to a lack of understanding of the importance of this part of the complete system. A well-designed, properly applied measuring system can do no better than give a correct analysis of the sample being supplied to it. If the sample is not representative of the process, there is nothing an analyser can do to correct the situation, and the analytical data cannot be used for control purposes. The results of poorly designed sample conditioning vary from the analyser not operating at all to an analyser operating only with extremely high maintenance requirements and/or giving erroneous or poor data.

Sample handling is a critical step affecting the analysis by e-noses. The quality of the analysis can be greatly improved by adopting an appropriate sampling technique.

To introduce the volatile compounds present in the headspace (HS) of the sample into the e-noses detection system, several sampling techniques have been used in literature [20].

1. The static headspace (SHS) technique consists of placing the sample in a hermetically sealed vial and then, once equilibrium has been established between the matrix and the gaseous phase, the compounds are carried onto the sensors. Sample temperature, equilibration time, vial size and sample quantity are the main parameters that have to be optimised. Due to the poor repeatability of the manual HS injection, it is recommended that an automatic HS sampler be used. Usually the vapour is transferred to the sensors by a constant flow of an inert gas. Usually the vapour is transferred to the sensors by a constant flow of an inert gas.
2. Purge and trap (P&T) and dynamic headspace (DHS) techniques have been used in some applications to increase sensitivity, since they provide a pre-concentration of volatile compounds. In these systems, the volatile components are purged by a stream of inert gas and trapped onto an adsorbent. In the case of P&T, the gas flow is injected through the sample, whereas, in the case of DHS, only the HS is purged with the gas. The constant depletion of the HS leads to a displacement of the equilibrium in favour of desorption of these molecules from the matrix. The trapped molecules are subsequently desorbed by heating and introduced into the detection system. Apart from the choice of trap, the main parameters to optimise are the temperature of the sample, the equilibration time, the flow rate of the extractor gas and the purge time of the HS.
3. Solid-phase micro-extraction (SPME) is a user-friendly pre-concentration method. The principle involves exposing a silica fibre covered with a thin layer of adsorbent in the HS of the sample in order to trap the volatile components onto the fibre. The adsorbed compounds are then desorbed by heating and introduced into the detection system. Apart from the nature of the adsorbent deposited on the fibre, the main parameters to optimise are the equilibration time, the sample temperature and the duration of extraction. This technique has a considerable concentration capacity and is very simple because, unlike P&T or DHS, it does not require special equipment.
4. Stir bar sorptive extraction (SBSE) is a magnetic bar coated with polymers, which can be held in the HS for sampling. Its loading capacity is much higher than that of SPME. Even though it has been developed only recently, SBSE is a promising extraction technique when a very high sensitivity is required.
5. Inside-needle dynamic extraction (INDEX) is also a pre-concentration technique [21]. The INDEX needles contain an absorbing polymer phase very much like a fixed bed. The volatile compounds are forced through the needle by repeated aspiration/ejection motions of the syringe plunger. The potential advantage of this system compared to SPME lies in its mechanical robustness and the possibility of increasing the amount of absorbing polymer as well as the surface area available for adsorbing volatile compounds.

3. Detection system: sensors

Over the past decades, several kinds of gas sensors have been developed based on different sensing materials and various transduction platforms forming integrated multisensors (electronic noses), which supposes the most advanced instruments for a global monitoring.

Among gas-sensing materials it is important to consider metal-oxide semiconductors, conducting and composite polymers, and other novel materials.

These devices can be applied on different transduction units including chemo-resistive, surface acoustic wave (SAW), quartz crystal microbalance (QCM), optical transducers and MOSFET (metal-oxide-semiconductor field-effect transistor) [22].

3.1. Metal-oxide sensors

Semiconductor metal-oxide based gas sensors have been studied for many years, despite this further research is ongoing mainly to improve their sensitivity, selectivity and stability. Several commercial available e-noses based on this technology are now available as PEN-3 for Airsense Analytics and Fox 4000 from Alpha Mos.

Sputtering, thermal vacuum deposition, chemical vapour deposition (CVD), and the sol–gel process are the most widely used deposition techniques to grow the sensitive layers. They are deposited either as a thick or thin film over different types of substrates mainly ceramic or silicon. Although they are strongly affected by water and ethanol, coupled with selective extraction techniques and a careful design, e-noses with a great discrimination power can be realised.

Chemiresistive semiconducting metal oxides are the main candidates due to their very low cost, high sensitivity, fast response/recovery time, simple electronic interface, ease of use, low maintenance and ability to detect large number of gases [23]. There are two main types of semiconducting metal oxide sensors including n-type whose majority carrier is electron (such as zinc oxide, tin dioxide, titanium dioxide, iron (III) oxide, etc.) and p-type whose majority carrier is hole (nickel oxide, cobalt oxide and others) [24,25]. The majority of semiconducting metal oxides are n-type because electrons are produced via oxygen vacancies.

The gas sensing characteristics such as gas response, response speed, and selectivity are greatly influenced by the surface area, donor density, agglomeration, porosity, acid-base property of the sensing material, the presence of catalysts, and the sensing temperature [26,27]. The response of metal oxide sensors generally depends on film thickness and operating temperature. The response to a particular gas can be greatly improved by adding a catalytic metal to the oxide but excessive loading can reduce response [28]. The grain size of the oxide also affects the response and selectivity to specific gases because grain boundaries perform as electron scattering centres [29–31]. Smaller grain metal oxide sensors would be more sensitive than larger ones.

3.2. *Conducting polymer sensors*

Gas sensors based on conducting polymers exhibit interesting properties that make them useful for gas sensors: room temperature operation, easy to prepare and quick response times amongst others. Different conducting polymers, as metalloporphyrines, poly-pyrrole, poly-N-methilpyrrole, polyaniline show important sensitivities when exposed to different volatile species as: methanol, ethanol, acetone, toluene, ether and aldehydes changing their electrical resistance [32–34]. Recently, gas sensors have been fabricated using multi-walled carbon nanotubes (MWCNTs) reinforced electrically by conducting polymer composites following the solution casting method [35].

In spite of some promising perspectives, these sensors lack specificity, show a limited reproducibility and display a marked cross sensitivity to water vapour.

3.3. *Optical sensors*

They have been widely used as chemical sensors in many applications because their response could be well defined and precisely measured. Although optical sensors are more complicated than other sensors, give alternative measuring possibilities. When the light source of sensors excites volatile molecules, a signal can be measured as an absorbance, reflectance, fluorescence, refractive index, colorimetric and chemo-luminiscence. The output signals from these sensors could be detected by photo diodes, CCD, CMOS cameras. The most classical method is the measurement of the absorbance of the analyte in a specific frequency range. Other alternative as simplest measurement is the colour change using indicators as metalloporphyrines in a LED and photodetector system. Majority of optical sensors, generally uses optical fibres coated with specific dyes generating different properties when exposed to various gases (VOCs, H_2, CH_4…) [36,37].

Imaging technologies seem new promising tools for identify chemical compounds for many areas of application. These technologies take advantage of the latest advances in optical principles for sensing, and data computing: optical imaging (OI) using new CCD sensing and photoluminescence (PL) of nano-materials. Optical imaging (OI) based on colorimetric sensor arrays, is a new technology for odour detection and differentiation. The basic principle is to use the colour change induced by reaction between volatiles and arrays of chemically-responsive dyes selected according to their sensitivity to volatile compounds that need to be detected. Organ-metallic compounds as metalloporphyrins are usually a choice for sensing metal-ligating vapours as they have sites, large spectral shifts upon ligand binding, and especially intense coloration [38,39]. The colorimetric array can be built up by printing selected dyes on a reversed-phase silica-gel plate. The array responses originate from selective and specific interactions between the vapour of interest and the metalloporphyrin deposits. The digital data representing the colour change profiles are then evaluated using the data-processing methods and pattern-recognition methods [40]. The colorimetric sensor array allows the visual identification of a wide range of ligating (amines, alcohols, ethers, phosphor compounds, thioethers, thiols, halocarbons, and ketones) vapours [38,39]. Taking advantage of the large colour changes induced in metalloporphyrins after ligand binding, we are able to obtain unique colour-change as finger prints for each analyte; besides the hydrophobic nature of reversed-phase silica, water vapour does not affect the performance of the device. The OI minimises the need for extensive signal-transduction, making up a colorimetric low-cost, sensor array for detection and identification of VOCs resulting from the environment, land fill, chemicals and chemical warfare agents [41,42]. The metal-oxide nano-wires as ZnO show interesting emission properties of photoluminiscence (PL) in the range of UV–vis at room temperature The surface interactions of metal oxides nanowires with gases can modify the intensity of PL: this effect allows the measurement of contents on gaseous species measuring the PL signal, permits arrays of optical chemical sensors that can be used at room temperature, and removes effects of thermal aging [42–44].These photoluminiscent (PL) sensors based on an optical transduction mechanism do not need electrical contacts thus avoiding the difficulties to handle nanowires. It has recently been shown that it is possible to excite the PL with an LED emitting in the UV, thus proving the possibility to set up a low cost wearable device using a photodiode to read the signal for detecting explosive and warfare agents.

3.4. *Gravimetric/acoustic sensors*

Arrays of acoustic wave (AW) devices are widely used in sensing applications, as, the environmental fields and security [45–48]. Some types of acoustic wave sensors are: quartz crystal microbalances, devices based on Rayleigh waves acoustic plated modes, transverse surface waves and Love waves. Love wave sensors are suitable to detect CWAs due to the high sensitivity, fast response, real time detection, stability and low cost.

3.4.1. *Quartz crystal microbalance sensors*

These sensors, essentially, weigh the amount of gas or vapour interacting with a sensing layer coated onto a microbalance [46,49,50]. If a quartz crystal oscillator is coated with a material such as a gas chromatographic stationary phase the resonance frequency decreases at a rate quantified by the Sauerbrey equation [51], provided the acoustic impedance of the coating material does not change and is similar to that of the quartz. This equation is used in quartz crystal microbalance measurements. The change Δf in the oscillation frequency of a piezoelectric quartz crystal is given as a function of the mass Δm added to the crystal.

3.4.2. *SAW sensors*

Saw sensors are based on the propagation of acoustic waves produced by piezoelectrical materials (quartz, ZnO, $LiNbO_3$, …) in a multilayer structure. Surface acoustic wave (SAW) devices have shown proved characteristics as chemical vapour sensors due to their compact structures, small size, low cost, high sensitivity and fast response. The basic principle of SAW gas sensors is the reversible sorption of chemical vapours by a sorbent coating which is sensitive to the vapour to be detected [52–54]. The vapour is adsorbed by the sensitive layer resulting in a mass increase of the coating, which alters the surface wave velocity in the device. The velocity changes are measured indirectly using the device as the resonant element in a delay line oscillator circuit and measuring the frequency shifts due to the vapour sorption. As 90% of the propagating SAW energy is focused at a depth of one wavelength from the surface, one of the alternative methods for fabricating SAW devices is to use layered structures containing piezoelectric thin films deposited on substrates. This is possible because of the availability of the techniques of deposition of thin piezoelectric films and by the compatibility of the technological process of fabrication of SAW sensors, with those of planar integrated circuits [55].

Thus, the research in this field is centred on the development of materials with good electro-acoustic properties allowing the fabrication of high frequency devices on silicon substrates with improved performances and at the same time with a low fabrication cost. Several polymers are chosen as sensitive layers: The most used are polymers such as: phtalocianines, ciclodextrins, organometallic compounds, and rubber polymers as polyepichlorohydrin (PECH), polyetherurethane (PEUT), polybutadiene (PBD), polydimethylsiloxane (PDMS), OV-225 and OV-275 silicones, and polyisobutylene (PIB) [56–58]. They are well known commercial polymers for SAW sensor applications with excellent properties such as low static glass transition temperature in order to obtain fast vapour diffusion and reversible response.

3.4.3. Love-wave sensors

The Love-wave sensors are based on a shear horizontal surface acoustic wave (SH-SAW) propagated on the ST-cut quartz perpendicular to the *x* crystallographic axis. This SH-SAW generated and detected by interdigited transducers (IDTs) which are made by the standard litho-graphic technique. Finally, the SH-SAW is guided in a film (SiO_2, Novolac, etc) in order to obtain a Love wave. Love sensors show larger sensitivity than SAW sensors and owing to the guided film are available for detecting gases solved in liquid samples and after a suitable functionalization of the sensing layer that allows placing antibodies that act as different immunosensors [59–61].

3.5. New materials and structures for sensors

3.5.1. Nanostructured sensors

Nano-crystalline and nano-structured materials are great candidates for improving sensitivity of gas sensing. A number of nanostructured materials such as quasi-1D metal oxides (nano-MOX), carbon nanotubes [62,63], nanoparticles, and nanoporous structures have been developed for sensing applications. Some of these materials have mono crystalline structures with well-defined chemical composition, surface terminations, free from dislocation and other extended defects, such variety of morphologies including nanowires, core-shell nanowires, nanofibres, nanobelts, hierarchical hollow nanostructures, nanorods, and mesoporous films [64–66]. The nanostructures exhibit several advantages with respect to their traditional thin/thick film counterparts including very large surface-to-volume ratio, dimensions comparable to the extension of surface charge region, superior stability owing to their high crystallinity, relatively simple preparation methods and possible functionalization of their surfaces with target specific receptor species [67–69]. In addition, nano-MOX may exhibit physical properties which are significantly different from their coarse-grained polycrystalline counterparts because of their nano-sized dimensions. Due to the increase of their specific surface area, surface effects are dominated, leading to the enhancement of surface related properties such as catalytic activity or surface adsorption, which are key properties for superior chemical sensors production [70–73].

Also several reports about nanofibres as sensitive layer of acoustic wave (AW) sensors have been published [74,75] and there is an increase in the use of the electrospinning technique to deposit them on AW sensors.The combination of Love-wave devices with different elesctrospun nanofibers can provide substantial advantages to detect VOCs, such as higher sensitivity and selectivity, and lower insertion losses of the devices. However, as far as we know, only there is a reference of the use of an array of Love-wave devices with electrospun nanofibres of polymers to detect VOCs, realised in our laboratory [76].

3.5.2. Graphene chemical sensors and biosensors

Recently, Graphene, RGO (reduced grapheno oxide) and some derived composites appear as important candidates for chemical and biological sensors, because they can detect even the lowest level of target species due to their extremely high surface to volume ratio with almost all the atoms exposed to the environment. Based on its two-dimensional monolayer of carbon atoms, as a building block of sp2 bonded carbon materials it should be well-suited in some cases for the detection of adsorbates when different functionalities are placed on the edge [77–79], which are very sensitive to changes in the chemical and biological environment. Their excellent electrical and mechanical properties, [80–83] showing very large electron mobility at room temperature, result in a very high sensitivity. Growing interest in graphene as a sensor is also due to its exceptional electronic properties [84–87] demonstrated experimentally and its potential application, in micro/nano electronic devices and chemical/bio-sensors. Recent improvements on graphene deposition methods have contributed to spread out the applicability for device integration. From the initial electrically isolated graphene fabricated by mechanical exfoliation of graphite, much effort has been devoted to develop methods to synthesise at a large scale for practical electronic applications. A variety of methods, such as epitaxial growth on SiC, chemical vapour deposition have been explored [88–93]. One of the most important and challenging goals is to grow graphene at large scale with uniform thickness [94]. Tacking account the precedent of carbon materials as chemical/bio-sensors since the environmental sensitivity of carbon-based molecules in the case of carbon nanotubes (CNTs) have already been extensively studied in a decade [95–101]. However, the diversity in CNTs' structure and chirality may lead to varied device characteristics, and thereby cause device reliability issues. On the contrary, graphene has a great potential to resolve these problems because its strictly two-dimensional (2D) structure, enabling devices based on graphene to behave identically on a large scale. The fabrication of chemical/bio-sensors in field effect transistor type structures based on graphene is also simpler than those of SWNT. In addition, with the 2D structure, the monolayer graphene has its whole volume exposed to the environment, which can maximise the sensing effect by changes in conductance due to chemical or biological species adsorbed on the surface, acting as electron donors or acceptors. Recently, graphene-based gas molecule sensors and biosensors have been reported. By using Wafer-scale synthesis of graphene monolayer, with uniform thickness, through CVD under ambient pressure it is expected to have an performance as pure graphene. Consequently, the commercialisation of graphene-based chemical/bio-sensors can be a near reality [102–104].

In the case of RGO (reduced grapheno oxide), the responses have been analysed by changes in electronic parameters as: conductivities, capacitances, and carrier effects by building electronic devices as FETs using RGO. The sensitivity of such sensor vs gas (or vapour phase) depends on the charge carrier transfer on GO/RGO surfaces due to the adsorption of gases and vapours as NO_2, NH_3, H_2O, CO [78,105–107].

Graphene based composite materials have been studied for gas sensors. For example, Pt/RGO/SiC based devices for hydrogen gas sensing [108]. The electrical characteristics and hydrogen gas sensing mechanism of the device were described by analysing the effect of hydrogen interaction at the graphene/SiC and Pt/graphene interfaces. High work function of Pt leads to a weak interaction energy at the interface and preserves the electronic structure of RGO and electrons transfer from RGO to

Pt to equilibrate the Fermi level. Upon exposure of hydrogen gas, the carrier concentration is increased due to dissociation of hydrogen molecules, which occurs on the Pt surface.

Also the basic SAW structure in which the propagation path is coated with a thin film of graphene or suitably functionalized graphene can adsorb the gas molecules of interest causing a delay in the path and a change in the frequency of operation [53]. Several studies have been demonstrated for RGO based biosensors as well [109]. In this case the fabrication and functioning of tree devices is proposed: a RGO-based (i) single-bacterium device, (ii) label-free DNA sensor, and (iii) bacterial DNA/protein and polyelectrolyte transistor.

The RGO FETs can also specifically detect biomolecules with high sensitivity using specific antibodies. The fabrication and characterisation of a highly sensitive and selective FET biosensor using Au NP antibody conjugates decorated with GO sheets have been reported [110]. The study demonstrates a GO-based immunosensor for detecting a rotavirus as a pathogen model. The sensor showed high sensitivity and selectivity by using GO. CdTe/RGO composite also exhibited the chemical–biological sensing where graphene worked as an amplified electrogenerated chemiluminescence (ECL) of quantum dots (QDs) platform [111].

4. Pattern recognition methods

The multivariate information obtained by the sensor array can be sent to a display so a human can read that information and take an action or an analysis. The information, which is an electronic fingerprint of the volatile compound measured, can be sent to a computer to perform an automated analysis and emulate the human nose. These automated analyses that come from methods of statistical pattern recognition, neural networks and chemometrics, is a key part in the development of a gas sensor array capable detecting, identifying or quantifying different volatile compounds. All these pattern recognition methods are composed by several stages of processing multivariate data. In the first stage the sensor data is pre-processed, usually the data curves are smoothed, drift compensated, outliers eliminated and also extracting of descriptive parameters can be extracted. In the second stage an extraction or selection of the features that will be used by the pattern recognition method is carry out. Some of these techniques extract the steady data of the response, such as Principal Components Analysis, and Fourier analysis. In the third part a classifier is used to decide to which class the neural networks trained with data coming from measured know samples but also fuzzy logic systems, linear and non-linear regression algorithms, Bayesian classifiers or other statistical methods. The final stage is to validate the model with additional data to estimate its accuracy. A good processing in this phase is essential to the performance of the subsequent stages of the pattern recognition method [112]. Usually this can be arranged in three steps [113]. Usually there is a reduction in the feature vectors to a smaller size by a feature selection or extraction. With feature extraction we transform the feature vector so we reduce the number of components preserving most of the information in the original feature vector. Techniques as PCA or LDA are used [114,115]. With feature subset selection we try to find an "optimal" subset of features preserving most of the information. In both cases we try to maximise the information contained in the new feature vector [116]. The prediction part can be a classification, quantification or clustering. The classification method aims to assign an unclassified feature vector to one class from a previously learned discrete set of labels. There are several methods such as the quadratic classifiers, kNN and neural networks [117]. The neural networks are the most popular classifiers in e-noses. Most of them are feed-forward networks of simple processing elements or neurons whose connectivity resembles that of biological neuronal circuitry. Others neural network models like radial basis functions or ART structures also have been used. The quantify method must do some kind of regression and has to establish a predictive model from the feature vector coming from the gas sensor responses to another set of continuous dependent variables, such as gas concentration. The regression can be of several types. To make a sensory analysis in which the dependant variable is the response of a sensory human panel to the same analyte (e.g. intensity, hedonic tone…). This situation is the more challenging and is a really complex regression problem. Ordinary least squares, ridge regression, principal components regression and partial least squares are some of the regression methods that can be used to solve those problems. Another method is the bootstrapping one in which we resample the data with replacement [118]. When the model has been selected a third independent set can be used to estimate the accuracy of the proposed model.

A new architecture called *m*Som (where *m* is the number of independent maps), has been developed on the basis of the self-organising map (SOM) theory developed by Kohenen. Unlike other neural techniques where the input–output learned mapping is static, the architecture here presented reduces the drift problem (thus increasing the time of re-calibration) by addressing the dynamic input–output mapping.

The principal goal of the self-organising map (SOM) is to transform an incoming signal pattern of arbitrary dimension into a two-dimensional discrete map, and to perform this transformation adaptively in a topological ordered manner. The embedded competition paradigm for data clustering is done by imposing neighbourhood constraints on the output units, such that a certain topological property in the input data is reflected in the output's unit weights.

The novelty in this architecture is the possibility to adjust the individual maps overtime to be able to predict gas measurements that have suffered from drift.

Other technique in use is the discrete wavelet transform: the filtering algorithm associated with the discrete wavelet transform is an effective tool for smoothing out the high-frequency content without losing the important features in the process signal. The wavelet transform decomposes signals over dilated and translated wavelets. It maps the input signal into a new space, the basic functions that are quite localised in space and provides a multiresolution signal decomposition. This signal analysis technique analyses the signal at different frequency bands with different resolutions by successively projecting it down onto two types of functions, which are obtained by applying shift and scaling operations to two prototype functions called the scaling function $\varphi(t)$ and the wavelet function $\psi(t)$, respectively [119].

5. Applications

5.1. Environment

Conventional monitoring methods for most chemical contaminants are costly, time intensive, and involve limited sampling and complicated analytical techniques. Today there are an increasing need for cheap, improved and reliable methods for rapid, accurate detection and quantification of environmental chemical pollutants.

Electronic noses resulting from the rapid development of gas multi-sensor technologies provide relatively cheap, portable electronic-detection devices with the flexible capabilities of detecting a wide range of organic and inorganic gaseous substances, including chemical pollutants. These devices based on diverse operational principles control chemical pollution in various environmental settings or applications. Their impact in the area of environmental-pollution monitoring is wide: detecting pollution range from monitoring air quality [120,121], the early or real-time area monitoring of diurnal urban pollution-emission events via sensor monitoring networks (outdoor pollution) [122], localisation of stationary (point-source) pollution sources [123], and mapping of chemical plumes [124,125] to detection of fires at chemical-storage facilities, maintaining chemical security at harbour entrances or importation ports [126], detection of leaks of toxic or hazardous materials from pipelines or industrial plants, and early warning of the accumulation of toxic fumes such as solvents or explosive fumes, carbon monoxide or carbon dioxide within enclosed areas of buildings or mines (indoor pollution) and soils contamination.

Metal oxide semiconductor (MOS) gas sensors are the most widely used e-nose sensor types for monitoring environmental pollution because they are relatively inexpensive, robust, lightweight, and long lasting with quick response and recovery times [127]. MOS sensors have high sensitivities as low as parts per billion (ppb) due to large surface areas for analyte adsorption [128,129]. The versatility of MOS sensors is indicated by capabilities of monitoring trace amounts of many environmentally-important gases such as carbon monoxide, ammonia, and nitrogen dioxide as well as a wide variety of VOCs.

As the production costs are relatively low for MOS sensors that can be manufactured quickly on a large scale with easily controllable processes that assure sensor uniformity. Previous research has revealed two possible approaches to increase the utility of e-nose instruments for pollution monitoring tasks. The use of either an array of gas sensors with different sensing materials (different sensor types within the array) for coverage of different classes of pollutants [130], or the use of temperature modulation of a single gas sensor have shown some demonstrated feasibilities [131,132]. Temperature modulation of high-power MOS gas sensors requires pre-calibration for both single gases and gas mixtures because the sensor response is nonlinear with gas concentration [133]. However e-noses show some weaknesses, in order a full incorporation and commercialisation because a pre-calibration would be necessary with all possible concentration combinations of component gases in polluted air mixtures since pollution monitoring requires both identification and quantification of the gases. The complexity and temporal variability in the composition of pollution discharges are two of the biggest challenges to utilising e-nose monitoring units within pollution-monitoring networks. Short-term variability in the composition of pollution mixtures, due to intermittent or accidental discharges of chemical pollutants, can greatly challenge any ability to readily identify such sources because of the immediate need to determine both the identities and concentrations of detected pollutants. These logistical problems suggest the need for more research to further develop e-nose technologies and methodologies to more effectively handle continuous monitoring of pollutants in wastewater emissions from sewage treatment plants and from industries that frequently release toxic pollutants into the environment. Similar solutions will need to be developed as well for random intermittent releases of complex pollutant mixtures that are encountered in air-pollution monitoring.

Another alternative technology to achieve high sensitivity is based on acoustic sensors, a polymer-coated surface acoustic wave (SAW) array is one of the best choices for organic gas sensing applications. Currently SAW devices are also used for chemical applications because of their high sensitivity, fully reversible behaviour, and high signal-to-noise ratio [57]. For the proposed portable e-nose system based on the SAW sensor array [134–137], a piezoelectric substrate was chosen for energy transformation between mechanical strains and electrics. The obtained results clearly demonstrate the ability to recognise a special component for similar families. We have demonstrated the possibility of to apply a SAW sensor array with different polymers to discriminate different gases. In addition, it is clear that the combination of sensor arrays of coated SAW devices and appropriate recognition algorithm [138–141], will provide a sensing system that can be extremely selective.

5.2. Security

Prevention and detection of explosives and chemical warfare agents (CWAs) has become a social priority due to increased demand for homeland security in the face of prevent terrorist threats as well the remediation of environments that already pose a high risk such as:clearing of minefields or the prevention of dangerous gases as: Sarin (GB), Soman (GD) or Distilled Mustard (HD), TNT, DNT, plastic explosive and nitrates, that are fast and effective weapons and, therefore, ideal for terrorist purposes. Knowledge of the processes that influence the fate and transport of CWAs in the environment can aid in the predictions of environmental persistence, estimates of exposure, and the development of decontamination and disposal strategies.

Usually the security at airports was solved using metal detectors to identify weapons by X-ray systems for viewing the contents of luggage by traditional methods but many terrorist groups have adapted to avoid the use of metallic objects.

Conventional detecting methods to detect volatile substances, such as ion mobility spectrometry (IMS) in routine use are largely only suitable for the screening the vapours in hand luggage. Here the sample vapours are ionised at atmospheric pressure before introduction into the drift tube and drift times, related to the mass of the ions and by determining the mass/charge ratio, is possible to identify components within the sample through comparison with known standards. Detection of traces of explosive substances in the air issues related to the low vapour pressures of many explosives are only hindered when these explosives are wrapped or packaged to avoid detection. Recently a new technology based on FIR (far IR radiation) called (Terahertz spectroscopy THz) emerges as a new very promising method of detection.

The terahertz (THz) spectroscopy has been investigated recently as a technique for the detection of explosive vapour signatures [142–144]. Some of these issues have been addressed and the technology is further being considered as not only an explosive detection method, but also a way to detect weapons and other concealed objects within luggage and beneath clothing. THz lies in the far infra-red region, from 0.1 to 10 THz. In this range waves can penetrate through many non-polar dielectric materials, such as wood or leather, and the low photon energies are at a level one million times less than that of X-ray photons. After the absorption spectra of seventeen explosives and explosive related compounds (ERC) using THz spectroscopy [145] most of the substances examined exhibited characteristic absorption features in the 0.1–2.8 THz range. These results may be used to form a fingerprint database of explosives and ERCs. Through improvements in emitters and sensors, new spectral features have also been established for explosives within the frequency region of 3–6 THz [146–148].

One of the most suitable and important aspects of these technologies is their portability and much research is being undertaken into the miniaturisation of existing technologies. Some of the nanotechnology based methods, utilising carbon nanotubes which may display rapid change in conductivity on adsorption of vapours of interest may also be suitable.

Nanotechnology has an important role to play in advanced detecting methods over the last decade has become increasingly important, with research focusing on incorporating new nano-based aspects into existing technologies to improve sensitivity, selectivity and portability.

Micro-sensors have been updated by the direct and selective growth of semiconductor SWCNT networks on their sensitive areas and these sensors have been used for the detection of three CWA simulants (DMMP, DPMGE and DMA). As CW involves high toxicity and its use is restricted in non-surety laboratories, an ideal chemical agent simulant would mimic all relevant chemical and physical properties of the agent without its associated toxicological properties. Although a number of compounds have been used as CWA simulants, no individual compound is ideal because a single simulant cannot satisfactorily represent all environmental fate properties of a given CWA. Thus, a number of different chemicals have been used as CW.

The most dangerous compounds are those that are harmful at very low concentrations (pico-mole range); electronic noses are utilised for military purposes as early-warning instruments to detect such compounds in air at concentrations below lethal contents [149]. There is a considerable demand for portable, handheld monitors, but previously they have not been employed to the fullest extent due to the great diversity of toxic compounds and mixtures [150]. Particular solutions are in the process of integrating complementarities of numerous e-nose instruments and sensors starting up platforms oriented for preventing in areas for special most-probable CWAs or pollutants.

The response of the micro-sensors may be considered linear in the range of the measured concentrations and the detection limits have been established well below the median lethal dose for each tested CWA. This is due to the porosity of Al_2O_3-SWCNT nanoparticles and to the tested analytes being strong electron donors.

Therefore electronic noses constitute a powerful tool applied towards the detection of explosives [77]. The development of these miniature and portable devices would increase the selectivity and sensitivity in a nano-electronic nose by a suitable integration of sensitive layers

A detailed description of electronic noses and their application to explosive and CWA detection has been reviewed elsewhere [52–58,151–154]. In these works, an array of chemical sensors, interacts with vapours in different ways and to different extents, and it is combined with a pattern recognition system such as an artificial neural network.

6. Conclusions and future

The present paper attemps to provide information about the recent advances in the electronic olfaction, checking the last improvements experimented on the three basic structural steps: sensing, sample handling and pattern recognition methods that configure the e-Noses and also their most important applications in the environment, and for citizen security. We show the conclusions and the prospects separately considering the two main considered issues: new sensors and advanced applications.

6.1. Conclusions about sensors

Sensing devices with improved sensitivity, selectivity and stability applied on different transduction units have been included on chemo-resistive detectors, by selecting characteristics such as the surface area, donor density, agglomeration, porosity, acid-base property of the sensing material in the case of MOS sensors. Nano-structured materials (quasi-1D metal oxides, nano-MOS), carbon nanotubes, nanoparticles and nanoporous structures have also been developed for sensing applications. Some of these materials have mono crystalline structures with well-defined chemical composition, surface terminations, free from dislocation and other extended defects. Due to the increase of their specific surface area, surface effects are prevailing, leading to the enhancement of surface related properties such as catalytic activity or surface adsorption, which are key properties for superior chemical sensors production. Taking into account the past experiences in CNTs as sensors, it is important to consider the growing interest in graphene and related materials as sensors due to their exceptional electronic properties. It has recently been demonstrated its potential application in micro/nano electronic devices and chemical/bio-sensors, due to the use of wafer-scale synthesis of graphene mono/multilayer, growth by CVD under ambient pressure, with an uniform thickness. Therefore applications in gas sensors are expected and the commercialisation of graphene-based chemical/bio-sensors could be a near reality. Chemo-resistive polymers exhibit interesting properties that make them useful for gas sensors: room temperature operation, easy to prepare and quick response among others. Different conducting polymers, as: poly-pyrrole, poly-N-methilpyrrole, polyaniline show important sensitivities when exposed to different volatile species.

SAW and LOVE devices shown suitable and contrasted characteristics as chemical vapour sensors due to their compact structures, small size, low cost, high sensitivity and fast response. The basic principle of AW gas sensors is the reversible sorption of chemical vapours by adsorbent coating which is sensitive to the vapour to be detected.

6.2. Conclusions about applications

6.2.1. Environment

With respect to the monitoring of environmental pollution that is a new field for the development of applications with the electronic nose (E-nose) and provides many new monitoring capabilities needed to overcome the limitations of conventional spectrometers. Large number of monitoring tasks may be also carried out using these relatively cheap devices increasing the number monitors building up large and cheaper networks. In such as a way, a more effective management of data for many complex urban pollution problems in real-time could be achieved and would help decision-making to minimise pollution damage.

At present, there is a considerable demand for portable, handheld gas monitors, but due to significant logistical problems, inherent to sensors that needs to be resolved, before these instruments are used extensively as pollution monitors. Metal oxide semiconductor (MOS) micro and nano-gas sensors are the main candidates for monitoring environmental pollution because they are relatively inexpensive, robust, lightweight, and long-lasting with quick response and recovery times MOS sensors have high sensitivities as low as parts per billion (ppb) due to their large surface areas for analyte adsorption. The versatility of MOS sensors is indicated by their capabilities of monitoring trace amounts of many environmentally-important gases such as carbon monoxide, ammonia, and nitrogen dioxide as well as a wide variety of VOCs. Gravimetric sensors (SAW, LOVE) are essentials in detection majority of VOCs having large sensitivities, quick responses, remote running and portability.

Optical imaging (OI) technologies constitute, at the present, one of the most advanced, powerful and low cost procedures for identifying organic molecules, using respectively new advances in colorimetric and photoluminescence properties of organ-metallic and nano-materials, both procedures show a large specificity to variety of noxious and warfare chemicals in environment and security situations.

6.2.2. Security

Citizen security, prevention and detection of explosives and chemical warfare agents (CWAs) has become a social priority due to increased demand for homeland security in the face of prevent terrorist threats as well the remediation of environments that already pose a high risk such as clearing of minefields. Recently a new technology based on FIR called (THz – Terahertz spectroscopy) emerges as a new very promising method for detection. Most explosives and explosive related compounds have spectral fingerprints within this range and, as many apparatus operate within the range 0.1–2.0 THz, thus highlighting THz radiation as a prospective sensor and imaging agent for the detection of hidden explosive substances. One of the most important aspects of these technologies is their foreseeable integration in arrays and portability for this reasons, much research is being undertaken into the miniaturisation of existing technologies. Nanotechnology has an important role to play in this as well as also enabling the development of new technologies. Improving the sensitivity and specificity of explosive detection technology are principles that continue to be important; lower detection limits for many materials have improved considerably and work in this area remains a competitive field of research. The most dangerous compounds are those that are harmful at very low concentrations (pico-mole range), electronic noses are utilised for military purposes as early-warning instruments to detect such compounds There appear to be many promising methods that are being developed as alternatives to these systems and the utilisation of these various technologies will depend on the particular application.

It has recently been shown that it is possible to excite the PL with an LED emitting in the UV, thus proving the possibility to set up a low cost wearable device using a photodiode to read the signal for detecting explosives and warfare agents.

In general, most of the applications represent limited feasibility studies with resulting poor validation especially in terms of reproducibility and predictive ability. There are very few long-term studies, which indicate excellent reproducibility without the need for extensive calibration and mathematical analyses of the sensor readings. The best results in the use of e-noses is an application-specific which may limit their use. There is much research even to be done with the interpretation of the results. Although differences can be measured by these devices, there is not a full agreement on sensory testing. There is also the requirement for considerable method development for specific applications. Finally, sensor arrays and pattern recognition techniques tend to give a quality index or alarm alert of a sample but not providing data with respect to composition.

6.2.3. The most recent advances

Optical imaging (OI) technologies constitute now cutting-edge research on gas sensing, is a powerful and low cost procedure for identify organic molecules, using respectively last advances in colorimetric and photoluminescence properties of organ-metallic and nano-materials [38,42]. Both procedures show a large specificity face to variety of noxious and warfare chemicals in environment and security situations. Actually wereable and remoting prototypes of such devices are in development for detecting VOCs, compounds as polyphenols, amines, methylamines and noxious gases of interest in air quality [155,156].

Structures of nano-particles, such as amine modified multi-walled carbon nanotubes (MWCNT-NH$_2$) and gold nanoparticle (AuNP) simultaneously, via electrospraying technique, were deposited onto interdigitated electrodes (IDE) fabricated on polyimide (Kapton$^{\circledR}$) substrate. These flexible sensors have great interest because to their low-cost, lightness, easy processing, conformability and flexibility, monitoring VOCs by an easy way, as it is the conductivity measurements. A current challenging issue because they have great influence in on the indoor air quality [157,158].

The latest developments in conductive and gravimetric sensor classical structures, due to the incorporation of micro/nano materials, for applications in environment and security are shown in the following researchs [159–162].

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