

Chemical Sensors for Environmental Monitoring and Homeland Security

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Chemical sensors consist of a recognition element that is sensitive to stimuli produced by various chemical compounds (analyte) and a transduction element that generates a signal whose magnitude is functionally related to the concentration of the analyte. Chemical sensors also include a special branch referred to as biosensors for the recognition of biochemicals and bio-reactions. The use of biological elements such as organisms, enzymes, antibodies, tissues, and cells as receptors differentiates biosensors from conventional chemical sensors. In general, the chemical sensors are broadly classified into gas, liquid, and solid particulate sensors based on the phases of the analyte. They are further categorized as optical, electrochemical, thermometric, and gravimetric (mass sensitive) sensors according to the operating principle of the transducer. Detailed sub-classification of the sensing schemes along with a comprehensive review of the merits and challenges of each modality can be found in the book authored by Jiri Janata.¹

Chemical sensors have become an indispensable part of our technology-driven society and can be found in chemical process, pharmaceutical, food, biomedical, environmental, security, industrial safety, clinical, and indoor monitoring applications to highlight a few.²⁻⁶ Like many fields in science, chemical sensors have benefited from the growing power of computers, integrated electronics, new materials, novel designs, and processing tools. Manifestation of such technological

changes can be seen in the development of miniaturized, inexpensive, portable, and mass manufacturable chemical sensors capable of static and continuous measurements even in remote environments. Moreover, research on nanostructured materials⁷ and the use of sensor arrays in electronic nose (e-nose) systems⁸ is addressing the need for better analyte selectivity. Breakthroughs over the last decade have pushed chemical sensors into new markets, as well as new applications⁹ within existing markets. In this brief article, we will discuss a few examples of emerging sensor technologies. The application of chemical sensors to environmental monitoring will be presented first. Then, the detection of chemical warfare agents and conventional explosives for homeland security applications will be discussed. Finally, the current challenges faced by chemical sensors and their future outlook are briefly presented.

Chemical Sensors for Environmental Monitoring

Chemical sensors are expected to play a critical role in environmental monitoring (both indoor and outdoor) and environmental control (air, water), facilitating a better quality of life. The projected increase in global energy usage and unwanted release of pollutants has led to a serious focus on advanced monitoring technologies for environmental protection, remediation, and restoration. Electronic nose (e-nose) and electronic tongue (e-tongue) have

been demonstrated to be promising technologies to address concerns over the degradation of the pristine environment. Behind the terms e-nose and e-tongue, one can find an array of biosensors or gas sensors whose signal output is analyzed with pattern recognition techniques. Using generic terminology, the e-nose can be defined as a chemical sensor composed of an array of independently semi-selective and reversible gas sensors combined with pattern recognition software with a potential to mimic the human olfactory system. Figure 1 illustrates the components of an e-nose system. There are several commercial systems based on a wide variety of sensing technologies available today for various applications.

Persaud and Dodd¹⁰ first reported the design of an engineered olfaction system to detect a variety of odorants using semiconducting transducers in 1982. Many sophisticated designs and commercial e-nose systems were developed thereafter and a number of review papers¹¹⁻¹⁵ were published on environmental monitoring using e-nose. The use of different transduction principles for specific scenarios, availability of commercial systems along with future outlook can be found as a common theme in all the above mentioned references. A common set of challenges is seen to resonate with all the authors when an e-nose is chosen for a field application. A major concern is the long-term stability of the sensing system without compromising the sensitivity or selectivity to the analyte of interest. Undoubtedly, the

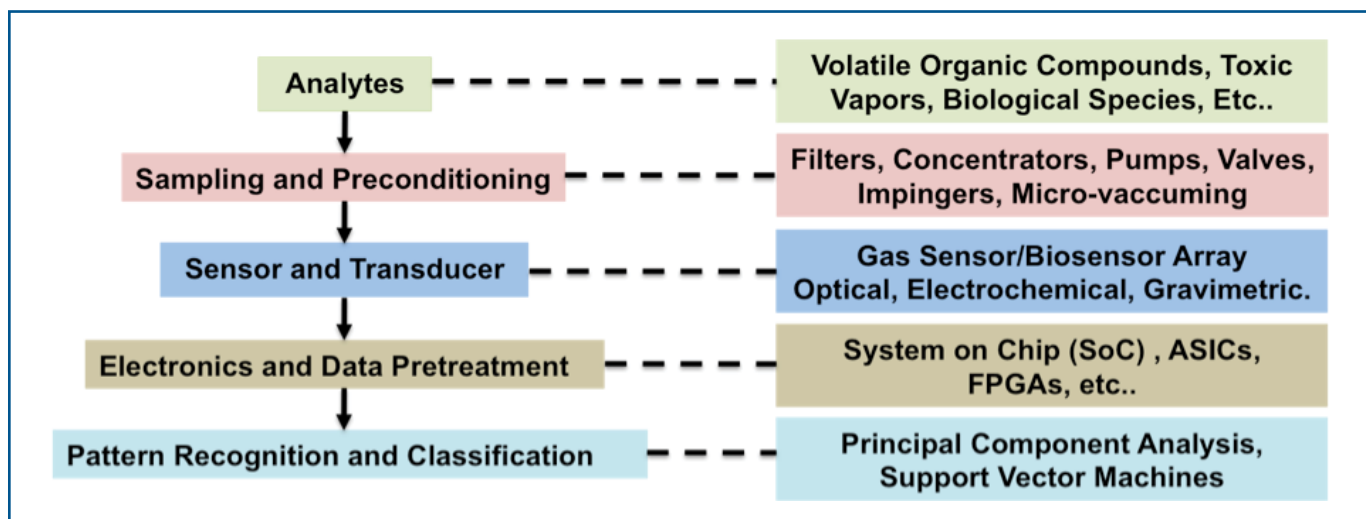


Fig. 1. Components of an e-nose system.

ever changing temperature, humidity, pressure, cyclic or seasonal variations, and fouling processes can lead to unacceptable selectivity and degrading sensitivity levels. It is to be noted the receptor plays a crucial role in averting nonspecific adsorption processes. Engineering the receptor to be stable and selective in varied environments is deemed essential for reliable operation of the sensor. Several gas-sensing technologies including conductometric, potentiometric, amperometric, surface acoustic wave, quartz crystal microbalance, calorimetric, and optical have been employed in e-nose systems. Two of the electrochemical gas sensor technologies that seems promising for their low cost and long-term stability are briefly discussed.

Metal oxide based gas sensor systems.—Metal oxide semiconductor (MOS) based conductometric sensors are one of the most commonly used sensors for environmental monitoring. They are also known as Taguchi or Figaro sensors (the inventor and the name of the company that commercialized the sensors respectively). With the metal oxide bulk or thin film acting as a receptor material, the detection mechanism is based on the change in material resistivity after exposure to the analyte gas. Chemical (change in surface oxygen concentration) and local carrier concentration change (change in redox state) mechanism is generally accepted as the origin of resistance change.¹⁶ A comprehensive treatment on the conduction mechanism prevalent in metal oxide gas sensors was carried out by Barsan *et al.*¹⁷ Recently, metal oxide nanostructures¹⁸ have been used as sensing elements targeting improved sensitivity and selectivity. The conductance of 1D metal oxide nanomaterials can be expressed as¹⁸

$$G = n_0 e \mu \pi (D - 2w)^2 / 4l \quad (1)$$

where n_0 represents carrier concentration, μ represents mobility, l is the length of the nanostructure, D is the diameter of the nanostructure, and w is the width of surface charge region that is related to the Debye length of the nanomaterials.

The Debye length of sensing materials, in turn, can be expressed as¹⁸

$$w = (eV_s/kT)^{0.5} L_D \quad (2)$$

$$L_D = (\epsilon \epsilon_0 kT / e^2 n_0)^{0.5} \quad (3)$$

where ϵ_0 is the absolute dielectric constant, ϵ is the relative dielectric permittivity of the structure, k is the Boltzmann's constant, T is the temperature, and V_s is the adsorbate-

induced band bending. The sensor response in these systems can be defined as¹⁸

$$S = (G_1 - G_0) / G_0 = 4(w_0 - w_1) / D \quad (4)$$

where G_0 and G_1 are the conductance before and after exposure to the analyte. As inferred from Eqs 1-4, applying an external gate voltage, doping metal impurities during material growth, modulating operating temperature, and changing the geometry of the nanostructures can improve the sensitivity. Though nanostructured metal oxide gas sensors look very attractive, the investigations on improving the signal to noise ratio, selectivity, and poisoning is still lacking. Further improvement in the overall nanoscale sensor performance along with good packaging schemes and seamless integration with electronics could rival other approaches in environment monitoring. In essence, if the issues of calibration, long-term stability, and selectivity can be resolved, e-nose systems will assume a valuable role in analytical systems for environmental monitoring and control.

Electrochemical mixed potential based gas sensor systems.—Electrochemical based non-nerstian, potentiometric gas sensors show exceptional long-term baseline and response stability and have the potential to be deployed in e-nose systems. Relying on differential catalysis, these sensors produce mixed potentials¹⁹ at each electrode using Ytria-Stabilized Zirconia (an oxygen-ion conducting) electrolyte. These sensors have been developed to detect a wide variety of gases including nitrogen oxide(s),²⁰ hydrocarbons,²¹ ammonia,²² and carbon monoxide.²³ The operating temperature, sensor bias voltage/current, and electrode materials impart the desired selectivity. Figures 2a, b, and c show the response to various gases (HCs, NO_x, NH₃, CO) of three different mixed potential sensor configurations with selectivity to non-methane hydrocarbons, NO_x/NH₃ and NH₃ respectively.^{24,25} As reported, the sensor design is very unique and possesses several inherent advantages. Two of the characteristic features leading to exceptional stability and sensitivity are the minimized electrode-electrolyte interface and its morphological stability. The sensor design uses dense electrodes and porous electrolyte unlike conventional oxygen sensors. A direct benefit from such a design was the enhanced NO_x sensitivity, which was directly attributed to a change in the interfacial impedance upon exposure to NO_x.²⁶ The applicability of mixed potential based sensing system for environmental monitoring will require a good packaging scheme and a multi-sensor element system, with each element tuned (material composition,

operating temperature and mode) to optimally detect a gas of interest on a single substrate with an integrated on-chip heater.

Chemical Sensors for Homeland Security

Chemical warfare agents.—Chemical warfare agents (CWA), along with biological and nuclear weapons, are considered weapons of mass destruction and as such their detection is of great interest for homeland security. Chemical weapons are relatively easy to produce, acquire, handle, and disperse when compared to nuclear and biological weapons. Therefore their detection acquires greater significance in the context of international terrorism and the ability of non-state actors to create mass casualties with minimal effort. Considerable research has been performed to develop detection systems and methods that are inexpensive, portable, and which achieve real time detection.

Hill and Martin²⁷ authored a review article on conventional analytical methods for the detection of chemical warfare agents. The authors classified the detection schemes by the number of dimensions of information they provide. The simplest approach (single dimensional) for chemical detection is to target the specific compound of interest and selectively detect it in the presence of other background compounds and interferences. When a separation method is coupled to single dimensional sensors to largely improve specificity, they are classified as two-dimensional detectors. Three-dimensional sensors (using separation and further filtration) are often preferred for high resolution screening applications with a drawback of complex instrumentation. Because of the complexity of these instruments, they are difficult to operate in the field without the support of a full mobile laboratory. This article focuses on single dimensional sensors and in particular, chemical sensors using spectrophotometric and millimeter wave technology incorporated into CWA detectors.

In the early 2000s, organophosphate nerve agents were detected using an amperometric enzyme based biosensor.²⁸ The biosensor incorporated the enzyme organophosphorus hydrolase by covalently immobilizing it on glass beads. In this approach, the enzyme hydrolyzes organophosphate to an electroactive species, which was then determined amperometrically. In addition, chemiresistive and chemicapacitive schemes have been investigated to detect CWA. Chemiresistive based sensing typically involves thin electrically conductive polymer films that swell in the presence

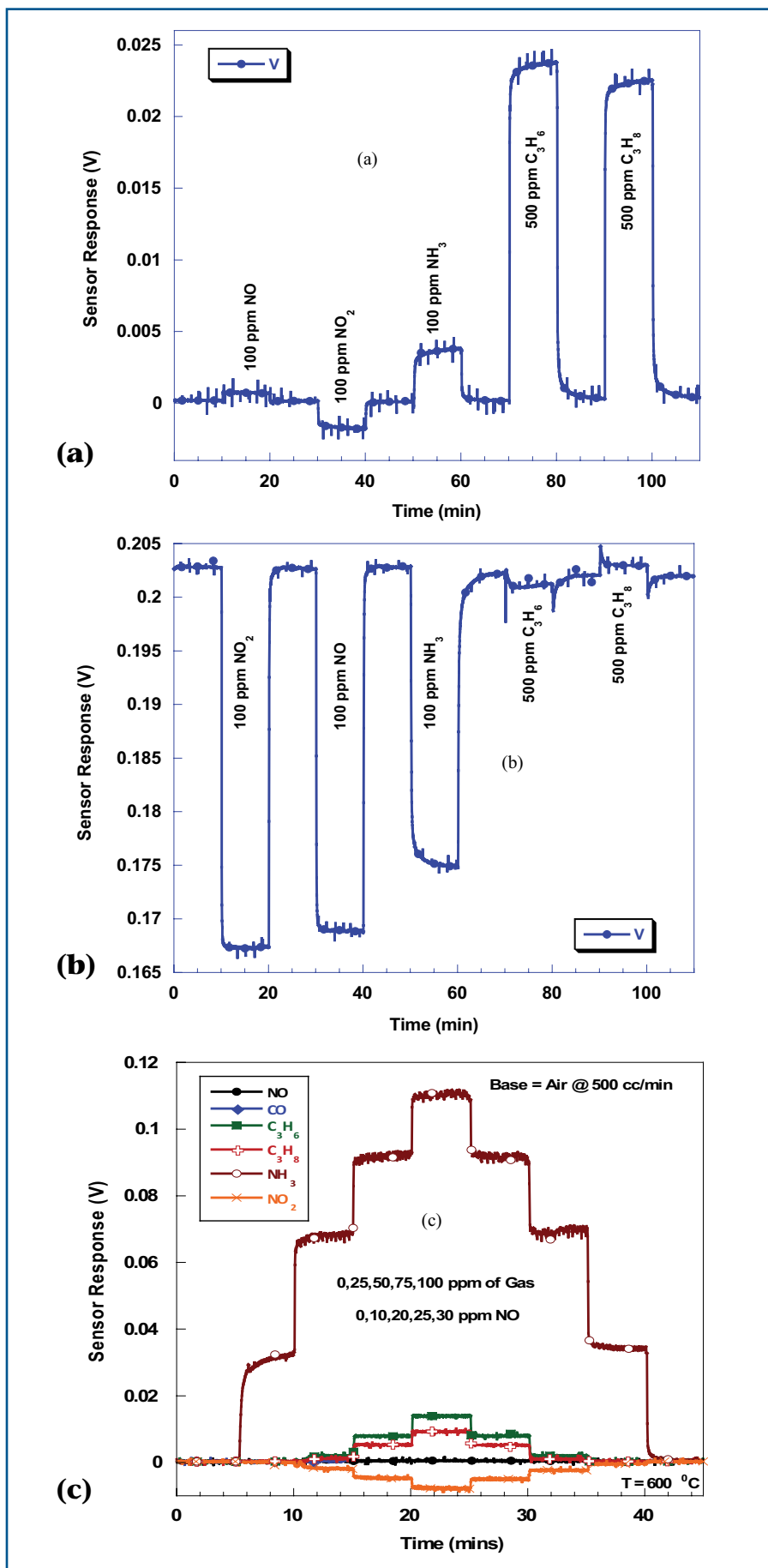


FIG. 2. Mixed potential response of different analytes: (a.) sensor configuration $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3/\text{YSZ}/\text{Pt}$, open circuit, 550°C , 200 sccm; (b.) sensor configuration $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3/\text{YSZ}/\text{Pt}$, biased $-1.4 \mu\text{A}$, 550°C , 200 sccm; and (c.) sensor configuration $\text{Au}/\text{YSZ}/\text{Pt}$, open circuit, 600°C , 500 sccm.

of volatile chemical compounds. The concentration of the species is indicated by the degree of swelling as measured through a change in electrical resistance across the film. Because the swelling of the polymer is reversible, the chemiresistor resets in the absence of the chemical from the environment. Therefore, it can be used repeatedly without component replacement. An array of these devices²⁹ is often used to detect different chemical signatures.

Mlsna *et al.*³⁰ has reported another type of transduction mechanism, a chemicapacitive microsensor consisting of 10 parallel plate (Fig. 3) capacitors with an absorbant dielectric material to measure the dielectric constant of an array of selectively absorbing materials. The dielectric permittivity of these polymer filled chemicapacitors changed upon absorption and desorption of the chemical vapors. The investigators were able to detect CWAs such as Sulphur Mustard, Sarin, Soman, and Tabun. Recently, Diakowski³¹ was able to screen nerve agent analogues using Electrochemical Impedance Spectroscopy (EIS) aided by a recognition layer formed by carbon nanotubes modified with a ferrocenyllysine conjugate. EIS measurements indicate a dramatic change in the electrical properties of the recognition layer upon adding the CWA mimic. The screening systems for CWA detection are under constant improvement with novel designs and new transduction principles. Lab-on-a-chip technology is being developed rapidly for chemical air monitoring systems with efforts to lower cost, reduce size, and power consumption.

Explosives detection.—The Intelligence Reform and Terrorism Prevention Act of 2004 (P.L. 108-458) directed the U.S. Department of Homeland Security (DHS) to place high priority on developing and deploying passenger explosives screening equipment. The recent Christmas Day bombing plot (December 25, 2009) using Penta erythritol tetranitrate (PETN) has constituted an immediate need to reliably detect bulk and trace amount of explosives in a cost-effective way. The focus of this subsection is on trace detection of explosives using the appropriate chemical sensors. Trace detection looks for residue or contamination from handling or being in proximity to explosive materials. Reviewing the techniques for trace detection of explosives,^{32,33} ion mobility spectrometry (IMS) seems to possess the required sensitivity and is also compatible with vapor detection of explosives. However, IMS instruments normally contain a small quantity of radioactive material as an ionizing source and are expensive to own and operate and require calibration when atmospheric conditions change. Chemical sensors,³⁴ as an alternate detection strategy, have the potential

to mimic the canine system (which is known to be the most reliable and mobile method of detection).

In many chemical sensor systems, a receptor layer is used to bind the target explosives of interest and trigger a change in physical or chemical parameter. For example, Caron *et al.*³⁵ described a system for the detection of nitroaromatic explosives consisting of a portable detector based on a specific fluorescent material—a diimine phenylene-ethynylene compound. In the presence of nitroaromatic vapors such as trinitrotoluene (TNT) or its derivative 2,4-dinitrotoluene (DNT), the fluorescence of the material was found to decrease due to the adsorption of nitroaromatic molecules on its specific adsorption sites. Further Capua *et al.*³⁶ reported on selective detection of triacetone triperoxide (TATP) using an array of field effect-like transistors based on GaAs. The gate in these devices has been replaced by a self-assembled monolayer of receptor (alkanephosphonates or alkanethiols) molecules. Following similar lines, Larsson *et al.*³⁷ investigated two types of thiols that are self-assembled to produce a biochip on gold, namely oligo (OEG)-alkyl thiols terminated with a hydroxyl group and a TNT-analogue (2,4-dinitrobenzene), respectively. Surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) techniques are used to monitor the dissociation of on-line immobilized monoclonal antibodies produced against TNT. In most of the cases, discrimination of explosives is perceived as a challenge.

Among the several classes of chemical sensors, electrochemical systems impart high selectivity, portability, a wide linear range, minimal space, and power requirements combined with the ability to lower the deployment cost of sensors using mass production. Such attributes are critical for the widespread deployment of explosive detection technologies to combat terrorist threats. The drawback of the electrochemical devices is their poor sensitivity in detecting explosive vapors, which necessitates a preconcentrator. Since vapor pressures of most explosives are extremely low, a large amount of air must be sampled in order to obtain enough explosive molecules for detection by the sensor element. The preconcentrator acts like a small vacuum cleaner that inhales vapors or extremely small particles onto a collection surface. The concentrated vapors can then be released on to an amperometric or potentiometric sensor for trace detection of explosives.³⁸ The combined preconcentrator-sensor system is a hand-portable device that is capable of detecting vanishingly faint odors (parts per trillion) of explosives, drugs, and other chemicals. Cizek *et al.*³⁹ reported amperometric detection

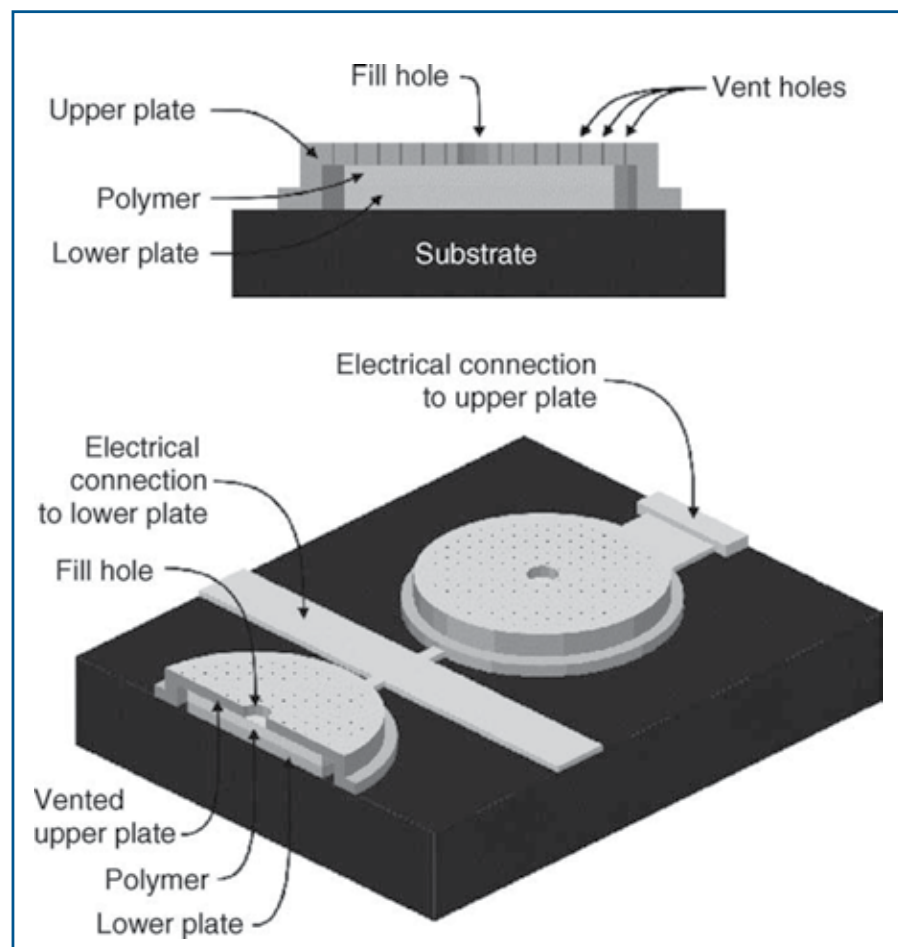


Fig. 3. Cross-sectional diagram of a chemicapacitive microsensor for the detection of chemical warfare agents. The device contains parallel plate sensor element with a polymer as a dielectric material. (Copyright permission obtained from Elsevier.³⁰)

of TNT, as nitroaromatic compounds such as TNT are readily reduced at mercury and carbon electrodes allowing their electrochemical determination. The reduction peaks resulting from the step-wise reduction of TNT to the corresponding hydroxylamine and amine compounds enabled its quantitative detection. The authors reported a linear signal dependence on TNT quantity exposed to the preconcentrator from 0.25 to 10 mg.

Recently, trace detection of (1-10 μg) of high explosives (PETN, TNT, and RDX in this study) using electrochemical, mixed potential gas sensors⁴⁰ based on Yttria Stabilized Zirconium (YSZ) solid electrolyte was demonstrated. This is an exciting development given that the sensors are a unique form of the ubiquitous O_2 lambda sensor used today in automobile engine control systems around the world. The use of the established front-end technology³⁸ to collect and concentrate the high explosives (HE) vapors emanating from areas and surfaces with trace HE contamination allows the detection of various low vapor-pressure explosives as the strength of the measured response from the sensors does not scale with the sample's relative vapor pressure for equal quantities of HE. In this

investigation, explosives were detected by using selective hydrocarbon (HC) and nitrogen oxides (NO_x) sensors in tandem through a customized hot wall set-up.

The area under each sensor peak was calculated and was found to be proportional to the amount of HE sample placed onto the hot wire and subsequently collected by the felt collector. Figure 4a is a plot representing HC and NO_x sensor response to 10 μg of trinitro toluene (TNT). A similar curve was obtained for pentaerythritol tetranitrate (PETN) as the analyte. Figure 4b shows the area under the curve for the HC and NO_x sensor as a function of PETN mass. The data indicate that the sensors responded to increasing trace amounts of HE (PETN). Further, the results show that by using multiple sensors with specifically targeted selectivity to HC and NO_x , different HE samples can be discriminated. The ability to use multiple sensors each tuned to one basic chemical component of the HE materials (*e.g.*, nitro, amino, and hydrocarbon groups) will permit the construction of detector systems with lower false positives than present day technologies.

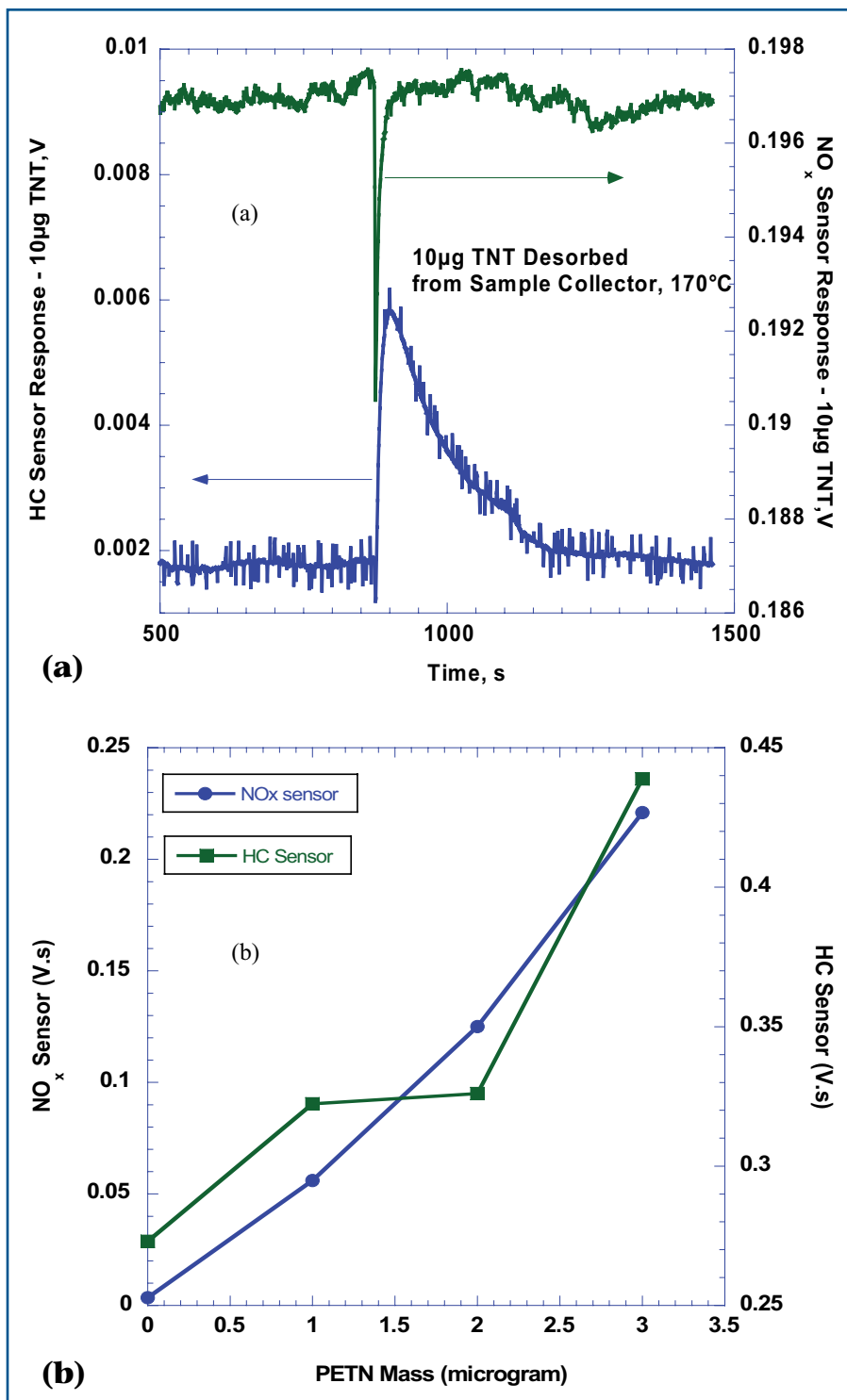


FIG. 4. Trace detection of explosives using mixed potential gas sensors as detectors and an established sampling and preconcentrator technology as the front end: (a.) HC and NO_x sensor response to 10 µg of TNT; and (b.) area under the curve for the HC and NO_x sensors as a function of PETN mass.

Challenges and Future Outlook

Chemical sensors have enjoyed commercial success in monitoring hazardous substances in many applications. Despite these successes, chemical sensors do require further development in terms of superior selectivity and stability over time. A

detailed understanding of the sensor-analyte interaction through (a.) quantitative study of the structure-activity relationships; (b.) investigation of the effect of physical variables such as humidity, temperature, and pressure on sensor performance; and (c.) experimental identification of the influence of diffusion, mass transport,

surface stress, and binding affinity on selectivity and sensitivity will possibly lead to better performing chemical sensors for a wide variety of applications.

Dictated by future applications, important trends in chemical sensors are higher-order or orthogonal sensors and chemical sensing arrays. Higher order implies that more than one transduction principle is applied to the receptor layer. For example, an electrochemical biosensor can be simultaneously interrogated optically thus producing orthogonal signatures of the analyte, thus providing an additional dimension for analysis. On the other hand, an array of different receptor layers with same transduction principle forms a sensor array of zero order. The increase in the number of individual sensors or the order of the sensor is expected to improve the sensitivity and selectivity. Majority of the applications require chemical sensors to be cost-effective, portable, and conducive to commercialization with minimal false negatives and false positives. A recent market report suggests that the U.S. demand for chemical sensors is projected to grow 7.6 percent per year to \$5.4 billion in 2012.⁴¹

Conclusions

Chemical sensors are transducers that incorporate a sensitive layer, which transforms a chemical interaction into an electrical signal. They tend to be physically small, operate in real time, and are controlled by the thermodynamics and kinetics of a chemical reaction. Chemical sensor and biosensor technologies have emerged as dynamic approaches for identifying and quantifying specific analytes for environmental, security, and human threats. Miniaturized chemical sensors and their derivatives are commercially available for specific applications.

Though the chemical sensors are sometimes robust enough to sense the desired analyte in a harsh environment, the sensitivity and selectivity obtained in a laboratory setting isn't necessarily achieved in field-testing. The selectivity, sensitivity, and reversibility of the sensors still remain a major concern. Addressing these concerns, the increase in sensitivity can be realized by appropriate sample pretreatment and preconcentration techniques, whereas filters and separation units can be used to increase the selectivity, minimize cross-interference, and reduce false positives and false negatives. Adopting such measures will inadvertently increase the complexity of the whole system, but learning from past experience and leveraging current technology is often more desired than developing a simple product with significant deficiencies. Future sensor systems will probably address this by using sensor arrays and

higher order sensors with advanced signal processing techniques to provide the selectivity and sensitivity. Chemical sensor systems will continue to provide a less expensive and portable alternative to bulky analytical systems for a wide variety of applications. ■

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