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Review of Electronic-nose Technologies and Algorithms to Detect Hazardous Chemicals in the Environment

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Abstract

Novel mobile electronic-nose (e-nose) devices and algorithms capable of real-time detection of industrial and municipal pollutants, released from point-sources, recently have been developed by scientists worldwide that are useful for monitoring specific environmental-pollutant levels for enforcement and implementation of effective pollution-abatement programs. E-nose devices are ideal instruments for measuring and monitoring carbon and greenhouse-gas emissions due to their sensitivity to a wide diversity of volatile organic compounds (VOCs). A large number of e-nose instrument types, based on a wide diversity of technologies and operational mechanisms, are available to monitor gaseous and particulate pollutants released into the atmosphere, or liquid and dissolved organic pollutants released into municipal and industrial waste-water systems. Some commonly used e-nose technologies include conducting polymers (CP), metal-oxide semiconductor (MOS), quartz crystal microbalance (QCM), and surface acoustic wave (SAW) sensors. Potential pollution-detection applications of e-noses range from atmospheric pollutant (gas-leak) detection of carbon emissions from biofuel production plants and fossil-fuel production sources in the oil and gas industry to VOC-releases from numerous other industries. E-nose technologies are potentially capable of monitoring all phases of industrial manufacturing processes to minimize production of pollutants and maintain efficient, clean production lines. E-nose devices are also useful in designing more environmentally-friendly, clean technologies for energy production, various industrial processes and product-manufacturing systems. This paper is a review of recent novel electronic-nose systems and algorithms, developed over the past decade, that have potential applications for detecting specific types of harmful VOC pollutants in the environment to meet carbon-capture and emission-reduction targets of worldwide environmental protection agencies.

Key words: Electronic aroma detection; E-nose devices; Environmental protection; Pollution; Multisensor arrays; Volatile organic compounds

1. Introduction

The detection and control of toxic chemical pollution in the environment has become a major challenge to

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modern developed and developing countries of the world. Billions of tons of organic and inorganic chemical pollutants are released into the air, water, and soil annually resulting in widespread potential health hazards to plants, animals, and humans worldwide. Monitoring of environmental pollution is necessary and required to protect the public in order to mitigate the many potential negative effects on environmental quality and human health. Potential adverse effects on ecological processes and functions within the United States have necessitated the establishment of strict regulations by the U.S. Environmental Protection Agency (U.S. EPA) on allowable tolerance levels for specific chemical contaminants based on concentration of emissions within air, water, and soil resources. Similar regulations have been developed by comparable environmental protection agencies within many developed countries of the global community.

Current conventional monitoring methods for most chemical contaminants are costly, time intensive, and involve limited sampling and analytical techniques. Thus, there is an increasing need for cheap, improved and reliable methods for the rapid, accurate detection and quantification of environmental chemical pollutants in order to facilitate the effective management and mitigation of harmful effects on society and the environment. Electronic-nose (e-nose) technologies have been widely explored within the past decade to evaluate the efficacy of utilizing e-nose devices, based on diverse operational principles, and to monitor chemical pollution in various environmental settings or applications. The impetus toward evaluation of electronic-nose devices has resulted from the rapid development of gas multi-sensor technologies that have provided relatively cheap, portable electronic-detection devices with the flexible capabilities of detecting a wide range of organic and inorganic gaseous substances, including chemical pollutants. This paper provides a review of numerous potential applications of e-nose devices, developed by scientists worldwide over the past decade, for the detection and quantification of environmental chemical pollutants.

2. Electronic-nose gas sensors for environmental pollution

The potential applications of electronic-nose devices in the area of environmental-pollution monitoring are many and varied. Some of the more important potential utilities of e-noses in detecting pollution range from monitoring air quality [1, 2], the early or real-time area monitoring of diurnal urban pollution-emission events via sensor monitoring networks (outdoor pollution) [3], localization of stationary (point-source) pollution sources [4, 5], and mapping of chemical plumes [6, 7], to detection of fires at chemical-storage facilities, maintaining chemical security at harbor entrances or importation ports [5], 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). The following discussion points out some of the differences between electronic-nose devices and current conventional spectrometric monitoring devices, some of the advantages and disadvantages of e-noses relative to conventional pollution monitors, and a summary of the efficacies of e-nose instruments for various pollution-monitoring applications as determined from recent scientific research.

2.1. Electronic-noses vs. conventional pollution-detection devices

Monitoring of urban pollution currently is carried out primarily by means of spatially-distributed networks of limited and fixed monitoring stations [8, 9]. A variety of chemical-detection technologies are utilized in these monitoring stations such as ion mobility spectrometry (IMS) [10], gas chromatography (GC) [11], and mass spectrometry (MS) [12]. Industrial spectrometers preclude the deployment of adequately dense pollution-detection networks due to the large size and high costs of these devices which require secure fixed stations. Complex air pollution diffusion in urban areas is heavily affected by atmosphere dynamics that often lead to inaccurate or misevaluated measurements of pollutant levels as a result of limited numbers of measurement nodes [8]. Electronic noses are likely to play an increasing future role in raising the density of pollution-monitoring networks due to their low costs, light weight, mobility, and capability of measuring a wide diversity of volatile organic compounds

(VOCs) and toxic inorganic chemicals.

A large diversity of electronic-nose technologies have been developed including acoustic sensors, such as Quartz crystal microbalance (QMB); surface and bulk acoustic wave (SAW, BAW), Carbon black composite detectors (CBCD), Catalytic bead (CB), Catalytic field-effect (MOSFET), Calorimetric, Complementary metal oxide semiconductor (CMOS), Conducting polymer (CP), Electrochemical (EC), Electrical porous silicon sensor (EPSS), Fluorescence, (FL), Infrared (IR), Metal oxides semiconducting (MOS), and Optical sensors [13,14]. Among all of these e-nose types, MOS sensors are the most widely used class of gas sensors for environmental pollution detection because they are capable of detecting both organic and inorganic toxins. MOS e-noses also have good reproducibility (precision) and limited manufacturing costs.

2.2. Efficacy of electronic-noses for pollution detection

Electronic-nose gas sensors have a number of advantages over current conventional pollution-monitoring systems in that they are relatively cheap, portable, highly versatile, and easily trained instruments that can be employed for a wide variety of pollution-detection applications. Low-cost e-noses reduce long-term operating costs allowing increased density of monitoring networks and reduced problems with security and capital losses that are associated with the potential damage of expensive spectrometer instruments. Overhead costs for secure buildings and instrument-maintenance, related to more-expensive analytical instruments, also are largely avoided. Because E-noses are relatively cheap instruments compared to spectrometers, they can be changed out rapidly and replaced with fresh units more frequently to maintain the pollution-monitoring network in full operation. Extra backup units may be held in equipment inventory to replace field units that stop functioning, need repairs, maintenance or recalibration.

Electronic nose devices also have some disadvantages that have hitherto largely limited their use for real-time pollution-detection monitoring functions. The toxicity of various organic and VOC pollutants is concentration dependent and thus environmental monitoring for these pollutants requires precise detection in terms of concentrations measured in the environment [15]. Some e-nose devices are very good at detecting and identifying the toxic compounds present (qualitative measurements), but are not so effective at measuring concentration (quantitative information) of the individual compounds detected, particularly in complex gas mixtures. This limitation must be overcome if e-noses are to be used successfully for quantifying toxic compounds in the environment. Complex gas mixtures also may contain high concentrations of interfering gases compared to the low concentration of target compounds. The typical lack of intrinsic selectivity of MOS e-noses for specific types of toxic chemicals is another limiting factor [15]. By contrast, CP e-noses can be customized to be much more selective in detecting certain classes of VOCs simply by the choice of specific types of sensors utilized in the sensor array. The sensor array of CP e-noses can contain a wide array of sensor types that are sensitive to a large diversity of VOC chemical classes. The flexibility of CP e-noses may be extended even further by the capability of selecting different specific combinations of sensors that are in operation at any one time. Thus, the combination of sensors that are turned on for monitoring certain types of pollutants at one instance (or monitoring episode) can be freely changed so that another combination of sensors is used in the same instrument to detect a different set of pollutants at another instance. Due to calibration problems associated with changing sensor combinations being used, a more likely scenario is to have different CP e-noses in the monitoring network to be dedicated and tuned to a different class of pollutants in order to cover the entire spectrum of pollutant classes likely to be present. Unfortunately, CP e-noses are only sensitive to VOCs and are unable to detect most inorganic toxic compounds that might be present. Thus, a combination of different e-nose types within the pollution-monitoring network may be necessary to cover all categories of organic and inorganic chemical pollutants that may be present.

Other difficulties associated with using electronic-nose devices for environmental pollution applications include the inability to effectively identify individual chemical gas components present in very complex gas mixtures. These situations often arise in cases where emissions from microbial fermentation are common such as in monitoring malodorous emissions from sanitary treatment plants, waste-treatment facilities, animal-production yards (feedlots), as well as industrial composting and fermentation systems, and other industries releasing effluents with organic

byproducts [16]. In these cases, an added problem is that the concentrations at which odorous substances become offensive to residents in urban areas are far below the legal threshold limit values that are acceptable by regulation since these concentrations are not directly toxic or harmful to human health. The identity of component gases present in complex gas mixtures become increasingly difficult for e-noses to detect as the concentrations decrease. Nevertheless, regulatory bodies require reliable methods to evaluate odor impact originating from individual industrial installations even though very low concentrations of analytes complicate the recognition of emissions originating from the monitored source [17].

MOS e-noses generally operate at high temperatures (ranging from about 300 °C to 550 °C) due to the requirement for high-temperature oxidations in the detection process [13]. At temperatures below 100 °C, the low vapor pressure of water molecules inhibits oxidative chemical reactions [18]. Associated with this high temperature requirement is high power consumption that increases long-term operating costs. CP e-noses operate at room temperature and thus may have lower long-term energy costs, but MOS sensors generally have much longer operational life compared with CP sensors that tend to have shorter operational life but are generally more sensitive to sensory overload by certain chemical substances that result in inactivation and loss of function. MOS e-noses have very high sensitivity, but limited sensing range, rapid response and recovery, but are susceptible to sulfur & weak acid poisoning, sensitive to high humidity, and have low recovery for high molecular weight analyte compounds. CP sensors have short response time, diverse sensor coatings, are inexpensive, resistant to sensor poisoning, but are also sensitive to humidity and temperature fluctuations.

Other e-nose types have variable lists of features and characteristics offering advantages and disadvantages for monitoring environmental pollution-type applications. Quartz crystal microbalance (QCM) e-noses have good precision, diverse range of sensor coatings, and high sensitivity, but they have complex circuitry, poor signal-to-noise ratio, and are sensitive to humidity and temperature [13]. Surface acoustic wave (SAW) e-noses have high sensitivity to virtually all gases, good response time, and diverse sensor coatings, are small and inexpensive, but are temperature sensitive and certain analyte compounds are affected by the polymeric-film sensor coatings. Optical sensors have very high sensitivity, are capable of identifying individual compounds in mixtures, and have multi-parameter detection capabilities, but are more expensive to operate and have low portability due to delicate optics and electrical components. Electrochemical sensors (EC) operate at ambient temperatures with low power consumption and are very sensitive to diverse VOCs, but are bulky in size and have limited sensitivity to simple or low molecular weight gases.

2.3. E-nose algorithms for calibration and data-analysis

E-nose algorithms and data-analysis methods are playing several important key roles in making electronic-nose devices suitable and competent instruments for real-life pollution-monitoring applications. The intrinsic long-term stability and selectivity of solid-state e-nose sensors can severely limit their reliability [9]. When e-nose units are calibrated for single-analyte quantification in the laboratory, they exhibit poor performance when operating in real-life field conditions with complex mixtures [19, 20]. In-field calibration strategies are needed to make sure field e-nose units are properly calibrated to the types of analyte pollutant mixtures the sensors will most likely come in contact with at any one point in time. Since air pollution mixtures change frequently due to unpredictable random emissions from various pollution point sources, the need for relatively frequent in-field calibrations become obvious. Such in-field calibrations are possible by periodically subjecting field e-nose units to sensor-proximal releases of previously prepared and precisely known pollution gas-mixture standards during calibration. The detection data collected from these calibration standards may be used in combination with specialized instrument-performance algorithms to determine how well the e-nose performed during calibration and what adjustments are needed in instrument settings to optimize performance of the sensor array. In this way, e-nose algorithms can prevent long-term degradation in instrument performance caused by temporal modifications in analyte species causing divergences between absolute and relative concentrations. Algorithm-based recalibration procedures are also useful for managing problems due to sensor-stability issues, often correctable by replacing individual sensors in the sensor array. In-depth analysis of in-field calibration results using e-nose algorithms can significantly help instrument-

feasibility assessments, guide the development of monitoring strategies (device positioning in the field relative to pollution-emission sources, calibration methodology, and long-term performance assessments), as well as instrument design and the validation process [9, 21]. Field-recorded data is essential for achieving effective field calibration methodologies with synthetic pollution-mixture standards using sensor-fusion algorithms that are properly tuned via supervised training [8, 19].

Pattern-recognition algorithms are essential for classifying and quantifying chemical constituents of pollution mixtures based on signal-signature outputs generated by the sensor array. Classification algorithms combined with data-analysis techniques such as Principle Component Analysis (PCA) enable the recognition of different sample types via aggregation of similar emissions into clusters representing compounds from related chemical classes. This clustering of data points in the sensor output following data analysis by algorithms is made possible by the variable sensitivity of individual sensors in the array to different classes of chemical compounds. Different gaseous mixtures of pollutants elicit variable responses from the cross-reactive sensor array. Thus, the capability of differentiation of different mixtures of pollutants in a gaseous sample is determined by all of the possible sensor-intensity combinations (permutations) that are possible for the sensor outputs which is proportional to the number of sensors present in the array, the overlap in cross-reactivity to different classes of compounds, and the diversity of chemical classes that the combined sensor array is capable of detecting. When sensor-fusion algorithms are combined with multivariate calibration and other statistical methods, problems of concentration estimation for complex gas mixtures can be more effectively resolved, particularly when Artificial Neural Networks (ANNs) are utilized with e-nose training for analyte recognition of complex mixtures [8, 13, 22-24].

3. Pollution-detection applications of e-noses

The primary applications of electronic-nose devices for monitoring environmental pollution may be categorized into four main areas based on types of chemical pollutants being detected, including 1) inorganic chemicals, such as heavy metals, and oxides of carbon, nitrogen, and sulfur as well as reduced forms of nitrogen and sulfur; 2) volatile organic compounds (VOCs); 3) point-source chemical pollutants; and 4) gases with multiple toxic compounds containing both organic and inorganic toxic chemicals. Sugimoto et al. [25] further subdivided VOC analytes into two groups: polar VOCs and nonpolar VOCs, based on the charge-polarity of these organic compounds. The following sections summarize e-nose applications for detecting and monitoring environmental pollutants that fall into these four main categories.

3.1. E-nose detection of inorganic and volatile organic compounds

Inorganic chemical pollutants detectable with electronic-nose technologies include heavy metals, various oxides of carbon, nitrogen, and sulfur, as well as hydrides of sulfur and nitrogen (Table 1). Heavy metals are mostly a pollution problem for water resources although certain heavy metals such as mercury can be a problem as an air pollutant in the gaseous form [26]. Major anthropogenic sources of mercury release include power plants, residential heating, waste incineration and production of cement, gold, caustic soda, iron, and steel [27, 28]. Heavy metals tend to be a major pollution problem primarily in water courses that are adjacent to highly acidic soils or areas where acids are released in sewage from industrial or mining facilities directly into local drainage systems and natural water courses. Acidic soil conditions cause heavy metals to be released from soil particles into solution and carried away by drainage water. Thus, acid mine tailings are a particularly important source of heavy-metal releases into the environment. Acid rain also contributes to the leaching of heavy metals from soils. E-noses are capable of detecting pollutants in water by sensing volatiles released into the airspace just above the water surface [29]. Sewage wastewater and polluted water emissions from residential and industrial sources release a continuous stream of volatile pollutants from the water surface into the atmosphere where they can be detected many miles from the source. Most of the major sources of inorganic air pollutants produced by urban industries include smog-type pollutants such as sulfur oxides and nitrogen oxides. Smog pollutants react to form acids that cause acid rain.

Organic chemical pollutants, often referred to as volatile organic compounds (VOCs), are important pollutants

alone, but VOCs also may react with nitrogen oxides in the atmosphere to produce peroxyacetyl nitrate (PAN) and ground-level ozone pollutants. Some important e-nose technologies that have been developed for the detection and monitoring of VOC environmental pollutants are presented in Table 1. Industrial organic solvents detectable with e-nose sensors include such highly volatile chemicals as methanol, toluene, chloroform, benzene, and xylene that are particularly toxic air pollutants because many of these are not only extremely flammable, but also are recognized as serious human carcinogens [30]. Biological VOCs that are released by microbes and multicellular organisms through respiration and fermentation processes can be serious sources of pollution, particularly from waste and sewage treatment plants and livestock feedlots. Microbial respiration products that become air pollutants detectable by e-nose devices include alcohols, aldehydes, and carboxylic acids [31, 32]. These are usually catabolic products resulting from fermentation of carbohydrates. Chlorofluorocarbons (CFCs) are halogen-containing methane and ethane derivatives, commonly used as refrigerants and previously as propellants in aerosol cans, which are important VOCs that threaten the degradation of the ozone (O_3) layer in the high atmosphere. Ozone is thought to be a major barrier to reduce the penetration of harmful ultraviolet rays (UV-radiation) into the lower atmosphere. A related group of aromatic hydrocarbons containing halogens, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDs) or dioxin, and polychlorinated dibenzofurans (PCDFs), are important toxins known to be potential teratogens [33].

Table 1. Electronic-nose technologies developed to detect hazardous inorganic and volatile organic compounds in the environment

Hazardous chemical pollutants	E-nose type[1]	Sensors[2]	Data processing method[3]	References
Inorganic chemicals				
As, Cd, Pb, Zn (in water)	BH-114	14 CP	PCA	[34]
CO, NO_2, NO_x	Exp. model	5 MOS	MVC	[9]
H_2S, NO_2, SO_2	Exp. Nepo	6 MOS	DFA	[35]
Hg (gas), heavy metals (in air)	Exp. E-dosimeter	DOS	RA	[26]
NH_3	Exp. model	6 QCM	RP, PCA	[30]
	PANi	MOS	ARA	[36]
	Kamina	38 MOS	PCA	[37]
Volatile organic compounds (VOCs)				
Carboxylic acids, organic acids	Exp. model	13 CBCD	PCA	[38]
	Exp. model	16 CBCD	PCA	[39]
	Exp. model	16 CBCD	PCA	[40]
Chloroform	Exp. model	FOS	GA	[41]
	Kamina	38 MOS	PCA	[37]
Diesel petroleum oils	ProSAT	8 CP	PCA	[31]
Ethanol	Exp. ITO	MOS	RA	[42]
	Exp. model	CMOS	CBM	[43]
	Exp. model	MOS	RA	[44]
	Exp. model	12 MOS	PCA	[17]
	Exp. model	6 MOS	DFA	[45]
Methanol	Exp. ITO	MOS	RA	[46]
	Exp. PPy	CP	SAE	[47]
	Exp. model	CBCD	RA	[48]
	Exp. model	MOS	RA	[44]
Organic solvents	Exp. model	EPSS	SPRM	[49]

	Exp. model	6 QCM	RP, PCA	[30]
	Exp. model	1 MOS	CA	[15]
	Exp. model	6 MOS	DFA	[45]
Toluene	Exp. model	FOS	GA	[41]
Trimethylamine	Exp. model	QCM	RA	[50]
Volatile amines	Exp. model	13 CBCD	PCA	[38]

[1]Electronic nose models utilized; commercially-available models are indicated by name.

[2]Number of sensors and sensor types used in the sensor array (as specified); CBCD = Carbon black composite detectors, CMOS = Complementary metal oxide semiconductor, CP = Conducting polymer, DOS = Dosimeter, EPSS = Electrical porous silicon sensor, FOS = Fiber optic sensor, MOS = Metal oxide sensors, QCM = Quartz crystal microbalance.

[3]Abbreviations for data-processing methods: ANN-PRA = Artificial neural network probability analysis, ARA = Absorption ratio analysis, CA = Chromatographic analysis, CBM = Competitive binding model, DFA = Discriminant factorial analysis, GA = Gravimetric analysis, MVC = Multivariate calibration, PCA = Principal component analysis, RA = Regression analysis (linear and nonlinear), RP = Radar plots, SAE = Sensitivity-Antoine equation, SPRM = Space charge region modulation.

Most e-nose technologies are experimental models consisting of 5-38 sensors within MOS, CP, CBCD or QCM sensor arrays. Generally, a minimum of 5-6 sensors are required within the sensor array of an e-nose to be capable of resolving and distinguishing between the many classes of VOCs that may be encountered as pollutants in the environment. Greater sensor numbers adds resolution, but increases instrument costs and reduces portability.

3.2. E-nose detection of point-source and multiple toxic chemicals

Point-source chemical pollutants, identified as being derived from specific known geographical locations and/or sources from which the offending chemical emissions, can be traced using various inductive and deductive scientific methodologies, such as distance-dilution models [8, 17]. E-nose methods and technologies have been developed for the detection of point-source pollutants from a variety of emission-source types (Table 2). These pollution sources

Table 2. Electronic-nose technologies developed to detect hazardous point-source and multiple toxic chemicals in the environment

Hazardous chemical pollutants	E-nose type[1]	Sensors[2]	Data processing method[3]	References
Point-source chemical emissions				
Agricultural pesticides	MOSES II	8 MOS, 8QMB	PCA	[51]
	Biosensors	FLS	OSA	[52]
Chemical warfare agents (CWAs)	Exp. model	MEMS	ANN-PRA, LDA	[53]
Composting, organic refuse plants	EOS 3, 9	6 MOS	KNNA	[16]
Environmental, microbial toxins	Exp. model	OF-LCS	OSA, RA	[54]
Food contaminated with mycotoxins	EOS 835	6 MOS	PCA	[55]
	PEN 2	10 MOS	PCA	[56, 57]
Residential organic compost piles	Exp. model	7 MOS	PCA, CCA	[32]
Toxic industrial chemicals (TICs)	Exp. model	MEMS	ANN-PRA, LDA	[53]
Waste-treatment facilities	PEN 2	10 MOS	PCA, DFA	[58]
Multiple toxic compounds				
CO, H_2S, NH_3, SO_2	FreshSense	4 ECS	DMRT	[59]
CO, H_2S, NH_3, NO_2, O_3, HCs, CH_4	Exp. model	4-7 MOS	PCA	[5]
CO, CH_4, ethanol, isobutane	Exp. model	4 MOS	PCA	[60]
CO, NO_x, NO_2	Exp. model	5 MOS	MVC	[9]

Alcohols, aldehydes, aliphatic HC, aromatic HC, chlorinated acids, ketones, NH_3, sulfur compounds	Exp. model	7 MOS	PCA, CCA	[32]
Alcohols, sulfur compounds	EOS 3, 9	6 MOS	KNNA	[16]
H_2S, SO_2, VOCs	Cyranose 320	32 CP	PCA, CCA	[29]
Benzene, toluene, xylene	Exp. model	1 MOS	CA	[15]
H_2S, NO_2, SO_2,	Exp. Nepo	6 MOS	DFA	[35]
Alcohols, aliphatic HC, CH_4, H_2	Exp. model	6 MOS	DFA	[45]
CO, NMHC, NO_X, NO_2, O_3, benzene	Exp. model	7 MOS	MPIs	[8]

[1]Electronic nose models utilized; commercially-available models are indicated by name.

[2]Number of sensors and sensor types used in the sensor array (as specified); CP = Conducting polymer, ECS = Electrochemical sensors, FLS = Fluorescence sensor, MEMS = Micro-electromechanical systems, MOS = Metal oxide sensors, OF-LCS = Optical fiber live cell sensor, QMB = Quartz microbalance.

[3]Abbreviations for data-processing methods: ANN-PRA = Artificial neural network probability analysis, CA = Chromatographic analysis, CCA = Canonical correlation analysis, DFA = Discriminant factorial analysis, DMRT = Duncan's multiple range tests, KNNA = K-nearest-neighbor algorithm (for pattern recognition), LDA = Linear discriminant analysis, MPIs = Multiple performance indexes, MVC = Multivariate calibration, OSA = Optical signature analysis, PCA = Principal component analysis, RA = Regression analysis (linear and nonlinear).

include agricultural pesticides, composting plants, specific industries, and waste-treatment facilities as well as multiple toxic chemicals (inorganic and organic compounds) that may be present simultaneously within polluted air, water, or soil. Sensor arrays capable of detecting multiple toxic compounds, particularly inorganic and organic types, are mostly MOS-type e-noses. Principal component analysis (PCA) is by far the most common method employed for discriminating between various inorganic and VOC pollutants using sensor output data. Regression analysis (RA) is most often used to determine the concentration of pollutants detected by the sensor array.

Emissions of odorous chemicals from many industrial hazardous waste sites, refineries, and combustion processes often are not regulated as primary air quality pollutants for which ambient environmental standards have been set because they do not cause immediate adverse health effects, even though they are offensive in odor [61, 62]. Other toxic compounds such as carbon monoxide and carbon dioxide are odorless, but highly toxic at high concentration. Many toxic chemicals produced for industrial purposes only pose a health hazard at higher concentrations. The most dangerous compounds are those that are harmful at very low concentrations (picomole range) such as the chemical warfare agents (CWAs) that can be detected with MEM-type e-nose sensors [53]. For these extremely hazardous compounds, electronic noses are utilized primarily for military purposes as early-warning instruments to detect these chemicals in the air at concentrations well below lethal levels. Highly toxic industrial chemicals (TICs) such as acrylonitrile, arsine, hydrogen cyanide, methyl isocyanate, and parathion also require use of e-nose devices as early-warning detectors around chemical plants that produce these chemicals as raw materials for the production of plastics, semiconducting materials, polymers, pharmaceuticals, and pesticides.

4. Conclusions

The monitoring of environmental pollution is a very promising new field for the development of new applications with the electronic nose. E-noses have the potential of providing many new monitoring capabilities to fill niches that are not currently possible with conventional expensive spectrometers. A multitude of monitoring tasks may be greatly improved by the use of these relatively cheap cross-reactive gas-sensor devices that offer the capability of increasing the density of sensing stations within pollution-monitoring networks. This function alone will provide significantly improved monitoring data allowing more effective real-time management of many complex urban-pollution problems. Utilizing e-nose assistance to on-line continuous measurements of pollution emissions should provide superior data, corroborated by pollution measurements from multiple e-noses in the network, which ultimately will improve real-time pollution-management decisions to minimize pollution damage to the environment through early detections of pollution-release events.

Currently, there is a considerable demand for portable, handheld gas monitors, but previously they have not been employed to the fullest extent of their potential due to significant logistic problems, inherent to e-nose sensors, that need to be resolved before these instruments are used extensive as pollution monitors. The great diversity of toxic gases that are encountered as pollutants in the environment is quite large, making it difficult for single e-nose units to identify and measure the concentration of individual chemicals that may be present, particularly in complex mixtures of pollutants [48, 63]. Cooperative efforts of numerous e-nose instruments within a monitoring network are needed to "divide the labor" for detecting different classes of pollutants that may occur in a given area based on the most-probable pollutants likely to exist in each monitored region. In-field e-nose calibration methodologies must be developed to make sure accurate readings are taken during continuous monitoring.

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 [64]. MOS sensors have high sensitivities as low as parts per billion (ppb) due to large surface areas for analyte adsorption [65-66]. 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. 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 [64].

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 [67], or the use of temperature modulation of a single gas sensor have shown some demonstrated feasibilities [67-69]. Developmental manufacturing costs for multiple types of e-noses are high and thus not suitable for ubiquitous sensing [48]. 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 [70]. Thus, feasibility of e-nose commercialization becomes difficult because pre-calibration would necessarily involve carrying out these calibrations for all possible concentration combinations of component gases in polluted air mixtures since pollution monitoring requires both identification and quantification of component gases detected [48]. This problem might be handled in the field by mechanical artificial pollution-dispersant devices that generate specific ratios of pollutant-calibration mixtures (standards) in the vicinity of e-nose units in order to achieve in-field calibrations, based on relayed data analyses of nearby spectrometers of the predominant pollution mixtures currently present in the monitoring area.

The complexity and temporal variability in the composition of pollution discharges are two of the biggest challenges to utilizing 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. This situation is particularly common for monitoring toxic pollutants in sewage wastewater as a result of the random and temporal nature of human activity relative to sewage disposal in both quantities and types of pollutants released as well as variable effects of environmental factors like rainfall [31]. All of these logistic 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.

Acknowledgements

gas-sensing technologies will be increasingly utilized by environmental protection agencies throughout the world.

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