Adaptive Microsensor Systems

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tunable sensors, integrated analytical systems, adaptive filtering, active sensing, integrated sensing and processing

Abstract

We provide a broad review of approaches for developing chemosensor systems whose operating parameters can adapt in response to environmental changes or application needs. Adaptation may take place at the instrumentation level (e.g., tunable sensors) and at the data-analysis level (e.g., adaptive classifiers). We discuss several strategies that provide tunability at the device level: modulation of internal sensing parameters, such as frequencies and operation voltages; variation of external parameters, such as exposure times and catalysts; and development of compact microanalysis systems with multiple tuning options. At the data-analysis level, we consider adaptive filters for change, interference, and drift rejection; pattern classifiers that can adapt to changes in the statistical properties of training data; and active-sensing techniques that can tune sensing parameters in real time. We conclude with a discussion of future opportunities for adaptive sensing in wireless distributed sensor systems.

1. INTRODUCTION

The objective of this article is to review advances in chemical sensing at the device, system, and data-processing levels that may enable the development of adaptive microsensor systems. A system is considered to be adaptive if its characteristics or parameters can be adjusted in response to the environment and the target analytes. A system may exhibit adaptability at multiple levels (e.g., device, system, or data analysis) in response to various factors (internal or external) and at different timescales (e.g., permanent versus reversible). As an example of these various strategies, an adaptive system may adjust its sensor parameters (device), its mode of operation (system), or its calibration parameters (data analysis); these adaptations may occur in response to sensor changes or sensor drift (internal) or upon the occurrence of cross-contaminants (external); and these adaptations may involve the regeneration of sensing surfaces (permanent) or adjusting sensor tunings (reversible).

We have organized this review according to which aspects of the adaptation take place at the hardware level (i.e., sensor device or instrument) and at the software level (i.e., data analysis). This is not to say that adaptation can occur only at one or the other level; adaptation may involve coordination at both levels (i.e., hardware changes can be triggered by the software in response to hardware events), and the boundaries between the two levels are becoming increasingly blurred (i.e., intelligent microsensors integrate sensing and data processing in the same device). Instead, this division between hardware and software should be viewed as a way to identify individual components of chemical microanalysis systems that may be targeted for adaptation. On the hardware side, there is also the large field of sensor interface electronics, such as auto-ranging and auto-zeroing circuits (1–4), which we deem to be outside the scope of this review.

2. HARDWARE APPROACHES

In most current applications of chemical sensors, the output of an individual sensor consists of a defined parameter, such as a resistance value measured at a fixed potential and temperature, in response to a chemical stimulus (5–11). This means that, usually, one predefined feature per sensor is monitored at a time, preferably during an equilibrium-type situation, in which a certain analyte concentration can be correlated to the resulting sensor response. Use of a single sensor and a predefined set of sensor-readout parameters, however, provides very limited performance in practical applications, in particular if the environment is challenging due to cross-interferences, or if it is rapidly changing.

Therefore, methods to effectively extend the so-called feature space or to provide a tunable feature space have received great attention. A feature space is an abstract space in which each sample, for instance a sensor measurement value, is represented as a point in n-dimensional space. Features are the individual measurable heuristic properties of the phenomena being observed, such as individual sensor measurements. Methods to extend the feature space and gain additional information include use of sensor arrays (arrays of identical transducers with different coatings or arrays of different transducers) and modification of transducer geometries (12–14). A tunable feature space can be realized by modulating and/or adapting sensor parameters and operation conditions to a certain sensing scenario. The tuning must be feasible during sensor operation; in other words, exchanging coating materials or changing the spacing of electrodes, for instance acoustic transducers (15), cannot be considered here, because they require a major reconstruction of the sensor. Following Göpel (12) and Weimar & Göpel (13), the parameters that can be varied during sensor operation may include internal parameters, such as sensor temperature, electrode bias voltage, or measurement frequencies, and external parameters, such as use of filters or catalysts to change the gas composition.

In this section we provide examples of hardware realizations of such tunable devices and discuss how tunability has been achieved. The devices are categorized according to internal and external parameter tuning (Sections 2.1 and 2.2); chemical microanalysis systems are described in Section 2.3.

MOX: metal oxide

2.1. Internal Sensor Tuning

One of the most prominent examples of an internally tunable sensor requires modifying the operation temperature of metal-oxide (MOX) gas sensors (16–19) to specifically detect target analytes in complex mixtures or in a background of interferants. The gas reactions at the MOX surfaces and, hence, the sensor selectivity or sensitivity patterns are highly dependent on the operation temperature (5, 20–23). Carbon monoxide (CO) is usually best detected at lower operation temperatures (e.g., 250°C) through use of, for instance, a tin dioxide–based sensitive layer, whereas higher temperatures (e.g., 350°C) are used for monitoring, for example, hydrocarbons such as methane. Therefore, one can vary the operation temperature of a single sensor or a small set of sensors to effectively tailor the sensor/array selectivity, and a carefully designed temperature program for a certain target analyte can be applied after a coarse qualitative detection of its presence. Fast temperature variations can also generate a large set of virtual sensors to analyze complex mixtures. A rather sophisticated temperature program that was used to examine a target matrix with five high-priority chemical hazards (ammonia, hydrogen cyanide, chlorine, ethylene oxide, and cyanogen chloride) is shown in **Figure 1*b*** (19). Ammonia and ethylene oxide are common toxic industrial chemicals that are also employed as precursors in the manufacture of explosives, narcotics, and polymers. Beyond their industrial uses, hydrogen cyanide and cyanogen chloride are blood agents, and chlorine is a pulmonary agent.

The temperature program used to operate the sensing elements toggles the temperature between (*a*) 32 ramp values that sample most of the temperature range of the device and (*b*) four different baseline temperature values to allow relaxation toward some initial state prior

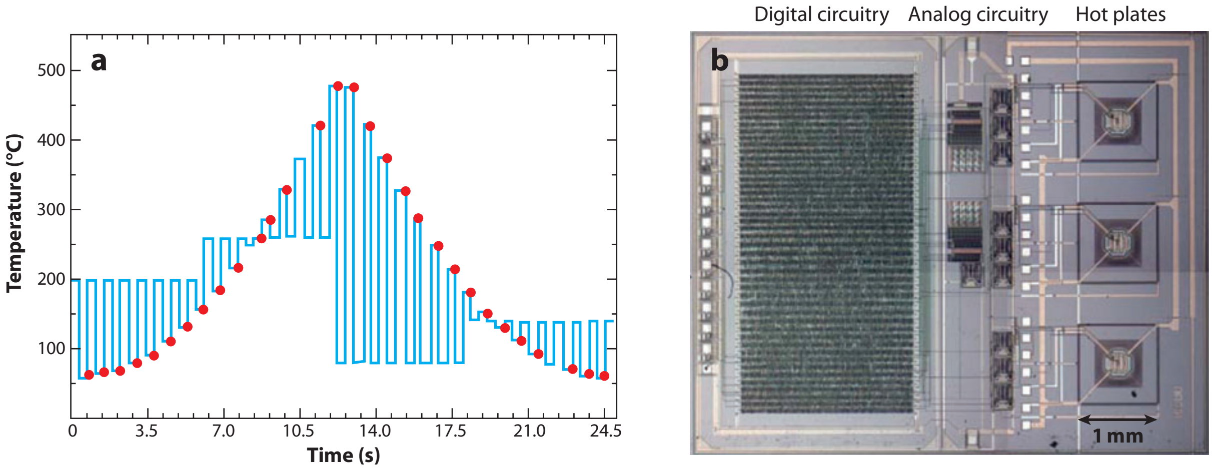

Figure 1

(*a*) Temperature program used for the detection of high-priority chemical hazards. Reprinted with permission from Reference 19. (*b*) Micrograph of a stand-alone micro–hot plate system. The digital circuitry (including three temperature controllers and converters) is on the left; it includes a control unit and the serial interface. The analog circuitry for biasing and analog-to-digital conversion is in the center, and the three micro–hot plates are on the right. Reprinted from Reference 32 with permission.

Micro–hot plate: a micromachined, thermally isolated stage, such as a membrane, bridge, or cantilever, with dimensions on the order of several tens of micrometers and featuring low thermal mass; allows millisecond-scale temperature variations

CMOS: complementary metal-oxide semiconductor

Voltammetry: a category of electroanalytical methods used in analytical chemistry and various industrial processes in which information about an analyte is obtained by measuring the redox currents at the electrodes as the potential is varied. The measured current is usually linearly proportional to the analyte concentration

to each ramp temperature. Moreover, different baselines allow different film-analyte interactions (adsorption/desorption, decomposition, and reaction) at the sensing surface prior to the ramp measurements.

The development of temperature programs for MOX sensors has been fueled by the appearance of micro–hot plates with low thermal mass (24), which allow for millisecond-scale temperature variations so that the temperature variations are faster or on the same time scale as the chemical processes occurring during gas/MOX interaction. There is an almost infinite number of target analyte–specific temperature-variation profiles (sinusoidal, ramp, rectangular, etc.) featuring arbitrarily selectable temperature intervals within which the variations can be realized. A variety of hot plate structures, including membranes (24–28), spider-like structures (18, 20, 29, 30), and bridge-like structures (31), have been developed. The most advanced developments in temperature-variable micro–hot plates include stand-alone complementary metal-oxide semiconductor (CMOS)-based microsystems featuring temperature-control loops, transistor heaters, digital circuitry, and standard interfaces (**Figure 1*b***), which allow for the application of any arbitrary temperature profile to three differently coated hot plates via standard software and a universal serial bus interface (32, 33). Moreover, algorithms have also been developed to optimize the operating temperature in real time, as we discuss in Section 3.3.

Another important parameter that can be tuned is the sensor's operating voltage. The sensors for which voltage tuning is most common are voltammetric sensors in the liquid phase (5, 11). Voltammetry is a method wherein the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept in time (34–36). This sweeping can be linear, stepwise, or cyclic (**Figure 2*a***); that is, the voltage can be ramped up and down (or vice versa) in a triangular pattern within a certain voltage interval (34–36). The reduction or oxidation of the target species is registered as a peak or trough in the current signal at the potential at which the species begins to be oxidized or reduced, according to its position in the electrochemical series (**Figure 2*a***). The charges transferred at the liquid-electrode interface, or the Faradaic component of the overall current, are the important measurand, and for the case of diffusion-limited conditions, they are linearly proportional to the target-analyte concentration. The measured current at any given potential difference depends on the material properties, the composition and geometry of the electrodes, the concentration of the electroactive species

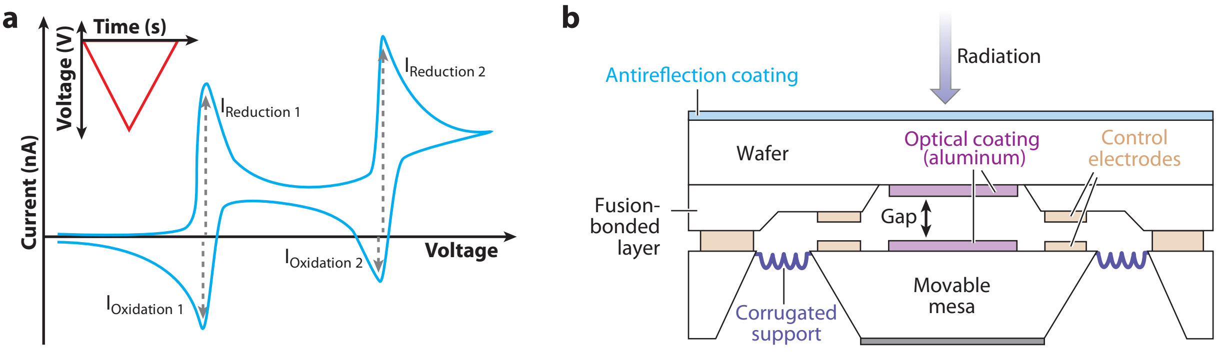

Figure 2

(*a*) Schematic representation of a cyclovoltammogram featuring two sequential, reversible one-electron transfer reactions at two different redox potentials. The applied voltage ramp is shown in the inset. (*b*) Schematic of a tunable Fabry-Pérot interferometer. The wavelength-defining gap width can be changed by applying direct current to the control electrodes. Aluminum has been used as optical coating material. Adapted from Reference 47 with permission.

(presumably the target analyte), and the mass-transport mechanisms in the analyte phase (9, 11, 34–36). Amperometry, a special case of voltammetry wherein the potential is kept constant as a function of time, is even more frequently applied in chemical sensors (11, 34, 35, 37) and also provides a linear current–analyte concentration relationship. The constant potential is then predefined by the nature or the redox potential of the target analyte (9, 11, 34).

Fabry-Pérot interferometer (FPI): an optical wavelength selector consisting of two partially reflecting, low-loss, parallel mirrors separated by a gap; its optical transmission characteristics consist of a series of sharp resonant transmission peaks that appear when the gap is equal to multiples of half a wavelength of the incident light

Applications of voltammetric and amperometric sensors include chemical analysis in the gas or liquid phase. If the target analyte is not an electroactive species [e.g., glucose, oxygen, or carbon dioxide (CO_2)], then enzymes (glucose oxidase) producing analyte-related ionic species may be used as components of the sensitive electrode coatings. Target analytes in the gas phase are nitrogen oxides or hydrogen sulfide using polymer electrolytes (38), as well as oxygen (37) using liquid electrolytes. Target analytes in the liquid phase comprise dissolved oxygen (39–41), glucose (42), hydrogen peroxide (43, 44), and chlorine in drinking water (45). One of the best-known voltammetric cells is the Clark cell (40), which is based on a two-step reduction of oxygen via hydrogen peroxide to hydroxyl ions in aqueous solution. The Clark cell is used to measure dissolved oxygen in blood and tissue (40, 41). The reference electrodes in the liquid phase are, in most cases, silver/silver-chloride elements.

The last internal parameter we describe herein is wavelength or frequency. One of the most commonly used devices to tune wavelength is the Fabry-Pérot interferometer (FPI), an optical element consisting of two partially reflecting, low-loss, parallel mirrors separated by a gap (**Figure 2*b***). The characteristics of the optical transmission through the mirrors consist of a series of sharp resonant transmission peaks, which occur when the gap is equal to multiples of half a wavelength of the incident light. These transmission peaks are caused by multiple reflections of the light in the cavity. Through the use of highly reflective mirrors, small changes in the gap (e.g., width and absorptivity) can produce large changes in the transmission response. Even though two reflective mirrors are used, transmission through the element at the peak wavelengths approaches unity.

The transmission is a function of both gap spacing and radiation wavelength. Usually, the gap width is tuned to achieve the desired wavelength and operate the device as a wavelength selector or monochromator. Tunable devices with a gap width that is variable by electrostatic actuation via electrodes on movable micromachined parts (**Figure 2*b***) have been reported by several groups (46–50). Such devices operate preferably in the near-infrared region at wavelengths longer than 1 μm, where silicon substrates become transparent. Typical applications include gas sensors and remote gas sensing in plumes (48–53). Characteristic absorption wavelengths are 4.7 μm for CO, 4.2 μm for CO_2, and 3.3 μm for methane or hydrocarbons (infrared region, molecular vibrations). CO_2 sensors based on tunable FPIs (dual-wavelength measurements) are commercially available from, for instance, Vaisala (Helsinki, Finland). The radiation source in most cases is a lightbulb or light-emitting diode. Single-chip CMOS optical microspectrometers based on FPI and operating in the ultraviolet/visible region, including operation in the liquid phase, have also been reported (54–56). These instruments, however, contain arrays of different Fabry-Pérot etalons with fixed resonant-cavity length, realized as a plasma-enhanced chemical vapor deposition silicon-oxide layer sandwiched between two metal layers (55–57).

More recently, quantum cascade lasers (58, 59) with wide tuning ranges in the infrared region between 3 μm and 24 μm have been developed and used for trace gas analysis of a variety of environmentally relevant gases (e.g., CO, CO_2, methane, and formaldehyde) and medically relevant gases (e.g., nitrogen monoxide, CO, CO_2, ethane, and CS_2), which are also important in spacecraft air quality and planetary atmospheric science (59–64). The wide tunability of the quantum cascade lasers is enabled through the use of so-called external cavities: Additional gratings are used as an end mirror of the laser cavity. When the diffraction grating is rotated, the wavelength can be tuned across the entire bandwidth of the quantum cascade laser chip. The detection limits for the different gases in mixtures are in the low parts-per-billion or even parts-per-trillion range (59, 62–64). Instruments are commercially available from, for instance, Daylight Solutions, Inc. (Poway, California) (63, 64).

Frequency variations are also applied to electrochemical sensors. Alternating current impedance measurements are, however, not generally used for analytical sensor applications. Impedance measurements are of special interest for membrane, electrode, and electrolyte characterizations that aim to find an equivalent electronic circuit model and to correlate that model with electrochemical or sensor-response phenomena (9, 11, 35).

2.2. Variation of External Parameters

An early example of external parameter variation includes the use of a catalyst located upstream from the sensor array in the analyte gas inlet (65–67). The noble-metal catalyst is heated to different temperatures, then decomposes (oxidizes) the incoming analyte molecules or promotes chemical reactions thereof. The resulting reaction products are then detected by an array of, for instance, electrochemical sensors (65–67). Through variation of the catalyst temperature, the sensor responses can be modified, and the operation regimes can be optimized for the detection of specific target compounds. Catalysts include, for example, rhodium or platinum filaments (65–67). The odor pattern of a spoiling fish sample, obtained with eight different electrochemical sensors (four CO sensors, two hydrogen sulfide sensors, one sulfur dioxide sensor, and one nitrogen monoxide sensor) and seven different catalyst temperature steps, is shown in **Figure 3*a*** (65). The sensor-response patterns vary according to temperature and sensor type upon exposure to the fish odor. Again, the use of the catalyst generates so-called virtual sensors and efficiently extends the feature space.

Another example of external modulation through variation of the sensor gas-exposure duration is shown in **Figure 3*b***: The exposure interval of the sensors to the analytes can be varied by actuating valves and by switching between analyte-loaded and pure carrier gas. The resulting

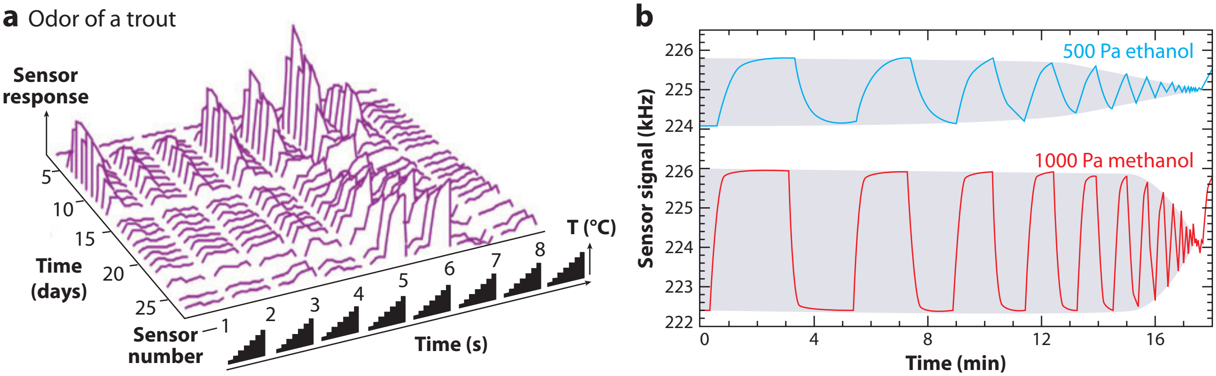

Figure 3

(*a*) Sensor signals of an array consisting of eight electrochemical sensors detecting the analyte gas-reaction products at seven different catalyst temperatures (30, 100, 200, 500, 600, 750, and 900°C) of an upstream platinum filament. The analyte included the odor of a spoiling trout sample. Reprinted from Reference 65 with permission. (*b*) Sensor signals for a series of concentration steps of decreasing lengths from 160 s down to 1 s. The capacitor was coated with a 4-µm-thick layer of poly(epichlorohydrin). The envelope of the response profile, highlighted in gray, is analyte specific and depends on the analyte absorption and desorption times in the polymer matrix. Reprinted from Reference 68 with permission.

transients of varying length can then be used to distinguish, for example, methanol from ethanol (68). For the experiments shown in **Figure 3**, a polymer-coated capacitive sensor was used, and the sensor signals are given in hertz, given that on-chip electronics convert the minute capacitive signals into the frequency domain in such experiments (69). Methanol and ethanol exposure steps of varying duration were applied to the sensor. For long exposure intervals, all analytes reach absorption equilibrium and maximum signal amplitude, whereas for short intervals this holds true only for fast-diffusing analytes. The sensor responses to methanol (**Figure 3*b***) reach saturation and sorption equilibria, even for relatively short exposure durations, whereas those to the larger and slower-diffusing ethanol do not. As a result, the signal amplitude of the ethanol response begins to decrease much earlier in comparison to methanol, allowing a discrimination of analytes that belong to the same homologous series to be performed.

Preconcentrator: a sampling device in which analytes are initially trapped and enriched in a sorptive matrix, then rapidly released using a heating pulse; in this manner, considerably higher analyte concentrations (depending on the enrichment time) reach the sensor or detection unit

2.3. Tunable Integrated Analysis Microsystems

In this section we briefly describe more complex gas sensor–based miniaturized analytical systems, which feature several parameters that can be tuned according to the sensing scenario. The sensor arrays act as detector units in those systems, so the parameter variations are external variations according to the terminology used here. In most cases, preconcentration and/or separation stages were combined with the sensor array acting as a detector unit for better analytical performance of the overall system, one of which is shown in **Figure 4** (70–79).

A preconcentration stage may be used to lower the detection limits for the sensors through enrichment of the target analytes in a sorptive matrix. After some time is allowed for the analyte enrichment, a sharp heating pulse is applied to the sorptive material so that all the analyte molecules, which were absorbed during a user-defined time span, desorb at once. In this way, considerably higher analyte concentrations hit the subsequent separation (micro–gas chromatography) and/or detection unit (sensor array) (71). The parameters that can be varied include the length of the enrichment time, the material of the sorptive matrix, and the temperature program for desorption. All these parameters influence how the analyte front hits the sensors. The preconcentration stages include dynamic headspace or purge-and-trap systems and solid-phase microextraction units that include fibers coated with absorbing materials (80). Nanoporous carbon, sol gels, ceramic matrices, polymers, and commercial packing materials are commonly used. In comparison to sensors without preconcentrators, improvements in the lower detection limit range between one and three orders of magnitude are achieved, so that the lower parts-per-billion range (relevant for many applications) becomes accessible.

The separation stage usually consists of miniaturized gas-chromatographic units, which were first presented in the late 1970s (81) and again in the mid-1990s (82). In most cases, the columns have been realized as spirals (column length 0.6 to 0.9 m, width 100 to 200 μm, depth 200 to 400 μm), micromachined into a planar silicon substrate (approximately 1 cm^2), with a glass plate bonded to the silicon substrate to close the column (see **Figure 4**). More recently, rather long (up to 3 m) square-type micromachined columns on 3.3–3.3-cm^2 dies have been developed (73). The variable parameters include the stationary-phase material (packed or coated column), the operation temperature or temperature program, and the flow speed (pressure) applied to the mobile gas phase.

The respective analytical microsystems were developed through broad-based efforts at the University of Michigan (70, 71, 73, 83, 84) and at Sandia National Laboratories (72, 78, 85, 86), respectively. They usually contain a sample inlet with particulate filter, a multistage preconcentrator/focuser, a gas-chromatographic separation module with pressure- and temperature-programmed separation tuning, an array of microsensors for analyte recognition and

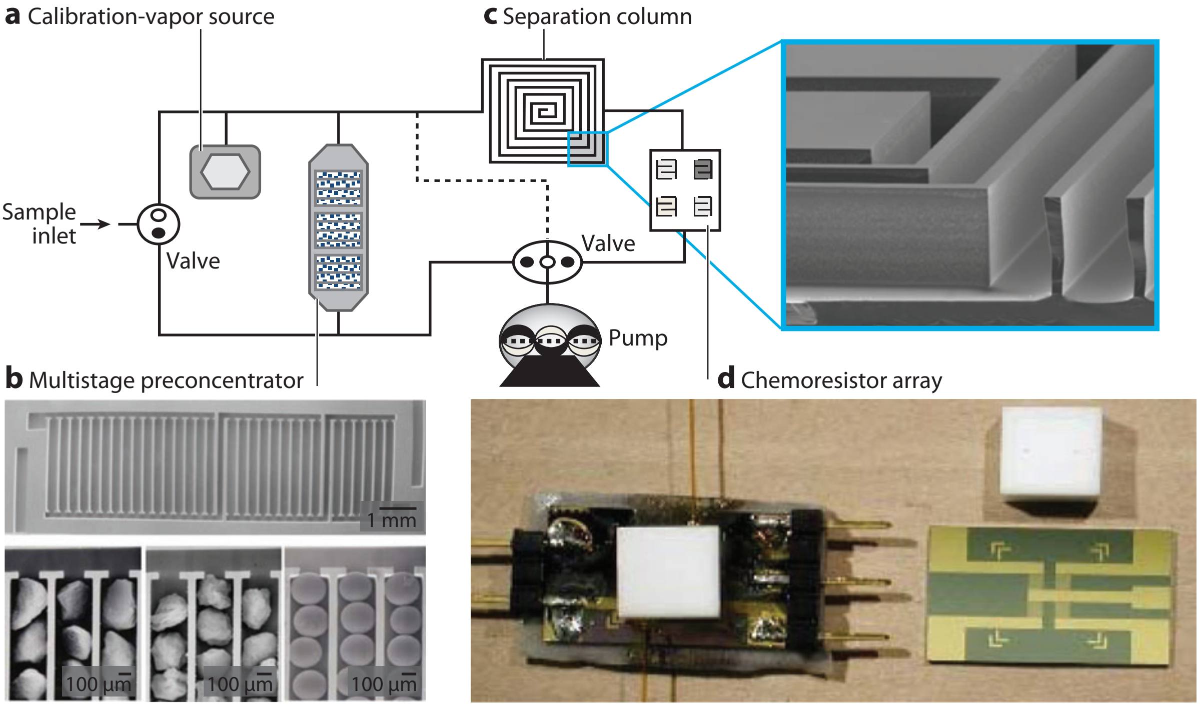

Figure 4

Schematic and components of the Michigan analytical microsystem. (*a*) Calibration-vapor source. (*b*) Three-stage adsorbent micropreconcentrator prior to loading and sealing (*lower left*), with close-up scanning electron microscopy images of each section loaded with adsorbents. (*c*) A 3-m separation column chip with close-up views of the channel cross sections prior to sealing (*top right*). (*d*) Detector assembly with four-chemiresistor-array chip (*bottom right*), Macor lid (*white square structure*), and sealed detector with connecting capillaries mounted on a custom fixture (*left*). Adapted from Reference 73.

quantification, and a pump and valves to direct the sample flow (**Figure 4**). Sometimes there is also an on-board calibration-vapor source to generate calibrant vapor at a constant rate by passive diffusion from a liquid reservoir. Analysis of this internal standard, along with vapors captured from the environment, provides the means to compensate for aging, drift, or other factors that might affect analytical performance. The systems are capable of separating, recognizing, and quantifying mixtures of moderate complexity (e.g., 11 vapors) in less than 1.5 min. The needed preconcentration time ranges from approximately 1 min (for industrial workplaces; analyte concentration in the single-part-per-million range) to 10 min or more (for less-contaminated office or residential environments; analyte concentration in the parts-per-billion range) (73).

Active sensing: a control strategy that adapts the configuration of the sensor system dynamically as it interacts with its environments (e.g., changing camera viewpoints to improve recognition of an object)

3. COMPUTATIONAL APPROACHES

Computational methods for adaptive sensing can be organized into three categories: adaptive filtering, adaptive classification, and active sensing. Adaptive filtering has had a long tradition in signal processing (87–89) and is the most common form of adaptation used with chemical sensors. Common to all adaptive filtering techniques is the assumption that the sensor system is subjected to unwanted phenomena that may originate either internally (e.g., sensor faults or drift) or externally (e.g., chemical backgrounds or environmental interferences). We also review adaptive classification techniques that compensate for nonstationary phenomena not during an initial stage (as done by adaptive filtering) but during the final stage in data processing: when a sample must be assigned to one of several known categories. Although other prediction problems exist (e.g., concentration estimation), classification has been the main focus of adaptive techniques for chemosensors. Finally, we review active sensing methods that allow a sensor system to adapt its parameters in response to the environment, thus providing a tight coupling between sensing and classification.

PCA: principal component analysis

3.1. Adaptive Filtering

Adaptive filtering schemes have been employed to address three classes of problems: detection of novel events (e.g., sensor failures or environmental changes), removal of interferences (e.g., backgrounds or environmental variables), and drift counteraction. Adaptation involves reacting to changes in the system or its environment. As such, the first step in any adaptive strategy consists of detecting such changes. Two basic strategies are commonly employed: knowledge-based models and analytical redundancy (90). Knowledge-based approaches involve building models of normal system operation and typical failure modes. These approaches are advantageous when prior knowledge about the system is available, but they may be too inflexible for use in adaptation. For this reason, our review focuses on the second (and also the most widely used) group of methods.

Analytical redundancy methods detect changes by exploiting redundancies in the sensor system, such as spatial and temporal correlations across multiple sensors. As an example, Pardo et al. (91) proposed a method for detecting faults in chemical sensor arrays. The method used a neural network to predict the response of each sensor through use of the remaining sensors as inputs, and it detected faults by analyzing residual errors. More recently, Perera et al. (92) proposed a novelty detection method to identify gas leaks in high-pressure lines. Because chemical sensors drift over time, static methods are unsuitable for long-term monitoring. Instead, the novelty detector must be adaptive so that it can factor out drift-related changes. The approach was based on recursive dynamic principal component analysis (RDPCA), a method closely related to the well-known technique known as evolving window factor analysis (EWFA) (93). EWFA models the covariance across sensors within a fixed time window; events in the system (e.g., a gas leak) act as new sources of variability, which can be detected by monitoring the PCA eigenvalues. In contrast, RDPCA models the covariance not only across sensors (as EWFA does) but also across time. RDPCA also uses the residual error rather than the eigenvalues, which speeds up the detection process. Wang et al. (94) described an adaptive method that detects anomalies in gas-sensor networks by analyzing spatiotemporal patterns across the network, such as cyclical changes in concentration, changes in the concentration of several gases, and joint events across sensing nodes. The method employs a Bayesian network to estimate the likelihood of events given new observations from the network; anomalies are detected whenever the likelihood of an event is low according to a hypothesis test. The above discussion provides a few recent examples of novelty detection with chemical sensors; the reader is referred to References 95 and 96 for a more extensive review of statistical and neural methods for novelty detection.

Environmental interferences and chemical backgrounds constitute a major source of noise in chemical sensors. When these interferences (e.g., temperature and humidity) are known and measurable, additional sensors may be used to quantify them and reduce their effect through calibration. The simplest form of compensation consists of modeling the sensor baseline response as a function of the interference, that is, through a static regression model (97). Such an approach, however, is unlikely to work when the two types of sensors have different dynamic characteristics. To address this issue, Perera et al. (98) employed the least-mean-squares algorithm (88) to remove humidity influences from the response of a gas-sensor array. Given an input signal $x(t)$

Blind source separation: the extraction of individual source signals from a set of their mixtures without knowledge of the sources or the mixing process (e.g., following individual conversations in a crowded room with multiple speakers)

ICA: independent component analysis

(e.g., the response of each gas sensor) and an interference signal $n(t)$ (e.g., the response of the humidity sensor), the least-mean-squares algorithm recomputes the parameters of a linear filter $\hat{x}(t) = \sum_{\tau=1}^{T} w(\tau)n(t-\tau)$ on the fly so as to minimize the residual error $\sum_t [x(t) - \hat{x}(t)]^2$. As a result, both static and dynamic effects of the interference signals can be removed. Furthermore, because the filter parameters $w(\tau)$ are recalculated over time, the algorithm can adapt to changes in sensor properties. In many cases, however, one does not have the luxury of measuring the interferences because they may be unknown or the required sensors may not exist. Several methods have been proposed to address this problem. One alternative is blind source separation, in which the response of the sensor array is modeled as a weighted sum of a number of independent sources. As an example, Di Natale et al. (99) applied independent component analysis (ICA) to a data set containing the response of thickness shear mode resonators to samples from two different types of peach cultivars measured in a nonconditioned room. In this study, ICA was used to separate temperature and humidity influences from discriminatory information. ICA was also applied by Wei et al. (100) to estimate the concentration of two gases from an array of MOX sensors and by Bermejo (101) to separate the effect of main and interferent ions from the response of ion-sensitive field-effect transistors.

A second group of techniques has sought inspiration from the processes of mixture segmentation and olfactory adaptation in the olfactory system. In earlier work, Gutierrez-Osuna & Raman (102) proposed a dimensionality-reduction method to cancel the effect of background chemicals from the multivariate response of a gas-sensor array. The method operated by adapting Fisher's linear discriminant solution so that the sensor response to previous odors becomes indistinguishable from the response to a neutral reference. Using neuromorphic models, the authors also proposed cortical feedback (103) and local habituation mechanisms (104, 105) that may be used to remove background odors and to segment odor mixtures into their individual constituents.

The most serious limitation of sensor arrays is the inherent drift of individual sensors, which results in a slow, random temporal variation of the sensor response even when the sensors are exposed to the same analyte under identical conditions. A number of algorithms have been developed to compensate for drift (14, 106). We focus on methods that are based on adaptive principles. One popular approach is to model the distribution of training examples with a codebook (i.e., a collection of cluster centers) and then adapt the codebook upon presentation of test data: An incoming (unknown) sample is assigned to the closest-matching class and then used to adapt the class parameters. Several variants of this approach have been used that update one cluster center per class (107), a single self-organizing map (SOM) for all the classes (108–110), or a separate SOM per class (111). A potential problem with these approaches, however, is that they rely on correct classification; misclassification errors eventually cause the model to lose track of the class patterns. Also, all analytes need to be sampled frequently to prevent their patterns from drifting away too much. Kermit & Tomic (112) have approached drift compensation as a blind source separation problem. Using experimental data from a hybrid sensor array exposed to two analytes at two dilution levels, the authors showed that ICA can separate the three sources of information in the sensor response: analyte identity, analyte concentration, and drift effects. A final approach that combines adaptive strategies with calibration techniques is to perform recalibration in an event-driven fashion. Such events may be triggered when unlabeled samples begin to fall outside the decision boundaries of the classifiers, when outliers are detected, or after interruptions in the data collection (113).

3.2. Adaptive Classification

Adaptive strategies for chemical sensors have also been explored at the classifier level, mostly in the context of incremental learning. Polikar et al. (114) proposed a learning algorithm (Learn^{++}) that builds an ensemble of classifiers online, that is, as training data arrives. The algorithm is closely related to AdaBoost (115), a machine-learning method that builds strong classifiers by forming ensembles of weak learners.[1] Learn^{++} builds the ensemble in a sequential manner. To ensure that each classifier learns a different decision boundary (otherwise the ensemble would be of little benefit), training samples are drawn according to an adaptive weight distribution; samples that are more difficult to classify receive higher weights, which increases their probability of being selected to train the next classifier. One interesting property of the algorithm is its ability to handle examples from classes that were not defined in the original training set: Because examples from these new classes cannot be correctly classified by the ensemble, these samples are highly likely to be selected for the next classifier. Along the same lines, Alippi & Roveri (116) proposed a just-in-time classifier for nonstationary environments. For this purpose, the authors used the *k*–nearest neighbors rule, which is ideally suited for adaptive classification because it lacks a proper training phase—all computations are deferred until new samples have to be classified. Their approach assumes that labeled training data is made available to the classifier in a sequential manner, and the goal is to optimize the performance of the classifier over time by adding new samples to the training set and removing samples that have become obsolete (i.e., as a result of drift). The approach consists of three steps: (*a*) adapting the value of *k* as the number of training samples changes over time, (*b*) detecting nonstationary behavior [described in a companion paper (117)], and (*c*) removing older samples from the training set once a nonstationary episode has been detected. Note that both approaches assume that training data arrive with their correct class label. This assumption may not be realistic in practical applications; in such cases, semisupervised learning strategies may be used when only a small proportion of the training data is labeled (118, 119).

Ensemble classifier: a machine-learning methodology that combines predictions from multiple individual classifiers to improve the overall classification rate of the system

Adaptive resonance theory (ART): a family of clustering/classification algorithms capable of adapting to changes in the statistical properties of the data without "forgetting" previously learned patterns

Methods based on adaptive resonance theory (ART) have been popular in the electronic-nose literature (120–123). The term ART refers to a family of algorithms originally developed to address the so-called stability-plasticity dilemma of incremental learning: How can a model adapt to changes in its environment without forgetting previously learned patterns? The basic approach shared by the various ART algorithms is a form of leader-follower clustering, where each incoming pattern is matched to the closest cluster in the model and either (*a*) the cluster is updated if it is close enough to the input pattern or (*b*) a new cluster is created. In this regard, ART is related to the adaptive methods for drift compensation (reviewed above). Although the original ART model was intended as a clustering algorithm, supervised versions, such as fuzzy ARTMAP, have been developed for classification problems (124). Fuzzy ARTMAP is significantly faster than other connectionist algorithms (e.g., multilayer perceptrons) but is sensitive to statistical overlap between the classes, which may lead to an uncontrolled growth in the number of categories. Other connectionist architectures have also been used for adaptive classification. As an example, Kurnik et al. (125) used the mixtures of experts (MOE) model, a modular neural network in which individual classifiers (i.e., experts) are trained on a subset of feature space and their predictions are linearly combined at the output. Unlike static classifier ensembles, in which the linear weights for the combiner are predetermined offline, the linear weights in an MOE are dynamically determined from the inputs by a gating network. This determination allows the model to adapt the classification rule depending on where a sample lies in feature space; such an approach may be used to adapt the classifier to the local environment of the instrument (e.g., temperature and humidity). More recently, Tang et al. (126) proposed a stochastic neural network, the continuous restricted Boltzmann machine (CRBM), to perform binary classification with chemical sensor arrays in the

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[1] A classifier is said to be a weak learner if its performance is only slightly better than chance (e.g., a 51% success rate for a binary classification problem). Such learners are also typically unstable in the sense that small perturbations in the training set can lead to large changes in the learned parameters.

presence of significant drift. The CRBM consists of three layers: (*a*) an input layer containing one node per sensor, (*b*) a hidden layer that provides a latent variable structure, and (*c*) an output layer to predict the class labels. Learning proceeds in two stages: an initial stage, in which the hidden layer is trained in an unsupervised fashion, and a final stage, in which the output layer is trained in a supervised fashion. Once learning is completed, all model parameters are frozen, with the exception of a hidden bias and an output bias. Freezing the parameters allows the model to adapt continuously in the presence of subsequent drift. Also, and unlike the other neural architectures, the CRBM training algorithm is amenable for very large-scale integration, which makes the model well suited for the development of intelligent sensors.

3.3. Active Sensing

Active-sensing strategies are inspired by the fact that perception (127) is not a passive process but an active one, in which an organism controls its sensory organs in order to extract behaviorally relevant information from the environment (see **Figure 5*a***). Active sensing has had a long tradition in robotics and computer vision (128–132) but has received only minimal attention in chemical sensing. In one of the earliest studies, Nakamoto et al. (133) developed a method for active odor blending, where the goal was to reproduce an odor blend by creating a mixture from its individual components. The authors developed a control algorithm that adjusted the mixture ratio so that the response of a gas-sensor array to the mixture matched the response to the odor blend. More recently, Gosangi & Gutierrez-Osuna (134) proposed an active-sensing approach to optimize the temperature profile of MOX sensors in real time. Consider the problem of classifying an unknown gas sample into one of M known categories $\{\omega^{(1)}, \omega^{(2)}, \ldots, \omega^{(M)}\}$ using a MOX sensor with

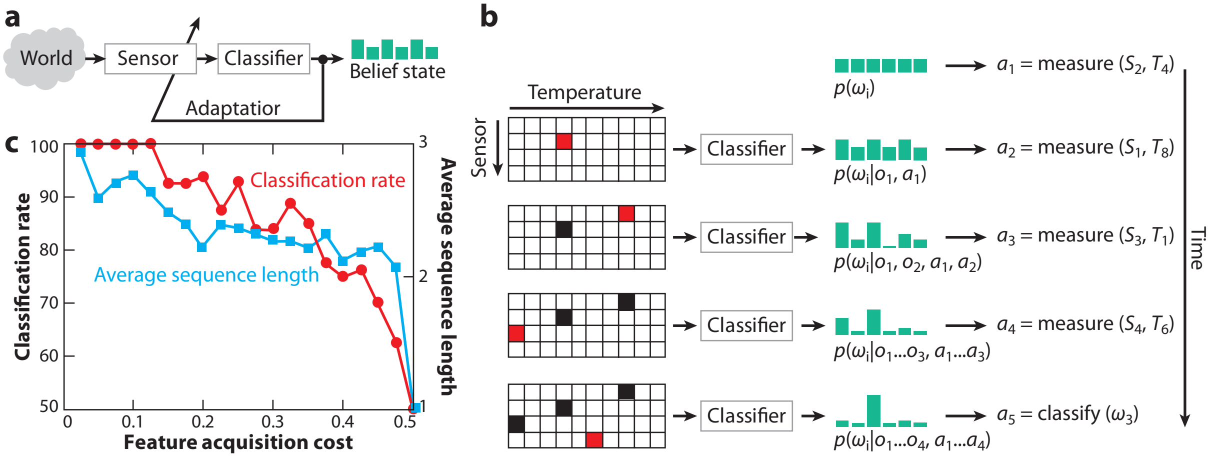

Figure 5

(*a*) In active sensing, the system adapts its sensing parameters on the basis of its beliefs about the world. (*b*) Illustration of active classification with an array of four metal-oxide sensors, ten temperatures per sensor, and a discrimination problem with six chemicals. At time $t = 0$, no information is available except that classes are a priori equiprobable: $p(\omega_i) = 1/6$. On the basis of this information, the active-classification algorithm decides to take the first sensing action (a_1, measure sensor S_2 at temperature T_4), which leads to observation o_1 and an updated posterior probability, $p(\omega_i \,|\, o_1, a_1)$. After four sensing actions, evidence accumulated in the posterior $p(\omega_i \,|\, o_1, \ldots, o_4, a_1, \ldots, a_4)$ and the cost of additional measurements are sufficient for the algorithm to assign the unknown sample to class ω_3. In this toy example, an accurate classification is reached with only 10% of all sensor configurations. (*c*) Classification performance and average sequence length as a function of feature acquisition costs. Adapted from Reference 134.

D different operating temperatures $\{\rho_1, \rho_2, \ldots, \rho_D\}$. To solve this sensing problem, one typically measures the sensor's response at each of the D temperatures, then analyzes the complete feature vector $x = [x_1, x_2, \ldots, x_D]^T$ with a pattern-recognition algorithm (135). Although straightforward, this passive sensing approach is unlikely to be cost-effective because only a fraction of the measurements are generally necessary to classify the chemical sample. Instead, we seek to determine an optimal sequence of actions $a = [a_1, a_2, \ldots, a_T]$, where each action corresponds to setting the sensor to one of the D possible temperatures (or terminating the process by assigning the sample to one of the M chemical classes). More importantly, we seek to select this sequence of actions dynamically on the basis of accumulating evidence. Our solution to this problem follows Reference 136. First, the authors modeled the dynamic response of a sensor to a sequence of temperature pulses by means of an input-output hidden Markov model, a machine-learning technique that can be used to learn a dynamic mapping between two data streams: (*a*) an input (temperature in this case) and (*b*) an output (sensor conductance). Once a dynamic sensor model has been learned, we then approach the temperature-optimization process as one of sequential decision-making steps under uncertainty, where the goal is to balance the cost of applying additional temperature pulses against the risk of classifying the chemical analyte on the basis of the available information. Following Reference 136, the problem is solved through a partially observable Markov decision process. Simulation results from this study are shown in **Figure 5*c***; these results indicate that the method can balance sensing costs and classification accuracy: Higher classification rates can be achieved by decreasing sensing costs, which in turns increases the length of the temperature sequence and the amount of information available to the classifier.

Integrated sensing and processing (ISP): a strategy in which part of the required computation is performed as the instrument collects measurements in order to reduce the need for subsequent signal processing

Active sensing has also been investigated in hyperspectral imaging (137), a domain in which acquiring the complete data cube is neither required nor even desirable in most applications. In these cases, adaptive techniques may be used in library-based spectral identification tasks to match a partial chemical spectrum to a known spectrum or to a mixture of spectra. Adaptive sampling may also be used to extend the dynamic range of imaging/spectrometric systems. As an example, when the dynamic range of a scene exceeds that of the imager, the result is an overexposed or underexposed image/spectrum or possibly both. In such cases, an adaptive technique may be used to select exposure durations at each spectral channel according to the signal level at that particular channel so that weak signals can be brought above the noise levels of the detector (138, 139).

A concept related to active sensing is that of integrated sensing and processing (ISP) (140). The basic idea behind ISP is to perform part of the required computation as the instrument collects measurements, thus reducing the need for subsequent signal processing. An early example of ISP is optical signal processing (141). An optical signal processing instrument consists of a dispersive element that directs wavelengths to various spatial locations in a transmission mask, where an inner product is computed between the incoming spectroscopic information and an orthogonal weight function stored in the mask. When the weight function is orthogonal to the emission spectra of interfering species (but not to the target's spectra), the output of the mask becomes a direct measure of the target's concentration, thus eliminating the need for further processing. A related approach was introduced in Reference 142 under the name of optical regression. The motivation behind optical regression is similar to that of ISP: avoiding the need to collect unnecessary variables. In a conventional instrument, a complete spectrum is first collected, and individual variables or wavelengths are subsequently selected algorithmically to form a regression vector. In optical regression, variable selecting is performed in an analog fashion: directly at the detector side. This is achieved through modification of the integration time at each wavelength such that the output of the detector is proportional to the inner product of the transmission spectrum and the regression vector. In this fashion, the output of the detector is made proportional to the concentration of the target analyte. Optical interference filters known as multivariate optical elements have also been designed to perform functions similar to those of optical regression. In this case, however, the multivariate optical element is designed to have a transmission spectrum that resembles the desired regression vector (143). This may be achieved by, for instance, identifying combinations of organic materials whose transmission spectra sum up to the desired regression vector and by placing various combinations in a rotating filter wheel (one combination for each target spectra).

ISP concepts have also been applied in the context of acoustic resonance spectrometry, an analytical technique that is known to generate very large data sets. As an example, Medendorp et al. (144) collected full spectra for two target analytes and applied Fisher's discriminant analysis to identify the most informative frequencies, namely those that are directly proportional to the physical property of interest. The resulting set of frequencies was then converted into the time domain and used as an excitation signal. As a result, once the excitation signal passed through the sample, its amplitude could be used as an estimate of the analyte concentration without the need for further data processing. Finally, Priebe et al. (145) developed a statistical pattern-recognition method for ISP that may also be used for active sensing. The approach consists of building a decision tree that partitions feature space in a hierarchical fashion: Nodes close to the root of the tree select features on the basis of their ability to provide clear partitions of examples regardless of class labels (i.e., clustering), whereas nodes at the leaves select sensors on the basis of their ability to discriminate examples from different classes. The method was evaluated on an experimental data set from an optical-sensor array exposed to trichloroethylene (a carcinogenic industrial solvent) in complex backgrounds. Experimental results show that the ISP decision tree can reduce misclassification rates by half, while requiring only 20% of the sensors to make any individual classification.

4. OUTLOOK

Most of the work reviewed in this article has focused on adaptation schemes for single sensors or, at most, sensor arrays within a single instrument. However, advances in chemical microanalysis systems along with the explosion of mobile computing and wireless communications capabilities will soon make it possible to deploy massively distributed sensor or microsystem networks with capabilities that, only a decade ago, were confined to the lab bench of research laboratories. The integration of chemical microanalysis systems and wireless networks may have a profound impact in applications ranging from environmental monitoring to personal health care (146), but it also presents formidable challenges to current practices for sensor management and data analysis. Approaches that work for a handful of sensors are unlikely to scale up to networks containing hundreds or thousands of geographically distributed heterogeneous detectors. In response to these projections, Yang et al. (147) have proposed the concept of autonomic sensing, a loosely defined term that envisions self-managed sensor networks requiring minimal or no human intervention. To deal with the complexity of large numbers of wireless sensors, autonomous sensing borrows inspiration from the study of biological systems. One example is swarm intelligence (148), an approach developed in artificial intelligence to manage large groups of agents (i.e., robots) through simple local rules. Intelligent behavior in such cases is considered to emerge as a result of interactions among agents, rather than through the imposition of a centralized control structure. As an example, Tsujita et al. (149) proposed an autocalibration method for networks of mobile gas sensors. In their approach, each sensor was recalibrated whenever (*a*) it was in close proximity of other mobile sensors, in which case the average concentration estimate across the neighboring sensors was used as an approximation of the true concentration, or (*b*) it was within range of one of several environmental monitoring stations distributed across the area of interest, which were assumed to provide accurate concentration estimates. Simulation results indicate that this simple mechanism may be used to compensate for additive sensor drift. A related approach, known as quorum sensing, is inspired by a molecular signaling process used by bacteria to communicate and coordinate behaviors with other bacteria in their vicinity. For example, Wokoma et al. (150) applied quorum sensing to the problem of environmental monitoring with wireless sensor networks, specifically to determine whether there were enough sensors in certain areas that would warrant the formation of a cluster to coordinate their monitoring operations. Simulation results indicated that the quorum-sensing protocol is more scalable and can adapt to changes in the environment more efficiently than a centralized method can, albeit at the expense of suboptimal clustering results and higher computational complexity. These examples illustrate that adaptation should not be considered only as residing at the sensor level, but rather as a property that pervades all levels of a system.

SUMMARY POINTS

1. Long-term operation of chemical detectors in unknown and variable environments requires adaptive techniques to (*a*) compensate for changes in the environment and in the detector itself and (*b*) reduce the power requirements of the system.
2. Several parameters can be modified to adapt the sensor or sensor system to a certain sensing scenario during operation. These parameters include internal parameters, such as frequencies and operation voltages, and external parameters, such as exposure timing and the use of catalysts.
3. Compact microanalysis systems featuring multiple tuning options, including preconcentration and separation stages, also constitute an important development.
4. By varying the parameters or changing the tuning options, one can tune the sensor or sensor system to detect specific analytes in a complex and changing environment or to increase the overall information gathered with such a system.
5. In many spectroscopy applications, the complete data matrix is neither required nor desirable, as it increases the computational complexity of subsequent stages.
6. Adaptation can take place at many levels and stages in the system, ranging from selecting sensor tunings to reestimating the parameters of the calibration models.

FUTURE ISSUES

1. The level of complexity of the sensor devices or systems massively increases with the provision of tuning options. Therefore, a major challenge involves keeping the sensors or systems user friendly and keeping small-volume production at a moderate price.
2. Sensor systems will enter into competition with miniaturized chemical analysis systems such as gas chromatography, infrared or ultraviolet spectroscopy, and mass spectroscopy. However, useful synergistic effects and combined instruments may also emerge.
3. The reliability and reproducibility of chemical sensors or systems must come close to those of purely physical detection and analysis methods (e.g., spectroscopy) to achieve general acceptance in industry.
4. A number of the adaptive methods reviewed herein have been tested on simulated data or short-term experimental studies. Few validation studies from long-term deployments of chemical sensors exist.

5. Current algorithms for wireless sensor networks assume that data transmission is the main source of energy expenditures. Although this may be true for the measurement of physical parameters (e.g., pressure, temperature, light, and vibration), a number of chemical detectors (e.g., high-temperature MOX sensors, preconcentrators, and infrared-based sensors) are power intensive and may require different assumptions about the relative energy budgets of sensing versus data transmission.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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