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Developments in electrochemical sensors for occupational and environmental health applications

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Abstract

This paper provides an overview of recent advances in electrochemical sensors for industrial hygiene monitoring applications. Currently available instrument technologies as well as new devices under development are both exemplified. Progress in ruggedization and miniaturization of electroanalytical devices has led to significant improvements for on-site monitoring applications, e.g. in harsh environments and in biological monitoring. Sensor arrays and modified electrodes offer considerable promise for improved electrochemical sensing, i.e. through multi-species detection and enhanced selectivity. On-site electroanalytical detection and measurement in the field may become more widely used for applications in occupational health monitoring.
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1. Introduction

Electrochemical sensors have been used for years in the occupational and environmental health fields, and they have proven to be valuable tools for screening and/or definitive analysis of workplace toxins. Significant improvements continue to be made in instrumentation and sensor methodologies and fabrication. Portable sensors and analytical devices based on electrochemical methods are commonly used on-site in the workplace for field monitoring of airborne exposures to toxic substances, and noteworthy emerging developments are described herein. Also, fixed-site laboratory methods based on electroanalytical techniques are used for industrial hygiene monitoring purposes. Moreover, electroanalytical methods are used widely for biomonitoring of certain toxins and metabolites in body fluids such as blood

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and urine. Electroanalytical measurement techniques for industrial hygiene monitoring purposes were reviewed a few years ago [1], and this paper will strive to provide an overview of recent developments in electrochemical sensors for applications in the occupational and environmental health arena. Apart from addressing commercially available electroanalytical technologies, some new advances which have not yet been commercialized are also covered.

Sensors for gases and vapors are used extensively in the industrial hygiene field, and research on new sensors and improved sensor designs has continued in recent years [2]. Many sensors that are commercially available are based on electrochemical transduction, and improvements in the materials, design, and construction of these types of sensors have led to better products for occupational and environmental health monitoring. Electrochemical sensors are used in industrial hygiene for the detection of inorganic gases and vapors such as carbon monoxide, carbon dioxide, sulfur dioxide, and nitric and nitrous oxides. Amperometric and other electrochemical sensing devices have also been employed for the determination of airborne organic compounds such as volatile organic hydrocarbons (VOCs), aldehydes, and ketones [3]. Electrochemical signal transduction is especially useful for sensing since extremely minute electrical signals (e.g. current, voltage, capacitance, conductance) can be detected and transmitted with very high sensitivity and low noise. New materials continue to be developed to enhance the performance of electrochemical instrumentation for monitoring purposes, in some cases allowing multi-gas sensitivity and specificity.

2. Ruggedization

For many years, a serious criticism of electrochemical techniques was the fragility of the instrumentation. Fortunately, dramatic improvements have been made recently in terms of ruggedization of electrochemical monitoring equipment. For on-site industrial hygiene measurement applications, clearly it is desirable to have monitoring devices that are able to withstand the rigors of use in the workplace. For applications in the fixed-site laboratory, the analyst prefers to utilize instruments that are reusable for long periods without requiring frequent maintenance. It is desirable that sensors be stable, sensitive, selective, and long-lived. Monitoring devices and electrode assemblies have been engineered that are much more rugged than two decades ago. Portable sensors are often meant for use by field technicians or analysts who may not be able to exercise the same level of instrumental care as those who used earlier versions of similar technology. Newer electrochemical sensors are much more user-friendly than the devices of previous generations. Improvements in both hardware and software have resulted in the commercialization of electrochemical sensors that can be employed for routine use by the industrial hygienist.

The advent of screen-printing techniques for the fabrication of inexpensive, disposable electrodes has been a boon to electroanalytical chemistry for various applications [4]. Screen-printed electrodes can be manufactured in bulk at relatively low cost, and their effective performance has been demonstrated for environmental, biomedical, and occupational hygiene monitoring [4,5]. For instance, such electrodes have recently been shown to provide a means for on-site monitoring of airborne lead at trace levels [6], and they have been used for the determination of this toxic metal in other matrices as well [7–11]. Disposable screen-printed electrodes have also been employed for measuring lead in human

Table 1
Examples of analytes measured using screen-printed electrodes (from [4–6], and references therein)

Analyte species	Matrix
Metals	Drinking water, ground water, blood, urine
Lead	Workplace air, paint, dust
Glucose	Body fluids, e.g. blood, urine
Lactate	Blood serum, foods
Cholesterol	Blood
Ethanol	Alcoholic beverages, vapor
Formaldehyde	Water
Thiols	Vapor
Uric acid	Urine
Nitrite	Ground water, drinking water
Phenols	Water
Pesticides	Standard solutions

blood samples [11–14]. An advantage offered by screen-printed electrodes is associated with their single-use application, which avoids problems from electrode fouling due to repeated analyses using the same electrode surface. Hence, there is no threat of electrode poisoning from reusing the same sensor surface for successive analyses. By employing these electrodes as sensors in field-portable, battery-powered instrumentation, it is now possible to obtain excellent sensitivity and selectivity for the on-site measurement of numerous analytes of interest. Table 1 lists some examples of analytes which have been measured using screen-printed electrodes. It is anticipated that more applications of screen-printed electrodes in environmental and biological monitoring will appear in the near future.

Over the years, electrochemical sensing devices as a class have been regarded by many as being overly subject to interferences, and such difficulties remain in many cases. However, advancements in materials chemistry and engineering are overcoming problems from interferences in electrochemical sensors. For example, the use of liquid interfaces in electrochemical sensing has led to greater specificity, better sensitivity, and longer electrode and cell lifetimes for the measurement of numerous gaseous analytes [15]. Workplace air species such as ozone, H_2S, NO_x, SO_2, formaldehyde, ammonia, and hydrogen peroxide have been successfully measured using electrochemical sensors employing porous membranes which can be used to preconcentrate the analyte. Membranes also prevent electrode fouling while eliminating interferences [15–19]. A classic example of where the use of a membrane dramatically improved sensor performance was demonstrated many years ago with the invention of the Clark oxygen electrode [20]. In the case of the Clark electrode, when a polymer membrane was placed over a metal electrode, poisoning of the electrode surface from blood proteins was prevented, thereby enabling the measurement of O_2 levels in blood.

Recently, improvements in power supplies through the use smaller, lighter and longer-lived batteries (notably lithium ion batteries) have overcome a major hurdle to field-portable technology. Advances in the materials and designs for batteries have resulted in the manufacture of instruments that out-perform previous models. Batteries required to power portable sensors have become more robust, enabling longer term monitoring with fewer and shorter charging periods. For instance, lithium ion batteries which have been used for years in cameras and more recently in cellular telephones offer significant improvements over nickel–cadmium batteries in terms of lifetimes and recharging capabilities. Engineering advances continue to be made in materials and designs of batteries for powering portable instruments.

A wide variety of commercial electrochemical sensors for gases and vapors are available [20,21]. Examples of applicable analytes include O_2, CO, CO_2, HCl, HCN, H_2S, NH_3, NO_x, SO_2, and halons; many instruments offer multi-analyte capability. Also, sensors for organic gases and vapors can be found on the market. These devices are all portable or transportable (e.g. via van or truck), and many are hand-held, battery-powered units. Electroanalytical instruments for continuous or short-term monitoring of toxic gases and vapors in air are numerous, and their stability and long-term performance have improved. While problems with interferences remain in many cases, advancements continue to made in the development of more rugged electrochemical sensors.

In short, there are numerous advances that have resulted in the manufacture of portable electroanalytical devices which are more rugged and user-friendly for making on-site measurements. These include the following examples: (a) disposable screen-printed electrodes for ease of use, enhanced sensitivity, reduced contamination and fewer interferences; (b) membrane electrodes for optimized specificity, increased sensitivity, and minimization of interferences; (c) lightweight, robust materials for the fabrication of rugged, light instruments; and (d) advances in battery technology for size minimization and longer device lifetimes.

3. Miniaturization

Sensors for on-site workplace monitoring tend to be more useful to the industrial hygienist if they are small and easily portable [1]. Biosensors are also of greater utility if they are minute in size, especially if such devices are intended for in vivo monitoring [20,22–24]. Much work has gone into miniaturizing electrochemical sensors for environmental and biological monitoring, analogous to the progressive miniaturization of computer chips. This effort is reflected in the availability of monitoring instruments and sensor probes that are generally considerably smaller than in earlier years [20–25]. Applications have been shown for inorganic and organic analysis as well as bioanalysis.

Developments in the design and fabrication of ultramicroelectrodes [26] offer considerable promise for advancements in electrochemical sensors. Ultramicroelectrodes have proven to be especially useful for biomonitoring purposes [23,24,27], and they also have been employed for environmental and industrial hygiene measurements [1,2]. These extremely minute electrodes provide fantastic sensitivity, for as their size is diminished the signal-to-noise ratio increases even though the magnitude of the detected signal is smaller [26,28]. Although the magnitude of the current signal is decreased as the electrode dimensions are reduced, with modern electronics it is possible to measure extremely small signals with low-noise operational amplifiers and associated instrumentation. In this way, the favorable mass-transport characteristics offered by electrodes of minute size can be used for analytical advantage. As electrode size is reduced, the rate of analyte diffusion to the electrode surface is increased dramatically, thereby enhancing sensitivity. Extremely low detection limits may be achieved with ultramicroelectrodes, and many hazardous substances demand that detection limits are as low as possible.

Another advantage of ultramicroelectrodes is that oftentimes no supporting electrolyte is necessary, owing to the favorable mass-transfer characteristics of tiny electrodes [26]. Hence, it may be possible to use ultramicroelectrodes to measure analytes having very high redox potentials [26,29]. In this way it may become possible to monitor toxic airborne species, e.g. polyaromatic hydrocarbons, which have previously been unattainable for measurement by electroanalysis. Arrays of ultramicroelectrodes can be employed to give increased sensitivity and selectivity for environmental monitoring [30], but applications of this technology for industrial hygiene monitoring have not yet been realized.

In addition to ultramicroelectrodes, chemistry in miniature has also been realized through chemical analysis on microchips [31]. Microdevices for electrochemical analysis on a micrometer scale have been fabricated using centimeter-sized chips comprised of glass, silicon or inert polymeric materials. Microfluidic circuits have been fabricated which provide a "total analysis" system including sample introduction and pretreatment, chemical reaction, detection, and separation or isolation of reaction products [32]. Analytical performance on a small scale is improved by means of speed and efficiency, as reactions can be completed effectively and rapidly through implementation of the lab-on-a-chip concept. In an application of "microelectrochemistry," potentiometric detection on a chip has demonstrated electrochemical behavior similar to conventional electrochemical cells and microelectrodes [33]. As an example, a microscale capillary electrophoresis system with amperometric detection has been fabricated [34]; the device has been employed in the assay of mixtures of nitroaromatic explosives and catecholamines. Another exciting related development is the fabrication of disposable microchips for blood chemistry biosensors [35]. Microscale electrochemical detection technology offers tremendous potential for many other analytical applications, especially for on-site screening measurements. It is only a matter of time before this "chemistry on a chip" technology becomes used in the manufacture of electrochemical sensors for occupational hygiene and related applications.

Other advances in the miniaturization of electronics for applications in chemical technology offer potential advantages in sensor design and performance. For instance, nanochemistry relying on non-lithographic techniques has permitted the fabrication of microscopic "single-electron transistors" (SETs) [36]. Transistor size has decreased by one-half about every 18 months since the original discovery of the transistor over 50 years ago, enabling the integration of over a million transistors into the space occupied by the first transistor. Nanometer-sized transistors have numerous potential applications, including ultrasensitive gas and vapor detection and biosensing. Single-electron conduction via reproducibly fabricated "nanotubes" has recently been demonstrated [37,38], and metallic "quantum wires" [39] have been investigated for their chemical sensing attributes. Research must continue in the characterization of electronic properties of nanotubes and related microscopic electronic materials before applications in sensor technologies will be realized.

4. Sensor arrays

As sensor size has decreased with corresponding increases in signal-to-noise ratios, it has become possible to use arrays of sensors to further increase sensitivity while also improving selectivity. For example, new sensor arrays based on amperometric detection, coupled with chemical modification and pattern recognition techniques, have been fabricated which significantly enhance analytical performance [40]. Arrays of microelectrodes have been commercialized which allow for voltammetric measurement of multiple metals. Electrode arrays for multicomponent analysis have shown applications in gas sensors, biosensors, and environmental analysis of other matrices such as water [41,42]. In one recent application, thin-film tin oxide sensor arrays were used to measure gaseous nitrous oxide, carbon monoxide, and methane, along with water vapor, simultaneously and at concentrations of interest for occupational health monitoring [43]. This and other nanotechnologies have been fabricated into arrays for enhanced electronic transmission at microscopic scales [37,44]. For example, a simple yet novel design for the preparation of analyte-specific chemical sensors has been proposed using nanotechnology [44]. Future sensors could enable the measurement of single-electron transfer events and, when arrays of nanoparticle sensors are fabricated, sensitivity may be significantly enhanced. Moreover, specificity and multispecies detection can be afforded through the attachment of various receptor types on metallic nanoparticles arranged in arrays. New microscale technologies may soon see extension to the design of useful electrochemical array sensors for occupational hygiene monitoring and related purposes.

Microlithographic and other novel engineering techniques for the fabrication of electrochemical array devices have enabled the development of ultramicroelectrode arrays which offer extremely novel environmental applications [30,45]. New developments in electrochemical sensor design include devices intended for use in harsh environments. Engineering challenges that still must be addressed in the manufacture of devices for use in workplaces sometimes remain difficult to overcome. With further advances we may expect that workplace monitoring applications of instrumentation based on arrays of electrochemical sensors should be forthcoming in the near future.

5. Modified electrodes

A vast literature exists on the subject of modified electrodes, for chemical modification of electrode surfaces is an essential key to sensor stability, sensitivity, and specificity. Numerous electrode-modification methods have been investigated for applications in electrochemical sensors, e.g. solid polymer electrolytes, membrane-modified electrodes, conducting polymers, sol–gel films, self-assembled monolayers, ceramic materials, and enzyme-modified electrodes, to name a few. Owing to the fact that there are a great number of published studies involving electrode modification for sensor applications, only a brief overview can be presented here, with representative examples given. Advances in materials science and engineering have made it possible and advantageous to employ numerous chemical detection and analysis techniques in the design and fabrication of electrochemical sensors, and work continues fervently in this research field.

Chief among the technologies employed in the ongoing development and evaluation of gas and vapor sensors are solid electrolytes. The immobilization of a conductive or semiconductive layer on the electrode surface, which demonstrates desired chemical properties, is an extremely useful technique for sensor design. Solid electrolytes have been used widely for the detection and monitoring of gaseous analytes, and they are especially appealing for this sensing application since no solution is required in which the analyte must be dissolved

Table 2
Some recent examples of applications of solid-state electrochemical sensors for gaseous monitoring

Solid electrolyte type	Analyte	Reference
Doped tin oxide	CO_2	[48]
Lithium ion conductor	CO_2	[49]
Nasicon (Na^+ conductor)	CO_2	[50,51]
Ba^{2+} conductor	CO_2	[52]
Zirconia (& Na^+ conductor)	CO_2	[53]
Zirconia (e^- conductor)	CO	[54]
Zirconia	O_2	[55]
Zirconia	SO_2	[56]
Zirconia	H_2S	[57]
Ag-β-alumina	SO_x	[58]
Galvanic (H^+ conductor)	Cl_2	[59]
Galvanic (H^+ conductor)	Explosives	[60]
H^+, Cl^- conductor	HCl	[61]
Doped indium oxide	O_3	[62]
Nafion (cation-exchange membrane)	Organics, SO_2	[63]
Nafion	H_2S	[64]
Plasticized polyvinyl chloride (e^- conductor)	NO_2	[65]
Prussian blue (e^- conductor)	CH_4, $EtCl_2$	[66]

prior to measurement. Rather, the solid-state sensor is simply exposed to the target analyte gas(es) or vapor(s), and the analyte(s) is (are) selectively intercalated into or adsorbed on the electrolyte layer. This interaction serves to alter the chemical potential of the electrolyte film, which results in an electrical signal that can be detected, transduced, and amplified with high sensitivity. Solid-state sensors employing this design have been developed for numerous analyte species of interest in occupational and environmental health. Ceramic materials such as Zirconia and Nasicon have been especially useful for the fabrication of solid electrolyte films in sensors for species such as CO_2, O_2, SO_2, and H_2S [46]. Nafion is another electrode modifier which has shown tremendous versatility in potential sensor applications, e.g. for detecting organic and inorganic gases and vapors [46,47]. A few recent examples of investigations of solid-state sensors for gaseous monitoring are listed in Table 2.

Possibilities for conducting polymers such as polypyrrole, polyphenylene, polyaniline, and polythiophene in electrochemical sensors have been recognized for many years [20,67]. Organic conducting polymers demonstrate tremendous versatility in terms of chemical properties and range of conductivities, and therefore offer considerable promise for many commercial applications, including polymer-modified electrochemical sensors [68–71]. However, short longevities of organic conducting polymer films attached to metal electrodes has restricted advances in sensor technology for many years. Nevertheless, great strides have been made recently in materials chemistry which have reintroduced organic conducting polymers and oligomers to the scientific limelight [72]. Novel organic polymers and copolymers are being produced and investigated that offer electronic and electrochromic properties which have long been sought but are now demonstrating longer-term stability which was, for well over a decade, not achievable. It is predicted that recent successes in organic conducting polymer research and development will soon pay dividends, specifically in terms of the availability of new electrochemical sensors that will be more robust and rugged. Electrochemical sensors based on conducting polymers hold promise for an expanded array of applicable airborne, environmental, and biological analytes.

An important methodology for immunological detection has been the development of electroanalytical techniques that utilize enzyme-modified electrodes [73]. Electrochemical immunoassays are based on electrode modification with enzymes which are used for specific assays of target analyte species. Enzyme/substrate activity is then measured potentiometrically or amperometrically. Examples of enzymes which have been used in this capacity include alkaline phosphatase, glucose oxidase, urease, and horseradish peroxidase [74]. These moieties are attached to electrodes via electroactive functional groups which act as electronic (redox) linkages between the immobilized enzyme and the electrode surface. Some of the electroactive linkages which have been utilized for this purpose are ferrocenyl-, dinitro-, 2,4-dinitrophenyl-, and azo groups, as well as organic conducting polymers [73]. A few example target substances which have been measured using electrochemical immunoassay include glucose, digoxin, immunoglobulins, atrazine, theophylline, thyroxin, and *p*-cresol [73]. Enzyme electrodes for environmental monitoring offer a viable means for field-based measurements [73,74]. Of course enzyme-modified electrodes also have numerous applications in biomonitoring [73,75]. Arrays of enzyme-modified electrodes show promise for multispecies detection while providing high selectivity and sensitivity.

Other chemical sensor treatments have been tried in attempts to provide better selectivity. For instance, macrocycles consisting of cavitands with different cavity shapes have recently been employed for organic sensor applications [76]. The use of macrocycles as receptor molecules for neutral and ionic species is well known [77], but applications in organic vapor monitoring are still in the developmental stages. Electrodes modified with microporous polytetrafluoroethylene (PTFE) membranes have been employed for HCN [78] and SO_2 [79] monitoring. High sensitivities for the target analytes were achieved, but interferences remained problematic. Ion implantation has been used in an effort to prepare sensitive ion-selective electrodes for sensor applications [80]. Membrane electrodes have been used widely for biomonitoring purposes, and many types of chemically modified electrodes have shown increasingly better performance in terms of sensitivity and selectivity of biosensors [81,82]. Sol–gel materials for antifouling [19] as well as chemical receptor immobilization [83] purposes have been used in the modification of electrodes for environmental monitoring and biosensing. Adsorption voltammetry is a technique which may be ideally suited for gas and vapor monitoring, and developments in this arena continue through the use of chemically modified electrodes, for instance in the determination of trace formaldehyde in air [84].

In recent work, modification of optically transparent electrodes (OTEs) with selective films has been used for ultraviolet-visible (UV-Vis) spectroelectrochemical sensing of target analytes [85,86]. The cell design is similar to that used years earlier for Fourier transform infrared (FTIR) spectroelectrochemical detection of adsorbed molecules on electrode surfaces, wherein an attenuated total reflection (ATR) prism is used to direct the light path [87]. A UV-Vis spectroelectrochemical cell, in which a chemically modified OTE is used to effect the desired redox reaction within the film, allows the reaction to be probed optically. The film acts as a path for analytes of interest and as a barrier to unwanted interferences, while also serving as a signal transducer. As another example, the analysis of traces of mercury in air has been carried out using an electrochemical device for years, but combination of the “gold trap” (Au–Hg amalgam) electroanalytical method with atomic spectrometry provides even better sensitivity and selectivity than previously [88]. Spectroelectrochemistry offers advantages of simultaneous electrochemical and optical detection [89,90], but this methodology has not been widely applied to sensor design and remains in the developmental stages.

6. Summary

Developments in electronics, miniaturization, materials science, and innovative melding of new technologies has led to the fabrication of chemical and biochemical sensors which are anticipated to see increased application in the environmental and occupational health field. Remote electrochemical sensors for environmental monitoring have been investigated [91], and further expansion of these technologies to the industrial hygiene and related fields is expected. Many challenges remain, such as sample extraction, overcoming interferences, multianalyte detection, and increasing sensitivity. For example, sample extraction techniques for field applications have been evaluated for the analysis of lead in airborne and dust wipe samples [92–95], but more research is required to develop sample treatment procedures that are more easily carried out by non-chemists. Another barrier to more widespread use of electrochemical techniques in the occupational and environmental health arena has been the matter of reference electrodes, which tend to require repeated maintenance and care and are not always rugged. But the development of disposable reference electrodes for chemical sensor and other applications [96] will overcome this obstacle to enable more widespread use of electrochemical methods by the non-chemist.

There have been numerous technological successes in the development of improved electrochemical sensor devices, and continued progress is anticipated. Sensor techniques range from qualitative to semi-quantitative to determinative, and their proper application for the evaluation of human exposures requires that the monitoring methods be evaluated appropriately and thoroughly [97,98]. Great strides in the development and evaluation of sensor technologies have been made over the last decade. For instance, the use of prefilters in sensor design has served to improve the selectivity of gas sensors [99–101], and polymer modification of mercury thin-film electrodes has been shown to eliminate interferences to trace metal analysis [102]. Novel fabrication techniques for sensor materials such as polymer electrolyte membranes [103,104], chalcogenide glasses [105], screen-printed electrodes [106], nanowires [107], and metal oxides [108] continue to be developed which offer improved characteristics for sensing purposes. Also, techniques to accurately predict sensor lifetimes during their use have recently been investigated [109]. We may soon expect to see new technologies being brought to market which will offer better performance than earlier generations of sensor devices.

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