REVIEW ARTICLE

Electroanalytical Applications in Occupational and Environmental Health

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ABSTRACT

Electroanalytical chemistry has been used for years in the occupational and environmental health fields. Portable sensors and analytical devices based on electrochemical (EC) methods are commonly used on-site in the workplace. Laboratory EC methods also have been used extensively for the analysis of industrial hygiene and related samples. Recent advances in electroanalytical methodology may lead to new analytical applications in the occupational health arena, both in the laboratory as well as on-site in the workplace. Applications in heavy metals analysis, analysis for inorganic and organic species, and bioanalysis are exemplified. This article provides an overview of the history of EC analysis for industrial hygiene purposes, and also summarizes current and newly developed applications of electroanalytical methods in occupational and environmental health.

KEY WORDS: Occupational health, Environmental health, Industrial hygiene, Electroanalysis.

INTRODUCTION

The objective of this article is to provide a review of the applications of electrochemical (EC) analysis in occupational and environmental health. This article is meant to be a thorough, but not necessarily exhaustive, review of the subject. Analytical methodology is a crucial component of industrial hygiene, because it is necessary to have the ability to detect and measure a wide variety of contaminants in the workplace, often at very low levels. The analytical challenges in the occupational health field are wide-ranging. The goal of the analysis can range from preliminary field screening, which is qualitative, to exposure assessments, epidemilogic investigations, control technology studies, etc., which require quantitative measurement of target toxic substances. Also, biological monitoring of suspected toxins is frequently necessary. A large variety of sample matrices must be dealt with, and sampling and analytical methodologies are many [1]. Examples of sample matrices that the industrial hygienist may need to consider include airborne particulates, soils, settled dusts, bioaerosols, fumes, etc. Methods used for biomonitoring purposes must be capable of performing analyses in blood, urine, sweat, and other body fluids. Health professionals in the occupational hygiene arena must rely on analytical information from the workplace environment as well as biological analyses. The main focus of this review will be on the electroanalytical techniques that may be used to analyze specific analytes following sample collection, with an emphasis on applications in occupational health.

Electroanalytical techniques have been used extensively in environmental analysis, and EC methodology for use in the environmental sciences is undergoing continued development and expansion [2]. Industrial hygiene chemistry may be viewed as a subdiscipline of environmental analytical chemistry, where the environment of concern is the workplace. While the focus of this article is on electroanalytical applications in occupational health and safety, applications in environmental health are also cited. Numerous electroanalytical methodologies have been used for industrial hygiene purposes, e.g., voltammetry, polarography, amperometry, potentiometry, etc. However, the use of EC techniques in industrial hygiene and related fields has not been extremely widespread. This may be due largely to a lack of familiarity (on the part of industrial hygienists) with modern EC methods of analysis. In addition, many potential applications may be forthcoming in light of new advances in electroanalytical chemistry, such as ultramicroelectrodes [3], chemically modified surfaces [4], and electrochemical immunoassay [5].

Electroanalytical methods offer several advantages for industrial hygiene purposes. Portability of analytical in-

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strumentation is an important attribute, because it is often the desire of the industrial hygienist to monitor pollutants on-site. Electrochemical techniques such as potentiometry, voltammetry, amperometry, and coulometry are readily made portable. Also, electroanalytical methods offer extremely low detection limits and large dynamic ranges for many toxins of concern. Another advantage of electroanalytical methods is that relatively little in the way of solvents and reagents is required to conduct analyses when compared to many other analytical methods. Also, the relative ease of use of electroanalytical techniques such as amperometry, potentiometry, or stripping voltammetry is a decided attribute, especially for applications in the field (i.e., on-site in the workplace).

Numerous commercial electroanalytical devices are available for a variety of analytes. For example, portable coulometric and potentiometric instruments are commercially available for measurements of a host of airborne pollutants [6]. Apart from field-portable devices, electroanalytical techniques have been used extensively in the laboratory as well. However, the use of laboratory-based EC methods for industrial hygiene samples is currently limited to relatively few analytes and source matrices. Certainly, there are numerous possibilities for expanded use of electroanalytical methods.

The purpose of this review is to provide some historical background on the use of EC techniques in industrial hygiene, and also to point out where new developments in electroanalytical methodology have led to new applications. Indeed, recent developments in chemical sensors and biosensors have resulted in significant advances in biological, environmental, process, and atmospheric electroanalysis [7–9]. Extensions of these novel applications to the industrial hygiene field should be forthcoming in the near future. However, there is a need to communicate these advances in electroanalytical methodology to industrial hygienists, physicians, chemists, and other professionals involved in various aspects of occupational and environmental health. Furthermore, it is important to make the electroanalytical chemist aware of potential applications of new technology in the occupational health arena.

General Overview

Electroanalytical methods in the occupational and environmental health fields have been used primarily for inorganic analysis, but EC measurements of organic and organometallic species have also been well represented [10]. In the bioanalytical area, the principal electroanalytical applications (for industrial hygiene and related purposes) have been in measurements of elements, usually heavy metals, in biological matrices. Virtually all common EC methodologies have been used for analyses of samples collected from workplace air [11]. Generally, voltammetric methods give better detection limits than potentiometric methods, but potentiometric instruments are usually easier to use and more readily made portable in comparison to voltammetric instruments. Laboratory-based methods in which a separation or preconcentra-

tion is accomplished prior to detection via EC means have also been used for some analytes. Examples of these techniques include high-performance liquid chromatography (HPLC) and flow-injection analysis (FIA) with EC detection (HPLC-EC and FIA-EC) [12].

Portable gas sensors (which are often potentiometric devices) are available for a large number of airborne inorganic species [6,13,14]; they are used frequently by industrial hygienists for workplace monitoring. Ion-selective electrodes have proven to be extremely useful in the construction of portable analytical devices for both ambient and source measurements of airborne contaminants [15]; these electrodes often form the basis of portable gas analyzers used for field industrial-hygiene measurements. Amperometric gas sensors have also been greatly used, and their use in environmental, industrial hygiene, and other applications has been reviewed recently [16].

There is increasing emphasis on the need to conduct analyses rapidly in the workplace, and electroanalytical devices afford a means to perform on-site measurements of many chemical species. However, it is not always possible to perform field analyses near the action level of the target analyte, especially if the detection limit of the instrument is above the action level. An "action level" is the concentration level of a target analyte in a given matrix above which some "action" must be taken, e.g., removal of employees from the worksite, implementation of control technologies, wearing of protective gear and clothing, etc. Examples of action levels used in the occupational and environmental health fields include National Institute for Occupational Safety and Health (NIOSH) "recommended exposure levels" (RELs) and Occupational Safety and Health Administration (OSHA) "permissible exposure levels" (PELs). In cases where it is not possible to conduct field measurements at concentrations below the action level of the target analyte, laboratory analysis of collected samples must be performed. Laboratory analyses, which are usually more accurate, more precise, more sensitive, and generally offer lower detection limits than field-portable analyses, are more time-consuming and require a higher level of technical expertise. Yet, the performance of field-portable electroanalytical instruments is improving to such an extent that, for many analytes, the necessity to obtain samples for laboratory analysis is decreasing in frequency.

Regarding electroanalytical devices, in cases where potentiometric methods may be used for field-screening purposes, voltammetric methods could potentially be used for on-site quantitative determinations. Also, there is more emphasis on the ability to conduct on-site multielement analysis. Electrochemical array sensors offer tremendous potential for multispecies analysis in the environment [17–20]. Furthermore, techniques such as anodic stripping voltammetry (ASV) not only can allow for trace element analysis but can provide speciation information as well (in some matrices) [21–23].

Extremely important issues that the analyst must consider are sample collection and preparation of in-

dustrial hygiene (and related) samples. While it is not within the scope of this article to exhaustively discuss sample collection and preparation, it is important to point out that these factors must be kept in mind at all stages of any analysis. For electroanalytical measurements, it is almost always necessary to solubilize the analyte of interest in a suitable solvent. This requirement can have a significant influence on the analytical strategy that is used. The large number of sample matrices which is encountered in the occupational and environmental health fields has already been mentioned. Appropriate sample size is also a crucial criterion. Types of sampling devices are many, including filters, impingers, sorbent tubes, wipes, syringes, etc. Sample preparation can require pretreatment, digestion or leaching, derivatization, and so on. For more specific information on sampling and sample preparation in occupational health and related subjects, a number of texts are available [1,11,24–32].

APPLICATIONS

Heavy Metal Analysis

Electrochemical analysis of heavy metals has been used extensively for occupational health and related applications. The most commonly used method for such applications is ASV [33,34]. Other techniques that have been applied to the analysis of heavy metals in samples that are of interest in industrial hygiene and related subjects include potentiometric and cathodic stripping [35], polarography [36], and other common electroanalytical methods. In this section, a compendium of studies are outlined in which electroanalytical techniques have been used in the occupational health and related fields to analyze heavy metals in nonbiological matrices. Heavy metal analysis in biological samples will be covered in a separate section on bioelectrochemistry.

Heavy Metals in Air. Electroanalytical methods for heavy metals in airborne particulates (e.g., fumes, dusts, mists, etc.) have been available for many years. Not surprisingly, conventional polarography was used for early investigations [37–39]. The use of EC methods for heavy metal analysis in air samples has not been exceedingly widespread. Atomic spectroscopic techniques (i.e., atomic absorption (AA) and atomic emission spectroscopy) have generally been favored over electroanalytical methods, since the spectroscopic methods are believed to be more user-friendly, and they also offer high sample throughput rates. A method for lead and cadmium in air based on ASV, developed by NIOSH researchers, was published in 1977 [40]. However, this method did not appear in the 1984 version of the *NIOSH Manual of Analytical Methods* (NMAM) [41], having been substituted by atomic spectrometric methods.

The general strategy for collection and EC analysis of airborne heavy metals must be considered. To perform a voltammetric or polarographic analysis of heavy metal species that may be present in air, particulate matter is first collected from air on a filter or other suitable collection device. For industrial hygiene applications, the filter of choice is usually a membrane with a small enough pore size so that no particulates pass through the membrane. The filter is placed in a cassette, and air is drawn through the filter at a predetermined flow rate. After sampling for a given period of time, the filter, which now contains trapped particulate, is digested in a strong acid mixture at elevated temperatures. The acid mixture, temperature, and duration of digestion may vary, depending on the principal metal(s) of interest. Following digestion, during which time the heavy metal element(s) of concern is/are extracted (solubilized), the acidic mixture is diluted with a buffer solution. Subsequently, the EC analysis is performed on this diluted, buffered solution. Electrodes that are most commonly used for voltammetric analysis of heavy metals include hanging mercury drop electrodes (HMDEs) and mercury film electrodes (MFEs), the latter of which are usually deposited on glassy carbon substrates. Polarographic analysis is, of course, conducted using a dropping mercury electrode (DME).

In an early industrial hygiene application, polarography was used for the determination of antimony, cadmium, cobalt, copper, manganese, nickel, lead, and other heavy metals in air [39]. This work was based in part on earlier investigations that were specific to certain metals such as chromium [38], lead [37,42], and thallium [43]. Since that time, detection limits for heavy metals have been improved significantly through the use of ASV, which was first applied to air samples in the mid-1960s [44]. Anodic stripping voltammetry of heavy metals in air samples has been conducted at both MFEs [44,45] and HMDEs [46] for many years, with applications in both environmental analysis and industrial hygiene. In general, detection limits are lower at MFEs versus HMDEs, but MFEs are more susceptible to electrode fouling and intermetallic effects than are HMDEs [34].

Detection limits for heavy metals by using ASV are generally in the range 10^{-8} to 10^{-10} M [35], allowing for trace element determinations in a variety of sample types, including air. Under optimum conditions, the ASV method is capable of measuring picogram quantities of a number of heavy metals [47]. Two decades ago, a study was conducted in which ASV was used to monitor cadmium, copper, lead, and zinc in airborne particulate matter; the results compared favorably with those from AA analyses [48].

An advantage that ASV offers over AA is the ability to conduct multielement trace analysis. Twenty years ago, ASV was used to monitor the temporal dependence of cadmium, copper, and lead concentrations in urban air [49]. Relative standard deviations (RSDs) for these metals ranged from 3 to 6%, and it was possible to analyze samples containing only a few nanograms of metal. Other ASV heavy metal analyses of atmospheric aerosols have appeared [50,51]. While these studies [49–51] focused primarily on air pollution monitoring, the potential application of ASV to industrial hygiene is apparent. An earlier application of ASV for industrial hygiene purposes was represented by the early NIOSH method for lead

and cadmium in workplace air [40], which remains a viable method for trace analysis of these two metals in occupational settings.

For several metals, simultaneous determination of trace levels by ASV is fraught with inherent limitations. For instance, a difficulty arises in efforts to determine thallium concurrently with lead and other heavy metals by ASV [52], because the thallium stripping peak overlaps with those of the other metals, especially lead. Additional problems have been noted in simultaneous ASV determinations of copper and zinc (especially in MFEs), due to the formation of intermetallic species between these two metals [53]. Other intermetallic compounds are known that can cause difficulties in the simultaneous measurement of certain metals after EC preconcentration [54]. In cases where intermetallic compounds are problematic, preferential deposition of only the metal species of interest may be accomplished.

More recently, the advent of pulse voltammetric techniques [55] has improved both precision and detection limits of electroanalytical methods. Differential-pulse anodic stripping voltammetry (DPASV) has, therefore, become a popular technique for trace metal analysis, and applications of DPASV to the analysis of heavy metals in air have appeared [56,57]. Pulse methods are used in order to subtract out the effects of background charging currents from the faradaic component of interest. Pulse voltammetric methods are recognized as being key to providing increased sensitivity while minimizing interferences from peak overlap, background currents, and other influences [55].

In one study in which DPASV was used for the analysis of airborne particulate samples, a novel EC cell was constructed that required no preliminary treatment of the air filter sample [56]. The heavy metals of interest (i.e., copper and lead) were extracted from atmospheric dust collected on the filter by a complexing agent, and the metals were then determined selectively by DPASV according to their chemical form. It was discovered that copper impurities were introduced during digestion of the filter media (used to collect air samples), leading to irreproducible results for this metal. Also, it was found that lead halide species were determined by DPASV using the extraction technique, while lead oxides were not.

In a separate study using pulse voltammetry, a small-volume electrolysis cell was used for the simultaneous determination of cadmium, copper, lead, and zinc in atmospheric aerosols [57]. A mixed stripping technique (differential pulse-alternating current-differential pulse, or DP-AC-DP) for potential scanning was used in an effort to minimize effects caused by the formation of intermetallic species. Analytical performance criteria were found to be comparable to those obtained by DPASV. In other work, differential pulse polarography (DPP) was used to determine trace heavy metals in air particulates [58]. Conditions were optimized to allow the simultaneous determination of cadmium, copper, lead, titanium, and zinc in air. In another investigation, both DPASV and DPP were used in strategies to measure trace levels

of thallium in the presence of other heavy metals and other potential interferences [59].

Differential pulse techniques form the basis for two methods, published by OSHA, that may be used for the determination of certain heavy metal species in workplace atmospheres. Differential pulse polarography is used by OSHA for the measurement of hexavalent chromium in air [60]. The OSHA method is based on earlier polarographic studies involving this chromium species [38,39] and offers increased sensitivity (while minimizing interferences) when compared with colorimetric methods [61]. A preliminary OSHA method for soluble uranium in workplace atmospheres is based on differential pulse cathodic stripping voltammetry (DPCS) [62]. The method was developed from a published electroanalytical protocol for uranium determination in plutonium-238 metal and oxide [63]. The electroanalytical method for uranium is viewed as an advantage over neutron activation analysis of this element [64], which is much more time-consuming and expensive, and requires special facilities (i.e., a nuclear reactor).

Although rather uncommon, potentiometric techniques may be used to determine certain heavy metals in airborne particulate samples. Voltammetric methods are generally more sensitive for any given element, but potentiometry may offer advantages in special cases. For example, potentiometric stripping has been used to determine mercury in air, using a computerized flow system [65]. Anodic stripping of mercury can be performed using gold substrate electrodes [66], but high background currents and other influences (arising mainly from impurities and intermetallic effects) have caused problems when ASV is applied to mercury determination. The potentiometric stripping method for mercury, when applied to the analysis of flue gas samples, was found to perform comparably to cold-vapor atomic absorption spectrometry (AAS) [65]. The detection limit was reportedly 0.2 μg m^{-3}, which is about 100 times higher than background atmospheric mercury concentrations.

Heavy Metals in Other Matrices. As a result of many successes, electroanalytical techniques have become widely used for the analysis of other environmental samples (besides air), which may also be of interest in the industrial hygiene/environmental arena. For instance, aside from applications of differential pulse techniques to air particulates already mentioned, the methodology has also been used to determine trace heavy metals in soils [67], natural waters [68,69], and other environmental samples [2,17–23]. Voltammetric investigations of transition metals in natural waters have demonstrated the ability to automate such techniques as stripping voltammetry [68]. Furthermore, stripping voltammetry of trace metals in water was found to compare favorably with results (i.e., detection limit, dynamic range, and precision) from graphite furnace AA spectrometry [68]. Other recent studies in natural waters have illustrated the portability of voltammetric techniques for the in situ measurement of trace metals, while maintaining excellent analytical performance [69]. Potentiometric stripping has

been applied to the analysis of heavy metals (e.g., cadmium, copper, lead, zinc, etc [70,71]), but applications to industrial hygiene, per se, have not been realized extensively to date.

The effects of dissolved oxygen and background electrolyte in stripping voltammetry have been well documented [35,72,73], and much work has been performed in efforts to reduce these contributions to the measured current. Square wave voltammetry is one method that has been used to reduce the effects of background currents in electroanalytical chemistry [74]. The technique also offers other advantages such as enhanced speed of analysis and improved detection limits [74]. Square wave anodic stripping voltammetry (SWASV) has been used successfully for the determination of trace lead and cadmium in untreated water samples at MFEs [75] and mercury-coated microelectrodes [76]. No deaeration of dissolved oxygen was required, even though the water samples were air-saturated. The SWASV results were found to agree very well with results obtained by electrothermal AAS, with detection limits of 5×10^{-10} M for each metal. The attributes of SWASV may prove to be extremely beneficial for industrial hygiene and environmental purposes, because on-site EC trace analyses can be made possible with this technique.

Chemically modified electrodes (CMEs) have been used extensively for electroanalytical studies of heavy metals [4,77]. The CMEs were shown to prevent electrode fouling due to the presence of organic surfactants, which are frequent interferents in environmental samples. Another advantage of CMEs is improved selectivity for the analyte species of interest. For example, MFEs coated with cellulose acetate [78] and poly(ester-sulfonic acid) [79] have been shown to provide very good detection limits for several heavy metals, which were determined by ASV. The CMEs also provided high selectivity while preventing electrode fouling from deliberately introduced organic surfactants [78,79]. In other work, CMEs containing crown ethers and cryptand ligands were used for DPV of lead and other metals [80]. In another study, hexavalent chromium oxyanions were determined selectively by linear sweep voltammetry at a platinum electrode modified with poly(3-methylthiophene) [81]. Numerous other investigations of CMEs for heavy metal analysis have been reported [4,7,9,77]; an exhaustive listing of pertinent references is outside the scope of this review. The few examples cited here demonstrate the use of CMEs for the determination of trace heavy metals and show promise for the potential applications of this technology in industrial hygiene analytical chemistry.

Ultramicroelectrodes, i.e., electrodes with a characteristic diameter of approximately 0.1 to 25 μm, demonstrate promise for electroanalytical applications in industrial hygiene and environmental analysis. Ultramicroelectrodes offer several analytical advantages over electrodes of conventional size [3]. Extremely small electrodes demonstrate much faster mass transport properties than do larger electrodes and also exhibit much lower ohmic drop at the electrode/solution interface [3,82].

These physical attributes lead to lower detection limits than can be achieved at larger electrodes, as well as the ability to conduct EC measurements in solutions containing no purposely added supporting electrolyte. Miniaturization of the electrode also enables experiments to be carried out in a minimal sample volume, e.g., a few microliters. Thus far, studies concerning the use of ultramicroelectrodes for heavy metals analysis have been limited mainly to water samples [17,18,83–85]. In one investigation, mercury-coated carbon fiber and platinum wire ultramicroelectrodes were used for ASV of lead and cadmium [83]. A subtractive technique, used previously for FIA of heavy metals with ASV detection [86], was used to eliminate the need for deoxygenation of sample solutions [83]. The detection limit was reportedly 5×10^{-9} M for a preconcentration time of only 10 seconds. Anodic stripping voltammetry at MFEs of conventional size requires preconcentration times in excess of 5 minutes to achieve this level of sensitivity. It is clear, then, that ultramicroelectrodes permit very fast, yet highly sensitive, analyses to be conducted.

Mercury-coated iridium ultramicroelectrodes have been used for the in situ determination of trace heavy metals in natural waters, using a portable voltammetric probe [84,85]. In other studies, multielement microelectrode arrays have been developed that can be used as field-portable sensors for a variety of analytes, including heavy metals [17,18]. Ultramicroelectrodes have not yet been used for heavy metals analysis of industrial hygiene samples, but the potential for such an application is readily apparent.

Other strategies have been used in efforts to improve the analytical performance of heavy metals electroanalysis. Increased sample throughput has been realized by batch-injection stripping voltammetry [87] and expert systems for voltammetric measurements [88,89] of trace metals. Screen-printed electrodes [90] and carbon-foam composite electrodes [91] for stripping analysis demonstrate a great deal of promise for field as well as centralized applications. Potentiometric stripping has been used for heavy metals analysis in several environmental samples [90–94]. Voltammetry following nonelectrolytic preconcentration may improve selectivity and detection limits [95]. The recent advances in electroanalytical chemistry bode well for industrial hygiene investigations of heavy metals and other analytes.

Analysis of Other Inorganics

A number of inorganic species (not including heavy metals) may be present in hazardous concentrations in workplace air. Electroanalytical methods for the determination of these species in the work environment are well represented. Most of the common EC techniques have been used, although the predominant electroanalytical method for industrial hygiene monitoring of airborne inorganics is potentiometry. Field-portable electroanalytical devices, which are usually based on ion-selective electrodes, are available commercially for a variety of analytes. For a number of inorganic species of

concern that may be encountered in workplace air, electroanalytical measurement devices are competitive with other analytical probes based on chemiluminescence, spectrophotometry, conductimetry, etc. In this ~ection, the use of EC methods for the analysis of inorganic species is reviewed, with an emphasis on applications in the occupational health field.

Halides in Air.   Airborne halide ions and their acids may pose potential health problems and can exist in various forms, such as particulate or gaseous. Halide species are usually measured potentiometrically by means of ion-selective electrodes. In general. the halide analyte is first trapped on an impregnated filter through which air is drawn. The halide species is then extracted from the filter medium, dissolved in solution, and analyzed by an ion-specific electrode (ISE). Knowledge of the volume of air sampled enables quantitative determination of the airborne halide concentration. Higher detection limits of the potentiometric techniques (compared to voltammetric methods) may often necessitate greater sampling volumes of workplace air.

Fluoride is commonly measured in numerous environmental matrices by means of the fluoride ion-selective electrode [96,97]. A NIOSH analytical method for fluoride in aerosol and gas, which is based on measurement by an ISE, is available [98,99]. Fluoride is first collected on a treated (if gaseous F^- is of interest) or untreated (if particulate F^- is the desired analyte) cellulose ester membrane filter by using a personal sampling pump. (A personal sampling pump is a battery-powered, portable air sampling pump that is attached to the body of a worker.) The filter is then wet-ashed in alkaline solution, and fluoride-determined by use of the fluoride ISE. The detection limit of the method is 0.003 mg F^- per sample, and the working range is 0.03 to 1.2 mg [98]. An ASTM standard method for fluorides in air, which is based on the same sample collection and analytical procedure as that outlined in the NIOSH method [98], is also available [100]. An interlaboratory comparison yielded a pooled RSD of 16.0% for the ASTM method. The collection recoveries for gaseous F^- standard samples (99.1%) were found to be greater than those for particulate standards (78.2%) [100]. The detection limits and quantitation limits of the F^- ISE for the measurement of this species in air are low enough to accommodate the action levels (i.e., OSHA PELs and NIOSH RELs) related to existing workplace exposure limits [98].

An ISE method for F^- and HF in air, in which the sample is collected in an impinger, was published [101]; the detection limit is similar to that for the filter collection method [98]. A continuous-flow method for fluoride with ISE detection was described for the analysis of air pollution samples [102]. The precision is 5% for F^- concentrations between 0.5 and 100 mg/L. Ion chromatographic and potentiometric (ISE) techniques for the determination of airborne fluoride were compared, and the detection limits of the two techniques were found to be similar [103]. The use of the fluoride ISE can allow for on-site measurements, although the collected fluoride

species must first be extracted (as F^-) from the sample collection medium. The F^- ISE is subject to potential interferences such as Fe^{3+}, Si^{4+}, and Al^{3+}.

A NIOSH method for airborne chloride, in which atmospheric Cl^- is collected by an impinger, uses a chloride ISE [104]. The detection limit of the Cl^- ISE for air samples is 18 $\mu g/m^3$ [105], and the precision of the analytical measurement is very good (coefficient of variation (CV) = 0.02) [104]. The greatest interference is due to sulfide. The Cl^- ISE has been used for the determination of HCl in humid air [106], and it has also been applied in instances where alternative sample collection procedures were used [107]. A new type of chloride ISE, in which a solid membrane ISE is prepared by ion implantation [108], shows significant promise for potential applications in field measurements.

An iodide ISE forms the basis of a NIOSH method for the analysis of iodine in air samples [109]. Airborne I_2 from an industrial site is first collected on a pretreated solid sorbent tube and is subsequently desorbed with sodium carbonate prior to measurement with the I^- ISE [110]. The detection limit of the NIOSH method is 0.001 mg I_2 per sample, the range is 0.008 to 0.2 mg, and the RSD of the method is better than ±10% [109]. Lower detection limits for iodide and iodine may be achieved by using ion chromatography with EC detection [111].

Portable, battery-powered, handheld coulometric and amperometric devices are available commercially for the detection and monitoring of gases such as F_2, Cl_2, and I_2 [6]. Often, such devices are rather nonspecific, but they are nonetheless useful for workplace monitoring, because they may respond to strong oxidant vapors in low, albeit hazardous, air concentrations. Portable electroanalytical monitoring devices that are specific for certain analytes are also available; these usually use a prefilter of some sort in order to trap potential interferents and large particles. The analyte species, i.e., F_2, Cl_2, and/or I_2, are allowed to pass on to the electrode surface, where they may then be reduced electrochemically to give a measurable current.

Other Airborne Inorganic Species.   Inorganic molecules and ions, such as ammonia, hydrogen peroxide, hydrazines, nitrogen oxides, sulfur dioxide, cyanide, carbon monoxide, etc., may exist in toxic concentrations in many workplace environments. Electroanalytical methods for these species include mainly potentiometry, polarography, coulometry, and amperometry. The operation principles of electroanalytical gas sensors have been described thoroughly in a recent text [112]. Highly sophisticated, portable EC measurement devices are available commercially for a number of analytes such as CO, SO_2, NO_x, and O_2. The portable devices may be battery powered, are usually handheld, and may include numerous special features such as audible alarms and battery strength indicators. The development of EC sensors for inorganic gases and vapors is currently a very active area of research.

Oxygen in workplace air can be readily measured in the field by portable direct-reading EC sensors. Solid-

state potentiometric devices for sensing gaseous oxygen have been reviewed [113], and many commercial devices are available [6]. A solid O^{2-} conducting electrolyte, which is sandwiched between two metal electrodes, will develop a gradient due to the difference in O_2 concentration between a reference gas (either pure O_2 or air) and the air being sampled. This concentration gradient results in a measurable electromotive force, enabling the concentration of oxygen in the sampled air to be determined. A NIOSH method for measuring O_2 in occupational settings, based on this technology, has been published [114]. Unlike many sample collection protocols in which a personal sampling pump is needed to obtain air samples from worksites, the portable direct-reading O_2 monitor gives a response to oxygen that diffuses to the sensor surface. The response time is on the order of a few seconds, and the calibration plot is linear from 0.1 to 25% O_2 (in N_2) [114]. No biases or interferences have been identified, and the precision is reportedly better than ±10% (RSD).

Battery-powered electroanalytical O_2 gas sensors are routinely used by industrial hygienists in order to monitor concentrations of this gas in worksites where oxygen depletion is a common problem. Some commercial instruments are equipped with alarms that are triggered when the oxygen concentration falls below a safe level. Portable electroanalytical monitors for ozone are also available [6], but these tend to be nonspecific. Portable potentiometric O_2 monitors have completely replaced "polarographic" (amperometric, really) oxygen sensors, which were formerly used for workplace air monitoring [115]. The so-called polarographic devices are based on the well-known Clark electrode, which is an amperometric membrane-based O_2 sensor [112]. Due mainly to slow response times, the Clark electrode has fallen into disfavor for on-site monitoring, owing to low permeation rates of oxygen through the membrane.

Carbon monoxide (CO) is another gaseous analyte for which portable EC sensors are available commercially [6]. Many of the commercial portable CO monitors are equipped with alarms that inform the user of hazardous concentrations of this lethal gas. Direct-reading EC CO sensors are frequently based on potentiometric, coulometric, or amperometric detection. In the NIOSH method for CO [116], gas bag samples are collected at low flow rates by means of a personal sampling pump, and the CO content is then determined by EC analysis. Because gas bag sampling is required, area samples are obtained to assess the potential CO hazard. The method was recently updated to allow direct measurements of CO concentrations via a portable EC monitor [117]. In this way, CO that diffuses to the surface of the sensor can be measured, precluding the need for sampling pumps. The applicable range of CO concentration is 5 to 120 ppm, with a very low CV (<1.5%) [117]. Several commercial devices reportedly extend the upper limit of the concentration range to over 1000 ppm of CO [6]. Interferences from other gases such as NO, NO_2, and SO_2 can bias the CO measurement [116].

A wide variety of CO EC monitors were developed and evaluated. In early work, polarographic (amperometric, actually) monitors for this poison were developed that used permeable metallized membranes to allow for diffusion of CO to the electrode surface [115,118]. Oxidation of CO at the electrode enables measurement of the resulting current [119]. Solid polymer electrolytes also have been used in the development of potentiometric gas measuring systems for CO and oxides of nitrogen [120]. These devices reportedly provide for better specificity than could be attained with earlier technology. An alternative method for improving the specificity of EC CO gas sensors has been proposed [121]. In this work, a portable gas chromatograph was used to separate CO from other gases, and the CO was then detected electrochemically. Portable instruments for CO that use "dynamic coulometry" have been devised and studied [122]. The technique involves the use of two amperometric gas sensors connected in series, and comparisons were made between several commercial devices using a theoretical treatment for this type of device [123].

Electroanalytical methods for oxides of nitrogen have been applied to industrial hygiene monitoring. Continuous NO and NO_2 monitors based on coulometric detection have been available for years [124]. In an early investigation, commercially available amperometric, coulometric, and chemiluminescent NO_2 sensors were compared [125]. The performances of the three sensing devices compared very favorably over a concentration range of 0 to 700 μg NO_2/m^3. In other work, DPP was used for the simultaneous determination of SO_2, NO, and NO_2 in air [126]. Detection limits for SO_2 (7 $\mu L/m^3$) were lower than those for nitric oxide species (50 $\mu L/m^3$). In a more recent study, high and low surface-area EC NO_2 gas sensors were used in order to elucidate the mechanism of the response of amperometric gas sensors [127]. In a separate study, NO_2 in ambient air was analyzed by ion-exclusion chromatography with EC detection [128]. NO_2 was trapped on a cartridge coated with sodium hydroxide, and the resulting NO_2^- species was determined amperometrically. This procedure gave better than part-per-billion sensitivity for NO_2 in air with ~0.3 L of sample [128], which was claimed to be a significant improvement in sensitivity over previous methods. A number of portable EC air-monitoring devices for NO_x species are commercially available for use in industrial hygiene and ambient air measurements [6].

Another analyte for which commercial air-monitoring instruments have been available for many years is sulfur dioxide. In an early investigation, a comparison was made between conductimetric, colorimetric, and coulometric analyzers for SO_2 in air [129]. The operation of EC devices for sulfur dioxide is based upon the oxidation of dissolved SO_2 to sulfuric acid [6]. Airborne sulfur dioxide is captured in solution by a bubbler or similar equipment, and the dissolved SO_2 is subsequently oxidized to yield a measurable current. The current is integrated to give the measured charge, which is proportional to the original SO_2 concentration. Early coulometric devices were found to perform well, in general,

but suffered from interferences such as H_2S and NO_2 [129]. Nevertheless, since coulometric analyzers have been developed, which are easily portable and give rapid response times, efforts to eliminate interferences have improved their performance. For example, filters have been used in SO_2 coulometric air sensors in order to improve selectivity [130]. Also, coulometric titration with bromine [130] or iodine [131] helps to diminish interferences from organic substances and allows for continuous monitoring of sulfur dioxide in air.

Differential pulse polarography has been applied to the determination of atmospheric SO_2 [132]. In the DPP method, the sampled gas is drawn through a bubbler containing dimethyl sulfoxide (and an appropriate electrolyte), and the extracted SO_2 is subsequently determined by cathodic reduction. The detection limit of the technique was reportedly 0.1 ppm [132], but much lower concentrations are probably accessible by DPP analysis with today's technology. In a novel application, a pneumatoamperometric device for the determination of SO_2 in air at the part-per-billion level is described [133]. The basis of operation involves gas extraction of the analyte into an aerosol, which transfers a large volume of airborne SO_2 into a small volume of solution. The resulting HSO_3^- and SO_3^{2-} species in solution are then determined amperometrically [133]. By using this enrichment, or preconcentration, technique, it was possible to obtain a detection limit for sulfur dioxide in air of less than 1 $\mu g/m^3$. In other studies, FIA with amperometric detection has been used for SO_2 determination in air samples [134,135]. (Alternatively, "The FIA/EC technique" FIA/EC has not been widely used for monitoring airborne contaminants, but there clearly is room for expansion of this technique in the occupational health and environmental hygiene fields.)

Electroanalytical methods may be used for the determination of various other sulfur-containing species (besides SO_2) in air. Sulfuric acid aerosol may be measured coulometrically (detection limit 0.03 μg H_2SO_4) following collection by impaction or filtration, which provides for separation of the analyte of interest from SO_2 [136]. Hydrogen sulfide can be determined at part-per-billion levels in air by potentiometric titration via a sulfide ISE [137]. In this method, H_2S is trapped in an aqueous solution containing ascorbic acid and sodium hydroxide. The resulting sulfide ion is then titrated at an S^{2-} ISE indicator electrode with a standard cadmium sulfate solution [137]. A similar potentiometric technique, in which a cadmium sulfide membrane electrode was used, has been applied to the determination of sulfur in other matrices such as natural waters, chemicals, metal ores and alloys, and fly ash [138]. Sulfide in air has also been determined by indirect potentiometric titration with a cadmium ISE [139]. The Occupational Safety and Health Administration has released a DPP method for hydrogen sulfide in workplace air [140]. In the OSHA method, air samples are collected (via a personal sampling pump) onto a filter that is impregnated with silver nitrate. In this manner, H_2S is converted to Ag_2S, which is subsequently dissolved in alkaline cyanide solution. The lib-

erated sulfide ion may then be analyzed by DPP, which yields a limit of quantitation (LOQ) of about 1 ppm and an RSD of better than ±4% [140]. Apart from these advantages of high sensitivity and low-percent error, the analytical protocol allows for the use of a much simpler sampling device than that required for a colorimetric analysis [141]. In other work, particulate sulfur in air has been analyzed by coulometric titration of SO_2 following pyrolysis at 1000°C [142].

According to an interim OSHA analytical method, hydrogen peroxide in workplace atmospheres may be determined by DPP after sampling with a midget bubbler that contains solubilized $TiOSO_4$ [143]. This reagent is reportedly highly specific for H_2O_2, and the method offers better sensitivity and has fewer interferences compared to the earlier OSHA method based on a colorimetric procedure [144]. The OSHA DPP procedure for H_2O_2 is based on a published method for the analysis of trace hydrogen peroxide in water [145] and yields an LOQ of 0.10 ppm and excellent precision (RSD <3%).

Dilute hydrogen gas (0.1 to 1.0%) can be detected in air using a solid-state EC device [146]. The H_2 sensor operates potentiometrically at open circuit, and the measured potential difference is a function of the oxidation of H_2 at one Pt electrode in concert with O_2 reduction at another Pt electrode. The device was also shown to be a useful humidity meter.

Ammonia in air may be determined by potentiometric analysis [147,148]. A method has been described in which ammonia is captured by a diffusion/denuder tube and is thereafter analyzed by an ammonia probe [147]. In the NIOSH method, ammonia is collected onto silica gel that is treated with sulfuric acid [148]. Ammonia is subsequently desorbed in 0.1 M H_2SO_2, diluted with deionized water, and made basic with 10 M NaOH before being analyzed by an ammonia ISE. The range of the method is rather narrow (17 to 68 mg/m^3), and the precision is ±6% RSD [148]. The upper limit of the range is limited due to breakthrough problems with the sampling method.

Cyanides are used extensively in the mining and plating industries, and represent a potential hazard to workers. CN^- in air may be converted to HCN in humid environments, so methods for both cyanide species are needed. Airborne cyanide can be determined by using an ISE following collection in an impinger [149]. An alternative potentiometric method for cyanides [150] calls for collection with a filter/bubbler system. After sample collection, cyanide is extracted and analyzed with a CN^- ISE [150]. The range of the method is 0.05 to 2.0 mg cyanide with a CV of about 4%. As the cyanide ISE is largely comprised of silver metal, interferences from sulfide, halides, and several metals may be problematic. Also, since the method is nonspecific for HCN or CN^- [150], it may be used to measure total cyanides. In recent work, polymer-modified electrode gas sensors, into which metal clusters are incorporated, have been devised for the detection of gaseous hydrogen cyanide in the concentration range 0.13 to 20 ppm [151]. The interaction of the gas with the metal-intercalated polymer layer induces a

change in the work function of the layer, which can then be measured by a Kelvin probe [152]. This technology shows potential for applications in the analysis of other inorganic, as well as organic, vapors.

In a very recent study, a coulometric method for the determination of hydrazines at part-per-billion concentration levels was reported [153]. A coulometric titration was used in conjunction with impingers to measure the amount of hydrazine and monomethylhydrazine in air. Following collection in an impinger, the hydrazine was titrated coulometrically with bromine. The dynamic range was reportedly 25 to 2500 ng for 10 L air samples, with an RSD of 2% at higher analyte concentrations.

Analysis of Organics

A wide variety of organic toxins may exist in the workplace air of many industrial environments. Airborne aldehydes, isocyanates, halogenated hydrocarbons, and other carbon compounds may pose potential hazards in numerous occupational settings, and methods for monitoring these compounds are required. Also, novel sample collection and extraction techniques are often needed in order to preserve the integrity of the sample and ensure good recoveries. Various electroanalytical methods, some of which are field portable, are available for a number of organic species that are of concern to the industrial hygienist.

Airborne Aldehydes. Polarography has been applied to the analysis of aldehydes in a variety of samples for several decades [154]. By using polarographic techniques, it is often possible to resolve current peaks arising from different aldehydes (e.g., formaldehyde and acetaldehyde). Portable polarographs were developed some years ago for workplace air monitoring of airborne aldehydes [155]. A polarographic method for formaldehyde was used by OSHA for a number of years [156] but has recently been replaced by alternative techniques. A review of industrial hygiene sampling and analytical methods (including EC) for formaldehyde is available [157].

In the OSHA polarographic method for formaldehyde [156,158], a known volume of air is drawn through a bubbler containing 10% methanol in water. The captured formaldehyde is reacted with hydrazine to form the hydrazone of formaldehyde. An aliquot of the reacted sample is then determined by DPP [158]. The method is purportedly selective for formaldehyde, because the formaldehyde-hydrazone half-wave potential $(E_{1/2})$ differs sufficiently from $E_{1/2}$ values for other low-molecular weight aldehydes. The detection limit of the method is about 2 μg per sample, which translates to 0.001 ppm for a 30 L air sample [156]. A NIOSH polarographic method for formaldehyde also has been published [159]. The NIOSH collection method is similar to that called for in the OSHA protocol, except that formaldehyde is reacted with Girard T reagent (trimethylammoniohydrazide chloride), which is dissolved in the bubbler. The resulting hydrazone may then be analyzed

by sampled dc polarography [159]. The applicable range of the NIOSH method is reportedly 20 to 220 μg per sample, and the precision is excellent (RSD ~2%). For an 18 L air sample, this converts to a working range of 1 to 10 ppm. A significant advantage of both the NIOSH and OSHA methods is that no sample workup is required prior to analysis. A disadvantage of the NIOSH polarographic method is the potential interference from other aldehydes such as acrolein, crotonaldehyde, and benzaldehyde. Also, bubblers are not generally desirable for personal monitoring, so alternative collection devices (requiring alternative analytical methods such as gas chromatography) are usually preferred for industrial hygiene sampling [157].

Electrochemical methods for the analysis of several other aldehydes have been devised. A DPP method for airborne chloroacetaldehyde, which is a mutagen, has been proposed for industrial hygiene analysis of this compound [160]. In this method, the aldehyde is reacted with semicarbazide in a citrate buffer, and the adduct is then determined by DPP. Unfortunately, formaldehyde is a serious interference [160], so alternative methods are required if the presence of formaldehyde is expected. A NIOSH method for crotonaldehyde has been published [161]. As for formaldehyde, a bubbler collection technique is used to extract crotonaldehyde from workplace air. The aldehyde is derivatized with hydroxylamine (which is dissolved in the bubbler), and the resulting crotonaldehyde oxime is measured by polarography [161]. The performance characteristics of the method are similar to those achievable with polarographic analysis of formaldehyde. However, other volatile aldehydes such as formaldehyde, acrolein, and benzaldehyde may cause significant interference. About 15 years ago, OSHA released a differential pulse polarographic method for acrolein in workplace atmospheres [162]. Unlike the bubbler sampling method, which has been popular for collecting other aldehydes, solid-sorbent sampling tubes are used to trap airborne acrolein (on molecular sieves). The aldehyde is subsequently desorbed in phosphate buffer and analyzed by DPP, which yields a detection limit of 0.01 ppm [162]. An advantage of this technique is that other volatile aldehydes do not interfere with the analysis. However, other substances (containing conjugated double bonds) that have an affinity for molecular sieves may interfere with DPP analysis of acrolein.

Halogenated Hydrocarbons in Air. Many organohalogen compounds, some of which are toxic, are used extensively in industry. Hence, methods are being developed for the detection and monitoring of these compounds in order to help ensure the safety of workers. Nearly 20 years ago, a coulometric technique was evaluated for its use in the determination of over a dozen atmospheric halocarbons [163]. The method involved initial separation of the collected compounds by gas chromatography, followed by EC (coulometric) detection. The technique was found to perform well for compounds that were easily ionized, with detection limits in the part-per-billion range. Species having ionization ef-

ficiencies of 90% or better exhibited an analytical error (RSD) of less than 5%, whereas compounds with lower ionization efficiencies gave poorer precision (e.g., RSD ≈ 25% for ~50% ionization efficiency) [163]. A similar technique was used for the determination of atmospheric dichloroacetylene and a series of other chlorinated hydrocarbons [164].

More recently, an EC sensor has been devised for the detection of Freons and other chlorinated hydrocarbons in air [165]. In this study, Freons and several other electrochemically inactive chlorinated hydrocarbons were detected amperometrically, following pyrolysis at a heated filament. This technique has been applied previously to other electroinactive gaseous species [166,167]. An HF EC sensor was used to detect fluorine-containing hydrocarbons, while an HCl EC detector was selective for chlorinated hydrocarbon species [165]. In other work, a coulometric device was described for the determination of "adsorbable" halocarbon compounds [168]. Quantitative determinations of individual halocarbon vapors are extremely difficult; therefore, techniques developed recently have sought to measure total atmospheric halocarbon content. In a separate investigation, phosgene in air at the sub-part-per-billion level was determined by pulsed flow coulometry [169]. Phosgene is used widely in industry, so it is an important species to consider for industrial hygiene monitoring.

Isocyanates in Air. Exposure to airborne isocyanates can result in a variety of respiratory disorders. Organic isocyanates are used in many commercial products and industries, and methods for monitoring these compounds in occupational settings are needed for worker protection purposes. For example, isocyanates are present in a variety of paints and coatings and, therefore, represent a significant hazard to workers involved in either the production or the use of paint. Methods for the determination of atmospheric isocyanates, including those in which electroanalysis has been used, have been reviewed [170,171]. In earlier work, a method based on high-performance liquid chromatography (HPLC) with EC detection was described for the determination of organic isocyanates in air [172]. In this study, 1-(2-methoxyphenyl)piperazine was used as an electrochemically active derivatizing agent for a series of isocyanates of occupational hygiene interest [172]. In addition, these derivatives absorb strongly in the ultraviolet (UV) region, enabling a combination of EC and UV detection following separation of the derivatized isocyanates by HPLC. Electrochemical (amperometric) detection was found to be significantly more sensitive than UV detection for a series of organic isocyanates [172].

In an effort to measure total isocyanate in air, an HPLC-EC method for organic isocyanate analysis has been combined with UV detection [173]. Based on the EC/UV response ratio, it was deemed possible to identify isocyanate-derived HPLC peaks, which could then be quantified by reference to a monomer standard. This reportedly precluded the need to isolate oligomeric derivatized isocyanates [173], for which no reference standards exist.

A NIOSH method for organic isocyanates, which is a modification of the previously reported method [173], is also based on HPLC separation with EC/UV detection [174]. In this method, samples are collected in an impinger by using a personal sampling pump, and isocyanates are reacted with 1-(2-methoxyphenyl)piperazine to form urea derivatives. Quantitation is allowed by the summation of peak areas that are recognized as being due to derivatized isocyanates. The NIOSH method has been found to perform well for monomeric isocyanate derivatives, but it is not appropriate for the analysis of isocyanate oligomers, as was previously thought [175,176]. The reason for this limitation is that the UV response to derivatized isocyanate dimers and trimers is not proportional to the number of isocyanate groups present [176]. As a proposed solution to the problems in identifying oligomeric isocyanate species, an alternative method has been suggested in which tryptamine is used as a derivatizing agent [177]. Subsequent to HPLC, the detection scheme used involves the ratio of fluorescence intensity to the EC (current) response, which allows accurate identification and quantification of isocyanate species for which no analytical reference standards are available [177]. Other derivatizing agents are being studied as possible solutions to the problems that are encountered in the analysis of oligomeric isocyanate derivatives [176].

Other electroanalytical methods for the analysis of organic isocyanates have been described. In one recent study, UV/EC detection was used in an effort to estimate isocyanate species by reagent loss [178]. It was found that reagent losses increased with the volume of air sampled, thereby biasing the analytical results. In another study, diisocyanate monomers in air were derivatized and determined by DPP [179]. The DPP method offers an alternative to the HPLC methods described earlier. The reported detection limit was 8 $\mu g/m^3$ for a 50 L air sample, which is an order of magnitude below the action level [179]. In other work, gas-phase toluene diisocyanate (TDI) was exposed to water vapor, and several techniques (including EC) were used in an attempt to discern any reaction between TDI and H_2O [180]. No evidence for the reaction of this isocyanate species with water vapor was found.

Other Airborne Organics. A variety of additional organic gases and vapors may be detected and analyzed by electroanalytical means. In efforts to develop responsive solid-state detectors, field-effect transistors (FETs) have been modified with conducting polymers and used as gas sensors [181]. For instance, FETs have been coated with electrochemically generated polypyrrole and used as gas/vapor sensors for alcohols [182,183] and aromatics [184]. This chemically sensitive FET, or CHEMFET, is a solid-state gas sensor that undergoes a change in its work function when it interacts with a gas or vapor. Efforts to impart greater selectivity in CHEMFETs have focused on polymer modification [182–184] and incorporation of desired functional groups into the polymer matrix [184]. The CHEMFETs may respond quickly and reversibly to gaseous analytes, so their potential in in-

dustrial hygiene monitoring is promising. The selectivity of these devices needs improvement, and current research is directed toward this goal.

In other work, HPLC with EC detection has be n used to determine bisphenol A in air that was collected on glass fiber filters [185]. A detection limit of 25 ng/m^3 was found for a 60 L air sample. An HPLC technique [186] with UV or EC detection forms the basis of a NIOSH method for 4,4'-methylenedianiline, which is a potential human carcinogen. In the NIOSH protocol, the analyte is collected on an acid-treated glass filter, extracted with methanolic KOH, and then analyzed by HPLC with UV or EC detection. The HPLC-EC method provides a much lower detection limit than the HPLC-UV technique, and the applicable working range is 0.025 to 0.50 μg per sample [186]. In a separate study, adsorptive (cathodic) stripping voltammetry was used for the determination of 1-butanethiol and cyclohexanethiol in air [187]. The thiol species are first trapped in a methanol-ammonium hydroxide mixture and then analyzed by cathodic stripping at an HMDE.

In a novel application, sensor arrays were used to analyze mixtures of vapors [188]. In this study, an amperometric sensor array was interfaced with a catalytic filament microreactor. Gaseous species are collected and exposed to the filament, and the reaction products are detected by amperometry. The device can be frequency and amplitude modulated, thereby enhancing the ability to discriminate between different compounds by use of information theory [189]. The response of the sensor array to CO, formaldehyde, benzene, trichloroethylene (TCE), and perchloroethylene was studied at different frequencies, and it was suggested that the modulated sensor may be applicable to the analysis of simple mixtures of organic vapors [188]. In the design of organic vapor sensors, it may be beneficial to use ultramicroelectrodes, which can be used successfully to oxidize compounds with high ionization potentials [190]. In this way, it may become feasible to omit the use of heated microfilaments, which are used for the pyrolysis of sampled vapors and are nonselective. A higher degree of selectivity, and greater ionization efficiencies, could (in principle) be afforded by using ultramicroelectrode-based sensors.

Bioelectrochemistry

A brief section on bioelectrochemical analysis is included here, because medical or biological monitoring by electroanalytical techniques is often conducted for purposes of exposure assessment, surveillance, epidemiologic studies, etc., in industrial hygiene and/or environmental health. For example, electroanalytical techniques may be used to measure the levels of toxic elements in the blood and urine of workers and members of the general public who are potentially exposed to harmful materials. Also, microorganisms that may pose hazards in the workplace can often be detected by electroanalytical means such as EC immunoassay. A number of biomolecules can be immobilized on electrode sur-

faces and used to perform analyses for specific toxic species. Some human carcinogens that may be present in certain work environments can be detected and/or determined by EC methods. Clinical chemistry represents an important facet of industrial hygiene, and electroanalytical methods are frequently used to conduct biological analyses. Bioanalytical chemistry is becoming increasingly important for occupational health and safety purposes, and there have been a few applications of bioelectrochemical analysis to issues relating to industrial hygiene and environmental health.

Heavy Metals in Body Fluids and Tissues. Voltammetric methods have been used for years to measure heavy metal concentrations in blood, urine, and other body fluids and tissues. Polarographic methods for the determination of lead and cadmium in urine were first reported in the 1950s and 1960s [191–194]. Improved detection limits were later afforded by ASV, which has been applied to heavy metals analysis in blood, urine, and other biological samples [194,195]. Pulse voltammetry also has been used for the analysis of heavy metals in biological fluids and tissues [196,197]. In an early survey study, ASV was compared with atomic spectrometric methods for measuring trace lead in blood [198], and applications of the analytical techniques for industrial hygiene control were cited. The performance of ASV has been found to compare favorably with atomic spectrometric methods such as flameless atomic absorption spectrophotometry [194,195,198,199]. However, lower rates of sample throughput by ASV (when compared to atomic spectrometry) have been cited as a drawback to using this electroanalytical technique for blood lead measurements [198]. Nonetheless, to this day, ASV continues to be used for blood lead measurements, and field-portable instruments are available.

The NIOSH methods for lead in blood and urine, based on ASV at a composite mercury-graphite electrode (CMGE), were published in the 1970s [200]. In the NIOSH protocols, whole blood or urine samples are first digested on a hotplate with a mixture of nitric, perchloric, and sulfuric acids. The resulting residue is dissolved in dilute perchloric acid, and the solution is then analyzed by ASV. For a 100 μL blood sample, the detection limit is 40 μg/L and the precision (CV) is 5% (at 1000 μg Pb/L blood); for a 1.0 mL urine sample, these values are 4.0 μg/L and CV = 6% (at 200 μg Pb/L urine), respectively [200]. Lower detection limits (with similar precision) were reported in separate studies [194]. The experiment may also be run at an HMDE, with comparable results.

In recent applications of ASV for heavy metals analysis in body fluids, this electroanalytical technique was used to measure trace metals in sweat [201] and blood [201,202]. Measurement of trace metals in sweat was proposed as a viable method for noninvasive industrial hygiene monitoring of workers [201], and ASV analyses of sweat samples were compared with ASV results from blood samples obtained from human volunteers [202]. Sweat samples were collected on membrane filters, and were subsequently extracted in a supporting electrolyte

solution or, alternatively, were analyzed directly by use of a novel thin-layer cell. The application of ASV heavy metals analysis of sweat for industrial hygiene monitoring of workers is an intriguing idea and shows some promise. However, this method may be subject to serious contamination problems in the workplace, and results from field studies are needed to assess the viability of the technique.

A number of interlaboratory comparisons of blood lead analyses by ASV (and other analytical methods such as flameless AA) have been conducted [203–205]. Biases were discovered in results obtained with commercial ASV instrumentation, which has been used widely by clinical laboratories [203,204], but software modifications have been made that successfully minimize the observed biases [203]. Rather than using hot plate/acid digestions, many clinical laboratories use hemolyzing reagents for the preparation of blood samples prior to ASV analysis. Blood-reagent mixtures are often allowed to stand overnight at room temperature and may be sonicated to achieve complete decomplexation of lead. This sample preparation protocol can provide for field-portable extraction and analysis and may enable blood lead monitoring of workers at worksites. Detection limits near 10 μg/L have been obtained, which compare favorably with the performance of graphite-furnace AAS [204]. The quantitation limit of the ASV technique is well below the action levels for blood lead concentrations in workers, so this analytical method is often used in the laboratory to monitor occupational lead exposures.

Anodic stripping voltammetry at graphite-epoxy microelectrodes has been applied to the analysis of trace metals in vitro, with the ultimate goal of using this technology for in vivo measurements [206]. Nanomolar concentrations of trace cadmium, lead, and copper could be determined by using preconcentration (deposition) periods of just a few minutes. The use of microelectrodes for in vivo measurements of trace metal concentrations may provide for real-time monitoring of workers in the near future. In other work, polymer-modified thin mercury film electrodes (on glassy carbon substrates) were used for the determination of trace metals in body fluids [207]. A perfluorosulfonated polymer membrane (Nafion) helped to prevent electrode fouling, a serious problem that is often encountered in bioelectroanalytical measurements. For the determination of trace lead, excellent results were obtained from whole blood, urine, and sweat samples which were pretreated with acid [207]. In a separate study, potentiometric stripping has been used for the simultaneous determination of cadmium and lead in whole blood and serum [208]. Unlike voltammetric techniques, potentiometric stripping analysis is not subject to interferences from other electroactive species (besides the cadmium and lead species of interest) that may be present in the matrix. Following a preelectrolysis time of only 2 minutes, potentiometric stripping reportedly gives detection limits of 25 nM for cadmium and lead, with a precision (RSD) of 4%. Throughput of up to 12 samples/h is possible, and sample volumes of 25 μL can be analyzed successfully [208]. It is clear from

these few examples that electroanalytical tools such as microelectrodes, polymer-modified electrodes, and anodic and potentiometric stripping analysis may, in the near future be used for the in vivo monitoring of trace metal concentrations in occupational environments.

Other Applications of Bioelectroanalysis. The fluoride ion-selective electrode was used to measure the concentration of this ion in urine and was used for industrial hygiene monitoring [209]. A NIOSH method for fluoride was published based on this technology [210]. The analysis is quite simple: urine samples are merely diluted with a buffer solution, and the buffered sample is then analyzed directly by the F$^-$ ISE. The reported range of the method is approximately 0.20 to 2000 mg/L urine [210]. Interferences from H_2O_2 and Ca^{2+} are eliminated by use of the pH buffer.

A variety of new techniques have been used for bioelectrochemical applications and may eventually find their place in the occupational health field. A potentially useful technology is EC immunoassay [5], which affords improved selectivity over other bioelectrochemical measurement methods. Other techniques that have been proposed for bioelectrochemical sensor applications include electrodes modified with immobilized enzymes, polymers, and other constituents [7,211,212]. These techniques may one day prove their usefulness in such applications as bioaerosol monitoring and in vivo sensing of toxic substances. Ultramicroelectrodes are being investigated for their biosensing and biomonitoring capabilities [3,7,9]. With the exception of but a few examples, these new bioelectroanalytical technologies have not yet been used for purposes relating to occupational health and safety. However, they are mentioned here because of the potential applications of these novel electroanalytical techniques in the industrial hygiene field.

SUMMARY

A vast array of electroanalytical techniques have been applied over the years to problems having to do with occupational health. Numerous examples that demonstrate the use of electrochemical (EC) analysis in the industrial hygiene and environmental health fields were given. New developments in EC measurement methodology were cited, such as ultramicroelectrodes, chemically modified electrodes, portable instruments, etc. Recent trends in electroanalytical chemistry such as miniaturization, biosensors, and sensor arrays have not yet been used for industrial hygiene purposes, and there is much promise for new applications in this area. Compared to other analytical methods, such as spectrometry, chromatography, etc., electroanalytical methods have been somewhat underutilized in the industrial hygiene and related fields. In the past, EC methods have suffered from problems of ruggedness and long-term reliability. So despite the high sensitivity offered by electroanalytical methods, alternative techniques have been employed. However, EC instrumentation is becoming much more rugged and user-friendly, thereby allowing for more routine application.

In light of new advances, there are many potential applications of novel electroanalytical technologies in the areas of occupational and environmental health.

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