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REVIEW ARTICLE

SENSOR TECHNOLOGY FOR ENVIRONMENTAL MONITORING: AN OVERVIEW

Jadav Jagruti N[1], Maind Sandip D[2a], Gajbhiye Suraj[2b] and Bhalerao Satish A[1]

[1]Environmental Sciences Research Laboratory, Department of Botany, Wilson College, University of Mumbai, Chowpatty, Mumbai-400007, (M.S.), India.

[2a]Department of Chemistry; [2b]Department of Botany, Bharatiya Vidya Bhavan's Hazarimal Somani college of Arts and Science, University of Mumbai, Kulapati K.M. Munshi Marg, Mumbai-400007, (M.S.) India.

ABSTRACT

Pollution of the environment is a problem of the modern age. The technology developed and used over the past decades has left serious consequences on human health and environment and implied the need for resolving them. Pollution which contaminates water, air & soil which affects ecosystems and creates new diseases which hazards human being. Preserving quality of water, air and soil are quite common issues in many countries. Sensor technology has significantly improved over the past few years. Sensors are smaller, lighter, more reliable and portable. They are capable of monitoring and measuring certain features of observed phenomena and can be placed anywhere. Sensors should allow one to move the measurement of numerous inorganic and organic pollutants from laboratory to the field and to perform them rapidly, inexpensively and reliably. Thus sensor technology plays a very important role to control and monitor the environment. In the present paper various types of sensors like electrochemical biosensors, chemically modified sensors & stripping based metals sensors and their applications in environmental monitoring and environmental protection is overviewed.

Keywords : Sensors, environmental protection, environmental monitoring.

INTRODUCTION

Environmental concern is present nowadays all over the world. The diversity and quantity of chemicals released into the environment has risen dramatically in recent years. These emissions and their impacts are varied and usually complex. This causes serious concerns about their adverse effects on the ecosystem and on human health. The legacy of land and groundwater contaminated by human activities affects quality of life. Increasing regulatory and economic requirements to monitor and treat pollution in the environment have created a pressing need for reliable, cost effective monitoring of contaminating compounds in water, soil and sediments. New low-cost effective tools are needed for monitoring pollution and detecting treads over time. Morden way of living has left some serious consequences on human environment. In recent years, one of the emerging technologies that have had big impact on the field of research is sensor technology and its diversity of features and applications.

Environmental monitoring and protection is an area where these sensor technologies are of huge importance. Data collected by sensors are sent through the network to the control centres where are than being processed and analysed. The environmental monitoring is one of the main areas of application of this technology due to its characteristics that allow the measurement of parameters in different environmental settings such as crop management, protection of forest fires, agriculture, earthquakes, and active volcano. It is also possible to use macro-instruments for measuring parameters of large-scale such as landslides, atmospheric meteorology, and finally pollution studies or even for planetary exploration.

Corresponding Author

Email: drsatish16@rediffmail.com

At present, global climate changes on the earth made a rational land use, environmental monitoring, forecasting of natural and technological disaster, and the tasks of great importance. The basis for the solution of these crucial applied problems consists in the integrated use of data of different nature: modelling data, in situ measurements and observations, and indirect observation such as airborne and space borne remote sensing data.

Electro-analytical chemistry can play a very important role in the production of in particular; electrochemical sensor and detectors are very attractive for on-site monitoring of priority pollutants, as well as for addressing other environmental needs and helping for protection of our environment. Such devices satisfy many of the requirements for on-site environmental analysis. Chemical sensors also include a special branch referred to as biosensors for the recognition of biochemical and bio-reaction.

ELECTROCHEMICAL BIOSENSORS:

The remarkable specificity of biological recognition processes has led to the development of highly selective biosensing devices. Electrochemical biosensors hold a leading position among the bioprobes currently available and hold great promise for the task of environmental monitoring. Such devices consist of two components: a biological entity that recognizes the target analyte and the electrode transducer that translates the biorecognition event into a useful electrical signal. A great variety of schemes for implementing the electrochemical biosensing approach, based on different combinations of biocomponents and electrode transducers have been suggested. These rely on the immobilization of enzymes, antibodies, receptors or whole cells onto amperometric or potentiometric electrodes. A general schematic diagram for the operation of electrochemical biosensors is shown in Figure 1. Fundamental aspects of these dives have been reviewed in the literature (Turner et al. 1987; Frew 1987 and Kobos 1994).

Electrochemical biosensors have been the subject of basic as well as applied research for nearly fifty years. Leland C. Clark introduced the principle of the first enzyme electrode with immobilized glucose oxidase at the New York Academy of Sciences Symposium in 1962 (Clark and Lyons was the YSI 23A Blood Glucose Analyzer; Yellow Miroslav Pohanka, Centre of Advanced Studies, Faculty of Military Health Sciences, University of Defense, Hradec Králové, Czech Republic).

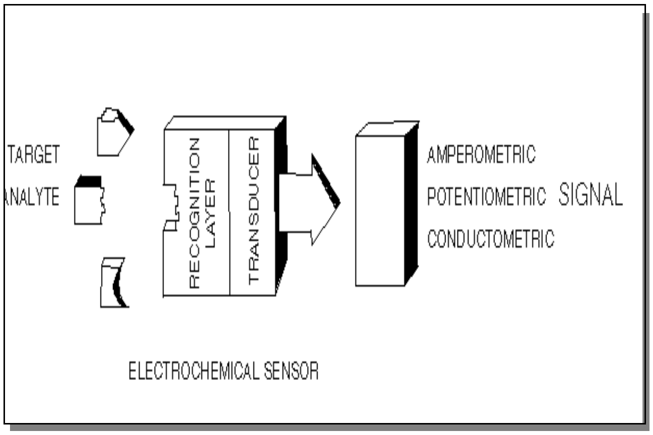

Figure.1. Electrochemical biosensors: biorecognition and signal transduction

The first commercially produced biosensor Springs Instruments (Yellow Springs, OH, USA) placed on the market in 1975. This device was applied to the fast glucose assay in blood samples from diabetics. At present, there are many proposed and already commercialized devices based on the biosensor principle including those for pathogens and toxins, some even based on a multi-channel configuration. The most typical part of electrochemical biosensors is the presence of a suitable enzyme in the biorecognition layer providing electroactive substances for detection by the physico-chemical transducer providing the measurable signal. A native enzyme can be used as the biorecognition component. In this case the analyte is equal to the enzyme substrate, alternatively it may function as its inhibitor and in addition, enzymes can be used. Electrochemical biosensors whose principles and applications labels bound to antibodies, antigens and oligonucleotides with a specific sequence, thus providing affinity-based sensors. A rather limited number of enzymes processed in biotechnology were chosen for the monitoring of clinical metabolites and, especially from the group of oxidoreductases: glucose oxidas and glucose dehydrogenase for glucose assays, alcohol oxidase for ethanol, NADH dependent lactate dehydrogenase and lactate: cytochromec oxidoreductase for lactate, urease for urea and cholesterol oxidase co-immobilized with cholesterol esterase for the cholesterol assay. Peroxidase and alkaline phosphatase are the most common enzyme labels for electrochemical affinity biosensors. Based on their operating principle, the electrochemical biosensors can employ potentiometric, amperometric and impedimetric transducers converting the chemical information into a measurable amperometric signal.

The design of enzyme electrodes is such that the current or potential measured is proportional to the rate limiting step in the overall reaction. For reactions limited by the Michaelis-Menten kinetics, a leveling off of calibration curves is expected at high substate concentrations. Mass-trasport limiting membranes can be used to greatly extend the linear range. This will also lead to a slower response. The signal may be dependent also upon the Ph of the water sample or its heavy metal content that affect the enzymatic activity. Attention should be given also to the long-term stability of these devices, due to the limited thermostability of the biocatalytic layer.

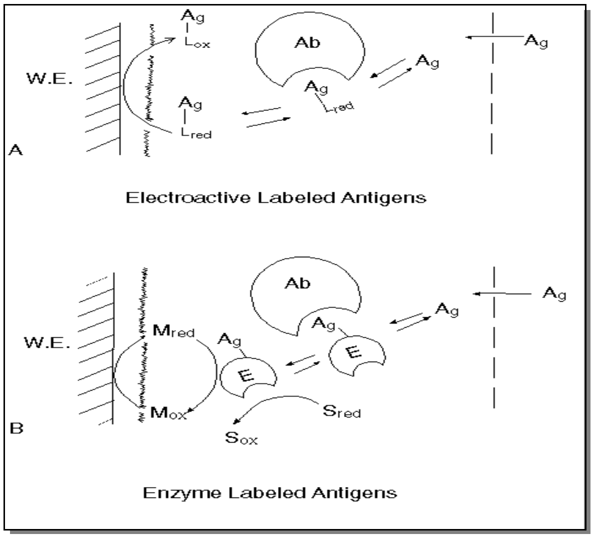

Figure. 2. Amperometric immunosensor based electroactive-(A) and enzyme (B) tagged antigen.

Several enzyme electrodes have already proven useful for the task of environmental monitoring. For example, several groups reported on highly sensitive amperometric biosensors for phenolic compounds. Such devices rely on the immobilization of tyrosinase onto carbon- or platinum transducers, and the low potential detection of the liberated quinone product (Figure 2.). Assays of industrial wastes or natural water have been documented, including possible remote phenol sensing (Wang and Chen) and single-use on-site sensing (Kotte et al. 1995 and Wang and Chen 1995). Similarly, low potential biosensing of organic peroxides or hydrogen peroxides or hydrogen peroxide can be accomplished at peroxidase-modified electrodes (Wang et al. 1991 and Csoregi et al. 1994). “class-selective” enzyme electrodes, based on tyrosinase or peroxidase, can be used for semiquantitative field screening. They can also be used as detectors for liquid chromatography, hence providing quantitation of the individual substrates (Ortega et al. 1994).

CHEMICALLY MODIFIED SENSORS:

The world seems to have a natural division between chemical and physical sensors. However, there are those that do not classify easily, like relative humidity sensors, a chemical sensor traditionally lumped with physical sensors. Also, sensors are often discussed along with the topic of actuators. Chemical sensors have a chemical or molecular target to be measured. Biosensors are defined as sensors that use biomolecules and/or structures to measure something with biological significance or bioactivity. More appropriately, bio- sensors target a biomolecule of interest for measurement. The biosensor can usually be considered a subset of chemical sensors because the transduction methods, sometimes referred to as the sensor platforms, are the same as those for chemical sensors. A useful definition for a chemical sensor is “a small device that as the result of a chemical interaction or process between the analyte gas and the sensor device, transforms chemical or biochemical information of a quantitative or qualitative type into an analytically useful signal. The lab-on-a-chip or m-TAS ~micro-Total Analytical System! is considered a sensor in only the broadest of definitions and is really a complete analytical system. The signal from a sensor is typically electronic in nature, being a current, voltage, or impedance/conductance change caused by changing analyte composition or quality. While chemical sensors contain a physical transducer and a chemically sensitive layer or recognition layer, the microinstrument or spectrometer sends out an energy signal, be it thermal, electrical, or optical, and reads the change in this same property caused by the intervening chemical and this is akin to molecular spectroscopy in the above example. In m-TAS, the system can include sampling system, separation or fluidic instrumentation system, as well as a detector. The users of sensors, of course, do not care about this division, but this paradigm is helpful in explaining the types of systems that exist and understanding how they work, why they have certain properties and analytical performance, and how new developments are made. ECS has had conferences that have included all of these types of sensors. A few types of electrochemical sensors are included in the following discussions. While the topic of sensors of interest to the Society is too broad to cover here, we can discuss a few electrochemical sensors by conventional definition, assigned to three categories: potentiometric, amperometric, and impedance or admittance based devices. Biosensors, while directed toward analysis for a specific or significant bio- logical material or bio-endpoint will utilize one or more of these principles. Optical and acoustic or similar approaches are also included in electrochemical sensors if a broad definition of these terms is used. Electrochemical sensors can be applied for solid, liquid, or gaseous analytes with the latter two most common. High temperatures can be accommodated using solid electrolytes and high temperature materials for sensor device construction. In the following brief discussion, we outline some common electrochemical sensors and, by illustration, the continued ECS interest in sensors.

Chemical layers can also be used for imparting a high degree of selectivity to electrochemical transducers. While conventional amperometric electrodes serve mainly for carrying the electrical current, powerful sensing devices can be designed by a deliberate modification of their surfaces. Basically, the modification of an electrode involves immobilization of reagents that change the electrochemical characteristics of the bare surface. Inclusion of reagents within the electrode matrix (e.g. carbon paste) is another attractive approach for modifying electrodes. Such manipulation of the molecular composition of the electrode thus allows one to tailor the response to meet specific sensing needs. The new "mercury-free" surface address also growing concerns associated with field applications of the classical mercury drop electrode. Theoretical details on modified electrodes can be found in several reviews (Murray et al. 1987; Wang 1991 and Arrigan 1994).

While sensor based on modified electrodes are still in the early stage of their lifetime, such preparation of structured interfaces hold great promise for the task of environmental monitoring. There are different directions by which the resulting modified electrode can benefit environmental analysis, including acceleration of electrone-transfer reaction, preferential accumulation or permselective transport.

Electrocatalysis invoves an electron transfer mediation between the target analyte and the surface by an immobilized catalyst (Figure 3.) Such catalytic action results in faster electrodes reactions at lower operating potentials. Various catalytic surfaces have thus been successuufully employed for facilitating the detection of environmentally relevant analytes. Theses enclude the electrocatalytic determination of hydrazines (Waang and Lu 1989) or nitrosamines (Gorski and Cox 1994) at electrodes coated with mixedvalent ruthenium films, monitoring of aliphatic aldehydes at palladium-modified carbon paste (Cai and Kalcher 1994), Sensing nitrite-based redox polymer (Doherty et al. 1991) of nitrate at a copper modified screen printed carbon electrode (Fogg et al. 1991), monitoring of organic peroxides at cobalt-phthalocyanine containing carbon paste (Wang et al. 1991), and of hydrogen peroxide at a copper heptacyanonitrosylferrate-coated electrode (Gao et al. 1992).

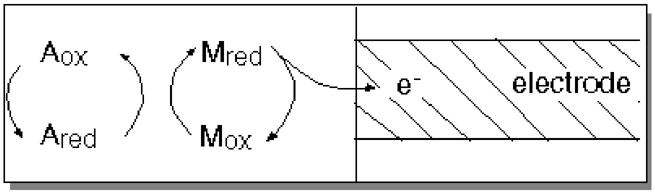

Figure.3. Electrocatalysis at modified electrodes; electron transfer mediated reaction between the target analyte and surface-bound catalyst.

STRIPPING-BASED METAL SENSORS:

Mercury-modified electrodes coupled with stripping techniques have been recognised as the most sensitive methods for determination of heavy metals. However, the potential dangers associated with mercury have led to developing mercury-free sensors.

Unmodified electrodes like bare carbon, gold or iridium2–4 graphite–epoxy composites5–7 recordable CDs8 or silver-plated rotograved carbon electrodes9 have been used as an alternative to mercury based electrodes. Efforts have been done also to use electrodes modified with various metal affinity compounds such as tetraphenylporphyrin, 10 Nafion11,12 N-p-chlorophenyl cinnamon- hydroxamic acid, 13 dithizone,14 etc. One of the excited alternatives to mercury based electrodes is that based on bismuth. Bismuth film electrodes (BiFE) display an attractive stripping voltammetric performance which compares favourably with that of common mercury-film electrodes (HgFE). The low toxicity of bismuth makes it an alternative material to mercury in terms of trace metal determination. The remarkable stripping performance of BiFE can be due to the binary and multicomponent ‘fusing’ alloys formation of bismuth with metals like lead and cadmium. Bismuth film, with an attractive stripping voltammetric behaviour, prepared by electrodeposition onto the micro disc,17 gold,18 carbon paste,19 glassy carbon, 20–23 rotating glassy carbon disc24 electrodes have been reported. In situ or ex-situ preparation 25 of the BiFE including the effect of bismuth precursor salt used to prepare the film and a variety of substrate surfaces (platinum, gold, glassy carbon, carbon paste, carbon fibre) 26 for bismuth plating were carefully examined for their effects in the preconcentration and stripping steps, including the constant-current potentiometric stripping.

Conducting composites represent another effort in designing mercury free sensors for stripping analysis. The capability of integrating various materials is one of their main advantages. Composite sensors offer many potential advantages including higher signal-to-noise (S/N) ratio 28–32 compared to more traditional electrodes consisting of single conducting phase. Composite electrodes can often be fabricated with great flexibility in size and shape of the material, permitting easy adaptation to a variety of electrode configurations. Their surfaces can be smoothed or polished to provide fresh active material ready to be used in a new assay. Each new surface yields reproducible results because all individual compounds are homogeneously dispersed or compressed in the bulk of the composite. Represents the schematic of the rigid graphite–epoxy composite electrode (GECE) configurations (I, II) that have been used by our group as well as the new one (III con- figuration) that is presented in this work. The first configura- tion was based on GECE sensors without modifications. These sensors have been studied firstly for PSA determination of heavy metals by using stripping with constant current mode or chemical oxidation by dissolved oxygen. Later on the same GECE without any modification have been characterised in their use in DPASV.6,7 The second configuration, Bi-GECE33 was based on GECE without modification but bismuth film formation due to the presence of bismuth in the measuring solution. In the present work we present a novel configuration (Bi(NO3) GECE, that represents GECE modified internally with bismuth nitrate salt which serves as a built-in bismuth precursor for bismuth film formation. This represents an integrated configuration of bismuth based GECEs for stripping analysis.

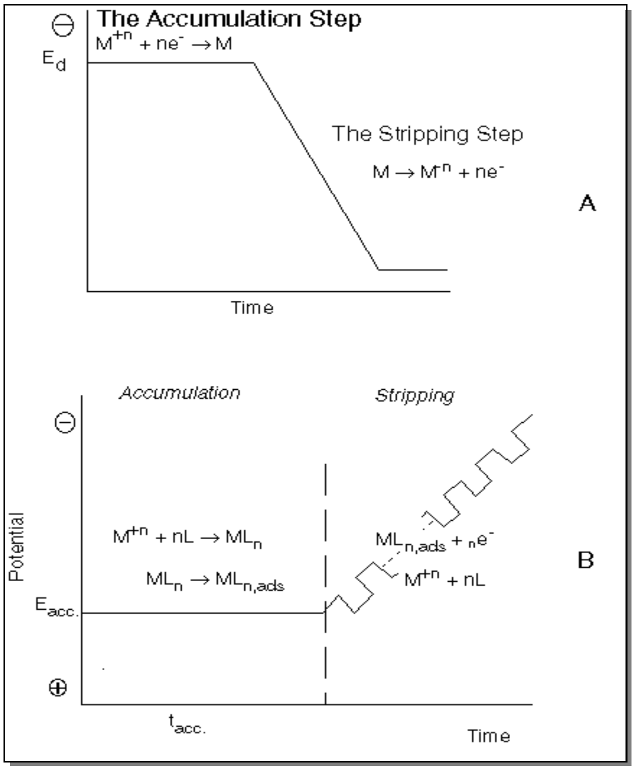

Figure 4. Steps in anodic (A) and adsorptive (B) stripping voltammetry of trace metals, based on electrolytic and adsorptive accumulation, respectively, of target metal analyte

The most sensitive electroanalytical technique, stripping analysis, is highly suitable for the task of field monitoring of toxic metals. The remarkable sensitivity of stripping analysis is attributed to its preconcentration step, in which trace metals are accumulated onto the working electrode. This step is followed by the stripping (measurement) step, in which the metals are "stripped" away from the electrode during an appropriate potential scan. About 30 metals can thus be determined by using electrolytic deposition or adsorptive accumulation of a suitable complex onto the electrode surface (Figure 4.). Stripping electrodes thus represent a unique type of chemical sensors, where the recognition and transduction processes are temporally resolved.

Various advances in stripping analysis should accelerate the realization of on-site environmental testing of toxic metals. New sensor technology has thus replaced the traditional laboratory-based mercury electrodes and associated cumbersome operation (oxygen removal, solution stirring, cell cleaning, etc.). Of particular significance are new stripping-based tools, such as automated flow systems for continuous on-line monitoring (Zirino et al. 1978; Wang et al. 1992 and Clark et al. 1988), disposable screen-printed sripping electrodes for single-use field applications (Wang and Tian 1992), or remote/submersible devices for down-hole well monitoring or unattended operation (Terciet et al 1990 and Wang et al. 1995).

In addition to trace metal pollutants, it is possible to employ new adsorptive stripping procedures for measuring low levels of organic contaminants that display surface-active properties (e.g. detergents, oil components). However, due to competitive adsorption such schemes usually require a prior separation step. Another version of stripping analysis, cathodic stripping voltammetry can be used for measuring environmentally-relevant anions (e.g. S^{2-}, I^{-}, Br^{-}) or sulfur or chlorine containing pollutants (e.g. pesticides) following their oxidative deposition onto the working electrode. Additional background information on stripping analysis and its environmental opportunities can be found in various reviews (Wang 1985; Wang 1982; Tercier and Buffle 1993 and Wang 1994).

CONCLUSION:

Sensor technology is very much useful for environmental monitoring, though having limited scope and cannot solve all environmental monitoring needs. Yet a vast array of sensor technology has been applied in recent years for monitoring a wide range of inorganic and organic pollutants.

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