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Electrochemical sensors for environmental monitoring. Strategy and examples*

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Abstract: The strategy and useful applications of electrochemical sensors for environmental monitoring are surveyed. Potential benefits and important design factors are outlined. Trends in important areas are focused on with illustrative examples, and future perspectives are considered.

INTRODUCTION

In recent years, increased concerns with the toxic effects of chemicals in the environment have led to the necessity of monitoring pollutant levels at various points in industrial processes and recycling processes, in effluents and wastewaters, and at industrial, agricultural, and urban sites. Additionally, continuous monitoring of environmental pollution in the field requires portable fast-response sensors that are robust and with sufficient sensitivity and long lifetime.

This paper examines the contribution electrochemical sensors and electroanalysis [1,2] can make to this strategy. Some of the criteria to be considered are shown in Fig. 1. First, the usefulness of elec-

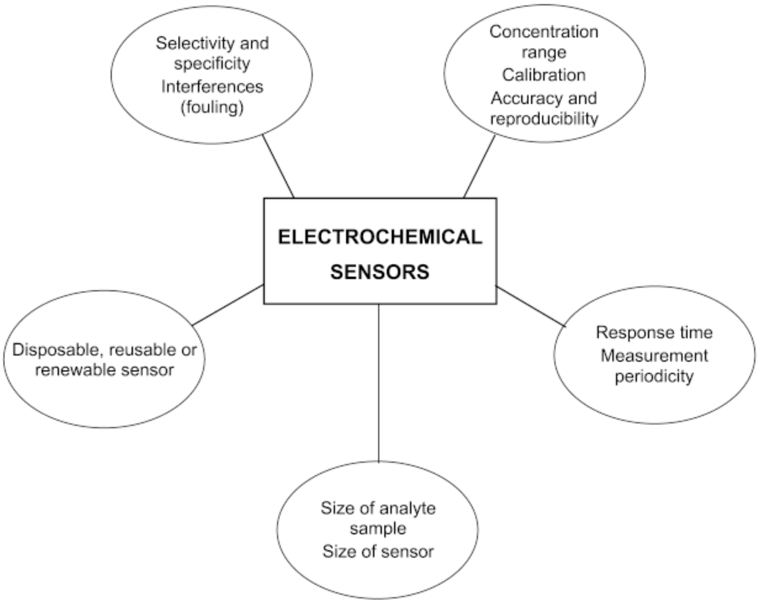

Fig. 1 Important aspects for choosing electrochemical sensors for environmental monitoring.

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trochemical sensors for environmental monitoring will be assessed, including the role they can play, design factors, and how selectivity can be achieved. Following this, recent examples from the literature will be given and an indication of future trends will be presented.

WHY ELECTROCHEMICAL SENSORS?

The three types of electroanalytical measurement that can be performed each offer different degrees of selectivity [1]:

Conductimetric. The concentration of charge is obtained through measurement of solution resistance and is therefore not species-selective. Conductimetric detectors can, however, be useful in situations where it is necessary to ascertain, for example, whether the total ion concentration is below a certain permissible maximum level or for use as an on-line detector after separation of a mixture of ions by ion chromatography. Such situations can arise in electroremediation.

Potentiometric. The equilibrium potential of an indicator electrode is measured against a selected reference electrode using a high-impedance voltmeter, i.e., effectively at zero current. Thus, the current path between the two electrodes can be highly resistive. At an inert redox indicator electrode such as platinum the potential measured is a mixed potential, a function of all species present in solution and their concentrations. In ion-selective electrodes, careful choice of electrode material can give good selectivity to one particular species, in many cases, with only minimal interference from other ions. Detection limits of the order of 100 nanomoles per litre of the total concentration of the ion present in a particular oxidation state, although down to 10 picomolar differences in concentration can be measured.

Voltammetric. Where the current is registered as a function of applied potential, more information and lower detection limits can usually be gained. Several species that react at different applied potentials can be determined almost simultaneously in the same experiment without the need for prior separation. Very low detection limits of down to the picomolar level can be reached using state-of-the-art instrumentation and preconcentration of the analyte on the electrode surface. In many practical sensors or detectors used after separation, e.g., by high-pressure liquid chromatography or capillary electrophoresis, or in detectors in continuous flow, after the voltammetric profile has been investigated, *amperometric* sensors at fixed potential can be employed.

The potential benefits of electrochemical monitoring, using the above types of measurement, in an environmental context are:

1. An applied potential in voltammetric sensors can lead to high selectivity and specificity, and thence probing of speciation. Each chemical species as well as each element or oxidation state has an associated potential for oxidation and reduction. Such specificity is not possible with most other analytical techniques.
2. The choice of electrode material can lead to selectivity, particularly in ion-selective electrodes. In voltammetric sensors and at some electrode materials, certain species do not react, so that interference problems may be resolved in this way. An obvious example is the high overpotential for hydrogen evolution at mercury electrodes.
3. Modern electrochemical instrumentation, particularly with controlled potential, associated with voltammetric sensors, leads to high sensitivity and low detection limits, since complex applied potential programs can be used together with accumulation of the species to be measured at the electrode surface.
4. There is the possibility of furnishing not only the results but also treated data in real time or close to real time, using computerized control and particularly in flow systems for on-line monitoring.
5. Portable sensors with dedicated instrumentation, possibly battery-powered, that can be used outside the laboratory.
6. Miniaturized sensors, for application in situations where other probes may not be usable.

Thus, electroanalysis is complementary to other analytical techniques. In the field, many of the existing analytical techniques cannot be applied as they require complex and large equipment, and so, electrochemical monitoring can bring many advantages. In the laboratory, the detection limits possible in electroanalysis make it a strong competitor for many other analytical techniques when alternatives exist.

The advantage of distinguishing oxidation states is highly important. The electrochemical approach can give a rapid answer, without digestion, as to the labile fraction of a given element in a particular oxidation state, and the experiment can be performed on-site in the field.

GENERAL SENSOR DESIGN CRITERIA

A useful electrochemical sensor must obey a number of experimental design criteria, many of which are linked to its potential benefits. Among the most important are:

(a) For amperometric and voltammetric sensors, the species to be determined is electroactive within the sensor's potential range, and whether there is the addition of an inert, supporting electrolyte to carry the current perturbs the equilibria in solution.
(b) For potentiometric sensors, there is an adequate electrode material, free from interferences.
(c) The concentration of electroactive species can be determined with sufficient accuracy and precision.
(d) The measurements are sufficiently reliable and repeatable.
(e) The response time of the sensor is sufficiently fast.
(f) The drift or diminution of sensor response with time owing to electrode degradation or surface fouling is sufficiently small.
(g) Calibration is simple and easy to perform, or not necessary.
(h) The detection limit is sufficiently low for the purpose envisaged.

The relative importance of these factors depends on the monitoring necessities as well as on the technique employed and the electrode and cell configuration.

It is important to bear in mind possibilities and advantages arising from:

- self-contained test modules
- specific assays
- miniaturization
- no external pretreatment or necessity of reagent addition.

RECENT TRENDS IN SENSORS

In this section, some recent trends and currently important aspects relating to the development and applications of electrochemical sensors for monitoring will be given, together with illustrative examples, see Table 1. Several of these have recently been discussed elsewhere [3–5]. Little emphasis will be given to hyphenated techniques in the context of this contribution.

Materials for potentiometric sensors

Recent tendencies in development of potentiometric sensors for monitoring have been the production of sensors that are more robust, more reliable (i.e., needing less calibration with smaller potential drift) and can be used in an ever wider range of situations with low maintenance.

Potentiometric sensors based on plasticized PVC membranes doped with neutral carriers have been extensively developed for many ions [6,7]. For example, crown and *bis*-crown ether ionophores can be incorporated into polymer membranes, the recognition coming from the size of the host cavity

Table 1 Trends, difficulties and examples in the development and applications of electrochemical sensors for environmental monitoring.

Materials for potentiometric sensors
New electrode materials for heavy metal detection
Flow and sample conductivity
Instrumentation
Poisoning of electrode surfaces
Biosensors and detectors for pesticides
Toxicity sensors

or through specific metal–ligand interactions; an alternative with similar properties is calixarenes (phenol-formaldehyde condensates) derivatized to bind metal ions. A different route is to electropolymerize conducting polymer monomers from a solution containing the counteranion that it is desired to measure in order to tailor the cavity size in the film to that ion. There is much effort in improving selectivity relative to interfering species through chemical recognition principles.

New electrode materials for heavy metal detection

The useful ranges of applied potential at electrode materials for voltammetry are determined by oxidation or reduction of the solvent, decomposition of the supporting electrolyte, oxidation/reduction of the electrode surface, or even electrode dissolution. It is also usually necessary that the electrode material is inert in the region of potential in which the electroanalytical determination is carried out.

For reduction reactions such as those of metal cations, liquid mercury was used extensively since the 1920s in the form of the dropping mercury electrode and later as the hanging/static mercury drop electrode. Mercury's useful potential range is limited by its oxidation, which means that essentially only reductions can be investigated.

In stripping voltammetry of heavy metals, the metal is reduced and accumulated at the electrode over a period of time and then reoxidized [8]. In order to avoid hydrogen evolution, this has meant that until recently the electrodes must be mercury, usually mercury thin film or incorporating mercury salts [9]. There have been many applications of stripping voltammetry in environmental monitoring [9], and many ways suggested of reducing the amount of mercury necessary. The preconcentration step enables detection limits that are well below the levels permitted by environmental legislation, and such analyses can often measure the amount of labile species or that which is weakly complexed, not the total amount. As a recent example of environmental importance, it was found that filtering of the analyte and medium exchange was sufficient to measure the speciation of heavy metals in wastewater from a sewage treatment plant [10]. Nevertheless, this strategy may well not work in the long term.

Although liquid mercury has been largely replaced by mercury thin films in recent years, these thin films have to be formed, and although the amount of mercuric ions can be regarded as very small, it is a route which may be unacceptable to the community in the near future. Thus, it is important to move toward different materials and non-mercury sensor materials.

Successes have been registered, particularly with regard to carbon materials, which have already had much application in recent decades, in the positive potential range for studying oxidations [11] as well as substrate for mercury thin films. Good results have been obtained in the negative potential range with thick carbon films [12], boron-doped diamond [13], and carbon film electrodes made from carbon resistors [14]. A short survey of recent progress is found in [14]. Environmentally important ions such as lead, cadmium, and copper can be determined at many of these carbon materials. A greater challenge is to be able to measure zinc ions at submicromolar levels, since reduction of zinc ions occurs at more negative potentials and is usually concurrent with hydrogen evolution at most electrode materials—this has been shown to be possible in [14] and holds much promise for the future. At the same time, the carbon film electrodes are cheap, so they can be used as disposable sensors.

Flow and sample conductivity

In many natural industrial and environmental situations, the analyte is under flowing conditions, which facilitates multicomponent detection either in parallel or sequentially, and ensures that there is no reagent depletion or build-up of reaction products. This is one way to approach the ideal of real-time analysis. Nevertheless, to obtain a reproducible response, it is important that any convective flow is understood, characterized, and modeled, or is constant. Alternatively, the effects of flow on sensor response are minimized as with microelectrodes, see below. Many sensors have been developed over the last decades for monitoring in flow systems [15].

A disadvantage of flow is that it can degrade the sensor surface (mainly in ion-selective electrodes), can foul or block it. Fouling is usually best prevented by protecting the electrode surface and/or minimizing contact between analyte and electrode. The latter is difficult in continuous flow, but in such cases microvolume [16] samples can be removed and injection methods can be usefully employed, which is well-known in flow injection analysis (FIA) [17] and can be adapted to electrochemical detection, even in the field. A hybrid scheme for using microvolumes together with convective flow over an electrode sensor during injection is to inject microlitre samples as a fine jet of solution over the center of a disc electrode immersed in electrolyte solution—batch injection analysis (BIA) [18–20]. The advantage of batch injection analysis is simplicity and that the electroactive species in the sample can be measured directly without electrolyte addition; sample dispersion is essentially zero.

The second question is that of sample conductivity, which determines whether added electrolyte is needed in order to increase the conductivity and suppress migration effects. While not necessary for potentiometric sensors, insufficient electrolyte, which increases the ohmic resistance between indicator and auxiliary electrodes, can severely distort the response in voltammetric sensors. Nevertheless, adding electrolyte can alter the sample speciation. Microelectrodes [21] can solve this problem, owing to the high-concentration gradients that are created near the electrode. Indeed, the use of BIA has the same effect, since only a very thin section of resistive solution from the injected sample jet contributes to the overall resistance. Microelectrodes have the added advantage of being small and so can be placed in otherwise inaccessible areas and are relatively immune to variations in flow.

Instrumentation

In the laboratory, it is now commonplace to use digitized applied potential waveforms such as differential pulse voltammetry and square wave voltammetry [22]. Many instruments allow the construction of applied potential waveforms by the user. Pulsed waveforms with current sampling are normal and allow the reaching of low detection limits—the accuracy of the electronics is such that highly reproducible responses can often be obtained even in the absence of convective flow. Square wave voltammetry has the additional advantage that it is fast, approaching a real time measurement and, consequently, in the negative potential range where dissolved oxygen is reduced, very often it does not have to be removed. This is the case in anodic stripping voltammetry where, after accumulation at a negative potential during which all oxygen near the electrode surface is reduced, there is no time for further oxygen to diffuse to the surface during the measurement. It is highly important for application outside the laboratory, where all necessary equipment should be reduced to a minimum.

With these advances in instrumentation and the decreasing size of electronic components, smaller and more dedicated instruments are beginning to appear in the marketplace, which will be usable in the field.

Poisoning of electrode surfaces

The poisoning of electrode surfaces has been a big limitation to the widespread use of electrochemical monitoring. Apart from regeneration of the surface through cleaning or polishing, which is time-consuming and to be avoided if possible for continuous or regular monitoring, there are three main ways of reducing these problems:

1. The time during which adsorption of the poisoning substance—possibly the product of the electrode reaction—occurs is reduced to a minimum via reduction of the contact time of the analyte with the electrode or the time during which the potential corresponding to adsorption is applied, as discussed above.
2. Making the surface of the electrode exposed to the solution incompatible with adsorption by modification or covering with a specially designed membrane.
3. Disposable electrodes, which are only employed for a short period of time during which adsorption problems are negligible.

With respect to the second strategy, polymer-modified electrodes have found widespread use for reducing the effects of surface blocking particularly from proteins and surfactants. Using as an example the measurement of heavy metals, cation exchange membranes such as Nafion can be used to protect the surface while permitting the metal ions to traverse the film through to the electrode below—usually a mercury thin film [23]. This concept has been combined with batch injection analysis, which is using microlitre volumes of analyte, with excellent results in the measurement of environmental samples. No memory effects were found between successive injections, and this strategy enables the measurement of the labile fraction of the heavy metals in the raw effluent analyte samples without pretreatment [24].

It was also shown that the technique is well suited to the measurement of labile heavy metal ions in toxicity tests undertaken with model organisms [25]. Additionally, carbon paste electrodes bulk modified with soil have been used to assess the labile fraction and thence heavy metal ion interactions, and it may be extremely useful for doing the same with nutrients used for toxicity tests [26].

Other routes involve placing the whole electrical circuit behind the ion-exchange membrane. The indicator electrode must then be porous, and the membrane acts as a polymer electrolyte—this also solves the problem of high electrolyte resistance in the outer solution as well as reducing the influence of flow [27].

Alternatively, the sensor can be placed behind a microdialysis membrane which serves to extract the component of interest in the analyte and prevent contamination. In [28] a submersible probe for chromium involves transport from the exterior through a microdialysis membrane, the inner solution containing a complexing ligand that makes the determination of Cr(III) possible.

Inorganic polymer layers, namely clays and zeolites, are also of current interest as these show different adsorption properties toward potential analytes, see [29] for a review.

The third strategy relies on the use of disposable sensors that are used only once or for a short period of time. Ideally, these would need no calibration. Examples of graphite film disposable sensors based on screen printing can be found in the literature, e.g., [30]. Miniaturized thin film sensors can also be made by lithographic techniques, and this subject has been recently reviewed [31].

Sonoelectroanalysis is a new route that holds promise as a way of keeping the electrode surface clean while simultaneously increasing convection. This has been reviewed [32]. Applications to metal ion determination in complex media with polymer-coated electrodes have been demonstrated, e.g., [33,34], although it is unlikely that this will be used outside the laboratory. Additionally, born-doped diamond electrodes have been used in the positive potential range [35].

Biosensors and detectors for pesticides

Organic pollutants have been investigated widely in the laboratory, particularly pesticides. This has usually been following separation of complex mixtures, and, if electrochemically, usually by oxidation at carbon electrodes; problems of electrode fouling can be acute. The use of biosensors, i.e., a modified electrode in which the modifier is a biologically active molecule, can lead to other possibilities [36].

These can either be highly specific, usually enzymes, or can be a general diagnostic, relying on the inhibitor action of a toxic pollutant—pesticide, other organic pollutant, metal ion, etc.—to reduce the response in some way. Many possibilities for environmental monitoring are illustrated in [37], particularly with respect to pollutant-related enzyme inhibition.

Toxicity sensors

Owing to the fact that measurements in the field can never be as accurate as those in the laboratory and that there are many factors, particularly complexation and other interactions, which can influence the response and may change with time, for some purposes it may often be better to consider diagnostic sensors, i.e., alarm sensors, for the field. Rather than furnishing levels of individual chemical species, these give the response to a number of species together or provide some sort of pattern which is characteristic of the whole, a concept very much linked to the concepts of pattern recognition and electronic tongues. In [38], multielectrode sensor arrays, of different materials, are employed together with pattern recognition to fingerprint a particular water. Any changes in the water composition alter the fingerprint, which is the essence of an alarm-type sensor. In a similar way, total metal ion concentrations can also be assessed by enzyme inhibition [39]. It is likely that this approach will be useful in the future, in the field.

On a more conventional note, for a number of years, electrochemical sensors have been used for *in situ* measurements in aquatic systems in conjunction with depth profiling, as well as 2D surface mapping of the oceans [40]. While this is used mainly to probe the biogeochemical processes occurring, clearly it can be used for detecting the effects of pollution close to effluent outlets and changes over time.

The toxicity of wastewaters has been measured using a microbial sensor in which oxygen-uptaking bacteria are attached to an electrode and general toxicity inhibits the bacteria action [41]. On the other hand, other ideas have been to use lipid-type sensors as a general toxicity sensor. This is based on the fact that cations increase the membrane potential of negatively charged membranes, while anions decrease that of positively charged membranes. Thus, a measure of the total cation and anion concentration can be obtained by multichannel potentiometric sensors [42].

CONCLUSIONS

It is fortunate that electrochemical sensors for environmental monitoring are conceptually very similar to those used for clinical or food analysis. Adaptation from one to the other can be relatively easy. One of the difficulties in natural environments is exactly the fouling of the electrode surface—this can also occur in a similar way in clinical or food analysis. Thus, sensor developments in various application areas are closely linked. Apart from this advantage, the real challenges for the future are those of good electrode materials, miniaturization and of measurements in as close to real time as possible. Although monitoring of an industrial process where the sample matrix is usually known can give accurate results, environmental analysis in the field, where the matrix is probably to some extent unknown, means that it is unlikely that results will be so accurate. The need for sample pretreatment should be minimized in order to reduce analysis time and allow the probing of natural speciation; thus, excellent and easy-to-use electrode protection strategies need to be developed. Field analyses should probably be used in the first instance in a diagnostic sense as an alarm sensor for environmental agencies, companies, etc. as to when closer control must be made, after which specific sensors can be installed if necessary. In this way, multispecies sensors of toxicity, as described above, can be extremely valuable. This also reduces the problem of accurate calibration of the electrochemical sensor for field use, particularly if disposable sensors are being employed.

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