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Novel sensor devices and monitoring strategies for green and sustainable chemistry processes*

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Abstract: The principles of green chemistry include a statement as to the necessity for real-time analysis for prevention of pollution. Methodologies need to be developed for real-time, in-process monitoring and control prior to the formation of hazardous substances. These should be carried out by (chemical) sensors. Monitoring also allows optimizing the efficient use of reagents and permits determination of the composition of waste and effluents. In this paper, new monitoring strategies are surveyed and some of the recent advances which have been achieved with respect to novel devices in terms of miniaturization and reliability are indicated. Emphasis is given to continuous and online flow and injection methodologies and the requirements for successful sensors. Particular attention is given to the future potential of electrochemical flow and batch injection sensors which can often be used without external sample pretreatment. Electrochemical sensors using carbon film-based electrodes, including their application in room-temperature ionic liquids (RTILs) for which electrochemical methodologies are directly suited are also described.

Keywords: chemical sensors; electrochemical sensors; flow injection; environment; lab on a chip; miniaturization.

INTRODUCTION

Recent research activity and innovation in green and sustainable chemistry have concentrated very much on new, more environmentally friendly synthetic routes with innocuous secondary products, the use of less toxic reagents, and atom economy. At an industrial level, where processes need to be automated as far as possible, these processes, as well as others which cannot reasonably avoid the production of toxic waste, need to be monitored. This was already recognized in the formulation of the 12 principles of green chemistry, which includes a statement in principle 11 as to the necessity for real-time analysis for prevention of pollution [1], in particular, the development of methodologies for real-time, in-process monitoring and control prior to, and in order to avoid, the formation of hazardous substances. Such control measures have to be carried out by (chemical) sensors. Online monitoring also allows for continuously optimizing the efficient use of reagents and permits determination of the composition of waste and effluents and their variation over time, necessary for a scenario of sustainable development. Sustainable development requires, at the same time, a hazard and operability analysis using "green engineering" criteria in the design and implementation of chemical processes [2]. This analysis can benefit from knowledge gained from previous monitoring of chemical processes and thus incorporate adequate points for sensor placement in the design of new plants and modified processes as a quality and environmental control measure.

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Recently, a different perspective has been considered with regard to the development of sensors themselves—the application of the principles of green chemistry in analytical chemistry [3]. The focus of this article is the reduction of sample size, the use of instrumental methods rather than conventional "wet" chemistry in separation methods, and micronization, with attention to the analytical process steps of sample preparation, separation, and detection (both quantification and identification). Particular emphasis is given to separation methods and the use of alternative solvents in designing new or modified analytical procedures and protocols.

To be efficient and effective, as mentioned above, analysis should be carried out in real time, i.e., the result of the analysis should be obtained "instantaneously" [4,5]. This implies that samples to be analyzed undergo no pretreatment or digestion, and if a chemical reaction has to be carried out to prepare the sample, then the kinetics is fast and does not lead to any time limitations. Such an approach does not allow for most derivitization reactions, which are used to increase the selectivity and sensitivity of the analytical procedure, and also assumes that appropriate steps have been taken to minimize interferences. Additionally, instruments or sensors should ideally not need to be calibrated, should need only a small amount of sample, and should furnish accurate results with an uncertainty that is sufficiently low for the purpose required. Therefore, the general challenges that need to be addressed for green or sustainable processes are the same as those that arise in the monitoring of any chemical process or environmental analysis.

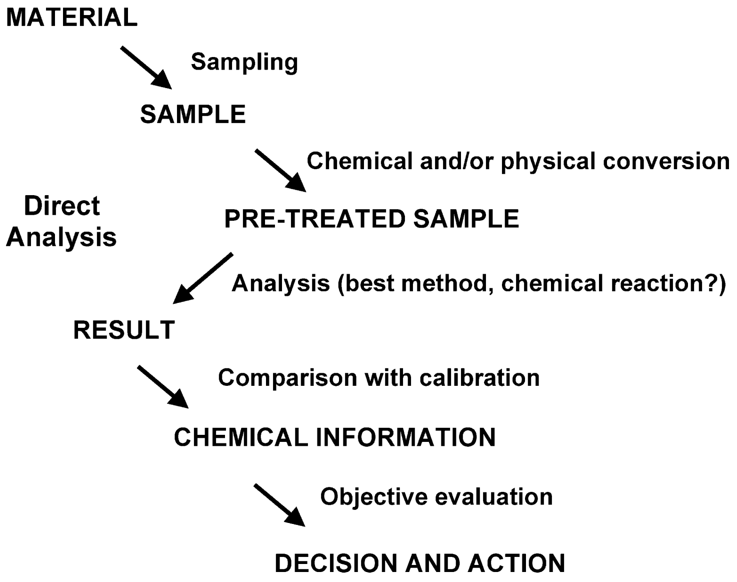
In this paper, current monitoring strategies will be presented and some of the recent advances which have been achieved with respect to novel devices in terms of miniaturization, integration, and reliability will be indicated, particularly with respect to continuous flow and injection methodologies. The requirements for successful sensors will be considered as well as inclusion into online monitoring systems. Particular attention will be given to the future potential of electrochemical flow and batch injection sensors which offer advantages in information on speciation and can often be used without external sample pretreatment in measuring the chemically labile fraction of an element. Examples will also be given involving electrochemical sensors using carbon film-based electrodes, including application in room-temperature ionic liquids (RTILs) for which electrochemical methodologies are directly suited.

NEW MONITORING STRATEGIES

Some of the present trends in the development of analytical chemistry are shown in Table 1. These rely on fundamental research undertaken in a number of fields, particularly materials chemistry and physical chemistry. Most of the topics will be discussed in this and in the following section. Nevertheless, it has to be remembered that any type of monitoring or analysis process using an instrument or sensor should follow a procedure such as that depicted in Scheme 1. Decisions have to be taken at various points along the path. First, how is the sampling carried out? Is it necessary to convert the analyte samples or separate their components before analysis? One of the objectives is to reduce the need for pretreatment as much as possible and perform "direct analysis" as shown in the scheme. The result of the analysis itself has to be compared with a reference (i.e., calibrated) value, and finally the information obtained must be interpreted objectively leading to a decision and possible (corrective) action. All these steps must be taken into account, as well as what lies behind them in terms of chemical reactions, and physical or chemical conversions, including the kinetics, in designing an online monitoring or other type of analytical procedure.

Table 1 Present challenges in analytical chemistry.

Microsystems	Control; data acquisition and analysis Miniaturization: lab-on-a-chip and total analysis systems Microfluidics New automated sampling strategies Remote (wireless) control
New materials	Polymers, composites, alloys, biomaterials Nanostructured materials, molecular imprinting
Information	Multiple, localized simultaneous measurements to give - Spectrum of information - Information on different species/processes Chemometrics and new data analysis techniques (recognition of standards, multivariate calibration, analysis in the frequency domain)
Sensors	Calibration-free: all sensors equal / total sample conversion Real time: "instantaneous" response, no kinetic effects



Scheme 1 Steps in an analytical procedure.

A recent special issue of *Trends in Analytical Chemistry* [6] highlights important advances that have been made over the last 25 years, many of which are applicable to the challenges faced with new regulation devices and reduced pollution requirements. Improved instrumentation and improvements in the fabrication of sensors have allowed a substantial increase in sensitivity and increase in signal-to-noise ratio, which has led to a decrease in detection limits. This also means that miniaturization of detectors has become possible. At the same time, physical characterization techniques, particularly based on local probe microscopies, now permit the routine examination of solids and surfaces at the nanometre dimension, which allows the nanoscale aspects of materials to be understood and exploited and new nanostructured materials to be developed. Nanosensors require nanomaterials such as nanotubes, nanoparticles, and nanowires [7], which are the focus of much research effort. The application of nanosensors in environmental analysis has been recently reviewed, focusing on the different types of structure that can be fabricated, including those formed by self-assembly, which can be adapted for monitoring of chemical processes [8]. Of particular interest as an extension of this concept is molecular recognition via molecular imprinted polymers (MIPs). Three approaches to make MIPs can be identified: (i) formation of a covalently bonded template–monomer adduct in solution prior to polymerization followed by cleavage of the bond and reformation when the MIP is exposed to a sample containing the analyte [9]; (ii) self-assembly where a noncovalent bond is formed between template and monomer that is used in the recognition reaction [10], (iii) a hybrid method in which covalent bonds are used during imprinting and recognition uses noncovalent interactions [11]. Ion-imprinted polymers, which could be of particular relevance in the future, are nanoporous polymeric materials which recognize metal ions after imprinting and which rely for their functioning on many of the ideas behind ion chromatography [12]. MIPs also have a role to play in sample pretreatment since they can be prepared to have tailor-made specificity to target analytes, thus being a form of solid-phase extraction, and consequently preconcentration, in this way avoiding many of the problems which can arise in trace analysis in complex matrices [13].

Many of the developments that have taken place are due to a concern with quality control. Quality control involves definition of a problem, the obtaining of representative samples, definition of the required accuracy and allowed uncertainty (perhaps from current legislation), data treatment, and communication of results. It began primarily in order to ensure that specified levels of product quality were attained, but the concept has clear “green” implications, since it is used simultaneously to measure impurity levels, toxicity, waste, etc. Current legislation deals with both aspects, and it is clear that the analytical devices and sensors that are being developed will be applicable in more complex and possibly difficult situations than up to now, such as in diverse industrial processes for online or periodic monitoring or in the field as a pollution diagnostic. The quality problem has been discussed in the European context with respect to the quality of water for drinking, environmental water, or wastewater [14]. Thus, methods and techniques are needed with portable instruments, with the ability to analyze complex matrices and decrease the response time.

Many analyses have been developed to work in flow systems. This is often compatible with the industrial context where flow-through reactors are used and a small portion of the reactor contents can be diverted for analysis purposes. Flow analysis was recognized many decades ago as an effective approach to improve the response time in analytical experiments—the convection leads to a sensitivity increase at the detector, a decrease in the detection limit, and an increase in reproducibility. Rather than using continuous flow, in 1975 the concept of flow-injection analysis (FIA) was introduced [15], see Fig. 1, and has since had a widespread effect on how chemical analyses are undertaken. Crucial factors in the correct working of such systems are: insertion by injection of an accurately defined volume of analyte into a carrier stream which is inert or is a reagent, with reproducible and accurately controlled timing; a constant carrier stream flow; and the creation of a concentration gradient by the time the detector is reached. This approach reduces reagent consumption, and the flow system can be switched on and off using computer-controlled valves and commutators. Very recently, the “lab-on-valve” approach has been invented using bead injection, essentially a further miniaturization, using the bead as a valve. This whole development can be viewed as a lab-on-a-chip device but larger, in which the manipulations are simpler to achieve. The whole evolution of FIA is elegantly summarized in a recent publication [16].

Another great challenge is the separation of complex mixtures and their analysis. The techniques of chromatographic separation have been used during the last decades in gaseous chromatography and high-performance liquid chromatography, further improved with the introduction of capillary columns and gradient elution. The separation technique of capillary electrophoresis needs only nanolitres of sample and has also increased its scope of application and ease of use, being an excellent potential tool for detailed mapping of environmental pollutants [17]. The coupling of gas and liquid chromatography with other efficient separation techniques such as mass spectrometry has been exploited and is a hyphenated technique which shows much promise [18].

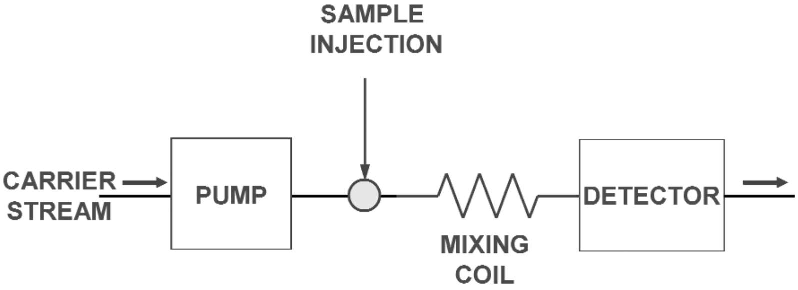


Fig. 1 Basic FIA set-up. Enhancements can include, for example, addition of extra carrier stream channels through the pump which join before the mixing coil, or the injection valve can be replaced by a commutator, etc.

MINIATURIZATION

The current trend in devices is toward the use of portable sensors that should be amenable to miniaturization. A chemical sensor can be defined as a tiny device which, as a result of a process of chemical interaction, transforms chemical or biochemical information into a signal; it contains three parts: a recognition element, a transducer, and a signal processor [19]. The function of the transducer is to transform the signal obtained by the sensor element into an electrical signal. Examples are shown in Table 2. Progress in electronics and in instrumentation has meant that extremely small electrical signals may be measured. With wireless technology, responses from individual sensors can be automatically received, the signals transformed into analytical information, and changes over time assessed from a remote location [20]. A particular challenge is that of periodic calibration, or complete removal of the need for calibration—if it can be guaranteed that all sensors within a batch are exactly equal within a stipulated uncertainty band, then only one of them needs to be calibrated. A second challenge is a "real-time" response without kinetic effects, which is one of the reasons behind using flow systems.

Table 2 Classification of types of sensor used in the detection and quantification of chemical species.

Type of sensor	Examples
Calorimetric	Thermistor
Electrochemical	Potentiometric: solid state, glass membrane, dissolved gas, polymer membrane, ISFETs[a], ENFETs[b] Voltammetric sensors and biosensors
Gas and solid electrolyte	Oxygen
Mass	Piezoelectric, surface acoustic wave
Optical	Spectrophotometric, colorimetric, fiber optic
Surface plasmon resonance	Interfacial "concentrations" of biomolecules

[a] Ion-selective field effect transistors.
[b] Enzyme field effect transistors.

Electrochemical voltammetric sensors are of particular interest because they respond to the chemically labile fraction of species present, i.e., the part that can be easily oxidized or reduced (assuming no pretreatment of samples has taken place). It is recognized that it is this fraction that is toxic to living organisms, although a full exploitation of these attributes has yet to be made.

Thus, miniaturization, together with simplification and automation, have become the focus of increasing efforts in recent years. The concept of miniaturized total analysis systems (μTAS) was invented in the 1990s [21], in part a response to the fact that a laboratory fully equipped to deal with a range of analytical problems requires a large investment, large amounts of reagents, and probably access to other physical techniques, and usually the instruments can only be used in the laboratory. Such miniaturization, implied by the term "lab on a chip", leads to consumption of fewer reagents, less than in FIA approaches, and often to the ability to use the system outside the laboratory.

The goal of "lab on a chip" is that all steps of the process are carried out using a microfluidic system on the same device—integration of pretreatment, separation, and detection. Investigation of different ways to construct microfluidic systems has undergone an explosive increase over the last decade, being fabricated in silica, glass, and polymers, and incorporating multiphase flows and membrane functionalities [22,23]. Since the channel dimensions are of the order of micrometres, instead of mm in FIA where flow is pump-driven, the consumption of analyte and reagent is correspondingly smaller. Special challenges arise with respect to their fabrication and, in use, their accuracy, reproducibility, and calibration, etc. that cannot be solved in the same way as for large systems [24]. The miniaturized systems, therefore, must be robust, probably disposable, and require only a minimum of direct operator intervention, particularly for environmental monitoring [25].

In the following sections, examples will be given of electrochemical flow-injection sensors which offer advantages in terms of information on speciation and of novel electrochemical sensors using carbon film-based electrodes, including application in RTILs for which electrochemical methodologies are directly suited.

ELECTROCHEMICAL FLOW-INJECTION SENSORS

As mentioned above, much interest has focused on flow-injection methods in solution. A small volume of a sample is injected into a carrier stream where, in the course of flow (which is imposed mechanically, gravitationally, or by pressure difference), a sample is diluted by dispersion and may be processed online on its way to a detector. The principal advantages are: mechanically carrying out various processes with the injected sample, high analysis efficiency, and reduction of contamination of the measuring system, especially important for trace analytes. In FIA with electrochemical detection, dispersion of the sample plug occurs within an electrolyte carrier stream, so that electrolyte is effectively added to the sample before reaching the detector electrode, as well as diluting it.

Batch-injection analysis (BIA), invented in 1991 [26], involves the injection of a small volume of analyte sample by an automatic micropipette directly above the sensing surface of the detector, which is immersed in a large volume of blank solution, and which records a transient signal during the flow of sample over the detector surface. The advantage of such measurements is their short response time, with essentially zero dispersion, while a drawback is the limited possibility of sample online processing. An important benefit of electrochemical BIA is that addition of electrolyte to the analyte sample is not necessary, since the injection is made into inert electrolyte; the contribution from the thin jet of analyte to the total solution resistance is so small that it can be ignored [27 and refs. therein]. Typically, a sample of volume 10–100 μL is injected directly from a micropipette, tip internal diameter ~0.5 mm, perpendicularly over the center of an electrode, see Fig. 2a. During the injection, after a short initial period to reach steady state, the hydrodynamics is wall-jet-type (a thin jet hitting a wall perpendicularly) and a time-independent current is registered over several seconds. Volume accuracy and reproducibility are excellent. An additional benefit, which can be important for the analysis of raw or environmental samples, is that the contact time of the sample with the electrode is only a maximum of several seconds, so that problems from poisoning of the electrode surface by components in the sample matrix are also correspondingly fewer.

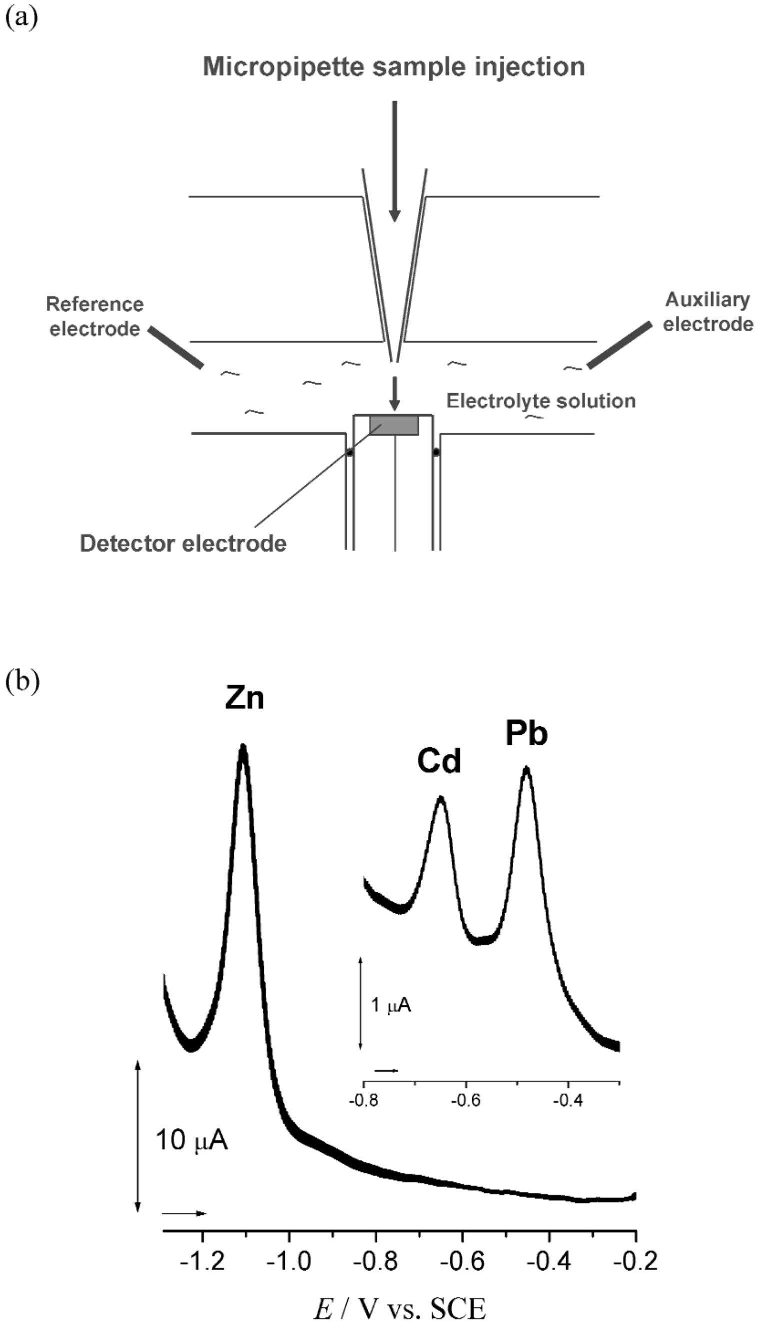


Fig. 2 (a) Scheme of an electrochemical BIA cell. The sample, up to 100 μL volume, is injected using a motorized electronic micropipette directly over the detector electrode which is immersed in electrolyte. The cell is usually constructed in Perspex. Typical micropipette tip internal diameter 0.5 mm, electrode diameter 5 mm. (b) Typical results from BIA with square-wave anodic stripping voltammetry, detection limit 5 nM, at a Nafion-coated mercury thin film electrode on glassy carbon substrate, of a diluted, heavily contaminated water, showing peaks due to three metal cations. The results correspond to 175, 0.33, and 0.36 mg L^{-1} Zn, Cd, and Pb in the original water. Preconcentration potential –1.4 V, for 120 s in 0.1 M acetate buffer, pH 4.45. After treatment to remove the ions from the water, these values decreased to 33, 7, and 5 μg L^{-1} (0.5, 0.062, 0.034 μM), respectively.

In BIA preconcentration methods, such as BIA stripping voltammetry, during injection the accumulation of trace analytes on the electrode surface takes place due to electrodeposition or adsorption, after which a potential scan is applied to oxidize or reduce the accumulated species—it is thus essentially a coulometric measurement. To make the system more robust for continued measurements in the presence of complex media such as industrial or domestic effluents, the electrode surface is protected by a thin polymer film which prevents fouling—an example is a mercury thin film electrode on a glassy carbon substrate coated by Nafion cation-exchange polymer for the measurement of trace metal ions [28,29]. Chemically labile metal cations are transported through the Nafion film and are reduced to the metal, followed by a square-wave voltammetric redissolution scan to positive potentials and quantification of the resulting current peaks: selectivity is achieved by the different potentials of the peaks. The standard addition method is used to determine the concentrations of components in analyte samples. Detection limits are of the order of 5 nm, and the linear range extends until 1 µm. This approach has been used successfully for probing ecotoxicological samples [30] and in measurements in the field of environmental samples both as a diagnostic and also to give quantitative information rapidly [31]. An example is shown in Fig.2b.

Finally, it is possible to carry out some online sample processing in the measuring system and reduce matrix effects by packing a small amount of solid sorbent in the micropipette tip. The sample is aspirated and then washed, the species of interest being held on the sorbent. They are then released by addition of an appropriate eluent. This was successfully tested with Chelex-100 chelating resin for the measurement of trace metal ions in complex matrices [32]. Such an approach can be used in other contexts in the future. It can be conveniently automated, is relatively simple, and is a miniaturized system, since very little sorbent or sample solution is needed.

ELECTROCHEMICAL SENSORS USING CARBON FILM ELECTRODES

Important directions of research in the field of chemical sensors, without moving to the ultimate goal of sensors of the type lab-on-a-chip, is sufficient miniaturization for the sensor to be able to be placed in different key locations, portability, reduction of poisoning problems, and sufficiently inexpensive to be disposable if necessary, as discussed above. To this end, over the last few years, one motivation in our research has involved the development of new materials for electrochemical sensors that are robust and give the necessary performance for use in sensors and biosensors. Additional criteria such as low cost and ease of use have also been taken into account. Some of these materials have involved the use of carbon film electrodes made from carbon film electrical resistors, which are sufficiently inexpensive to be able to be used as disposable electrodes if required. Resistors are fabricated by pyrolysis of methane in a nitrogen atmosphere at 1100 °C onto cylindrical ceramic substrates, typically of 6 mm length and 1.5 mm diameter [33]. As electrical resistors, each end is covered with a metal cap plus external connecting wire, Fig. 3a. To make electrodes, one of the contacts is removed and the other plus wire is covered with plastic tube and epoxy resin; the procedure is quick and effective. Examination of these electrodes by electrochemical techniques of cyclic voltammetry and electrochemical impedance spectroscopy shows that they are at least as good, and often better, than other forms of carbon as electrode material [34,35]. Owing to their small size, they can be inserted in places where larger “normal” electrodes cannot whilst being more robust than microelectrodes. Various types of sensing strategy for sensors and biosensors have been investigated using these electrodes.

An important application investigated is to the measurement of trace metal ions that are common contaminants in environmental matrices, in waters used in industrial processes, etc. Electrochemical methodologies are powerful and allow the measurements to be carried out in the field, as for BIA. The problems that can arise derive from the complexity of the matrices, so that coating the electrodes with an inert polymer coating can be particularly useful. The application of a nanoporous ion-exchange coating prevents the passage of organic and biological molecules, whilst permitting the trace metal ions to pass through. It was demonstrated by electrochemical impedance that they can be used for a long time

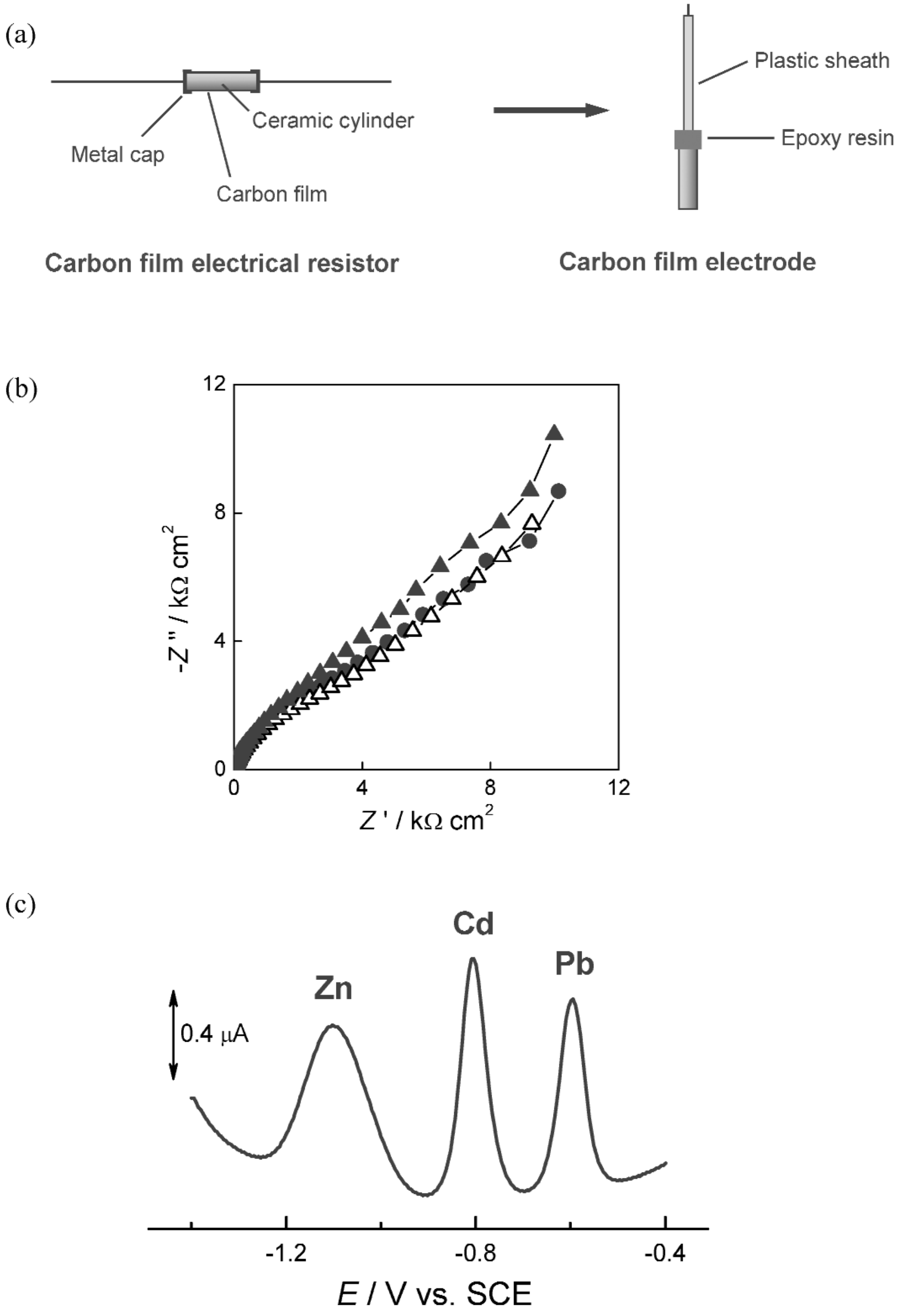


Fig. 3 (a) Fabrication of a carbon film cylinder electrode, diameter 1.5 mm, length 4 mm, from a C film electrical resistor. For disc electrodes, the cylinder surface is covered with epoxy resin, leaving only the end exposed. See text for further details. (b) Complex plane electrochemical impedance plots for Nafion-coated C film disc electrodes at –1.0 V vs. SCE in: (●) pH 4.4 0.1 M acetate buffer solution, (▲) 10^{-7} M [Pb^{2+}] and [Cd^{2+}] + 2 mg L^{-1} Triton in acetate buffer and (△) acetate buffer after stripping voltammetry, showing that there are no memory effects. (c) Anodic stripping voltammetry of 10 µg L^{-1} metal ions at Bi-film-coated carbon film electrode. Preconcentration potential –1.4 V, for 120 s in 0.1 M acetate buffer, pH 4.45.

without causing any changes in the structure of the polymer film after initial reconstruction, Fig. 3b and [35].

Bismuth-film-coated electrodes, formed by electrochemical deposition on carbon film resistor electrode substrates at constant applied potential, by potential cycling or at constant applied current, have been investigated [36]. These films, on carbon substrates, extend the negative potential range of the sensor almost as much as mercury, but without toxic effects. After voltammetric and electrochemical impedance characterization, they were applied to the determination of zinc, cadmium, and lead by preconcentration techniques (Fig. 3c), showing nanomolar detection limits, which augurs well for future application as small, short-term-use sensors. The influence of contaminants in the analyte samples, such as surfactants, can be reduced by polymer coatings [37]; the effect of the coating on electrode response was tested and probed with electrochemical impedance spectroscopy. It was demonstrated that this strategy allows measurement of these trace metals in environmental samples containing surfactants. Using a similar idea, bismuth-film-coated glassy carbon electrodes were used in a flow-injection system for measuring trace metals [38], so that such an approach can also be followed with these carbon film electrodes.

The use of these carbon film sensors in flow systems has been investigated. A dedicated flow cell was designed, and although the application uses an oxysilane sol-gel coated carbon film electrode with redox mediator for enzyme biosensor purposes [39], the cell plus sensor electrode is sufficiently stable to be applied in other contexts. Such sol-gel coatings have been made from a number of different precursors and precursor mixtures, their nanoporosity has been investigated using electrochemical techniques and atomic force microscopy [40], and they may find use as substitutes for other polymer coatings in the future. Choosing the length and polar or nonpolar character of the substituent groups in the oxysilane sol-gel precursor should lead to tailoring of the polymer film porosity. Currently, the influence of toxic metal ions on inhibiting enzyme activity is being probed as a means of measuring toxicity levels.

Finally, electrode processes at carbon film electrodes have been used in several RTILs [41]. After characterization of ferrocene derivatives, they were used to study two sensor redox mediators. With the increasing use of ionic liquids in industrial processes [42], monitoring is a very real concern and the advantages and limitations associated with online chemical sensing need to be addressed. Since RTILs can act simultaneously as solvent and electrolyte, electrochemical sensing is ideally suited for monitoring the process so that such applications hold much promise for the future.

CONCLUSIONS

There is a well-recognized need for real-time monitoring of chemical processes and their products. Some of the considerations to be borne in mind and the directions in which the developments of these devices are heading have been outlined in this article. New devices and monitoring strategies both need to be developed. The extent to which and how rapidly this will occur in the future will be dictated not only by legislative requirements but also by advances in the use of materials and electronics, as well as in fundamental aspects of the chemistry, physics, and biological and toxicological aspects involved. Particular challenges are sample preparation and interfacing of the sensor device with its environment, and ease of use, with a minimum of sample pretreatment. Nevertheless, significant progress can be expected in the coming years.

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REFERENCES

1. P. T. Anastas, J. C. Warner. *Green Chemistry: Theory and Practice*, Oxford University Press, New York (1998).
2. J. Garcia-Serna, J. L. Martinez, M. J. Cocero. *Green Chem.* **9**, 111 (2007).
3. M. Koel, M. Kaljurand. *Pure Appl. Chem.* **78**, 1993 (2006).
4. C. M. A. Brett. *Electroanalysis* **11**, 1013 (1999).
5. C. M. A. Brett. *Pure Appl. Chem.* **73**, 1969 (2001).
6. A. Crawford (Ed.). *Trends Anal. Chem.* **26**, Issue 1 (2007).
7. L. He, C.-S. Toh. *Anal. Chim. Acta* **556**, 1 (2006).
8. J. Riu, A. Maroto, F. X. Ruis. *Talanta* **69**, 288 (2006).
9. G. Wulff, A. Sarhan. *Angew. Chem., Int. Ed.* **11**, 341 (1972).
10. R. Arshady, K. Mosbach. *Makromol. Chem.* **182**, 687 (1981).
11. M. J. Whitcombe, M. E. Rodriguez, P. Villar, E. N. Vulfson. *J. Am. Chem. Soc.* **117**, 7105 (1995).
12. T. P. Rao, R. Kala, S. Daniel. *Anal. Chim. Acta* **578**, 105 (2006).
13. F. Qiao, H. Sun, H. Yan, K. H. Row. *Chromatographia* **64**, 625 (2006).
14. Ph. Quevaullier. *Trends Anal. Chem.* **26**, 52 (2007).
15. J. Ruzicka, E. H. Hansen. *Anal. Chim. Acta* **78**, 145 (1975).
16. E. H. Hansen, M. Miró. *Trends Anal. Chem.* **26**, 18 (2007).
17. G. Chen, Y. Lin, J. Wang. *Talanta* **68**, 497 (2006).
18. D. Barceló, M. Petrovic. *Trends Anal. Chem.* **26**, 2 (2007).
19. R. W. Cattrall. *Chemical Sensors*, Oxford University Press, Oxford (1997).
20. R. Shepherd, S. Beirne, K. T. Lau, B. Corcoran, D. Diamond. *Sens. Actuators, B* **121**, 142 (2007).
21. A. Manz, N. Graber, H. M. Widmer. *Sens. Actuators, B* **1**, 244 (1990).
22. J. de Jong, R. G. H. Lammertink, M. Wessling. *Lab Chip* **6**, 1125 (2006).
23. A. Günther, K. F. Jensen. *Lab Chip* **6**, 1487 (2006).
24. A. Rios, A. Escarpa, M. C. González, A. G. Crevillén. *Trends Anal. Chem.* **25**, 467 (2006).
25. L. Marle, G. M. Greenway. *Trends Anal. Chem.* **24**, 795 (2005).
26. J. Wang, Z. Taha. *Anal. Chem.* **63**, 1053 (1991).
27. C. M. A. Brett. *Comprehensive Chemical Kinetics*, R. G. Compton, G. Hancock (Eds.), **37**, Chap. 16, Elsevier, Amsterdam (1999).
28. C. M. A. Brett, A. M. Oliveira Brett, F.-M. Matysik, S. Matysik, S. Kumbhat. *Talanta* **43**, 2015 (1996).
29. C. M. A. Brett, D. A. Fungaro, J. M. Morgado, M. H. Gil. *J. Electroanal. Chem.* **468**, 26 (1999).
30. C. M. A. Brett, J. M. Morgado. *J. Appl. Toxicol.* **20**, 477 (2000).
31. H. Dias, J. A. P. Piedade, C. M. A. Brett. *Proceedings, Senspol – EU Technical Meeting on Sensors for Characterization and Monitoring of a Contaminated Site*, Sevilla, Spain, S. J. Alcock, M. Valente (Eds.) (2002).
32. M. Trojanowicz, P. Kozminski, H. Dias, C. M. A. Brett. *Talanta* **62**, 394 (2005).
33. C. M. A. Brett, L. Angnes, H.-D. Liess. *Electroanalysis* **13**, 765 (2001).
34. O. M. S. Filipe, C. M. A. Brett. *Electroanalysis* **16**, 994 (2004).
35. C. Gouveia-Caridade, C. M. A. Brett. *Electroanalysis* **17**, 549 (2005).
36. R. Pauliukaite, C. M. A. Brett. *Electroanalysis* **17**, 1354 (2005).
37. C. Gouveia-Caridade, R. Pauliukaite, C. M. A. Brett. *Electroanalysis* **18**, 854 (2006).
38. A. Economou, A. Voulgaropoulos. *Talanta* **71**, 758 (2007).
39. M. M. Barsan, J. Klinčar, M. Batič, C. M. A. Brett. *Talanta* **71**, 1893 (2007).

40. R. Pauliukaite, A.-M. Chiorcea-Paquim, A. M. Oliveira Brett, C. M. A. Brett. *Electrochim. Acta* **52**, 1 (2006).
41. R. Pauliukaite, A. P. Doherty, K. D. Murnaghan, C. M. A. Brett. Submitted for publication.
42. H. Zhao. *Chem. Eng. Commun.* **193**, 1660 (2006).