PERSPECTIVES FOR ELECTROANALYSIS WITH SOLID AND HYDRODYNAMIC ELECTRODES

Christopher M.A. Brett and Ana Maria C.F. Oliveira Brett

Departamento de Química, Universidade de Coimbra,

3049 Coimbra, Portugal

ABSTRACT

Recent advances in the use of solid electrodes in electroanalysis are reviewed and future directions indicated, focussing particularly on hydrodynamic and pulse techniques and new electrode materials.

KEYWORDS: electroanalysis, solid electrodes, hydrodynamic electrodes, pulse voltammetry, stripping voltammetry, electrode materials, biosensors.

INTRODUCTION

Analysis by electrochemical methods has grown tremendously in recent years, reflected in the relevance given to electrochemistry in special issues of journals devoted to physical and general chemistry [1]. It is now generally recognised that electrochemical sensors form an important part of techniques available for analytical use. This is particularly so when answers are required rapidly, and the sample to be analysed is already in the form of a solution. Electrochemical detectors are well suited to use in flow systems [2] and can be used on line, more difficult with other types of technique. Most of the important recent advances have been in systems involving forced convection and with new solid electrode materials. In this review we will concentrate on these two aspects. We are mindful of the important contributions made at liquid mercury electrodes, i.e. polarographic techniques, but the subject has already been treated in some depth [3]. The emphasis will be on why particular methods are used and perspectives for their future use.

The reasons for the recent surge in electroanalysis can be traced to a number of factors, besides their useful application to on-line

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analysis. Firstly, advances in instrumentation mean that the degree of understanding required by the experimentalist doing routine analysis is reduced to that necessary for other analytical techniques such as atomic absorption spectroscopy. Secondly, better understanding of the fundamentals of electrode processes and methods to study them [4] has enabled the development of relatively sophisticated electrochemical sensors that give reliable, reproducible results. The investigation of the fundamentals of any new electrode reaction to be used for electroanalysis is important, so as any nuances in the mechanism of the electrode reaction or interferences which might affect the response will be detected, and the correct interpretation of the results made.

Electroanalysis at present is particularly useful when we are interested in good accuracy, particularly near the detection limits, the precision being a little less important. To test unknown samples we can either construct calibration curves and work directly from these, or use theoretical equations. Best confidence in the results will be obtained when we can use both simultaneously.

STRATEGY FOR USING ELECTROCHEMICAL SENSORS

The most commonly used electroanalytical techniques can be divided into potentiometric and amperometric (fixed potential/current) or voltammetric (varying potential/current). Since the former rely on measurements of equilibrium potential at zero current, to be useful sensors the electrode material needs to be selective to a particular species. For the latter, selectivity results only partly from the electrode material, depending much more on the applied current/potential and possibly the electrolyte; judicious control of these and the transport of species to the electrode surface by forced convection can increase the sensitivity and reproducibility and improve the detection limit of the experiment. Species which are electrochemically active at small applied potentials (i.e. roughly -1.3V to +1.3V vs SCE in aqueous solution) can be detected voltammetrically. The kinetic factors are a function of electrode material and applied potential, which hopefully we can tailor to the aim of easy results without interferences..

The decision on whether to use a particular analytical technique can be complex. Electrochemical sensors are, as shown above, uniquely suitable for analysis in flowing streams and for on-line analysis. Other advantages are:

(a) Portability and, for flow-through detectors, easy placement at any point in a flow system;

(b)Facile automation, particularly given that the response of the system is already an electrical signal. This enables automatic periodic calibration;

(c) Relatively small capital expenditure.

The interests of accuracy, reproducibility and high sensitivity determine the way we control the current or potential of an amperometric sensor or electrode material and pre-conditioning of a potentiometric sensor. It is best to choose conditions where the effect of the kinetics of the electrode reaction is negligible, or at least well defined.

For a non-equilibrium process, and assuming that migration effects can be neglected in the presence of a sufficiently large quantity of inert electrolyte, the electrode reaction is described by the equation

$$\partial c/\partial t = D\nabla^2 c - v\nabla c + \text{kinetic terms} \qquad (1)$$

for each species i, with the appropriate boundary conditions. ∇ is the Laplace operator, v is the fluid velocity caused by convection and the kinetic terms represent any homogeneous reactions coupled to the electrode reactions. Without these we have pure diffusion (Fick's 2nd Law). Applying a potential step or pulse, initially the concentration gradients close to the electrode surface will be very high, resulting in large currents that decay with time. On the other hand if we arrange for $\partial c/\partial t = 0$, then we have a steady state; this can be achieved by constant forced convection at fixed applied potential/current. Use of both these strategies gives a powerful set of electroanalytical techniques.

The capacitative current that appears on changing the potential of the electrode, if not corrected for, can limit the usefulness of these techniques through

$$i_c = C_d(dE/dt) \qquad (2)$$

where C_d is the differential capacity of the electrode/solution interface. In the steady-state there is obviously no capacitative contribution. Fortunately in the other cases i_c decays faster than the faradaic current, i_f, so that judicious current sampling in potential pulse techniques can resolve the problem. Alternatively, one can use a subtraction technique relying on the fact that C_d is due almost entirely to the inert electrolyte and not to the electroactive species.

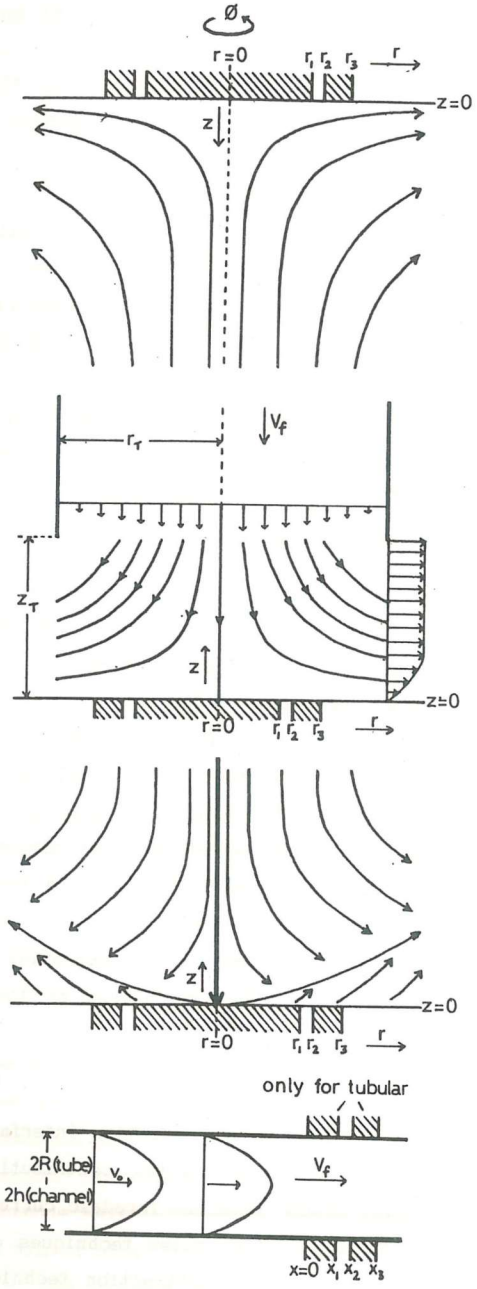

Fig.1 Laminar flow patterns at commonly used hydrodynamic electrodes, coordinates and electrode configuration; for symbols see Table 1.

HYDRODYNAMIC TECHNIQUES

The enhanced mass transport caused by forced convection increases sensitivity, and reproducibility; the dependence of the electrode response on the physical properties of the solution is weak. These factors are extremely useful in the study of electrode kinetics, but also for electroanalysis [5]. In general one arranges for $\partial c/\partial t = 0$ (although this is not the case if the applied potential or current varies faster with time than the electrode response). Thus, in the absence of coupled homogeneous reactions the governing equation is

$$D\nabla^2 c = v\nabla c \qquad (3)$$

for each electroactive species. Since the current is greatest when all electroactive species react, for electroanalytical purposes the best is to fix the applied potential at a value corresponding to the diffusion limited current plateau. If the solution flowing past the electrode has constant composition, then a constant current will be measured. If, at the other extreme, we inject a small volume of sample into a stream of flowing electrolyte, such as in HPLC with electrochemical detection or flow injection analysis (FIA) [6,7], a peak will appear in the i vs. t plot - in general, peak height is proportional to concentration. High sample throughputs are possible. This configuration is referred to as an amperometric sensor, as the applied potential does not vary.

Commonly used hydrodynamic electrodes are shown in Fig.1, together with the streamlines for laminar flow. In all cases, except for the rotating electrode, the electrode is fixed and the solution moves, thus being directly usable in a flow system for on-line electroanalysis or FIA. Although the forced convection caused by electrode movement (rotating electrode) is in principle a discontinuous process, it could be coupled into a flow system designed such that the solution flow does not perturb the hydrodynamics. The correct operation of hydrodynamic electrode detectors under diffusion-limited current conditions is a prerequisite for their electro-analytical use: the equations for the hydrodynamic detectors of Fig.1 are given in Table 1.

A hydrodynamic electrode voltammetric sensor has clear advantages over amperometric for a fuller elucidation of the content of a solution. For flow-through sensors this may imply the necessity of a fast potential scan if solution composition varies with time. How this can be achieved will be described in following sections.

Table 1. Diffusion-limited currents at commonly employed hydrodynamic electrodes under laminar flow conditions[a]

Rotating disc/ring[b,c]	$i_L = 1.554nFD^{2/3}\nu^{-1/6}W^{1/2}C_\infty\pi(r_n^3-r_{n-1}^3)^{2/3}$
Wall-tube disc/ring[b,c]	$i_L = 1.53nFD^{2/3}\nu^{-1/6}(V_f/r_T^3)^{1/2}C_\infty\pi(r_n^3-r_{n-1}^3)^{2/3}$
Wall-jet disc/ring[c]	$i_L = 1.38nFD^{2/3}\nu^{-5/12}V_f^{3/4}a^{-1/2}C_\infty(r_n^{9/8}-r_{n-1}^{9/8})^{2/3}$
Tubular	$i_L = 5.43nFD^{2/3}V_f^{1/3}C_\infty x_1^{2/3}$
Channel	$i_L = 0.925nFD^{2/3}V_f^{1/3}C_\infty(h^2d)^{-1/3}wx_1^{2/3}$

[a] Adapted from Ref.8.
[b] Rotating disc and wall-tube disc electrodes are uniformly accessible.
[c] Disc electrode; n=1 and r_1 is disc radius. Ring electrode; n=3, r_2 is inner and r_3 is outer disc radius.
Symbols; W rotation speed, Hz; V_f volume flow rate; r_T radius of wall-tube; a diameter of impinging jet; x_1 length of tubular/channel electrode; h half-height of channel; d width of channel; w width of channel electrode.

Double hydrodynamic electrodes [5,9,10] can also be very useful in electroanalysis. In the steady state a certain fraction of species which are produced at the upstream electrode reach the downstream electrode - the steady-state collection efficiency, N_o. N_o is solely a function of geometric parameters and independent of the degree of forced convection (assuming laminar flow), but is reduced if the upstream electrode products decompose (1st order kinetics) or react with a species in solution (2nd order kinetics). The latter can be used to probe the concentration of non-electroactive species by measurement of the downstream electrode current. An example is production of bromine from bromide and reaction with proteins [11] previously separated in an HPLC column.

Another, little exploited, aspect of double electrodes which can be advantageous, is shielding of the downstream electrode by the upstream electrode [9]. Supposing that the solution contains, in addition to what we wish to analyse, an interferent that reacts with the electrode reaction product, for example. A fraction of the interferent can be removed at the

upstream electrode, described by the shielding factor. This removal will be most effective when the distance between upstream and downstream electrodes is small and when the latter is thin in relation to the former.

With respect to potentiometric sensors, it is a simple matter to introduce their tips into flow streams. Problems that can arise are solution movement between indicator and reference electrodes leading to non-stable equilibrium potentials, and enhanced leaching of species from or dissolution of the indicator electrode surface [12].

POTENTIAL STEP AND PULSE TECHNIQUES

The high initial current and associated concentration gradient on application of a potential step, or a series of potential steps at stationary electrodes, is an alternative way of probing solution composition, which has had much success [13]. The simultaneous capacitative current (which fortunately decays with t rather than with $t^{1/2}$ for the faradaic current) makes current sampling too rapidly after application of the perturbation prone to error, so that much of the increased sensitivity can be lost without appropriate measures being taken. If a succession of potential pulses is applied we have possible extra advantages of:

(i) Causing the maximum variation in the concentration gradient at the electrode surface, i.e. maximum sensitivity;

(ii) Minimising the blocking effect of interfering adsorbable substances in the region of the redox reaction;

(iii) In stationary solution minimising the depletion of electroactive species.

The schematics of the commonly used techniques are shown in Fig.2: the "direct" technique of normal pulse voltammetry (and its complement reverse pulse voltammetry, where the base potential is on the diffusion-limited current plateau and the pulses are backwards, useful for probing the products of the electrode reaction) and the differential techniques.

As originally evolved at the DME, these techniques permitted one independent pulse per mercury drop - the theoretical analysis of the response was relatively simple. At solid electrodes the theoretical problem is more complex, since the current observed for each pulse may be dependent on the previous history of transport of electroactive species. For differential pulse voltammetry at solid electrodes where this is the case, it has been shown theoretically by numerical calculation that peak

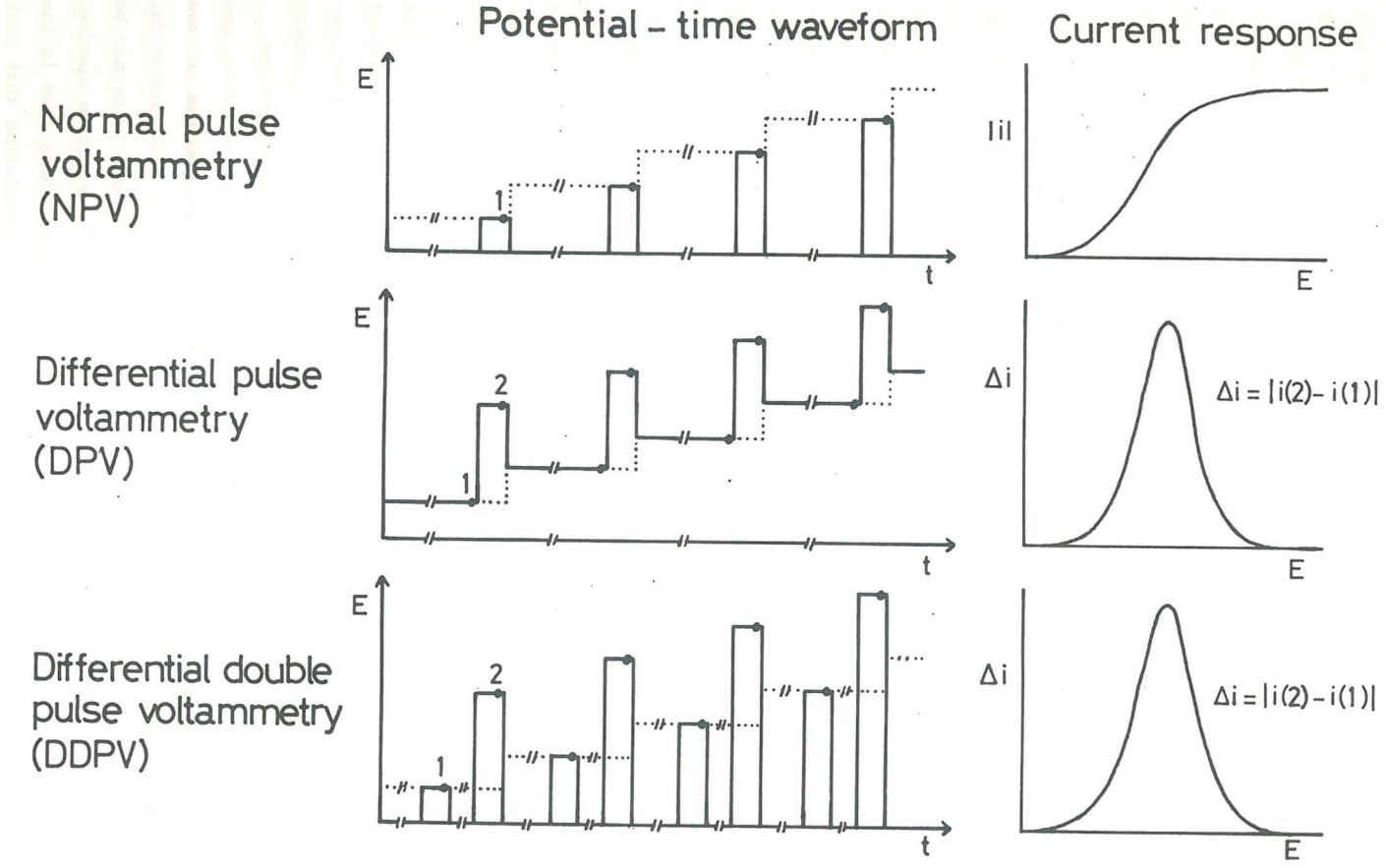

Fig.2 Pulse voltammetric techniques, potential-time waveform and current response, showing their relation to staircase voltammetry (dotted line); current sampling (●) just before end of pulse. Pulse widths typically 5→50ms and staircase step width 0.5→5s; step height 10/n mV and pulse height 50/n→100/n mV. In square wave voltammetry 'pulse width' 0.5→100ms and staircase step width 1→200ms.

current should nevertheless be proportional to bulk concentration [14], a confirmation of experiment. Differential double pulse [15] and differential normal pulse [13] voltammetry are ways of avoiding this "memory" problem and also reducing to an absolute minimum the time spent in electrolysis and discriminating against capacitative currents by subtraction. This is important because a typical scan can take up to 200s.

In pursuing the goals of elimination of capacitative currents and the blocking effect of adsorbable substances, the pulse techniques described above have been quite successful. In terms of rapidity however, the relatively newly exploited technique of square wave voltammetry [16] is far superior, and satisfies the other criteria: capacitative currents are virtually eliminated by direct subtraction and the experiment is done in 2s so that very little time is available for adsorption to occur. Additionally, on the diffusion-limited current plateau the difference current registered will be zero (see Fig.2), facilitating the elimination of an unwanted interferent in the zone of interest such as oxygen. Detection limits and sensitivity are better than for differential pulse, although the advantage becomes small for irreversible reactions. Thus it is quite reasonable to assume that square wave will be the pulse technique to be preferred in the future. The reason for its appearing only recently is due to the need for microprocessor based instrumentation to operate efficiently.

PRE-CONCENTRATION METHODS

The detection limits of any of the techniques mentioned above can be decreased by pre-concentration methods, often referred to globally as stripping voltammetry [17] (this is in reality a misnomer since in adsorptive stripping voltammetry the species usually remains on the electrode and is not "stripped"). Essentially the methods consist in a pre-concentration step on the electrode surface and a determination step - the difference in time scale between the two steps decreases the detection limit. Table 2 shows the types of experiment that can be performed. Many of these applications are at solid electrodes or at mercury thin film electrodes (MTFE) deposited on a solid substrate such as glassy carbon - this latter offers higher sensitivity than the HMDE and can be used in hydrodynamic detectors. The determination step, if potential controlled, relies generally on the proportionality between

Table 2. Electrochemical preconcentration methods for determination of trace species in solution[a]

Method	Preconcentration step control variable	Stripping step control variable	Measurement
Stripping voltammetry	Potential	Potential	i vs. t
Adsorptive stripping voltammetry	Adsorption (with/without applied potential)	Potential	i vs. t
Potentiometric stripping analysis	Potential	Reaction with oxidant or reductant in solution (no applied potential)	E vs. t
Stripping chronopotentiometry	Potential	Current	E vs. t

[a] Adapted from Ref.18.

peak height and concentration, obtained by linear scan, differential pulse or square wave stripping. Conventionally although the determination step was carried out with convective-diffusion, the determination step was in stationary solution which has obvious drawbacks for use in flow systems, for example. Recently it has been shown that anodic stripping from mercury thin film electrodes in flowing solution does give useful experimental results [19], and wave shape and position for linear scan stripping have been explained theoretically at rotating and wall-jet electrodes [20]. Square wave stripping holds considerable promise for the future in this area judging by preliminary work [21]. An alternative is the hydrodynamic double electrode collection technique where the stripped species from the upstream electrode is collected at the downstream electrode and the area of the current peak measured [18]: the collection technique will probably find most application in systems where the double electrode is already being used for other determinations.

Problems that arise in pre-concentration methods result primarily from interferences in mixtures in analytes, especially in MTFE's where intermetallic compounds can be formed. Although these can often be removed by judicious subtraction of signals obtained in different

experiments or addition of appropriate complexing agents, in the future one expects more use will be made of tailoring the electrode material to the specific needs of the experiment. This is particularly pertinent in the analysis of biological fluids - at present elaborate pre-treatment procedures are necessary [22].

ELECTRODE MATERIALS - MODIFIED SURFACES

The choice of an electrode material for electroanalysis depends on its usable potential range, surface reactions, usable time span without surface renewal and kinetic considerations. Most solid electrode materials form oxides on their surfaces in aqueous solution in certain potential zones and cannot be regarded as inert - this fact can however be exploited, as in the anodic generation of platinum oxide at platinum electrodes in achieving oxidative desorption of adsorbed (principally organic) species and consequently higher currents [23]. At negative potentials there is no doubt that mercury offers significant advantages: in the form of a thin mercury film on a suitable solid substrate it can be used, removed and renewed as required. Nevertheless, the necessity that the substrate does not dissolve in mercury and that the latter forms a thin uniform layer limits the range of possible substrates considerably [24]. Glassy carbon, whilst not perfect, is the preferred substrate for mercury films at present, although it seems that iridium may offer some advantages. Procurement of better substrates is one direction of research. In favour of glassy carbon is that it can be used at positive potentials simply by removing the mercury film electrolytically and without changing the electrode, being versatile in this sense.

The strategy in investigating new electrode materials is seeking greater selectivity and specificity and materials which are not blocked rapidly by use in organic and biological matrices. The answers to these questions will probably be found in the modification of the electrode surfaces [25] in one of three ways:

- creation of a porous film over the electrode surface that physically excludes species over a certain size from reaching the electrode. For example, partially hydrolysed cellulose acetate coatings have been used to exclude proteins [26], and Nafion has been used to reduce interference from surface-active substances in anodic stripping voltammetry [27]. Obviously the thickness of the coatings must not be too great, or the electrode response time will be affected.

- a chemically modified surface, the attached groups having an electrocatalytic effect. This can also be very useful for biological compounds that easily block the unmodified electrode surface, such as reduction of haemoglobin and myoglobin at methylene blue modified graphite [28].

- a non-porous conducting polymer film on the surface of which the electrode reaction occurs; hopefully it will be catalysed and parallel reactions inhibited. There is, in this way, a possibility of analysis of non-electroactive species by homogeneous reaction with the covering [29]: this affects the current that is passed on cycling the applied potential.

DETECTORS AND INSTRUMENTATION

The new generation of microprocessor-based instruments permits a flexibility in the generation of signals to apply to an electrochemical cell and analysis of the response, especially when microcomputer controlled [30]. This advance has contributed in a very large way to the evolution of electroanalysis, especially pulse techniques [31]. There is still a place for dedicated, non-flexible, instruments for routine analysis. Both types and intermediate versions will no doubt be seen. The 'black-box' aspects such as signal filtering in all types of instrument with automatic or semi-automatic operation must be treated with caution - these can be much more problematic in digital than in analogue instruments as electrical noise tends to be enhanced. Nevertheless, the possibilities are tremendous: collection of much information in a short space of time, allowing both quantitative analysis and species identification with much reduced ambiguity, as exemplified by chromatovoltammograms [32].

A related problem is in instrumental detection limits: the limit is determined by the signal to noise ratio, with high quality modern integrated circuits 10^{-12}A can be measured with confidence [33]. The important fact is that this is much better than the detection limit determined by the electrochemical system parameters.

Instrumentation for a.c. voltammetry has also undergone improvements. A.c. techniques are very powerful for electrode reaction mechanism diagnostic and can be used as a concentration probe [34]. Application of the Fourier transform to a.c. voltammetry experiments [35] should increase the rapidity and amount of information collected, making it an extremely viable alternative in electroanalysis.

Detector design can be very important in determining sensitivity. In principle one should go for high solution transport, such as in flow systems [36,37], and a high percentage electrolysis. The latter implies a thin-layer cell or porous electrode - however, both these produce constraints on flow system design with regard to pressure differences. A low efficiency electrolysis together with increased ease of maintenance of cell parts, such as the wall-jet or tubular configurations, may be preferable. Since rapid data collection implies that the electrode reaction can be studied at the same time that concentrations are being measured with voltammetric techniques, the different kinetics on different sections of a non-uniformly accessible electrode may be of interest. This can also act as a check on the electrode reactions over a period of time.

ELECTROANALYSIS IN BIOLOGY AND MEDICINE

The advances described above with respect to pulse techniques, electrode materials, instrumentation etc. mean that application of electrochemical sensors to complex organic compounds [38] and biological matrices [39], is becoming more a reality. Analyses *in vitro* [40] and *in vivo* [41] are both important. For *in vivo* studies microelectrodes [42], are almost obligatory as well as their biocompatibility - carbon electrodes seem to be good in this regard. In any case the use of enzyme-modified electrode biosensors [43] will increase specificity - present problems of electrode lifetime are being currently addressed. An *in vivo* sensor must also have a fast response time (<30s) and not be affected by other components of the biological fluid, which may be at abnormal levels, and it is not feasible to replace the electrode with great frequency. Whereas the future of *in vivo* sensors for research on experimental animals into metabolic pathways, stimuli response, drug action etc. seems assured, in clinical medicine with human patients the stringent criteria with regard to safety, reliability and possible infection risks may mean that the use of electrochemical or any other type of *in vivo* biosensor is a long way from being medically acceptable. In external analyses, however, the criteria are less stringent. For instance, one of the most studied systems, glucose, due to its importance for diabetics, now has a commercialised throw-away-enzyme-electrode amperometric sensor; the goal would be a reusable sensor with immobilised enzyme where the enzyme is regenerated amperometrically.

REFERENCES

1. J. Chem. Ed., April 1983; J. Chem. Soc. Faraday Trans. I, April 1986; Chem. in Britain, December 1986.
2. K. Štulik and V. Pacakova, "Electroanalytical Measurements in Flowing Liquids", Ellis Horwood, Chichester, 1987.
3. A.M. Bond, "Modern Polarographic Methods in Analytical Chemistry", Dekker, NY, 1980.
4. A.J. Bard and L.R. Faulkner, "Electrochemical Methods: Fundamentals and Applications", Wiley, NY, 1980.
5. C.M.A. Brett and A.M.C.F. Oliveira Brett, "Hydrodynamic Electrodes", in Comprehensive Chemical Kinetics Vol.26 ed. C.H. Bamford and R.G. Compton, Elsevier, Amsterdam, 1986, Chapter 5.
6. G. Nagy, Zs. Feher and E. Pungor, Anal. Chim. Acta, 1970,**52**,47.
7. J. Ruzicka and E.H. Hansen, "Flow Injection Analysis", 2nd Edn., Wiley, New York, 1988.
8. C.M.A. Brett, Port. Electrochim. Acta, 1985,**3**,259.
9. S. Bruckenstein and B. Miller, Acc. Chem. Res., 1977,**10**,54.
10. W.J. Albery and M.L. Hitchman, "Ring Disc Electrodes", Clarendon Press, Oxford, 1971.
11. W.J. Albery, L.R. Svanberg and P. Wood, J. Electroanal. Chem., 1984,**162**,45.
12. K. Toth, J. Fucsko, E. Lindner, Zs. Feher and E. Pungor, Anal. Chim. Acta, 1986,**179**,359.
13. J.G. Osteryoung and M.M. Schreiner, CRC Crit. Rev. Anal. Chem., 1988,**19**,S1.
14. K. Aoki, K. Tokuda and H. Matsuda, J. Electroanal. Chem., 1984,**175**,1.
15. R.F. Lane and A.T. Hubbard, Anal. Chem., 1976,**48**,1287.
16. J. Osteryoung and J.J. O'Dea, Electroanalytical Chemistry ed. A.J. Bard, Dekker, NY, Vol.14,1986,pp.209-308.
17. J. Wang, "Stripping Analysis. Principles, Instrumentation and Applications", VCH Publishers, Deerfield Beach, Florida, 1985.
18. C.M.A. Brett and M.M.P.M. Neto, J. Chem. Soc. Faraday Trans. I, 1986,**82**,1071.
19. H. Gunasingham, K.P. Ang and C.C. Ngo, J. Electroanal. Chem., 1986,**215**,123.
20. C.M.A. Brett and A.M.C.F. Oliveira Brett, J. Electroanal. Chem., 1989, in press.

21. C. Wechter, N. Sleszynski, J.J. O'Dea and J. Osteryoung, Anal. Chim. Acta, 1985,**175**,45.
22. J. Wang, J. Electroanal. Chem., 1982,**139**,225.
23. D.C. Johnson, J.A. Polta, T.Z. Polta, G.G. Neuberger, J.Johnson, A.P.-C. Tang, I.-H. Yeo and J. Baur, J. Chem. Soc. Faraday Trans. I, 1986,**82**,1081.
24. S.P. Kounaves and J. Buffle, J. Electroanal. Chem., 1987,**216**,53.
25. R.W. Murray, Electroanalytical Chemistry ed. A.J. Bard, Dekker, NY, Vol.13, 1984, pp.191-368.
26. J. Wang, T. Golden and R. Li, Anal. Chem., 1988,**60**,1642.
27. B. Hoyer, T.M. Florence and G.E. Batley, Anal. Chem., 1987,**59**,1608.
28. J. Ye and R.P. Baldwin, Anal. Chem., 1988,**60**,2263.
29. e.g. L.M. Wier, A.R. Guadalupe and H.D. Abruña, Anal. Chem., 1985,**57**,2011; J. Ye and R.P. Baldwin, Anal. Chem., 1988,**60**,1982.
30. P. He, J.P. Avery and L.R. Faulkner, Anal. Chem., 1982,**54**,1313A.
31. e.g. J. Tacussel, P. Leclerc and J.J. Pombon, J. Electroanal. Chem., 1986,**214**,79; A.M. Bond, I.D. Heritage and W. Thormann, Anal. Chem., 1986,**58**,1063.
32. R. Samuelsson, J.J. O'Dea and J. Osteryoung, Anal. Chem., 1980,**52**,2215.
33. S.G. Weber and J.T. Long, Anal. Chem., 1988,**60**,903A.
34. D.E. Smith, CRC Crit. Rev. Anal. Chem., 1971,**2**,247.
35. D.E. Smith, Anal. Chem., 1976,**48**,221A,517A.
36. H.B. Hanekamp and H.J. van Nieuwkerk, Anal. Chim. Acta, 1980,**121**,13.
37. R.J. Rucki, Talanta, 1980,**27**,147.
38. W.J. Albery, B. Fleet and A.M. Oliveira Brett, J. Appl. Electrochem., 1984,**14**,550.
39. B. Hoyer and T.M. Florence, Anal. Chem., 1987,**59**,2839.
40. J.D. Czaban, Anal. Chem., 1985,**57**,345A.
41. e.g. D.J. Claremont and J.C. Pickup in "Biosensors" ed. A.P.F. Turner, I. Karube and G.S. Wilson, OUP, 1987, Chapter 20; R.M. Wightman, L.J. May and A.C. Michael, Anal. Chem., 1988,**60**,769A.
42. M. Fleischmann, S. Pons, D.R. Rolison and P.P. Schmidt eds., "Ultramicroelectrodes", Datatech Systems Inc., Morganton, NC, 1987.
43. J.E. Frew and H.A.O. Hill, Anal. Chem., 1987,**59**,933A.

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Determination of copper by adsorptive stripping voltammetry of its complex with diazo-1H-tetrazole

Josino C. Moreira and Arnold G. Fogg

Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire, LE 113TU, UK

Introduction

Copper is an essential element to all living organisms. It takes part in a range of biological processes, from electron transport to oxidation of a range of substrates [1,2]. As an essential element and because of the ability to form complexes with organic substances, copper is virtually present in all living tissues [3]. Despite its essentiality copper is also toxic . In some cases, the gap between the concentration levels where copper is essential or toxic is very narrow [4]. This and the low concentration of copper found in the environment make it necessary to use very sensitive analytical procedures for its determination.

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