MICROELECTRODES IN ANALYSIS

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Abstract

Although electroanalytical techniques are familiar to most analysts, few will fully recognize the new opportunities offered by replacing a conventional electrode by a microelectrode (an electrode with at least one dimension smaller than 100 μm, commonly 1-10 μm). Hence, the purpose of this review is to emphasize the application of microelectrodes in analysis. The use of microelectrodes can improve both sensitivity and selectivity in the laborarory and also extend the use of voltammetric methods to, for example, on-line analysis in flowing streams, *in vivo* monitoring, gas chromatographic detection and direct analytical determinations in media as diverse as pure water, oil and strawberries!

Introduction

In the context of this review microelectrodes are defined as electrodes with at least one dimension smaller than 100 μm, typically 1-10 μm [1]. During the last ten years their advantageous properties for many electrochemical experiments have become recognized and today they are well established as powerful tools in many areas of research [1-7]. The properties and advantages of microelectrodes have been described by several authors and it is not the intention to repeat this material here. The purpose is to review present thinking about their role in analysis.

The most common geometry of microelectrodes is the disc. Inlaid discs can be prepared by sealing carbon fibers or microscopic wires of noble metals into glass tubes and exposing the cross section of the wire. Other geometries such as cylinders, bands, lines, spheres, rings and arrays, however, have been used; each present their own specific advantages. Materials of manufacture include Hg, C, Pt, Au, Ir, Cu, Ni, etc., while the insulating surround is commonly glass or epoxy resin.

The electrochemical response at microelectrodes may differ greatly from that observed at conventional sized electrodes and this is because the diffusion flux to the electrode surface is very large leading to high steady-state current densities, which are insensitive to convection. Other unique features of microelectrodes include (a) reduced

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ohmic losses in the cell, allowing measurements to be carried out in highly resistive media, (b) low polarization currents, which lead to the use of two-electrode systems and the elimination of expensive equipment, and (c) a reduced capacitive component of the current, enhancing the signal-to-noise ratio.

In 1981, a paper by Wightman [8] catalysed the development of the theory and applications of microelectrodes and since then, publications in this field have appeared at an increasingly fast rate. It is expected that this interest will continue and that in the near future microelectrodes will be used routinely for investigations in electrochemistry and many other fields of science and technology.

The advantages of applying microelectrodes in analysis derive, firstly, from the high steady state rate of diffusion which (a) improves rate of concentration in techniques such as anodic stripping voltammetry and (b) leads to a high steady state current in voltammetry and, hence, to increased sensitivity for steady state measurements. In non-steady state experiments it is possible to obtain good quality responses at very short times. Hence, it is possible to reconsider cyclic voltammetry at high scan rates for analysis (e.g., good quality cyclic voltammetry is easy to obtain at 1000 Vs^{-1} and pulse voltammetry with measurements of current at less than 1 ms intervals. This may lead to lower detection limits in analytical applications. Also, much smaller volumes of the analyte solution are required, not only because the electrode has smaller dimensions but also due to the simplicity of a two-electrode cell configuration. Moreover, direct electrochemical measurements (without sample preparation) may now be possible in media of low conductivity such as foodstuffs and pure water. On the other hand, since diffusion can be the predominant mode of mass tranfer to microelectrodes, even in conditions of forced convection, they can be used as detectors in flowing systems. Since the interference from iR drop is minimal they can be used successfully as highly sensitive detectors in gas and liquid chromatography without addition of electrolyte or solvent.

Microelectrodes are also particularly attractive for the determination of chemical concentrations in the mammalian brain. Neurotransmitters, for example, have a very important role in the brain since they provide the communication link between neurons. The very small size of these electrodes allow their implantation in the brain and, therefore, to follow *in vivo* the changes in chemical concentrations as a result of a variety of stimulations. Moreover, the currents obtained are very small and, therefore, virtually non-destructive of the species being electrolysed.

In addition to the advantages described above, it should be emphasized that experiments with microelectrodes are based on sound fundamental concepts and that the circuitry and cells used in microelectrode experiments are often simple and inexpensive. Certainly, very simple and cheap electronics will suffice for many analyses.

Difficulties with the preparation of microeletrodes have been cited as a problem. In fact, this view point has probably been overemphasized Particularly, microdiscs are commonly made by the users in their own laboratory and the difficulties are rapidly overcome provided the dimensions are above a few μm. Certainly, in the submicrometer region, real difficuties appear in the fabrication but, then, most analytical applications do not require such small sizes. Comercial microdiscs are now provided by a number of suppliers such as Biolanalytical Systems and EG&G Princeton Applied Research but the cost is relatively high. Moreover, microfabrication techniques, such as vapor deposition and screen printing, commonly used in the microelectronics industry, will in the future allow the manufacture of line microelectrodes in large numbers at low cost and, therefore, it is easy to envisage, in the near future, the use of microelectrodes as inexpensive, disposable sensors in a variety of applications. Both discs and line microelectrodes are very suitable for analysis.

Because microelectrode dimensions are very small, the measured currents are normally in the range 10^{-10} to 10^{-6} A and noise can be a problem if the system is poorly designed. It is generally found, however, that modern electronics and the appropriate use of shielding provide good quality data free of noise.

Finally, it should be pointed out that fouling in microlectrodes may be a more difficult problem than in electrodes of conventional size because low concentration impurities will collect more rapidly (again due to the higher diffusive flux). Still, many analytical applications are exemplified in the literature that are not affected by electrode poisoning.

In the following examples, it will be shown that microelectrodes allow the use of voltammetric methods to be successfully extended to non-conventional media (i.e., media without electrolyte, gas phase), used as detectors in flowing systems, and as sensors for in *vivo* determinations. Furthermore the sensitivity and selectivity are improved when compared to conventional size electrodes.

Determination of Metal Ions

In the analysis of metal ions, mercury is the electrode material with most favorable electrochemical properties and is often used in conjunction with stripping techniques. Mercury microelectrodes have been prepared by electrodeposition of mercury ions onto substrates such as carbon, iridium and silver.

Potentiometric and voltammetric stripping analysis [9] have both been used coupled to mercury microelectrodes, the first method differing from the second in that the preconcentrated analyte is stripped chemically rather than electrochemically. A very important advantage of the use of microelectrodes in stripping analysis is the possibility

of carrying out determinations of multicomponents in extremely small volumes of solution. Also, the microelectrode accumulates metal into the mercury much more rapidly (due to high rates of diffusion) and, hence, stirring is not required during the deposition step and the deposition time may be short. Furthermore, the metal is accumulated during the electrodeposition period in a very small volume of electrode and, therefore, is completely reoxidised during the anodic scan. This feature gives rise to well defined and abrupt peaks similar to those observed with mercury films. The sensitivity of stripping techniques are greatly enhanced at microelectrodes.

In potentiometric stripping analysis, the measured potential is independent of the area of the electrode. Some preliminary results were presented by Baranski *et al* [10] in the determination of Cd^{2+}, Pb^{2+} and Cu^{2+}, in concentrations of 5×10^{-6} mol dm^{-3} in the presence of Hg^{2+}, in a 10^{-4} mol dm^{-3} concentration. Using the same technique Jagner *et al* [11] report results for the determination of Cd^{2+}, Pb^{2+}, Cu^{2+} and Bi^{2+} in a flowing stream (the response is independent of flow rate).

Anodic stripping voltammetry employing mercury films is one of the most sensitive techniques in the analysis of heavy metals. Carbon fibers are often used as the base material for mercury film electrodes and their properties have been reviewed [12, 13].

Several authors used mercury coated microdiscs by electrodeposition of mercury at constant potential and negative enough to ensure diffusion control. In the lead analysis it was observed that the peak currents are proportional to the concentration in the region 7×10^{-10} - 1×10^{-7} mol dm^{-3} (with only 5 minutes of pre-concentration) and the precision was superior to that obtained with conventional stripping techniques [14]. The sensitivity of this method increases with sweep rate and Cd^{2+} and Pb^{2+} were detected at sweep rates between 1 and 100 V s^{-1}. The detection limit was close to 5×10^{-9} mol dm^{-3} for only 10 s of pre-concentration time [15]. These ions were also determined using short pulse rapid scan stripping voltammetry and figure 1 presents a typical voltammogram for a solution containing Pb^{2+} and Cd^{2+}, demonstrating that the peaks obtained are sharp and well defined for concentrations below 1 μg dm^{-3} and deposition periods of 60 s [16].

Mercury coated carbon discs were used for the determination of Cd(II) using square wave anodic stripping voltammetry [17]. Microelectrodes offer several useful features when employed for square wave voltammetry since the charging current can be virtually eliminated and the current generated may be demodulated by a lock-in amplifier to provide high sensitivity voltammetric analysis [18,19].

The capabilities of mercury film microelectrodes were explored in the detection of metals in media of low ionic strength, such as aquatic systems [20]. Solutions containing known concentrations of ligands and metal were analysed using anodic stripping voltammetry and the potentialities of microelectrodes in speciation studies were demonstrated. This work comes in the sequence of another [21] where the authors

determine traces of metals (Pb, Cd, and Zn) in non-aqueous solvents such as acetonitrile, methanol and ethylene glycol. The stripping voltammograms are not distorted even in the absence of electrolyte, and the possibility of measuring low metal concentrations in very resistive media allows a wide spectrum of new applications of microelectrodes in stripping voltammetry such as the analysis of oils and petrols. This technique was also applied to the determination of Pb(II) sulphate in sulphuric acid solutions at mercury microelectrodes obtained by electrodeposition of mercury on Pt discs [22]. The method was tested in real systems, in particular, in the determination of Pb in acid battery electrolytes.

Recently, there has been a fast growth of interest in the analysis of trace metals in human fluids. Several studies indicate that an excess or depletion of certain metals is associated with several types of illnesses, thus, justifying the interest in the detection and quantification of metals in solution. Microelectrodes have also contributed in this area, allowing both *in vivo* and *in vitro* determinations. Mercury films on carbon microelectrodes and anodic stripping voltammetry were used to study systems *in vitro* with the objective of extending the method to systems in *vivo* [23]. Several experiments were carried out in nanomolar solutions of different metal ions (Cd^{2+}, Pb^{2+}, Cu^{2+}) and different electrodeposition periods between 1 and 5 minutes. The dissolved O_2 affects the voltammograms by increasing the background current, although some experimental factors may diminish the effect (e.g., increase of the deposition period).

It has been shown that in differential pulse anodic stripping voltammetry, carbon fibers plated with mercury films give very low background currents, better peak resolution when compared to the hanging mercury drop electrode, and good reproducibility. Cadmium was determined using this technique in solutions of organocadmium compounds and cadmium salts in the 1 - 10 μg l^{-1} concentration range, using differential pulse anodic stripping voltammetry. The limit of detection was 0.04 μg Cd l^{-1} [24]. Schutze *et al* [25] used stripping potentiometric analysis and differential pulse stripping voltammetry to determine zinc, cadmium and lead in solutions containing concentrations between 100 and 1 μg l^{-1} and tested different geometries of carbon fiber preplated with a thin film of mercury. The results obtained were compared with respect to reproductibility, sensitivity and practical aspects.

Mercury cylinder microelectrodes have also been used and the codeposition of Pb(II) with Hg(II) has been described [26] and it was shown that the square wave stripping peak increased linearly with lead concentration up to 4 μM.

Several contributions in the literature employed various types of mercury microelectrodes by amalgamation and coating or by suspending droplets on carbon or other conductors [10,16,17,22,27]. Amalgamated electrodes may be useful for specific applications but are difficult to reproduce and hanging drop microelectrodes are short

lived, cannot be reused and are also difficult to reproduce. Pons *et al* [28] have described a simple polarographic capillary that delivers droplets in the microelectrode range. The application of this device to analytical problems remains to be tested. The same applies to a dropping mercury microelectrode developed by Sluyters *et al* [29] which offers distinct advantages in double layer research but has not been applied in analysis yet.

Despite the successful determinations on mercury carbon-based microelectrodes it should be emphasized that the electrodeposition of mercury on carbon gives rise to a collection of nuclei dispersed across the surface and the connection between these droplets and the substrate is sufficiently weak that they slide easily, at a rotating disc electrode, across the carbon surface. On iridium substrates, however, coherent films of mercury are formed but in both direct and stripping wave voltammetry, anomalies occur at higher square wave frequencies. Osteryoung *et al* [27] have used linear scan and square wave voltammetry in the direct and anodic stripping modes at an iridium-based mercury film electrode (63.5 μm), for the determination of lead and compared experimental results with existing theoretical models. Silver-based mercury film electrodes were used under square wave conditions over a wide range of mercury film thicknesses and square wave frequencies [30]. The usefulness of these film electrodes under square wave conditions was established even at high frequencies. Theoretical predictions were confirmed by experimental results for Pb(II)/Pb(Hg).

Although mercury has been the electrode material of choice in the quantification of many metals, other substrates have been used. Edmonds *et al* [31] used carbon fiber electrodes to study the reduction of Cu(II) in hydrochloric acid, by means of differential pulse voltammetry. Calibration curves were plotted for solutions containing concentrations between 10 and 50 mg l^{-1} of Cu^{2+}. The variation of the peak current with ion concentration was linear. It was observed that an electrochemical pre-treatment of the electrode surface increased considerably the sensivity of the method.

In another report, amounts of Hg(II) in very dilute solutions were determined using a cylindrical gold microelectrode [32] and it is pointed out that for concentrations below 100 μg l^{-1} in Hg(II) the detection limit was 3.7 μg l^{-1}, while for solutions containing concentrations above 100 μg l^{-1}, the peak corresponding to the stripping of Hg(II) is shifted to less positive values, the peak height being proportional to the concentration of Hg(II). The authors explain this shift in terms of stabilization of the first few layers of bulk mercury by interacting with the gold-mercury amalgam. As the bulk mercury layer increases, less of the mercury interacts with the amalgam and less positive values are necessary to oxidise the mercury film. Mercury, copper and bismuth were also determined in urine with gold microdisc electrodes and using the technique of flow constant current stripping potentiometry which was fully automated [33]. During the stripping period, the potential transient was recorded and differentiated. Interferences

resulting from the reduction of species such as Sb(III), As(III), Ag(I) and Pt were tested. On the other hand it has been shown that the incorporation of Pt microdiscs in a wall-jet flow cell offers low limits of detection for the determination of copper in urine by flow injection analysis compared with standard methods based on a conventional sized glassy carbon disc in a thin-layer cell [34]. An increase in the limit of detection was observed with a decrease in electrode radius below 28 μm. The dependence of peak current on flow rate, however, does decrease as the electrode radius decreases, and this can be an advantage in some circumstances.

Special attention was given to natural waters as shown in the work by Jagner *et al* [35] who tried to determine Sb(III) and Sb((V) in river and sea waters. This metal occurs in natural waters in concentrations low enough (0.1 - 1 μg l^{-1}) that the use of conventional sized elctrodes is excluded. The analysis was carried out with the technique of flow constant current stripping potentiometry using a gold fiber electrode where a fresh layer of gold was electrodeposited. The same electrode was used in the analysis of Hg(II) and Cu(II) in tap water [36]. In this case, other electrode materials were tested, namely, platinum and carbon. The results obtained have shown that Hg(II) can be determined in the presence of Cu(II) in a concentration 10^5 times larger in media with chloride concentrations below 0.05 mol dm^{-3}. Mercury was also determined in air samples in concentrations above 0.2 μg m^{-3} using gold microdisc electrodes and stripping potentiometry at constant current [37]. This technique was tested by applying it in the analysis of carbonate and permanganate traps used in the determination of water soluble and metallic mercury in flue gases.

The behaviour and utility of a cylindrical platinum microelectrode was demonstrated [38]. The authors have shown that for usual analytical purposes, square wave voltammetry at microcylinders does not display any inconvenient distortions in shape or potential due to cylindrical diffusion. In the case of anodic stripping voltammetry it is desired that a stripping peak current be proportional to deposition time. Although the limiting current at a stationary cylinder depends on time, over the timescale of interest it was shown that the deposition charge is linear with time to an acceptable degree of accuracy. A Pt microcylinder electrode was used to perform square wave anodic stripping voltammetry of silver. Linear calibration curves were obtained in the 10 μM to 1 mM concentration range, demonstrating that this system provides analytically useful data.

In vivo Determinations

It is well recognized that electrochemical methods provide some useful new approaches to neurochemistry and neurophysiology [39-41]. An obvious application of microelectrodes in this area is to make chemical measurements in the extracellular fluid of
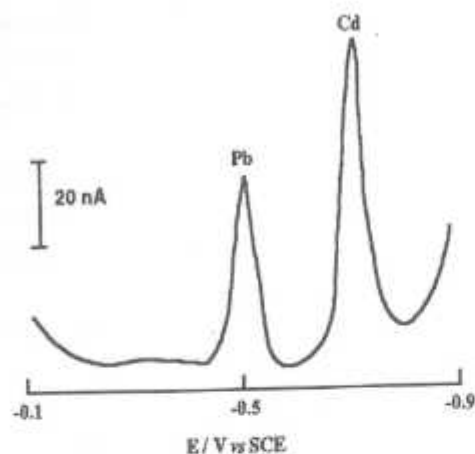
Figure 1. Short-pulse rapid scan stripping voltammogram of a 0.52 µg/dm³ Pb²⁺, 0.65µg/dm³ Cd²⁺, 0.25 M HCl and 4mg/dm³ Hg²⁺ solution. [After Anderson *et al*, in ref. 16].
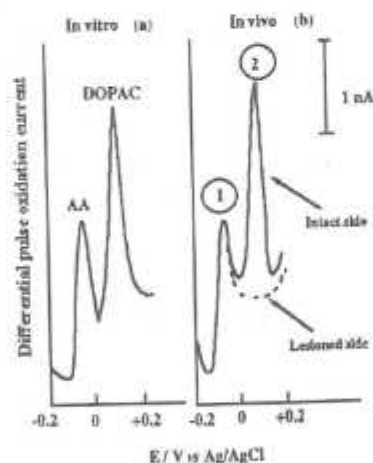

Figure 2. Differential pulse voltammograms from *in vitro* experiments and from the neostriatum of anaesthetized rats (*in vivo*). Electrochemically treated carbon fiber electrodes were tested in phosphate-buffer saline containing ascorbic acid (AA) (200 µg) and 3,4-dihydroxyphenylacetic acid (DOPAC) (20µg). (a) Shows typical differential pulse voltammogram. (b) Represents one typical example of differential pulse recorded in one rat with the same electrode implanted alternately in both striata. The lesioned side corresponds to a striatum in which the dopaminergic terminals were selectively destroyed. Peak 2 supression was observed with all the lesioned rats. [After Gonon *et al*, in ref. 58].

the brain without the need to sacrifice the animal. Therefore, carbon fiber microelectrodes implanted in small animal brains have been used to monitor changes of electroactive species *in vivo* [42-45]. The reason for using carbon is related to its compatibility with biological tissues. Some of the most important neurotransmitters are catechols or phenolic compounds and, hence, are readily determined by anodic oxidation [8, 41, 42, 46-54].

Of particular importance is dopamine which is a transmitter found in a region of the brain known as the caudate nucleus. Several studies are concerned with its release or inhibition in the presence of a variety of drugs, hence, providing fundamental information in the design of therapies for diseases associated with dopamine systems. The oxidation of dopamine at carbon electrodes was shown to involve the adsorption of both reactant and product of the electrode reaction [55-57]. Carbon ring microelectrodes fabricated by the pyrolysis of methane gas on the inner walls exhibit charge-selective enhancement of oxidation rates for a series of catechols following anodic electrochemical treatment [57]. Voltammetry at these electrodes suggests that the carbon formed by the pyrolysis step contains charge-selective sites which are responsible for catechol adsorption prior to electron transfer.

The monitoring of dopamine, however, is complicated by the presence of ascorbic acid and 3,4-dihydroxyphenylacetic acid which are easily oxidizable and are present at 10^4 to 10^3 times greater concentration. Gonon *et al* [50, 51, 58] have shown that an electrochemical pre-treatment of the pyrolitic carbon fiber electrodes combined with differential pulse voltammetry enables the resolution of dopamine, ascorbate, and 3,4-dihydroxyphenylacetic acid. Figure 2 shows voltammograms from *in vitro* and *in vivo* experiments performed on anaesthetized rats. The interference of compounds in the electrochemical measurement of dopamine can also be minimized, to a large degree, by using fast scan cyclic voltammetry [59]. Adams *et al* [60] have used Nafion coated microelectrodes to improve the selectivity for dopamine, norepinephrine, and 5-hydroxytryptamine. The combination of fast scan voltammetry with Nafion modified carbon microdiscs, provides the requirements for a selective, *in vivo* sensor of dopamine and other biogenic amines [61-63]. Selectivity of these electrodes for dopamine over ascorbate was enhanced to better that 2000:1 and concentrations as low as 35 nM were detected [62].

Recently, the effects of physiological concentrations of various biological precursors and metabolites of dopamine on the detection of the parent compound have been investigated by fast cyclic voltammetry at carbon microelectrodes [64].

Most studies have been carried out employing carbon fiber electrodes, either in cylindrical (typically 250-500 µm length and 8 µm diameter) or disc geometry (8 µm diameter). Their size and form makes them inadequate for intracellular measurements and

hence, smaller microelectrodes have been developed to probe dynamic changes inside cells [65,66].

Microelectrodes as Chromatographic Detectors

Analytical determinations in flow systems has become an area of increasing interest in electrochemistry with special emphasis on the development of amperometric detectors for liquid chromatography and flow injection analysis. This interest derives from the lower detection limits obtained and also from the reasonable selectivity displayed (by controlling potential) and low cost. Tubular, planar, and wall-jet cell / electrode configurations have been commonly used.

The application of microelectrodes in continuous-flow analysis increases considerably the practical advantages of electrochemical detectors [67-73]. Firstly, as mentioned earlier, the problems related to ohmic losses are greatly decreased and, therefore, they can be used in highly resistive media such as organic solvents with very low dielectric constants. It, therefore, becomes unnecessary to add electrolyte and, perhaps, a higher dielectric constant solvent between the column and the detector. This is particularly important in normal-phase liquid chromatography where purely organic solvents are commonly used instead of mixed aqueous-nonaqueous solvents [74]. The absence of electrolyte also eliminates specific adsorption and ion-pairing effects and interferences resulting from impurities which tend to increase the background currents. Secondly, the use of a two electrode cell configuration simplifies the electronics and also the dead volume is much smaller than when macroelectrodes are used. Thirdly, due to the high rate of diffusion, the current densities are higher as compared to conventional sized electrodes and, therefore, a better sensitivity is to be expected. Finally, microelectrodes are much less dependent on flow rate, when compared to larger electrodes [72].

The reduced dependence on flow rate at a carbon fiber array channel-type cell and the advantages of rapid scanning electrochemical detection have been discussed by Wightmann et al [75,76]. Staircase voltammetry with background subtraction provided low picomole detection capabilities of dopamine and other catechols. This method also provides the capability of obtaining voltammograms of small volumes of sample.

Koo et al [77] have used a carbon disc array and a platinum thin ring microelectrode in conjunction with a wall-jet cell as an amperometric detector in liquid chromatography. The detection limit was 100 pg for catecholamines. The ring was preferred over the array because it has more uniform accessibility and a higher current is obtained.

The form of carbon can also be important; for example, Tallman and co-workers [78,79] investigated the optimum composition of a compression-molded Kel-F-graphite composite electrode for the electrochemical detection of efluents, including phenolic compounds, separated by reversed-phase high-performance liquid chromatography. The electrode surface is considered to consist of an array of microelectrodes and, as a result of signal enhancement due to radial diffusion, composite electrodes are predicted to possess a signal-to-noise advantage compared to continuous carbon electrodes. Experimental results characterizing the flow response and favorable properties of the Kel-F-graphite (Kelgraf) electrode at high applied potentials have been further discussed [80]. It was applied as an electrochemical detector in HPLC for the direct measurement of selected carbamate pesticides and a nitroaminophenyl pesticide spiked into a river matrix.

Other contributions include the use of single graphite fiber electrodes for open-tubular liquid chromatography using scanning electrochemical detection [81-84] and also a potentiometric detector [85], based on an ion-selective microelectrode. Chi et al [86] applied a novel carbon fiber flow electrode to use as a detector in liquid chromatography which is easy to prepare and is stable in organic solvents. The detection limit for 3,5-orcinol and 2,7-dihydroxynaphthalene was ca. 1ng.

Supercritical CO_2 is a HPLC solvent of growing importance and Wightman et al [87,88] developed an electrochemical sensor for use for use as a detector in this medium. A film of an ionically conducting polymer, Nafion, placed over an electrochemical probe consisting of both a microdisc working electrode and a quasi reference electrode was used. The results obtained for ferrocene, 4-methylcatechol and 3,4-dihydroxybenzylamine dissolved in supercritical CO_2 in the presence of small quantities of water demonstrate the potential utility of membrane coated microelectrodes as chromatographic detectors. Figure 3 shows a voltammogram of ferrocene performed with a Nafion-coated probe in modified supercritical CO_2 and illustrates the good quality of the electrochemical response.

Microelectrodes can also be used successfully as sensitive and selective detectors in gas chromatography. Pons et al [89] report the use of carbon and gold microelectrodes in the gas phase and demonstrate their use as electrochemical detectors in gas-phase chromatography as well as a sensitive electrochemical gas sensor. Conduction is thought to occur across the glass surface between the micro and counter elecrodes and limiting currents measured are typically on the order of 10^{-10} to 10^{-16} A. The microelectrode assembly was mounted in a Faraday cage to reduce the capacitatively coupled noise. A gas chromatograph was set up adjacent to the cage so that the gas outlet port extended inside the Faraday cage. The tip of the microelectrode was inserted inside the outlet port so that the dead volume between the column and the detection was minimized. The authors have compared, for a wide variety of compounds (about 30), the relative

response of microelectrode detection to thermal conductivity detection and concluded that the electrochemical method gives higher sensitivity. This method was extended to electrochemical detection in pure liquid chromatographic phases [90]. A thin-gap microelectrode assembly which operates by a different mechanism has been reported [91] and its performance is compared with the previous assembly.

A new type of electrochemical gas chromatographic detector consists of a film of polymer electrolyte $PEO_{16}/LiCF_3SO_3$, coating a microelectode-based electrochemical cell and in contact with the efluent stream of a gas chromatograph [92]. Several electrochemical techniques were employed for collecting data: saw tooth, square wave, cyclic potentital sweep, and constant potential, but from the stand point of sensitivity all approaches were similar.

Determination of Inorganic, Organic, and Biological Compounds

As emphasized above, microelectrodes are particularly suited for analytical determinations in non-conventional, extremely resistive and difficult media. For example, it has been shown possible to determine directly antioxidants such as phenothiazine and phenyl-1-naphtylamine in lubricating oils simply by dilution in acetonitrile and without treatment [93]. Similarly, gold microband electrodes have been demonstrated to be suitable as sensors for ascorbic acid in foodstuffs such as fruit, potatoes, syrups and sauces [94]. These electrodes were made by printing techniques and such procedures are capable of very reproducible manufacture of electrodes with $0.12 \mu m$ thickness. Moreover, this approach to manufacture could be used for mass production and would be relatively cheap. Another application uses a copper microelectrode to measure nitrate concentration in pure water [94].

Microelectrodes are also gaining popularity for analytical determinations in flowing systems and various instrumental and electrode configurations for flow-through cells [69, 70, 73] have been developed and tested. Pletcher *et al* [95] have demonstrated the usefulness of a microelectrode based sensor for chlorine in flowing water streams and since microdiscs are difficult to manufacture in large numbers, some experiments were carried out with microband electrodes as described by Williams *et al* [94]. For quantitative analysis the potential step method was used and figure 4 shows chronoamperometric responses for a 12 μm thickness Au microband electrode in solutions of various concentrations of chlorine in water containing phosphate buffer. It can be seen that a reasonable pseudo-steady state is reached after 50 s and a good linear relationship between current and chlorine concentration was found for the range 0.1-1 ppm chlorine. The phosphate buffer concentration used may be as low as 0.5 mM
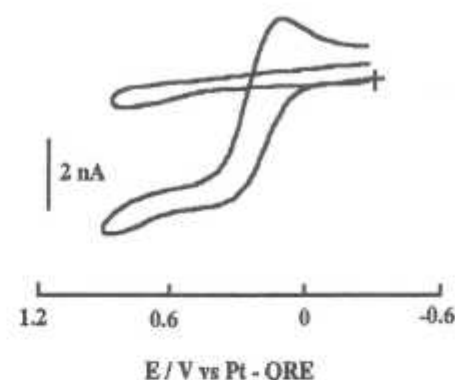
E / V vs Pt - QRE

Figure 3. Background and ferrocene (2×10^{-4} M) voltammogram in $SC\text{-}CO_2$ with 0.1 M H_2O added (0.1 V/s; i = 2 nA). [After Wightman *et al*, in ref. 88].
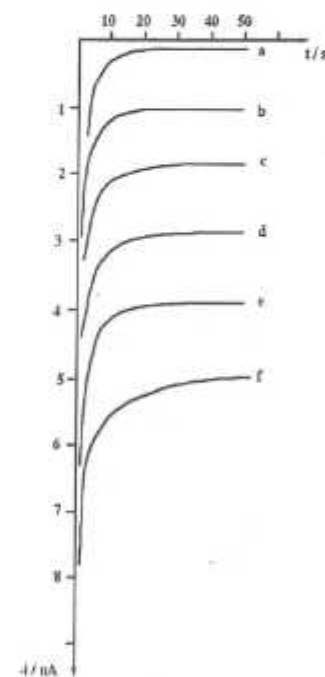

Figure 4. Chronoamperometric responses to a potential step from +0.85 V to +0.2 V vs SCE for a 12 μm thickness Au microband electrode. (a) 0; (b) 0.19; (c) 0.38; (d) 0.57; (e) 0.76; (f) 0.95 ppm chlorine in 0.5 mM phosphate buffer, pH 6.6. [After Pletcher *et al*, in ref. 95].

without the addition of other electrolytes and, within normal operating range, the response was found to be independent on solution flow rate.

The diminute size of microelectrodes offers advantages in the field of clinical assay where it becomes important to miniaturize sensors to be used in microvolume samples. For this reason, the oxygen electrode (i.e., the Clark Electrode) has been made quite small [96] and a theoretical description of this electrode has been developed [97]. The micro oxygen electrode has been combined on a chip with enzymatic layers to make an amperometric sensor for glucose, glutamate, and CO_2 [96]. A glucose sensor was developed by immobilizing glucose oxidase in an electropolymerized poly(N-methylpyrrole) film on a gold microelectrode [98].

Suaud-Chagny *et al* [99] immobilized lactate dihydrogenase on a carbon fiber electrode in order to develop an electrode sensitive to pyruvate. The presence of the enzyme is confirmed by the catalysis of its enzymatic reaction with the nicotinamide adenine dinucleotide (NAD / NADH). Therefore, by using voltammetry it is possible to measure the concentration of NADH in solution and after addition of pyruvate, it is observed a decrease in NADH oxidation current due to local consumption of NADH. Hence, it is possible to measure pyruvate concentrations. With this sensor it was possible to estimate that the pyruvate concentration in a rat cerebrospinal fluid sample of 50 µl was 10^{-4} M.

The selectivity offered by polymer modified electrodes has also been used to detect biological compounds. The water-soluble polymer poly(N-vinyl pyrrolidone) immobilized on a carbon microelectrode surface by gamma irradiations, was used to detect catechol compounds in the presence of the interferent ascorbic acid [100].

Abruña *et al* [101] used modified electrodes with antipyrylazo(III) for the determination of Ca^{2+}. Previous studies were made, for the determination of the sensivity of the method, using Fe(II) and concentrations of the order of 5×10^{-8} mol dm^{-3} were determined. The methods used were cyclic, differential pulse and square wave voltammetry and it was observed that the process of identifying Ca^{2+} is much more sensitive and selective, specially with respect to Mg^{2+}. The interest of studying this system is related to the fact that it is similar to the intracellular fluids where the Mg^{2+} concentration is about 100 times above that of Ca^{2+}.

Although the most widely used microelectrode geometry is the disc, other geometries offer specific advantages. Microcylinder electrodes have been shown, both theoretically and experimentally, to have an enhanced signal due to non-planar diffusion at all experimental times. Their small area results in lower background currents. In contrast with that of a microdisc, however, it is typically large enough that currents can be measured with conventional instrumentation. Osteryoung *et al* [102] have used a microcylinder electrode made from a single carbon fiber, with electrochemical

conditioning and square wave voltammetry, for the determination of N-acetylpenicillamine thionitrite. The method gave a detection limit of 2.7 µM with a sensivity of 2.92×10^{-3} µA/µM. A disadvantage of microcylinder electrodes, however, is that they cannot be polished reproducibly, which prevents their use in many analytical applications.

Conclusions

Perusal of the extensive literature of recent years indicates that microelectrodes have many advantages in analysis and that these should be further explored. Many contributions have shown that microelectrodes are attractive in the determination of trace metals, inorganic, organic and biological compounds and that their virtues include *in situ* and *in vivo* measurements. Several papers have demonstrated the particular importance of analysis in difficult media and in real systems, such as lubricating oils, foodstuffs, gas phase, etc. and many others emphasized the application as sensors and electrochemical detectors in GC, HPLC, and other flowing systems.

Despite the widespread interest in the exploitation of the unique properties of microelectrodes for analytical purposes, it is clear that there are many further fields to conquer. In particular, the relative merits of different geometries (discs, spheres, rings, lines, bands, cylinders and interdigitated filar microelectrodes [103, 104], and ensembles [105]) should be deeply understood. With respect to analytical techniques coupled to microelectrodes it seems clear that pulse and square wave voltammetry have a lot to offer in terms of sensitivity and selectivity. On the other hand, the modification of the electrode surface with polymers [106] and immobilized enzymes [99] appears to increase the selectivity and decrease the detection limits of many systems, thus, promising to be another way to go in the selection of new and exciting analytical methods employing microelectrodes.

Acknowledgement

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VOCABULARIO EM CORROSÃO E PROTECÇÃO

ANTICORROSIVA

Parte I

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Resumo

Apresenta-se uma colectânea, tanto quanto possível completa, dos vocábulos em português sobre corrosão e protecção anticorrosiva. Indica-se o seu equivalente em francês e inglês.

Palavras chave: corrosão, electroquímica, terminologia de corrosão.

Abstract

Vocabulary in corrosion and corrosion protection

A comprehensive compilation of Portuguese vocabulary in corrosion and related areas is presented with the indication of the French and English equivalent expressions. Follows an alphabetic list of the words used and respective entry in the previous text.

Key words: corrosion, electrochemistry, corrosion terminology