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<td>A. Beagleyhole</td>
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STUDIES WITH VOLTAMMETRIC MICRODISK ELECTRODES.

by

Darryl L. Luscombe

BSc(Hons.) Deakin

Being a thesis submitted for the degree of Doctor of Philosophy,
Deakin University, School of Sciences, 1991.
I certify that the thesis entitled "Studies with voltammetric microdisk electrodes" and submitted for the degree of Doctor of Philosophy is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution.

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Dated: 21/9/82
DEDICATION

to my father,

Leslie Henry Luscombe

(1940-1990)
ACKNOWLEDGEMENTS

During the past four years, many people have contributed to the work contained in this thesis. Some people have contributed directly in a practical sense, while others have helped in less tangible ways.

I extend my appreciation to you all.

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PUBLICATIONS

1. R.N. Bagchi, A.M. Bond, R. Colton, D.L. Luscombe, J.E. Moir,
   "Electrochemical oxidation of [dibenzo-18-crown-6-K][Cr(CO)₆F] and

2. A.M. Bond, D.L. Luscombe, "The influence of ultra-violet irradiation on the
determination of nickel and cobalt in natural waters by adsorption

   "Continuous monitoring of copper and cadmium in zinc plant electrolyte using
   a microprocessor based battery operated data acquisition system, multiple ion

   chronoamperometric response at inlaid and recessed disk microelectrodes", *J.

5. C.L. Colyer, D.L. Luscombe, K.B. Oldham, "Growth of mercury electrodeposits

   microprocessor controlled, programmable function generator for field based
   stripping voltammetry with conventional and microsized electrodes",

   by flow injection analysis with electrochemical detection at platinum disk

8. D.L. Luscombe, A.M. Bond, "Determination of tocopherols by reversed phase
   liquid chromatography and electrochemical detection at a surface oxide
   modified platinum microelectrode, without added electrolyte", *Talanta*, 1991,
   **38**, 65.
# GLOSSARY

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<td>cᵇ</td>
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<td>cᵐ</td>
<td>concentration at mouth of recessed microdisk electrode</td>
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<td>transient concentration</td>
<td>mol l⁻¹</td>
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<td>distributed capacitance element</td>
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<td>Cᵦ</td>
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<td>d.c. current</td>
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<td>( \gamma )</td>
<td>surface free energy</td>
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<td>kinematic viscosity</td>
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<td>specific solution resistance</td>
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<td>( \sigma )</td>
<td>(nvF/RT)</td>
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<td>dropping mercury electrode</td>
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<td>electrochemical impedance spectroscopy</td>
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<td>EPROM</td>
<td>erasable programmable read only memory</td>
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<td>Meaning</td>
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<td>ethyl</td>
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<td>flow injection analysis</td>
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<td>GC</td>
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<td>hanging mercury drop electrode</td>
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<td>HPLC</td>
<td>high performance liquid chromatography</td>
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<td>infrared</td>
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<td>liquid crystal display</td>
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<td>methyl</td>
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<td>mercury thin film electrode</td>
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<td>micro mercury thin film electrode</td>
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<td>ppm</td>
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<tr>
<td>ppb</td>
<td>part per billion</td>
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<td>random access memory</td>
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<td>reference electrode</td>
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<td>ultra violet</td>
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<td>voltmeter</td>
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<tr>
<td>1.</td>
<td>Voltammetric microelectrodes.</td>
</tr>
<tr>
<td>2.</td>
<td>Characterisation of inlaid and recessed microdisk electrodes in quiescent solutions.</td>
</tr>
<tr>
<td>3.</td>
<td>Examination of an impinging-jet flow cell.</td>
</tr>
<tr>
<td>4.</td>
<td>A comparison of copper determination in urine by flow injection analysis with electrochemical detection at glassy carbon and platinum microelectrodes.</td>
</tr>
<tr>
<td>5.</td>
<td>The determination of tocopherols using reverse-phase liquid chromatography and electrochemical detection at a surface-oxide modified platinum microelectrode without added electrolyte.</td>
</tr>
<tr>
<td>6.</td>
<td>Examination and use of micro-mercury thin film electrodes for trace analysis.</td>
</tr>
<tr>
<td>7.</td>
<td>Electrochemical oxidation of dibenzo-18-crown-6-K [Cr(CO)<em>{6}F] and [Cr(CO)</em>{6}].</td>
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<tr>
<td>8.</td>
<td>The influence of ultra-violet irradiation on the determination of nickel and cobalt in natural waters by adsorption voltammetry.</td>
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<tr>
<td>9.</td>
<td>General summary</td>
</tr>
</tbody>
</table>
CHAPTER 1

VOLTAMMETRIC MICROELECTRODES.

1.1. INTRODUCTION ................................................................. 2
  1.1.1. General .............................................................................. 2
  1.1.2. Definition of a microelectrode ........................................... 3
  1.1.3. Historical perspective ....................................................... 5
1.2. FABRICATION OF MICRODISK ELECTRODES ...................... 7
  1.2.1. Previous methods of fabrication ......................................... 7
  1.2.2. Inlaid microdisk electrodes ............................................... 8
  1.2.3. Polishing of electrodes ..................................................... 9
  1.2.4. Recessed microdisk electrodes .......................................... 10
1.3. INSTRUMENTATION ............................................................... 10
1.4. NOISE .................................................................................... 13
  1.4.1. Noise arising from within the electrochemical cell ............... 13
    1.4.4.1. Johnson noise ............................................................. 13
    1.4.4.2. Shot noise ................................................................. 15
    1.4.4.3. Flicker noise .............................................................. 16
  1.4.2. Noise arising from connections to the cell ......................... 16
    1.4.2.1. Dissimilar metals ....................................................... 16
    1.4.2.2 Dirty connections ....................................................... 16
    1.4.2.3 Triboelectric effects ..................................................... 17
  1.4.3. Noise arising from electronic equipment ......................... 17
  1.4.4. Noise arising from environmental factors ......................... 17
1.5. SCOPE OF THESIS ................................................................. 18
1.6. REFERENCES .......................................................................... 19
1.1. INTRODUCTION

1.1.1. General

The experimental technique of voltammetry has been in use since the pioneering work of such people as Daneel[1] and Salomon[2] in the late 1890's. In a voltammetric experiment the electrochemical behaviour of a material, the analyte, is characterised by recording the rate of oxidation or reduction of the material which occurs at a given electrical potential. The rate of oxidation or reduction is recorded as an electrical current, the rate at a given potential is called amperometry, and the rate over a range of potentials is called voltammetry. The resulting plot of potential versus current is known as a voltammogram.

A voltammogram is usually recorded at an inert electrode which does not actively participate in the electrochemical process, but provides the necessary electrically conducting pathway into the test solution. This electrode is termed the working electrode. Commonly used working electrode materials are platinum (Pt), gold (Au), mercury (Hg), silver (Ag), nickel (Ni), glassy carbon (GC), and graphite (C).

Apart from mercury which is a liquid at room temperature[3], all other common electrode materials are solids and may be used in a variety of different geometric shapes and sizes[4]. In the past, the relatively large size of the solid electrodes used (eg. $10^{-4}$ to $10^{-6}$ m$^2$) has restricted the application of voltammetry from many useful areas of study. These limitations have arisen from the inability of conventional solid electrodes to:

(a) maintain a uniform surface finish across the entire electroactive surface of the electrode, eg. chemical and physical inhomogeneities,

(b) maintain a uniform surface activity, especially when electrocatalytic processes are involved (eg. hydrogen evolution reaction at a Pt electrode),

(c) examine discrete electrode processes, eg. nucleation and growth of a single growth centre,
(d) conduct voltammetric experiments in confined areas, e.g. in biological tissue,
(e) achieve a diffusive steady state in an experimentally accessible time scale,
(f) conduct voltammetric experiments in highly resistive environments, e.g. in solutions of low specific conductivity without added electrolyte, in frozen solutions, in the gas phase, and
(g) conduct experiments in very short time domains, e.g. fast scan rate voltammetry ($10^4$ to $10^6$ V s$^{-1}$), high frequency a.c. experiments, etc.

In order to overcome these difficulties, a number of workers have demonstrated the benefits of reducing the active area of the working electrode down to the range $10^{-10}$ to $10^{-12}$ m$^2$. Electrodes with these dimensions are referred to as microelectrodes.

1.1.2. Definition of a microelectrode.

A voltammetric microelectrode (hereafter referred to simply as a microelectrode) may take any number of geometric forms. This has led to a problem in the nomenclature of microelectrodes. Electrodes of micrometer dimensions are variously referred to as microelectrodes[5], ultramicroelectrodes[6], microvoltammetric electrodes[7], microneedle electrodes[8], or microcathodes[9]. Further, the geometry of the electrode may be referred to in its name, e.g. microdisk, microring, microline. This proliferation of nomenclature has led to much confusion in the literature.

As a result of this confusion, a microelectrode will be defined arbitrarily for purposes of this thesis as:

"An electrode consisting of an electronic conductor whose geometry is constrained by a surrounding electronic insulator, such that the electronic conductor has a characteristic dimension which has a numerical value less than 100 µm."

Further, the geometry of the particular electrode will be referred to in the name. Hence a microdisk electrode is a disk electrode with a radius of less than 100 µm, a microcylinder has a circular radius of less than 100 µm, etc.
Virtually all conceivable geometries of microelectrode have been fabricated or described theoretically, with microdisk, microring, microline, and microcylinder being the most popular[10-12]. The reason for the preference of these geometries over others (e.g. microsphere[13], microhemisphere[14], microhemi-toroid[15]) relates to the fact that disks and lines are easier to fabricate in practice.

The work to be reported in this thesis describes the behaviour of inlaid and recessed microdisk electrodes in flowing and quiescent solutions. An inlaid microdisk electrode consists of a circular metal disk surrounded by an insulating medium that forms a geometric continuation of the electrode plane, as shown in cross section in figure 1.1. A recessed microdisk electrode has a geometry shown in figure 1.2. In practice some deviations from ideal geometries will occur during the fabrication process. Hence an electrode may be referred to as having a microdisk geometry, even though the true geometry may be somewhat less than that of a perfect disk.

![Diagram of an inlaid microdisk electrode](image)

**Figure 1.1** Diagram describing an inlaid microdisk electrode.
1.1.3. Historical perspective

The first report of the fabrication and use of a voltammetric microelectrode was for the cathodic determination of oxygen in animal tissue, in 1942 by Davies and Brink[5]. In the paper they described the fabrication and application of Pt inlaid and recessed microdisk electrodes with radii of 12.5 μm. Many workers in the biological and physiological fields have continued to develop and refine the use of microelectrodes for pH and pO2 determinations in in-vivo and in-vitro analysis since Davies and Brink's pioneering work[16-19].

The reason for using such small electrodes was three-fold; the ability to penetrate biological tissue with a minimum of disruption; fine spatial resolving power, enabling a
map of oxygen levels to be obtained with resolution down to ≈ 2 μm; and low oxygen consumption during the measurement. As the use of microelectrodes for *in-vivo* work increased in popularity, many unique properties due to the size of the electrodes were noted, but received little or no interest from outside the biological disciplines. These properties included:

(a) non-linear diffusion to inlaid microdisk electrode[20],

(b) ability to model diffusion to an inlaid microdisk by assuming hemispherical diffusion[21],

(c) reduced time required to achieve diffusion limited steady state currents[21], and

(d) reduced effects of convection on the limiting current[6,9,22,23].

Hence until the early 1970's the entire body of microelectrode literature was dedicated to the determination of oxygen in biological tissue and fluids, with only a basic understanding of the underlying theory involved[5,20,21,24,25]. At about this time Adams et. al.[26-28], and Hubbard et. al.[29,30] began to apply microelectrodes to the *in-vivo* voltammetric determination of catecholamines in brain tissue, using transient electrochemical techniques. Also, Fleischmann et. al. reported the use of Pt microdisk electrodes for the study of nucleation and growth of individual growth centres of electrodeposited α-PbO₂ [31].

The first use of microelectrodes as anything other than simply small electrodes appears to be that of Lines and Parker[32], who examined voltammetry in high resistance solutions of benzene and chlorobenzene. Thus utilising the ability of microelectrodes to minimise the effects of solution resistance.

During the early 1980's an explosion of interest occurred in the fundamental and applied aspects of microelectrode behaviour. This interest may be attributed to the heightened profile of microelectrodes in the chemical literature at the beginning of the decade[33]. This interest in microelectrodes by the electrochemical community was followed by a flood of papers covering an enormous range of fundamental and applied studies, including
(a) electrode kinetics \([34-37]\),
(b) anodic stripping voltammetry \([38-41]\),
(c) steady state voltammetry \([42,43]\),
(d) spectroelectrochemistry \([44]\),
(e) fast scan rate voltammetry \([45-47]\),
(f) voltammetry in the absence of deliberately added electrolyte \([42,48-50]\),
(g) voltammetry at extreme potentials \([51,52]\),
(h) amperometry in the gas phase \([53]\),
(i) amperometry and voltammetry in convective systems \([54-58]\)
(i) adsorption studies \([59]\), and
(j) a theoretical understanding of (a) - (i) \([43,60-70]\).

Electrochemistry at microelectrodes is such a rapidly expanding area of research that it is virtually impossible to provide a comprehensive review of all papers published in this multi-disciplinary field. The above list is indicative of the breadth of research into microelectrode behaviour and application, much of which is still in progress.

1.2. FABRICATION OF MICRODISK ELECTRODES

1.2.1. Previous methods of fabrication

There is considerable prior art in the area of microdisk electrode fabrication \([17]\). Microdisk electrodes are most easily fabricated by sealing a microwire of the appropriate diameter into a length of glass tubing, then polishing the end of the tubing to expose the cross-sectional area of the microwire. This technique has been the most popular method of fabricating electrodes down to radii of 2.5 \(\mu m\), mainly due to the ready availability of microwires of a wide variety of materials and sizes \([71,72]\). In order to fabricate electrodes of smaller radii it was necessary to use more exotic forms of materials, or modify existing materials.

Wollaston wire consists of a thin core of platinum (radii 0.25 to 5.0 \(\mu m\)) encased in a thicker (\(\approx 50 \mu m\)) sheath of silver. The core is exposed by dissolving away the silver
in nitric acid, then the Pt may be sealed into an insulator in the same way as the bare microwire[6,17,42]. Taylor wire consists of a core of Pt (radius = 0.5 \, \mu m) encased in a glass sheath, and was also used to fabricate Pt inlaid microdisk electrodes[6].

Another method that has been employed to fabricate sub-micrometer sized electrodes was to etch the tip of a thicker microwire to a very fine point. Electrodes with tip radii of less than 0.1 \, \mu m have been prepared in this manner[6,17,73]. The main problem with using this type of electrode is that as the electrode is polished, the radius of the electroactive tip will increase due to the conical nature of the etched microwire.

The methods used in the construction of a wide variety of electrode materials and geometries are available in the literature[11,12,17], with the review by Rolison[74] providing an extremely detailed cookbook of methods.
1.2.2. Inlaid microdisk electrodes

In this work, durable inlaid microdisc electrodes were prepared from gold and platinum microwires (Goodfellow Inc., England) having nominal radii 2.5 to 100 μm (figure 1.3). A 10 cm length of soda glass tubing (7.0 mm outer diameter and 5.0 mm inner diameter) was thoroughly cleaned with successive rinses of dichloromethane, acetone, and distilled water. The glass tubing was then soaked for a minimum of 1 hour in 5M nitric acid, rinsed with distilled water, and oven dried. The cleanliness of the glass was found to be essential for a good glass-to-metal seal, free from air bubbles.

One end of the tubing was slowly collapsed by continuously rotating the tip in a quiet gas/oxygen flame until a 1-2 mm hole remained (figure 1.3(a)). The tubing was then quickly removed from the flame to ensure that the tip did not close completely. A 1.5 cm length of microwire was then inserted into the small hole, leaving 2-3 mm of microwire protruding out of the end, as figure 1.3(b) illustrates. Holding the tubing
horizontally without rotation, the orifice was heated slowly in the flame until the glass reached a temperature at which the microwire stuck to the glass. The electrode was then rotated in the flame until the glass tip melted around the wire forming a bubble free seal (figure 1.3(c)). The electrode tip was ground to a flat surface on successively finer grades of silicon carbide( emery) paper (150, 320, 600, and 1200 grades), then polished on microcloth with successively finer grades of alumina (5, 2, and 0.3 µm) until a mirror smooth finish was obtained.

Electrical contact was made with the sealed microwire by placing small lumps of Woods Metal (melting point 68°C) inside the tubing, together with a 12 cm length of copper wire. The electrode was then heated in a water bath at 80°C to melt the Woods Metal, removed and allowed to cool, leaving a reliable electrical contact between the gold and copper wires. The electrode body was filled with either polystyrene or wax to immobilize the copper wire and Woods Metal (figure 1.3(d)).

1.2.3. Polishing of electrodes

The inlaid microdisk electrodes were routinely polished on a microcloth with 0.3 µm alumina slurry, placed in an ultrasonic bath in distilled water for 30 seconds to remove any adhered alumina, rinsed again in distilled water, then the solvent of interest before wiping with a lint-free tissue. Electrodes were polished using this procedure prior to all experiments, unless otherwise stated.

1.2.4. Recessed microdisk electrodes.

The recessed microdisk electrodes were prepared by immersing the tip of a Au inlaid microdisc electrode in aqua-regia for 5-30 minutes depending on the depth of the etch required. The aqua regia, freshly prepared from one part analytical grade hydrochloric acid and three parts analytical grade nitric acid, was stirred continuously during the etching step. After etching, the now recessed electrode was rinsed thoroughly with distilled water followed by rinsing with acetonitrile for 5 minutes, each in an ultrasonic bath.
The depth of the recess was determined after the experiments were performed by grinding and then polishing the glass away from one side of the wire until less than 100 μm of glass remained. The depth of the recess was then measured to within 10 μm using a calibrated microscope. The surface of the etched electrode was noticeably rough, though microscopy showed no obvious convex or hemispherical shape resulting from the etching procedure.

The recessed disk electrodes were stored in pure acetonitrile or in acetonitrile (0.1 M Et₄NClO₄) solutions.

1.3. INSTRUMENTATION

The instrumentation used to perform voltammetric experiments has developed from the relatively simple apparatus used until the mid 1950's, to the sophisticated digital equipment available today. There are two basic voltammetric systems that need to be considered with respect to voltammetry at microelectrodes, the two-electrode system and the three-electrode system.

The two-electrode system is the most simple of all possible voltammetric systems, consisting of an electrical circuit comprising a working electrode (WE), counter electrode (CE), an ammeter (A), and a variable voltage source (V), with the electrolyte solution completing the circuit between the working and counter electrodes (figure 1.4)[3]. The counter electrode in the two-electrode system performs two vital functions, it provides

(a) a stable potential reference, and
(b) a current path through the solution.

The problem with these two functions being provided by the one electrode is that they are not completely exclusive. The passage of large currents through the counter electrode will adversely affect its ability to maintain a stable reference potential. Also, the passage of large currents (i), through the solution will result in a voltage drop due to the solution resistance (R) equal to the product iR. The net result of this is that the potential applied to the working electrode interface is in error by the term iR. Another
problem due to the iR term is that the quality of the voltammetric response degrades with a large iR drop, leading to distorted voltammograms[3].

In order to overcome these problems, the three-electrode system was developed. The potential at the working electrode interface is controlled between the working electrode and reference electrode (RE), while virtually all of the current passes between the working electrode and the auxiliary electrode (AE), thus separating the two roles assumed by the counter electrode in the two-electrode system. The net result of this approach is that potential control is maintained regardless of the magnitude of the current, and the effects of iR drop are minimised, though not completely eliminated. The device employed to control the potential and supply the necessary current is called a potentiostat[3].

The magnitude of the current generated at a microelectrode in a typical voltammetry experiment rarely exceeds $10^{-7}$ A, and may be as low as $10^{-15}$ A. Due to the extremely low currents encountered when using microelectrodes, the two-electrode system has been favored over the three-electrode system in many studies[10,11]. The reasons for this are threefold: (a) simplified instrumentation, (b) lower instrumental noise, and (c) low cost. Further, the main justifications for using a three-electrode system, the ability to handle large currents and minimise iR drop, are not relevant when using microelectrodes. For these reasons the bulk of work reported in this thesis was performed using the two-electrode system. Details of the equipment used for a given experiment is detailed in the relevant chapters of the thesis.

At the initiation of this thesis in 1986, there was no instrumentation which was specifically designed for use with microelectrodes commercially available. For this reason, most of the work detailed in this thesis used discrete instruments (e.g. battery powered function generator, picoammeter, digital electrometer) to perform the tasks of applying the potential, and measuring the low currents. At the time of writing this thesis, there are a number of commercial electrochemical instruments available which are capable of these tasks.
Figure 1.4. Schematic description of a two electrode cell.

Figure 1.5. Schematic description of a three electrode cell.
1.4. NOISE

There are a number of intrinsic and extrinsic noise sources which may contribute to the overall level of noise in an electrochemical experiment[75,76]. In order to optimise the signal-to-noise ratio (S/N) in a given experimental design, it is necessary to understand the processes which lead to noise, and therefore how to minimise it[77,78]. Noise may be contributed from any of four major sources: (a) from within the electrochemical cell, (b) from the connections made to the cell, (c) from the electronic equipment used to control the experiment, and (d) from external environmental factors.

1.4.1. Noise arising from within the electrochemical cell.

1.4.4.1. Johnson noise.

At any temperature above absolute zero, thermal motion of charged particles in any resistive material will generate a noise voltage, variously referred to as Johnson, Nyquist, or resistance noise[75]. The power (P) available from this source of noise is given by:

\[ P = 4kT \Delta f \]  \hspace{1cm} (1.1)

where \( k \) = Boltzmann's constant, \( T \) = absolute temperature. The noise bandwidth (\( \Delta f \)) in an electrochemical cell will be determined by the time constant (RC) of the cell. The noise bandwidth will be equal to[76]:

\[ \Delta f = \frac{1}{4RC} \]  \hspace{1cm} (1.2)

where \( R \) is the effective cell resistance (i.e. the total of the solution, electrode, and lead resistances), and \( C \) the effective cell capacitance (i.e. the total of the double layer, stray, connection, and lead capacitances).

Alternatively the Johnson noise may be expressed in terms of an rms voltage or current noise in a resistance by[76]:
\[ V_{\text{rms}} = \sqrt{4kRT\Delta f} \]  

(1.3)

and

\[ I_{\text{rms}} = \sqrt{\frac{4kT\Delta f}{R}} \]  

(1.4)

Peak-to-peak (p-p) values for these expressions can be calculated from equations 1.3 and 1.4, so at a temperature of 300 K, the peak-to-peak noise levels are given by:

\[ V_{p-p} = 6.5 \times 10^{-10} \sqrt{R \Delta f} \]  

(1.5)

and

\[ I_{p-p} = 6.5 \times 10^{-10} \frac{\sqrt{\Delta f}}{R} \]  

(1.6)

Johnson noise is the fundamental limitation to any electrical measurement. Johnson noise is a white noise, which means that it displays a constant power per unit bandwidth relationship.

It can be seen from the above relationships that there are a number of ways to minimise the effects of Johnson noise, although these methods may not be practical in all cases. Johnson noise may be reduced by cooling the experiment, as the noise current varies with \( \sqrt{T} \) (equation 1.4). Decreasing the bandwidth of the measurement by the introduction of a filter circuit will also help to minimise Johnson noise, or by increasing the RC time constant of the electrochemical cell (equation 1.2). The final option to decrease current noise is to increase the source resistance (equation 1.4), as would be accomplished by decreasing the supporting electrolyte concentration. A decrease in supporting electrolyte concentration would also result from decreasing the temperature of the cell, due to solubility arguments. It could therefore appear that if Johnson current noise is the major noise source in an experiment, that cooling of the cell would be the optimum strategy to minimise it.
1.4.4.2. Shot noise.

Shot noise is believed to arise when the passage of current is governed by random single electron processes (cf. metallic conduction where electrons migrate as a cloud of charge), and is usually associated with discrete electronic components (eg. diodes, transistors, vacuum tubes, etc.)[75]. However, it has been shown that an electron transfer event at the electrode/solution interface may also give rise to shot noise[79-81].

The level of shot noise is directly proportional to the dc current flowing through the signal source. The rms power ($P_{rms}$) and current ($I_{rms}$) expressions for shot noise are given by[75]:

$$P_{rms} = 2eRI\Delta f$$  \hspace{1cm} (1.7)

and

$$I_{rms} = \sqrt{2eI\Delta f}$$  \hspace{1cm} (1.8)

where $e =$ electron charge ($1.60 \times 10^{-19}$ C), and $I =$ dc current. Shot noise like Johnson noise displays the characteristics of a white noise.

Shot noise may be minimised in two ways, decreasing the bandwidth of the measurement, or decreasing the magnitude of the dc current involved.

1.4.4.3. Flicker noise.

Flicker noise is not well understood, but appears to arise from discrete conduction processes[75]. Flicker noise displays a $1/f$ dependence, which results in flicker noise being the predominant noise source below 100 Hz in many cases. Further implications of the $1/f$ dependency of flicker noise are that very low frequency measurements, down to dc, may suffer greatly. The effects of flicker noise on electrochemistry of the hydrogen evolution reaction at mercury plated silver electrodes has been examined[82].
1.4.2. Noise arising from connections to the cell.

The connections from the control instrumentation to the cell may contribute significantly to the level of noise, if a number of relatively simple precautions are not observed. The major sources of noise involving the connections to the cell result from dissimilar metals in contact, dirty connections, and triboelectric phenomena.

1.4.2.1. Dissimilar metals.

If the terminal connections involve dissimilar metals in contact, there may arise the possibility of currents from thermoelectric and galvanic effects. Thermoelectric currents may be minimised by using the same material for all connections, and by ensuring that the cell and all equipment is maintained at a uniform temperature[76].

Galvanic currents arise because of the difference in potential which occurs between different metals when placed in a moist conducting environment, leading to corrosion of the connector. Galvanic currents may be minimised by ensuring that connections are kept dry and free from corrosive chemicals.

1.4.2.2 Dirty connections.

Electronic plugs and connectors should be kept free of grease and dust which may give rise to noise due to unreliable connections, and from leakage currents to earth.

1.4.2.3 Triboelectric effects.

Triboelectric phenomena arise in insulated cables through friction at the conductor\insulator boundary[76]. The friction causes electrons to rub off the conductor leading to a charge imbalance, and a resultant current flow. Triboelectric currents may be of the order of $10^{-10}$ to $10^{-12}$ A, and must therefore be considered a significant potential noise source in microelectrode experiments.

Triboelectric currents may be minimised by ensuring that all leads are fixed and not capable of any free movement. If fixing the cable is inappropriate, special cables in which the conductor\insulator interface is lubricated with graphite should be used[76].
1.4.3. *Noise arising from electronic equipment.*

The instrumentation used to apply the potential waveform to the cell, and measure the resulting current may also contribute to the overall noise level. Intrinsic noise factors such as were discussed in section 1.4.4.1 also apply to the electronic components used in modern instrumentation, and may only be minimised by a careful choice of components at the initial design stage. Power supplies are of particular concern, as they can be significant sources of radio-frequency (RF) noise, as will be discussed in the next section.

Noise associated with instrumentation is usually beyond control of the experimenter, although some instrumentation is designed to enable cooling with liquid nitrogen. If excessive noise levels are found in a particular instrument the only practical solution may be to have the instrument repaired (if faulty), or replaced by an instrument with lower inherent noise levels. Fortunately there are a number of well designed commercial instruments available for measuring currents down to $10^{-17}$ A.

1.4.4. *Noise arising from environmental factors.*

Noise resulting from sources extraneous to the experiment, i.e. environmental noise, are a common feature of any laboratory[75]. Environmental noise may result from stray magnetic fields (eg. the Earth's magnetic field, electromagnets contained in electron spin resonance or nuclear magnetic resonance spectrometers), mains and high-tension power lines (eg. 50 Hz noise), vibration of the experiment (eg. wind, people, traffic), high voltage equipment (eg. laser power supplies, elevator motors, air conditioners), etc[75].

Radio-frequency (RF) noise and high frequency (HF) noise may not at first appear to present a problem to measurements carried out at low frequency (eg. dc measurements), which constitute the bulk of work in this thesis. However, when the wavelength of the RF noise is of a similar magnitude to the path length of the instrument ground, interference will occur[83]. For example, consider an RF noise source with a frequency of 100 MHz, which corresponds to a wavelength ($\lambda$) of 3.0
metres. A ground path will cease to act as a ground when the ground path length exceeds $\frac{\lambda}{4}$ [83], or 0.75 metres. There are many possible sources of RF noise including; fluorescent lights, power tools, exhaust hood fans, laser power supplies, refrigerator motors, etc.

The best method of eliminating environmental noise is to isolate the source from the experiment, and ideally the problem should be tackled at the source[76,83]. However, this is generally not possible, and environmental factors must be controlled in the laboratory. In order to isolate the experiment it is necessary to construct a shield of suitable material around the experiment to attenuate the incoming noise source, and then ground the shield to earth. In order to minimise any possibility of ground loops forming, all equipment should be grounded at a single point [83]. Such an enclosure is known as a Faraday shield.

1.5. SCOPE OF THESIS

This thesis seeks to investigate some of the fundamental and applied aspects of the voltammetric behaviour of microdisk electrodes, in quiescent and flowing solutions. Microelectrodes based on geometries other than that of the disk were not examined.

Chapter 2 deals specifically with the behaviour of inlaid and recessed microdisk electrodes in quiescent solutions, whereas the characterisation of inlaid microdisk electrodes in flowing solutions is examined in chapter 3. A number of applications of microdisk electrodes to analytical and fundamental studies is detailed in chapters 4 - 7. Chapters 4 and 5 involve the application of microdisk electrodes to analytical determinations involving flowing solutions, whereas chapters 6 and 7 apply the benefits of microelectrode behaviour to quiescent solutions.

Chapter 8 examines the influence of ultra-violet irradiation on the adsorptive stripping determination of cobalt and nickel using conventional mercury electrodes, and does not involve the application of microelectrodes.
1.6. REFERENCES

CHAPTER 2

THE RESPONSE OF INLAID AND RECESSED MICRODISK ELECTRODES
IN QUIESCENT SOLUTIONS.

2.1. INTRODUCTION ................................................................. 24
   2.1.1. General ............................................................................. 24
   2.1.2. Electrochemical Impedance Spectroscopy ......................... 25
   2.1.3. Linear and cyclic sweep voltammetry ............................... 27
   2.1.4. Chronoamperometry ...................................................... 28

2.2. EXPERIMENTAL ................................................................. 29
   2.2.1. Instrumentation .............................................................. 29
   2.2.2. Chemicals ...................................................................... 30
   2.2.3. Software ......................................................................... 30
   2.2.4. Glassware ...................................................................... 30
   2.2.5. Procedures ..................................................................... 31
     2.2.5.1. Electrochemical Impedance Spectroscopy ..................... 31
     2.2.5.2. Voltammetry ............................................................ 31
     2.2.5.3. Chronoamperometry ................................................. 32

2.3. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY .............. 33
   2.3.1. Theory .......................................................................... 33
   2.3.2. Magnitude of applied sinusoidal voltage ......................... 37
   2.3.3. Effect of electrode radius on the measured impedance ....... 37
   2.3.4. Roughness effects ........................................................ 40
   2.3.5. Summary ........................................................................ 44

2.4. LINEAR SWEEP AND CYCLIC VOLTAMMETRY .................... 45
   2.4.1. Qualitative theoretical description of voltammetry at a microdisk electrode .............................................. 45
   2.4.2. Quantitative description of steady state voltammetry at an inlaid microdisk ...................................................... 47
   2.4.3. Quantitative description of voltammetry under linear diffusion conditions ....................................................... 49
   2.4.4. Analysis of a steady state voltammogram at an inlaid microdisk electrode ...................................................... 51
   2.4.5. Analysis of a voltammogram at a recessed microdisk electrode ................................................................. 52
   2.4.6. Effect of scan rate on wave height at inlaid microdisk electrodes ................................................................. 52
   2.4.7. Effect of scan rate on wave height at recessed microdisk electrodes .......................................................... 55
   2.4.8. Effect of solution resistance on inlaid microdisk electrodes ................................................................. 56
2.4.9. Effect of solution resistance on recessed microdisk electrodes .......................... 58
2.4.10. Concentration dependence .............................................................................. 59
2.4.11. Calibration of inlaid microdisk electrodes ......................................................... 60
2.4.12. Summary ........................................................................................................... 61

2.5. CHRONOAMPEROMETRY .............................................................................. 62
   2.5.1. Theory of the Steady state ................................................................................ 62
   2.5.2. Theory of the transient response ..................................................................... 65
   2.5.3. Results and discussion ..................................................................................... 70
   2.5.4. Summary ......................................................................................................... 74

2.6. REFERENCES ....................................................................................................... 75
2.1. INTRODUCTION

2.1.1. General

Electrochemistry refers to any chemical process in which electrical potential or flow of current is directly or indirectly involved. Voltammetry, the principle technique used throughout this thesis, involves chemical reactions in which electron transfer occurs. Typically the electron transfer occurs between the electrode and a chemical species in solution.

One of the principal differences between voltammetric and most spectroscopic techniques is that electrochemistry involves reactions occurring at surfaces, whereas most spectroscopic techniques (e.g. ultraviolet, visible, infra-red, electron spin resonance) analyse bulk materials[1]. Another important distinction between voltammetry and the other spectroscopic techniques mentioned is that in a voltammetric experiment, the material being examined is altered by the removal or addition of electrons, hence voltammetry is a destructive method of analysis. However, in most voltammetric experiments only a very small fraction, perhaps less than 2 - 5% of the total amount of material being analysed, is destroyed[2].

In voltammetry a molecule must approach the electrode surface closely enough so that electron transfer can occur[2]. The means by which the molecule gets to the surface, and the condition of the surface once it gets there will also influence the resulting electron transfer reaction. In other words, the rate of an electron transfer reaction is partially determined by the mass transport processes involved, and partially by the kinetics of the actual electron transfer step.

Mass transport may occur through three distinct physical processes[3]; (i) diffusion, as a result of concentration gradients in solution; (ii) migration of charged species due to electric field gradients in solution; and (iii) convection, caused either by deliberate stirring, or density gradients in solution.

Voltammetric techniques in quiescent solutions generally utilise diffusion as the mass transport mode of choice, and via judicious choice of experimental conditions,
attempts are usually made to minimise the effects of migration and convection. The dominant form of the diffusion which occurs in a given voltammetric experiment will be determined by the geometry and size of the electrode, together with the time scale of the experiment.

The popularity of voltammetric microelectrodes in recent times has been reflected in the level of interest in their behaviour in quiescent solutions. This interest arises because of a number of demonstrated benefits of using microelectrodes over conventional sized macroelectrodes including:

(a) low ohmic polarization, reducing the requirement to add supporting electrolyte,

(b) the achievement of diffusive steady states in experimentally accessible time scales,

(c) small size, enabling fine spatial resolution in analysis,

(d) reduced effects of convection, and

(e) enhanced mass transfer due to non linear diffusion,

as was detailed in chapter 1.

2.1.2. Electrochemical Impedance Spectroscopy.

Electrochemical Impedance Spectroscopy (EIS), also known as AC Impedance has been used for many years in the elucidation of the structure of the double layer through differential capacity measurements[4], as well as studies of corrosion[5], reaction mechanisms[6], kinetics[7], electrodeposition[8], and the physical morphology of the electrode-solution interface[9]. The ability to determine the physical morphology of the electrode-solution interface is of particular interest in the case of microelectrodes, where the integrity of the electrode surface may often be unknown due to the difficulty in examining micron sized electrodes visually. By far the largest body of literature regarding EIS measurements have been reported at mercury electrodes, with differential capacity measurements leading directly to many of the advances in a general understanding of the role and behaviour of the double layer in modern
electrochemistry[2,4,10-13].

EIS measurements at solid electrodes have also been reported[9,14-17], but in contrast to the measurements at mercury electrodes the impedance measurements at solid electrodes often show a dispersion of the measured impedance with frequency which has been attributed to the effects of surface morphology[9]. There was originally some controversy regarding this interpretation[18], however surface morphology is now widely accepted as a primary cause of frequency dispersion at solid electrodes[9,19,20].

Baranski[21] recorded the frequency dependence of the measured impedance of a carbon fibre microdisk electrode in acetonitrile (LiAsF₆) solutions. The carbon fibre electrode exhibited considerable frequency dispersion over the measured frequency range. Values of 33 pF (86 μF cm⁻²) to 90 pF (230 μF cm⁻²) at 100 kHz and 1 Hz respectively, were typical. Baranski also reported similar behaviour for a platinum inlaid disk microelectrode, and made the comment that all electrodes made in his laboratory displayed some degree of frequency dispersion.

Howell and Wightman[22] reported impedance data for gold inlaid disk microelectrodes in acetonitrile (Bu₄NClO₄) solutions. They observed no frequency dispersion of the measured cell impedance over the frequency range of 10⁴ to 10⁴ Hz. However, this frequency range is insufficient to guarantee that no dispersion is present[21]. Photomicrographs of the gold microdisk electrode presented in reference [22] clearly show the presence of small scratches and pits on the electrode surface, which could be expected to lead to some degree of frequency dispersion[9].

Wehemeyer and Wightman[23] examined the behaviour of gold microdisk electrodes sealed in soda glass, and demonstrated a frequency dependence of the apparent capacitance in aqueous potassium nitrate solutions. The area normalised capacitance of the microelectrode varied considerably more than that of a one millimetre radius electrode. This was interpreted in terms of an imperfect gold to glass seal, leading to microcracks which give rise to the frequency dispersion. The possibility of microcracks in gold/soda glass electrodes is due to the different coefficients of expansion of the gold and soda glass. Silanisation of the electrodes, which would render
the microcracks hydrophobic was suggested and demonstrated to be effective in reducing the background current. However, examination of the voltammograms obtained for before and after the silanisation treatment show a decrease in the faradaic current of approximately 20%. This may suggest that surface features are being rendered hydrophobic as well, thus leading to a decrease in the electroactive area, and a diminution of the faradaic current.

Finally it is worth dispelling a popular misconception regarding the measurement of ac impedance behaviour of microelectrodes. That is, the belief that due to the small size of the microelectrodes that the ac impedance response will be difficult to observe. This is not correct as was reported by Harman and Baranski[24], who examined the capacitance response of 25 μm diameter electrodes in aqueous solutions. They pointed out that as the solution resistance of a hemispherical electrode varies inversely in proportion to the radius of the electrode, and the capacitive reactance varies inversely in proportion to the surface area (i.e. radius squared), that the ratio of capacitive reactance to solution resistance becomes more favourable as the radius of the electrode decreases. Thus facilitating the measurement of double layer capacitance in poorly conductive media with microelectrodes.

The present work will examine the use of ac impedance techniques to effectively characterise the presence of surface roughness and imperfect sealing of electrodes using microelectrodes in the blocking configuration.

2.1.3. Linear and cyclic sweep voltammetry.

Many spectroscopic techniques (e.g. ultraviolet, visible, infrared) rely on the ability to scan the compounds of interest through a range of wavelengths, generating a spectrum which may be used to identify the components[25]. In electrochemistry the equivalent technique is linear sweep voltammetry (LSV), in which the potential is varied at a constant rate and the corresponding current response recorded. The shape of the potential/current plot, called a voltammogram, may be related to the mass transport of the analyte to the electrode, the kinetics of the reactions involved, and bulk properties
of the solution[26].

A related technique in which the potential is swept first in one direction, then the
direction of the scan is reversed, is called cyclic voltammetry(CV), and may be
considered as two consecutive LSV experiments. Cyclic voltammetry is a powerful tool
in the elucidation of reaction kinetics, and most useful as a qualitative probe of the
electrochemical reactivity of compounds of interest. LSV and CV have been used
extensively to characterise the behaviour of various microelectrodes[27-30], and for the
study of reaction kinetics at microelectrodes[31-35].

The present work will examine the response of inlaid and recessed microdisk
electrodes to LSV and CV perturbations, in order to characterise the response of the
electrodes, and to evaluate the suitability of the ferrocene/ferricinium redox couple for
use as a reversible test couple for further characterisation of microelectrode behaviour.

2.1.4. Chronoamperometry.

Chronoamperometry involves the application of a potential step to the working
electrode, and the recording of the current transient which results. A plot of the current
transient versus time is called a chronoamperogram. Chronoamperometry is arguably
the simplest of all potentiostatic techniques, from both an experimental and a theoretical
point of view[2]. For this reason, much of the initial evaluation of the diffusional
behaviour of microelectrodes was based on chronoamperometry[36-40].

In this chapter the chronoamperometry of inlaid and recessed microdisk electrodes
will be discussed. At times short in comparison with L^2/D, where D is the diffusion
coefficient of the electroactive species, and L the recessed depth, a recessed microdisk
electrode behaves as a classical "shrouded planar electrode" where the predominant
mode of diffusion is semi-infinite linear diffusion, and therefore it should obey the
Cottrell equation exactly during chronoamperometry [41-43]. However, at longer times,
this behaviour breaks down and eventually a steady-state is attained.

The situation at the inlaid microdisk electrode is considerably more complicated
than the recessed microdisk, as the predominant mode of diffusion changes during the
course of the experiment. Initially semi-infinite linear diffusion will predominate. However, this dependence will only last for a brief time, before hemispherical diffusion becomes the dominant diffusion mode, and a steady state diffusion limited current is established.

2.2. EXPERIMENTAL

2.2.1. Instrumentation

AC impedance measurements were performed on either a Hewlett Packard 4192A LF Impedance Analyzer, fitted with a 16047A test fixture enabling direct attachment 4-terminal pair measurements, or a Wayne Kerr 4225 Automatic LCR meter. All experiments were performed in inert supporting electrolyte solutions at room temperature. Working electrodes were inlaid disk microelectrodes, and the counter electrode used was a Pt flag (area = 2 cm²).

Linear sweep voltammetry and cyclic voltammetry were carried out with a BAS 100A electrochemical analyser (Bioanalytical Systems Inc.). The BAS 100A system used in this work consisted of a BAS100A workstation based on the Z80A CPU, controlling a BAS 100 Low Current Module with software selectable gain. Potential sweep experiments were carried out over a wide range of scan rates from 5 mVs⁻¹ to 50 Vs⁻¹.

Chronoamperometric experiments were carried out using a PAR 273 digital potentiostat/galvanostat (Princeton Applied Research Corp). Current data were acquired digitally at 10 ms intervals, for 10 seconds after the potential was applied using the PAR 273 in conjunction with a DASH 16F A/D interface board (Metrabyte Corp) installed in an Olivetti M24 personal computer. All experiments were performed in a two-electrode mode and in a grounded Faraday cage. A length of silver wire was employed as the second electrode.

2.2.2. Chemicals

Acetonitrile (HPLC grade, Malinckrodt, Australia) was dried over alumina.
Distilled deionized water was obtained by passing distilled water through a Barnstead Sybron Nanopure water purification system (Barnstead Sybron Corp., Boston, MA), then through a Millipore Organex-Q cartridge to remove any trace organics. Tetraethyl ammonium perchlorate($\text{Et}_4\text{NClO}_4$, Electrochemical grade) was recrystallised from methanol/water, dried in a vacuum oven at 90 °C overnight. Ferrocene (E. Merk Damstardt) was resublimed onto a cold finger, then stored in a desiccator over phosphorus pentoxide. Potassium Chloride(AR grade, BDH, England) was used as supplied.

2.2.3. Software

Analysis of the ac impedance data was facilitated with the Equivalent Circuit software package available from Dr Bernard A. Boukamp, Dept. of Chemical Technology, PO Box 217, 7500 AE Enschede, the Netherlands. The Equivalent Circuit package incorporates data reduction, non linear least squares fitting, transformation, and plotting of impedance data.

Control of the PAR 273, the Metrabyte A/D card and subsequent data conversion and analysis was performed by the Axystant plus software package (MacMillan Software).

2.2.4. Glassware

All glassware was thoroughly cleaned, then dried in an oven at 105 °C prior to use.
2.2.5. Procedures

2.2.5.1. Electrochemical Impedance Spectroscopy

AC impedance data were collected in a two electrode format at open circuit potential. A minimal connecting lead length between the electrochemical cell and the impedance analyser was used to minimise stray capacitive and inductive effects. The impedance of the leads was estimated prior to each set of experiments by measuring the impedance response of the empty cell. The connecting leads were found to have a mainly reactive impedance equivalent to a capacitance of approximately 3pF, which was corrected for either instrumentally or manually in all subsequent measurements.

The HP 4192A instrument was used for the bulk of measurements reported, and was used typically with the following settings: applied sinusoidal voltage = 10 mV r.m.s., frequency range = 5 Hz to 1MHz, measurement mode = average, three or five individual experiments were carried out and averaged for each data set, and data was collected in series equivalent circuit mode as either impedance and phase angle, real and imaginary impedance, or capacitance and dissipation factor.

A Wayne-Kerr 4225 Automatic LCR Meter was used to measure the capacitance of a range of different radii microelectrodes typically with the following settings: applied sinusoidal voltage = 250 mV r.m.s. (fixed), frequency = 100Hz, 1kHz, and 10kHz, five individual measurement were taken at each frequency and averaged for the final value.

2.2.5.2. Voltammetry

Cyclic and Linear Sweep Voltammograms were obtained over a range of scan rates using the BAS 100A in a three electrode mode. All experiments were performed in a shielded Faraday cage. Electrodes were polished prior to each experiment on 0.3 μm alumina slurry, and rinsed with the appropriate solvent prior to use.
2.2.5.3. Chronoamperometry

The electrode reaction used to compare the experimental performance of the inlaid and recessed disk electrodes was the oxidation of ferrocene to produce the ferrocinium cation

\[(\text{C}_5\text{H}_3)_2\text{Fe} \text{ (solution)} \rightarrow (\text{C}_5\text{H}_3)_2\text{Fe}^+ \text{ (solution)} + e^- \quad (2.1)\]

Solutions containing 0.98 mM ferrocene in 0.10 M Et₄NCIO₄ + acetonitrile were prepared by spiking a 10.0 ml blank solution of 0.10 M Et₄NCIO₄ + acetonitrile with 200 μl of 0.050 M ferrocene in acetonitrile. Ferrocene (Merck) was sublimed prior to use. Tetraethyl ammonium perchlorate (Southwestern Analytical Chemicals Inc) was recrystallized from methanol, dried in vacuo, and stored over phosphorus pentoxide. Acetonitrile (Mallinckrodt, ChromAR HPLC grade) was used as received. The temperature was 22 °C throughout.

In all reported experiments, the potential was stepped from 0.20 V to 0.80 V. Experiments were performed first on the blank solution and then on the solution spiked with ferrocene. Both the blank and ferrocene experiments were replicated ten times and the averaged currents were stored serially. Between experiments the electrode surface was cleaned electrochemically by stepping the potential to -0.80 V for 30 seconds and then to +0.20 V for 30 seconds. Background subtraction was performed offline.

For the recessed electrodes it was necessary to ensure that the ferrocene solution had diffused into the hole. This was accomplished by performing repeated cyclic voltammetry experiments until a constant response was obtained.
2.3. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

2.3.1. Theory

Consider an electrochemical cell which consists of an inlaid microdisk working electrode, a large area counter electrode, and contains only inert supporting electrolyte solution. The working electrode in such a cell is termed a 'blocking electrode', because no faradaic reactions are possible[9]. In this section the ac impedance response of the blocking microelectrode will be examined. In order to simplify the cell impedance response the counter electrode is generally designed to be significantly larger than the working electrode, such that the impedance of the counter electrode is relatively insignificant in comparison to that of the working electrode.

The cell impedance may then be represented using a number of discrete electronic components intended to represent the major features of the blocking electrode cell. A series combination of the double layer capacitance \( C_{dl} \) and the solution resistance \( R_{sol} \) has been used to represent the blocking electrode under most circumstances. However, at high frequencies (approx. 1 MHz) the geometric capacitance of the cell may also need to be included in parallel to \( C_{dl} \) and \( R_{sol} \), as shown in figure 2.1. Such a model has been applied to inlaid disk electrodes by Newman[45], who examined the response of the blocking electrode cell with frequency in an attempt to explain the so-called "frequency dispersion" of the measured impedance. His analysis demonstrated that any perfect inlaid geometry would give rise to frequency dispersion of both
resistive and reactive impedances. Of particular note is the fact that the capacitance would tend to zero as frequency increases to infinity, but only if the electrode were a perfect inlaid electrode. If the electrode was recessed into the insulating boundary the capacitance would tend to a limiting value, rather than zero. In practice a perfect inlaid geometry where the electrode material is a perfect continuation of the surrounding insulator is difficult to achieve and maintain for any length of time. Scratches, pits, defects in fabrication, imperfect metal-to-glass seals will effect the response of the electrode.

DeLevie[9,46] modelled the rough surface of an electrode with a simple model based on the representation of surface features as parallel V shaped grooves (*figure 2.2*), and derived an expression for the cell impedance,

\[ Z_{a} = \frac{\rho}{\tan \beta} \frac{M_{0}}{zM_{1}} (\cos \theta - j \sin \theta) \]  
(2.2)

where \( Z_{a} \) = apparent impedance of groove, \( \rho \) = specific solution resistance, \( z \) = length of groove in \( z \) direction, and \( \theta \) = phase angle. Values for the functions \( M_{0} \) and \( M_{1} \) have been tabulated[9]. Further, the individual expressions for \( R_{\text{sol}} \) and \( C_{\text{dl}} \) were derived,

\[ R_{\text{sol}} = \rho \cot \beta \frac{M_{0}}{zM_{1}} \cos \theta \]  
(2.3)

and

\[ C_{\text{dl}} = 4\pi b \sec \beta \frac{M_{1}}{zM_{0}} \cot \sec \theta \]  
(2.4)

Although this model is based on assumptions which may appear unrealistic, it is likely that a carefully polished electrode will end up with a distribution of small parallel grooves on the surface[47]. Some experimental data has been presented which indicate that this type of model does indeed represent some of the characteristic behaviour of surface roughness on inlaid electrodes[9].
Figure 2.2. Simplified model of surface roughness based on a V shaped groove.

Combinations of ideal electronic components (R, C, and L) only approximate the response of a real electrochemical cell over very limited frequency ranges. Even a real resistor (R), for example, will display some capacitance and inductance effects at higher frequencies. Such a component will exhibit a distributed response which may be represented by a transmission line model. This type of approach is also useful for modelling electrochemical systems.

Two types of distributed response are encountered in modelling electrochemical cells, the finite length Warburg Impedance ($Z_w$), and the Constant Phase Element (CPE) response[48]. The Warburg Impedance occurs due to finite length diffusion and may be derived from Fick's Laws of diffusion. The finite length Warburg Impedance may be written,

$$Z_w = R_D \left( \frac{\tanh(\sqrt{js})}{\sqrt{js}} \right)$$

(2.5)

where $s = l (\omega/D)$, $l =$ finite region length, $D =$ diffusion coefficient, and $R_D =$ diffusion resistance.

The finite length Warburg Impedance is characterised in the complex plane by a straight line with $\theta = 45^\circ$. $Z_w$ may be considered the diffusion analog of the impedance of a uniformly distributed RC transmission line, as shown in figure 2.3.
The CPE response is typified by a straight line in the impedance plane with $\theta$ not equal to $45^\circ$. Such behaviour may be written in admittance representation as

$$Y_{CPE} = \Lambda_0(j\omega)^n$$

(2.6)

where $\Lambda_0$ and $n$ are frequency independent parameters which generally vary with temperature. When $n = 1$ the CPE corresponds to an ideal capacitance, when $n = 0$ the CPE corresponds to an ideal resistance, and when $n = -1$ the CPE corresponds to an ideal inductance.

CPE behaviour has been used extensively in the fitting of impedance data, and has been ascribed to the presence of inhomogeneities in the electrode/solution system, and is best considered in terms of a distribution of relaxation times. This is analogous to the Cole-Cole complex dielectric constant[49]. One possible interpretation of CPE behaviour is in terms of a distribution of relaxation times arising from a distribution of length scales at the electrode surface due primarily to roughness features.

---

**Figure 2.3.** Example of a uniformly distributed transmission line network.
2.3.2. **Magnitude of applied sinusoidal voltage.**

In order to perform meaningful ac impedance experiments it is essential for the magnitude of the applied sinusoidal waveform ($E_0$) to be small enough that a linear response is obtained [50]. **Figure 2.4.** illustrates the result of varying the magnitude of $E_0$ on the real and imaginary components of the measured ac impedance. It is clear from these results that ac impedance data in acetonitrile solutions at microdisk electrodes should be obtained at applied sinusoidal voltage levels of less than 0.2V, and preferably less than 0.1V. All experiments which will be described in the remainder of this chapter have been recorded with $E_0 = 0.010V$, unless otherwise stated. Similar results were obtained for electrode sizes up to $r = 50 \mu m$.

2.3.3. **Effect of electrode radius on the measured impedance.**

The ac impedance behaviour of a range of microdisk electrodes in aqueous solution was studied. As expected the impedance response is shifted to lower frequencies as the resistance of the inlaid microdisk electrode increases. This is demonstrated in **figure 2.5**, which confirms that the low frequency intercept of the real
Figure 2.5. A plot of inverse radius of a range of Pt inlaid microdisk electrodes versus the low frequency intercept of the real impedance. Solution: 2.0 M KCl (aqueous), T = 20 °C.

impedance varies inversely with radius as predicted from the primary current distribution[45]. A plot of the frequency behaviour of the real impedance is shown in figure 2.6. The variation of the high frequency behaviour (ie. $10^6$ Hz) confirm the dependence of the impedance response on the inverse of the radius of the microdisk electrode.

The variation of capacitance is also of interest in the case of microdisk electrodes. The results obtained for a range of inlaid Au microdisk electrodes in acetonitrile containing different concentrations of supporting electrolyte are shown in figure 2.7. The area of the electrode should be proportional to the measured capacitance, as the capacitance of any electrode is derived from the double layer. However, the analysis of the data indicates a dependence of $C \propto A^{5}$, not a direct proportionality as expected. this may be due to an inconsistency in the determination of the area of the electrodes.
Figure 2.6. A plot of the magnitude of the real impedance versus frequency for a range of Pt inlaid microdisk electrodes. Solution: 2M KCl (aqueous), T = 20 °C, radii of electrodes (a) 2.5 μm, (b) 5.0 μm, (c) 12.5 μm, (d) 25.0 μm.

Figure 2.7. A log-log plot of area of Au inlaid microdisk electrodes versus capacitance measured at 100 Hz in acetonitrile with the indicated additions of supporting electrolyte (Et₄NClO₄).
Table 2.1. Fitting results* from the analysis of the data contained in figure 2.8.

<table>
<thead>
<tr>
<th>Fitting parameter</th>
<th>Surface Finishb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Resistance (Ω)</td>
<td>1.51x10⁻³</td>
</tr>
<tr>
<td>C.P.E.</td>
<td>7.28x10⁻¹⁰</td>
</tr>
<tr>
<td>n</td>
<td>0.937</td>
</tr>
</tbody>
</table>

* Data analysed using Equivalent Circuit software. b Surface finish: (A) polished to 0.3 μm alumina; (B) 1000 grade emery paper; (C) 500 grade emery paper; (D) 220 grade emery paper.

2.3.4. Roughness effects

An electrode was prepared with a series of different surface finishes by polishing with different grades of silicon carbide paper, or alumina polishing powder. The finest finish used was a polish with 0.3 μm alumina, with successively rougher finishes being provided by 1000, 800, 500, and 220 grade emery (silicon carbide) papers. Each of the electrodes so prepared exhibited different impedance responses, indicative of the different degrees of surface roughness (figure 2.8). The data obtained from these series of experiments was fitted to an equivalent circuit of a resistance and CPE in series, over the frequency range of interest (i.e. 500 Hz to 1 MHz). The results for the fitted data are shown in table 2.1, and in each case the fitted data matched the experimental results to within 0.5% over the entire frequency range; indicating an excellent match between theory and experiment. A general trend in the data is observed for the CPE element and the value for the parameter n, which suggests that as the electrode surface is purposely roughened the distribution of responses increases. This would be expected for a rougher surface in which a larger range of both length and time scales would be present.

This behaviour may also be interpreted by examining the measured capacitance of the electrode for each surface finish over a range of frequencies. Figure 2.9. clearly shows the increase in the dispersion of measured capacitance with frequency for the rougher electrodes, as was predicted by DeLevie[9] for rough surfaces.
**Figure 2.8.** Impedance plane diagram (Nyquist plot) for the impedance of a Pt inlaid microdisk electrode (a=25.9 μm) in an aqueous solution of KCl (1.0M), with different levels of surface finish; (a) 0.3 μm alumina polish, (b) 1000 grade emery paper, (c) 800 grade emery paper, (d) 220 grade emery paper. Temperature = 19 °C, each data point represents the average of three measurements.

**Figure 2.9.** A plot of the dispersion of the measured capacitance at a Pt inlaid microdisk electrode (a=25.9 μm) in aqueous KCl (1.0M) solution, for a series of different surface finishes; (a) 220 grade emery paper, (b) 500 grade emery paper, (c) 800 grade emery paper, (d) 1000 grade emery paper, and (e) 0.3 μm alumina polish.
Another possible cause of frequency dispersion of measured capacitance is imperfect glass to metal seals of the gold microdisk electrodes[23]. This can arise due to the difference in the coefficients of expansion of gold and soda glass. While no electrodes used in the current work were found to possess such cracks, one electrode was accidentally cracked during the course of the experiments. The glass insulator surrounding the microdisk was cracked, but did not separate from the electrode body, a sketch of the cracked electrode is shown in figure 2.10. Readings taken both before and after the cracking of the electrode demonstrate clearly the difference in the cracked and precracked electrode (figure 2.11).

The standard surface finish used during the course of this thesis was a 0.3 μm alumina polish, and this was used for all electrodes in stationary and flowing solution experiments. An examination of the variation of the measured capacitance with frequency for three different radii Au microdisks was undertaken for each electrode to ensure that there was little frequency dispersion, indicative of a rough surface finish or poor glass-to-metal seal. An example of the type of response obtained from three acceptable electrodes is shown in figure 2.12.

![Crack](image)

**Figure 2.10.** Sketch of the cracked microdisk electrode used to determine the effect of an imperfect seal on the measured impedance.
Figure 2.11. A plot of the capacitative dispersion associated with a (a) cracked (shown in figure 2.10), and an (b) acceptable Au inlaid microdisk electrode (a=4.7 μm) in acetonitrile (0.10M Et₄NClO₄). Temperature = 22 °C.

Figure 2.12. Example of the variation of capacitance with frequency for three different radii Pt inlaid microdisk electrodes in an aqueous KCl (1.0M) solution, temperature = 22 °C. Radii: (a) 27.4 μm, (b) 12.6 μm, and (c) 5.0 μm.
2.3.5. Summary

1. Electrochemical impedance spectroscopy was found to be a powerful tool in the elucidation of the surface morphology of microdisk electrodes in aqueous and non-aqueous solutions.

2. The measured value of the capacitance of inlaid microdisk electrodes was found to vary with the area of the electrode, confirming the assumption that the capacitance is derived from the electrical double layer.

3. The impedance response of inlaid microdisk electrodes was found to shift to higher frequencies as the radius of the electrode was decreased.

4. An increase in surface roughness was found to induce a frequency dispersion and an increase in the absolute value of the measured capacitance.

5. The presence of surface roughness is indicated by a constant phase angle response in the measured impedance, which varies as the surface roughness increases.

6. EIS was found to be useful in the detection of cracked electrodes, and promises to be a powerful tool in the detection of sealing defects.
2.4. LINEAR SWEEP AND CYCLIC VOLTAMMETRY

2.4.1. Qualitative theoretical description of voltammetry at a microdisk electrode.

Consider an inlaid microdisk electrode (radius = 5.0 μm) in a quiescent solution of 1mM ferrocene in acetonitrile containing 0.1M Et₄NCIO₄, and examine the current response if the potential is swept at a very slow rate (eg. 10 mV s⁻¹) from zero volts to one volt versus a Ag/AgCl reference electrode. The potential waveform that is applied to the working electrode is illustrated in figure 2.13.

At the initial potential no electron transfer reactions occur. However, as the potential is increased towards the oxidation potential of ferrocene, some of the ferrocene molecules at the electrode surface oxidise according to[51]

\[ \text{Fe} \xrightarrow{\text{+e}} \text{Fe}^+ + e^- \] (2.7)

This electron transfer process will lead to a concentration gradient near the surface of the electrode as the concentration of ferrocene near the surface with respect to the bulk solution will be depleted, and the concentration of the ferricinium cation will be enriched. The concentration gradient will lead to a diffusion of the ferrocene from the
bulk of solution to the electrode and a diffusion of the ferricinium cation into the bulk. As the potential is swept further positive more of the ferrocene will oxidise until a potential is reached where the rate of diffusion becomes the limiting factor, and a steady state current is achieved. Such a steady state voltammogram is illustrated in figure 2.14(a). If the potential sweep is reversed the experiment becomes a cyclic voltammetric experiment, and the response will be seen to trace back over the forward sweep trace. This is due to the fact that the oxidised material has diffused away from the electrode surface and is not present to be reduced back to the original neutral species. The reverse scan traces over the forward scan due to the decrease of the oxidation current as the potential moves away from the oxidation potential of ferrocene.

If the rate at which we vary the potential is increased considerably (e.g. 1000 V s⁻¹) then different electrochemical behaviour will be observed. The ferrocene will still oxidise as the potential approaches the oxidation potential of ferrocene. However, in this case the rate of potential sweep is so fast that a steady state current does not have sufficient time to occur, and only the ferrocene very close to the electrode surface will oxidise leading to a rapid depletion of the material at the electrode surface. In this case a peaked shape voltammogram will result, and a peak on the reverse scan will occur due to the reverse electron transfer reaction occurring (figure 2.14(b)).

It is useful to visualise these processes in terms of the shape of the diffusion layer of ferrocene. In the steady state experiment the ferrocene diffusion layer resembles an ever increasing 'hemisphere', so an ever increasing number of molecules can diffuse towards the surface so that the mode of mass transport may be termed hemispherical diffusion (figure 2.15(a)). In the fast scan rate experiment the diffusion layer is confined to a layer very close to the electrode surface, and the molecules essentially diffuse straight to the electrode surface forming a uniform layer over the electrode (figure 2.15(b)). This mode of diffusion is often termed linear diffusion. Linear diffusion may also be constrained by the geometry of the electrode used, for example a recessed microdisk electrode. The efficiency of the hemispherical diffusion mode is much greater than the linear diffusion mode as a greater amount of material has
access to the electrode surface as the experiment progresses, leading to an enhanced current density. At scan rates intermediate between the two extremes a hybrid mode of diffusion will apply.

2.4.2. Quantitative description of steady state voltammetry at an inlaid microdisk.

Saito[52] was the first person to derive the expression for the diffusion limited steady state current ($i_d$) at an inlaid disk microelectrode,

$$i_d = 4nFe^{b}Da$$  \hspace{1cm} (2.8)

where $n =$ number of electrons, $F =$ Faraday's constant, $c^b = $ bulk concentration, $D =$ diffusion coefficient, and $a =$ radius of disk.

A general treatment of the shape of steady state voltammograms was given by Bond et al.[53] who generated analytical and numerical solutions enabling the
Figure 2.15. Example of the form of (a) hemispherical diffusion, and (b) linear diffusion to a microdisk electrode during voltammetry.

prediction of steady state voltammetric waves under reversible, quasi reversible, and irreversible conditions. Only the reversible cases will be described here, and the original reference may be consulted for information regarding quasi reversible, and irreversible cases. Consider the following reaction,

\[
\text{O (solution)} + n\text{e}^- \rightleftharpoons \text{R (solution)} \tag{2.9}
\]

For the reversible case, the expression relating the current and potential is given by,

\[
i = \frac{4nFD_O D_R Kac_0^b}{D_O + KD_R} = \frac{i_m}{1 + (D_O/KD_R)}
\]

where

\[
\frac{1}{K} = \frac{c_o(r,0)}{c_R(r,0)} = \exp \left( \frac{nF}{RT} (E - E^o) \right) \quad 0 < r < a \tag{2.10}
\]

hence it follows that,

\[
\frac{i_d - i}{i} = \frac{D_O}{KD_R} = \exp \left( \ln \left( \frac{D_R}{D_O} \right) + \frac{nF}{RT} (E - E^o) \right) \tag{2.11}
\]
therefore the half wave potential \( i = \frac{1}{2} i^* \) may be given by,

\[
E_{\frac{1}{2}} = E^o + \frac{RT}{nF} \ln \left( \frac{D_2}{D_0} \right) \tag{2.12}
\]

rearranging gives,

\[
E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \left( \frac{1 + i}{1 - i} \right) \tag{2.13}
\]

The Tomé's criteria for reversibility is given by,

\[
E_{\frac{1}{4}} - E_{\frac{3}{4}} = \frac{RT}{nF} \ln(9) = \frac{56.45}{n} \text{ mV} \tag{2.14}
\]

2.4.3. **Quantitative description of voltammetry under linear diffusion conditions.**

The expression relating the shape of a reversible voltammogram under linear diffusion conditions has been derived[53],

\[
\int_0^\sigma \chi(z) \frac{dz}{(\sigma t - z)^{\frac{1}{2}}} = \frac{1}{1 + \xi \Theta (\sigma t)} \tag{2.15}
\]

where

\[
\chi(z) = \frac{i(\sigma t)}{nFAc(b(\pi D_0)\sigma)^{\frac{1}{2}}} \tag{2.16}
\]

and \( S(\sigma t) = e^{-\sigma t}, \Theta = \exp[(nF/RT)(E_1 - E^o)], \sigma = (nF/RT) \nu, E^o \) = formal potential, \( \nu = \) scan rate, and \( z = \sigma t, \) where \( t = \) dummy Laplace variable. Hence the current may be obtained from the expression,
\[ i = nFAc^b(\pi D_c \sigma)^{1/2} \chi \sigma t \] (2.17)

Tables of values for the solution to the integral, hence the current expression have been calculated[2], making the analysis of linear diffusion voltammograms possible. Further to this the value for the peak current can be derived,

\[ i_p = (2.69 \times 10^5) n^{3/2} A D_c^{1/2} \nu^{1/2} c^b \] (2.18)

If we define the potential at half the peak height to be \( E_{p/2} \), and the peak potential to be \( E_p \), then a criteria for a reversible wave is given by,

\[ |E_p - E_{p/2}| = 2.2 \frac{RT}{nF} = 56.5/n \text{ mV at 25 °C}. \] (2.19)

So for a reversible wave \( E_p \) is independent of scan rate, and \( i_p \) will be proportional to \( \nu^{1/2} \). For the case of cyclic voltammetry a further criteria for a reversible system is the separation of the cathodic \( (E_{pc}) \) peak and the anodic peak \( (E_{pa}) \), which is given by[54],

\[ |E_{pa} - E_{pc}| = \frac{59.5}{n} \text{ mV at 25 °C} \] (2.20)
2.4.4. Analysis of a steady state voltammogram at an inlaid microdisk electrode.

A steady state voltammogram of ferrocene oxidation at a gold microdisk electrode (a = 5.0 μm) in acetonitrile containing 0.1M Et₄NClO₄ supporting electrolyte is shown in figure 2.17. The steady state wave demonstrates the sigmoidal shape which is so familiar to electrochemists who are used to working with steady state currents in d.c. polarography. An evaluation of the steady state voltammogram was carried out utilizing equations 2.7 and 2.8, in order to ascertain the suitability of the ferrocene/ferricinium couple as a reversible test system for further work. A plot of log(\((i_d - i)/i\)) vs potential (figure 2.16) is linear, with the reciprocal slope equal to the expected value of 57 mV. The Tomès criteria was calculated to be 56.0 mV, confirming the reversibility of the ferrocene oxidation reaction in acetonitrile at a gold microdisk electrode.
2.4.5. Analysis of a voltammogram at a recessed microdisk electrode.

A cyclic voltammogram of 1mM ferrocene in acetonitrile 0.1M Et$_4$NCIO$_4$ solution at a recessed Au microdisk electrode ($a = 12.5$ $\mu$m, depth of recess = 30 $\mu$m) is shown in figure 2.18. Note the prominent peaks typical of linear diffusion processes, and the much reduced current caused by constraining the diffusion to be linear. The peak separation in this case was found to be 62.5 mV, which is slightly higher than expected, as is the value of $|E_p - E_{pc}| = 60.5$ mV calculated for the oxidation wave (forward sweep). This may be attributed to iR drop which would tend to draw these values out.

2.4.6. Effect of scan rate on wave height at inlaid microdisk electrodes.

The effect of scan rate on the current response of the ferrocene oxidation wave was examined at a range of different radii inlaid disk microelectrodes, the data obtained are listed in table 2.2 smallest electrode ($a = 2.8\mu$m) exhibited steady state behaviour over a considerable scan rate range, until a scan rate of 5 V$s^{-1}$ when the peak shaped response characteristic of linear diffusion was observed. The larger radius electrode demonstrated a rapid progression to linear diffusion with the characteristic scan rate to the half power dependence, clearly demonstrating the utility of using smaller electrodes for achieving steady state voltammograms.

Table 2.2. Comparison of the effect of scan rate on the peak height of 1mM Ferrocene solution in 0.1M Et$_4$NCIO$_4$ in acetonitrile for inlaid microdisk electrodes.

<table>
<thead>
<tr>
<th>radius ($\mu$m)</th>
<th>Wave height for a given scan rate (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>2.79 2.79 2.84 2.79 2.84 2.89 2.93 3.17 3.47 4.20</td>
</tr>
<tr>
<td>5.2</td>
<td>5.16 5.16 5.16 5.26 5.37 5.58 5.81 6.29 7.16 8.27 10.5</td>
</tr>
<tr>
<td>12.2</td>
<td>12.5 12.9 13.3 14.1 14.8 16.4 18.7 23.7 29.6 38.0 52.2</td>
</tr>
<tr>
<td>30.6</td>
<td>30.3 34.5 38.7 43.2 51.7 62.1 76.8 106 139 185 265</td>
</tr>
</tbody>
</table>
Figure 2.17. A cyclic voltammogram of $1 \times 10^{-3}$ M ferrocene in acetonitrile (0.010 M Et$_4$NClO$_4$) at a gold inlaid microdisk electrode ($a = 5.0 \mu$m). Scan rate = 5 mV s$^{-1}$, $T = 19^\circ$C.
Figure 2.18. A cyclic voltammogram of $1 \times 10^{-3}$ M ferrocene in acetonitrile (0.010 M Et$_4$NClO$_4$) at a gold recessed microdisk electrode ($a=12.5$ $\mu$m). $L = 30$ $\mu$m, scan rate = 5 mV s$^{-1}$, $T = 19$ °C.
2.4.7. Effect of scan rate on wave height at recessed microdisk electrodes.

The situation with recessed disk microelectrodes is not as straightforward as the inlaid microdisks, due to the added complication of the recess constraining the diffusion to a linear form. This means that, the diffusion at a recessed microdisk electrode would be expected to be linear at short to medium time scales, then 'switch' to a steady state hemispherical diffusion mode as the diffusion layer reaches the mouth of the recess.

A plot of peak height versus the square root of scan rate is shown in figure 2.19 for the oxidation of ferrocene in acetonitrile (0.1M \( \text{Et}_4\text{NClO}_4 \)) at a recessed gold microdisk electrode. The scan rate to the half dependence is found to begin at a scan rate of approximately 20 - 50 mVs\(^{-1}\), in the region where the inlaid microdisk is still demonstrating steady state behaviour.

**Figure 2.19.** Plot of the square root of scan rate versus peak height for a recessed Au microdisk electrode. \( a = 5.0 \mu m \), solution = 1mM ferrocene in 0.1M \( \text{Et}_4\text{NClO}_4 \) acetonitrile, depth of recess = 60 \( \mu m \).
2.4.8. Effect of solution resistance on inlaid microdisk electrodes.

The solution resistance of an inlaid disk microelectrode may be calculated from the primary current distribution and is given by[3],

\[ R = \frac{1}{4 \kappa a} \]  \hspace{1cm} (2.21)

where \( R \) = resistance, \( \kappa \) = solution conductivity, and \( a \) = disk radius. This resistance can severely hamper the measurement of electrochemical data in high resistivity solvents (eg. dichloromethane, toluene, heptane, etc.), due to the resultant voltage drop in solution. This is because the passage of current through a resistance causes a voltage drop equal to the product of the current times resistance, the so called iR drop. A high iR drop in solution will lead to distorted voltammetric data, and is a particular problem at conventional sized electrodes.

The resistance of inlaid disk microelectrodes should obey the above relationship under all circumstances; however many workers have reported that the iR drop in solutions with little added electrolyte is less than anticipated, enabling electrochemical characterisation of a number of systems in high resistance media[27,55,56]. The most likely explanation involves a number of factors, including the production of charged species in solution and migration effects. If the product of the redox reaction is charged then a population of charged species will exist near the electrode surface where the maximum iR drop is to be found (ie. current density is greatest), thus leading to an increase in the conductivity, and a decrease in the iR drop. Another factor which may help to explain this data is that without the presence of a large amount of inert supporting electrolyte migration effects will be felt by any charged species in solution, leading to enhanced mass transfer for those species. Oldham[57] and Bruckenstein[58] have recently shown that all electrodes have the same iR drop when they are in the steady state regime regardless of geometry or size.

Tables 2.3 and 2.4 contain the concentration dependence for ferrocene in
acetonitrile at different radii microelectrodes in the presence and absence of deliberately added supporting electrolyte. There is in fact little difference in the wave height data for the two sets of data, however some distortion of the wave shape does occur. This is conveniently demonstrated by performing a plot of \( \log \left( \frac{i_0 - i}{i} \right) \) versus potential as shown in figure 2.20. The reciprocal slope of this wave is 105 mV, considerably greater than the previously determined value of 57 mV in the presence of supporting electrolyte. Further confirming the drawn out nature of the wave in the absence of supporting electrolyte is the value calculated for the Tomès criteria of 90 mV, which compares with the previous value of 56 mV. In spite of the apparent distortion of the wave shape, the wave height is virtually unaffected by the absence of supporting electrolyte, a characteristic which may enable the use of electrochemical detection in high resistance solvents in flow injection analysis, and high performance liquid chromatography to be detailed in later sections.

**Table 2.3.** Limiting current data for the oxidation of ferrocene at various radii Au microdisk electrodes in acetonitrile with 0.1M Et₄NClO₄ supporting electrolyte.

<table>
<thead>
<tr>
<th>Radius (μm)</th>
<th>Limiting current for given concentrations of ferrocene (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10⁻³M</td>
</tr>
<tr>
<td>2.8</td>
<td>2.6x10⁻⁹</td>
</tr>
<tr>
<td>4.7</td>
<td>4.5x10⁻⁹</td>
</tr>
<tr>
<td>12.4</td>
<td>1.2x10⁻⁸</td>
</tr>
<tr>
<td>32.5</td>
<td>3.1x10⁻⁸</td>
</tr>
</tbody>
</table>

**Table 2.4.** Limiting current data for the oxidation of ferrocene at various radii Au microdisk electrodes in acetonitrile with no deliberately added supporting electrolyte.

<table>
<thead>
<tr>
<th>Radius (μm)</th>
<th>Limiting current for given concentrations of ferrocene (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10⁻³M</td>
</tr>
<tr>
<td>2.8</td>
<td>2.6x10⁻⁹</td>
</tr>
<tr>
<td>4.7</td>
<td>4.8x10⁻⁹</td>
</tr>
<tr>
<td>12.4</td>
<td>1.3x10⁻⁸</td>
</tr>
<tr>
<td>32.5</td>
<td>3.4x10⁻⁸</td>
</tr>
</tbody>
</table>
2.4.9. **Effect of solution resistance on recessed microdisk electrodes.**

The advantages of reduced iR drop are not observed to any great degree with the recessed microdisk electrodes displaying linear diffusion behaviour. However under steady state conditions the same iR drop benefits as inlaid disk electrodes may be anticipated. It was found that as the amount of added electrolyte decreases the wave shape of the ferrocene oxidation process is found to become drawn out, which is expected under linear diffusion conditions. This behaviour is typified by an increase in the separation between the anodic and cathodic peaks with an increase in the iR drop (table 2.5). For comparison, peak to peak separations at a conventional (a = 1.5 mm) inlaid disk electrode obtained under identical conditions are shown in table 2.6. The distortion introduced by decreasing the supporting electrolyte concentration by just two orders of magnitude is severe, and contrasts the data obtained at inlaid microdisk electrodes under steady state diffusion conditions discussed in section 2.4.8.
The results presented here clearly demonstrate the advantage of steady state voltammetry at inlaid microdisk electrodes in solutions with reduced amounts of added electrolyte. These data also emphasise that the iR drop benefits at microelectrodes are not simply due to the low currents, but are related to the ability to achieve steady state currents in experimentally accessible time scales.

2.4.10. Concentration dependence

According to equation 2.2 the steady state limiting current at an inlaid disk microelectrode should be proportional to the concentration of the analyte in solution. The concentration dependence for four inlaid disk microelectrodes of different radii is illustrated in figure 2.21, with data taken from table 2.3. The response was found to vary linearly with concentration over three orders of magnitude examined in the present work.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>5 mV s⁻¹</th>
<th>10 mV s⁻¹</th>
<th>20 mV s⁻¹</th>
<th>50 mV s⁻¹</th>
<th>100 mV s⁻¹</th>
<th>200 mV s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻¹ M</td>
<td>0.065</td>
<td>0.055</td>
<td>0.055</td>
<td>0.055</td>
<td>0.065</td>
<td>0.075</td>
</tr>
<tr>
<td>10⁻² M</td>
<td>0.100</td>
<td>0.090</td>
<td>0.105</td>
<td>0.145</td>
<td>0.180</td>
<td>0.235</td>
</tr>
<tr>
<td>10⁻³ M</td>
<td>0.160</td>
<td>0.175</td>
<td>0.225</td>
<td>0.340</td>
<td>0.470</td>
<td>0.640</td>
</tr>
</tbody>
</table>

Table 2.5. Peak separation data for a recessed microdisk electrode (a = 12.5 μm) in acetonitrile containing the indicated concentrations of supporting electrolyte.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>5 mV s⁻¹</th>
<th>10 mV s⁻¹</th>
<th>20 mV s⁻¹</th>
<th>50 mV s⁻¹</th>
<th>100 mV s⁻¹</th>
<th>200 mV s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻¹ M</td>
<td>0.070</td>
<td>0.070</td>
<td>0.075</td>
<td>0.075</td>
<td>0.105</td>
<td>0.165</td>
</tr>
<tr>
<td>10⁻² M</td>
<td>0.100</td>
<td>0.110</td>
<td>0.130</td>
<td>0.170</td>
<td>0.205</td>
<td>0.305</td>
</tr>
<tr>
<td>10⁻³ M</td>
<td>0.265</td>
<td>0.295</td>
<td>0.365</td>
<td>0.510</td>
<td>0.650</td>
<td>0.735</td>
</tr>
</tbody>
</table>

Table 2.6. Peak separation data for a conventional gold inlaid disk electrode (a = 1.5 mm) in acetonitrile containing the indicated concentrations of supporting electrolyte.
Figure 2.21. Concentration dependence of the limiting current for a range of inlaid Au microdisk electrodes. Analyte = ferrocene in acetonitrile (0.10M Et₄NClO₄), radius of electrodes: (a) 32.5 μm, (b) 12.4 μm, (c) 4.7 μm, (d) 2.8 μm.

2.4.11. Calibration of inlaid microdisk electrodes.

The expression for the steady state current (equation 2.2) provides a useful tool for the calibration of microdisk electrodes. Provided that the system of interest is well characterised (e.g. ferrocene/ferrocinium) the 'electroactive' radius of the electrode may be determined. To illustrate this point a range of microdisk electrodes was calibrated using slow scan LSV on a 1mM ferrocene in acetonitrile (0.1M Et₄NClO₄) solution. All microdisk electrodes used in the course of the present work were calibrated after fabrication, then at regular intervals afterwards.

While it is true that the value calculated for the radius of the electrode closely matches the nominal radius in almost all cases, it is worth considering what is being determined in this experiment in a little more detail. The relationship expressed in equation 2.2 applies for steady state currents which implies that the size of the diffusion layer is considerably larger than the characteristic length of the microdisk electrode. Further, any features which are present on the electrode surface (e.g. cracks, roughness, grain boundaries, etc.) which have a characteristic length smaller than the
diffusion layer will NOT effect the magnitude of the measured current. Hence the value of radius determined in a steady state experiment only applies when the electrode is used in steady state experiments.

If a microdisk electrode is calibrated using the steady state expression (equation 2.2.), the radius value determined should not be assumed to apply in other time domains. For example if the radius of a microdisk electrode is calculated in a steady state experiment, that value may not apply if that same microdisk electrode is used in fast scan rate experiments, where the diffusion layer will be considerably thinner. This implies that if there are surface features on a microdisk electrode the diffusional area of the electrode will vary with the thickness of the diffusion layer (ie. scan rate). This behaviour will be further examined in chronoamperometric experiments at recessed microdisk electrodes(section 2.5.3) where the process of etching the recessed microdisk electrodes produced a noticeable surface roughness leading to anomalously high currents at shorter time scales.

2.4.12. Summary

1. Steady state voltammetry is achievable in experimentally accessible time scales at inlaid microdisk electrodes.

2. The ferrocene/ferrocinium redox couple is a reversible system in acetonitrile solutions, suitable for the characterisation of microdisk electrodes.

3. The time scale of the experiment will dictate the diffusion mode which will predominate in a given experiment at a microdisk electrode. At short time scales linear diffusion will predominate, whereas at long time scales hemispherical diffusion will apply.

4. Steady state voltammetry is possible in high resistance solutions with inlaid microdisk electrodes.

5. The steady state limiting current varies with concentration of ferrocene in acetonitrile in the presence and absence of deliberately added supporting electrolyte.

6. Recessed microdisk electrodes display peaked voltammograms indicative of
linear diffusion.

7. Calculation of the electroactive radius of a microdisk electrode is possible using the steady state current expression (equation 2.2), enabling calibration of recently fabricated microdisk electrodes.

8. The effect of iR drop at inlaid microdisk electrodes is reduced to the extent that steady state voltammograms are obtainable in the absence of deliberately added electrolyte.

9. The effect of iR drop at recessed microdisk electrodes is extreme at low concentrations of added electrolyte, confirming that the iR drop benefits of inlaid microdisks is due to the steady state current, and not the absolute value of the current.

2.5. CHRONOAMPEROMETRY.

2.5.1. Theory of the Steady state.

Consider a sudden change, at \( t=0 \), of the potential applied to the working electrode, initially at its rest potential, that is sufficiently extreme so as to cause complete concentration polarization (figure 2.22). In the case of the oxidation

\[
R \rightarrow O + e^- \tag{2.22}
\]

this implies stepping the potential to a value of several hundred millivolts more positive than the standard potential. An exact solution for the steady-state current, namely

\[
i = 4nFbc^bDa \tag{2.23}
\]

eexists for the inlaid disk [52,53].

---

1 Chronoamperometric theory derived in collaboration with Prof. K.B. Oldham and Dr C.G. Zoski.
The steady-state for a recessed disk may be modelled assuming the approximation that the concentration of R is uniform across the mouth of the electrode tube, with a value of \( c^m \). This value will differ from \( c^b \) if the bulk solution is unstirred but will equal \( c^b \) when stirring occurs.

For a steady-state current to exist in the tube portion of the recessed disk assembly, there must be a linear concentration profile of R within the tube, with concentration values of zero at the electrode itself and \( c^m \) at the mouth. Therefore

\[
\frac{i}{\pi n F a^2} = D \frac{dc}{dx} = \frac{D c^m}{L} \tag{2.24}
\]

Moreover, diffusion from the bulk of the solution to the mouth must mimic steady-state diffusion to an inlaid disk, as given by equation 2.23 but with \( c^b \) replaced by \( c^b - c^m \), thus

\[
i = 4nF(c^b - c^m)D a \tag{2.25}
\]

Because equations 2.24 and 2.25 relate to the same current, the concentration at the mouth is given by
\[ e^m = \frac{4Lc^b}{4L + \pi a} \] (2.26)

and hence the steady-state current

\[ i = \frac{4\pi nFcbDa^2}{4L + \pi a} \] (2.27)

The value obtained by equation 2.27 is smaller than that of the inlaid disk electrode by the factor

\[(4L/\pi a) + 1 \] (2.28)

when the solution is unstirred. When convection beyond the mouth maintains a uniform concentration \( c^b \) there, the steady-state current is increased only slightly to

\[ i = \frac{\pi nFcbDa^2}{L} \] (2.29)

To determine the ohmic polarization, or "iR drop", for the inlaid and recessed disk electrodes in the steady-state, it is sufficient to calculate the resistance \( R \) of two electrode cells, one of which is a disk (inlaid or recessed) microelectrode and multiply this value by the current.

If the counter electrode is large and effectively at infinity, the resistance of the solution in contact with an inlaid disk electrode of radius \( a \) is simply [3]

\[ R = \frac{1}{4\kappa a} \] (2.30)

The resistance of the recessed electrode is well approximated by the resistance of the column of electrolyte solution in the tube, plus the resistance beyond the mouth, as
given by equation 2.30; that is

\[ R = \frac{L}{\pi \alpha^2} + \frac{1}{4\alpha} \]  

(2.31)

which is larger than that of the inlaid disk by the factor given in equation 2.28.

Multiplying these two values of \( R \) by the steady-state currents given in equations 2.23 and 2.24 leads to

\[ iR = \frac{nF \beta D}{\kappa} \]  

(2.32)

for both inlaid and recessed disk electrodes. Of course, this is not a coincidence. In fact, in a given solution the steady-state \( iR \) drop during concentration polarized conditions is a constant, irrespective of electrode size or cell geometry, as has recently been shown elsewhere [57,58]. This statement naturally presupposes that the electrode geometry is such that a steady-state will be attained and applies only when transport is wholly diffusive. Thus the steady-state \( iR \) drop is slightly larger for a recessed disk electrode when there is convection beyond the mouth.

2.5.2. Theory of the transient response

In this section the time evolution of the transient current following a potential step will be compared for both the inlaid and recessed disk electrodes. Initially, the Faradaic currents at both disk electrodes obey the Cottrel equation, which may be written

\[ it^{1/4} = nF \beta a^2 (\pi D)^{1/4} \]  

(2.33)

but the duration of this obedience is very brief for the inlaid disk electrode. After a time of only
\frac{a^2}{361 \pi D}

(2.34)

departures from Cottrellian behaviour represent 5% of the total current for the inlaid disk. This conclusion follows from the equation [59-62]

\[ i = nF b a^2 (\pi D t)^{\frac{1}{2}} \left( 1 + \frac{(\pi D t)^{\frac{3}{2}}}{a} + 0.135 \frac{\pi D t}{a^2} + \ldots \right) \]  

(2.35)

which describes the short-time behaviour of the inlaid disk electrode.

For a recessed disk electrode, planar diffusion will initially govern the concentration profile of R within the electrode tube, resulting in a steadily lengthening column of solution from which species R is significantly depleted. Eventually, this depleted zone will reach the end of the tube and, shortly thereafter, this will cause a repercussion in the Faradaic current. If convection maintains the mouth concentration of R at its initial value, then

\[ c = c^b, \quad x = L \quad \text{all} \quad t \]  

(2.36)

where \( x \) denotes distance measured normally to the disk electrode and \( c \) is the concentration of R at distance \( x \) and time \( t \).

The other boundary condition, resulting from our prescription of complete concentration polarization, is

\[ c = 0, \quad x = 0 \quad \text{all} \quad t > 0 \]  

(2.37)

while the initial condition is

\[ c = c^b, \quad \text{all} \quad x \geq 0, \quad t = 0 \]  

(2.38)
Fick's second law must be solved

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]  \hspace{1cm} (2.39)

subject to conditions 2.36, 2.37, and 2.38.

The Laplace transform of equation 2.39 gives

\[ \frac{d^2 \tilde{c}^*}{dx^2} = \frac{1}{D} [s \tilde{c}^* - c^0] \]  \hspace{1cm} (2.40)

after the initial condition 2.38 is incorporated. A general solution of this differential equation may be written

\[ \tilde{c}^* = \left( \frac{c^0}{s} \right) + P(s) \exp \left\{ -x s^D \right\} + Q(s) \exp \left\{ x s^D \right\} \]  \hspace{1cm} (2.41)

where \( P(s) \) and \( Q(s) \) are arbitrary functions of the dummy Laplace variable. Boundary condition 2.36 implies that \( \tilde{c}^* = c^0 / s \) at \( x = L \), while boundary condition 2.37 shows that \( \tilde{c}^* = 0 \) at \( x = 0 \). These two results permit the two arbitrary functions to be identified as

\[ P(s) = \frac{-c^0/s}{1 - \exp(-2Ls^D)} \]  \hspace{1cm} (2.42)

and

\[ Q(s) = \frac{c^0/s}{\exp(2Ls^D)} - 1 \]  \hspace{1cm} (2.43)

in the present circumstances.

By differentiating equation 2.41 with respect to \( x \), and then setting \( x = 0 \), one determines that the concentration gradient of R at the electrode surface has a Laplace
transform given by

\[
\left( \frac{dc}{dx} \right)_{x=0} = s^{+}D^{-\xi}(Q(s) - P(s))
\]

\[
= \frac{c^b}{s^{+}D^{\xi}} \left( \exp \{-Ls^{+}D^{-\xi} \} + \exp \{Ls^{+}D^{-\xi} \} \right) \left( \exp \{Ls^{+}D^{-\xi} \} - \exp \{-Ls^{+}D^{-\xi} \} \right)
\]

(2.44)

equations 2.42 and 2.43 having been used. The term in square brackets is simply
\[
\coth \{Ls^{+}D^{-\xi} \} \text{ and Laplacian inversion of equation 2.44 then yields [63]}
\]

\[
\left( \frac{dc}{dx} \right)_{x=0} = \frac{c^b}{L} \theta_3 \left[ 0 , \frac{Dt}{L^2} \right]
\]

(2.45)

a simple result involving one of the theta functions [63]. The current, found by
application of Fick's first and Faraday's laws, is \( \pi nF \alpha^2 dc/dx \) \_x=0 and if this is
combined with equation 2.45 then

\[
i = \left( \frac{\pi nF \alpha^2}{L} \right) \theta_3 \left[ 0 , \frac{Dt}{L^2} \right]
\]

(2.46)

describes the behaviour of the recessed disk electrode at all times, when the mouth
concentration is maintained at \( c^b \).

Similarly, if a short-time expansion of the theta function [63] is employed, the
result is

\[
i = nF c^b \alpha^2 \left( \frac{\pi D}{t} \right)^{\frac{1}{2}} \left[ 1 + 2 \exp \left\{ -\frac{L^2}{D} \right\} + 2 \exp \left\{ -\frac{4L^2}{D} \right\} + ... \right]
\]

(2.47)
in which the leading term is simply the Cottrell term.

Similarly, if a long-time expansion of the theta function [63] is employed, the
result

\[ i = \frac{\pi n F c_b D a^2}{L} \left[ 1 + 2 \exp\left( \frac{-\pi^2 D t}{L^2} \right) + 2 \exp\left( \frac{-4\pi^2 D t}{L^2} \right) + \ldots \right] \quad (2.48) \]

predicts a steady-state current of \( \pi n F c_b D a^2 / L \) and permits a calculation of the time required to reach the steady-state, akin to equation 2.51.

At short times the behaviour of a recessed disk electrode is given by equation 2.33 irrespectively of whether there is (natural or forced) convection or not. Note that this equation does not involve the tube length \( L \). At long times, the steady-state equations 2.29 and 2.27, respectively, apply with and without convection. For typical experimental conditions, the magnitude of the steady-state current is seen to depend only marginally on whether or not there is convection. The algebraic difference between equations 2.29 and 2.27 is simply that the \( L \) term for the convective case is replaced by \( L + (\pi a/4) \). Hence it is possible to approximate the behaviour of the recessed disk without convection by simply replacing \( L \) in equation 2.45 by \( L + (\pi a/4) \), so that

\[ i = \frac{4\pi n F c_b D a^2}{4L + \pi a} \theta_3 \left\{ 0, \frac{16 D t}{4L + \pi a} \right\} \quad (2.49) \]

and assume that this equation applies at all times during the chronoamperometric experiment. This approximation is assumed to be valid provided that the recess is not too shallow.

From the short-time expansion of the \( \theta_3 \) function (equation 2.47) it can be concluded that the departure from Cottrellian behaviour for a recessed disk in the absence of convection does not exceed 5% until the time

\[ \frac{(4L+\pi a)^2}{16 D \ln(38)} \quad (2.50) \]

Similarly, the use of a long-time expansion of the \( \theta_3 \) function (compare equation
2.48) shows that the time required for the current at a recessed disk electrode to come within 5% of its steady-state value is

$$\frac{(4L+\pi a)^2 \ln(38)}{16D\pi^2} \quad (2.51)$$

For comparison, the approach to the steady-state value by the current at an inlaid disk is complete to within 5% by the time

$$\frac{(38a)^2}{(\pi^3D)} \quad (2.52)$$

This conclusion follows from the equation [59-62]

$$i = 4nFbDa \left(1 + \frac{2a/\pi}{(\piDt)^{1/2}} + \frac{0.039a^3}{(\piDt)^{3/2}} + \ldots \right) \quad (2.53)$$

which describes the long-time behaviour of an inlaid disk electrode during chronoamperometry.

2.5.3. Results and discussion.

Using log/log scales, figure 2.23 shows theoretical chronoamperograms for the inlaid disk and recessed disk electrodes in the absence of convection. Apart from the larger steady-state current value of the inlaid disk, the most noticeable feature of this diagram is the very slow transition of the inlaid disk from Cottrelian to steady-state behaviour. In comparison, the recessed disk almost "switches" from one regime to the other. An indication of how slowly the inlaid disk approaches its steady-state is given by noting that, for the parameters we adopt, the current is within 10% of its steady-state value after 680 ms but requires 82 s to come within 1%.

Considering ohmic polarization in the transient state, the resistance expressions from equations 2.30 and 2.31 are used because $R$ is time-independent when supporting electrolyte is present in excess (though not otherwise [27,64,65]). Thus to construct
*figure* 2.24, which shows the evolution of ohmic polarization during chronoamperometric experiments at inlaid and recessed disk electrodes, required only the multiplication of the currents in *figure* 2.23 by the corresponding resistances.

Inspection of *figure* 2.24 shows that the ohmic polarization is much more severe for a recessed disk microelectrode than for an inlaid microdisk electrode of identical area. This is despite the fact that the current is smaller at the recessed disk electrode, as *figure* 2.23 illustrates. Thus we see that the small iR drop characteristic of some microelectrodes does not arise simply because the current is small. It is the convergent geometry of the inlaid disk electrode that is beneficial in conferring a low ohmic overpotential. These remarks are true only in the transient state because as we have seen, all microelectrodes suffer the same iR drop in their steady-states.

The diffusion coefficient for ferrocene was determined from the diffusion limited steady-state current \( i_d = 4nFDCb \) [53,66] of ten averaged and background corrected voltammograms. The calculated value of \( D = 2.4 \times 10^{-9} \text{ m}^2\text{s}^{-1} \) is in excellent agreement with a literature value of \( 2.42 \times 10^{-9} \text{ m}^2\text{s}^{-1} \) [67]. Using logarithmic scales, *figure* 2.25 shows experimental chronoamperograms for an inlaid disk electrode and a recessed disk electrode of depth \( L = 90 \pm 10 \mu\text{m} \). Qualitatively the behaviour of these chronoamperograms compares well with the theoretical chronoamperograms of *figure* 2.23. The inlaid disk electrode approaches a steady-state diffusion current leisurely, in contrast to the recessed disk electrode where the transition to a steady-state current is more abrupt.

The inlaid disk evidently approaches a steady current of about 11 nA, in agreement with the 12 nA predicted in *equation* 2.23. There is no evidence in *figure* 2.25 of Cottrellian behaviour for the inlaid disk electrode, nor would any be expected
Figure 2.23. Plot of theoretical current for the chronoamperometric response of an inlaid and a recessed microdisk electrode. Experimental conditions as for figure 2.25.

Figure 2.24. Plot of the evolution of iR drop during the course of the chronoamperometric experiment detailed in figure 2.23, at an inlaid and recessed microdisk electrode.
in the light of equation 2.34, which predicts a duration of obedience of Cottrellian behaviour of the inlaid disk of only 57 μs.

The results with the recessed disk show a transition behaviour at about 2 seconds, in conformity with the times calculated from equations 2.50 and 2.51. This indicates a duration of obedience of current on the Cottrell equation approximately 19000 times that of the inlaid disk. The steady-state current obtained at the recessed microdisk electrode was 0.8 nA (as shown by the solid line in figure 2.25), slightly lower than the prediction of 1.1 nA (equation 2.27). The slope $\frac{\Delta i}{\Delta n}$ of the transient results from the recessed disk electrode equals -0.7 (also indicated by the solid line), compared with the theoretical Cottrellian value of -0.5. This discrepancy may be explained by the nature of the surface generated in the fabrication process. As was noted previously the etching procedure generated a rough surface finish to the recessed microdisk electrodes. Recent publications have related the fractal nature of a rough surface to the effect on the Cottrellian current[68,69], and demonstrated that at time scales where the diffusion length was comparable to the dimensions of the surface roughness that significant deviation from crottellian behaviour would be expected.

The fractal model of electrode behaviour replaces the $t^{-1/6}$ term of the Cottrell equation with $t^{-D_f - 1/2}$, where $D_f$ is the fractal dimension of the surface roughness. This relationship has recently been demonstrated experimentally at polycrystalline TiO$_2$ electrodes, with slopes of up to 0.8 being reported [70]. It therefore appears as if the surface roughness has a significant effect on the development of the current at the recessed microdisk electrodes, leading to higher than expected slopes, and initial currents which are higher than the inlaid microdisk electrode.

The measured resistances (at 10kHz) of the inlaid and recessed disk electrodes in acetonitrile containing 0.1M Et$_4$ClO$_4$ were 24 kΩ and 240 kΩ respectively. The ratio of the resistance values is exactly that predicted theoretically (equation 2.25) though the individual values are somewhat larger than the values of 17 kΩ and 170 kΩ predicted by equations 2.30 and 2.31.
The steady-state iR products of 0.26 mV and 0.19 mV were calculated for the inlaid and recessed disk electrodes and are to be compared to the theoretical common value of 0.19 mV reported in equation 2.29.

2.5.4. Summary.

1. During chronoamperometry, a recessed disk electrode displays Cottrellian behaviour initially and then switches suddenly to a constant steady-state current. In contrast, Cottrellian behaviour is not observable at an inlaid disk microelectrode and the approach to steady-state is remarkably slow.

2. It is also the convergent geometry of the inlaid disk electrode that lowers the cell resistance, leading to a diminished iR drop during the transient phases of chronoamperometry. However, once the steady-state is reached, all microelectrodes have the same ohmic overvoltage.
2.6. REFERENCES


CHAPTER 3

EXAMINATION OF AN AMPEROMETRIC IMPINGING JET FLOW CELL.

3.1. INTRODUCTION ................................................................................................................. 78
  3.1.1. General .......................................................................................................................... 78
  3.1.2. Flow injection analysis ................................................................................................. 80
3.2. THEORY ............................................................................................................................. 82
  3.2.1. Theory of jet flow ......................................................................................................... 82
3.3. EXPERIMENTAL ............................................................................................................... 85
  3.3.1. Chemicals ................................................................................................................... 85
  3.3.2. Flow injection analysis system ..................................................................................... 85
3.4. RESULTS AND DISCUSSION .......................................................................................... 86
  3.4.1. Effect of electrode size ............................................................................................... 87
  3.4.2. Flow rate dependence ................................................................................................. 89
  3.4.3. Electrode rotation ....................................................................................................... 92
  3.4.4. Effect of electrode-jet separation ............................................................................... 93
  3.4.5. Effect of short term variations in flow rate ................................................................. 97
  3.4.6. Concentration dependence ....................................................................................... 101
3.5. SUMMARY ......................................................................................................................... 103
3.6. REFERENCES ................................................................................................................... 104
3.1. INTRODUCTION

3.1.1. General

The properties that distinguish microelectrodes from conventional sized electrodes in stationary solution experiments include a predominance of radial diffusion to the electrode, yielding a true steady state in experimentally accessible time scales; a reduced requirement for deliberately added supporting electrolyte; a reduced ohmic iR drop in solution; a fast cell response time (i.e. short RC time constant); and the ability to operate by using a simple two-electrode system rather than the more complex potentiostated system due to the low iR drop involved, as discussed in chapters 1 and 2.

The first reported application of a microelectrode in a flowing system was by Hill[1] in 1948. Hill evaluated a recessed microdisk electrode (a = 20 μm) in a purpose built flow cell for the determination of pO₂ in biological fluids, and reported that the electrode was insensitive to variations in flow rate. Other workers also reported the insensitivity of inlaid microdisk electrodes (radii 0.5 μm to 50 μm) to flow rate[2-4]. Saito[5] attributed the reduced flow rate behaviour of microelectrodes to the fact that the diffusion layer at the smallest microelectrodes is contained within the stagnant boundary layer which occurs at the wall of any flowing system.

Microelectrode detection for flow injection analysis (FIA) and high performance liquid chromatography (HPLC) was introduced by Caudill et. al. in 1982[6]. They reported that an array of 100 inlaid carbon microdisk electrodes in a thin-layer cell configuration was insensitive to variations of flow rate caused by pump pulsations, and that the analytical response of the array was substantially better than a conventional inlaid disk electrode (a = 1.5 mm). The same group utilized the fast RC time response of their array of microdisk electrodes to apply rapid scanning and pulse voltammetric techniques to HPLC detection[7]. Scanning detection at microelectrodes has also been applied to microcolumn based HPLC [8-11] and FIA determinations[12].

Amperometric detection in an impinging jet flow cell was first reported in 1985 by Belal and Anderson[13], who used an array of carbon inlaid disk electrodes for the
analytical determination of phenothiazine drugs. Bixler and Bond[14] examined the response of single inlaid microdisk electrodes placed in the stagnation region of an impinging jet cell, and discussed the flow behaviour and analytical response in detail. The limitations of purpose-built and commercial instrumentation for use with microelectrodes has also been described[15]. Geometries other than the disk have also been utilised in impinging jet flow cells, with band and ring geometries providing low flow rate dependences, and enhanced analytical sensitivities[16-19].

This chapter will evaluate inlaid and recessed microdisk electrodes in an impinging jet flow cell, and the parameters which effect the optimisation of the detector response. FIA methodology was employed in the evaluation to provide a rapid and reproducible means of introducing an analyte into the flow cell, hence to the microelectrode.
3.1.2. Flow injection analysis

Flow injection analysis involves the controlled manipulation of dispersion in a flowing environment, and offers a methodology by which many analytical processes and analyses may be routinely automated[19-21]. A typical FIA system consists of a solvent reservoir, pump, injection valve, analytical detector, and sundry electronics to record the detector response to the injected analyte (figure 3.2).
PIA relies on the reproducible flow behaviour of a fixed experimental system.

Many processes will effect the dispersion of a sample passing through a conduit system, with the two most basic processes being related to mass transport: convection and molecular diffusion. An example of the effect that convection and diffusion have on a sample injected into the flow stream is illustrated in figure 3.1[19], together with the form of the response a typical detector would record. Initially convection is the prevalent mode of mass transport, which results in a bullet shaped profile of the sample bolus, and a very sharp asymmetrical peak. In the next stage diffusion as well as convection effect the sample bolus, and a more drawn out profile results. Finally if the sample is allowed to continue through the flow system for a sufficiently long time, radial diffusion will predominate, and the sample bolus will tend to a normal distribution of analyte molecules.

Provided the experimental system is fixed, the mass transport of each injected sample will be identical, leading to a very reproducible response, and short analysis times. Thus this basic PIA system was considered the ideal methodology to employ in the evaluation of the microelectrode impinging jet flow cell, as it provided a rapid and reproducible environment for the introduction of standard samples into the detector system.
3.2. THEORY.

3.2.1. Theory of jet flow

A fully developed submerged laminar impinging jet is shown in schematic form in figure 3.3, with the relevant flow regions within the impinging jet being indicated[22].

I. Potential core region. In this region the fluid begins to mix with the surrounding body of fluid, resulting in a change in the velocity profile from tube flow to jet flow. The velocity profile of the central core of fluid within the potential core region remains unchanged from that inside the jet nozzle, and may extend several nozzle diameters from the nozzle exit.

II. Established flow region. The fluid in the established flow region has a well developed velocity profile in which the centerline velocity decreases with distance from the jet nozzle.
III. *Stagnation region.* As the jet approaches the wall the velocity profile alters from that of an axial jet to radial flow, with the subsequent conclusion that the centerline velocity must decrease to zero at some point, hence the name, stagnation region. There is considerable turbulence at this point, with the net result that local mass transfer rates and the boundary layer thickness remain fairly constant in the region of the stagnation point.

IV. *Transition region.* The fluid in this region is undergoing the transition from axial jet to radial flow.

V. *Wall jet region.* The radial flow of liquid over the wall is influenced by both the wall and the surrounding fluid. The radial velocity decreases and boundary layer thickness increases with radial distance from the stagnation point.

Most reported impinging jet electrodes reported in the literature fall in to the category of wall-jet electrodes. This is due to the fact that with a larger electrode the bulk of the electrolysis occurs in this region with the stagnation and transition regions occupying only 15-20% of the total current. For this reason, most previous theoretical descriptions of flow cell behaviour do not apply in the case of microelectrodes, where the electrode sits in the stagnation region.

In order to quantify the behaviour of an impinging-jet flow cell it is necessary to solve the relevant continuity and boundary layer (eg. momentum and mass diffusion) equations for axisymmetric jet flow [23].

**continuity,**

\[
\frac{\partial (ux)}{\partial x} + \frac{\partial (vx)}{\partial y} = 0 \quad (3.1)
\]

**momentum,**

\[
\frac{\partial c}{\partial x} + \frac{\partial u}{\partial y} = -\frac{1}{\rho} \frac{dp}{dx} + v \frac{\partial^2 u}{\partial y^2} \quad (3.2)
\]
mass diffusion,
\[ \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \]  
(3.3)

These equations have been solved by a number of workers [22-26], with Scholtz and Trass [23], solving them for the case of stagnation point mass transfer. The paper of Chin and Tsang [22], collated a total of 13 equations from various references relating the rate of mass transfer near the stagnation region and dimensionless nozzle height \((H/d)\). All the reported equations were of the form

\[ Sh = \alpha Re^{1/2} Sc^{1/3} g(Sc)f(H/d) \]  
(3.4)

where \(Sh\) = Sherwood number (mass transport), \(Re\) = Reynolds number (flow rate), \(Sc\) = Schmidt number (ratio of mass to momentum transfer), are all dimensionless groups related to fluid properties, and may be defined by

\[ Sh = \frac{k a}{D} ; \quad Re = \frac{U a}{\nu} ; \quad Sc = \frac{\nu}{D} . \]  
(3.5)

where \(k\)=mass transfer rate constant, \(D\)=diffusion coefficient, \(\nu\)=kinematic viscosity, \(U\)=fluid velocity, and \(a\)=electrode radius.

Although no given function was found to be adequate for the entire range of \(H/d\) values studied, correlation was obtained for selected regions of \(H/d\) values. In the range \(0.2 \leq H/d \leq 6; 0.1 \leq a/d \leq 0.5; \text{ and } Re < 2000\) (i.e. laminar flow at nozzle exit), the data was fitted (numerically) to the equation

\[ Sh = 1.51 Re^{1/2} Sc^{1/3} g(Sc) (H/d)^{-0.054} \]  
(3.6)

where the function \(g(Sc)\) is given by the asymptotic series.
\[ g(\text{Sc}) = \left( 1 - \frac{0.084593}{\text{Sc}^{1/3}} - \frac{0.016368}{\text{Sc}^{2/3}} - \frac{0.0057398}{\text{Sc}} + \frac{0.0014288}{\text{Sc}^{4/3}} + \ldots \right) \quad (3.7) \]

Now since the electrode current is related to the local mass transfer rate constant (in the case of a microelectrode), the current at any time \( i_t \) is defined by

\[ i_t = kFc_t \quad (3.8) \]

where \( c_t \) = concentration at electrode surface at any time; a value dependent on the degree of dispersion of the sample in the flow stream. It follows from *equations 3.5, 3.6 and 3.8* that the FIA peak current should be proportional to both the concentration of the analyte species and the square root of the flow rate.

### 3.3. EXPERIMENTAL

#### 3.3.1. Chemicals

Chemicals were of Analytical Grade purity, and used without further purification, unless otherwise stated. Acetonitrile (Mallinckrodt, Australia) was of Liquid Chromatography grade. Tetraethylammonium perchlorate \((\text{Et}_4\text{NClO}_4)\) (Southwestern Analytical Chemicals Inc.) was recrystallized from methanol, then dried and stored in a vacuum desiccator prior to use.

#### 3.3.2. Flow injection analysis system.

The microelectrode based FIA system was assembled from commercially available chromatographic components as shown in *figure 3.2*. The system consisted of an ICI LC1500 chromatographic pump (ICI Instruments, Australia), a Rheodyne 7125 sample injection valve (Rheodyne Inc., USA), fitted with one of a variety of different injection loops (e.g. 20 µl, 50 µl, and 100 µl), and a Metrohm 656 Wall-Jet flow cell (Metrohm AG, Herisau, Switzerland). The microelectrode wall jet cell operated in the two
electrode mode, with either a Ag/AgCl (3M KCl) reference electrode, or a large area gold disk (a = 2.5 mm) as the second electrode. The gold disk was found to be suitable for use as a pseudo reference electrode[27] provided that the current did not exceed 1.0 nA, to avoid polarisation of the electrode. The current was measured with a Keithley 614 electrometer, and the cell voltage was applied by a precision voltage source as described in reference [14].

A pulsation dampener was constructed from an empty 15.0 cm x 4.6 mm chromatography column, by blocking off one end, and allowing the column to partially fill with mobile phase forming an air-lock in the column. The pulsation dampener was connected between the pump and injector as shown in figure 3.4.

Nozzle-to-electrode spacing was determined by a pair of vernier callipers (accuracy=0.01mm) with the aid of a reference mark on each electrode and on the flow cell body.

3.4. RESULTS AND DISCUSSION

The rate of mass transport of material to the electrode surface is a limiting factor in Faradaic electrochemistry. In electrochemical techniques such as linear sweep voltammetry and chronoamperometry, the dominant mode of mass transport is through molecular diffusion. In a flowing stream of solution such as that found in an impinging jet flow cell, convection and molecular diffusion need to be considered. As
was discussed previously, the local mass transfer rates in an impinging jet flow cell vary considerably depending on the relative location of interest. For the present study the response of a range of gold microdisk electrodes was examined.

3.4.1. Effect of electrode size.

The effect of electrode size on the response of the impinging-jet flow cell was examined for a range of gold microdisc electrodes (a = 2.5 \( \mu \text{m} \), 5.0 \( \mu \text{m} \), 12.5 \( \mu \text{m} \) and 30 \( \mu \text{m} \)). A log-log analysis of the electrode radius versus peak current indicated a dependence of \( a^{1.72} \) at \( H/d=0.3 \) and \( a^{1.48} \) at \( H/d=11.7 \).

Conventional wisdom suggests that mass transport is uniform within the stagnation region of an impinging jet. This would lead to uniform accessibility of the electrode surface[22], and uniform current densities at all sized electrodes, hence an \( a^{2.0} \) dependence. However, this does not take into account the non-linear diffusion field associated with microelectrodes. On converting the peak current data to current density, the current density was found to increase with a decrease in the radius of the working electrode, indicating a substantial non-linear diffusion contribution to the total current (figure 3.5).
**Figure 3.5.** Plot of current density (pA/μm²) versus radius (μm) for injections of 5x10⁻⁵ M ferrocene, at a flow rate of 1.09 ml/min, and H/d=0.3, E_{app}=0.70V.

**Figure 3.6.** Plot of log(flow rate) versus log(peak height) for an inlaid gold microdisk electrode. Carrier solution = acetonitrile (0.010M Et₄NClO₄), injected volume = 20 μl, analyte = 5x10⁻⁶ M ferrocene in acetonitrile (0.010M Et₄NClO₄), H/d=0.3, E_{app}=0.70V.
3.4.2. Flow rate dependence

The flow rate dependence of the current response (i) at an amperometric detector has the form [28]

\[ i \propto U^x \]  \hspace{1cm} (3.9)

where \( U \) = flow rate, and \( x \) = flow rate dependence. The major factor that influences the value of the flow rate dependence is the relative thickness of the boundary layer and diffusion layers. If, for example, the diffusion layer was entirely contained within the boundary layer, the electrode would not directly respond to variations in the flow rate. The relative boundary/diffusion layer thickness will be influenced by many factors, including [19,22,28], (i) size and geometry of the electrode, (ii) fluid dynamics of the flow cell, (iii) physical properties of the fluid medium, and (iv) environment.

From a practical point of view, there are two experiment routes to determine the value of the flow rate dependence, under steady-state, or transient conditions. In a steady state experiment, the analyte is present in the mobile phase continuously during the experiment, thus maintaining a uniform concentration profile within the flow cell. In a transient experiment, the mobile phase is allowed to flow freely through the flow cell and discrete samples of the analyte are introduced into the flow stream at discrete time intervals. The transient experiment closely matches the situation encountered in analytical applications of amperometric detection in FIA and HPLC, and for this reason the transient technique was used in this work.

The exponential flow rate dependence of an inlaid gold microdisc electrode of radius 5.0 \( \mu \text{m} \), was measured at the dimensionless electrode/jet separations \( (H/d) \) of 0.3, 11.7, and 16.7. The 5.0 \( \mu \text{m} \) microdisc electrode was chosen for this measurement as the gold microdisc was found to lie in the exact centre of the electrode face, thus ensuring the continuity of the stagnation region at the electrode during different experiments at differing electrode/jet separations.
The value of the exponential flow rate dependence is determined from the slope of a plot of log(flow rate) versus log(peak height). An example of such a plot is shown in figure 3.6 for an Au microdisk electrode (a=5.0 μm). The data at high flow rates tended to a linear response, whereas at lower flow rates the peak current varied in a complex way with flow rate. Similar results were obtained in reference [22] for electrodes with radii ranging from 0.127 mm to 19.1 mm, although they obtained two separate linear regions to the plot, corresponding to laminar and turbulent flow conditions at the nozzle exit, with an intermediate transition region. Calculation of the Reynolds number for the experimental conditions used in the present work indicate that laminar flow conditions would be predicted at all flow rates employed, as the Reynolds number at the nozzle exit at no time exceeded 300. Turbulent flow is generally characterised by Re=2000 or greater, although geometry of the flow path is important[28]. A further possibility is that the flow of the solution issuing from the nozzle was in some way impeded by the close proximity of the impinging surface, leading to turbulent flow in the vicinity of the electrode.

The magnitude of the FIA peak current($i_p$) will respond according to the relationship[22]

$$i_p = kF(c_0)p$$  \hspace{1cm} (3.10)

where $k$ = mass transfer coefficient, $F$ = Faradays number, and $(c_0)_p$ = transient concentration. Hence according to equations 3.5, 3.6 and 3.8 a plot of $i_p$ versus $\sqrt{flow\ rate}$ should be linear. The flow rate dependence calculated from the data in figure 3.6, gives a value of 0.64, which is higher than the value of 0.5 expected. Data at H/d=11.3 gave the same flow rate dependence (0.64), whereas the data at H/d=16.7 was lower at 0.43. The higher value of the flow rate dependence may be attributed to some contribution of the enhanced mass transfer rate at the edge of the jet when H/d ≤ 0.3 [23], but this would not account for the higher than expected value at H/d=11.3.

The greatly reduced flow rate dependencies reported previously[1-6, 14, 16-18] have occurred when the diffusion layer surrounding the electrode was well within the
stagnant boundary layer of solution on the electrode face. Such behaviour was not observed in this work due to the flow properties of the stagnation region of the impinging jet. The boundary layer is at its thinnest at the stagnation region, being virtually zero at the impingement point, and it rapidly increases in depth with distance along the face of the electrode. Reduced flow rate dependences could presumably be obtained with the current sized electrodes by placing them in the wall-jet region of the jet, or by using alternative flow geometries.

The flow rate behaviour of a recessed microdisk electrode was also examined and compared with the inlaid microdisk. The peak recorded at the recessed disk electrode displayed a slight asymmetry, with the trailing edge of the peak dropping below baseline level in the form of an inverted peak, as shown in figure 3.7(b). This is not observed at the inlaid microdisk electrode. The flow rate dependence also was much reduced. The flow rate dependence at H/d=0.3 was only 0.08, indicating virtually no dependence of flow rate on the response of the recessed microdisk electrode. The recessed tube forms a definite barrier to the unrestricted flow of material to the electrode, so a low flow rate dependence is expected[1].

![Figure 3.7](image_url)

**Figure 3.7.** A comparison of the FIA response obtained at (a) inlaid microdisk (a=12.5 μm), and (b) recessed microdisk (a=12.5 μm, L=30 μm) in an impinging jet cell. Carrier solution: acetonitrile (0.010M Et₄NClO₄), analyte=ferrocene (10⁻⁵ M), injected=20 μl, E_app=0.70V, flow rate=1.1 ml min⁻¹.
Figure 3.8. The effect of rotating a Au inlaid microdisk electrode (a=12.7 μm), on the measured FIA peak height for a 20 μl injection of 10⁻⁵ M ferrocene in acetonitrile (0.010 M Et₄NClO₄). Flow rate = 1.10 ml/min, Eₚ₀₉₀=0.70V.

3.4.3. Electrode rotation.

The effect of rotating the electrode if it is centrally located within the flow cell, should have no effect on the electrode response, as the mass transport to the stagnation region of the impinging jet is uniform across the region. Data reported previously [14], and data for most of the electrodes used in this study also confirmed this view, with little variation of measured peak height with electrode rotation. However if the electrode is not centrally located, a large variation was observed. A typical example of this behaviour is shown in figure 3.8. The actual metal microdisk of this example was situated 0.22 mm off the centre axis of the glass electrode body, and the electrode body itself was slightly asymmetrical. As the diameter of the nozzle is only 0.3 mm, the net result of rotation of the electrode is that the microdisk is passing out of the stagnation region into the transition region, with a subsequent decrease in the rate of mass transport[23], hence decreased peak current.
3.4.4. Effect of electrode-jet separation

The measured peak height was found to vary in an exponential manner with nozzle-to-electrode spacing (H/d) as shown in figure 3.9. Analysis of these results shows that there are two distinct regions of interest, H/d ≤ 3, and 3 < H/d ≤ 20. In the latter region, the data follows an exponential dependence of 0.33, but changes to 0.19 at H/d<3. This is similar to the data reported on heat transfer from a laminar slot jet reported by Miyazaki and Silberman[29] for the point of impingement, but is in contrast to the report of stagnation region mass transfer at laminar slot jets[30], in which little variation of mass transfer in the stagnation region was found over the range 0 ≤ H/d ≤ 6 (also cf. [31]).

The greatest response was obtained at the smallest H/d used in all cases, and with all electrode radii used. The baseline noise level did not change with decreasing H/d, remaining constant at a value of 0.03 pA during the course of the experiments. Thus the effect of placing the electrode so that the H/d value is low is to increase the signal-to-noise ratio (S/N), indicating a genuine benefit in operating the electrode as close as possible to the jet nozzle.
The low baseline noise level obtained here (i.e. 0.03 pA) consists mainly of electronic noise, indicating very low levels of electroactive impurities in the solvents and supporting electrolytes used. If the impurity levels were significantly higher, it would be expected that the baseline noise would increase as H/d decreased, negating the benefits of an enhanced S/N.

The effect of flow rate on response at large H/d values was examined to determine if the break up of the jet could be determined. Instead what was observed was a splitting of the FIA peak at \( 9 \approx H/d \leq 20 \) (figure 3.10 and 3.11). The splitting of the FIA peak was only observed at low flow rates and large H/d values, and was found not to depend on mode of pumping, or mode of injection of the sample. The data presented in figure 3.11 was obtained using gravity flow to eliminate the possibility of pulsations from the pump distorting the wave.

\[ \text{Figure 3.10. Plot of the variation of peak height with } H/d \text{ for an Au (r=12.5 } \mu \text{m) microdisk electrode, at a flow rate of 0.26 ml/min (under gravity feed). Injected volume=20 } \mu \text{l, analyte= ferrocene (5x10^{-5}M) in acetonitrile (0.010M Et_4NClO_4), E_{app}=0.70V.} \]
Figure 3.11. Development of a split peak FIA response at a Au inlaid microdisk (a = 12.5 μm) as H/d is varied. Conditions as for figure 3.10.

One particularly interesting feature of the splitting of the peak at different H/d values was that a finite amount of time was required for the peak shape to evolve into a stable configuration (figure 3.12(a)). Although in some cases a stable configuration was not achieved in the time scale of the experiment, with apparent random (chaotic?) behaviour observed (figure 3.12(b)). Also notice that the relative peak heights of the split peak, with the leading peak decreasing in proportion to the trailing peak as the value of H/d is increased.

Split peaks have been reported in FIA previously[24, 33-35], however the causes previously elucidated do not correspond to the present case. Mixing of reagents leading to a time dependent reaction may cause splitting of peaks, if there is incomplete mixing of the reagent zones[35]. The nature of the sample plug may also lead to peak splitting. As was mentioned in the introduction to this chapter, the sample undergoes dispersion due to effects of convection and diffusion. It has been shown that under various convection/diffusion conditions the sample bolus may form in the flow tubing such that a split peak will result[32], although this mechanism will
not usually lead to two peaks with almost baseline resolution. Unfortunately the flow conditions required for this behaviour do not correspond with those in the present experiment, and the dependence on splitting of the H/d value would be difficult to reconcile with this mechanism.

The most likely explanation derives from the work of Law and Masliyah [36], on mass transfer due to a confined laminar impinging jet, who used real time holography to establish flow profiles within the body of solution in a confined two dimensional impinging jet cell. They were able to show that a number of vortices were formed around the central jet at low Reynolds numbers. A toroidal vortex was also visualised by Scholz and Trass[37] at low Reynolds numbers in a laminar radial impinging jet.
In this case the vortex only appeared at Re < 1000, and was particularly stable at Re=300. Above Re=300 the vortex was easily destroyed by the slightest variation in flow rate, or vibration of the cell. Glauert [38] accounted for this behaviour in terms of vortex formation by entrainment in the jet of fluid from outside the boundary layer.

The presence of vortices such as these in the flow cell could easily lead to entrainment of some of the sample plug in the vortex, causing a delay in the arrival time of part of the sample, resulting in a split peak such as we observe here. The time dependent nature of the peak splitting, may also be explained by the development of a stable vortex with time. Law and Masliyah described the effect of variation of flow rate on the position and intensity of the vortex, and showed that there was a considerable effect. It is not difficult to imagine that by increasing the length of the free jet path (i.e. H/d) the flow distribution within the cell would also affect the vortex behaviour. It is therefore possible that the variation of peak heights may be related to a variation in the nature of the vortex, with more or less of the sample plug being effected.

3.4.5. Effect of short term variations in flow rate

The most common forms of pumps used to propel solutions in analytical systems are peristaltic, and piston type pumps. Both of these types of pumps introduce variations into the instantaneous flow rate delivered. Piston type pumps are commonly used for HPLC determinations, and may also be used (as in the present study) for FIA experiments. Piston type pumps may be either single or dual piston pumps, and flow variations will be introduced at the end of a piston stroke, with single piston pumps giving a more noticeable pulse.

Electrochemical detectors based on faradaic electrochemistry are susceptible to variations in flow rate, as indicated by the flow rate dependence determined for the
microdisk electrodes in section 3.4.2. Pulsations introduced by the pump may therefore effect the detection limits of microelectrode detectors.

A comparison of the type of response obtained when using a dual piston pump for FIA with and without pulsation dampening is shown in figure 3.13. The effect of pulsations in the flow is most evident at low flow rates with this type of pump, and it is clear that there are large variations in the instantaneous flow rate delivered under these conditions.

The magnitude of the pulsations recorded by the microelectrode are surprisingly large in comparison to those previously reported for macroelectrodes[39]. The most likely explanation for this relates to the fact that the microelectrode is responding to the localised mass transfer in one flow region (i.e. stagnation region) which may be high in relation to other flow regions, whereas the macroelectrode responds to the cumulative effect of several regions of jet flow (i.e. average effect of stagnation, transition, and wall jet regions).
Figure 3.14. Effect of a pulsed flow on the FIA response of a Au microdisk electrode ($a=12.5 \, \mu m$) to repeated 50 $\mu l$ injections of $1.06 \times 10^{-7} M$ ferrocene in acetonitrile (0.010M Et$_4$NClO$_4$); carrier solution = acetonitrile (0.010M Et$_4$NClO$_4$), flow rate=0.48 ml/min, $E_{app}=0.70V$. 
Introduction of a simple pulsation dampener into the flow stream situated between the pump and injector, virtually eliminates the effects of flow variation (figure 3.13). It is important to realise that the average flow rate, as typically measured by recording the time to deliver a certain volume of liquid, is the same with and without the pulsation dampener fitted, so simply measuring flow rate in this way will not ensure uniform flow rates are obtained.

This behaviour may not at first appear to be useful analytically, however modulation of flow behaviour at a rotating disk electrode has been suggested[40] as a means of reducing background current, and enhancing sensitivity, and the use of a reproducible pulsation derived from the pump may be one means of achieving this without the need for a rotating disk electrode. Another useful feature of this behaviour of microdisk electrodes is that the local mass transfer in selected regions of the flow cell may now be amenable to determination, and a more detailed picture of the overall flow behaviour of impinging jet flow cells may be determined.

![Figure 3.14](image)

**Figure 3.14.** Concentration dependence for the oxidation of ferrocene at a Au microdisk electrode (d=5 μm) in the presence and absence of pulsation dampening. Flow rate = 0.54 ml min⁻¹, mobile phase = acetonitrile (0.010 M Et₄NClO₄), temperature = 22 °C.
3.4.6. Concentration dependence.

Data for the concentration dependence over the range 1.07x10^-7M to 1.07x10^-4M of ferrocene in a damped and undamped flow system is illustrated in figure 3.14 for a flow rate of 0.54 ml/min, and data for other flow rates given in table 3.1. The data at 0.54 ml/min clearly demonstrates the effect of pulsations in the flow with the ratio of the analytical responses obtained for the damped to undamped systems varying by a factor of 1.36 (average of the ratio of the five different concentration responses). All work reported in this thesis was therefore recorded using a pulsation dampener, unless otherwise specified.

Correlation data for the concentration dependence for Au microdisk electrodes in the range 2.5 μm ≤ a ≤ 30 μm are included in table 3.2. All the electrodes provided a linear response with concentration, over the range 5x10^-8M to 5x10^-5 M of ferrocene in acetonitrile containing 0.010M Et4NCIO4. The calculated detectivity[17] for each electrode clearly demonstrates the high sensitivity of using Au microdisk electrodes in an impinging jet flow cell for analytical purposes. Virtually identical data was obtained for Pt microdisk electrodes of the same size, indicating little dependence of the ferrocene oxidation on electrode material.
Table 3.1. Data for the concentration dependence at a Au inlaid microdisk electrode (a=5.0 µm), H/d=0.3, temperature = 22 °C.

<table>
<thead>
<tr>
<th>Flow</th>
<th>Flow rate (ml min⁻¹)</th>
<th>1.07x10⁻⁶M</th>
<th>8.00x10⁻⁷M</th>
<th>5.30x10⁻⁷M</th>
<th>2.70x10⁻⁷M</th>
<th>1.07x10⁻⁷M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damped</td>
<td>0.54</td>
<td>9.10</td>
<td>6.95</td>
<td>4.78</td>
<td>2.48</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td>11.2</td>
<td>8.70</td>
<td>5.70</td>
<td>3.05</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>1.07</td>
<td>12.3</td>
<td>9.43</td>
<td>6.28</td>
<td>3.30</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>1.36</td>
<td>13.2</td>
<td>10.1</td>
<td>6.85</td>
<td>3.55</td>
<td>1.63</td>
</tr>
<tr>
<td>Undamped</td>
<td>0.54</td>
<td>12.7</td>
<td>9.70</td>
<td>6.43</td>
<td>3.40</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td>14.5</td>
<td>11.2</td>
<td>7.30</td>
<td>3.93</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>1.07</td>
<td>15.0</td>
<td>11.4</td>
<td>7.73</td>
<td>4.10</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>1.36</td>
<td>17.0</td>
<td>12.9</td>
<td>8.55</td>
<td>4.60</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Table 3.2. Correlation data for the concentration dependence of a range of Au inlaid microdisk electrodes in acetonitrile (0.010 M Et₄NCIO₄).

<table>
<thead>
<tr>
<th>Electrode Radius (µm)</th>
<th>Noise (pA)</th>
<th>H/d</th>
<th>Correlation data</th>
<th>Detectivity$^#$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>slope (pA M⁻¹)</td>
<td>intercept (pA)</td>
</tr>
<tr>
<td>2.7</td>
<td>0.03</td>
<td>0.3</td>
<td>3.59x10⁶</td>
<td>0.122</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>11.7</td>
<td>1.99x10⁶</td>
<td>0.069</td>
</tr>
<tr>
<td>4.9</td>
<td>0.02</td>
<td>0.3</td>
<td>1.37x10⁷</td>
<td>0.373</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>11.7</td>
<td>6.35x10⁶</td>
<td>0.128</td>
</tr>
<tr>
<td>12.5</td>
<td>0.03</td>
<td>0.3</td>
<td>4.14x10⁷</td>
<td>0.905</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>11.7</td>
<td>3.60x10⁷</td>
<td>1.52</td>
</tr>
<tr>
<td>32.7</td>
<td>0.04</td>
<td>0.3</td>
<td>2.79x10⁸</td>
<td>8.28</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>11.7</td>
<td>1.05x10⁸</td>
<td>6.52</td>
</tr>
</tbody>
</table>

$^\#$ Detectivity = \( \frac{2 \times \text{peak-to-peak baseline noise}}{\text{slope of calibration curve}} \)
3.5. SUMMARY

1. Microdisk electrodes centrally located in an impinging jet flow cell have been found to provide an analytically useful response when examined in a flow injection analysis mode.

2. The microdisk electrode response was found to vary with the relative position (i.e. vertical and horizontal) of the microdisk electrode in relation to the jet nozzle.

3. The flow rate dependence of the centrally located inlaid microdisk electrodes examined in this work did not differ substantially from that obtained at conventional sized electrodes. This results from the relatively thin nature of the boundary layer in the stagnation region of the impinging jet.

4. The flow rate dependence of a recessed microdisk electrode was found to be much reduced over the inlaid microdisk electrode, and was attributed to the constricted flow path which results from the nature of the recessed electrode.

5. The microdisk electrode was found to be useful in the elucidation of the flow characteristics of an impinging jet, providing detailed information on mass transfer rates (i.e. current) with spatial position.

6. Anomalous split FIA peaks were obtained at low flow rates and have been attributed to the presence of a vortex in the flow path of the impinging jet flow cell.

7. A linear concentration dependence ($5 \times 10^{-5}$ to $5 \times 10^{-8}$ M) was found for the oxidation of ferrocene in acetonitrile at a range of microdisk electrodes ($2.5 \leq \text{radius} \leq 30 \ \mu\text{m}$).
3.6. REFERENCES

CHAPTER 4

A COMPARISON OF COPPER DETERMINATION IN URINE BY FLOW INJECTION ANALYSIS WITH ELECTROCHEMICAL DETECTION AT GLASSY CARBON AND PLATINUM MICROELECTRODES

4.1. INTRODUCTION..............................................................106
4.2. EXPERIMENTAL............................................................108
  4.2.1. Chemicals.............................................................108
  4.2.2. Flow Injection System............................................108
  4.2.3. Procedures..........................................................110
    4.2.3.1. Urine Collection..............................................110
    4.2.3.2. Glassware..................................................110
4.3. RESULTS AND DISCUSSION...........................................110
  4.3.1. General Methodology.............................................110
    4.3.1.1. Determination of copper as the diethyldithiocarbamate............................................110
    4.3.1.2. Sample determination......................................111
  4.3.2. Macroelectrode Studies..........................................111
    4.3.2.1. Mobile phase composition................................111
    4.3.2.2. Analytical considerations................................112
    4.3.2.3. Urine samples.............................................112
  4.3.3. Microelectrode Method...........................................112
    4.3.3.1. Instrumental Considerations..............................112
    4.3.3.2. Mobile phase.............................................113
    4.3.3.3. Analytical response of microelectrodes..................115
    4.3.3.4. Flow rate effects.......................................119
    4.3.3.5. Urine Samples...........................................120
4.4. SUMMARY......................................................................120
4.5. REFERENCES...................................................................121
4.1. INTRODUCTION

Copper is the third most abundant trace metallic element in the human body [1], and there is considerable interest in the role played by copper in biological systems [2]. Copper proteins and copper enzymes are involved in a wide variety of biochemical processes [3]. The average daily intake of copper ranges from 1mg to 5 mg [4-7], with up to 70% being absorbed by the body [8]. The main excretion route for copper is via the bile [8,9], followed by salivary, gastric and pancreatic secretions. Urinary copper excretion amounts to only about 1% of the total copper excreted (approx. 20 µg/day) in a normal healthy adult [7,9,10].

Urine is considered to be one of the most complex biological fluids due to the larger number of components which may be present (> 200 components), and the enormous variation which they may display even in a completely healthy individual [11]. In such a complex and varied medium as urine the possibility of interactions between individual components must be considered. In the case of urinary copper analysis, the daily intake of molybdenum has been found to directly effect urinary copper levels. Low molybdenum intake corresponds to a low urinary copper concentration, whereas a high intake of molybdenum results in a high urinary copper concentration [12].

Despite the low level of copper excretion through the urine, and the variation due to molybdenum, urinary copper determinations can be of considerable use especially in the diagnosis of Wilson's Disease [12-17]. In Wilson's Disease, urinary copper excretion is greatly enhanced by an order of magnitude or greater. Higher than normal levels of urinary copper are also evident in other diseases, for example chronic active hepatitis [18], primary sclerosing cholangitis [19], thermal injury [20], and nephrotic syndrome [21]. Methods for rapid, accurate, inexpensive and relatively simple assay for urinary copper, with a minimum of sample pretreatment are therefore desirable. Analytical methods currently in use include atomic absorption spectrometry [22-24], anodic stripping voltammetry [14,25-28], gel chromatography [29], inductively coupled
plasma emission spectrometry [30,31], Zeeman effect atomic absorption spectrometry [32], mass spectrometry [33], and neutron activation analysis [34]. Most of these techniques require extensive pretreatment of the urine in the form of ashing or digestion, or utilize expensive instrumentation which may not be readily available.

Recently, Bond et al. [35] published a chromatographic method for the simultaneous determination of copper, nickel, and lead in urine. The method utilized a direct injection of freshly acidified and filtered urine into a reversed-phase chromatographic system, containing a dithiocarbamate ligand in the mobile phase. The dithiocarbamate ligands readily form stable complexes with a large number of metal cations [36-37]. The metal complexes so formed were then rapidly separated on the reversed-phase column, and detected either spectrophotometrically or electrochemically. However, the need to use a chromatographic separation effectively dilutes the sample and results were relatively close to the limits of detection.

Flow injection analysis (FIA) does not lead to as much dilution as found with liquid chromatographic methods, and is inherently more sensitive and rapid. The determination of copper by flow injection analysis has been examined with spectrophotometric detection [38] and produces a much shorter analysis time and lower detection limits. However, interferences would mitigate against the use of spectrophotometric detection in urine samples. On the other hand electrochemical detection may be more specific and more sensitive under appropriate conditions.

In chapter 3, FIA methodology was used in the evaluation of the response of inlaid and recessed microdisk electrodes in an impinging jet flow cell. This chapter will examine the use of FIA methodology for the specific determination of copper in urine, using electrochemical detection at conventional, and microelectrodes. A comparison with detection at a glassy carbon electrode in a thin layer cell is presented to demonstrate the advantages of the microelectrode method over what might be regarded as the conventional method. A chromatographic column is not required for the separation of the different metals which may be present in a urine sample, as a judicious
choice of applied potential discriminates against the response due to the presence of other metal complexes.

4.2. EXPERIMENTAL

4.2.1. Chemicals

Chemicals were of Analytical Grade purity, and used without further purification, unless otherwise stated. Chromatographic solvents (Mallinckrodt, Australia) were of Liquid Chromatography grade. The water used in this study was obtained from a Millipore Water Purification system. Acetate buffer was prepared according to Vogel [39]. Tetraethylammonium perchlorate (Et₄NClO₄) (Southwestern Analytical Chemicals Inc.) was recrystallized from methanol, then dried and stored in a vacuum desiccator prior to use.

Sep-pak cartridges (C₁₈) were obtained from Waters/Millipore Corp. and treated as described in figure 4.1.

4.2.2. Flow Injection System

The macro-electrode system consisted of a Waters 6000A pump coupled to a Rheodyne 7125 sample injector (20 µl or 50 µl loop), then to a BAS LC4B Thin Layer Cell/Detector, using a glassy carbon working electrode, stainless steel auxiliary electrode, and Ag/AgCl (3 M KCl) reference electrode. The microelectrode system consisted of an ICI LC1500 pump (ICI Instruments, Australia), a Rheodyne 7125 ample injector (20 µl loop), and a Metrohm 656 wall-jet flow cell. The microelectrode cell was operated in the two electrode mode, with a microelectrode as the working electrode, and either a Ag/AgCl (3 M KCl) reference, or large area gold disk as the second electrode. The gold disk was found to be suitable for use as a pseudo reference electrode if the current was maintained below 1.0 nA. The current was measured using a Keithley 614 Electrometer, and the cell voltage was applied using a home built precision voltage source, as described previously [43].
**Sample dilution**
Sample aliquot of 3.0 ml diluted with water to 5.0 ml

**Sample preparation**
To sample solution add 5.0 ml of 0.0003M DDTC in acetonitrile.
Reaction time = 15 minutes

**Sep-pak cartridge treatment**
Sep-pak soaked in 0.01M NaDDTC/acetonitrile overnight. Cartridge rinsed with water (10 ml)

Slowly load total solution volume onto Sep-pak over 3 minutes.

**Sep-pak washed with:**
1. 3.0 ml water to remove excess NaDDTC
2. 3 x 2.0 ml aliquots of 50/50 acetonitrile/water

Sample eluted into a 5.0 ml standard flask with 4.0 ml 80/20 acetonitrile/water solution, pH = 6, over a 2 minute period.

Standard flask made up to 5.0 ml with 80/20 acetonitrile/water solution, pH = 6.

**Volume suggested for analysis is 20 - 100 microlitres**

*Figure 4.1.* Analytical procedure for the sample preparation and analysis of copper in urine, using FTA with electrochemical detection. Note: When microelectrodes were used the sample was eluted with 100% acetonitrile solution.
4.2.3. Procedures

4.2.3.1. Urine Collection

All urine samples were collected as random specimens by the clean-catch/midstream technique described by Schumann [40].

4.2.3.2. Glassware

All glassware used in these determinations was precleaned in an acid bath (2 M HNO₃) for a minimum of seven days, then thoroughly rinsed with distilled/deionized water prior to use.

4.3. RESULTS AND DISCUSSION

4.3.1. General Methodology

4.3.1.1. Determination of copper as the diethylidithiocarbamate

Sodium diethylidithiocarbamate (NaDDTC) and other dithiocarbamate ligands form stable complexes with a wide variety of transition metals [41]. The non-specific nature of NaDDTC has meant that careful selection of experimental conditions is necessary to increase the selectivity of the reagent.

In the present study selectivity is obtained from the differences in oxidation potentials of the metal-DDTC (MeDTTC) complexes [42], shown in table 4.1. For example, an applied potential of 0.60 V vs Ag/AgCl will selectively oxidize the Cu(DTTC)₂ complex according to a reversible one electron oxidation reaction [42],

\[
\text{Cu(DTTC)₂} \rightleftharpoons [\text{Cu(DTTC)₂}^+] + e^- \tag{4.1}
\]

It may therefore be considered that the mode of detection is performing the separation, thus eliminating the need for a chromatographic column, and allowing flow injection analysis to be used as the method of choice.
Table 4.1. Oxidation potentials\textsuperscript{a} of various metal dithiocarbamate complexes in acetonitrile (0.1 M Et\textsubscript{2}NClO\textsubscript{4}).

<table>
<thead>
<tr>
<th>Metal dithiocarbamate</th>
<th>Oxidation potential\textsuperscript{a,b} (V vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(DDTC)\textsubscript{2}</td>
<td>+ 0.52</td>
</tr>
<tr>
<td>Ni(DDTC)\textsubscript{2}</td>
<td>+ 0.74</td>
</tr>
<tr>
<td>Co(DDTC)\textsubscript{2}</td>
<td>+ 0.96</td>
</tr>
<tr>
<td>Cr(DDTC)\textsubscript{2}</td>
<td>+ 1.08</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Values taken from reference 42. \textsuperscript{b} At a platinum electrode.

4.3.1.2. Sample determination

As previously mentioned, urine contains a large number of components, many of which may interfere with the analytical copper response. In a FIA determination where no analytical column is employed, no separation of components is possible during the analysis hence the sample clean-up must occur prior to the injection of the sample. A simple and efficient means of sample preparation has been found in the small disposable solid-phase extraction cartridges (Sep-pak (Waters)), which are available in a wide range of solid-phases. A reversed-phase (C\textsubscript{18}) Sep-pak was found to be a suitable choice for the sample preparation and clean-up, as detailed in figure 4.1.

4.3.2. Macroelectrode Studies\textsuperscript{1}

4.3.2.1. Mobile phase composition

The optimum mobile phase composition when macroelectrode detection with a glassy carbon electrode and thin layer cell was employed was found to be 80% acetonitrile/20% acetate buffer, pH = 6.0, with 0.2 M NaNO\textsubscript{3} added. It was noted that a decrease in the aqueous component of the mobile phase lead to a decrease in the limit of detection for copper. Higher concentrations of acetonitrile cause problems with ohmic iR drop. The addition of 5 ppb Cu(DDTC)\textsubscript{2} to the mobile phase was found to improve long term baseline stability. This addition meant that slight variations of background

\textsuperscript{1} Macroelectrode determination carried out in collaboration with Dr D.E. Davey, S.A.I.T., The Levels, Ingle Farm, South Australia, 5098.
current due to variable copper impurity levels is effectively eliminated. Naturally occurring copper levels in urine are well above this level, so detection limits are not effected.

4.3.2.2. Analytical considerations

An example of the FIA response to a standard series of copper solutions is shown in figure 4.2. The calibration curves for both the 50/50 and 80/20 (acetonitrile-buffer) mobile phases are illustrated in figure 4.3. Although both mobile phases yield an excellent linear response, the response per unit concentration of the 80/20 mobile phase is considerably greater than the 50/50 mobile phase. Hence the lowered limit of detection found with the former.

4.3.2.3. Urine samples

Recoveries from urine samples were determined by comparison of macroelectrode results with atomic absorption spectrometry. In all cases excellent recoveries of 100±2% were obtained. The possibility of contamination from the Sep-pak cartridges was examined and found to be negligible. This is demonstrated in figure 4.4, where a duplicate series of standards was compared. The first was prepared without the use of Sep-pak cartridges, and the second according to figure 4.1. Within the limits of experimental error no difference was noted, indicating excellent recovery and minimal contamination.

4.3.3. Microelectrode Method

4.3.3.1. Instrumental Considerations

Most of the measurements in the present work were performed using a 5 mm diameter gold disk as reference electrode. This was found to be entirely satisfactory unless a current exceeding approximately 1.5 nA was obtained. If this occurred the baseline current was found to oscillate, slowly settling out to an equilibrium value. It was therefore necessary to ensure that the magnitude of the current did not exceed 1.5 nA during the course of an experiment, and as a general rule the peak current was
maintained under 1.0 nA. The applied potential was determined from a hydrodynamic voltammogram prior to an FIA analysis.

4.3.3.2. Mobile phase

The effect of increased detector response with a decrease in the aqueous component of mobile phase noted for macroelectrode detection was also noted for microelectrodes. However, a further decrease in the aqueous component of the mobile phase was possible with the use of microelectrodes without introducing problems from ohmic iR drop. In fact, the use of a microelectrode detection system enabled a 100% acetonitrile mobile phase to be used, with the addition of only 0.001 M Et₄NClO₄ supporting electrolyte.

This type of high resistance mobile phase would lead to a distorted potential-current profile at macroelectrodes which would require the applied potential to be raised considerably. Since microelectrodes minimise the iR drop problem their use simplifies the potential control problem in the determination of copper in urine.

![Figure 4.2](image)

*Figure 4.2.* Flow injection response of Cu(DDTC)₂ standards in acetonitrile/acetate buffer (80/20), containing 0.2 M NaN₃. Flow rate 0.7 ml/min, sample volume 50 μl, applied potential +0.60 V vs. Ag/AgCl. Working electrode conventional glassy carbon in a thin layer cell. Concentrations (as Cu) (a) 0.01 ppm (b) 0.02 ppm (c) 0.04 ppm (d) 0.06 ppm.
**Figure 4.3.** Concentration dependence of FIA peak height for copper using a conventional glassy carbon electrode in a thin layer cell. Applied potential +0.60 V vs. Ag/AgCl. (a) Mobile phase 80/20 acetonitrile/acetate buffer, flow rate 0.4 ml/min. (b) Mobile phase 50/50 acetonitrile/acetate buffer, flow rate 0.6 ml/min.

**Figure 4.4.** Comparison of concentration dependence of FIA peak height for standards of Cu. Prepared by (▲) analytical procedure detailed in figure 4.1, or (■) injecting previously prepared Cu(DDTC)$_2$ standards. Other conditions as figure 4.2.
4.3.3.3. Analytical response of microelectrodes

In the analytical problem being considered, FIA provides a simple and efficient means of transferring the samples and standards to the electrochemical cell. One feature of FIA is that the sample solution passing from the injector to the cell, forms a distinctive "bullet" shaped concentration profile in the flow stream. A consequence of this is that the response obtained by a conventional (macroelectrode) detector is in the form of a slightly skewed peak (figure 4.2). The copper concentration may be derived either from the peak height (current) or peak area (charge). The response of a microelectrode in a flow cell is identical in form to the macroelectrode, and may be treated in an analogous manner. A typical f.i.a.-microelectrode response to a series of Cu(DDTC)$_2$ standards is shown in figure 4.5. The dependence of injected concentration to peak height was determined to be linear for a range of microelectrode sizes, in the concentration range of interest (figure 4.6).

In a stationary solution, microelectrodes are predicted to experience a relatively enhanced mass transfer to the electrode surface over that expected at conventional sized electrodes [5]. The enhancement is due to the radial nature of the diffusion zone associated with electrodes of micro size. Steady state currents are also observed more rapidly at microelectrodes and under these conditions a very favourable faradaic current to charging current ratio is predicted. It was therefore anticipated that decreasing the size of the electrode would lead to greater analytical sensitivities (faradaic to charging current ratios) in flowing systems as would be predicted for stationary solutions.
Table 4.2. Detection limits for the determination of copper using the microelectrode and macroelectrode methods coupled with flow injection analysis.

<table>
<thead>
<tr>
<th>Electrode radius (μm)</th>
<th>Analytical sensitivity (pA ppm⁻¹)</th>
<th>Normalised sensitivity (pA ppm⁻¹ m²)</th>
<th>Limit of detection (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.7</td>
<td>1732</td>
<td>1.27 x 10¹¹</td>
<td>0.83</td>
</tr>
<tr>
<td>28.1</td>
<td>768</td>
<td>3.10 x 10¹¹</td>
<td>0.70</td>
</tr>
<tr>
<td>13.2</td>
<td>143</td>
<td>2.62 x 10¹¹</td>
<td>1.08</td>
</tr>
<tr>
<td>4.7</td>
<td>58</td>
<td>8.22 x 10¹¹</td>
<td>1.40</td>
</tr>
<tr>
<td>2.5</td>
<td>20</td>
<td>1.06 x 10¹²</td>
<td>3.80</td>
</tr>
<tr>
<td>1500</td>
<td>6.0 x 10⁵</td>
<td>8.45 x 10¹⁰</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Detection limits and sensitivities calculated in units of concentration of copper which was added as Cu(DDTC)₂. Cu(DDTC)₂ determined in acetonitrile (0.001M Et₄NClO₄), applied potential 0.65 V vs. Au disk reference electrode, flow rate 1.0 ml/min. Large area inlaid glassy carbon disk in thin layer cell, mobile phase 80% : 20% acetonitrile : acetate buffer (0.02M, pH = 6.0) containing 0.2 M NaNO₃, applied potential 0.60 V vs Ag/AgCl (3.0M KCl).

Figure 4.5. Flow injection response of Cu(DDTC)₂ standards in pure acetonitrile containing 0.001 M Et₄NClO₄, for a 28 μm Pt disk electrode in a wall jet cell. Flow rate 1.0 ml/min, applied potential +0.70 V vs. Au pseudo reference electrode.
Figure 4.6. Concentration dependence of FIA peak height for copper using a range of Pt microdisk electrodes, (a) 65.7 µm (b) 28.1 µm (c) 13.2 µm (d) 4.7 µm (e) 2.5 µm. Other conditions as in figure 4.5.

Figure 4.7. Example of the calculation of noise levels for a 28.1 µm Pt microdisk electrode. Conditions as in figure 4.5.
Table 4.3. Magnitude of noise and signal-to-noise (S/N) ratio for microelectrodes of different radii under conditions of flow injection analysis.

<table>
<thead>
<tr>
<th>Electrode radius (µm)</th>
<th>Noise level (pA)</th>
<th>Normalised noise (pA m²⁻¹)</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.7</td>
<td>0.40</td>
<td>2.95 x 10⁷</td>
<td>65</td>
</tr>
<tr>
<td>28.1</td>
<td>0.17</td>
<td>6.85 x 10⁷</td>
<td>70</td>
</tr>
<tr>
<td>13.2</td>
<td>0.050</td>
<td>9.13 x 10⁷</td>
<td>45</td>
</tr>
<tr>
<td>4.7</td>
<td>0.035</td>
<td>4.96 x 10⁸</td>
<td>31</td>
</tr>
<tr>
<td>2.5</td>
<td>0.024</td>
<td>1.27 x 10⁹</td>
<td>13</td>
</tr>
</tbody>
</table>

a Noise levels calculated as shown in Figure 4.7.

b Signal-to noise ratio calculated for injections of 2 x 10⁻⁷ M Cu(DDTC)₂ standard.

However, experimental data obtained in this work indicate that decreasing the size of the electrodes below a = 28.1 µm leads to a less favourable limit of detection (poorer signal to noise ratio), as shown in table 4.2. The area normalized analytical sensitivity does indeed increase as the radius was decreased, but this did not result in a concomitant decrease in detection limits because of the dependence of noise on the electrode radius.

The reason for this theoretically unexpected behaviour required a detailed examination of the short term variation in the background current (noise), figure 4.7. The background noise was found to vary with electrode radius (table 4.3), where a decrease in radius corresponded to a decrease in noise level, as would be expected if the background noise level was caused by an impurity in the mobile phase in contrast to the data obtained previously for the oxidation of ferrocene in acetonitrile (section 3.3.6).

However the noise level decreases at a slower rate as the radius is decreased than does the faradaic response, as evidenced by the signal-to-noise ratio (S/N) calculated for the 2 x 10⁻⁷ M Cu(DDTC)₂ standard. Similar results were obtained for all concentrations of Cu(DDTC)₂. An increase in S/N from the a = 65.7 µm to 28.1 µm is followed by a progressive decrease in S/N as the radius decreases. In this case there appears to be no analytical benefit in incorporating microelectrodes less than 28.1 µm in wall-jet type detectors in the determination of copper.
4.3.3.4. Flow rate effects

When an electrode is placed in a flowing stream, the effects of convection play an increasing role in the mass transport to the electrode, for fast electron transfer processes. As a result the rate at which the analyte reaches the electrode surface governs the magnitude of the current-flow rate response. This variation of current with rate of mass transport, or flow rate therefore also varies with the geometry of the flow cell employed.

The dependence of peak height on flow rate has the form (see chapter 3 for a more detailed discussion of flow rate dependence),

\[ i \propto U^x \]  

(4.2)

where \( i \) = peak current, \( U \) = flow rate, and \( x \) = flow rate dependence. When a sample of electroactive species is injected into the flow stream, a transient or peak shaped response is the result. When the electroactive species is present in the mobile phase, such that a constant uniform concentration of the analyte is flowing into the detector cell, then a steady state response is observed. The experimentally determined flow rate dependencies for these two kinds of experiment are shown in table 4.4.

The flow rate dependencies obtained do not appear to match the theoretically expected value of 0.5 (section 3.3.2), and in fact show considerable variation with radius. The reasoning for this would appear to relate to the actual position of the

<table>
<thead>
<tr>
<th>Electrode radius (( \mu \text{m} ))</th>
<th>Flow rate dependence Transient response</th>
<th>Flow rate dependence Steady-state response</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.7</td>
<td>0.80</td>
<td>0.90</td>
</tr>
<tr>
<td>28.1</td>
<td>1.11</td>
<td>0.85</td>
</tr>
<tr>
<td>13.2</td>
<td>0.95</td>
<td>0.61</td>
</tr>
<tr>
<td>4.7</td>
<td>0.72</td>
<td>0.59</td>
</tr>
<tr>
<td>2.5</td>
<td>0.43</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 4.4 Exponential flow rate dependencies for a range of microelectrodes

Flow rate dependence of the form \( i \propto U^x \) where \( U \) = flow rate, and \( x \) = flow rate dependence. Concentration of copper = 1.0 x 10^{-6} M Cu(DDTC)\(_2\) \( \) in acetonitrile (10^{-3} M Et\(_4\)NClO\(_4\)). Flow rate varied from 0.4 ml/min to 1.6 ml/min, in 0.2 ml/min increments, H/d=11.7.
individual electrodes in the impinging jet cell. Small deviations from the centre of the impinging jet may lead to large variations in peak current, and mass transfer (section 3.3.2). It is therefore likely that in the present case the actual microdisks were offset from the centre, and are responding to mass transfer in the transition region of the jet. The low flow rate dependence of the smallest electrode is a distinct advantage when flow rate variations are introduced into a chromatographic system by the pump. This is most beneficial at high applied potentials where background currents increase due to the reduction/oxidation of the mobile phase components.

4.3.3.5. Urine Samples

The results for two urine samples collected from the same subject on subsequent days determined using a 28.1 μm microelectrode, were 26.7 ppb and 34.4 ppb Cu respectively. These results fall within the limits expected for a normal healthy adult.

4.4. SUMMARY

1. The method for the determination of copper in urine as described in figure 4.1 was found to be rapid, accurate and relatively simple to perform with both conventional glassy carbon electrode-thin layer cell configurations and microelectrode-wall jet cell configurations.

2. The microelectrode method exhibits a considerable increase in sensitivity over that found with conventional sized electrodes, although both methods are sufficiently sensitive for the determination of copper in urine at naturally occurring levels.

3. There was found to be limited benefit in using extremely small microelectrodes, as an increase in the limit of detection was observed with a decrease in electrode radius below 28.1 μm. However the dependence of peak current on flow rate does decrease as the electrode radius decreases and this can be an advantage in some circumstances.
4.5. REFERENCES


CHAPTER 5

THE DETERMINATION OF TOCOPHEROLS USING REVERSE PHASE LIQUID CHROMATOGRAPHY AND ELECTROCHEMICAL DETECTION AT A SURFACE OXIDE MODIFIED PLATINUM MICROELECTRODE WITHOUT ADDED ELECTROLYTE.

5.1. INTRODUCTION ................................................................. 124
5.2. EXPERIMENTAL ............................................................... 126
  5.2.1. Reagents ................................................................. 126
  5.2.2. Chromatographic system ........................................... 126
  5.2.3. Electrode pretreatment .............................................. 127
5.3. RESULTS AND DISCUSSION ............................................. 127
  5.3.4. Stationary cell voltammetry ....................................... 127
  5.3.5. High Performance Liquid Chromatography .................... 133
5.4. REFERENCES ....................................................................... 139
5.1. INTRODUCTION

When electrochemical detection (ECD) is employed in conjunction with separation by liquid chromatography, it is generally considered to be a requirement that a sufficiently high concentration of an inert "supporting electrolyte" be dissolved in the mobile phase, to ensure the mobile phase is electrically conducting and to reduce the cell/solution resistance, i.e. reduce the so-called "iR" (voltage) drop across the cell. It is also considered necessary to add electrolyte to overcome the effects of the migration current of charged electroactive species in solution. A rule-of-thumb is to have a one hundred fold excess of supporting electrolyte over the concentration of the analyte, in order to eliminate the effects of migration[1]. So for example if the concentration of analyte is $10^{-6}$ M, then the supporting electrolyte concentration would need to be $10^{-4}$ M in order to negate migration effects. Such a low concentration of supporting electrolyte would not usually be regarded as providing the necessary conductivity to reduce the cell resistance to a functional level in conventional ECD, and concentrations of the order of $10^{-3}$ to $10^{-1}$ M are usually added.

The need to add electrolyte is a distinct disadvantage, adding to the risk of contamination and increasing the cost of experiments. Methods for eliminating the need for addition of electrolyte are therefore desirable. Recently, it has been demonstrated that when microelectrodes are substituted for conventional sized electrodes, electrochemistry without deliberately added supporting electrolyte is possible[2]. Presumably self dissociation of the solvent (or impurities) provide the necessary background conductivity in such experiments. The ability to combine liquid chromatography or flow injection analysis with electrochemical detection at microelectrodes without adding large quantities of supporting electrolyte, makes electrochemical detectors more economical to use[3].

Electrochemical detection at positive potentials is usually undertaken at solid electrodes constructed from platinum, gold, or various forms of carbon[4]. In the case of platinum electrodes the background response of noble metal electrodes, particularly
platinum in aqueous media, is characterized by surface oxide formation and hydrogen sorption/desorption[5]. The nature of the surface oxide layer on platinum electrodes has been subject of considerable debate over the last thirty years. Particular interest has centred on both the catalytic properties of the oxide layer with respect to electrochemical oxidation reactions of compounds of interest, and conversely the ability of the oxide layer to inhibit the oxidation of organic compounds[6-8]. It is now generally agreed that the surface oxide layer initially consists of a reversibly chemisorbed OH species probably in the form of PtOH. This species may be stabilized by exchange reactions with the Pt surface, and converted to the irreversibly bound PtO[9]. While the exact nature of the surface oxide phases may not be settled, the important point to note is that while the PtOH phase has been implicated in the catalytic oxidation of a number of species (e.g. As(III), carbohydrates, alcohols, amino acids, etc)[10], the PtO phase appears to inhibit many oxidation reactions[6]. Thus while some properties of the platinum electrode surface at positive potentials related to oxide film formation restrict the analytical usefulness of platinum as an electrode material, some properties of the surface can be advantageously modified to provide a selective response by passivating the surface towards interfering species[11].

In this chapter the analytical utility of the surface PtO oxide phase in achieving selectivity at a platinum microelectrode is demonstrated with respect to the electrochemical detection of tocopherols in a reverse phase h.p.l.c. separation. The electrode surface is oxidised to form the PtO surface layer which inhibits the methanol adsorption/oxidation processes, enabling the selective detection of the tocopherols. If this modified platinum electrode is used as a microelectrode, the oxidative detection of α-, γ-, and δ-tocopherol (structures shown in figure 5.1) can be undertaken in a methanol/water (95:5) mobile phase without the need to deliberately add supporting electrolyte.
The addition of supporting electrolyte interferes with the chromatographic separation of tocopherols as demonstrated by Ikenoya et al. [12] in their studies employing electrochemical detection in methanol using a conventional sized glassy carbon electrode. An increase in the sodium perchlorate supporting electrolyte concentration above 0.05M led to the observation of band broadening of the peaks, and increased retention times. Thus, the addition of supporting electrolyte is something to be avoided if possible in the detection of tocopherols, and the use of microelectrodes offers a means of achieving this aim.

5.2. EXPERIMENTAL

5.2.1. Reagents

The three tocopherol isomers (α, γ, δ) were obtained from Kodak, and used as received. Methanol, and water were both of chromatographic solvent grade, and supplied by Waters Associates. Tetraethylammonium perchlorate (Southwestern Chemicals) was recrystallized from ethanol/water, then dried in a vacuum desiccator over phosphorous pentoxide.

5.2.2. Chromatographic system

The chromatographic system used in this work was assembled from the following

\[
\begin{align*}
\text{α - tocopherol} & : 5,7,8 \text{ trimethyl} \\
\text{β - tocopherol} & : 5,8 \text{ dimethyl} \\
\text{γ - tocopherol} & : 7,8 \text{ dimethyl} \\
\text{δ - tocopherol} & : 8 \text{ methyl}
\end{align*}
\]

*Figure 5.1. Structures of α-, β-, γ-, and δ-tocopherol.*
components, an ICI LC1500 HPLC pump (ICI Scientific Instruments, Australia), a Rheodyne 7125 sample injector fitted with a 20 μl loop (Rheodyne Corp.), a Spherisorb ODS2 15 cm x 4.6 mm column, an ICI TC1900 temperature controller, a Metrohm 656 electrochemical detector (Metrohm Herisau, Switzerland), a Keithley 614 digital electrometer (Keithley Instruments Inc., USA), an ICI SD2100 UV-Vis detector, and an ICI DP600 dual pen chart recorder.

Electrochemical detection measurements were carried out using a two electrode system, with a platinum disc microelectrode as the working electrode and either a Ag/AgCl (KCl 3M) reference electrode, or a gold disc (a = 1.5 mm) acting as pseudo reference electrode. UV detection was performed at 296 nm, and all chromatographic determinations were carried out at a temperature of 30 ± 0.5 °C.

5.2.3. Electrode pretreatment

The following oxidative pretreatment of the platinum disc microelectrodes was performed prior to the electrodes being used in the detector cell. Each electrode was placed in a beaker containing 2M HNO₃, and a potential of +1.80V vs. Ag/AgCl was applied for the desired length of time. The evolution of oxygen gas from the electrode surface was noted during the course of the electrode pretreatment. Following the oxidation, the electrode was rinsed several times in distilled water, then several times in methanol/water (95:5) solution before being placed into the electrochemical detector cell. No attempt to polish or dry the electrode was made.

5.3. RESULTS AND DISCUSSION

5.3.4. Stationary cell voltammetry

The ability of voltammetric microelectrodes to provide useful information in high resistance solvents with a minimum of distortion has been demonstrated[2]. This feature is particularly useful in the elucidation of mechanisms of processes involving adsorption in the absence of deliberately added electrolyte[13].
Repeated scans of cyclic voltammograms obtained with a platinum microelectrode (a=12.6 μm) in methanol/water (95:5) without deliberately added supporting electrolyte are shown in figure 5.2(b). The response is characterized by the growth of the wave at 0.75V vs Ag/AgCl on the forward (positive potential direction) scan, and the growth of a wave on the reverse scan direction which occurs at a less positive potential (0.45V vs Ag/AgCl). Both processes have the same current sign despite the different scan direction. This anomalous behaviour has been reported previously for the oxidation of methanol in acidic solutions at conventional sized electrodes[14,15], but has not been described at microelectrodes, or without electrolyte being present.

The positive potential scan direction can be characterized into a number of distinct potential regions (vs Normal Hydrogen Electrode)[16]:

(a) 0.0V < E < 0.2V double layer region
(b) E > 0.2V region where oxygen and methanol adsorption occur at electrode surface, and where an oxidation wave is observed
(c) E > 0.75V region where a peak is formed due to the displacement of methanol by the more strongly bound oxide film
(d) E > 0.90V region where an increase in current occurs due to oxide formation and possible methanol oxidation on oxide film

It should be noted that the initial scan (figure 5.2(a)) where PtOH is absent from the electrode surface shows almost no oxidation response. This oxidation response grows as the surface coverage of oxide increases up to an equilibrium value (figure 5.2(c)).
The behaviour displayed in the reverse scan direction has also been described at conventional sized electrodes in acidic methanol solutions, with the most substantiated explanation being presented by Giner[14]. On the reverse scan some of the oxide film formed at positive potentials is reduced. This leads to an increasing number of sites free of inhibiting oxide becoming available and also free of adsorbed methanol. Consequently this leads to an increased rate of oxidation of methanol, evidenced by an increased oxidative current response observed on the reverse scan.

It therefore appears that at a platinum microelectrode, even in the absence of electrolyte, that the oxide layer inhibits the oxidation response of methanol at potentials greater than 0.75V vs Ag/AgCl. However since the oxidation of methanol is not observed at all at a clean electrode (figure 5.2(a)) the formation of an oxide layer can also be said to catalyse the response over a limited potential range. At a potential less positive than 1.2V vs Ag/AgCl the most likely oxide phase giving rise to the catalysis is PtOH[9]. Similarly scanning to very positive potentials, which is likely to lead to the formation of PtO, also appears to inhibit the response.

Since the application of very positive potentials appears to inhibit the potentially interfering background process, the response of an electrode which had previously been oxidized at 1.80V vs Ag/AgCl in 2M HNO₃ was examined. Results in methanol/water (95:5) after the electrode had been held at this potential in 2M HNO₃ for 60 seconds and then transferred to the methanol/water solvent mixture is shown in figure 5.3(a). Repeated cycling over the potential range of interest had little effect on the response, indicating that the coating is strongly bound to the surface, and effectively inhibits the methanol adsorption/oxidation response. The most likely composition of the surface film formed at very positive potentials would be PtO[9], which unlike the PtOH film is deposited irreversibly.
Figure 5.2. Cyclic voltammograms observed at positive potentials in methanol/water (95:5) containing no added electrolyte with a 12.5 μm radius platinum microdisc electrode (a) initial scan (b) response observed with repeated cycling of the potential and, (c) equilibrium response obtained after approximately 30 scans. Scan rate 100 mV s⁻¹, temperature 22 °C.
While the background response has been reduced to an acceptable level by pre-oxidation at 1.8V, this is of little use if the response of the species to be detected at the platinum microelectrode is also inhibited. A cyclic voltammogram of 1.33x10^{-3} M $\alpha$-tocopherol in methanol/water (95:5) at a surface modified platinum microelectrode is shown in figure 5.3(b). The sigmoidal shaped response expected for a faradaic process at a microelectrode is observed demonstrating that the tocopherol oxidation process is not inhibited.

However the response for tocopherol at the mM concentration level is slightly distorted by iR drop effects in the absence of electrolyte. Hysteresis effects are commonly observed at this type of coated electrode[16]. To determine the extent to which iR drop was the cause of this hysteresis in the absence of electrolyte, experiments were repeated in the methanol/water(95:5) solution containing 10^{-1}M tetraethylammonium perchlorate. In the presence of electrolyte, the response of the tocopherol oxidation did not exhibit any hysteresis indicating that iR drop is the most likely cause of this effect.

The above results demonstrate that the pretreatment of the platinum surface effectively discriminates against the methanol adsorption/oxidation reaction in favour of the tocopherol response. The utility of this preoxidized microelectrode was then examined in a high performance liquid chromatographic separation of a number of tocopherols using a methanol/water mobile phase without added electrolyte.
Figure 5.3. Cyclic voltammograms observed at positive potentials in methanol/water (95:5) containing no added electrolyte with a 12.5 μm radius platinum microdisc electrode preoxidised in 2M HNO₃ at a potential of 1.80V for 60 seconds. (a) blank, (b) 1.33x10⁻³ M α-tocopherol. Scan rate 100 mV s⁻¹, temperature 22 °C.
5.3.5. High Performance Liquid Chromatography

Normalized hydrodynamic voltammograms in 95:5 methanol/water of α-, γ-, and δ-tocopherol obtained in a flow cell at a microelectrode which had been preoxidized for 30 seconds in nitric acid are shown in figure 5.4. Although the oxidation waves are drawn out and occupy a 600 mV potential range, well defined sigmoidal shaped curves are observed. The half-wave potential for oxidation of α-tocopherol (0.63 V vs Au) in the absence of electrolyte was found to be 70 mV less than γ-tocopherol (0.70 V vs Au), which agrees with data reported at a glassy carbon electrode in methanol[12]. The halfwave potential for oxidation of δ-tocopherol is almost the same as that of α-tocopherol in contrast to that previously reported. Apart from slight differences in oxidation potentials, the different tocopherols show essentially the same voltammetry.
Figure 5.5. Amperometric detection of $\alpha$-, $\gamma$-, and $\delta$-tocopherol at an applied potential of 0.9V vs Au following chromatographic separation in methanol/water (95:5) at (a) polished 65.7 $\mu$m radius platinum microdisc electrode, and (b) preoxidized electrode. Other conditions are as for figure 5.4.
Based on data obtained from hydrodynamic voltamograms, the reversed-phase chromatographic separation and electrochemical detection of α-, γ-, and δ-tocopherol was examined in detail. Amperometric detection without added electrolyte was employed at an applied potential of 0.90V vs Au, and the mobile phase consisted of methanol/water (95:5). The electrode was a platinum microdisc (a=65.7 μm). Figure 5.5(a) shows the response at a freshly polished electrode, and figure 5.5(b) shows an electrode that has been preoxidized as described in the experimental section in HNO₃ for 60 seconds. The preoxidised electrode shows three distinct peaks at 3, 3.8 and 4.6 minutes corresponding to γ, δ, and α-tocopherol respectively. The freshly polished electrode shows no response to these compounds at all! Preconditioning of the electrode surface also reduces the background current observed in the mobile phase by approximately an order of magnitude.

Pretreatment of microelectrodes at a very positive applied potential (eg. +1.80V) in the methanol/water (95:5) mobile phase was found to be an inefficient method of preparation relative to pretreating the electrodes externally to the cell in 2M HNO₃ at an applied potential of +1.80V vs Ag/AgCl. Pretreatment in 2M HNO₃ at applied potentials less than the oxygen evolution wave was found to give higher background currents and a reduced response for tocopherol, indicating a lessened coating of PtO. Pretreatment in acid solution (for up to two hours) without application of a an applied voltage had little effect on the response obtained at a freshly polished electrode.
Figure 5.6. Short term variation of the chromatographic peak height observed with electrochemical detection of \(\alpha\)-tocopherol after preoxidation of a 65.7 \(\mu\)m radius platinum microdisc electrode for (\(\Delta\)) 30 seconds, (\(\Box\)) 60 seconds and (\(\bigtriangledown\)) 120 seconds. Other conditions and experimental parameters are as for figure 5.4 and 5.5.

The short and long term stability of the externally oxidized platinum microelectrode maintained at a potential of 0.90V vs Au, was monitored by examining the chromatographic response due to repeated injections of \(\alpha\)-tocopherol. The response of a freshly prepared electrode was found to change over a period of approximately 30 minutes (figure 5.6) before a constant peak height was obtained. A likely explanation for the short term instability is the influence on the oxide film of a lower applied potential of the amperometric detection (+0.90V vs Au) compared with the pretreatment potential (+1.80V vs Ag/AgCl)). A mixed oxide containing PtOH and PtO will probably be present at a potential of +0.90V.

The long term stability was found to be excellent, with the response remaining relatively constant for at least 10 hours (figure 5.7). Thus reproducible measurements may be obtained over extended periods of time from a single electrode without the need for further treatment. The electrochemical response of \(\alpha\)-tocopherol was found to decrease significantly if the electrode was left in the cell at open circuit for extended...
Figure 5.7. Long term dependence of chromatographic peak height observed with electrochemical detection of (△) α-tocopherol, (■) γ-tocopherol, and (◇) δ-tocopherol after preoxidation of a 65.7 μm radius platinum microdisc electrode for 60 seconds. Other conditions and experimental parameters are as for figure 5.4 and 5.5.

periods of time. This implies that the applied potential of +0.90V vs Au stabilizes the oxide coating in the methanol/water system.

The response observed at platinum microelectrodes was also found to be critically dependent upon the length of time the pretreatment was carried out. An optimum pretreatment time of 60 seconds was established based on the data demonstrated in figure 5.8. A plausible explanation for the data in figure 5.8 is that a minimum surface layer thickness of PtO is required to inhibit the methanol adsorption/oxidation reaction. After an oxidation time of 60 seconds, the surface layer becomes so thick that it begins to inhibit the oxidation of the tocopherols.

A linear dependence of concentration on peak height was recorded over the concentration region of interest (figure 5.9). The limit of detection for α-, γ-, and δ-tocopherol was calculated to be 1x10⁻⁷ M, or 2pmol on column for a 20 μl injection, based on signal to noise ratio of 2:1 for the 67.5 μm platinum microdisc electrode with a pretreatment time of 60 seconds. Detection limits at the 2:1 signal to noise ratio with UV detection were found to be 2x10⁻⁷ M, indicating that a slight increase in sensitivity
is obtained when electrochemical detection is employed instead of UV detection. Improved sensitivity of electrochemical detection over UV detection for the determination of tocopherols has been noted previously[12]. The relative standard deviation for repeated 20 µl injections of 5x10⁻⁶ M α-tocopherol on the same electrode was found to be 5%. A similar reproducibility was obtained with UV detection implying that the variation is due to the chromatographic system, not the electrode response. The variation of the peak height for 5x10⁻⁶ M α-tocopherol from electrode-to-electrode, or pretreatment-to-pretreatment, was generally better than 10%.

**Figure 5.8.** Variation of the chromatographic peak current for α-tocopherol with duration of preoxidation of the microdisc electrode. Electrode stabilized in flow cell for 30 minutes prior to determination. Other conditions and experimental parameters are as for figure 5.4 and 5.5.
CHAPTER 6

EXAMINATION AND USE OF MERCURY PLATED INLAID DISK MICROELECTRODES FOR TRACE ANALYSIS.

6.1. INTRODUCTION........................................................................................................... 141
  6.1.1. General .................................................................................................................. 141
  6.1.2. Mercury electrodes in chloride media .................................................................... 141
  6.1.3. ASV ...................................................................................................................... 143
  6.1.4. Portable battery powered devices ........................................................................ 145

6.2. THEORY ..................................................................................................................... 146
  6.2.1. Hg drop growth theory ....................................................................................... 146

6.3. EXPERIMENTAL ....................................................................................................... 153
  6.3.1. Hg plating experiments ...................................................................................... 153
  6.3.2. Battery powered purpose built equipment ....................................................... 153
    6.3.2.1. CMOS Function Generator .......................................................................... 154
      6.3.2.1.1. General design features ......................................................................... 154
      6.3.2.1.2. Hardware description ........................................................................... 155
      6.3.2.1.3. Software ............................................................................................... 158

6.4. RESULTS AND DISCUSSION .................................................................................. 158
  6.4.1. Hg growth ............................................................................................................ 158
  6.4.2. The behaviour of mMTE's in chloride media .................................................... 160
  6.4.3. Pb\(^{2+}\) model system ........................................................................................ 164
    6.4.3.1. Effect of scan rate at the mMTE ................................................................ 167
    6.4.3.2. The effect of stirring ................................................................................... 167
    6.4.3.3. The effect of deposition time variation ...................................................... 170
  6.4.4. Simultaneous determination of Pb\(^{2+}\) and Cd\(^{2+}\) using battery powered equipment ................................................................................................................ 170
  6.4.5. Cu in tap water using a battery powered system ............................................. 174

6.5. SUMMARY ............................................................................................................... 176

6.6. REFERENCES .......................................................................................................... 177
6.1. INTRODUCTION

6.1.1. General

Mercury is the electrode material of choice in many areas of electrochemistry[1]. This is due to the many attributes which make liquid mercury unique over the solid electrode materials platinum, gold, carbon etc., including high hydrogen overvoltage, ability to generate fresh clean surfaces, freedom from surface roughness, and the ability to dissolve metal species[1].

The most popular mercury electrode is the dropping mercury electrode (d.m.e.), in which liquid mercury is passed through a glass capillary to form droplets of mercury which act as the electrode surface. Another technique for producing a mercury electrode is to electrodeposit mercury onto a solid substrate (e.g. Pt, Au, C) from solutions of a soluble mercury salt. This type of electrode is known as a mercury thin film electrode (MTFE).

6.1.2. Mercury electrodes in chloride media

The anodic response of a mercury electrode is dominated by the oxidation of the mercury electrode itself. In the presence of chloride ions, the oxidation wave of mercury will be displaced cathodically[2], and the electrocrystallization of calomel (Hg₂Cl₂) on the mercury surface will dominate the response[3], and lead to the electrode's passivation.

The electrocrystallization of calomel occurs initially through the deposition of a monolayer at the surface, via a two dimensional growth of two dimensional nuclei[3] i.e.,
Growth of the film then proceeds via the laying down of further monolayers orientated parallel with the {110} face of the monolayer substrate. The rate determining step appears to be the incorporation of new material into the film, which occurs by ionic migration through, or disruption of the film to enable mercury ions to react with the chloride ions. Thus an overall mechanism of film growth may be described,

\[
\text{Cl}^-\text{(solution)} \rightleftharpoons \text{Cl}^-\text{(adsorbed)} \rightleftharpoons \text{Cl}^-\text{(lattice)} \quad (6.1)
\]

\[
\text{Hg(metal)} \rightleftharpoons \text{Hg}^+\text{(adsorbed)} + e^- \quad (6.2)
\]

\[
\text{Hg}^+\text{(adsorbed)} \rightarrow_{\text{slow}} \text{Hg}^+\text{(lattice)} \quad (6.3)
\]

It has also been shown that the dissolution of \(\text{HgCl}_2^+\) is important, leading to the overall reaction scheme [4],

\[
2\text{Hg} + 2\text{Cl}^- \rightleftharpoons \text{Hg}_2\text{Cl}_2 + 2e^- \quad (6.4)
\]

\[
\text{Hg} + 4\text{Cl}^- \rightleftharpoons \text{HgCl}_4^2 + 2e^- \quad (6.5)
\]

The morphology of the resultant calomel film has been found to be dependent on many factors, of which the most important appear to be current density, and chloride ion concentration[2,5-7]. Low current densities give smaller crystals on the surface of
the electrode [2], reaching a point at very low current densities (e.g. 1 μA cm⁻²) where
the deposit formed an intimate mixture of mercury and calomel at the surface. At high
current densities more structure was noted in the film, which was found to be thicker,
with many holes and ridges forming. Kemula et. al. [5] reported that the electron
transfer reaction of the ferri/ferrocyanide couple was still observable through the film,
indicating the porous nature of the calomel layer. The thickness of the calomel layer
was found to vary depending on the chloride ion concentration, with dilute chloride
solutions giving thicker layers[6].

6.1.3. ASV

Anodic stripping voltammetry (ASV) is one of the most sensitive and selective of
the range of electroanalytical techniques available, enabling simultaneous detection of a
number of elements at concentrations down to the sub part-per-billion level. The
analytical procedure used in ASV is very simple, and involves three main steps; (i)
deposition of the metal ion into the mercury electrode, (ii) rest period, and (iii) the
quantitative stripping of the dissolved metal from the mercury.

The deposition step involves the reduction of metal ions in solution to the metal,
which then dissolves in the mercury electrode,

\[ M^{n+} + ne^- \rightleftharpoons M(Hg) \quad (6.6) \]

this step explains the incredible sensitivity of ASV. The longer the deposition step is
maintained, the greater the concentration of metal built up in the mercury. The solution
is normally stirred during this step in order to maximise the mass transport of the
dissolved metal ions to the electrode surface, and hence maximise the concentration of
dissolved metal in the mercury.

The rest period enables the solution to become quiescent, and also allows the metal
concentration in the mercury electrode to become uniform throughout the mercury
drop, as shown in figure 6.1.
The stripping step is where the actual quantitation takes place. The dissolved metal is stripped (oxidised) back out of the mercury drop, according to the reaction

$$
M(\text{Hg}) \rightleftharpoons M^{n+} + ne^- \quad (6.7)
$$

producing a stripping peak for each metal present. In general peak height, or wave height is proportional to concentration. Any form of potential waveform may be used for the quantitation (eg. linear sweep, differential pulse, normal pulse), with the various pulse techniques being the most popular at conventional sized electrodes.

A number of workers have examined the use of micro-mercury drop electrodes for ASV analysis, and have generally relied on the deposition of a mercury film onto an inlaid microdisk electrode to produce a sufficiently small mercury electrode. Almost all of the electrode materials which have been used for inlaid microdisk electrodes have been used as substrates for mercury films, including carbon fibres[8-10],

*Figure 6.1.* Distribution of dissolved metal species versus normalised radius in a mercury drop for different rest periods[27]. (a) 30 s, (b) 20 s, (c) 10 s, (d) 0 s.
platinum[11,12], iridium[13], and graphite[14].

There are several advantages claimed when using mercury microelectrodes for ASV. These include the enhanced mass transfer due to the non linear diffusion field reducing the need to stir the solution during deposition[11]; the ability to scan more rapidly than at conventional electrodes during the stripping step, thus decreasing analysis time, and increasing reproducibility[12]; decreased charging current enhancing detection limits[8]; the ability to use linear sweep waveform during the stripping step, simplifying the analytical requirements of the technique; and finally the ability to work in solutions without adding electrolyte[15].

Most of the work reported to date on the use of mercury microelectrodes has involved the examination of standard solutions of metal ions, and little analysis of real samples. In the present work results will be reported for the determination of both standard solutions and natural water samples.

6.1.4. Portable battery powered devices

The rapid development of low-power, complementary metal oxide semiconductor (CMOS) devices in recent years, has led to a concomitant rise in the development of portable battery-powered field based analytical instrumentation[16,17]. As a direct result of these developments it is now feasible to take the analytical equipment into the field directly to the location of analytical interest. This situation is much more desirable than that which currently exists where samples are collected in the field and transported back to the laboratory for analysis. The inherent problems with this latter methodology have been well documented[17-20], and include; an increased risk of contamination, possible alteration of the speciation of elements of interest, storage and transport problems, and the time lapse between sampling and analysis of the sample. Many of these problems are minimised if the analysis may be performed at the location of sampling.

Electroanalytical techniques, by their very nature, are eminently suited to this type of approach, and much work is being directed to achieve this aim. For example Mann
et. al. [18] have described a commercially available battery powered instrument based on anodic stripping voltammetry, the PDV 2000 portable digital voltameter (Chemtronics, Australia). This instrument utilizes conventional sized glassy carbon electrodes onto which a thin mercury film is deposited, enabling the determination of a range of environmentally important elements (eg Pb, Cu, Zn, Cd), by this menu driven instrument. Other workers have made developments along similar lines [20].

In the present work the development and use of a low powered programmable function generator based on CMOS technology will be described. When coupled with a battery powered potentiostat, and recorder, field based ASV is possible.

6.2. THEORY

6.2.1. Hg drop growth theory

The deposition of mercury from a solution of soluble mercury salts onto a platinum microdisk electrodes will proceed according to the reaction,

$$
\text{Hg}^{n+}_{m} + ne^{-} \rightarrow m\text{Hg (liq)}
$$

(6.8)

Mercury growth may then occur in a number of different ways depending on the relative specific surface energies of the interfaces involved at an inlaid disk electrode plated with mercury (i.e. disk/solution (ds), disk/mercury (dm), mercury/solution (ms), insulator/mercury (im), and insulator/solution (is)). If the surface energies obey the relationship

$$
\{\gamma_{ds} - \gamma_{dm}\} > \gamma_{ms} < \{\gamma_{im} - \gamma_{is}\}
$$

---

1 Theory derived in collaboration with Ms. C.L. Colyer and Prof. K.B. Oldham.
then the growth of the mercury on the inlaid microdisk electrode will follow the sequence shown in figure 6.2, this type of electrode will be referred to as a micro mercury thin film electrode (μMTFE). The growth of such a geometry, termed a penned configuration, is assumed to grow through an infinite series of steady states, as justified by Fletcher [21]. Analytical solutions exist for three of the geometries through which the electrode grows during the deposition process, these are listed in table 6.1, and illustrated in figure 6.3. The area of the mercury/solution interface and the volume of the mercury deposit may be related to the contact angle by

\[
A = \pi a^2 \sec^2 (\theta/2) \quad (6.9)
\]

and

\[
V = \frac{\pi a^3}{6} \left( \sec^2 \left( \frac{\theta}{2} \right) + 2 \right) \sqrt{\sec^2 \left( \frac{\theta}{2} \right) - 1} \quad (6.10)
\]

From examination of equations 6.9 and 6.10 it is evident that there is a cubic relationship between \( A \) and \( V^2 \) which can be solved such that the area is given by
\[ A = \pi a^2 \left[ (1 + v^2 + \sqrt{(v^4 + 2v^2)})^{1/3} + (1 + v^2 - \sqrt{(v^4 + 2v^2)})^{1/3} - 1 \right] \quad (6.11) \]

where \( v \) is the volume normalised by division by \( \frac{\pi a^3}{\sqrt{18}} \).

The second column in table 6.1 lists the steady state current expression (i) for that geometry, the third column lists the area of the mercury solution interface (\( A_{ms} \)), the final column lists the ratio of steady state current to the square root of area. The values for \( i / \sqrt{A_{ms}} \) are worthy of further investigation, due to the similarity of the magnitude of the numerical expressions \( 4 / \sqrt{\pi}, \sqrt{2\pi}, \text{ and } \sqrt{4\pi \ln(2)} \). It has been proposed \([22]\) that the equation

\[ i = \sqrt{2\pi \alpha(\theta)} \text{nFCD} \sqrt{A_{ms}} \quad (6.12) \]

**Table 6.1.** Expressions relating the limiting current and surface area to the geometry of a \( \mu \text{MTFE} \) at different stages of growth of the electrodeposit.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>( i )</th>
<th>( A_{ms} )</th>
<th>( i / \sqrt{A_{ms}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlaid disk</td>
<td>( 4\pi FcDa )</td>
<td>( \pi a^2 )</td>
<td>( 4\pi FcD/\sqrt{\pi} )</td>
</tr>
<tr>
<td>Shrouded hemisphere</td>
<td>( 2\pi nFcDa )</td>
<td>( 2\pi a^2 )</td>
<td>( \sqrt{2\pi} \text{nFCD} )</td>
</tr>
<tr>
<td>Sphere on a plane</td>
<td>( 4\pi \ln(2)nFcDR )</td>
<td>( 4\pi R^2 )</td>
<td>( \sqrt{4\pi \ln(2)}nFcD )</td>
</tr>
</tbody>
</table>
be used to describe the diffusion limited steady state current at the complete range of geometries involved in the growth of the mercury deposit. The term $\alpha(\theta)$ is a number which is dependent on the contact angle, all other terms have their usual meanings. Values for the $\alpha(\theta)$ term have been calculated [22] and are reproduced in table 6.2.

Combining equations 6.11 and 6.12 leads to an expression for the voltammetric current during the mercury deposition,

$$i = \sqrt{2\pi} \alpha(v) nFCDa \left[ (1 + v^2 + \sqrt{(v^4 + 2v^2)})^{1/3} + (1 + v^2 - \sqrt{(v^4 + 2v^2)})^{1/3} - 1 \right]^{\frac{1}{2}} \quad (6.13)$$

where the function $\alpha(v)$ is also included in table 6.2.

The total charge passed during the experiment is given by $q$, which may be derived by applying Faraday's law, giving

$$q = \frac{nFpV}{mM} = \frac{\pi nFpa^3v}{\sqrt{18} \text{ mM}} \quad (6.14)$$

where $n$ and $m$ are integers defined in equation 6.8, $F$ is Faraday's constant, $M$ is the atomic weight of mercury, and $p$ the density. Further, it is possible to define

$$t = \int \frac{dq}{i}$$

hence

$$t = \int \frac{dv}{\alpha(v) \left[ (1 + v^2 + \sqrt{(v^4 + 2v^2)})^{1/3} + (1 + v^2 - \sqrt{(v^4 + 2v^2)})^{1/3} - 1 \right]^{1/2}} \quad (6.15)$$
gives the time required to grow a penned mercury deposit of volume $\frac{\pi a^4 y}{\sqrt{18}}$ on a disk of radius $a$. From the values of $\alpha$ contained in table 6.2, a numerical integration of equation 6.15 is possible, with the results shown in table 6.3. The second column in table 6.3 is proportional to $q$, and the values in the third column are proportional to $t$. This data was used to generate the theoretical curves reported in figure 6.6.
Table 6.2. Values of the $\alpha$ term as a function of either $\theta$, or $\nu$.

<table>
<thead>
<tr>
<th>$\cos(\theta)$</th>
<th>$\alpha(\theta)^1$</th>
<th>$\alpha(\nu)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.9003</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.9</td>
<td>0.940*</td>
<td>0.4952</td>
</tr>
<tr>
<td>0.8</td>
<td>0.962*</td>
<td>0.7333</td>
</tr>
<tr>
<td>0.7</td>
<td>0.975*</td>
<td>0.9436</td>
</tr>
<tr>
<td>0.6</td>
<td>0.985*</td>
<td>1.1490</td>
</tr>
<tr>
<td>0.5</td>
<td>0.992*</td>
<td>1.3608</td>
</tr>
<tr>
<td>0.4</td>
<td>0.9948</td>
<td>1.5871</td>
</tr>
<tr>
<td>0.3</td>
<td>0.9972</td>
<td>1.8360</td>
</tr>
<tr>
<td>0.2</td>
<td>0.9988</td>
<td>2.1170</td>
</tr>
<tr>
<td>0.1</td>
<td>0.9997</td>
<td>2.4421</td>
</tr>
<tr>
<td>0.0</td>
<td>1.0000</td>
<td>2.8284</td>
</tr>
<tr>
<td>-0.1</td>
<td>0.9997</td>
<td>3.3007</td>
</tr>
<tr>
<td>-0.2</td>
<td>0.9990</td>
<td>3.8971</td>
</tr>
<tr>
<td>-0.3</td>
<td>0.9979</td>
<td>4.6805</td>
</tr>
<tr>
<td>-0.4</td>
<td>0.9964</td>
<td>5.7607</td>
</tr>
<tr>
<td>-0.5</td>
<td>0.9945</td>
<td>7.3485</td>
</tr>
<tr>
<td>-0.6</td>
<td>0.9923</td>
<td>9.8995</td>
</tr>
<tr>
<td>-0.7</td>
<td>0.9897</td>
<td>14.5882</td>
</tr>
<tr>
<td>-0.8</td>
<td>0.9869</td>
<td>25.4558</td>
</tr>
<tr>
<td>-0.9</td>
<td>0.9837</td>
<td>67.8086</td>
</tr>
<tr>
<td>-1.0</td>
<td>0.9803</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

$^1$ Data taken from reference [22]. Data marked with an asterisk not reported in reference, but interpolated from their data.
Table 6.3. Values for the integral in equation 6.15. as a function of the ratio \( \frac{V}{V_{\text{hemi}}} \) of the volume of deposit to the volume of a hemisphere of radius \( a \), and the normalised volume \( v \).

<table>
<thead>
<tr>
<th>( \frac{V}{V_{\text{hemi}}} )</th>
<th>( v )</th>
<th>integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.25</td>
<td>0.7071</td>
<td>0.7484</td>
</tr>
<tr>
<td>0.50</td>
<td>1.4142</td>
<td>1.402</td>
</tr>
<tr>
<td>0.75</td>
<td>2.1213</td>
<td>1.980</td>
</tr>
<tr>
<td>1.00</td>
<td>2.8284</td>
<td>2.502</td>
</tr>
<tr>
<td>1.25</td>
<td>3.5355</td>
<td>2.982</td>
</tr>
<tr>
<td>1.50</td>
<td>4.2426</td>
<td>3.420</td>
</tr>
<tr>
<td>2.00</td>
<td>5.6569</td>
<td>4.256</td>
</tr>
<tr>
<td>2.50</td>
<td>7.0711</td>
<td>5.007</td>
</tr>
<tr>
<td>3.00</td>
<td>8.4853</td>
<td>5.705</td>
</tr>
<tr>
<td>5.00</td>
<td>14.142</td>
<td>8.154</td>
</tr>
<tr>
<td>10</td>
<td>28.284</td>
<td>13.06</td>
</tr>
<tr>
<td>20</td>
<td>56.568</td>
<td>20.67</td>
</tr>
<tr>
<td>50</td>
<td>141.42</td>
<td>37.76</td>
</tr>
<tr>
<td>100</td>
<td>282.84</td>
<td>59.42</td>
</tr>
<tr>
<td>200</td>
<td>565.68</td>
<td>93.81</td>
</tr>
<tr>
<td>500</td>
<td>1414.2</td>
<td>172.1</td>
</tr>
<tr>
<td>1000</td>
<td>2828.4</td>
<td>272.7</td>
</tr>
<tr>
<td>2000</td>
<td>5656.8</td>
<td>432.6</td>
</tr>
<tr>
<td>5000</td>
<td>14142.</td>
<td>797.5</td>
</tr>
</tbody>
</table>
6.3. EXPERIMENTAL

6.3.1. Hg plating experiments

A solution containing 5.0 mM HgCl₂ (analytical grade, Ajax, Sydney) and 10.0 mM HCl (Aristar grade, BDH, England) was prepared in water that was purified by reverse osmosis/deionization/organic cartridge treatment. The high mobility of H⁺ ions will make the migration of Hg²⁺ ions negligible in this solution. Prior to each experiment, high purity nitrogen was passed for 5 minutes to deoxygenate the solution.

The electrodeposition of mercury onto the inlaid platinum microdisk electrode, from the mercuric ion solution described above, was carried out in a three electrode cell using a Ag/AgCl (3M KCl) reference electrode and a platinum wire counter electrode. Application of a constant -100 mV potential by a Bioanalytical Systems (BAS) 100A potentiostat ensured total concentration polarization of the working electrode during the deposition experiments. The total charge passed was monitored by the potentiostat and was recorded at one minute intervals during each 10 minute experiment.

Linear sweep stripping experiments were performed using a BAS 100A potentiostat, or a combination of a Keithley 614 Electrometer and either the battery powered function generator(described in section 6.3.2) or a Metrohm VA Scanner E612.

6.3.2. Battery powered purpose built equipment.

A completely battery powered system for dc stripping analysis was constructed from a purpose built CMOS based function generator(description follows), an AMEL model 554 battery powered potentiostat, a Keithley 614 Electrometer, and a Goerz Electro MINIGOR X-Y recorder.
6.3.2.1. CMOS Function Generator

6.3.2.1.1. General design features

The function generator constructed utilizes CMOS integrated circuits exclusively and is based on a CMOS microprocessor unit (MPU), which, in line with current practice, utilizes a multiplexed (address, then data) bus. The function generator is based on the Hitachi eight bit MPU (type HD6303RP, Hitachi Microcomputer Systems, Semiconductor Division). The MPU has two main functions: (1) the provision of all signals required for data transfer and control of all internal operations, and (2) the provision of all signals to indirectly interface to the outside world via the digital-to-analog converter (DAC) and the liquid crystal display (LCD). (see figure 6.4).

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Figure 6.4. Block diagram showing the major components of voltammetric instrumentation.

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2 Function generator designed and constructed by Mr F. L. Walter from initial design concept by present author, with further design and development by Ms S.N. Tan.
A firmware monitor program and the applications programs are contained in a CMOS 8192 x 8 bit erasable programmable read only memory (EPROM) device. The monitor program contains all of the general purpose routines for handling timing, display, and mode selection that are needed in analytical voltammetry. It should be noted that no provision has been made for external random access memory (RAM) in this function generator because there is no need to store a large number of parameters or data with the modular design being employed. The on-board RAM in the MPU is sufficient for the housekeeping and storing the limited number of parameters used.

6.3.2.1.2. Hardware description.

Figure 6.5 shows the circuitry and components used in the function generator. The heart of the system is the Hitachi HD6303RP MPU, which utilizes a multiplexed address/data bus format in order to reduce the number of pins allocated to address and data functions. This allows the pins released from these functions to be used as input or output (I/O) lines. All of the I/O lines are fully used in the design of this function generator. System timing is provided in a conventional way by a 4MHz crystal. The problem of handling mode selection, reset, and the port 2 I/O lines (P20-P24) is overcome by using a 14053B multiplexer device (CMOS Integrated Circuits, Motorola Inc.). On system reset, the required mode is read from the port 2 I/O lines P20, P21, and P22, which then revert to normal I/O lines for interfacing the thumbwheel switches S7-10, which are used for setting all of the potentials required by the operator. Switches S3-S5, which are connected to port 1, carry out the operator functions of <Enter>, <Start>, and <Stop>. The buzzer, BU1, functions as an audible indication of the end of a particular step in an analysis, and as a warning signal that the batteries are weak and in need of replacement. The remaining I/O lines required by the thumbwheel switches are also connected to port 1.
Figure 6.5. Detailed circuit diagram of the battery powered function generator.
The DAC is an AD7545KN (Integrated Circuits, Vol 1, Analog Devices, 1984) which is connected directly to the bus. The analog unipolar output of the first operational amplifier (op amp) ICL7611CPA (Hot Ideas in CMOS, Intersil Inc., 1983) is suitably scaled and level shifted by the second op amp (ICL7611CPA) to provide analog outputs between -4.096 and +4.095 V. The minimum increment available to the operator for setting the potential with the thumbwheel switch is 10 mV, and the software incorporates level checking to ensure that the output is between -4.00 and +4.00 V.

Memory space is limited to 64K, which for simplicity is paged in 8K blocks by using the 74HC138 and 74HC00 devices. The lower page is allocated to on-board addresses (namely the stack and MPU ports), while the EPROM is located at the top of memory at $E000$ hexadecimal (hex) and the LCD is located at $4000$ (hex). Because the EPROM requires a nonmultiplexed bus, a 74HC373 is provided to demultiplex the low order address signals for the device and as required elsewhere.

The LCD is a DMC40218 (Dot Matrix LCD Module, User's Manual, Optrex Corp.) two line by 40 character display; it is connected directly to the bus and, thus, appears as two memory locations to the MPU. The fact that 80 characters are available ensures that meaningful prompts can be provided even for an inexperienced operator.

The power source for the instrument is four 1.5V AA dry cells. The necessary regulation of this 6V input is carried out by a low-dropout regulator LM2931AZ (linear Databook, National Semiconductor Corp., 1982), that provides +5V; -5 V is produced by a voltage converter ICL7660CPA (Hot Ideas in CMOS, Intersil Inc., 1983). A micropower undervoltage/overvoltage detector ICL7665PA (Hot Ideas in CMOS, Intersil Inc., 1983) is used to signal the MPU via port I/O line P14 that the battery condition is suspect and that the dry cells should be changed. In practice, 10 hours of continuous use of the function generator is possible when alkaline cells are used.
6.3.2.1.3. Software.

All software has been written at the assembly level using a cross assembler named CRASMB produced by Lloyd I/O and marketed by Frank Hogg Ltd. This package runs under the FLEX-09 operating system in a South West Technical Products Corp. 6809 MPU system.

The initial potential, deposition potential (these two potentials can be the same), final or switching potential, and rest potential can be set from the thumbwheel switches. The deposition/equilibrium time can also be set via the thumbwheel switches between 0 and 999 seconds. The scan rates can be set between 10 mVs⁻¹ and 40 Vs⁻¹. The number of scans can be specified. Timing for scanning or stepping the analog output is provided by suitable software delay routines. Visual and audio program prompts are provided to the operator at all times, which allows the easy entry of all of the potentials required in a stripping experiment. In the event of a spurious entry, a prompt is provided to the operator. In addition, the software continually monitors the battery status and provides both visual and an audible prompt when the battery condition deteriorates to an unsuitable level.

The function generator has been designed to provide all of the features required for dc voltammetric techniques (eg. dc cyclic voltammetry, dc linear sweep voltammetry, dc stripping voltammetry).

6.4. RESULTS AND DISCUSSION

6.4.1. Hg growth

The results of thirty experimental μMTFE electrodepositions are shown in figure 6.6. Each experimental point represents the average of six deposition experiments, which were carried out under identical conditions. The data was background corrected by subtracting the charge at equivalent times in the absence of mercuric ions, however it is worth noting that the background in each case was less than 1%, and could easily have been disregarded.
The theory/experimental correlation for the two largest electrodes (radius = 12.5 and 5.0 μm) is poor for all but the first one or two points. This may be explained by the fact that a finite time is required for a steady state to be achieved. For the case of a 5 μm radius electrode it has been calculated that it takes approximately 8 seconds for the current to come within 2% of the steady state value, and 20 seconds for a hemispherical electrode of the same radius[23]. A reasonable interpretation of the results at the 12.5 μm and 5.0 μm radius microdisk electrodes may be that the current approaches, but never achieves the true steady state values. Therefore the current in the non steady state would exceed those at the steady state, and larger values would be observed, which is what was found in this case.

**Figure 6.6.** Comparison of theoretical (curves) and experimental (*) dependence of faradaic charge passed during the diffusion controlled electrodeposition of mercury. Analyte: \(5.0 \times 10^{-3} \text{M HgCl}_2\) in 0.010M HCl solution. Electrode radii (a) 0.5 μm, (b) 1.0 μm, (c) 2.5 μm, (d) 5.0 μm, (e) 12.5 μm.
The ability to reach a steady state in an accessible timescale is related to the square of the microelectrodes characteristic dimension[23]. So it is not unreasonable to expect that smaller electrodes will be able to approach the steady state values whereas larger electrodes will not. The three smaller μMTFE’s all demonstrate an excellent fit between theory and experiment as shown in figure 6.6. The fit is all the more remarkable when it is realised that no adjustable parameters have been used in the present analysis.

Of interest is the relative size of the mercury deposit in relation to the microdisk it was grown from. For the smallest electrode used in these experiments (0.5 μm radius), the total volume of electrodeposited mercury corresponds to approximately 6000 times the hemispherical volume of \(2\pi a^3/3\) and the question of the gravitational stability of such a pendant near sphere must be questioned. The gravitational force on this near sphere is calculated to be about \(2 \times 10^{-10}\) N and this can be balanced by the retaining force \(2\pi a\gamma_{dm}\) with \(\gamma_{da}\) as small as 0.06 mN/m. So pendant near-spheres (eg. figure 7.3(c)) much larger than any grown in this work could be supported easily.

6.4.2. The behaviour of μMTFE’s in chloride media

A cyclic voltammogram of a μMTFE in 0.1%(\(\gamma_s\)) HCl is shown in figure 6.7. The forward (oxidation) sweep displays two important features; a small prewave at 0.175V, which appears as a symmetrical peak which returns to baseline, and the main oxidation peak at 0.185V, which appears as a sharp asymmetrical peak which also returns to baseline, although more slowly than the prewave.
The prewave appears to be related to the formation of a monolayer of oriented calomel (Hg₂Cl₂) on the electrode surface, as reported by Armstrong et. al. [4] at the DME. The main oxidation wave involves the bulk formation of calomel at the surface, leading to a blocking of the electrode reaction after sufficient calomel has formed at the surface. After this film growth can only occur by the diffusion of ions through the film to the reaction front, thus explaining the slow return to baseline of this peak.

The nature of the response was found to alter dramatically in dilute solutions (figure 6.8). At the lowest concentration of chloride ions examined (2.32 x 10⁻⁴ M HCl) the oxidation features appeared as a diffusion limited plateau, with a small plateau just visible corresponding to the prewave. The reverse scan revealed two overlapping processes with the first being present only as a shoulder to the main stripping peak. As the concentration was increased the oxidation wave increased in proportion, and the stripping peak became a single asymmetric wave.
Figure 6.8. Cyclic voltammograms of a μMTFE in 2.32x10^{-4}M HCl solution. Scan rate (a) 20 mV s^{-1}, (b) 50 mV s^{-1}, (c) 100 mV s^{-1}, other conditions as for figure 6.7.

The effect of varying the scan rate on the oxidation wave was particularly interesting. As can be seen in figure 6.8, at the fastest scan rate (100 mV/s) the oxidation wave has the form of a diffusion limited plateau. However, as the scan rate was decreased to 20 mV/s, the wave began to take on the form of an asymmetric peak, indicating that the passivation of the surface by the growing calomel film was occurring on the time scale of the slowest scan rate. As the concentration was further increased the differentiation of peak shape became indistinguishable.

The stripping of calomel from a mercury electrode has been used for the determination of soluble chloride[24], however the linear range was found to be restricted to 10^{-4} - 10^{-5} M. The present work confirms the non-linear response of the cathodic stripping of calomel from a μMTFE in the concentration range 2.32 x 10^{-4} to 4.87 x 10^{-3} M HCl, as shown in figure 6.9. This is not surprising in view of the
variation in the nature of the stripping response over this range. However, a surprising
result was found for the main oxidation wave, as demonstrated by the results plotted in
*figure 6.10*, for the scan rate of 100 mV s\(^{-1}\). Two regions of linear correlation of the
peak current versus concentration were found. The first region corresponds to the
concentrations where the response was of the form of a diffusion limited plateau. The
second linear region corresponds to the response as a peak. Similar behaviour was
recorded for the scan rates 50 mV s\(^{-1}\) and 20 mV s\(^{-1}\).

*Figure 6.9.* Plot of chloride ion concentration versus cathodic peak height for a μMTFE. Scan rate =
100 mV s\(^{-1}\), other conditions as for *figure 6.7*. 
6.4.3. \textit{Pb}^{2+} \textit{model system}

The analytical determination of aqueous \textit{Pb}^{2+} by ASV using conventional mains powered laboratory based equipment was chosen as a test system for the mercury microelectrode. A typical ASV response curve for a \textmu MTFE is shown in figure 6.11., and the peak is quantitated by measuring peak height, as illustrated. The sloping background illustrated in figure 6.11. arises from the fact that the analyte solution was not purged of dissolved oxygen prior to the stripping experiment. As can be seen in this example it is easy to differentiate the peak shaped stripping peak from the sigmoidal shaped diffusion limited oxygen reduction wave. The ability to perform ASV without the need for oxygen removal is a particularly attractive feature of the use of \textmu MTFE's. While this is obviously a benefit in this case, it cannot be assumed to apply to the ASV determination of all species, as the oxygen reduction process may complicate the chemistry of the stripping reaction of some metals[25].
Figure 6.11. Stripping curve for 100 ppb Pb$^{2+}$ in 0.1%($V/V$) HCl solution at a μMTFE. Scan rate 500 mV s$^{-1}$, $t_{don} = 60$ s, $E_{don} = -800$ mV vs. Ag/AgCl (sat. KCl), other conditions as for figure 6.7.

This response is typical of that which was observed on all determinations except the initial stripping experiment on a freshly prepared μMTFE. Figure 6.12(a) illustrates the type of response found at a freshly prepared μMTFE surface. A number of baseline excursions can be seen in the region -0.20 to -0.50V, which do not occur on subsequent scans (figure 6.12(b)). These features are attributed to the freshly prepared mercury film rearranging itself on the electrode surface. It is known[26] that the mercury film may not wet the entire surface of the platinum substrate initially, but on subsequent scans will tend to distribute itself evenly over the platinum surface.
Figure 6.12. Baseline response of a μMTFE in 0.1% HCl solution. (a) freshly prepared electrode, (b) subsequent scans. Scan rate = 20 mV s\(^{-1}\), other conditions as for figure 6.7.

The deposition potential was varied in the range -600 to -1000 mV (vs. Ag/AgCl) to determine an optimum deposition potential for the determination of Pb\(^{2+}\) in 0.1% HCl solution. In the range studied there was very little difference in the results (table 6.4.), with -800 mV giving a slightly higher response. This value was chosen for the remainder of this work.

Table 6.4. Variation of stripping peak current with deposition potential at a mMTE electrode for a 100 ppb Pb\(^{2+}\) solution.

<table>
<thead>
<tr>
<th>Deposition potential (mV)</th>
<th>Peak current (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 600</td>
<td>1.43</td>
</tr>
<tr>
<td>- 700</td>
<td>1.48</td>
</tr>
<tr>
<td>- 800</td>
<td>1.53</td>
</tr>
<tr>
<td>- 900</td>
<td>1.48</td>
</tr>
<tr>
<td>-1000</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Solution purged, stirred between runs, scan rate 500 mV s\(^{-1}\), \(\lambda_{\text{dep}} = 60\) s, Hg drop volume = 1.23x10\(^{-12}\).
6.4.3.1. Effect of scan rate at the μMTFE

For a MTFE the stripping peak current is expected to vary directly with scan rate[27]. A plot of scan rate versus stripping peak height is linear as shown in figure 6.13, indicating that the μMTFE is behaving similarly to a conventional MTFE. This should not come as a surprise as the thickness of the deposited mercury layer at a conventional MTFE may be only a couple of micrometers, similar to that of the μMTFE. The scan rate dependence is derived from the diffusion of the material through the mercury layer, which is of a similar dimension in both cases.

6.4.3.2. The effect of stirring

One of the principal causes of variation in stripping analyses at conventional sized HMDE’s is attributed to the use of mechanical stirring during the deposition step[28]. It has been suggested that because of the enhanced diffusive mass transport at microelectrodes, and the reduced susceptibility to convection, that it may be possible to eliminate the use of mechanical stirring[11] during deposition.

A series of stripping experiments was performed at a range of scan rates, under both convective/diffusive, and purely diffusive mass transport conditions at a μMTFE.
The results are contained in table 6.5. The effect of stirring at a rate of 2500 rpm only increased the response by a factor of two, and varied little at other stirring rates. Similar data at a conventional HMDE would vary by considerably more, as discussed in reference 27. It is obvious from these results that stirring of the solution during deposition is much less effective at a μMTFE than at a conventional HMDE at increasing the efficiency of mass transport to the electrode. Also notice from the data in table 6.5 that the standard deviations for the two sets of experiments differ considerably for scan rates greater than 0.20 V s⁻¹, with the results for the stirred solutions being up to five times worse than those for the quiescent solutions.

It therefore appears that the absence of stirring during the deposition step would not greatly effect the limit of detection of Pb²⁺, and would also increase the overall precision of the results. However, it was found that if the solution was not stirred, or purged during the deposition step of a series of identical stripping experiments, that the peak height increased considerably with successive repetitions. One such series of experiments is illustrated in figure 6.14. The reason for this increase in response is simply due the fact that on successive experiments the solution surrounding the μMTFE is enriched in Pb²⁺ from the stripping experiment, which is not carried away by convection. This material will tend to diffuse away. However, the time required may be considerably longer than the time between replications (15 - 20 seconds in the present case). On the basis of this data stirring, either deliberately with a stirrer, or purging with nitrogen, is recommended at μMTFE's. The stirring for the remainder of this work was carried out between experiments, rather than during the deposition step, to improve the precision of the results.
Table 6.5. Comparison of the effects of stirring during deposition step at different scan rates.

<table>
<thead>
<tr>
<th>Scan rate (V s⁻¹)</th>
<th>Peak height (nA)</th>
<th>Stirred¹</th>
<th>Not stirred</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.239 (0.03)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>0.686 (0.05)</td>
<td>0.399 (0.04)</td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>1.54 (0.07)</td>
<td>0.813 (0.03)</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>4.07 (0.36)</td>
<td>1.99 (0.07)</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>7.56 (0.9)</td>
<td>3.66 (0.33)</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>13.8 (0.9)</td>
<td>6.77 (0.13)</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>27.0 (1.0)</td>
<td>13.1 (0.3)</td>
<td></td>
</tr>
</tbody>
</table>

¹ Stirred at approximately 2500 rpm. Values in brackets are standard deviations.

Analyte=100 ppb Pb²⁺ in 0.1% HCl. tₜₕₜₜₚ=60 seconds. Hg drop volume = 2.46x10⁻¹² l, Eₜₕₜₜₘₜₜₜ = -800 mV, stirred between runs.

Figure 6.14. Plot of stripping peak height for a number of identical stripping determinations of a 100 ppb Pb²⁺ in HCl (0.1%(V/V)) solution at a µMTFE. Scan rate 50 mV s⁻¹, tₜₕₜₜₚ=60 sec, Eₜₕₜₜₘₜₜₜ = -800 mV, other conditions as for figure 6.7.
6.4.3.3. The effect of deposition time variation.

The effect of varying the deposition time was studied for the case of 100 ppb Pb\textsuperscript{2+} at a scan rate of 500 mV s\textsuperscript{-1}, with stirring between scans. A plot of deposition time versus stripping peak height is shown in figure 6.15. The response was found to be linear over the range 30 to 480 seconds, indicating that the mercury was not becoming saturated by the Pb, even after 480 seconds deposition.

6.4.4. Simultaneous determination of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} using battery powered equipment.

The following experiments were performed on a range of battery powered equipment, in order to demonstrate the functional ability of battery powered devices, for use in stripping analysis. The simultaneous determination of Cd\textsuperscript{2+} and Pb\textsuperscript{2+} was chosen for this study.

One of the problems which may be encountered when using mercury coated

---

**Figure 6.15.** Plot of the variation of deposition time versus stripping peak height for 100 ppb Pb\textsuperscript{2+} in HCl (0.1% (v/v)) solution at a \(\mu\)MTFE. other conditions as for figure 6.7.
platinum electrodes is the formation of intermetallic compounds with the platinum substrate. At a μMTFE this possibility is great as the depth of the mercury is very small. Such behaviour was noticed in the simultaneous determination of Pb²⁺ and Cd²⁺, as shown in table 6.6. The difference in the stripping response of Cd²⁺ at a freshly prepared μMTFE, and one that had been used for more than twenty determinations, was found to be ≈ 50%. Results for the determination of lead were found to decrease slightly (≈ 10%). The formation of a PtCd intermetallic has been previously reported[28], and would account for this behaviour. At the fresh electrode many active platinum sites would be available for formation of an intermetallic compound. With the passage of time the amount of intermetallic at the mercury-platinum interface would reach an equilibrium level, leading to a constant response for the stripping of cadmium. The slight decrease in the Pb²⁺ stripping response may be related to the CdPt intermetallic as the decrease observed here was not noticed when Pb²⁺ only was being determined.

The ability to vary scan rate using the battery powered equipment is not as great as at the mains powered equipment, due to the slower response time of the Keithley Electrometer used for this work. However the simultaneous linear sweep stripping response of both the Cd²⁺ and Pb²⁺ was found to be linear over the range 20 to 400 mV s⁻¹.

The variation of deposition time for the simultaneous stripping determination of Cd²⁺ and Pb²⁺ was studied at an aged electrode to eliminate the problems associated with intermetallic compound formation. At the aged electrode the stripping response of the Cd²⁺ and Pb²⁺ was found to vary linearly with deposition time (figure 6.16, and table 6.7), with the slopes of the calibration curves being 0.052 nA s⁻¹ and 0.053 nA s⁻¹ for Cd²⁺ and Pb²⁺ respectively.

These results clearly demonstrate that battery powered equipment is capable of providing data comparable to that obtained with mains powered equipment.
Figure 6.16. Plot of variation of stripping peak height with deposition time. 1 ppm Cd$^{2+}$ and Pb$^{2+}$ in 0.1%($\%_w$) HCl solution. Solution not purged. Other conditions as for figure 6.7.

Table 6.6. Comparison of drop history on the scan rate dependence of stripping peak height of 1 ppm Pb$^{2+}$ and Cd$^{2+}$ in 0.1% HCl solution.

<table>
<thead>
<tr>
<th>Scan rate (mV s$^{-1}$)</th>
<th>Peak height (nA)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>Pb$^{2+}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fresh drop</td>
<td>Old drop</td>
<td>Fresh drop</td>
</tr>
<tr>
<td>20</td>
<td>0.4</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>50</td>
<td>0.7</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>100</td>
<td>1.4</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>200</td>
<td>2.6</td>
<td>4.3</td>
<td>3.6</td>
</tr>
<tr>
<td>300</td>
<td>3.5</td>
<td>5.8</td>
<td>5.1</td>
</tr>
<tr>
<td>400</td>
<td>4.8</td>
<td>7.2</td>
<td>5.6</td>
</tr>
</tbody>
</table>

* $t_{\text{dep}} = 30$ seconds, other conditions as for figure 6.7.
Table 6.7. Variation of peak height with deposition time\textsuperscript{*} for 1ppm Cd\textsuperscript{2+} and Pb\textsuperscript{2+} in 0.1% HCl solution.

<table>
<thead>
<tr>
<th>Deposition time (sec)</th>
<th>Peak Height (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd\textsuperscript{2+}</td>
</tr>
<tr>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>30</td>
<td>2.1</td>
</tr>
<tr>
<td>60</td>
<td>3.6</td>
</tr>
<tr>
<td>90</td>
<td>4.7</td>
</tr>
<tr>
<td>120</td>
<td>6.7</td>
</tr>
<tr>
<td>150</td>
<td>8.1</td>
</tr>
</tbody>
</table>

\textsuperscript{*} t\textsubscript{dep} = 30 seconds, other conditions as for figure 6.7.
6.4.5. Cu in tap water using a battery powered system.

Figure 6.17(a) shows the d.c. stripping voltammogram obtained at a μMTFE for the determination of copper in a Barwon River water sample acidified to a concentration of $8 \times 10^{-4}$ M HNO$_3$ and the standard addition peaks for the addition of copper to the river water sample, without stirring during deposition or oxygen removal. The copper level was determined to be 104 ppb. Cadmium and lead could not be detected in this water sample under these experimental conditions. This determination was not performed in chloride media as the previous determinations of Pb$^{2+}$ and Cd$^{2+}$ were, as the copper stripping process was found to be modified in HCl solutions, rendering quantitation impossible.

The concentration of acid used in this determination ($8 \times 10^{-4}$ M HNO$_3$) is much less than would be required when using a conventional HMDE, due to the iR drop considerations. The extremely low concentration of supporting electrolyte used in this example is obviously beneficial in minimising sample contamination and analysis cost.

The successful determination of copper in a natural water sample using a completely battery powered system with a μMTFE, clearly demonstrates the possibility of analytical determinations in the field, with portable battery powered equipment.
Figure 6.17. Anodic stripping voltammograms for the determination of copper in river water (8.0x10^{-6} M HNO₃) using a μMTPE (radius = 5 μm), together with a battery powered function generator and electrometer current measuring device. Scan rate 100 mV s⁻¹, solutions not purged or stirred, t_d = 60 seconds. (A) original sample, (B) addition of 100 ppb Cu(II), (C) addition of 200 ppb Cu(II).
6.5. SUMMARY

1. The deposition of mercury onto a Pt inlaid microdisk electrode may be modelled theoretically by assuming a simple free energy argument, which enables an accurate assessment of the volume and surface area of the resultant mercury electrodeposits. Experimental data were found to match theory for the three smallest electrodes used in this study to within 2%. The larger electrodes were found to deviate substantially from the predicted values, and this was attributed to an inability to reach a steady state current.

3. The behaviour of a mercury microelectrode in chloride media provided a clear picture of the passivation of mercury due to the electocrystallization of calomel on the mercury electrode surface. The µMTFE was found to be suitable for the quantitative determination of chloride in the concentration range $2.32 \times 10^{-4}$ to $4.87 \times 10^{-3}$ M HCl. The main oxidation wave was found to give a two distinct linear concentration dependences.

4. Anodic stripping voltammetry at a µMTFE was found to be a reliable and practical means of determining a range of heavy metals using both laboratory based and field based instrumentation. Freedom from the requirements of removing oxygen and convective mass transfer during the deposition step are particularly appealing features of µMTFE's, although some caution must be observed when doing so.
6.6. REFERENCES


CHAPTER 7

ELECTROCHEMICAL OXIDATION OF [DIBENZO-18-CROWN-6-K]
[Cr(CO)₅F] AND Cr(CO)₆ : CHARACTERIZATION OF [Cr(CO)₅]⁺ AND ITS
SUBSTITUTION REACTIONS WITH FLUORIDE AND
TRIFLUOROACETATE.

7.1. INTRODUCTION.............................................................................. 179

7.2. EXPERIMENTAL........................................................................... 181
   7.2.1. Reagents.............................................................................. 181
   7.2.2. Solvents.............................................................................. 181
   7.2.3. Synthesis............................................................................. 181
   7.2.4. [Dibenzo-18-crown-6-K][Cr(CO)₅X] (X = F, Cl, Br, I).............. 181
   7.2.5. Instrumentation................................................................. 182
      7.2.5.1. Electrochemical.............................................................. 182
         7.2.5.1.1. General................................................................. 182
         7.2.5.1.2. Conventional cyclic and rotating disc electrode
                      voltammetry............................................................. 182
         7.2.5.1.3. Fast scan rate voltammetry.................................... 183
         7.2.5.1.4. Coulometry and controlled potential electrolysis....... 183
      7.2.5.2. Electron spin resonance............................................... 183
      7.2.5.3. Infrared spectroscopy.................................................... 183

7.3. RESULTS AND DISCUSSION......................................................... 184
   7.3.1. General.............................................................................. 184
   7.3.2. Electrochemistry of Dibenzo-18-crown-6-K.......................... 184
   7.3.3. Electrochemistry of [Dibenzo-18-crown-6-K][Cr(CO)₅F]...... 186
   7.3.4. Electrochemistry of [Dibenzo-18-crown-6-K][Cr(CO)₅X] (X = Cl, Br, I)........ 193
   7.3.5. Electron spin resonance................................................... 193
   7.3.6. Electrochemistry of Cr(CO)₆............................................... 197
   7.3.7. Electrochemical synthesis of Mo(CO)₅(dpe)₂F........................................ 206

7.4. REFERENCES.............................................................................. 207
7.1. INTRODUCTION

The chemistry of complexes where halide (chloride, bromide, and iodide) and carbonyl ligands are both bonded to a transition metal has been studied extensively as perusal of references 1-10 would indicate. In contrast, comparatively few carbonyl fluorides are known. Indeed early review articles implied they may not exist[11]. However, a number of examples have been well documented (e.g. Mo(CO)$_4$F$_2$, W(CO)$_4$F$_2$, Re(CO)$_5$F, etc.[12-17]), but references to carbonyl fluorides are still relatively rare.

Although the electrochemistry of the Group 6B pentacarbonyl halides anions [M(CO)$_5$X] (M = Cr, Mo, W; X = Cl, Br, I) has been previously examined[18,19], studies on analogous carbonyl fluorides have not been reported. Oxidation of [Cr(CO)$_5$F] will be considered in this chapter. Fluoride being an electronegative element ($\sigma$-donor), favours the formation of high oxidation state complexes. Carbon monoxide ($\pi$-acceptor), by comparison, favours formation of low oxidation state complexes. In view of this substantially differing preference for high and low oxidation states, electrochemical studies could be expected to enhance the understanding of the stability and/or reactivity of carbonyl fluorides.

To study the influence of fluoride as a ligand when oxidizing [Cr(CO)$_5$F], it turned out that the electrochemistry of the parent carbonyl Cr(CO)$_6$ needed to be reinvestigated. While formation of [Cr(CO)$_6$]$^+$ seems well substantiated in solvents such as acetonitrile[20,21], in dichloromethane some workers have claimed that no oxidation step is observed prior to the solvent limit[22], whereas an oxidation process complicated by surface phenomena has been described by another report[23]. Molten salt media[24] also provide stabilization of [Cr(CO)$_6$]$^+$. Interestingly, the ESR spectrum [Cr(CO)$_6$]$^+$ is reported to be very broad, with a low g-value[20], in contrast to the relatively sharp signals observed with some of the well characterized 17-electron substituted chromium carbonyl complexes. [Cr(CO)$_6$]$^+$ is of course expected to be highly reactive and is known to be prone to disproportionation[20,21]. Kochi et al.[25]
have also observed that electrochemical oxidation of Cr(CO)$_6$ in acetonitrile leads to a substitution labile product. Intuitively, [Cr(CO)$_6$]$^{\text{+}}$ is expected to be more stable in a non coordinating solvent (e.g. dichloromethane), than a coordinating solvent such as acetonitrile. The simple well defined electrochemistry reported in acetonitrile, contrasted with the reported data in the non coordinating solvent dichloromethane, is surprising.

In addition to investigating possible anomalies in the literature it was felt that if fluoride is present, in situ, during the electrolysis of a carbonyl compound in a non coordinating solvent that the possibility of replacement of carbon monoxide by fluoride ion exists. Kochi et al.[25] have already presented data in acetonitrile for the oxidation of Cr(CO)$_6$ in the presence of anionic ligands such as trifluoroacetate. The irreversible electrochemistry observed in the presence of trifluoroacetate was explained by these authors in terms of slow electron transfer accompanying substitution of [Cr(CO)$_6$]$^{\text{+}}$ but it is not clear why the rate of electron transfer should be affected. Fluoride may be expected to act in an analogous fashion to trifluoroacetate, with respect to substitution. The mechanism of any substitution and variation of rate of electron transfer for both fluoride and trifluoroacetate has therefore been examined in addition to undertaking further investigations on the properties of the [Cr(CO)$_6$]$^{\text{+}}$ redox couple.

Fluoride, unlike chloride, bromide, and iodide, is not readily oxidized to the corresponding halogen. Consequently, application of the relatively positive potentials required to oxidize Cr(CO)$_6$(1.46V vs. SCE in acetonitrile[20]) will not give rise to the simultaneous oxidation of Cr(CO)$_6$ and the fluoride ligand. Electrochemical oxidation of carbonyl compounds is therefore suggested to provide a systematic approach to the synthesis of carbonyl fluoride complexes. An example of this synthetic route is presented with respect to electrochemical synthesis of Mo(CO)$_3$(dpe)$_2$F (dpe = 1,2-bis-(diphenylphosphino)ethane) since chromium carbonyl fluoride complexes formed via oxidation of Cr(CO)$_6$ in the presence of fluoride were too reactive to isolate.

The main aim of this chapter is to elucidate the reaction mechanism involved in the oxidation of Cr(CO)$_6$ and [Cr(CO)$_6$X], X = F, Cl, Br, I, in a range of non-aqueous
solvents. As was described in chapter 2, cyclic voltammetry under linear diffusion conditions, is an ideal technique for the study of the reversibility of electrode reactions. In order to use cyclic voltammetry in this work, microelectrodes had to be employed to provide sufficiently fast scan rates to observe rapid oxidation processes, while still maintaining linear diffusion conditions. This is possible due to the very short RC time constants displayed by microelectrodes.

7.2. EXPERIMENTAL

7.2.1. Reagents

Dibenzo-18-crown-6 (EGA CHEMIE), tetraethylammonium fluoride (Fluka AG), chromium hexacarbonyl (Pressure Chemical Co.) lithium trifluoroacetate (Alfa Products), and lithium acetate (BDH) and other compounds were used as supplied by the manufacturer except for drying under vacuum. Tetraethylammonium perchlorate and tetra-n-butylammonium perchlorate (G. Frederick Smith Chemical Co.) were dried in vacuo, at 60°C for 4 hours prior to use.

7.2.2. Solvents

All solvents were of either Analytical or HPLC grade and were used as supplied except for drying by standard procedures[26].

7.2.3. Synthesis

All preparations were carried out under a nitrogen atmosphere in a Labconco 5004 Controlled Atmosphere Glovebox. All solvents were degassed with nitrogen prior to use.

7.2.4. \([\text{Dibenzo-18-crown-6-K}]\left[\text{Cr(CO)}_5X\right] \ (X = F, \ Cl, \ Br, \ I)\).

The method of preparation was based on that of Cihonski and Levenson[13]. Chromium hexacarbonyl(1.7 mmol), dibenzo-18-crown-6 (2.7 mmol), and the potassium halide salt (3.4 mmol) in 40 ml of tetrahydrofuran and 40 ml of dichloromethane were irradiated with a Phillips HPK 125W mercury lamp for 4 hours.
The resulting yellow/orange solution was cooled on dry ice for 30 minutes and then quickly filtered. To the filtrate was added petroleum ether (bp 40-60 °C) to precipitate the crude product. Typical yields were of the order of 30-40% following recrystallization from dichloromethane/pet. ether. All compounds synthesized were stored under nitrogen, in the dark at less than 0 °C.

Mo(CO)$_2$(dpe)$_2$ was prepared according to the literature method[27].

7.2.5. Instrumentation.

7.2.5.1. Electrochemical

7.2.5.1.1. General

All electrochemical experiments were performed in a Labconco Controlled Atmosphere Glovebox under a nitrogen atmosphere.

7.2.5.1.2. Conventional cyclic and rotating disc electrode voltammetry.

Cyclic voltammograms at conventional sized electrodes were recorded on a Bioanalytical Systems Inc. BAS CV-27 cyclic voltammograph. Conventional working electrodes used were BAS platinum(Pt), gold(Au), and glassy carbon(GC) electrodes. A platinum wire auxiliary electrode was used in all experiments, and the reference electrode Ag/AgCl(saturated LiCl in ethanol) was separated from the test solution by a salt bridge containing the same solvent and supporting electrolyte as the test solution. A Metrohm rotating disc electrode assembly (628-10) was used with Metrohm Electrodes for all rotating disc electrode voltammetry. Supporting electrolytes used were 0.1M tetrachloroethylene perchlorate in acetone and acetonitrile, and tetra-n-butylammonium perchlorate in dichloromethane at 20 °C. At the lower temperature of -70 °C saturated solutions of electrolyte were used.

Oxidation of a 1 x 10$^{-3}$ M ferrocene solution in the appropriate solvent was used as a calibration standard throughout the course of this work.

7.2.5.1.3. Fast scan rate voltammetry.
Fast scan rate voltammetry experiments were performed with a PAR 175 Waveform Generator providing the potential waveform to a two electrode cell consisting of a Pt inlaid microdisk working electrode and a length of silver wire acting as the pseudo reference electrode. A purpose built current-to-voltage converter[43] based on a OP-37 operational amplifier was used to measure current, and data was acquired by a Gould 4035 series Digital Storage Oscilloscope initially, then to a 8088 based microcomputer for further data analysis.

All fast scan rate voltammetry experiments were performed in the relevant solvent with typically 0.5M supporting electrolyte added to minimise iR drop effects.

7.2.5.1.4. Coulometry and controlled potential electrolysis.

Controlled potential electrolysis experiments were undertaken with a Princeton Applied Research PAR 173 potentiostat/galvanostat fitted with a PAR 176 digital coulometer. A platinum gauze basket was used as the working electrode, together with a platinum gauze auxiliary electrode separated from the test solution by a salt bridge containing the same solvent/supporting electrolyte as the test solution. The reference electrode used was the same as for cyclic voltammetry.

7.2.5.2. Electron spin resonance.

Electron spin resonance data were obtained using an X-band reflection type spectrometer employing 100 kHz modulation[28]. The oxidized 17-electron carbonyl compounds were generated in situ, using the PAR 173 potentiostat/galvanostat and electrochemical cell consisting of platinum working and auxiliary, and Ag/AgCl reference electrodes[29].

7.2.5.3. Infrared spectroscopy.

Infrared spectra were recorded on a Perkin Elmer 457 grating spectrophotometer in the range 2500-1700 cm⁻¹ with the use of NaCl solution cells. All spectra were recorded in degassed chloroform and calibrated against the polystyrene 1602 cm⁻¹ peak.
Table 7.1. Infra-red spectra of the Chromium Pentacarbonyl Halides, [dibeno-18-crown-6-K][Cr(CO)_5X] (X = F, Cl, Br, I).

<table>
<thead>
<tr>
<th>Halide</th>
<th>Infra-red bands in the carbonyl region (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A_1^{eq})</td>
</tr>
<tr>
<td>F</td>
<td>2065 (w)</td>
</tr>
<tr>
<td>Cl</td>
<td>2055 (w)</td>
</tr>
<tr>
<td>Br</td>
<td>2055 (w)</td>
</tr>
<tr>
<td>I</td>
<td>2050 (w)</td>
</tr>
</tbody>
</table>

(s) = shoulder, (w) = weak, (m) = medium, (s) = strong. All values calibrated against the polystyrene 1602 cm\(^{-1}\) peak.

For the [Cr(CO)_5X]\(^-\) complexes, infrared spectra were consistent with literature values[13].

7.3. RESULTS AND DISCUSSION.

7.3.1. General.

As described in the Experimental Section, all of the complexes were isolated as yellow diamagnetic solids which were stable in air for short periods of time. The solution stability of the [Cr(CO)_5X]\(^-\) complexes showed a general trend I > Br > Cl > F and dichloromethane > acetone > acetonitrile. The stability of [Cr(CO)_5F]\(^-\) in dichloromethane and acetone was found to be markedly increased at lower temperatures, and much of the experimental data was obtained at -70 °C rather than at ambient temperatures.

The complexes themselves exhibit a distorted C\(_4\)v symmetry, as indicated by their infra-red spectra. The band assigned to the \(B^1\) stretching mode is remarkably intense considering that it is infra-red forbidden (table 7.1.).

7.3.2. Electrochemistry of Dibenzo-18-crown-6.

The compounds of interest in this study contain a crown ether in the cation. In acetonitrile on platinum electrodes, dibenzo-18-crown-6 (figure 7.1(a)) exhibits an irreversible oxidation process involving strong adsorption at a potential of about
+1.5V vs. Ag/AgCl. Upon repeated scans the electrode response is found to become inhibited (figure 7.1(b)). LeBerre et al.[30] have reported that the oxidation of dibenzo-18-crown-6 leads to the formation of a polymeric film on the electrode surface. The response on gold and glassy carbon electrodes occur at a similar potential to that on platinum but vary somewhat in detail.

Fortunately the oxidation of the crown ether occurs at a very positive potential (+1.4V vs. Ag/AgCl) in all solvents and would therefore not be expected to interfere with the electrochemistry of [dibenzo-18-crown-6-K][Cr(CO)\textsubscript{2}X] (X = F, Cl, Br, I) which occur at less positive potentials. It was also observed that the polymerization reaction did not occur when the crown ether forms part of the crown ether/chromium halide complexes.

**Figure 7.1.** Cyclic voltammogram of dibenzo-18-crown-6 in acetonitrile (0.1M Et\textsubscript{4}NCIO\textsubscript{4}) at a conventional Pt disk electrode after (a) first scan, and (b) repeated scans. Scan rate=200 mV s\textsuperscript{-1}, temperature=20 °C.
7.3.3. Electrochemistry of [Dibenzo-18-crown-6-K][Cr(CO)₅F].

Two well defined one electron oxidation processes are observed under conditions of cyclic (figure 7.2) and rotating disc (figure 7.3) voltammetry for [dibenzo-18-crown-6-K][Cr(CO)₅F]. The first process remains chemically reversible under all conditions (table 7.2) and data are essentially independent of electrode material (Pt, Au, GC) and solvent (dichloromethane, acetone, acetonitrile). This process can be defined as

$$[\text{Cr(CO)}_5\text{F}]^- \rightleftharpoons \text{Cr(CO)}_5\text{F} + e^-$$ (7.1)

Deliberate addition of fluoride does not alter the electrochemical response nor does the deliberate addition of carbon monoxide. Results are essentially independent of concentration, except for evidence of ohmic (iR) drop at higher concentrations.

The second process is chemically irreversible at room temperature and conventional scan rates (table 7.2). However, at low temperatures (-70 °C) the second oxidation process is also a chemically reversible one-electron step in both acetone and dichloromethane. Fast scan rate voltammetry in acetonitrile at a Pt microdisk electrode also demonstrates the reversibility of the second wave at room temperature (figure 7.4). Thus the second process at low temperature and fast scan rates is

$$\text{Cr(CO)}_5\text{F} \rightleftharpoons [\text{Cr(CO)}_5\text{F}]^+ + e^-$$ (7.2)
Figure 7.2. Cyclic voltammogram of 10^{-3}M [dibenzo-18-crown-6-K][Cr(CO)_5F] in acetone (0.1M Et_4NClO_4) at a conventional Pt disk electrode. Scan rate=200 mV s^{-1}, and temperature (a) 20 °C, (b) -70 °C.
Figure 7.3. Rotating disk voltammograms of $10^{-3}$M [dibenzo-18-crown-6-K][Cr(CO)$_3$F] in dichloromethane (saturated Bu$_4$NClO$_4$) on a glassy carbon electrode; (a) before oxidation with NOPF$_6$, (b) after oxidation with NOPF$_6$. Scan rate=200 mVs$^{-1}$, temperature=-70 °C, rotation rate=2000 rpm.
At room temperature in dichloromethane, the second step is essentially independent of both fluoride and carbon monoxide concentration. In acetonitrile at conventional scan rates, however, the second process is modified by the addition of carbon monoxide (figure 7.5). The appearance of a shoulder on the second wave is probably due to a solvent substituted species being formed. This would not be expected for dichloromethane as the coordinating ability if the solvent is very poor. Fast scan rate voltammetry data for this process are not available.
Chemical oxidation with NOPF$_6$ in dichloromethane at -70 °C yields a yellow solution of Cr(CO)$_3$F. In situ monitoring of this reaction via rotating disc voltammetry (figure 7.3) confirms the formation of the neutral chromium(I) species. The instability in solution was evidenced by a change in color from yellow to colorless after a few minutes. [Cr(CO)$_3$F]$^-$ is reformed after decomposition and a gas, presumably carbon monoxide is evolved. At ambient temperatures, no electrochemical or infra red evidence could be obtained for formation of a carbonyl fluoride. Coulometric data at potentials in the limiting current region of the first wave are consistent with a two electron oxidation. This fact together with the low temperature data suggest that disproportionation occurs on longer time scales.

$$2\text{Cr(CO)}_3\text{F} \rightarrow [\text{Cr(CO)}_3\text{F}]^- + \text{Cr}^{2+} + 5\text{CO} + \text{F}^-$$ (7.4)

Electrochemical data for the complexes [(CH$_3$CH$_2$)$_4$N][Cr(CO)$_3$X]$^-$ (X = Cl, Br, I) have been reported[18,19]. The overall behaviour of the fluoride is very similar to that of the other halides, except that the fluoride complex is far more reactive.
Table 7.2. Cyclic voltammetric data\(^a\) for oxidation of $5 \times 10^{-4}$ M [Dibenzo-18-crown-6-K] [Cr(CO)\(\text{X}\) (\(X = \text{F, Cl, Br, I}\)) at a scan rate of 200 mV s\(^{-1}\).

<table>
<thead>
<tr>
<th>Halide</th>
<th>Electrode</th>
<th>Solvent</th>
<th>First oxidation process</th>
<th>Second oxidation process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>($E_{p}^{o}$(\text{X}))</td>
<td>($E_{p}^{\text{red.}}$)</td>
</tr>
<tr>
<td>$X = \text{F}$</td>
<td>Pt</td>
<td>DCM</td>
<td>0.50</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.60</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.54</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>DCM</td>
<td>0.51</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.62</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.55</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>G.C.</td>
<td>DCM</td>
<td>0.51</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.55</td>
<td>0.47</td>
</tr>
<tr>
<td>$X = \text{Cl}$</td>
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<td>0.51</td>
<td>0.42</td>
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<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.64</td>
<td>0.57</td>
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<td></td>
<td>MeCN</td>
<td></td>
<td>0.56</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>G.C.</td>
<td>DCM</td>
<td>0.52</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.63</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.57</td>
<td>0.46</td>
</tr>
<tr>
<td>$X = \text{Br}$</td>
<td>Pt</td>
<td>DCM</td>
<td>0.54</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.67</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.60</td>
<td>0.52</td>
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<tr>
<td></td>
<td>Au</td>
<td>DCM</td>
<td>0.54</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.64</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.59</td>
<td>0.51</td>
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<tr>
<td></td>
<td>G.C.</td>
<td>DCM</td>
<td>0.54</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.64</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.59</td>
<td>0.52</td>
</tr>
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<td>$X = \text{I}$</td>
<td>Pt</td>
<td>DCM</td>
<td>0.55</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.71</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.62</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>DCM</td>
<td>0.56</td>
<td>0.47</td>
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<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.66</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.63</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>G.C.</td>
<td>DCM</td>
<td>0.55</td>
<td>0.46</td>
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<tr>
<td></td>
<td>Ac</td>
<td></td>
<td>0.67</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td></td>
<td>0.63</td>
<td>0.56</td>
</tr>
</tbody>
</table>

\(^a\)All potentials V vs Ag/AgCl. E\(_{1/2}\) for oxidation of $10^{-3}$M ferrocene = 0.49 V (DCM), 0.61 V (Ac), 0.54V (MeCN), all electrodes were disks with radius = 2.0 mm.

\(^b\)Data obtained at -78 °C, all other data obtained at 20 °C.

\(^c\)Chemically irreversible process.

Abbreviations: DCM = Dichloromethane, Ac = acetone, MeCN = acetonitrile, G.C. = glassy carbon,

Electrode ($E_{p}^{o}$\(\text{n}\)) = peak oxidation potential for process n (n = 1, 2), and ($E_{p}^{\text{red.}}$\(\text{n}\)) = peak reduction potential for process n (n = 1, 2).
7.3.4. *Electrochemistry of [Dibenzo-18-crown-6-K][Cr(CO)$_3$X] (X = Cl, Br, I)*.

*Table 7.2* also summarizes the electrochemical data for the oxidation of the crown ether complexes of [Cr(CO)$_3$X]$^+$ (X = Cl, Br, I). The ease of oxidation shows a trend with the (E$_{1/2}$) being

$$[\text{Cr(CO)}_3\text{F}]^+ < [\text{Cr(CO)}_3\text{Cl}]^+ < [\text{Cr(CO)}_3\text{Br}]^+ < [\text{Cr(CO)}_3\text{I}]^+$$

as would be expected from simple electronegativity arguments. Alternatively, this may be interpreted as a correlation between the donor/acceptor nature of the halide ligands and the oxidation potentials. The ligands in this type of substituted carbonyl complex may affect the highest occupied molecular orbital (HOMO) of the complexes in two ways[22]:

(i) the energy of the $\pi$ - type HOMO may be modified indirectly by the Lewis base $\sigma$ - donation of the ligand, or

(ii) if the ligand has vacant orbitals capable of participating in $\pi$ - back bonding, then a lowering of the HOMO energy would result. Hence a net corresponding increase in the oxidation potential would be observed.

The halide ions have filled p-orbitals. However, except for the fluoride ion they have empty d-orbitals. Fluoride, an exclusive $\sigma$ - donor with no available d-orbitals for back donation, would therefore be expected to have the least positive oxidation potential, as is observed. The decreasing ability for $\sigma$ donation and availability of empty d-orbitals for back-donation accounts for the trend observed for Cl, Br, and I.

In summary, thermodynamically Cr(CO)$_3$F is more stable than the other halides in the sense that less energy is required for it's formation via oxidation. However, kinetically it is the most reactive.

7.3.5. *Electron spin resonance.*

The neutral chromium(I) species Cr(CO)$_5$F is considered to be a 17 electron paramagnetic species that may generate an ESR signal, although none was reported.
for the related \( \text{Cr(CO)}_3 \text{I} \) species[31]. If coupling occurs with fluorine \((I = 1/2)\) a doublet may be observed.

In situ electrolysis, in the esr spectrometer, of \( \text{Cr(CO)}_3 \text{F}^- \) in dichloromethane at \(-80^\circ \text{C}\) occurs slowly and generated two single line signals of unequal intensity with \( g\)-values of 1.982 and 1.969, rather than the expected doublet (figure 7.6.). This indicates that they arise from two different paramagnetic species. Both of these signals vanish on increasing the temperature. Coupling may not be observed because of

(i) rapid electron exchange of \( \text{Cr(CO)}_3 \text{F} \) with \( \text{Cr(CO)}_3 \text{F}^- \) as is the case with the mer-[\( \text{Cr(CO)}_3 \text{P}_3 \text{I} \text{v}^0 \)] system \((P = \text{phosphorus ligand})[32]\), or

(ii) the coupling constant is too small.

The one electron oxidation to produce \( \text{Cr(CO)}_3 \text{F} \) described in equation 1 is obviously not the only reaction occurring, as it is necessary to account for the second

![ESR spectra](image)

**Figure 7.6.** ESR spectra obtained from in-situ electrolysis of [Dibenzo-18-crown-6-K] \( \text{Cr(CO)}_5 \text{F} \) in dichloromethane (sat'd \( \text{Bu}_4 \text{NClO}_4 \)) at \(-80^\circ \text{C}\).
ESR signal. Oxidation of Cr(CO)$_6$ generates the 17 electron species [Cr(CO)$_6$]$^+$. In situ electrolysis in dichloromethane at -80 °C generated the signal shown in figure 7.7. This signal also disappears as the temperature is raised to 0 °C. Chromium exists in two isotopes, $^{52}$Cr (I = 0) and $^{53}$Cr (I = 3/2). Hence the central intense signal at $g = 1.982$ can be attributed to $^{52}$Cr and the four satellite features to $^{53}$Cr. The spectrum is characterized by a small line width, indicating isotropic g-value which is consistent with octahedral symmetry. The coupling constant, $A_{Cr}$, is 2.16 mT at -80 °C. The differing intensities are due to the ratio of natural abundance of $^{52}$Cr : $^{53}$Cr, viz. 90.45% : 9.55%. The signal assigned to $[^{52}$Cr(CO)$_6]$ corresponds within experimental error to one of the signals obtained in the electrolysis of [Cr(CO)$_5$F]$^-$. Therefore, the peak of $g = 1.969$ can be assigned to Cr(CO)$_5$F. Consequently, on the
experimental error to one of the signals obtained in the electrolysis of \([Cr(CO)_3F]^-\). Therefore, the peak of \(g = 1.969\) can be assigned to \(Cr(CO)_3F\). Consequently, on the time scale of preparative electrolysis the oxidation mechanism must account for the generation of \([Cr(CO)_6]^+\) as a product.

A reaction scheme of the kind

\[
[Cr(CO)_3F]^- \Leftrightarrow Cr(CO)_3F + e^- \quad (7.5a)
\]

\[
2[Cr(CO)_3F] \Leftrightarrow [Cr(CO)_3F]^+ + [Cr(CO)_3F]^- \quad (7.5b)
\]

\[
[Cr(CO)_3F]^+ \rightarrow Cr^{2+} + F^- + 5CO \quad (7.5c)
\]

\[
Cr(CO)_3F + CO \Leftrightarrow [Cr(CO)_6]^+ + F^- \quad (7.5d)
\]

is consistent with all the available data, including the chemical oxidation with NOPF_6, which is considerably more rapid than the controlled potential electrolysis experiments. Pickett and Pletcher[20] reported an ESR spectra for \([Cr(CO)_3]^+\) in acetonitrile. The signal they obtained was extremely broad (approx. 1000 mT) in contrast to the very sharp (0.5 mT) signal obtained in dichloromethane. Also, they did not observe any chromium coupling, and the \(g\) value of 1.842 differs considerably from the value of 1.989 obtained in this study. Comparison with data reported for other chromium(I) complexes as summarized in table 7.3 indicates that the \(g\) and \(A_{Cr}\) values obtained in dichloromethane for \([Cr(CO)_6]^+\) are consistent with the values for other complexes. Finally, deliberate addition of acetonitrile to a dichloromethane solution containing \([Cr(CO)_6]^+\) leads to the rapid decay of the ESR spectrum and appearance of a broad signal as reported by Pickett and Pletcher. The broad signal is not believed to be due to \([Cr(CO)_6]^+\). More likely this is due to a complex formed by reaction of \([Cr(CO)_3]^+\) with acetonitrile such as \([Cr(CO)_2CH_3CN]^+\). The large line width is consistent with a large \(g\) anisotropy commonly associated with solution spectra of low symmetry.
Table 7.3. ESR data for various chromium (I) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>g value</th>
<th>$A^c_{Cr}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(CO)$_3$]$^+$</td>
<td>1.989</td>
<td>2.16</td>
<td>a</td>
</tr>
<tr>
<td>Cr(CO)$_3$F</td>
<td>1.969</td>
<td>-</td>
<td>a</td>
</tr>
<tr>
<td>[Cr(C$_{10}$H$_8$)]$^+$</td>
<td>1.986</td>
<td>1.82</td>
<td>b</td>
</tr>
<tr>
<td>[Cr(CN)$_3$(NO)]$^-$</td>
<td>1.9949</td>
<td>1.85</td>
<td>b</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_2$(NO)]$^{2+}$</td>
<td>1.979</td>
<td>2.35</td>
<td>b</td>
</tr>
<tr>
<td>[Cr(OH)$_2$(NO)]$^{2+}$</td>
<td>1.9671</td>
<td>2.69</td>
<td>b</td>
</tr>
</tbody>
</table>

*a* Present work.  
*b* Reference 38 and references cited therein.  
*c Coupling constants in mT.

7.3.6. *Electrochemistry of Cr(CO)$_6$.*

Results are summarized in table 7.4. In acetonitrile, two well defined oxidation waves are observed on Pt electrodes in agreement with Pickett and Pletcher[20]. On Au, the response is characterized by significant adsorption. In dichloromethane, the

![Cyclic voltammograms for the oxidation of 10^{-3} M Cr(CO)$_6$ on a Pt electrode. First oxidation process shown only: (a) acetonitrile (0.1 M Et$_4$NCIO$_4$), (b) dichloromethane (0.1 M Bu$_4$NCIO$_4$). Scan rate 200 mV s$^{-1}$, temperature 20 °C.](image-url)
first process at a Pt electrode appears complex and is also characterized by strong adsorption (figure 7.8). The second oxidation process in dichloromethane is masked by the solvent oxidation. The observed electrochemistry in dichloromethane is in contrast to that reported by Cook and Morse[22], who could not observe a response in dichloromethane. However provided dry solvents are used, the oxidation process is clearly observable, and ESR data at low temperatures (see previous discussion) support the formation of \([\text{Cr(CO)}_6]^+\).

The first oxidation step can be explained by the reaction

\[
\text{Cr(CO)}_6 \rightleftharpoons [\text{Cr(CO)}_6]^+ + e^- \quad (7.6)
\]

Klinger and Kochi[25] have indicated that \([\text{Cr(CO)}_6]^+\) may be kinetically labile. In demonstrating this they provide data for the first oxidation process in the presence of lithium trifluoroacetate\((\text{CF}_3\text{CO}_2\text{Li})\) or lithium acetate \((\text{LiAc})\) and attributed the reaction to the sequence

\[
\text{Cr(CO)}_6 \rightleftharpoons [\text{Cr(CO)}_6]^+ + e^- \\
[\text{Cr(CO)}_6]^+ + \text{CF}_3\text{CO}_2^- \rightarrow \text{Cr(CO)}_5(\text{CF}_3\text{CO}_2) + \text{CO} \quad (7.7)
\]

If a simple EC mechanism is operative with reversible charge transfer, then theoretically the oxidation process should show a small shift to less positive potentials on addition of \(\text{CF}_3\text{CO}_2^-\). Surprisingly Klinger and Kochi reported a large shift \((200\text{mV})\) to more positive potentials, which they attributed to a decrease in the rate of electron transfer accompanying irreversibility. In view of this apparent anomaly, the work of Klinger and Kochi was repeated.
Figure 7.9. Cyclic voltammograms for the first oxidation wave of Cr(CO)$_6$ in acetonitrile (0.1M Bu$_4$NClO$_4$) at a conventional Pt electrode, showing the effect of successive additions of CF$_3$CO$_2$Li: (a) $10^{-3}$M Cr(CO)$_6$; (b) $10^{-3}$M Cr(CO)$_6$ + 1.0 ml of $10^{-2}$M CF$_3$CO$_2$Li; (c) $10^{-3}$M Cr(CO)$_6$ + 2.0 ml of $10^{-2}$M CF$_3$CO$_2$Li; (d) $10^{-3}$M Cr(CO)$_6$ + 3.0 ml of $10^{-2}$M CF$_3$CO$_2$Li; (e) $10^{-3}$M Cr(CO)$_6$ + 4.0 ml of $10^{-2}$M CF$_3$CO$_2$Li; (f) $10^{-3}$M Cr(CO)$_6$ + 5.0 ml of $10^{-2}$M CF$_3$CO$_2$Li. Scan rate 200 mV s$^{-1}$, temperature 20 °C, initial cell volume 20 ml.
Figure 7.10. Rotating disk voltammograms for the oxidation of Cr(CO)₆ in acetonitrile (0.1 M Et₄NClO₄) on a glassy carbon electrode: (a) 10⁻³ M Cr(CO)₆; (b) 10⁻³ M Cr(CO)₆ + 1.0 ml of 10⁻² M CF₃CO₂Li; (c) 10⁻³ M Cr(CO)₆ + 2.0 ml of 10⁻² M CF₃CO₂Li; (d) 10⁻³ M Cr(CO)₆ + 3.0 ml of 10⁻² M CF₃CO₂Li; (e) 10⁻³ M Cr(CO)₆ + 4.0 ml of 10⁻² M CF₃CO₂Li; (f) 10⁻³ M Cr(CO)₆ + 5.0 ml of 10⁻² M CF₃CO₂Li. Scan rate 10 mV s⁻¹, rotation rate 2000 rpm, temperature 20 °C, initial cell volume 20 ml.
Table 7.4. Cyclic voltammetric data\textsuperscript{a} for oxidation of Cr(CO)\textsubscript{6} at 20 °C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Electrode</th>
<th>Conc'n</th>
<th>Scan rate</th>
<th>Oxidation processes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>\textsuperscript{First}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(E_{p}^{\text{ox}})</td>
</tr>
<tr>
<td>MeCN</td>
<td>Pt</td>
<td>5x10\textsuperscript{-3}</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5x10\textsuperscript{-4}</td>
<td>200</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1x10\textsuperscript{-4}</td>
<td>200</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1x10\textsuperscript{-5}</td>
<td>200</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>Glassy Carbon</td>
<td>5x10\textsuperscript{-3}</td>
<td>200</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5x10\textsuperscript{-4}</td>
<td>200</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1x10\textsuperscript{-4}</td>
<td>200</td>
<td>1.62</td>
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<td></td>
<td></td>
<td>1x10\textsuperscript{-5}</td>
<td>200</td>
<td>1.61</td>
</tr>
<tr>
<td>DCM</td>
<td>Au\textsuperscript{c}</td>
<td>5x10\textsuperscript{-3}</td>
<td>200</td>
<td>1.61</td>
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<tr>
<td></td>
<td>Pt</td>
<td>5x10\textsuperscript{-3}</td>
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<td></td>
<td>5x10\textsuperscript{-4}</td>
<td>200</td>
<td>1.86</td>
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<td></td>
<td>1x10\textsuperscript{-4}</td>
<td>200</td>
<td>1.83</td>
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<td></td>
<td>1x10\textsuperscript{-5}</td>
<td>200</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>Glassy Carbon</td>
<td>5x10\textsuperscript{-3}</td>
<td>200</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5x10\textsuperscript{-4}</td>
<td>200</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1x10\textsuperscript{-4}</td>
<td>200</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1x10\textsuperscript{-5}</td>
<td>200</td>
<td>1.84</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All potentials V vs. Ag/AgCl. \textsuperscript{b} Chemically irreversible process. \textsuperscript{c} Complex behaviour observed consistent with strong adsorption. \textsuperscript{d} Not recorded.

\textit{Figure 7.9} shows the effect of the addition of CF\textsubscript{3}CO\textsubscript{2}Li on the first oxidation wave of Cr(CO)\textsubscript{6} in acetonitrile at a conventional electrode. Within experimental error (\(\pm 20\) mV), no potential shift was observed on addition of CF\textsubscript{3}CO\textsubscript{2}\textsuperscript{-}. However, a significant increase in the height of the oxidation peak occurs, as does a decrease in the peak height of the reduction peak observed on the reverse scans of the cyclic voltammogram. Data are more easily interpreted by rotating disc voltammetry(\textit{figure 7.10}). It can be seen that the limiting current of the first oxidation process, increases concomitant with the disappearance of the second oxidation process.
This behaviour can be explained if the substituted species Cr(CO)₅(CF₃CO₂) is oxidised at less positive potentials than for the oxidation of Cr(CO)₆. Since CF₃CO₂⁺ is an anionic ligand, as is F⁻, this is possible since the process \( \text{Cr(CO)}_6 \leftrightarrow \text{Cr(CO)}_6^+ + e^- \). Under this circumstance, the overall process can be described by equations 7.8 to 7.11.

\[
\text{Cr(CO)}_6 \leftrightarrow \text{[Cr(CO)}_6]^+ + e^- \quad (7.8)
\]

\[
\text{[Cr(CO)}_6]^+ + \text{CF}_3\text{CO}_2^- \rightarrow \text{Cr(CO)}_5(\text{CF}_3\text{CO}_2) + \text{CO} \quad (7.9)
\]

\[
\text{Cr(CO)}_5(\text{CF}_3\text{CO}_2) \leftrightarrow \text{[Cr(CO)}_5(\text{CF}_3\text{CO}_2)]^+ + e^- \quad (7.10)
\]

Then by analogy to equation 7.3

\[
\text{[Cr(CO)}_5(\text{CF}_3\text{CO}_2)]^+ \rightarrow \text{Cr}^{2+} + \text{CF}_3\text{CO}_2^- + 5\text{CO} \quad (7.11)
\]

Alternatively, Cr(CO)₅(CF₃CO₂) may simply disproportionate as is the case with many 17 electron complexes

\[
2\text{Cr(CO)}_5(\text{CF}_3\text{CO}_2) \rightarrow \text{[Cr(CO)}_5(\text{CF}_3\text{CO}_2)]^- + \text{Cr}^{2+} + 5\text{CO} + \text{CF}_3\text{CO}_2^- \quad (7.12)
\]

This would also lead to an observed two electron oxidation.
Figure 7.11. Fast scan cyclic voltammogram of $10^{-3}$ M Cr(CO)$_6$ + $10^{-3}$ M Et$_4$NF in acetonitrile (0.5M Et$_4$NCIO$_4$) at a Pt inlaid microdisk electrode ($a = 65.7 \mu$m). $T = 22 \, ^\circ$C, scan rate: (a) 1 V s$^{-1}$, (b) 20 V s$^{-1}$. 
Figure 7.12. Rotating disk voltammograms for the oxidation of Cr(CO)$_6$ in acetonitrile (0.1M Et$_4$NClO$_4$) on a glassy carbon electrode: (a) $10^{-3}$M Cr(CO)$_6$; (b) $10^{-3}$M Cr(CO)$_6$ + 1.0 ml of $10^{-2}$M Et$_4$NF; (c) $10^{-3}$M Cr(CO)$_6$ + 2.0 ml of $10^{-2}$M Et$_4$NF; (d) $10^{-3}$M Cr(CO)$_6$ + 3.0 ml of $10^{-2}$M Et$_4$NF; (e) $10^{-3}$M Cr(CO)$_6$ + 4.0 ml of $10^{-2}$M Et$_4$NF; (f) $10^{-3}$M Cr(CO)$_6$ + 5.0 ml of $10^{-2}$M Et$_4$NF. Scan rate 10 mV s$^{-1}$, rotation rate 2000 rpm, temperature 20 °C, initial cell volume 20 ml.

If fluoride is present in situ, instead of CF$_3$CO$_2^-$, a similar substitution reaction may be expected to occur, although it should be noted from the ESR data that CO may replace F$^-$, rather than the reverse. Figure 7.12 shows successive additions of fluoride monitored by platinum rotating disc voltammetry in acetonitrile. A comparison of figures 7.10 and 7.12 indicates that the reactions occurring for the fluoride are different to those for trifluoroacetate. In order to explain the significant decreases in the limiting current on addition of fluoride, some form of mechanism involving interaction between reactants and products must be operative. Possible examples would be

$$\text{Cr(CO)}_6 \rightleftharpoons [\text{Cr(CO)}_6]^+ + e^-$$
\[
[\text{Cr(CO)}_{6}]^{+} + \text{F}^- \rightarrow \text{Cr(CO)}_{5}F + \text{CO} \quad (7.13)
\]

\[
\text{Cr(CO)}_{5}F \quad \cancel{\leftrightarrow} \quad \text{Cr(CO)}_{5}F^{+} + e^- \quad (7.14)
\]

\[
[\text{Cr(CO)}_{5}F]^{+} + 2\text{Cr(CO)}_{6} + \text{F}^- \rightarrow [\text{Cr}_{2}(\text{CO})_{10}(\mu-\text{F})] + 2\text{CO} + \text{Cr(CO)}_{5}F \quad (7.15)
\]

Alternatively

\[
[\text{Cr(CO)}_{6}]^{+} + \text{Cr(CO)}_{6} + \text{F}^- \rightarrow [\text{Cr}_{2}(\text{CO})_{10}(\mu-\text{F})] + 2\text{CO} \quad (7.16)
\]

The dimeric species \([\text{Cr}_{2}(\text{CO})_{10}(\mu-\text{F})]\) postulated in equations 7.15 and 7.16 has not been reported previously. However the Cl\(^+\), Br\(^+\), and I\(^-\) analogues of the reduced form of this dimer\(^{[34]}\) \([\text{Cr}_{2}(\text{CO})_{10}(\mu-X)]^{+}\), and the neutral iodide dimer \(\text{Cr}_{2}(\text{CO})_{10}(\mu-I)\) have been reported\(^{[35-38]}\) so this seems to be a likely product. Analogous bridged species have also been reported \(^{[37-40]}\).

Fast scan rate voltammetry at a Pt microelectrode (figure 7.11) of the oxidation of \(\text{Cr(CO)}_{6}\) in the presence of fluoride shows that the reversible response is obtained at scan rates as low as 20 V s\(^{-1}\), with a peak-to-peak separation of only 70 mV. Data at lower scan rates (e.g. 1 V s\(^{-1}\)) still appears irreversible at the microelectrode.

To ensure no reaction was occurring between chromium hexacarbonyl and fluoride before oxidation, the addition of fluoride to \(\text{Cr(CO)}_{6}\) was monitored by infra red spectroscopy. No change was observed in the carbonyl region. The bridged fluoride complex is expected to be extremely reactive, and it is not surprising that it could not be isolated in the present work. However, this study has demonstrated the potential for synthesizing carbonyl fluoride complexes via electrochemical oxidation.
7.3.7. *Electrochemical synthesis of Mo(CO)$_2$(dpe)$_2$F.*

The electrochemistry of [Cr(CO)$_2$F]$^-$ has shown that previously unreported complexes Cr(CO)$_2$F and [Cr(CO)$_2$F]$^+$ are stable, at least on the electrochemical time scale at low temperatures. Furthermore, electrochemical oxidation appears to offer prospects of making a wide range of carbonyl fluoride complexes. For example, oxidation of molybdenum or tungsten carbonyl complexes in the presence of fluoride may be expected to lead to stable carbonyl fluoride complexes. Chemical oxidation of cis-Mo(CO)$_2$(dpe)$_2$ (dpe = 1,2-bis(diphenylphosphino)ethane) with NOPF$_6$ actually produces Mo(CO)$_2$(dpe)$_2$F [41]. Electrochemical oxidation of cis-Mo(CO)$_2$(dpe)$_2$ in CH$_2$Cl$_2$ occurs via two one electron oxidation steps [42]. Controlled potential oxidative electrolysis in the presence of deliberately added fluoride, as might be expected, produces the stable seven-coordinate complex Mo(CO)$_2$(dpe)$_2$F (identified by infra red spectrum and comparison of other properties with an authentic sample) which has been well characterized[41]. This example confirms our contention that electrochemical synthesis should provide a general route to the preparation of carbonyl fluoride complexes.
7.4. REFERENCES.

CHAPTER 8

THE INFLUENCE OF ULTRA VIOLET IRRADIATION ON THE DETERMINATION OF NICKEL AND COBALT IN NATURAL WATERS BY ADSORPTION VOLTAMMETRY.

8.1. INTRODUCTION ........................................................................................................... 209

8.2. EXPERIMENTAL ............................................................................................................. 211

8.2.1. Reagents and solutions .......................................................................................... 211

8.2.2. Glassware and plasticware ..................................................................................... 211

8.2.3. Instrumentation ....................................................................................................... 211

8.2.4. Procedures ................................................................................................................ 212

8.2.4.1. Samples .............................................................................................................. 212

8.2.4.2. Voltammetric ..................................................................................................... 212

8.3. RESULTS AND DISCUSSION. .................................................................................... 213

8.3.1. The use of a µMTFE for ADPV determinations ...................................................... 213

8.3.2. Reagent blank analysis ........................................................................................... 214

8.3.3. Natural water analysis at conventional Hg electrodes .......................................... 215

8.4. SUMMARY ................................................................................................................... 222

8.5. REFERENCES. ............................................................................................................... 223
8.1. INTRODUCTION

The complexation of trace metals in natural waters (rivers, lakes, oceans, etc.) by dissolved organic matter has been well documented as perusal of references 1-6 would indicate. One of the important techniques for the determination of trace concentrations of metals in aqueous media is anodic stripping voltammetry (ASV) at conventional and micro-mercury electrodes, as was discussed in detail in chapter 6. The technique of ASV has been used extensively for the determination of copper, lead, cadmium, and zinc in natural water systems[7,8].

Despite the wide use of anodic stripping voltammetry, and its proposed role in speciation studies[9-11], it is still not always clear what fraction of the total metal concentration is being measured, particularly when the technique is applied directly to the natural water sample. Obviously uncomplexed metal ion and labile metal complexes are likely to be determined, but the fraction of organic complexes accessible to the anodic stripping voltammetric method cannot be easily ascertained nor can the effect of organic reagents on the electrode process. For example, Brainina et. al.[12] have recently described the effect of organic substances on the results of the anodic stripping voltammetric determination of lead, copper, and cadmium in aqueous media. By addition of organic compounds such as enzymes, fulvic acids, humic acids, and polyethylene glycol, natural water systems were simulated and the metals determined by the standard addition method. The presence of these organic reagents affected the anodic stripping determination of copper and lead, and made results unreliable. In contrast, the determination of cadmium was not hampered by the presence of these organic substances.

As a result of uncertainties concerning the influence of dissolved organics, it has been suggested that the determination of zinc, cadmium, lead, and copper be undertaken by anodic stripping voltammetry after pretreatment by irradiation with an ultraviolet (UV) source to destroy the dissolved organics. This method, studied extensively
by Nurnberg and co-workers[7,13-17], is assumed to release the organically bound fraction of these metals and lead to the determination of the total dissolved metal concentration.

More recently, the technique of adsorption voltammetry has been developed for trace determination of many metals[7,18-27]. Whilst UV irradiation or equivalent procedures may be mandatory for most total metal determinations in natural waters when employing anodic stripping voltammetry, the situation with respect to adsorption stripping voltammetry has yet to be extensively investigated. In the adsorption stripping method for the determination of nickel and cobalt, as described by Nurnberg et. al., dimethylglyoxime adsorbed on the electrode surface is employed as part of the analytical procedure. Dimethylglyoxime is a specific organic ligand for the two metals. It forms complexes having very high stability constants with cobalt and nickel, and relatively low stability constants with most other metals. Hence, with the combination of a high stability constant and its presence at relatively high concentration in the analytical procedure, it may be postulated that this ligand could effectively compete with the vast majority of naturally occurring ligands present in natural waters to provide a direct determination of total dissolved cobalt and nickel concentrations without the need for UV irradiation. That is, the adsorption stripping method is intrinsically different to anodic stripping voltammetry and may be less prone to interferences of the kind frequently associated with dissolved organic matter in anodic stripping voltammetry.

In this chapter, the influence of UV irradiation on the determination of nickel and cobalt by adsorption stripping voltammetry at conventional and micro-mercury electrodes in natural water samples will be discussed. Data are compared with that obtained for the determination of copper, lead, cadmium, and zinc by anodic stripping voltammetry to demonstrate that the different stripping techniques have fundamentally different characteristics with respect to the fraction of metal they determine in natural water samples. That is, speciation studies are technique dependent even within the
framework of analytical voltammetry and the exact nature of the stripping method needs to be carefully evaluated.

8.2. EXPERIMENTAL

8.2.1. Reagents and solutions.

Distilled deionized water was obtained by passing distilled water through a Barnstead Sybron Nanopure water purification system (Barnstead Sybron Corp., Boston, MA), then through a Millipore Organex-Q cartridge to remove any trace organics. Standard solutions of lead, copper, cadmium, zinc, cobalt, and nickel were prepared by dissolution of analytical reagent grade salts in distilled deionized water, acidified to pH 2.0 with 10M HCl (Aristar grade, BDH).

8.2.2. Glassware and plasticware.

All glassware, electrochemical cells, the UV irradiation cell, stirring bars, and polyethylene bottles were precleaned by washing in 0.5M HCl for seven days. Prior to use each item was rinsed repeatedly with distilled/deionized water, then dried with lint free tissue.

8.2.3. Instrumentation.

Differential pulse anodic stripping voltammetric (DPASV) determinations of Cu, Pb, Cd, and Zn, and adsorption differential pulse voltammetric (ADPV) determinations of Co and Ni were undertaken on either a Metrohm 646 VA Processor using a 647 Multimode Electrode in the stationary mode (hanging mercury drop electrode), or an EG&G Princeton Applied Research Corporation Model 384 Polarographic Analyzer and Model 303 static mercury drop electrode (hanging mercury drop electrode mode).

Microelectrode ADPV experiments were carried out on a BAS 100A Electrochemical Analyzer (Bioanalytical Systems Inc.), at a μMTFE prepared as described in section 6.3.1.
The UV irradiation of all samples was carried out for 4 hours in a closed quartz glass cell fitted with a water cooled insert containing a 125W Philips HPK mercury lamp.

8.2.4. Procedures.

8.2.4.1. Samples.

Water samples were stored in the precleaned polyethylene bottles after filtration (0.45 μm filter) and acidification to pH 2 with hydrochloric acid. Samples, after collection, were cooled and maintained at a reduced temperature of 4 °C prior to use. All analytical determinations were performed within three weeks of collection of samples.

8.2.4.2. Voltammetric.

All experiments were undertaken at 22 °C. Then samples were purged with nitrogen for a minimum of 5 minutes prior to commencement of the experiments. All determinations were carried out in triplicate using the method of standard additions with individual data points being the average of three determinations.

DPASV determination of Cu, Pb, Cd, and Zn was undertaken directly on a 20.0 ml aliquot of the acidified and filtered water sample. A deposition potential of -1.15V vs. Ag/AgCl(sat. KCl) was used when all four elements were determined simultaneously.

Appropriately less negative potentials were chosen when Zn was not being determined. The deposition time was normally 5 minutes with longer times up to 20 minutes being used if the concentrations were extremely low. Constant stirring of the solution was used throughout this deposition time. The pulse amplitude was 50 mV with a duration of 0.5 seconds between pulses. The scan rate was 4 mV s⁻¹ and an equilibration time of 15 seconds without stirring was used prior to the commencement of the stripping scan.
ADPV of Co and Ni required the addition of 300 μl of 4M NH₃/NH₄Cl buffer and 20 μl of 10⁻⁴M dimethylglyoxime in 95% ethanol to the 20.0 ml sample volume. An adsorption potential of -0.70 V vs. Ag/AgCl(sat. KCl) was used with an accumulation time of 100 seconds (or longer for ultra trace levels). The pulse amplitude was -50 mV in ADPV, with other parameters being the same as for DPASV.

8.3. RESULTS AND DISCUSSION.

8.3.1. The use of a μMTFE for ADPV determinations.

The successful use of μMTFE's for the ASV determination of heavy metals in aqueous solutions was detailed in chapter 6. It was therefore anticipated that a comparison of the fraction of metals determined by anodic and adsorption stripping voltammetry at a μMTFE in the presence and absence of UV irradiation of natural water samples would be carried out. However, the adsorption stripping technique for the determination of cobalt and nickel using dimethylglyoxime in acetate buffer systems, was found to provide non-reproducible data when attempted at a μMTFE. In many cases no peaks were observed at all. Such behaviour has been reported by other workers in the field, who similarly reported anomalous behaviour when attempting to use a μMTFE for adsorption stripping determinations[28].

Adsorptive stripping analysis relies on the ability to adsorb the analyte species at the mercury-solution interface in a deterministic manner, prior to the quantitative analysis of the adsorbed analyte via a Faradaic redox process. However, when the size of the mercury electrode is reduced, as is the case with a μMTFE, the subtleties of the adsorption process may become apparent[29]. In particular, the nucleation of the adsorption process may arise from a single nucleation event, which occurs at an indeterminate time.

The stochastic nature of the nucleation and growth of condensed thymine films at a mercury microelectrode has been examined by Sridharan and DeLevie[30]. Delay times for the nucleation of the thymine film ranged from 0 - 4 seconds. However, under
Table 8.1. Blank levels from reagents with and without UV irradiation.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Trace metal concentration* (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Unirradiated</td>
<td>0.002(0.001)</td>
</tr>
<tr>
<td>Irradiated</td>
<td>0.002(0.001)</td>
</tr>
</tbody>
</table>

* Average values of two determinations with three standard additions with a 20 minute time, with standard deviation shown in brackets. Cd, Pb, and Cu determined by ASV, and Co & Ni determined by ADPV as per experimental section. b UV irradiation time 4 hours.

certain conditions the nucleation rate was observed to become so low that the electrode surface was poisoned by adsorbable impurities from solution. In this case no nucleation of the thymine film was observed for the duration of the experiment (10 seconds).

In the present work, the anomalous behaviour of the μMTFE is probably due to the stochastic nature of the adsorption of the analyte species, and the concomitant poisoning of the electrode surface by adsorbable impurities.

All experimental determinations reported in the remainder of this chapter refer to conventional mercury electrodes only.

8.3.2. Reagent blank analysis.

In trace metal determinations on natural water, reagent blank levels can be important. In distilled deionized water acidified to pH 2 and after addition of reagents as required for the cobalt and nickel determinations (see experimental section), the concentration levels in both UV irradiated and non-irradiated samples were found to be as given in table 8.1. These data provide important information on several features relevant to the present investigations. Firstly, for cadmium, lead, copper, cobalt, and nickel, data in table 8.1 represent maximum blank values. This is a maximum value since it contains reagents plus distilled water, with the distilled water not being required when examining natural water samples. All reagent blank values are sufficiently low to enable natural water systems to be examined. For copper, blank levels are of the order of 0.5 ppb and significantly higher than for the other metals.

However in the natural waters examined in this work, copper levels are generally well in excess of the 1 ppb level so that reagent contamination is still not a critical
factor in determining the overall reliability of copper data. We have aimed to achieve at least a 5:1 excess of trace metal to the maximum possible blank value reported in Table 8.1. Secondly, data show that the 4 hour irradiation procedure does not in itself introduce a contamination problem. Thirdly, the data on distilled deionized water demonstrate that within experimental error no electrochemically inert organic metal complexes are present in the reagents, as results are independent of the presence or absence of the irradiation step.

Nurnberg et. al. [13] have suggested the use of hydrogen peroxide in conjunction with UV irradiation (typically 2 hours) to destroy dissolved organic matter. This step was avoided because of increased reagent blanks and development of poorer backgrounds on some occasions. However, a 4 hour UV irradiation period for all samples was used, which is considerably longer than that proposed by Nurnberg. The extended irradiation period is aimed at ensuring complete destruction of the organic matrix in natural water systems without risking possible contamination introduced by the addition of peroxide. Data, within experimental error, are time independent for irradiation periods of 4 hours or longer for all samples examined in this work which suggests that this strategy is successful.

8.3.3. Natural water analysis at conventional Hg electrodes.

Figures 8.1 and 8.2 show typical differential pulse adsorption and anodic stripping voltammograms for natural water samples with and without UV irradiation. Whereas data obtained with the DPASV method shows substantial change after UV treatment, this is not the case for the cobalt and nickel determination by ADPV. Tables 8.2 and 8.3 contain an extensive set of 9 replications per data point on a sample obtained from Corio Bay, Geelong, Victoria, Australia. This is a sea water sample from a bay in the southern part of Australia which is known to be severely contaminated with toxic heavy metals, particularly cadmium [31]. For the determination of both Co and Ni by adsorption differential pulse voltammetry, using the standard addition method, results
as indicated in table 8.3 are independent of the presence or absence of the 4 hour UV irradiation step.

In the particular example described in table 8.3, the slope of the cobalt response is slightly altered by the UV irradiation step but the matrix effect presumably associated with the surface active organic compounds is nullified by the standard addition method. No equivalent alteration is observed for nickel in this particular sample. Dissolved organic matter may influence voltammetric data by complexation to provide electroinactive species, or by altering electrode surface properties via adsorption. The latter mechanism may alter the observed current per unit concentration. However, this matrix effect may be eliminated by the standard addition method under ideal circumstances.

Table 8.2. Standard addition data for Corio Bay samples with and without UV irradiation.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Peak heighta (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Original (i)</td>
<td>4.55(0.65)</td>
</tr>
<tr>
<td>(ii)</td>
<td>4.77(0.57)</td>
</tr>
<tr>
<td>+ standard (i)</td>
<td>12.1(0.8)</td>
</tr>
<tr>
<td>additionc (ii)</td>
<td>12.2(1.1)</td>
</tr>
<tr>
<td>+ standard (i)</td>
<td>18.9(1.5)</td>
</tr>
<tr>
<td>addition (ii)</td>
<td>19.9(0.5)</td>
</tr>
<tr>
<td>+ standard (i)</td>
<td>25.7(1.6)</td>
</tr>
<tr>
<td>addition (ii)</td>
<td>26.4(1.0)</td>
</tr>
</tbody>
</table>

*a Average value of nine determinations with standard deviations in brackets.

b UV irradiation time 4 hours. (i) Unirradiated (ii) Irradiated
cSerial standard additions of each element as follows: Cd(0.4ppb), Pb(1.6ppb), Cu(10ppb), Co(0.2ppb), Ni(2ppb)
Table 8.3. Linear regression data for results in table 8.2.

<table>
<thead>
<tr>
<th>Regression parameter</th>
<th>Sol</th>
<th>Cd</th>
<th>Pb</th>
<th>Cu</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>slope</td>
<td>(i)</td>
<td>17.5</td>
<td>13.2</td>
<td>7.6</td>
<td>99.6</td>
<td>56.2</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>18.1</td>
<td>13.8</td>
<td>7.0</td>
<td>130.6</td>
<td>62.8</td>
</tr>
<tr>
<td>y intercept</td>
<td>(i)</td>
<td>4.8</td>
<td>14.5</td>
<td>63.3</td>
<td>16.7</td>
<td>323</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>4.9</td>
<td>27.8</td>
<td>78.6</td>
<td>17.5</td>
<td>339</td>
</tr>
<tr>
<td>correlation coefficient</td>
<td>(i)</td>
<td>0.9996</td>
<td>0.9985</td>
<td>0.9999</td>
<td>0.9972</td>
<td>0.9955</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>0.9994</td>
<td>0.9994</td>
<td>0.9979</td>
<td>0.9978</td>
<td>0.9921</td>
</tr>
<tr>
<td>calculated concentration</td>
<td>(i)</td>
<td>0.27(0.03)</td>
<td>1.10(0.12)</td>
<td>8.31(0.58)</td>
<td>0.16(0.02)</td>
<td>5.83(0.23)</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>0.27(0.02)</td>
<td>2.01(0.12)</td>
<td>11.26(0.79)</td>
<td>0.13(0.02)</td>
<td>5.40(0.22)</td>
</tr>
</tbody>
</table>

*(i) Unirradiated, (ii) Irradiated. * Concentration in ppb, with standard deviation in brackets.
Figure 8.1. Typical adsorption differential pulse voltammograms of cobalt and nickel from a Northern Australian estuarine water sample, before (---), and after (----) UV irradiation. $E(\text{ads}) = -0.7 \ \text{V}$ vs. Ag/AgCl (sat. KCl), adsorption time = 100 s, scan rate = 4 mV s$^{-1}$. 
Figure 8.2. Effect of UV irradiation on the determination of copper, lead, cadmium, and zinc by differential pulse anodic stripping voltammetry in an Northern Australian estuarine water sample. (a) before irradiation; (b) after irradiation. $E_{(dep)} = -1.15$ V vs. Ag/AgCl (sat. KCl), deposition time = 5 minutes, scan rate = 4 mV s$^{-1}$, pH = 2.00.
Table 8.4 contains data from fresh (river) and estuarine seawater samples obtained from the tropical regions of Northern Australia near a heavily industrialized region where elevated metal levels are expected. Again, as for the samples obtained from the temperate climate regions of Southern Australia, the adsorption differential pulse voltammetric method for the determination of cobalt and nickel is not influenced by UV irradiation treatment when using the method of standard additions. This observation has been found to be generally true for all Australian river, estuarine and coastal seawater samples examined in these laboratories and is attributed to the highly specific and very strong nature of the nickel and cobalt complexation via adsorbed dimethylglyoxime. Unlike anodic stripping voltammetry; where no complexation mechanism is associated with the determination, dimethylglyoxime is presumed to be able to compete effectively with naturally occurring organic ligands in natural waters and binds preferentially to nickel and cobalt. The dimethylglyoxime is present in a huge concentration excess relative to naturally present organic ligands, is specific for nickel and cobalt and is therefore well suited to the task of providing total metal determinations.

Table 8.4. Trace metal levels in Northern Australian water samples with and without UV irradiation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal concentrationa (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td>1b</td>
<td></td>
</tr>
<tr>
<td>(i)d</td>
<td>8.21 ± 0.88</td>
</tr>
<tr>
<td>(ii)</td>
<td>8.83 ± 0.71</td>
</tr>
<tr>
<td>2b</td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>1.26 ± 0.21</td>
</tr>
<tr>
<td>(ii)</td>
<td>3.62 ± 0.25</td>
</tr>
<tr>
<td>3c</td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>3.03 ± 0.27</td>
</tr>
<tr>
<td>(ii)</td>
<td>5.91 ± 0.44</td>
</tr>
<tr>
<td>4c</td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>7.54 ± 0.86</td>
</tr>
<tr>
<td>(ii)</td>
<td>11.2 ± 1.20</td>
</tr>
</tbody>
</table>

a Average value of two determinations with three standard additions ± standard deviation.
b Fresh water sample.  c Estuarine sample.  d UV irradiation time 4 hours.  (i) Unirradiated, (ii) Irradiated.
However, the application of dimethyl glyoxime to compete with the naturally occurring ligands may not provide determination of total Co and Ni in all cases. But will depend on the organic composition of the seawater at a given geographic location, as was recently indicated by Van den Berg for the determination of Ni[32].

As mentioned previously, adsorption voltammetric methods are now becoming widely available for many metal determinations. Furthermore, detection limits are usually adequate for direct trace metal analysis in natural waters. Clearly speciation schemes developed for voltammetric methods based on anodic stripping voltammetry may not necessarily be extended to methods based on adsorption voltammetry, since different detection principles are involved. For example, direct injection of urine into a voltammetric high performance liquid chromatographic system utilizing dithiocarbamate complexation leads to direct determination of total copper[33] despite the presence of a large fraction of copper as organically bound copper. That is, ligands with a very strong capacity to complex with a particular metal may overcome the problem of organic complex formation with voltammetric detection by anodic stripping voltammetry where pre-treatment methods are required for copper determinations in urine. Data in tables 8.2 and 8.4 show that treatment of natural water samples lead to markedly enhanced copper levels when detection is undertaken by differential pulse anodic stripping voltammetry. We have found this to be true for all natural water samples examined in these laboratories. Voltammetric speciation studies[10] have supported the hypothesis that large fractions of copper in natural waters are bound organically and these are said to be non-detectable by anodic stripping voltammetry. These findings raise the important question as to whether the recently described highly sensitive adsorption methods for the determination of copper[18-27] actually measure the same fraction of copper levels as do widely used anodic stripping methods. Based on these findings with Ni and Co it is possible to speculate that intrinsic and fundamentally different answers may be obtained unless UV irradiation or equivalent pre-treatment methods are implemented to ensure that total copper is being determined irrespective of the voltammetric method applied.
Tables 8.2 and 8.4 also provide data on lead, cadmium, and zinc determination by differential pulse anodic stripping voltammetry in the presence and absence of pretreatment by UV irradiation. Figure 8.2 shows an example of the profound influence on anodic stripping curves that may be introduced by UV irradiation. The effect on results is always pronounced for copper and lead, but may be small or even nondetectable with some samples when cadmium is being determined. Zinc data is not necessarily strongly influenced by the application of UV irradiation. In view of their lower sensitivity to dissolved organic species it may be postulated that development of adsorption voltammetric methods for cadmium and zinc, as is the case with the cobalt and nickel method, may lead to total metal determinations irrespective of the presence of dissolved organic matter in many natural water samples.

8.4. SUMMARY

In conclusion, these studies on cobalt and nickel suggest that speciation studies by voltammetric methods may be aided by the advent of specific and sensitive techniques of adsorption voltammetry at conventional Hg electrodes. Furthermore, this implies that the already excellent sensitivity of anodic stripping methods should not hinder research aimed at developing alternate adsorption voltammetric methods since they need not be redundant in their applications. The deliberate introduction of a specific reagent which involves adsorption and metal complexation can fundamentally alter the fraction of metal detected in a natural water system. However, the anomalous behaviour reported when a µMTFE was used for ADPV determinations of cobalt and nickel using dimethylglyoxime, is unexplained and requires further investigation.
8.5. REFERENCES.

28. S.N. Tan, personal communication.
CHAPTER 9

GENERAL SUMMARY.
Microelectrodes have been in existence since the early 1940's, although a fundamental understanding of their behaviour has only been achieved in the last 15 years. This thesis has examined the fundamental behaviour and analytical applications of inlaid and recessed microdisk electrodes in quiescent and flowing solutions.

The use of electrochemical impedance spectroscopy was shown to be a powerful tool in the evaluation of the surface morphology, and electrode integrity of inlaid microdisk electrodes. The nature of the diffusion to both inlaid and recessed microdisk electrodes was found to depend on the time scale of the experiment. Slow scan rates at inlaid microdisk electrodes result in hemispherical diffusion of the analyte to the electrode surface, while fast scan rates result in linear diffusion. Recessed microdisk electrodes constrain diffusion to be linear by nature of their design, but do switch to a steady state diffusion once the diffusion layer reaches the mouth of the recess. Diffusion limited steady state voltammetry was used to evaluate the reversibility of the ferrocene oxidation reaction, and then to calibrate all microdisk electrodes used in this work. The insensitivity of the diffusion limited steady state response to surface roughness was noted.

The response of inlaid and recessed microdisk electrodes was evaluated in an impinging jet flow cell, using the oxidation of ferrocene in acetonitrile as the test system. The response was found to be dependent on the relative position of the electrode to the jet nozzle, the flow rate, and the concentration of material injected. The flow rate dependence of a inlaid microdisk electrode centrally located in the stagnation region of the jet, was found to be the same as for a conventional electrode. In contrast the flow rate dependence of the recessed microdisk electrode was found to be much reduced when compared to that of the inlaid microdisk electrode.

The application of a microdisk based flow cell was examined in a flow injection analysis based method for the detection of copper in urine, and a high performance liquid chromatographic procedure for the determination of a range of tocopherols. In the copper determination the detection limits were found to be dependent on the radius of the inlaid microdisk electrode, and an optimum radius was noted. Noise was found to
severely limit the analytical usefulness of the smallest microelectrodes used in this thesis. The tocopherol determination demonstrated the ability of microelectrodes to provide analytically useful data in the absence of deliberately added electrolyte, a feature which should enhance the appeal of microelectrodes as detectors for high performance liquid chromatography and flow injection analysis.

The deposition of mercury onto an inlaid microdisk electrode was described theoretically and confirmed experimentally. The resultant mercury microelectrodes were then used in the study of the calomel electrocrystallisation reaction, and were also applied to the analytical determination of heavy metals by the technique of anodic stripping voltammetry.

Finally the effects of ultra violet irradiation on the speciation of cobalt and nickel in natural waters was examined using adsorption stripping voltammetry at a conventional hanging mercury drop electrode. The results for cobalt and nickel were then compared with the effects of ultraviolet irradiation on the speciation of cadmium, lead, copper, and zinc as determined by anodic stripping voltammetry.