1993

Some analytical applications of chemically modified electrodes

Peter John Riley

University of Wollongong

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SOME ANALYTICAL APPLICATIONS

OF

CHEMICALLY MODIFIED ELECTRODES

A thesis submitted in fulfilment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

THE UNIVERSITY OF WOLLONGONG

by

PETER JOHN RILEY, BSc (Hons)

Department of Chemistry
1993
To my wife,

Beth

and my parents,

Arthur and Jean Riley
"The conclusion, when all has been heard, is: fear God and keep His commandments, because this applies to every person."

Ecclesiastes 12:13
ACKNOWLEDGMENTS*

I wish to thank all of those who assisted in the completion of this thesis. First of all I wish to thank my supervisor Professor Gordon Wallace for his advise, support, friendship and encouragement throughout the duration of this project. My thanks also go to the other members of the IPRL especially Mark Imisides, Norm Barisci, Kerry Gilmore, Peter Teasdale, Richard John, Chee on Too, Karin Maxwell, Lin Yuping and Zhao Huijin for their friendship during my time in the laboratory. To my proof readers Will Price and Gill Middleton I extend my heartfelt thanks for diligence in an enormous task.

Finally, I wish to thank my family for their love and support. To my wife, Beth, I owe a great debt for the many hours spent typing and editing this work and holding the fort whilst I was away from home, all too often. To my children, Erin, Joel and Thomas, thanks for your patience. To my entire family, this thesis is as much yours as it is mine.

---

* I wish also to thank my current employer BHP Coated Product Division, Research and Technology Centre for their flexibility in, wherever possible, allowing me the time required to finally complete this work.
PUBLICATIONS

1 A New Electrochemical Sampling Device.  
Manthey, M., Riley, P. J. and Wallace, G. G.  

2 Controlled Release of the Dithiocarbamate Ligand from a Polypyrrole Polymer: A Basis for On-line Electrochemically Controlled Derivatisation.  
Lin, Y. P., Riley P. J. and Wallace, G. G.  

3 Ion Exchange Based Chemically Modified Electrodes  
Riley P. J., and Wallace, G. G.  
New Developments in Electrode Materials and their Applications  
A. Jones and L. Wood (eds.)  

4 Determination of Gold using Anion Exchange Based Chemically Modified Electrodes.  
Riley, P. J. and Wallace, G. G.  

5 The use of Electropolymerisation to Produce New Sensing Surfaces - A review emphasising electrodeposition of heteroaromatic compounds.  
Imisides, M. D.; John, R.; Riley, P. J. and Wallace, G. G.  

6 Intelligent Polymers  
Riley, P. J. and Wallace, G. G.  

7 Use of Authoring Tools in the Development of Instructional Resources for Scientific Equipment.  

8 Intelligent Chemical Sensors Based on Conductive Electroactive Polymers.  
Riley, P.J. and Wallace, G.G.  
9 Conductive Polymeric Systems.
Riley, P.J. and Wallace, G.G.

10 A Computerized Electrochemical System for Teaching and Analysis.

11 ElectroLab. A New Electrochemical Workstation.
Barisci, J.N.; Hodgson, A.J; Riley, P.J. and Wallace, G.G.
*Amer. Lab.* In Press
ABSTRACT

The continued advancement of electrochemical sensing is inextricably linked with the development of modified electrodes. New preconcentration schemes, utilising analyte-electrode interactions not normally employed in conventional sensors, open up a number of potential applications for these electrodes. One flexible route to the generation of electrode modifiers is through the use of electrochemically generated polymers to functionalise the electrode surface.

This work has investigated the use of a number of monomers for electrode modification. Monomers studied include pyrrole, thiophene, 3-methylthiophene, 2,2'-bithiophene, N-ethyltyramine and 4-vinylpyridine. The electrochemical generation of polymers from these monomers was studied and those found to deposit as reproducible coherent modifier layers were further investigated with a view to practical applications. Of the polymers studied polypyrrole was found to provide the greatest scope for use as an electrode modifier. This was due to the fact that, during the oxidation of the monomer to form the polymer, anions from the polymerisation solution are incorporated into the polymer matrix. As polypyrrole may be generated from either aqueous or acetonitrile solutions of the monomer and supporting electrolyte it is possible to incorporate a number of water soluble and water insoluble anions into the polymer matrix during electrosynthesis. None of the other monomers studied give this degree of flexibility in polymer growth.

The application of polypyrrole modified electrodes for sensing purposes and polypyrrole modified Reticulated Vitreous Carbon for sampling purposes has been the focus of this study. The interaction of mercury(II) with a dithiocarbamate functionalised polypyrrole has formed the basis of a preconcentration device for this cation. Gold has also been preconcentrated onto polypyrrole coated RVC. The mode of interaction in this application appears to be a redox reaction between the polymer and the analyte.

Polypyrrole was found to be unsuitable for sensing applications that required modifiers with a low background signal. In this case polymers formed from either 4-(vinyl pyridine) [gold sensor] or N-Ethyltyramine [methylmercury sensor] were employed. The mode of electrode-analyte interaction with these electrodes was thought to be ion-exchange and complexation respectively.

The effect of applied potential on the electrode-analyte interaction was studied and it was found that in some cases it could be used to enhance this interaction.
<table>
<thead>
<tr>
<th>Abbreviation</th>
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<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
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<tr>
<td>AC</td>
<td>Alternating Current</td>
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<td>AIBN</td>
<td>Azoisobutylnitrate</td>
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<td>APDC</td>
<td>Ammonium pyrolidinedithiocarbamate</td>
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<td>CV</td>
<td>Cyclic Voltammogram</td>
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<td>CME</td>
<td>Chemically Modified Electrode</td>
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<td>Cold Vapour AAS</td>
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<td>DPSV</td>
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<td>EC-PVP</td>
<td>Electrochemically generated PVP</td>
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<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
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<td>FAB-MS</td>
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<td>FPE</td>
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<td>GAME</td>
<td>Gold Amalgamated Mercury Electrode</td>
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<td>Graphite Furnace AAS</td>
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<td>GOD</td>
<td>Glucose Oxidase</td>
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<td>HgRVC</td>
<td>Mercury Coated RVC</td>
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<td>HMDE</td>
<td>Hanging Mercury Drop Electrode</td>
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<tr>
<td>HPLC</td>
<td>High Pressure Liquid Chromatography</td>
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<td>HSA</td>
<td>Human Serum Albumin</td>
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<td>ICPAES</td>
<td>Inductively Coupled Plasma Emission Spectroscopy</td>
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<td>INAA</td>
<td>Instrumental Neutron Activation Analysis</td>
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<td>LOD</td>
<td>Limit Of Detection</td>
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<td>LSV</td>
<td>Linear Sweep Voltammetry</td>
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<td>LSSV</td>
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<tr>
<td>MIP</td>
<td>Microwave Induced Plasma Emission Spectroscopy</td>
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<td>MTIE</td>
<td>Mercury Thin Film Electrode</td>
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<td>NET</td>
<td>N-Ethyltyramine</td>
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<td>OSWSV</td>
<td>Osteryoung Square Wave Stripping Voltammetry</td>
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<td>PP/Cl⁺</td>
<td>Polypyrrole Chloride</td>
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<tr>
<td>PSA</td>
<td>Potentiometric Stripping Analysis</td>
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<tr>
<td>PVC</td>
<td>PolyVinyl Chloride</td>
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<tr>
<td>PVP</td>
<td>Poly (4-Vinylpyridine)</td>
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<tr>
<td>RVC</td>
<td>Reticulated Vitreous Carbon</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Micrograph</td>
</tr>
<tr>
<td>TBATFB</td>
<td>Tetraethyl ammonium tetrafluoroborate</td>
</tr>
<tr>
<td>TEAP</td>
<td>Tetraethyl ammonium perchlorate</td>
</tr>
<tr>
<td>TOPO</td>
<td>(n-octyl)phosphine oxide</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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</tbody>
</table>
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GENERAL INTRODUCTION

The current awareness of the impact of many anthropogenic pollutants has led to a renewed interest in the determination of these pollutants in the biosphere[1-3]. Determination of these metals is often a complex task. A task that can be made more difficult if the sample collection point and analytical laboratory are separated by significant distances or if a significant time elapses between sample collection and analysis. To provide meaningful information the analysis obtained must accurately reflect the composition of the bulk sampled.

There are two approaches to obtaining the required information [4]:

a) Collect the sample in a manner that preserves the sample integrity (including speciation) or,

b) Perform the analysis at the sampling site with sensors capable of directly measuring the species of interest.

Either approach is viable and both suffer from a number of limitations.

This introductory chapter will evaluate each approach, review Chemically Modified Electrodes (CMEs) and delineate the proposed benefits of using CMEs to add a new dimension to each of the above approaches when sampling aqueous systems.

1.1 TRACE METAL SAMPLING

The difficulties encountered in sample collection and storage have been reported by a number of workers [4-14]. These problems are particularly evident when sampling aqueous systems for trace metal analysis [4-10]. It is an often stated fact that many early studies of heavy metal concentration in deep ocean waters suffered from a significant
positive bias caused by severe contamination of the water during sample collection and manipulation [11, 15, 16]. This fact is evidenced in dramatic changes in baseline metal concentrations recorded over a number of decades (Tables 1.1 and 1.2*).

To minimise these effects the materials used for sample containers must be carefully chosen [4, 17] and containers must be scrupulously cleaned prior to use [8]. Sample acidification is often necessary to prevent losses due to adsorption or precipitation of the analyte [4, 9]. Such pretreatment regimes may affect both the chemical form or oxidation state of the analyte [4]. Coupled with this, there is often a need to obtain large volumes of sample which must be transported and stored until analysis.

Following transportation to the laboratory a sample pretreatment step is often required to remove matrix interferences and raise analyte concentrations to a level above the limit of detection of the method chosen for analyte quantification.

A variety of laboratory methods have been devised to achieve this. Solvent extraction, ion exchange, complexation, precipitation and electrodeposition have all been used in sample pretreatment. It is those techniques based upon the immobilisation of the analyte on the surface of a solid preconcentration medium that are of interest here.

1.1.1 SOLID PHASE ADSORBENTS

Solvent extraction techniques provide a useful, but often complex, method of analyte preconcentration and interference removal. A more convenient approach uses solid phase adsorbent to collect the analytes of interest [18]. With this technique a variety of preconcentration mechanisms are available, the most popular of which involve either adsorption or chemisorption (where the analyte forms a chemical bond with the surface

* Both tables taken from reference 16
to which it has been adsorbed). It is this latter phenomenon of chemisorption that will be the focus of this section.

Table 1.1

<table>
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<th>Reference</th>
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<th>Pb</th>
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Original Data

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* Surface water samples
‡ All concentrations expressed in μg.L⁻¹

Table 1.2

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<th>Year</th>
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<td>0.26</td>
<td>0.27</td>
<td>0.050</td>
</tr>
</tbody>
</table>

* Filtered samples collected at 1 m depth. All concentrations expressed in μg.L⁻¹

Given the wealth of information available concerning liquid phase extraction it was an obvious extension of this work to design solid phase extractants that mimic the liquid-
liquid systems. There are several approaches to the production of these functionalised phases. The first involves the generation of a phase containing the appropriate functional group on the surface of the sorbent, for example, an ion exchange resin that contains surface bound sulphonate groups [19]. Alternatively, a relatively inert substrate may be chemically functionalised to provide the desired characteristics. This approach has been used extensively and quite successfully with silica based materials [20]. Other methods involve the use of an inert binding agent to fix the active reagent to the substrate surface [21] or the adsorption of the complexing agent onto a suitable support [22]. Each solid phase adsorbent to be discussed here will be classified according to the type of interactions involved in analyte immobilisation, rather than the mode of attaching the functional group to the substrate.

1.1.1.1 Iminodiacetate resins

Resins containing the iminodiacetic acid group have been the subject of extensive studies for many years. Since as early as 1965 [23] workers have been evaluating the suitability of this type of resin for the preconcentration of various metals. Two most commonly used and commercially available forms of this material are Dowex-A1 and Chelex 100 (50 -100), a sized and purified form of Dowex-A1 [23]. Muromac A-1 [24] is another commercially available iminodiacetate resin. Iminodiacetate resins have been reported to form complexes with a variety of metals [23 - 25] however, the complexation reactions have been shown to be very pH dependant [23, 26, 27].

The ability of the iminodiacetate resins to form complexes with a wide variety of metals has resulted in the development of a number of applications utilising this resin. One of the earliest applications of Chelex 100 to environmental samples was the work of Riley and Taylor [28]. In this study seawater samples were passed through a 60 x 120 mm bed of resin that had been converted to the hydrogen form. Eighteen of the thirty metals studied were successfully collected and re-eluted. A characteristic of chelex noticed by
these workers was the dramatic change in resin volume with significant changes in pH. This is, in fact, one of the major problems with Chelex 100 and will be discussed later.

Other workers [27] have also found that both the pH and ionic strength of the samples have a dramatic effect on the efficiency of uptake of metals on the resin. Sample pH has been shown to dramatically effect the nature of metal-resin binding with alkaline earth ions. Ion exchange is the predominant mechanism at pH<4 and chelation at pH>6 with mixed mode interactions at pH values between these. A survey of the literature shows no universally accepted procedure for the use of Chelex.

It should be noted that there is a great diversity of opinion regarding the suitability of this technique for the collection of Mn, Cr [29, 30, 37] and to a lesser extent Fe [37]. The reason for this variation may be the geometry of the columns used. A study by Su [40] showed that both Mn and Fe are distributed throughout a bank of 10 columns arranged in series, whereas the other metals studies were restricted to the first 2 or 3 cartridges, except Cd (5 cartridges) and Cr (no retention).

Chelex resin has been employed in flow injection analysis (FIA) with AAS detection providing a rapid technique for metal preconcentration and detection. The tendency of Chelex to swell with changes in pH causes problems with sample flow rate [33]. As the resin swells it restricts sample flow. To circumvent this problem the resin is converted to the appropriate form, usually the ammonium form [33, 25] or the magnesium form [40], and packed to 75% of the column volume [33]. Despite it's limitations Chelex 100 has found application with a variety of matrices. These are listed in Table 1.3.
1.1.1.2  8-Hydroxyquinoline functionalised adsorbent.

The immobilisation of 8-Hydroxyquinoline (oxine) and its derivatives onto various supports has provided a wide range of efficient preconcentration phases. By far the most
popular support material has been silica [42-47]. Attachment of the reagent to silica is generally achieved by silation of the silica surface with an appropriate reagent which subsequently couples with the oxine via a diazo coupling route [42, 44, 46].

Silica provides a support with mechanical properties superior to macroporous resins. Swelling of the support does not occur (compare with Chelex 100), and the material is readily available in a selection of particle sizes and porosity. This latter characteristic has a significant effect on the performance of the adsorbent. It has been found that pore size affects preconcentration efficiency with the optimum pore size being about 6 nm [45]. Alternate approaches involve the immobilisation of oxine by adsorption onto macroporous resins or silica [22, 48], or the collection of metal-oxine complexes, formed in solution, onto appropriate resins [49, 50]. A recent publication details the use of an oxine functionalised water-soluble polymer gel to collect metals from solution. The gel forms complexes with the metals to be removed and is subsequently collected by filtration through a suitable size exclusion membrane [51].

As with the iminodiacetate resins, the attraction of oxine based phases is their selectivity towards transition metals. These generally form stable 1:1 complexes [43] with high binding coefficients, whereas alkali and alkaline earth metal ions form complexes with low binding coefficients [47].

A number of applications utilising immobilised 8-hydroxyquinoline phases are listed in Table 1.4.
## Applications of 8-hydroxyquinoline functionalised adsorbents

<table>
<thead>
<tr>
<th>Metals collected</th>
<th>Sample matrix</th>
<th>Support</th>
<th>Determination method†</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu, Mn, Zn</td>
<td>Water</td>
<td>Silica</td>
<td>Colorimetry</td>
<td>46</td>
</tr>
<tr>
<td>Al, Cu, Mn, V</td>
<td>Water</td>
<td>Silica</td>
<td>INAA</td>
<td>48</td>
</tr>
<tr>
<td>Cd, Cu, Pb, Zn</td>
<td>Supporting electrolyte for A.S.V. determinations</td>
<td>Silica</td>
<td>ASV</td>
<td>52</td>
</tr>
<tr>
<td>Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb</td>
<td>Seawater</td>
<td>C$_{18}$, Silica (externally formed complexes)</td>
<td>GFAAS</td>
<td>49</td>
</tr>
<tr>
<td>Al, Cu, Co, Fe, Mo, Ni, T, W, Zr</td>
<td>Ultrapure water</td>
<td>Silica</td>
<td>Colorimetry</td>
<td>53</td>
</tr>
<tr>
<td>Cu</td>
<td>Water</td>
<td>Silica</td>
<td>AAS</td>
<td>54</td>
</tr>
<tr>
<td>Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn</td>
<td>Seawater</td>
<td>Silica</td>
<td>GFAAS</td>
<td>55</td>
</tr>
<tr>
<td>Cu, Pb</td>
<td>Water</td>
<td>C$_{18}$ Silica (externally formed complexes)</td>
<td>FIA-AAS</td>
<td>56</td>
</tr>
<tr>
<td>Cd, Co, Cu, Ni, Pb, Zn</td>
<td>Water</td>
<td>Silica</td>
<td>FIA-AAS</td>
<td>43</td>
</tr>
<tr>
<td>Ag, Al, Bi, Cd, Cu, Fe, Ga, Mn, Ni, Pb, Tl</td>
<td>Seawater</td>
<td>Macroporous resin (XAD-4)</td>
<td>GFAAS</td>
<td>22</td>
</tr>
<tr>
<td>Ca, Cd, Cu, Mg, Mn, Ni</td>
<td>Water</td>
<td>SDVB* anion exchange resin (collection of preformed complexes)</td>
<td>ICPAES</td>
<td>50</td>
</tr>
<tr>
<td>Cu</td>
<td>Water</td>
<td>Silica</td>
<td>FIA-AAS</td>
<td>47</td>
</tr>
<tr>
<td>Al, Bi, Cd, Co, Fe, Hg, Ni, Pb, Zn</td>
<td>Water</td>
<td>Membrane</td>
<td>ICPAES</td>
<td>51</td>
</tr>
</tbody>
</table>

* SDVB - Styrene divinylbenzene  
† INAA - Instrumental neutron activation analysis
1.1.1.3 Dithiocarbamate functionalised adsorbents

Dithiocarbamates are widely used in solvent extraction of many metals [57]. One of the most widely used reagent of this class is sodium diethyldithiocarbamate (NaDDC)

\[
\text{C}_2\text{H}_5 \quad \text{S}^- \quad \text{N} \quad \text{C} \quad \text{S} \quad \text{C}_2\text{H}_5 \quad \text{Na}^+ \\
\text{N} \quad \text{C} \quad \text{S} \\
\text{C}_2\text{H}_5 \quad \text{S}^-
\]

(1)

which forms complexes with over thirty metals [57]. Dithiocarbamates find application in environmental analysis because of their ability to form complexes with many metals of environmental concern without forming complexes with the main interferences, alkaline earth and alkali metal ions.

It is not surprising therefore, that dithiocarbamate based adsorbents have proven to be quite popular in solid phase extraction applications. There are a variety of routes to immobilising dithiocarbamates on appropriate supports.

Silating reagents have been used to bond ethylene diamine as well as several primary and secondary amines to the surface of silica gel. The amine groups are then converted to dithiocarbamates by reacting with alkaline carbon disulphide. The functionalised silica produced is stable at pH > 2.5 and was used to collect a variety of metals prior to XRF determination [58]. Silation has also been used to bond the mercaptopropyl moiety to silica. In this case the adsorbent was used to collect Cd, Cu, Pb and Zn from seawater [59] and to selectively collect arsenite from natural water containing various other arsenic species [60].

Many workers [61-67] have synthesised polydithiocarbamate resins. The general scheme used follows that of Hacket and Siggia [62], who in turn used a method first described by Dingman et al. [63]. This involves the formation of a polyamine-polyurea resin from polyethyleneimine and an appropriate diisocyanate, the resin is further
derivatised with alkaline carbon disulphide to form the dithiocarbamate resin. The derivatisation period initially used was three weeks [63], however, Miyazaki and Barnes [66] indicate that overnight derivatisation is sufficient. Despite this, most authors follow the initial method [61, 67]. Applications of these resins are listed in Table 1.5.

As with other chelating resins pH control is an important parameter in achieving quantitative preconcentration. In an extensive study, Miyazaki and Barnes [66] have shown that at the optimum pH it is possible to collect 22 metals, including 14 rare earth, on polydithiocarbamate resin. This study has also shown that it is possible to separate Cr(VI) and Fe(III) from Cr(III) and Fe(II), as the former are collected on the resin whereas the lower oxidation state metal ions are not. Barnes and co-workers have used polydithiocarbamate resins to preconcentrate heavy metals from urine [65, 68-70,]. The metals of interest were collected whereas magnesium and calcium were not retained on the resin.

There appears to be only one commercially available dithiocarbamate resin, Sumichetate Q-10. This has been used by 2 groups [71, 72] for the collection of mercury compounds. Quantitation was achieved by cold vapour AAS in the former study and head space gas chromatography in the latter.

The functionalisation of other supports provides yet another route to dithiocarbamate resins. Chen et al. [64] have functionalised polystyrene beads which were subsequently used to collect a number of metals.

Various cellulose substrates have also been derivatised [73] to dithiocarbamates or xanthates and the adsorption behaviour of 15 different metals studied. The resins produced had a relatively high capacity for Ag, Cr(VI), Cu, Hg, Pb and Se(IV).
<table>
<thead>
<tr>
<th>species collected</th>
<th>Sample matrix</th>
<th>Support</th>
<th>Determination method†</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag, Cu, Cr, Hg, Mn, Zn</td>
<td>Water</td>
<td>Silica</td>
<td>XRF</td>
<td>58</td>
</tr>
<tr>
<td>Cd, Pb, Zn, Cu arsenite</td>
<td>Seawater</td>
<td>Silica</td>
<td>AAS</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>Water with other arsenic species present</td>
<td>Silica</td>
<td>AAS</td>
<td>82</td>
</tr>
<tr>
<td>Au, Pd, Pt, Ag</td>
<td>Digested geological samples</td>
<td>Polydithiocarbamate resin</td>
<td>ICPAES</td>
<td>61</td>
</tr>
<tr>
<td>22 metals</td>
<td>Water</td>
<td>Polydithiocarbamate resin</td>
<td>ICPAES</td>
<td>66</td>
</tr>
<tr>
<td>Ag, Cd, Cu, Hg, Pb, Sb, Co, Ni</td>
<td>Water</td>
<td>Polydithiocarbamate resin</td>
<td>AAS</td>
<td>63</td>
</tr>
<tr>
<td>Bi, Cd, Cu, Hg, Ni, Pb, Se, Sn, Te, U</td>
<td>Urine</td>
<td>Polydithiocarbamate resin</td>
<td>ICPAES</td>
<td>65</td>
</tr>
<tr>
<td>Hg, Cu, Zn, Cd, Co, Au, Ag, Pb</td>
<td>Water</td>
<td>Polystyrene</td>
<td>uptake study</td>
<td>64</td>
</tr>
<tr>
<td>Au, Pt, Ir, Ru</td>
<td>Digested Ore</td>
<td>Polydithiocarbamate resin</td>
<td>INAA</td>
<td>83</td>
</tr>
<tr>
<td>CH₃Hg⁺</td>
<td>Natural waters</td>
<td>Commercial resin</td>
<td>Headspace GC</td>
<td>72</td>
</tr>
<tr>
<td>Hg</td>
<td>Water</td>
<td>Commercial</td>
<td>Cold vapour AAS</td>
<td>71</td>
</tr>
<tr>
<td>CH₃Hg⁺, C₈H₅Hg⁺, Hg</td>
<td>Natural waters</td>
<td>Polyurethane</td>
<td>XRF</td>
<td>78</td>
</tr>
<tr>
<td>Pb</td>
<td>water</td>
<td></td>
<td>ESCA</td>
<td>79</td>
</tr>
<tr>
<td>species collected</td>
<td>Sample matrix</td>
<td>Support</td>
<td>Determination method†</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------</td>
<td>------------------------------</td>
<td>-----------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Bi, Co, Cr, Cu, Hg, Ni, Pt</td>
<td>Water</td>
<td>XAD-4</td>
<td>ICPMS</td>
<td>80</td>
</tr>
<tr>
<td>Cd, Co, Cu, Pb, Ni, Sb, Zn</td>
<td>Snow,tap-water milk, seawater river water</td>
<td>Polydithiocarbamate resin</td>
<td>AAS</td>
<td>62</td>
</tr>
<tr>
<td>Cr(III), Cr(VI) speciation</td>
<td>Water</td>
<td>Polydithiocarbamate resin</td>
<td>ICPAES</td>
<td>85</td>
</tr>
<tr>
<td>Be, Co, Cu, Fe,Hg, Mn, Mo, Te,Ti, V, Zn</td>
<td>Urine</td>
<td>Polydithiocarbamate resin</td>
<td>ICPAES</td>
<td>68</td>
</tr>
<tr>
<td>Cd, Co, Cu, Fe, Mo, V, Zn</td>
<td>Serum</td>
<td>Polydithiocarbamate resin</td>
<td>Hydride generation ICPAES</td>
<td>46</td>
</tr>
<tr>
<td>Cr(III), Cr(VI) speciation</td>
<td>Urine and dextrose</td>
<td>Polydithiocarbamate and Polyacrylamidoxime resins</td>
<td>ICPAES</td>
<td>70</td>
</tr>
<tr>
<td>As, Bi, Sb,Se, Te</td>
<td>Urine</td>
<td>Polydithiocarbamate resin</td>
<td>ICPAES</td>
<td>69</td>
</tr>
<tr>
<td>Cd, Co, Cu, Mo,Ni, Ti, V</td>
<td>Bone</td>
<td>Polydithiocarbamate resin</td>
<td>ICPAES</td>
<td>86</td>
</tr>
<tr>
<td>Cu, Pb</td>
<td>Water</td>
<td>C18-silica</td>
<td>FIA-AAS</td>
<td>56</td>
</tr>
<tr>
<td>Co, Cu, Hg,Mn, Pb, Zn</td>
<td>Ultrapure water Lake water</td>
<td>Silica</td>
<td>XRF</td>
<td>87</td>
</tr>
<tr>
<td>Ca, Fe, Mn, Co,Ni, Cu, Zn, Ag,Cd, Hg, Pb, UO22+</td>
<td>Water</td>
<td>Thiol functionalised hydrophilic resin</td>
<td>FIA</td>
<td>77</td>
</tr>
<tr>
<td>As, Sb, Se, Te</td>
<td>Water</td>
<td>Thiol Cotton</td>
<td>AAS</td>
<td>74</td>
</tr>
<tr>
<td>CH3Hg⁺</td>
<td>Natural waters</td>
<td>Sulphydryl cotton</td>
<td>GC</td>
<td>76</td>
</tr>
</tbody>
</table>

† GC - gas chromatography  ICPMS - Inductively coupled mass spectrometry

Closely related to the dithiocarbamate resins is the sulphydryl cotton adsorbent. This has been produced by various workers [74-76] and used for the collection of precious metals.
methyl mercury, As, Sb, Se, and Tl. Thiol functionalised resins have also been studied for the immobilisation of selected heavy metals [77].

Finally, two other approaches involved the use of solid phase adsorbents and dithiocarbamates. The first involves loading diethylammonium dithiocarbamate onto polyurethane foam disks [78, 79]. This technique was used to collect methyl, phenyl and inorganic mercury from natural waters. Quantification was achieved by XRF.

The second approach uses the formation of metal dithiocarbamate complexes in solution. These are subsequently collected onto a suitable sorbent after which they are eluted and determined [80, 81]. For example, Plantz et al. have used bis(carboxymethyl)dithiocarbamate to complex Bi, Co, Cr, Cu, Hg, Ni, Pt and V. The complexes were collected onto a styrene-divinylbenzene resin, the metal complexes are then eluted with an alkaline solution and determined by ICPES. This technique provides a twofold concentration factor with a concomitant reduction in alkali and alkaline earth metal ions.

1.1.1.4 Other sorbents

Although the three classes of adsorbents listed previously account for a large portion of the published literature on metal preconcentration with solid phase adsorbents, there remains a significant body of work investigating the use of other functional groups for metal preconcentration. A brief discussion of these follows, the grouping of references reflects the approach to reagent immobilisation rather than any group classification.

The simplest materials used are untreated adsorbents such as activated carbon [75, 88]. These however have limited applications, and have been applied primarily to the preconcentration of gold.

A convenient method of incorporating functional groups onto relatively inert substrates has been to utilise the adsorption of the reagent onto the support material. To achieve this the desired reagents is usually loaded onto the support from a non-aqueous system and
the solvent allowed to evaporate leaving the immobilised reagent. For the successful implementation of this approach both the chelating agent and metal-chelate complexes need to be insoluble in water or they will be eluted during sample collection.

Utilising this approach dithizone has been coated onto activated carbon [89], 2-mercaptobenzothiozole cellulose acetate [90] loaded onto silica and controlled pore glass [21] and 1-(2-Pyridylazo)-z-napthol coated onto XAD-4 [95]. A major problem with this approach is that the complexing agent is also eluted during sample elution. The extent of this effect varies, but limits the scope for reuse of the adsorbents.

To circumvent these problems many workers have immobilised reagents to the surface of the support by various chemical reactions. The most popular approach has been the use of silanising reagents to immobilise collectors onto silica. This method has been employed with a variety of amines, attaching them to either silica gel or controlled pore glass [55, 58, 87, 91, 92]. Other workers have used this technique to graft 2-[(2-(triethoxysilyl)ethyl)thio]aniline [93] and salicaldimine [94] to silica.

A similar approach to this is the use of other chemical reactions to graft collectors onto supports. The carbodiimide reaction has been used to attach a chelating agent to sepharose gel [96], ring opening reactions to derivatise a polymethacrylate copolymer [97], cyanuric chloride to bind anthranilic acid to a cellulose support [98]. Picolinic acid [99] and dithizone [100, 101] have been attached to polystyrene-divinylbenzene polymers utilising the appropriate synthetic route. A summary of the aforementioned approaches and the metals collected is found in Table 1.6. A more extensive review of the various chelating polymers used for metal preconcentration can be found in references 18 and 102.
### Table 1.6 Applications of alternative solid phase adsorbents

<table>
<thead>
<tr>
<th>Species collected</th>
<th>Matrix</th>
<th>Substrate</th>
<th>Functional group</th>
<th>Determination method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Natural water</td>
<td>Activated carbon</td>
<td></td>
<td>GFAAS</td>
<td>103</td>
</tr>
<tr>
<td>Ag, Bi, Cd, Cu, Hg, Pb, Zn</td>
<td>Acidic samples</td>
<td>Activated carbon</td>
<td></td>
<td>GFAAS</td>
<td>89</td>
</tr>
<tr>
<td>Cd, Co, Cu, Ni, Zn</td>
<td>Water</td>
<td>Methacrylate polymer</td>
<td>Imidazole groups</td>
<td>AAS</td>
<td>97</td>
</tr>
<tr>
<td>Au, Pt, Pd</td>
<td>Acid matrix</td>
<td>Silica</td>
<td>γ-Aminopropyl triethyloxysilane</td>
<td>AAS</td>
<td>91</td>
</tr>
<tr>
<td>Ag, Cd, Co, Cr, Cu, Fe</td>
<td>Water</td>
<td>Silica</td>
<td>Z 6020</td>
<td>XRF</td>
<td>58</td>
</tr>
<tr>
<td>Co, Cu, Hg, Mn, Pb, Zn</td>
<td>Water</td>
<td>Silica</td>
<td>Z 6020</td>
<td>XRF</td>
<td>87</td>
</tr>
<tr>
<td>Co, Cu, Hg, Zn oxyanions</td>
<td>Water</td>
<td>Silica</td>
<td>Z 6020</td>
<td>XRF</td>
<td>92</td>
</tr>
<tr>
<td>Cu</td>
<td>Seawater</td>
<td>Sepharose 4B gel</td>
<td>Diethylenetriamine-N,N,N',N'-pentaacetic acid</td>
<td>AAS</td>
<td>96</td>
</tr>
<tr>
<td>Co, Cu, Ni, Zn</td>
<td>Seawater and fresh water</td>
<td>Polyamine-polyurea</td>
<td>Amine</td>
<td>GFAAS</td>
<td>104</td>
</tr>
<tr>
<td>Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb</td>
<td>Pure water</td>
<td>Acrylic ester resin</td>
<td></td>
<td>GFAAS</td>
<td>105</td>
</tr>
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</table>
### Table 1.6 (continued)

<table>
<thead>
<tr>
<th>species collected</th>
<th>Matrix</th>
<th>Substrate</th>
<th>Functional group</th>
<th>Determination method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd, Cu, Pb, Zn</td>
<td>Water</td>
<td>Phenol-formaldehyde resin</td>
<td>Salicylic acid</td>
<td>FIA-AAS</td>
<td>46</td>
</tr>
<tr>
<td>Cd, Cu, Pb, Zn</td>
<td>Water</td>
<td>Silica</td>
<td>2-Mercapto benzothiazole</td>
<td>AAS</td>
<td>21</td>
</tr>
<tr>
<td>Cd, Co, Cu, Pb, Zn</td>
<td>Seawater</td>
<td>Cellulose acetate</td>
<td>Dithizone</td>
<td>Polarography</td>
<td>90</td>
</tr>
<tr>
<td>Cd, Cu, Fe, Ni, Pb, Zn</td>
<td>Water</td>
<td>XAD-4</td>
<td>1-(2-Pyridylazo)-2-naphthol</td>
<td>AAS</td>
<td>95</td>
</tr>
<tr>
<td>Pd</td>
<td>Water</td>
<td>Silica</td>
<td>2-[[2-((Triethylxysilyl)ethyl)thio]aniline]</td>
<td>Colorimetry</td>
<td>93</td>
</tr>
<tr>
<td>Ag, Au, Pd</td>
<td>Water</td>
<td>Silica</td>
<td>2,2'-Dipyridyl-3-[[4-amino-5-mercapto]-1,2,4-triazolyl]hydrazone</td>
<td>AAS</td>
<td>106</td>
</tr>
<tr>
<td>Cu</td>
<td>Water</td>
<td>Silica</td>
<td>Salicaldimine</td>
<td>AAS</td>
<td>94</td>
</tr>
<tr>
<td>Hg</td>
<td>Water</td>
<td>Polystyrene</td>
<td>Picolinic acid</td>
<td>AAS / colorimetry</td>
<td>99</td>
</tr>
<tr>
<td>Au and Pt group metals</td>
<td>Water</td>
<td>Polystyrene</td>
<td>Dithizone and dehydrodithizone</td>
<td>dc plasma emission spectroscopy</td>
<td>101</td>
</tr>
</tbody>
</table>

Z 6020 = $\beta$-Aminoethyl - $\gamma$-aminopropyl trimethoxysilane

### 1.1.2 ELECTROCHEMICAL PRECONCENTRATION

An alternative method of immobilising analytes onto a solid collection medium is to utilise an electrochemical reaction. To achieve this the collector must possess sufficient conductivity to enable it to be used as the working electrode in an electrochemical cell. This in turn puts a number of restrictions on the materials that can be employed in...
electrochemical preconcentration. Despite these limitations electrochemical preconcentration techniques are in theory, a very attractive approach to metal preconcentration. All they require is a clean substrate onto which the metals of interest can be deposited, an appropriate holder (cell) for the solution and electrodes. Control is achieved by a suitable voltage or current source. The addition of other reagents is often unnecessary, as samples usually have sufficient ionic conductivity to allow the passage of current. Thus, the only reagent added to the system is electrons and hence not a source of contamination, provided the electrode is inert in the sample solution.

The most common form of electrochemical preconcentration involves electrodeposition of the metals of interest. Metals may be deposited directly as metallic films onto a solid electrode such as graphite [107, 108] or platinum wire [109]. Alternatively, some metals may be deposited onto mercury electrodes where they form amalgams [110]. Another immobilisation route available with mercury based electrodes is the formation of insoluble mercury-analyte films. Recent reviews of the subject [111, 112] provide an extensive discussion of electrolytic preconcentration methods.

It is evident from the available literature that although electrolytic methods possess many desirable characteristics they are not used extensively in analyte collection and preconcentration. There appears to be several reasons for this:

- Only a limited number of metals may be successfully collected
- only labile metals may be collected
- organic materials may foul the electrode and reduce collection efficiency
- 100% collection efficiency is extremely difficult to achieve, particularly for dilute solutions

As a result of these limitations only one group of routinely used instrumental techniques have an electrochemical preconcentration step prior to quantification. These techniques, collectively known as stripping analysis [113] have an electrochemical preconcentration
step, followed by a voltammetric determination step. During this determination step the
current flowing at the electrode is monitored as a function of applied potential. This
technique is known as stripping voltammetry (SV). When the applied potential is
ramped in a positive direction the technique is known as anodic stripping voltammetry
(ASV). When applied in a negative direction the technique is known as cathodic
stripping voltammetry (CSV). Alternatively, the potential of the electrode is monitored
as a function of time. This is known as potentiometric stripping analysis (PSA). With
either technique the requirement is not 100% collection efficiency, but rather reproducible
collection efficiency that is independent of analyte concentration. This requirement is
usually met over a limited range of analyte concentrations depending both on the metal to
be determined and the experimental conditions used.

One form of electrolytic preconcentration that has shown some promise is the use of
flow through porous electrodes (FPEs). In this technique the sample is pumped through
a large surface area electrode where it is subsequently deposited. The attraction of this
technique is that high preconcentration efficiencies are possible, although Sioda has
shown [114-116] that the system will reach an equilibrium condition where the rate of
metal deposition is equal to the rate of metal dissolution from the electrode. Thus, the
rate of metal uptake can be expressed as:

\[
\frac{dc}{dt} = -k_1c + k_2 \frac{S}{V}
\]  \hspace{1cm} (1.1)

Where [112]
- \(c\) = concentration at time \(t\)
- \(k_1\) = rate coefficient of deposition
- \(k_2\) = specific rate of dissolution
- \(S\) = surface area of the deposited metal
- \(V\) = solution volume
- \(t\) = time

A variety of materials have been used to construct FPEs. These range from fine metal
screens (eg. Ni, Pt, Au), to carbon cloth, carbon particles [117] or reticulated vitreous
carbon (RVC) [112]. Of these, RVC possesses both the mechanical and chemical properties that make it a superior preconcentration medium. As such it is worthy of further investigation.

1.1.2.1 Reticulated vitreous carbon

Reticulated vitreous carbon is particularly attractive for sample preconcentration because:

- it is chemically inert
- it is supplied clean and easily cleaned if contaminated
- it has high surface area/volume ratio
- it is amenable to chemical modification
- it has high mechanical strength.

These properties make the material very suitable for manufacture into analyte preconcentration cartridges that can be used both in the field and the laboratory.

RVC is manufactured by the pyrolysis of reticulated polyurethane in an inert atmosphere [118] and it is essentially a honeycomb of glassy carbon like material (Figure 1.1), it has been suggested [118] that, like glassy carbon, RVC possesses a crosslinked turbostratic structure.

![Electron micrograph of RVC](image)
The physical properties that make RVC attractive are [119]:*

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.048 ( \text{g.cm}^{-3} )</td>
</tr>
<tr>
<td>Void volume</td>
<td>97%</td>
</tr>
<tr>
<td>Hardness</td>
<td>6 - 7 (mohs)</td>
</tr>
<tr>
<td>Specific resistivity</td>
<td>0.47 - 0.69 ( \text{ohm/cm @ 25}^\circ \text{C} )</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>3 - 12 ( \text{kg.cm}^{-2} )</td>
</tr>
</tbody>
</table>

From this data it can be seen that RVC possesses both mechanical stability and very good electrical conductivity. Coupled with this, RVC is chemically and electrochemically very stable, it is only effected by severe chemical attack and has a potential range of +1.2 to -1.0V (vs SCE) at pH 7 [120].

The first reported use of RVC in an electrochemical application was as part of an optically transparent electrode, in this case the extremely high surface area to volume ratio of 65 \( \text{cm}^2.\text{cm}^{-3} \) [120] meant that thin slices of RVC could be fabricated into low dead volume (400 - 550 \( \mu \text{l} \)) cells.

The first use of RVC as a flow through electrode was reported by Curran and Strohl [121]. These workers [121-124] and Wang et al. [125-129] have extensively studied RVC in flowing systems. Both groups reported extremely high conversion efficiencies (>95%) for the oxidation of ferrocyanide, ascorbic acid and catechol at relatively low flow rates.

In the work of Strohl and Curran, RVC electrodes were used as the detection electrode in an FIA system for the oxidative determination of ascorbic acid, epinephrine, catechol, hydroquinone, ferrocyanide and L-dopa [121-123]. The authors reported very low limits of detection and high reproducibility of analyses. Tougas and Curran [124, 130] improved on the design of the cell used in the previous work and produced an RVC electrode based coulometric detector with a low (150 \( \mu \text{l} \)) dead volume.
Wang and co-workers have used an RVC electrode for solution clean up in on-line stripping analysis [128, 129]. In this application a coulometric cell using an RVC electrode, was placed, in a flow system, downstream of the voltammetric cell. The coulometric cell was set at a potential to remove species that were interfering with the analysis being performed in the voltammetric cell. Using this system, copper was removed from a solution being analysed for zinc, thus preventing the formation of the copper-zinc intermetallic. In a similar application oxygen was removed from a solution to be analysed for cadmium, lead and zinc.

Wang and Blaedel have also used mercury coated RVC (HgRVC) for the construction of a rotating porous carbon electrode and have used it in flow systems for ASV measurements of Cd, Cu, Pb and Zn [131]. In a similar study Alzand and Langford [132] investigated the use of HgRVC as an electrode for the stripping voltammetry of Copper in natural water. These authors also investigated the feasibility of collecting the samples onto HgRVC, in the field, with simple instrumentation. Quantification of the copper was performed in the laboratory at a later date, using more sophisticated electrochemical instrumentation.

The results of this study showed that although labile copper could be collected onto HgRVC cartridges, subsequent analysis indicated that some of this copper was lost on storage. They concluded that field sampling with HgRVC was plausible but probably only with some form of on-line sample digestion.

Other workers have studied the use of RVC or HgRVC as electrodes for voltammetric analysis. Osteryoung [133] has used an inert epoxy to fill the voids in the RVC. The electrode produced when polished, behaved like a microelectrode array. Zampori et al. [134] used a HgRVC electrode for the determination of Cd and Pb.

Apart from coating with mercury, there have been few attempts to chemically modify RVC. Anderson and Lung [118] used a variety of reactions to covalently bond ferrocene to the surface of RVC. Wieck et al. have used RVC as a support for the immobilisation
of glucose oxidase and used this in a FIA system for the determination of glucose [135]. More recently [136] Heider et al. electrochemically platinized RVC and attached glucose oxidase to the partially platinised surface to form a glucose sensor with enhanced sensitivity. Only one report to date has used electropolymerisation techniques to modify the RVC surface [137]. In this work the electropolymerised 1,2 diaminobenzene was used to both stabilise an enzyme attached to the surface of platinised RVC and to provide a layer that prevents electrode fouling.

This lack of work on RVC is somewhat surprising given that RVC is essentially a porous glassy carbon electrode and that much work has been performed attaching electrochemically generated polymers to glassy carbon. It is this literature that provides much background information regarding the techniques of polymer synthesis and the properties of the polymers generated. It should be noted however, that many of these studies concentrate on the physical, electrical and to a lesser extent, electrochemical properties of the polymers produced.

The only reported use of RVC for the preconcentration of metals prior to a non-voltammetric determination step has been reported by Oragam and Snook [118]. In this work they used a specially designed cell to preconcentrate copper and release it on-line into the nebuliser of an inductively coupled atomic emission spectrometer (ICPAES). Using a sample flow rate of 3.4 mL.min⁻¹ they achieved a 35% plating efficiency for copper at -400 mV. This lowered the limit of detection (LOD) for copper, using a 5 minute plating time, from 20 ng.mL⁻¹ to 100 pg.mL⁻¹. To date, all work performed using electrochemical techniques as a means of quantitative analyte preconcentration have been restricted to the use of unmodified conventional electrode materials. Chemically modified electrodes are yet to find application in this area.
1.2 ELECTROCHEMICAL SENSORS

As stated in the introduction, there are 2 approaches to the selective determination of analytes. The first, selective sampling, has been reviewed in the previous section. In this next section the use of selective sensors will be evaluated.

One requirement for performing analyses at the sampling site is that any instrumentation used must be portable and robust. Consequently, many laboratory based techniques are not suitable for use in on-site analysis because they lack portability. The portability and size requirement have become so important that in a recent review Wolfbeis [138] gives the following definition for a chemical sensor;

"small sized devices comprising a recognition element, a transduction element, and a signal processor capable of continuously and reversibly reporting a chemical concentration".

The author then stated that only electrochemical or optical (particularly those based on fibre optics) techniques successfully fulfilled this requirement.

It is electrochemical techniques that are the focus of this work, however the working definition of sensor used throughout this study does not relate to the whole instrument but rather the most important component of it - The Recognition Element; as the electronics required to convert the signal into a chemical concentration are readily available.

The advent of low power electronics has enabled the development of portable electrochemical instruments. Portable, even pocket size, pH meters are readily available and portable voltammetric instruments have been described in the literature [139]. At least one of these, the Chemtronics PDV 2000 is now commercially available.

Only a limited number of electrodes are suitable for use with portable voltammetric instruments. As a result of this only a limited number of analytes can readily be detected,
specifically those that are determinable by stripping voltammetry. The most common technique used is ASV, although some elements may be determined by CSV. The range of elements detectable may be expanded by the use of adsorptive stripping voltammetry [140, 141]. However, it is often difficult to achieve reproducible results using this technique as the instruments use a mercury thin film electrode (MTFE) as the sensing element. This problem may be circumvented by stripping the mercury film from the electrode at the completion of each analysis and replating it either prior to the next determination or in-situ during the determination [142].

If electrochemical instruments are to find widespread use, the range of compounds that can be detected must be expanded. Also, recognition elements must be developed that are more resistant to fouling and able to preferentially detect one species in the presence of others. To achieve this it is necessary to develop electrodes that possess new preconcentration schemes, different signal generation mechanisms or have improved stability. It is with this aim in mind that many workers in recent years have investigated and developed chemically modified electrodes for use as sensing elements.

1.2.1 CHEMICALLY MODIFIED ELECTRODES (CMES)

As with stripping voltammetric techniques, voltammetry with CMEs often involves specific application of selective preconcentration. Similarly it is an application requiring not 100% collection efficiency but rather reproducible collection efficiency.

When considering the operation of CMEs it is convenient to consider the action of an electrochemical sensor as a combination of several steps:

- movement of analyte to the sensing element
- selective binding of the analyte to the sensor surface
- signal generation at the sensor surface
- transmission of that signal through the bulk of the sensor to the electrochemical instrument
Chemically modified electrodes add a new dimension to both the binding and signal generation steps.

The modification of electrode surfaces can be achieved by a number of approaches. In the past few years a variety of reviews dealing with modified electrodes have appeared in the literature [138, 143-152]. Consequently, this section will only provide an overview of modification techniques used and review recent advances in the areas that are relevant to this study.

To successfully produce a modified electrode it is necessary to impart analyte recognition properties to the electrode surface. This may be achieved in a variety of ways. It can be as simple as adding the modifier to the sample solution and relying on adsorption of the modifier onto the electrode, as is done in adsorptive stripping voltammetry [140, 141]. Alternatively, the modifier may be added to the electrode prior to electroanalysis by techniques such as spin coating, dip coating, evaporative coating, physical admixing, surface immobilisation and electrochemical generation of modifier layers [150]. Once present either in or on the electrode surface, the modifier makes the electrode capable of determining or collecting specific analytes.

### 1.2.1.1 Physical admixing

With this method of electrode modification the chemically active agent is mixed with the electrode material prior to electrode manufacture. This technique of electrode preparation is particularly suited to the modification of carbon paste electrodes, as the carbon powder is mulled with a binding agent as part of electrode construction. To modify these electrodes it is simply a matter of adding the modifier to the binding mixture during the mulling operation. A recent publication by Kalcher [151] reviews this technique in detail.

The main consideration when producing this type of electrode is to obtain a homogenous mixture. A number of different modifiers have been used including resin based ion-
exchangers [153, 154-157], liquid ion exchangers [158], complexing agents [159-164],
coupling reagents [165], zeolites or other minerals [166] and crown ethers [167].

The major advantage of this approach to electrode modification is the ease with which the
modifier is incorporated into the electrode. This facilitates rapid production of modified
electrodes and allows the experimenter to readily vary the amount and type of reagent
used.

Although carbon paste based electrodes are the most popular composite electrodes used
there is another type of composite electrode that warrants mention. This was reported by
Shaw and co-workers [168, 169] and involves the formation of a composite electrode
produced by the polymerisation of a mixture containing a monomer (eg styrene), cross
linking agent (divinylbenzene), an initiator (azoisobutynitrile), the modifier (either
vinylpyridine or vinylferrocene) and carbon black. Electrodes prepared in this manner
were reported to be robust and reproducible and have a better signal/noise ratio than
glassy carbon [168]. This approach is yet to be used by other workers despite providing
the advantage of reusable electrodes.

1.2.1.2 Chemical binding

The use of surface functional groups as anchoring points for modifiers has also found
application in modified electrode synthesis.

Silanization reactions have been used extensively to immobilise reagents onto silica
substrates (see section 1.1.2) and it is an obvious extension of this principle to use this
method of attachment to bind modifiers to glassy carbon electrodes. In this technique,
the silanizing reagent reacts with the surface hydroxyl groups of the substrate to produce
a modified surface [149] which may be used as is or further modified. This approach
has been used by a number of researchers who have successfully attached reagents to
glassy carbon [170]. Other surface immobilisation reactions used include the
Carbodiimide reaction [149], the thionyl chloride reaction [149] and the Williamson reaction [149].

1.2.1.3 Coating with preformed polymers

The techniques of spin coating, dip coating and evaporative coating belong to this class of modification scheme. Using this technique the modifier, usually a polymer, is dissolved in a suitable volatile solvent. The solution is then applied to the electrode surface by one of the techniques mentioned above and the solvent allowed to evaporate leaving only the modifier on the electrode surface. Film thickness is controlled by the contact time of the electrode with the solution or by the volume of solution dispersed onto the electrode surface.

Using this method a number of modifiers, including poly(4-vinylpyridine) [171-174], nafion [175-177] tri-n-octylphosphine in PVC [178] and poly(ester-sulfonic) acid [179] have been applied to electrodes. Electrodes prepared this way however have been found to lack robustness and as a result some workers have tried to stabilise these by either treating them with heat to promote cross linking in the modifier [173] or by coating with a more stable polymer layer [180]. The stabilisation methods have increased electrode life but not to the extent that they would be suitable for long term use.

The use of preformed polymers, although possessing limited reproducibility provides a simple method for screening the activity of various modifiers. All that is required is that the modifier be soluble in a volatile solvent but insoluble in the supporting electrolyte to be used for analysis.

1.2.1.4 Electropolymerisation

Electropolymerisation provides a convenient route to electrode modification. In its simplest form all that is required is a voltage applied to two electrodes immersed in a solution containing a monomer amenable to electropolymerisation. In practice however,
there are many other criteria to be considered when modifying an electrode with electrochemically generated polymers.

The review articles previously cited (section 1.2.2) provide a general overview of the topic. A detailed evaluation of the electrodeposition of polymers is given in a review article by F. Beck [181] and more recently by Imisides et al. [152], in a review of the use of electropolymerisation to produce new sensing surfaces.

Historically, the first electrochemically generated polymers were those produced by electro-reductive means. These were synthesised primarily from vinyl containing monomers [181] and have found little application in sensor development.

Most current interest in electrochemically generated modifiers is focussed on those that can be formed by oxidative polymerisation schemes. These can be represented generally by the equation for the oxidation of pyrrole or thiophene to their respective polymers.

\[
\begin{align*}
\text{X} = \text{NH} \text{ or } \text{S} \\
\text{M}^+ \text{A}^- \rightarrow \text{salt in supporting electrolyte}
\end{align*}
\]

(1.2)

The polymer product of this reaction has several important features:[182]

- it contains conjugated double bonds and as such possess significant conductivity
- during polymerisation the polymer is oxidised to contain a net positive charge. To maintain overall electrical neutrality the polymer incorporates anions from the polymerisation solution.
- once formed the polymer may be switched from its oxidised state to the reduced state by the imposition of an external potential. This reduction of
the polymer backbone is accompanied by an expulsion of anion incorporated during synthesis.

It is the combination of these characteristics that makes conducting polymers so suitable for sensor development. The inherent conductivity means that potentials are easily applied to the sensor surface. The ability to incorporate anions during synthesis has been investigated by many workers as a means of incorporating reagents into the electrode [152 and references contained therein] and the ability to release anions under potential control has been used to release reagents from electrodes [184, 185].

It is the ability to incorporate specific chemically active agents during electropolymerisation that has been most often used in the fabrication of sensors from these polymers. An excellent example of the flexibility of this approach is the variety of glucose sensors developed with polymer modified electrodes. These sensors use glucose oxidase (GOD) immobilised in a conducting polymer membrane composed of either polyaniline [186] or polypyrrole [187-189]. Glucose concentration is estimated by measuring oxygen consumption [190], hydrogen peroxide formation [191], reduction of iodine [192] or the oxidation of a reduced mediator [193, 194].

In the above mentioned cases the polymer layer serves only to immobilise the active agents [191] and prevent electrode fouling. This approach has also been used in the fabrication of glucose sensor employing immunoglobulin immobilised in polytyramine [195] and a human serum albumin (HSA) sensor based on anti HSA entrapped within a polypyrrole film [196].

The use of reagent entrapment is not restricted to biological molecules, Wallace and Lin [197] have incorporated complexing agents into polypyrrole to form the basis of a silver sensor.

Interaction with the polymer backbone has been used by various workers. Phom et al. [153, 198] have polymerised 8-hydroxyquinolines and studied the interaction of both cobalt and copper (II) and cobalt (II) with the polymer produced. Wallace et al. have
derivatised polypyrrole to form dithiocarbamate modified electrodes suitable for the determination of copper [199, 200] and mercury [201]. Also reported is the use of Poly(3-methylthiophene) modified electrode for the determination of chromium (VI) [202], in this case the analytical signal is derived from non-faradaic signal that occurs as the Cr (VI) anion is expelled from the polymer matrix.

Electrodes exhibiting size exclusion characteristics have been developed [203, 204], the various selectivities were achieved by controlling electropolymerisation conditions. Similarly, over oxidised polypyrrole films have been shown to exhibit anion exclusion properties [205]. In this application an electrode coated with an over oxidised polypyrrole film was shown to be suitable for the determination of dopamine whereas no response was seen for the ascorbate anion at the same electrode. Wang and Li [206] have used poly(3-methylthiophene) as a protective layer to prevent the fouling of glassy carbon electrode during the voltammetric and amperometric determination of phenolic compounds. The mechanism of protection is not given but it appears that the phenols are oxidised at the polymer film. The poly(3-methylthiophene) film exhibits a greater resistance to fouling than unmodified glassy carbon.

The anion exchange properties of conducting polymers have been an area of great interest. Both polypyrrole [207] and polyaniline [208] modified electrodes has been used for the determination of electroinactive anions. In both cases the analytical signal observed is attributed to doping/undoping processes in the polymer. Other workers have developed ion exchange polymers [209], although these polymers have not been used in sensor design it is feasible that they will eventually be utilised, particularly when they can be made to exhibit the type of ion exchange specificity seen with ion exchange based carbon paste electrodes.
1.3 AIM AND SCOPE OF THIS WORK

Chemically modified electrodes have increased the scope of electrochemical sensing by providing improvements in electrode selectivity and enabling the detection of a number of electroinactive materials. Both of these benefits are a result of the modifiers present at the electrode surface, modifier which enable the use of a wide range of analyte-electrode interactions in the generation of an analytical signal. These interactions can be further utilised in analyte preconcentration steps, both electrolytic and non-electrolytic, to enable the use of CMEs in stripping voltammetry. The generation of an analytical signal is no longer restricted to redox reactions but now may include changes in the electronic properties of the electrodes. This may be evidenced as changes in electrode capacitance or resistance [210].

Therefore, with these advantages in mind, the objective of this work has been to investigate a number of chemically modified electrodes with the aim of developing sensors and sampling electrodes. Specifically, sensing electrodes for the detection of gold and methylmercury were investigated. Sampling electrodes studied were developed for the collection of gold and inorganic mercury(II) from solution.

The detection and collection of the various mercury species was studied because of the environmental significance of these compounds. The detection of gold, on the other hand, finds application in geochemical exploration and the processing of gold bearing ores.

The use of electrochemical techniques for the detection of methylmercury has only been studied by a small number of workers (reviewed in chapter 3) and the use of CME's for the detection of gold by electrochemical techniques has been the subject of investigation almost since the development of polarography. Various electrodes have been used for the detection of gold (see chapter 4 for a review) yet the only modified electrodes studied have been those based on modified carbon paste electrodes. In either case, ie.
methylmercury or gold, the development of an appropriate CME would enhance the applicability of electrochemical techniques for the detection of each species.

An extension of the study of interactions at the polymer modified electrodes has been to investigate the suitability of utilising these interactions, on a larger scale, in the development of sampling electrodes. This application requires the use of porous, large surface area electrodes that are amenable to further modification.

Reticulated vitreous carbon was chosen as the electrode material for this aspect of the study. RVC combines the requisite physical robustness with the appropriate chemical and electrochemical characteristics to make it particularly well suited to electrochemical preconcentration applications. Interest in the use of RVC in this type of application has waned dramatically since the early reports of this application. This is due, to the fact that the only collection mechanisms available with unmodified RVC is electrodeposition.

There appears, however, to be a facet of electrochemical sampling with RVC or any other porous electrode that has not been investigated, that is the use of chemically modified electrodes. These introduce a further dimension to sample collection with the ability to use both chemical and electrochemical interactions for analyte collection. In this study we have sought to modify RVC and investigate the collection of various metals at these modified electrodes. The modification schemes investigated have ranged from simple mercury coating through modification with conducting polymers to polymer modification followed by chemical derivatisation of the modified electrode. Many approaches used have been borrowed from sensor applications and adapted to sampling.

The modification of the electrode surfaces was achieved by the electropolymerisation of the appropriate aromatic monomers. Electropolymerisation was chosen as the electrode modification technique because it allows the operator to maintain fairly tight control over the properties of the polymers generated. This is achieved by limiting either the potential or current drawn at the electrode during the electropolymerisation step.
Finally, application of a potential to conducting polymers has been shown to change both the oxidation state and hydrophobicity of these polymers [211]. Such changes can be expected to affect the polymer-analyte interactions. It is feasible that these changes at the solution/electrode interface may be used to improve analyte collection efficiency and specificity. As such, the effect of applied potential upon both the preconcentration efficiency of sampling electrodes and the sensitivity of sensors has been studied.

To deal with the separate areas covered in this work the thesis has been divided into 3 major sections. Part 1 (chapters 3 and 4) deals with the development of chemically modified electrode sensors for methylmercury and gold respectively. Part 2 (chapters 5 and 6) details investigations into the use of chemically modified RVC for the collection of mercury and gold. Parts 1 and 2 are preceded by chapter 2, dealing with the generation and characterisation of the polymers studied in parts 1 and 2 of the thesis. The third component of this work is dealt with in chapter 7. This chapters deal with the development of ElectroLab, an electrochemical workstation. Specifically, it deals with development of Design-a-waveform, a new waveform definition protocol that may find application in the development of CME based sensors. Finally, chapter 8 reviews the entire work and delineates the conclusions reached.
CHAPTER 2
POLYMER GENERATION AND RVC MODIFICATION

2.1 INTRODUCTION

The generation and characterisation of conducting polymers has been the focus of considerable research effort in the past 10 - 15 years. This work has been driven by the desire to produce "synthetic metals" for utilisation in a diverse range of applications including light weight batteries, electromagnetic shielding, sensing devices, biomedical applications, non metallic electronic circuits and many other applications.

The field of conducting polymer research has its genesis in studies on polysulphur nitride [182], this rather unstable material can be regarded as the first intrinsically conducting polymer, the study of which marked the beginning of this dynamic field of research. Research which was given further impetus with the discovery that polyacetylene could readily be doped from an insulating state to a conductivity approaching that of metals [182, 183]. To achieve this the polymer was first prepared in the dedoped form and then exposed to iodine vapours, other halogens or oxidising agents to induce conductivity in the polymer.

Finally, the report of a useable electrochemical method for the production of a doped, conducting polymer from a solution containing a pyrrole monomer and supporting electrolyte [212] led to the current interest in the preparation of polypyrroles. This work has been quickly followed by studies involving the oxidation of other heterocyclic monomers including thiophenes, furans and indole or aromatic monomers such as phenylene and aniline.
It is those polymers, prepared by the oxidative polymerisation of heterocyclic monomers, that have been the primary focus of this work.

2.1.1 **ELECTROCHEMICALLY GENERATED CONDUCTING POLYMERS**

Since the first report [212] of the useable electrochemical synthesis of a conducting polymer, research in this area has increased rapidly. The most studied of these polymers appears to be those based on pyrrole, with thiophene and aniline based polymers also attracting a great deal of attention.

The oxidation of many other aromatic monomers have also been investigated by various workers. Monomers that have been successfully polymerised include indole [213], furan [214], azulene as well as pyrrole and thiophene [214]. The conductivity of the films formed which varied from $5 \times 10^{-3} \, (\Omega \text{cm})^{-1}$ (polyindole) to $10^2 \, (\Omega \text{cm})^{-1}$ (polythiophene or polypyrrole). Other monomers polymerised include fused thiophene rings [215, 216], benzo-b-thiophene [217], aniline [204, 208, 218, 219], diphenylamine [220], dibenzofuran [221], N-3-thienylphthalimide [222], thianaphthene-indole [223] and many others [152, 224-228]. It should be noted however that most of the polymers mentioned above were studied for their electrical properties only, with little interest in their chemical function.

2.1.1.1 **Polypyrrole**

Although the first preparation of a pyrrole polymer was achieved by Dall Olio et al. [230], it was not until the work of Diaz and co workers, who a decade later carried out the first systematic studies of pyrrole based polymers, that this material attracted significant attention [212, 231-233].

In their first study [212] they found that films grown from acetonitrile had higher conductivity than those grown from aqueous media, although 1% water was added to the acetonitrile solutions to improve both adhesion and uniformity of the films produced.
VoCymer Çeneration and^J/C Modification

The effect of water in the electropolymerisation solutions was later studied by Downard and Pletcher [234] who, like others, confirmed the improved film characteristics. They attribute this to the influence of water on the initial nucleation and growth steps during polymerisation.

Diaz also found that the use of very high current density yielded films with very rough surfaces and recommended ramping the current density from zero to 1 mA.cm\(^{-2}\) over a period of three minutes during the polymer growth. This produced films with improved adherence and morphology. These workers also proposed a mechanism of polymerisation involving \(\alpha-\alpha\) coupling of the pyrrole rings, an observation supported by the fact that monomers substituted in the \(\alpha\) position fail to form films whereas those substituted in the \(\beta\) position are readily polymerised. The incorporation of anions during synthesis was confirmed by elemental analysis, with the ratio of monovalent anion to pyrrole being 1:4, both infrared and Raman spectroscopic studies support this hypothesis.

In subsequent studies Diaz et al. investigated the effect of N substitution of pyrrole on polymer formation [231], this was found to adversely effect film conductivity. Studies of the electrochemistry of \(\alpha\) substituted pyrroles [232] showed that although these monomers were amenable to oxidation they did not form polymer films. In a complementary study Cross et al. [235] investigated the electrochemistry of twelve pyrrole based monomers and the polymers formed from these. The monomers were chosen such that all substituent permutations were studied, ie N substitution, \(\alpha\) substitution, \(\alpha,\alpha\) substitution, \(\alpha,\beta,\beta\) substitution and \(\beta,\beta\) substitution. Their results indicate that it is possible to form films with monomers that were restricted to \(\alpha-\beta\) linkages only, although the films formed exhibited poor conductivity. Monomers restricted to \(\beta-\beta\) coupling were found to form soluble oligomers only.

Mono-\(\alpha\)-substituted pyrroles were found to form films with very low conductivity. This was attributed to the effect of \(\alpha-\beta\) coupling. These observations were taken to indicate that some \(\alpha-\beta\) coupling may be possible in polypyrrole.
Another variable studied by Diaz's group at IBM was the effect of changing the anion present in the electropolymerisation solution [233]. This was found to have significant effect on both the physical and electrical properties of the polymers formed. Again, conductivity provides a suitable yardstick for film performance, with films prepared containing FSO$_3^-$ as the counter ion having a conductivity of 0.01 (Ω cm)$^{-1}$ whereas those prepared from ClO$_4^-$ had conductivities in the range 60-200 (Ω cm)$^{-1}$.

This effect has subsequently been studied by other workers [236-243]. The most recent of these [243] investigated the effect of the anion on film conductivity, smoothness and redox behaviour. These workers varied the anion studied to include chloride, perchlorate, p-toluenesulphonate and mono, di and trisulphonated benzene. They found that 1,3,5 benzotrisulphonate produced films with the highest conductivity whereas chloride and perchlorate films possessed the lowest conductivity. One feature that held true for all anions was that increased current density during polymerisation caused decreased conductivity. The rate of polymer discharge and charge was found to decrease with anion size (for monovalent anions). Similarly, it was found to approach the fastest monovalent behaviour as the charge on the large sulphonated benzene species was increased; i.e. it increased from mono to di to tri sulphonated benzene.

Shimidzu et al. [237] synthesised polypyrrole with an anionic polyelectrolyte as the counter ion. This could not be expelled from the polymer during the reduction process and hence the polymer incorporated cations to maintain electrical neutrality. This formed the bases of a cation exchange membrane.

Other functionalised pyrroles polymerised include 3 substituted pyrroles [244-246], N-methylpyrrole [231, 247, 248], other N substituted pyrroles [209, 232] and 3-methylpyrrole-4-carboxylic acid [249]. The last 2 groups have been used to form anion and cation exchange polymers respectively [209, 249].
2.1.1.2 Polythiophenes

A second group of conducting polymers that have been extensively studied are those based on the thiophene monomer [250-257]. Waltman, Bargon and Diaz reported the electropolymerisation of a series of β substituted thiophenes, many of which formed conductive polymer films [251]. A particularly interesting observation from this study was that 2,2'-bithiophene polymerised at a much lower potential (1.32 V vs SSCE) than thiophene (2.06 V vs SSCE). This effect was further studied by Heinze et al. [258] who found a similar trend for the polymerisation of thiophene, α bithienyl and α quaterthienyl (E_p = 1.9, 1.2 and 0.8 V vs Ag/AgCl respectively). These authors also give evidence from cyclic voltammetric data that the quaterthienyl films have a regular structure (primarily α–α' linkages) and low molecular weight distributions, whereas the thiophene derived films have a complex cross linked structure involving α–α, α–β and β–β linkages. Krische and Zagorska have studied this phenomenon along with other characteristics of polythiophene and polybithiophene [259-261] and attribute increased cross linking to the fact that the thiophene monomer is oxidised at a potential greater than that required to oxidise the polythiophene polymer formed. Thus, the potential for polymerisation leads to the generation of more active nucleophiles, hence more side reactions, and the formation of a partially oxidised polymer [259].

Thiophene is amenable to substitution in the 3 position and the polymerisation of a wide variety of 3 substituted monomers have been studied [251]. Substituents studied include short length alkyl chains [215, 251, 262-265], aromatic substituents [266, 267] ethers [268, 264] and sulphonated sidechains [267, 269]. Two of these proved particularly interesting, the sulphonated monomers possess a flexible anionic side chain which has been shown to self dope the polymer and uptake cations during potential cycling [269]. The ether substituted thiophene has been shown to polymerise to form a poly pseudo-crown ether [270].

2.1.1.3 Electropolymerisation techniques

There are three main modes of electropolymerisation:

**Galvanostatic (constant current) polymerisation**

In this mode a constant current is applied between the working and auxiliary electrodes. The voltage at the working electrode reaches a potential that allows the required current to flow. This potential usually corresponds to that required to oxidise or reduce one or more of the species present in solution. If we consider that the redox reactions occurring must gain or lose electrons to maintain the current flow then it is evident that the reaction rate will be directly effected by the current drawn and that the total charge consumed will be proportional to the amount of active species reacted. Thus, by controlling current, or more specifically current density, it is possible to control the rate of polymer growth and by controlling the total charge passed during polymerisation it is possible to control the amount of polymer formed and hence polymer thickness. The current density affects the surface morphology of the resultant material [271], polymer conductivity [272] and potential drawn during polymerisation.

Another advantage of galvanostatic polymerisation is the ability to obtain qualitative information on the polymer quality during the polymerisation process. This is achieved by monitoring the potential at the working electrode during polymerisation. As soon as the current is applied the potential at the electrode rises to a level required to initiate the nucleation process [271] after which it either continues to rise, indicating that the polymer formed has a significant iR drop across the polymer film, alternatively it may plateau or even decrease a little indicating that there is negligible iR drop across the polymer film.

Galvanostatic polymerisation, although the method of choice in most cases, is not suitable for all applications. This is a particular problem when one solution component is oxidised at a potential less anodic or reduced at a potential less cathodic than that required
VoCymer Çeneration and RVC Modification

To initiate polymerisation. Under these conditions polymerisation can only be achieved by controlled potential techniques.

**Potentiostatic (constant potential) polymerisation**

To achieve potentiostatic polymerisation the potential at the working electrode is set at a predetermined value. This value is usually chosen such that the reaction of interest is occurring whilst undesirable side reactions are minimised.

The hardware required to achieve this is a constant voltage source. This usually takes the form of a potentiostat, although some workers simply apply a DC voltage across the two electrodes. A potentiostatic system provides much better voltage control than that achievable with a simple DC voltage source.

In a potentiostat the voltage difference between the working and auxiliary electrode is set such that the actual potential at the working electrode is maintained at the required value. To achieve this a third electrode, a sensing or reference electrode, is placed adjacent to the working electrode. The potential at the working electrode is monitored with any changes in the working electrode potential being fed back into the control loop. As a result of this the voltage at the auxiliary electrode is altered to restore the working electrode to the required potential. Thus, this system will automatically compensate for any changes in solution conditions that may effect the working electrode.

**Potentiodynamic (sweeping/pulsed potential) polymerisation**

There are some applications where unwanted side reactions occur at potentials much lower than that required to initiate polymerisation. In this case a suitable method of polymer synthesis may be to repeatedly sweep the potential at the electrode past the polymerisation potential and back to a potential at which no unwanted reactions occur. In this way, if the rate of polymerisation is faster than the rate of the unwanted side reaction, polymerisation is achieved and the unwanted reactions are minimised. A feature of controlled potential polymerisation is that the current flow is not regulated. Therefore
there is little control on both reaction rate and total charge consumed, although the latter may be monitored. Hence, properties such as polymer thickness, conductivity and morphology are not readily controlled. This in turn makes obtaining reproducible electrodes a difficult task.

2.1.2 POLYMER CHARACTERISATION TECHNIQUES

To develop reproducible electrode surfaces requires an understanding of the chemistry and physical characteristics of these surfaces. This can only be achieved by accurate characterisation of the polymer surfaces, an extremely difficult task due, primarily to the amorphous nature and intractability of conducting polymers. By far the most widely used tool for characterising conducting polymers is dry state conductivity measurements. This, however, gives no indication of chemical activity of the polymer or of the effect of potential on this activity.

Electrochemical methods have found widespread application in the characterisation of conducting polymers [225, 273-275], scanning electron microscopy has been used to probe the physical structure [233], and X-ray photoemission spectroscopy (XPS) has been used to investigate both the electronic structure and anion content of conducting polymers [193, 276-278].

Other characterisation techniques used include Infra-red spectroscopy [276, 279], Cross Polarisation Magic Angle Spinning NMR Spectroscopy (Solid State NMR) [279], thermogravimetric methods [279, 280] and scanning electrochemical microscopy [281]. Quartz crystal microbalance has been employed to monitor the incorporation and expulsion of ions from polypyrrole during the doping/dedoping cycle under electrochemical control [282, 283].

In the following section of work a brief overview of the various characterisation techniques used in this work will be given.
2.1.2.1 Electrochemical characterisation methods

Electrochemical methods have found extensive application in the characterisation of conducting polymers [225, 273-275]. Cyclic voltammetry [225, 248] has been used to probe both the polymerisation mechanism and redox activity of conducting polymers. AC impedance studies have been used to study the electronic structure and ionic transport in a polypyrrole based polymer [284, 285] and chronoamperometry has found application in the study of doping/dedoping processes of polymers [286].

Cyclic voltammetry

Cyclic voltammetry (CV) is probably one of the most versatile techniques available for the study of redox systems [287] and, as such, is often the method chosen to conduct initial studies of these. In one experiment the researcher is able to determine the potential of the redox reactions of interest and obtain qualitative data pertaining to both the electrochemical reversibility and kinetics of electron transfer for the reactions of interest.

In cyclic voltammetry the potential applied to the electrode is swept repeatedly between two potential limits, with the current flowing at the working electrode being monitored and plotted as a function of applied potential. A cyclic voltammogram for an ideal, electrochemically reversible single electron transfer reaction is shown in Figure 2.1.

![Cyclic voltammogram of an ideal system](Figure 2.1)
There are several terms used in the figure that require definition. The first of these, $E_{pc}$ is the potential at which the reduction reaction occurs. Similarly $E_{pa}$ is the potential at which the oxidation reaction occurs, $i_{pc}$ and $i_{pa}$ are the reduction and oxidation peaks currents respectively. The relative position, magnitude and scan rate dependence of these parameters provide useful insights into nature of the redox couple under investigation [287].

The use of cyclic voltammetry to characterise conducting polymers has been the subject of a number of publications [274, 225]. Using this technique it is possible to determine the potential at which the polymer is reversibly oxidised or reduced, the potential at which irreversible oxidation of the polymer occurs and any changes to the polymer electrochemistry caused by interaction with analyte species in solution.

A typical polypyrrole voltammogram is shown in Figure 2.2. There are two distinct features in the voltammogram that are characteristic of polypyrrole [274]. The first of these is the reversible oxidation of the reduced polymer as the potential is swept from -1000 mV vs Ag/AgCl to the positive limit of 700 mV. The transition commences at -500 mV and is associated with the change in the polymer from the reduced or non-conducting* form to the oxidised or conducting form. This step is electrochemically reversible as can be seen from the second feature, the reduction response seen at -300 to -500 mV on the reverse scan. This redox response has been shown to be due to changes in the oxidation state of the polymer [274, 282, 283] and for polymers incorporating small mobile anions can be represented by equation (2.1).

\[ \begin{array}{c}
\text{Oxidation} \\
\text{Reduction}
\end{array} \]

\[ n_{1} = 3-6 \]  

(2.1)

* It should be noted here that the terms conducting and non-conducting are used in a relative sense, for if the pyrrole was truly non-conducting it would be impossible to electrochemically oxidise the reduced polymer due to its insulating nature.
It can be seen from the previous equation that oxidation of polymer occurs with a concomitant inclusion of anions into the polymer, to maintain electrical neutrality. Conversely, reduction of the polymer is accompanied by the expulsion of counterion, again to maintain electrical neutrality.

For polypyrrole prepared with large immobile counterions the opposite phenomenon is exhibited. Oxidation results in the expulsion of cations from the polymer, whilst reduction is accompanied by the inclusion of cations into the polymer. In both cases the movement of ions is necessary to maintain a charge balance in the polymer [282, 283].

A second use of cyclic voltammetry in conducting polymer research is to characterise the electrochemistry of the monomer chosen for electropolymerisation [213]. From the voltammogram the potential at which monomer oxidation occurs may be determined. This in turn may be used to set the potential limits chosen for the potentiostatic and potentiodynamic polymerisation techniques (see earlier discussion in section 2.1.1.3).
**Chronopotentiometry**

This technique is used to monitor the potential of the working electrode during galvanostatic polymerisation. In brief, it provides a qualitative measure of the conductivity of the polymer formed.

The trends evident in the chronopotentiograms give a good indication of the conductivity of the polymer formed. If the potential drawn at the working electrode remains constant throughout the polymerisation process it can be inferred that the polymer layer adds no extra resistance to the circuit and as such will be conducting. In contrast, if the polymer synthesised at the electrode has a significant resistance it will add to the overall resistance of the electrochemical cell. The changes in resistance will manifest themselves in a chronopotentiogram with a rising potential transient throughout the polymerisation process [197].

There is a significant body of theory relating to the time and current dependence of chronopotentiometric data acquired during galvanostatic experiments [289]. However this theory has been developed to deal with solution responses and is not valid for the case of electropolymerisation. This is because with electropolymerisation we are dealing with deposition onto the electrode, not solution responses.

### 2.1.2.2 Spectroscopic and spectrometric techniques

A number of researchers have investigated the use of spectroscopic and spectrometric techniques for the characterisation of conducting polymers. Optical spectroscopy [231, 246, 290], Raman spectroscopy [231] and infra red spectroscopic techniques [214, 231, 276, 279, 290-293] have all found application in both identifying reagents incorporated into these polymers and monitoring any changes in the polymer.

X-ray photoelectron spectroscopy (XPS) has been used to study anion exchange processes in polypyrrole [193, 294, 295], to probe the structure of polypyrrole [193, 277] and to investigate the interaction of copper with polypyrrole [296]. Finally, mass
spectrometry has been used to characterise polymers, although not conducting polymers. Fragmentation is usually achieved by either fast atom bombardment or field desorption techniques [297]. Only those techniques used in the experimental work are described here.

**Fast atom bombardment mass spectrometry (FAB-MS)**

Fast atom bombardment mass spectrometry is a technique that is extremely useful for the identification of species included in the polymer, particularly cations and anions.

Both positive ion and negative ion spectra of conducting polymers can be recorded. In general the spectra are far too complex to provide definitive information on the polymer structure, the presence of cations in the polymer can be confirmed using this technique. However, the negative ion spectra of these polymers has proven a very useful tool in the identification of anions present in the polymer.

**Scanning electron microscopy/ EDX**

Scanning electron microscopy (SEM) provides an extremely powerful method for the determination of the morphology and surface topography of conducting polymers. Changes in surface morphology brought about by altering polymerisation conditions [212] or altering the anions present during polymerisation [233] have been detected by SEM studies. Electron microscopy has also been used for studies of the comparative morphology of different polymers.

The conductivity of the polymers studied is generally too low to permit direct analysis of the polymer surface without charging problems. Therefore samples are generally coated with a gold layer prior to electron microscopy.

Sample for microanalysis (EDX) are not gold coated prior to analysis. This technique has been used to identify the presence of various elements at the surface of the polymers.
One limitation of this technique is that elements lighter than nitrogen cannot be detected and that the detection limits for some metals is quite poor.

2.1.3 AIM AND SCOPE OF THIS WORK

The objective of this component of the research work has been to determine the appropriate techniques for polymer generation, characterise the polymers formed and, wherever necessary, apply the polymer generation techniques to the modification of RVC.

Preliminary polymerisation studies and electrochemical characterisation of the polymers formed were conducted using either platinum or glassy carbon electrodes. During these studies the electrochemical characteristics of the polymers were determined. Once this was completed the polymers were used for either sensor development or solid phase sampling applications discussed in later chapters.

Whilst there are a number of monomers suitable for electropolymerisation, the focus of this study has been those polymers based upon either pyrrole or thiophenes. Pyrrole based polymers were chosen for these studies because it is possible to polymerise pyrrole in both aqueous and non aqueous solutions. This ability to polymerise the monomer in both types of solution increases the scope for inclusion of reagents into the polymer as the chance of finding a suitable solvent for the required reagent is much greater when either aqueous or non-aqueous systems can be used. Unlike pyrrole, thiophenes can only be polymerised from non-aqueous solutions and as such are more restricted terms of the supporting electrolytes that may be used during polymerisation. Interest in these polymers was primarily due to the claims that they have a more positive working potential limit than polypyrroles [182].
2.2 EXPERIMENTAL

2.2.1 REAGENTS

Unless otherwise stated, all supporting electrolytes were used as received (generally LR or AR grade), all solvents used were analytical reagent (AR) grade and all water used was Milli Q grade deionised water.

Liquid monomers (ie pyrrole, thiophene, furan and 3-methylthiophene) were distilled just prior to use. Typically, approximately 10 mL of monomer was distilled, with the first 1 mL of distillate being discarded. The next 5 - 7 mL of distilled monomer was collected and stored under refrigeration when not in use. All solid monomers were used as received without further pretreatment.

2.2.2 POLYMERISATION SOLUTIONS

Unless otherwise stated, all pyrrole solutions were prepared with a pyrrole concentration of 0.5 M and a salt concentration of 1.0 M. Polymers generated from aqueous solution were prepared using NaCl as the supporting electrolyte unless other electrolytes were used for specific studies. Non-aqueous solutions were prepared using similar monomer and counterion concentrations in acetonitrile solution. 1% v/v water was added to all acetonitrile solutions.

Thiophene solutions were prepared in dry acetonitrile using a monomer concentration of 0.5 M and an electrolyte concentration of 1.0 M. The salts used in the preparation of these supporting electrolytes were dried envacuo prior to use.

3-Methylthiophene solutions were prepared in dry acetonitrile using a monomer concentration of 0.5 M and an electrolyte concentration of 1.0 M. The salts used in the preparation of these supporting electrolytes were dried envacuo prior to use.
2,2'-bithiophene polymerisation solutions were prepared with a monomer solution concentration of 0.5 M and a supporting electrolyte concentration of 1.0 M. All solutions were prepared in acetonitrile.

2.2.3 EQUIPMENT

Voltammetric experiments were performed on either a Bioanalytical Systems (BAS) 100A Electrochemical analyser or a BAS CV 27 voltammograph connected to a Houston 2000 X - Y recorder.

Galvanostatic experiments were performed using either a Princeton Applied Research (PAR) 173 constant current source or a purpose built constant current source (Science Faculty Workshop). Chronopotentiograms were recorded with an ICI DP600 y - t chart recorder.

Scanning electron microscopy and EDX analyses were performed with a JEOL JSM 840 scanning microscope.

Fast atom bombardment mass spectroscopy (FAB-MS) was performed on a VG model MM 12-12 mass spectrometer fitted with a purpose built electrode holder to enable modified electrodes to be placed in the spectrometer sample chamber for analysis.

X-ray photoelectron spectroscopy was performed on a Perkin Elmer Physical Electronics Industries model 551 X-ray photoelectron spectrometer/scanning Auger microprobe spectrometer.

2.2.3.1 Electrodes

Platinum wire electrodes were prepared by sealing 0.5 mm diameter Pt wire in soda glass. Electrical connection was achieved by the use of Wood's metal and copper wire. Electrode length was generally maintained at 1 cm, thus most electrodes had the same surface area; 0.157 cm². Electrodes were pretreated by soaking in chromosulphuric acid.
prior to use. This treatment was also used to remove polymer films after each experiment.

Glassy carbon electrodes used were BAS 3 mm diameter glassy carbon electrodes. These were polished on 0.3 μm γ alumina coated pad and ultrasonicated prior to use. Polymer films were removed by polishing on γ alumina coated pads.

Reference electrodes used were either a BAS Ag/AgCl (3M KCl) electrode, for aqueous work, or a Metrohm Ag/Ag⁺ electrode for non-aqueous work. All reference electrodes were isolated from the working solution by a vycor tipped salt bridge containing the supporting electrolyte being used in the working solution.

Reticulated Vitreous Carbon (RVC) was obtained from Energy Research and Generation (ERG). Cylindrical RVC working electrodes were punched out of the RVC sheet with a laboratory cork borer. The electrodes prepared were 9 mm diameter and 19 mm long. These were initially flushed with acetone to facilitate wetting the surface of the RVC, after which they were flushed with Milli Q water. The wetted electrodes were then boiled for a minimum of 10 minutes in 1:1 HNO₃ to remove any metal contamination present on the surface as a result of the electrode fabrication process. Acid treated electrodes were then rinsed several times with Milli Q water and subsequently stored in Milli Q water.

As these electrodes possess a large surface area a specially designed electrochemical cell was produced for use with RVC electrodes. This cell (Figure 2.3) uses a large surface area platinum gauze cylinder as the auxiliary electrode. This has sufficient surface area to be used with RVC and, as the RVC electrode is located in the centre of the gauze cylinder it is subject to an even electric field at all points on the cylinder surface. This promotes even polymer growth on the RVC.
2.2.4 POLYMER GROWTH

To investigate the polymerisation of the monomers studied and the modification of RVC with these polymers the following experimental protocol was followed:

(i) Using cyclic voltammetry at either a platinum wire or glassy carbon disc working electrode the electrochemistry of the monomer and the monomer oxidation potential were determined.

(ii) Wherever possible galvanostatic polymerisation was used to achieve polymer growth

(iii) Investigate the electrochemistry of any polymer formed to determine the potential window within which the polymer is stable.

(iv) Attempt polymer growth at RVC using constant current conditions

(v) If (iv) is unsuccessful attempt to achieve polymerisation at RVC by potentiostatic techniques.
Polymers produced were studied by cyclic voltammetry and any other relevant characterisation technique as required.

2.3 RESULTS AND DISCUSSION

2.3.1 PYRROLE POLYMERISATION

The polymerisation of pyrrole was extensively studied because this monomer is easily oxidised and polymerisation can be performed in both aqueous and non aqueous media thus allowing a wider range of counterions to be incorporated into the polymers produced.

2.3.1.1 Pyrrole electropolymerisation techniques

Initial studies investigated the polymerisation of pyrrole in acetonitrile with tetraethylammonium perchlorate as the supporting electrolyte. A cyclic voltammogram recorded during pyrrole electropolymerisation is shown in Figure 2.4a. On the first oxidative scan the current begins to increase at 400 mV(vs Ag/Ag⁺), the current continues to rise until the upper potential limit is reached, at which time the scan direction is reversed and the current drawn begins to decrease. The reverse current crosses the forward current forming a hysteresis loop typical of a process involving nucleation and growth [225, 234, 298]. This trend continued with subsequent scans. Formation of the polymer is evidenced by the production of a black deposit on the electrode and the emergence of a CV pattern typical of polypyrrole (Figure 2.4b). An upper potential of 700 mV is required to achieve polymer growth on the electrodes used (Table 2.1).
### Table 2.1 Effect of upper potential limit on polymer formation

<table>
<thead>
<tr>
<th>Potential Upper limit (mV)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>+500</td>
<td>No polymer deposited after 3 cycles</td>
</tr>
<tr>
<td>+700</td>
<td>Small amount of polymer deposited</td>
</tr>
<tr>
<td>+900</td>
<td>Polymer deposited</td>
</tr>
<tr>
<td>+1200</td>
<td>Polymer deposited but over oxidised</td>
</tr>
</tbody>
</table>

**Conditions:**  
$E_{\text{initial}} = -1000 \text{ mV}$; $E_{\text{lower}} = 1000 \text{ mV}$,  
Scan rate $= 100 \text{ mV.s}^{-1}$  
Number of cycles: 3  
Solution: 0.5 M pyrrole, 1.0 M NaClO$_4$ in 99% CH$_3$CN, 1% H$_2$O  
Electrode: Glassy Carbon  
Reference electrode: Ag/Ag$^+$

---

**Figure 2.4** Cyclic voltammogram recorded during polymerisation of pyrrole  

* a) Scan 1  
* b) Scan 7

**Conditions:**  
$E_{\text{initial}} = -1000 \text{ mV}$; $E_{\text{lower}} = -1000 \text{ mV}$;  
$E_{\text{upper}} = 700 \text{ mV}$; Scan rate $= 100 \text{ mV.s}^{-1}$  
Number of cycles: 7  
Solution: 0.5 M pyrrole, 1.0 M NaClO$_4$ in 99% CH$_3$CN, 1% H$_2$O  
Electrode: Glassy Carbon
Constant current (galvanostatic) polymerisation of pyrrole was also investigated as a means of polymer growth. Polymers were produced using current densities of at least 0.1 mA.cm\(^{-2}\) (Table 2.2). The effect of varying the current density on polymer properties was investigated and it was found that, for a given charge consumption, higher current densities produced rougher polymers. This is seen in Figure 2.5 (a - b) which shows the surface topography of 2 polymers grown at differing current densities.

Apart from surface characteristics, all other attributes of the polymers are essentially the same. Table 2.2 lists the effect of current density on the polymerisation of pyrrole and the electrochemical characteristics of the polymer formed.

The potential at the working electrode was monitored during the electropolymerisation experiment and it can be seen from table 2.2 that the increase in current density causes an increase in the potential at the working electrode. This is due to the need to drive the electrode reaction at a greater rate in order to maintain the required current density. Despite the higher final potential reached chronopotentiograms recorded during polymerisation (Figure 2.6) have the same general trend for all current densities.

![Figure 2.5: Scanning Electron micrographs of polypyrrole produced at various current densities](image)

a) 0.25 mA.cm\(^{-2}\)

b) 3.0 mA.cm\(^{-2}\)

(Both polymers synthesised with the same total charge)
They rise initially then settle to a potential which is maintained during the entire electropolymerisation. This indicates that the polymer formed is conductive.

Table 2.2  
Effect of current density on polymerisation of pyrrole*

<table>
<thead>
<tr>
<th>Current Density (mA.cm⁻²)</th>
<th>Time (min)</th>
<th>Polymerisation potential (mV)</th>
<th>Cyclic Voltammetry* Epa   Epc</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>30</td>
<td>380</td>
<td>-250 -810</td>
</tr>
<tr>
<td>0.50</td>
<td>6</td>
<td>380</td>
<td>-360 -860</td>
</tr>
<tr>
<td>1.0</td>
<td>3</td>
<td>400</td>
<td>-300 -790</td>
</tr>
<tr>
<td>2.5</td>
<td>1.2</td>
<td>460</td>
<td>-300 -810</td>
</tr>
<tr>
<td>5.0</td>
<td>0.6</td>
<td>540</td>
<td>-320 -720</td>
</tr>
<tr>
<td>10</td>
<td>0.3</td>
<td>540</td>
<td>-320 -620</td>
</tr>
</tbody>
</table>

*Conditions:  
Polymerisation Solution: 0.5 M pyrrole/1.0 M NaClO₄ 99% CH₃CN, 1% H₂O  
Supporting electrolyte: M NaCl  
Electrode: Pt wire  
# Peak notation as in Figure 2.2

Cyclic voltammograms of the polymer coated electrode indicate that all polymers are oxidised (ie change from insulating to conducting state) at -300 mV. Whereas the reverse reaction, polymer reduction, is achieved at a more positive potential for polymers synthesised at higher current density. This may be due to the fact that for a given quantity of polymer, those polymers grown at a higher current density are more porous and hence have a greater surface area of polymer exposed to solution, therefore the change from the oxidised to reduced state occurs more rapidly.
Figure 2.6 Chronopotentiograms for the polymerisation of pyrrole at various current densities

a) 10 mA cm\(^{-2}\)

b) 0.5 mA cm\(^{-2}\)

Solution 0.5M pyrrole and 1.0M NaCl in H\(_2\)O

The polymerisation of pyrrole from aqueous solutions of pyrrole was also investigated. In all cases polymerisation was achieved galvanostatically from a 0.5 M solution of
pyrrole in water with 1.0 M NaClO₄ as a supporting electrolyte. Chronopotentiograms recorded during polymerisation again indicate that a polymer with adequate conductivity was formed. A cyclic voltammogram recorded after polymerisation shows the typical polypyrrole cyclic voltammogram with well defined oxidation and reduction responses.

Some authors have indicated that growth of polymers from aqueous solution adversely effects their dry state conductivity [234] however, for the purpose of this work no significant differences were seen in the performance of polymer grown from either solutions.

2.3.1.2 Effect of anion on polymer properties

Changes in the physical properties of polypyrrole brought about by varying the anion incorporated during polymerisation, have been the subject of a number of studies [236-240, 242, 243]. This interest has arisen primarily because the parameter of greatest concern to most investigations, conductivity, is dramatically effected by the anion incorporated into the polymer. Reports indicate that the polymer conductivity can vary over 3 or 4 orders of magnitude depending upon the anion incorporated during polymerisation [233, 243]. Polymer electroactivity is also dramatically effected by the anion incorporated into the polymer [237].

Given the significance of the anion in determining both the physical and electrochemical characteristics of polypyrrole a series of experiments were undertaken to ascertain the differences between the polymers to be used in later studies. To achieve this, a number of anions were studied, in all cases the sodium salt was used in electrolyte preparation and polymerisation was conducted using aqueous solutions of the desired anions.

The first characteristic of interest was the effect of the anion on the polymerisation process. This was determined in a similar manner to the cation studies with the polymerisation of each solution being achieved using galvanostatic techniques at a current density of 0.5 mA.cm⁻². In contrast to the cation study, the various anions investigated
caused significantly different polymerisation potentials to be drawn at the electrode during polymer growth. These data (Table 2.3) indicate that the larger organic anions, for example salicylate, require a higher polymerisation potential than the smaller inorganic anions such as chloride.

Table 2.3  
Polymerisation potential and CV data for polypyrrole prepared with various anions

<table>
<thead>
<tr>
<th>Anion</th>
<th>Polymerisation potential (mV)</th>
<th>Cyclic Voltammetry data*</th>
<th>ΔE†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>E_{pa} (mV)</td>
<td>i_{pa} (µA)</td>
</tr>
<tr>
<td>Cl⁺</td>
<td>580</td>
<td>-100</td>
<td>83</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>530</td>
<td>-19</td>
<td>154</td>
</tr>
<tr>
<td>SDS⁻</td>
<td>580</td>
<td>-375</td>
<td>138</td>
</tr>
<tr>
<td>Sal⁻</td>
<td>640</td>
<td>433#</td>
<td>38</td>
</tr>
<tr>
<td>BF₄⁻</td>
<td>530</td>
<td>-66</td>
<td>123</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>520</td>
<td>-22</td>
<td>207</td>
</tr>
<tr>
<td>CH₃COO⁻</td>
<td>4280</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Conditions: As in Table 2.3

# Oxidation peak broad and indistinct - value indicative only

† A measure of peak-peak separation between E_{pa} and E_{pc}

Cyclic voltammograms recorded for each polymer also exhibit significant differences in voltammetric responses. This is evident in both the shape and potential of the redox changes in the cyclic voltammograms. The chronopotentiogram for polypyrrole-salicylate (Figure 2.7) shows an increase in potential throughout the polymerisation process and the resulting voltammogram is very poorly defined with broad oxidation and reduction peaks. Whereas Polypyrrole chloride has a chronopotentiogram that remains constant throughout polymerisation and the polymer voltammogram is well defined with distinct redox peaks attributable to the polymer switching between the oxidised to reduced form as shown in Figure 2.8.
Chronopotentiogram and cyclic voltammogram of polypyrrole/salicylate showing reduced electroactivity

**Figure 2.7**

**Conditions:**

- a) current density = 0.5 mA.cm$^{-2}$
- b) $E_{\text{lower}} = -1000$ mV  $E_{\text{upper}} = 700$ mV  Scan rate = 100 mV.s$^{-1}$
- Supporting electrolyte: M NaCl
Thus, cyclic voltammetry and chronopotentiometric data indicate that the anion present during polymer synthesis has a marked effect on the properties of the polymers produced, particularly the electroactivity of the resultant polymer. This in turn may have
an effect on the applicability of a particular polymer to a sensing or sampling application and as such this aspect must be borne in mind when choosing polymers for these particular applications.

The second aspect of this study was to ascertain the effect of the anion used during polymerisation on the resulting surface morphology of polypyrrole. This has been well documented by other authors. Therefore, the object of this investigation was to gain an appreciation of the differences between the polymers studied and the potential impact of these differences on sampling and sensing applications. Electron microscopy was used to determine the surface characteristics of the polymers studied. The electron micrographs recorded are shown in Figure 2.9 (a-f) respectively and indicate significant variations in the surface morphology of the polymers produced.

From these Figures it can be seen that the polymers produced containing either Cl\textsuperscript{-} or BF\textsubscript{4}\textsuperscript{-} as the counterion have very similar surface morphology, typified by an underlying bulk phase that exhibits a moderate degree of granularity. This phase is covered with a moderate density of nodular outbursts of polymer growth, this is probably slightly greater in the case of the BF\textsubscript{4}\textsuperscript{-} polymer.

Polypyrrole/NO\textsubscript{3}\textsuperscript{-} has a slightly less granular surface and a lower density of the nodules. The polypyrrole/ClO\textsubscript{4}\textsuperscript{-} polymer has a relatively smooth surface that is essentially devoid of any granularity. However, the nodular outbursts of polymer growth are still present on the surface of this polymer, albeit at a lower density than on the previous 3 polymers.
Figure 2.9  Electron micrographs of polypyrrole synthesised in the presence of
a) NaCl   b) NaNO₃  c) NaSO₃
d) NaSalicylate e) NaBF₄  f) NaClO₄
2.3.1.4 Polypyrrole functionalisation

The desire to produce polymers functionalised with specific chemically active groups has meant that a number of synthesis routes have been investigated in order to produce polymers functionalised with the appropriate reagents.

The techniques used can be classified into two groups:

1. those that achieve functionalisation during polymer synthesis and;
2. those that use post synthesis derivatisation techniques to incorporate the desired functional group into the polymer.

Both techniques have been investigated as means of preparing modified electrodes in this work.

**Polypyrrole: functionalisation during synthesis**

Previous studies [197, 236-238] have shown that the anion present in the polymerisation solution during polymer growth is incorporated into the resulting polymer. Thus, the simplest route to producing polymers incorporating specific reagents is to ensure that these reagents are the anions present in the polymerisation solution.

Table 2.4 lists some of the combinations of supporting electrolytes and solvents investigated throughout this study. Also listed in this table is the polymerisation technique investigated to achieve polymer growth and some observations of the polymer characteristics.

The electrolyte used were chosen to provide a counterion for incorporation during the polymerisation process that would impart specific chemical properties to the polymer. In particular anionic complexing agents were used because these are amenable to inclusion as a result of their anionic charge. The specific use and evaluation of RVC cartridges modified with these polymers is dealt with in the following chapters. A number of polymers listed in this table were not used in further studies, primarily because the
modification of RVC with these polymers was not possible. The discussion of several of these is warranted here.

The incorporation of the dithiocarbamate anion into polypyrrole is of particular interest, as the dithiocarbamates are known to form stable complexes with a significant number of metals [57]. Solid phase adsorbents utilising the dithiocarbamate moiety have also found widespread use in the collection of metals from aqueous samples (see 1.1.2.3).

In order to ascertain whether it is possible to use electrochemically enhanced techniques to improve the collection efficiency of the dithiocarbamate group it was necessary to produce polymers containing various dithiocarbamates. However, as can be seen from Table 2.4, it was not possible to form polymers when dithiocarbamates were present. This is due to the fact that the dithiocarbamate is oxidised at a potential lower than that required for pyrrole oxidation.

Dithiocarbamates are known to oxidise to thiuram disulphide according to:

\[
2 \text{R}_1\text{N} \text{C}(-\text{S})_2 \xrightarrow{\text{Oxidation}} \text{R}_1\text{N} \text{C}(-\text{S})_2 \text{S} \text{S} \text{C}(-\text{S})_{\text{R}_1} \quad (2.2)
\]

The oxidation potential of a number of dithiocarbamate salts was investigated and is given in Table 2.5. As can be seen from these data in all cases the potential required to oxidise the dithiocarbamate to the corresponding thiuram disulphide is lower than that of pyrrole oxidation. However, as this oxidation potential approaches the pyrrole oxidation potential the chance of polymer formation increases. For example Zn(HDTC)\text{3$^-$} is oxidised at 560 mV and can be used to form polymers at platinum wire electrodes. These polymers can only be prepared by potentiodynamic methods, are rather patchy and have poor electrochemical properties but this example is a useful indication of the approach necessary to directly incorporate dithiocarbamate ligands into polypyrrole.
**Table 2.4**  
**Supporting electrolyte/solvent combinations investigated for pyrrole polymerisation**

<table>
<thead>
<tr>
<th>Electrolyte#</th>
<th>Solvent</th>
<th>Polymerisation* technique</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>LiCl</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>CsCl</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>NaSdS</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>NaClO₄</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>NaSalicylate</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>NaNO₃</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>Nadtc</td>
<td>H₂O</td>
<td>PS/G</td>
<td>No polymer due to oxidation of the dithiocarbamate.</td>
</tr>
<tr>
<td>mpa</td>
<td>H₂O</td>
<td>PD</td>
<td></td>
</tr>
<tr>
<td>Oxalic Acid</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>TBABF₄</td>
<td>CH₃CN</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>Zn(BHDC)₃⁻</td>
<td>MeOH/H₂O</td>
<td>PS/G</td>
<td>Patchy Polymer.</td>
</tr>
<tr>
<td>K₃Fe(CN)₆</td>
<td>H₂O</td>
<td>PD</td>
<td></td>
</tr>
<tr>
<td>NaBF₄</td>
<td>H₂O</td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>NaClO₄/Quinone</td>
<td>H₂O</td>
<td>PD</td>
<td>Presence of quinone confirmed by Cyclic Voltammetry</td>
</tr>
<tr>
<td>HgCl₂</td>
<td>pyridine</td>
<td>PD</td>
<td>only on Pt wire</td>
</tr>
</tbody>
</table>

*G = galvanostatic polymerisation, PS = potentiostatic polymerisation, PD = potentiodynamic polymerisation  
#mpa = mercaptopropanoic acid, sds = sodium dodecylsulphate, TBA = Tetrabutyl ammonium, Nadtc = sodium diethyldithiocarbamate, Zn(BHDC)₃⁻ = Zinc (bis 2 hydroxydiethyl dithiocarbamate) anion.
For sampling purposes the use of other metal dithiocarbamate complexes, except cadmium, is precluded both because of the relative stability of these complexes and because zinc is one of the few metals to form anionic dithiocarbamate complexes. Zinc dithiocarbamates are known to be relatively labile and the zinc ion is readily displaced by most metals. Cadmium dithiocarbamates were not used because the sampling of Cd\(^{2+}\) from aqueous systems was a potential use for the modified electrodes produced. Other metals are not as easily displaced which would mean that any dithiocarbamate incorporated would not be readily available for metal collection.

The incorporation of metallic mercury centres into polypyrrole was achieved by polymerising the pyrrole monomer from a solution containing Hg\(^{2+}\) ions. It was not possible to achieve this in aqueous solution as the mercury salts used were sufficiently strong oxidants to cause spontaneous polymerisation in solution.

The use of pyridine as a solvent enabled the combination of Hg\(^{2+}\) and pyrrole without the formation of a polymer. Using this solution it was possible to achieve polymerisation by
the potentiodynamic technique. The potential limits used were such that on the oxidative
cycle monomer oxidation could occur, as would the oxidation of metallic mercury that is
on the electrode surface. During the reductive scan mercury (II) ions are reduced and
deposited onto the polymer surface.

The judicious choice of potential limits and scan rate enable the deposition of a
polypyrrole layer into which centres of metallic mercury are dispersed. This is confirmed
by the cyclic voltammogram of the polymer which has a mercury response
superimposed onto a typical polypyrrole voltammogram. The polymer formed by this
technique combines the electrochemical activity of mercury with the added advantages of
polymer electrodes. However, the potentiodynamic preparation technique renders it
unsuitable as a means of RVC cartridge modification.

Whilst the examples shown above demonstrate the feasibility of incorporating functional
groups into the polymer during the polymerisation process it is also evident from this
work that there are instances where this approach is not suitable. To achieve the desired
polymer functionalisation and alternative approach is required. Such an approach is post
synthesis functionalisation.

**Polypyrrole: post synthesis functionalisation**

The need to investigate the use of post synthesis reactions as a means of modifying
polypyrrole came about as a result of the inability to directly incorporate various
dithiocarbamate groups into the polymer. As stated earlier, the reason for this was
investigated and it was found that in all cases the dithiocarbamate oxidation potential was
significantly lower than that required to oxidise the pyrrole monomer (500 - 700 mV).
Thus, an alternate method for the production of polypyrrole-dithiocarbamate electrodes
was required.

To achieve this two approaches were investigated. The first involved utilising the anion
exchange capabilities of the polymer to exchange the anion incorporated during
polymerisation for a dithiocarbamate anion. This was achieved by soaking cartridges in saturated solutions of the required anion.

The second approach involved the post-synthesis chemical derivatisation of the polymer backbone. This approach has been used previously for sensor application [201] but has not been used in metal sampling with polypyrrole, although it is similar to the approach normally employed for the generation of dithiocarbamate functionalised resins.

**Ion exchange derivatisation**

Conducting polymers are known to incorporate anions during polymerisation [233, 241, 243], various studies have also shown that this anion in expelled when the polymer is reduced from its conducting to non-conducting state [300]. In this work the use of this phenomenon was investigated to ascertain whether dithiocarbamates could be exchanged under electrochemical control. It was also desirable to achieve ion exchange by non-electrochemical methods and the effect of simply soaking the electrodes in saturated dithiocarbamate solution was studied.

Initial investigations focused on the general aspects of the ion exchange phenomenon. From these studies it was found that it was possible to use ion exchange to replace the chloride in the polymer with a dithiocarbamate anion.

Given that it is possible to exchange the chloride anion for a dithiocarbamate anion the next investigations were aimed at determining the possibility of carrying out this ion exchange reaction without applied potential. This reaction is thought to occur through the displacement of the chloride anion, incorporated into the polymer during synthesis, with the diethyldithiocarbamate anion from solution. This process may be depicted schematically by the following equation:
This was achieved by soaking polypyrrole electrodes in a saturated dithiocarbamate solution for various times. Table 2.6 lists the results of this investigation, it can be seen that the dithiocarbamate anion is exchanged into the polymer and that the time required to achieve a significant level of exchange into polypyrrole is several hours, thus for all sampling applications PP/RVC cartridges were soaked in the saturated dithiocarbamate solution for a minimum of 24 hours.

Table 2.6  
Dithiocarbamate oxidation response at various soaking times for PP electrodes

<table>
<thead>
<tr>
<th>time (min)</th>
<th>Dithiocarbamate oxidation response (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Not detected</td>
</tr>
<tr>
<td>15</td>
<td>1.6 x 10^{-5}</td>
</tr>
<tr>
<td>30</td>
<td>3.8 x 10^{-5}</td>
</tr>
<tr>
<td>60</td>
<td>5.8 x 10^{-5}</td>
</tr>
<tr>
<td>120</td>
<td>3.6 x 10^{-4}</td>
</tr>
</tbody>
</table>

* Conditions: Polypyrrole Electrode soaked in saturated Na₂dtc CV in MnNO₃  
E_{initial} = 0 mV; E_{lower} = -1000 mV  
E_{upper} = 700 mV  
Scan Rate = 100 mV.s⁻¹
Electrochemical investigation of the derivatised electrodes shows two significant features. The first, seen on the forward scan, is the oxidation of the incorporated dithiocarbamate. This oxidation peak is seen at 285 mV was attributed to the oxidation of the dithiocarbamate anion. This potential is close to that seen for the oxidation of the free dithiocarbamate (Table 2.5). If however a negative going scan is performed first a significant reduction peak is seen at approximately ~800 mV. This peak corresponds to the expulsion of the dithiocarbamate anion from the polymer. This has been confirmed by adding Cu$^{2+}$ to a solution in which a PP/dtc electrode had been cycled. The solution turned bright yellow characteristic of the presence of the copper dithiocarbamate complex. This characteristic has since been developed into a device for the controlled release of dithiocarbamate [184]. For sampling applications however, this restricts the negative potential that may be applied to PP/dtc to approximately ~800mV. This approach proved quite successful for the incorporation of several dithiocarbamate anions (Table 2.7). The specific applications of the dithiocarbamate derivatised electrodes will be discussed in chapter 5.

Table 2.7  Dithiocarbamate anions incorporated by ion exchange

<table>
<thead>
<tr>
<th>Dithiocarbamate Incorporated</th>
<th>Salt used</th>
</tr>
</thead>
<tbody>
<tr>
<td>diethyldithiocarbamate</td>
<td>Sodium Salt</td>
</tr>
<tr>
<td>bis-2-hydroxydiethyldithiocarbamate</td>
<td>Ammonium salt</td>
</tr>
<tr>
<td>pyrrolidine dithiocarbamate</td>
<td>Ammonium salt</td>
</tr>
</tbody>
</table>

Confirmation that the dithiocarbamate was incorporated was achieved by FAB-MS, Figure 2.10 shows the FAB-MS spectrum for diethyldithiocarbamate incorporated into polypyrrole.
Chemical derivatisation

An alternate approach to electrode derivatisation involved the functionalisation of the polymer backbone to produce a polymer that has the dithiocarbamate group grafted to the polymer backbone. Secondary amines are known [301] to undergo reaction with alkaline carbon disulphide according to:

$$R_1NH_2 + 2CS_2 \rightarrow R_1N=C=S + 2CS$$

(2.4)

This approach has been used to produce sensors for mercury determination [201, 288, 302] and as the first step in the production of a novel mercury thin film electrode [303]. In this work we have used the synthesis conditions reported by Imisides and Wallace [201] to produce dithiocarbamate derivatised polypyrrole electrodes.
One significant advantage of this approach is that the dithiocarbamate group is securely attached to the electrode surface and is not expelled at negative potentials, thus offering a more negative potential limit for the polymer use. The addition of copper into a solution in which this electrode had been cycled gives no evidence of the presence of dithiocarbamate in solution.

23.1.5 Polymerisation of pyrrole onto RVC

The synthesis of polypyrrole at planar glassy carbon and platinum wire electrodes has been demonstrated in the previous section. However, these electrodes do not possess sufficient surface area to be useful for sampling purposes. Therefore, polymerisation onto a RVC support was investigated as a means of producing large surface area modified electrodes.

Polymerisation onto RVC provides a number of challenges, caused primarily by the physical properties of the substrate. The large surface area to volume ratio of the RVC dictates that very large surface area auxiliary electrodes are used during polymerisation and the 3 dimensional nature of the electrode causes difficulties in obtaining even potential/charge density over the entire electrode surface. As such, the polymerisation of monomers onto RVC has been dealt with as a separate issue to the formation of polymers on platinum or glassy carbon.

This study was carried out using RVC cartridges in the electrochemical cell described previously (2.2.3.1) and a solution of pyrrole in acetonitrile/water(99:1) with NaClO₄ as the supporting electrolyte. Initial studies focused on the use of potentiodynamic polymerisation techniques. This approach was quickly abandoned as the uneven voltage profile across the cartridge resulted in the deposition of an uneven polymer layer. Electrodes coated in this manner tended to have dense polymer coatings on the outer surface of the cylinder with little or no polymer at the centre of the cartridge.
Galvanostatic polymerisation proved to be much more successful, producing RVC electrodes with an even coating of polypyrrole on all surfaces. Chronopotentiograms recorded during polymerisation (Figure 2.11) indicate that a conducting layer is being formed. The modification of RVC with polypyrrole generated from aqueous systems was also achieved using galvanostatic polymerisation, the polymers formed were uniform and conducting.

The presence of pyrrole on the surface of the electrode can be confirmed visually by the fact that the derivatised electrode appears matt black whereas the non-derivatised RVC has a black/grey appearance.

![Chronopotentiogram for the polymerisation of pyrrole at RVC electrode](image)

**Figure 2.11 Chronopotentiogram for the polymerisation of pyrrole at RVC electrode**

- Conditions: 20 mA; 10 min polymerisation
- Solution: 0.5 M pyrrole and 1.0 M NaCl in H₂O

Electron microscopy also confirmed the presence of the polymer on the electrode surface. Figure 2.12a shows the electrode surface photographed at 50 times magnification. The presence of fibrous polymer growths at some places on the electrode is clearly evident. A photograph taken at 10,000 times magnification (Figure 2.12b) shows a polymer morphology very similar to that seen for PP/ClO₄⁻ on glassy carbon.
All attempts to synthesis polymers onto RVC by potentiodynamic or potentiostatic techniques failed with the polymerisation inevitably occurring at the outside of the cartridge only.

2.3.2 THIOPHENE POLYMERISATION

The polymerisation of various thiophenes has also been the subject of a number of studies [250-257]. It was felt that the higher anodic potential limit available with this group of polymers may offer advantages in sampling applications, particular for those applications requiring higher positive potentials to achieve analyte collection.

2.3.2.1 Thiophenes: electropolymerisation techniques

As with the pyrrole based systems, both potentiodynamic and galvanostatic polymerisation protocols were attempted with each monomer studied. The results of these studies are detailed in the following sections.

Thiophene polymerisation

The polymerisation of thiophene was studied and it was found that in solutions containing 0.5 M thiophene polymerisation could only be achieved at potentials greater
than 1500 mV (vs Ag/Ag+). If the thiophene concentration was decreased to 0.1 M the potential required to achieve polymerisation was increased. This dependence of polymerisation potential on thiophene concentration has been reported previously [260, 261, 304].

The potential required to achieve thiophene polymerisation is significantly greater than that required to oxidise the polymer formed. This phenomenon, known as the thiophene paradox [261], causes the polymers formed to have poor electrochemical properties. It was felt that this would lead to a lack of reproducibility in sensor generation. Consequently, thiophene was deemed to be unsuitable for this application.

3-Methylthiophene polymerisation

Given that thiophene was unsuitable for electrode modification the polymerisation of 3-methylthiophene was investigated as an alternate route to thiophene based CMEs. Various reports [262, 305] indicate that the oxidation potential of this monomer is significantly lower than that of thiophene and hence the thiophene paradox may be avoided. To study this a cyclic voltammogram of 3-methylthiophene in CH₃CN was recorded and it was found that monomer oxidation commences at 1200 mV (Figure 2.13). At potentials above this, black polymeric films were seen to form on the electrode surface. The presence of the polymer layer was also confirmed by the appearance of a voltammetric response for poly(3-methylthiophene) in the polymerisation cyclic voltammogram (Figure 2.13).
Further investigations showed that potentials greater than 1500 mV were required to achieve potentiostatic polymerisation. The polymers formed by this method showed poor adherence and uneven coverage.

The potentiodynamic polymerisation of 3-methylthiophene was subsequently investigated and it was found that polymerisation could be achieved by cycling the potential applied to the electrode between 0 and 1700 mV at a scan rate of 100 mV.s\(^{-1}\). This was typically continued for 10 - 20 cycles during which a relatively even polymer layer was formed on the electrode surface. Galvanostatic polymerisation of 3-methylthiophene was also studied and it was found that polymerisation could be achieved providing the current density was greater than 10 mA.cm\(^{-2}\). However, if care was taken to remove all traces of water from the polymerisation solution it was possible to achieve consistent polymerisation at 5 mA.cm\(^{-2}\) current density.
As was the case with thiophene, the potential required to achieve polymerisation was
greater than the potential that caused irreversible damage to the polymer once formed.
Consequently, the use of poly(3-Methylthiophene) as an electrode modifier was not
studied any further.

2,2'-Bithiophene polymerisation

The implication of the high oxidation potential required for the polymerisation of either
thiophene or 3-methylthiophene is that these polymers are not suitable for use in sensing
applications. An alternate route to the generation of a thiophene based CME is to
polymerise the thiophene dimer 2,2'-bithiophene.

The polymerisation of the thiophene dimer, 2,2'-bithiophene has been reported in the
literature and it has been shown to be oxidised at a potential significantly lower than that
required to polymerise thiophene [251, 258]. Therefore, polymerisation of this monomer
may be a suitable route to the preparation of polythiophene modified electrodes.

Studies of the electrochemistry of 2,2'-bithiophene show an increase in the oxidation
current commencing at approximately 700 mV vs Ag/Ag+ (Figure 2.14 scan1) the
current continues to increase as the potential is swept to the positive potential limit.
During this period polymer growth was observed at the electrode. This was evidenced
by the appearance of a deep red polymer on the surface of the Pt wire electrode. As the
potential is swept from the positive limit back to the starting potential the voltammogram
crosses over itself, this is characteristic of polymer nucleation and growth at the
electrode. The reverse scan also has a reduction peak at approximately 300 mV (Figure
2.14) attributable to the reduction of polymer formed on the electrode. Subsequent scans
(Figure 2.14 scans 2 and 3) exhibit a polymer oxidation peak at 550 mV, along with an
increase in magnitude of the 300 mV reduction peak as the amount of polymer on the
electrode surface increases.
Given the relatively low oxidation potential of 2,2'-bithiophene, galvanostatic polymerisation techniques were investigated. The results of this study are given in Table 2.7 and indicate that polymerisation is successfully achieved at a current density of 0.1 mA.cm⁻², however a current density of 0.5 mA.cm⁻² was used for all further work.

<table>
<thead>
<tr>
<th>Current Density (mA.cm⁻²)</th>
<th>Time (min)</th>
<th>Polymerisation potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>30.0</td>
<td>670</td>
</tr>
<tr>
<td>0.25</td>
<td>12.0</td>
<td>750</td>
</tr>
<tr>
<td>0.50</td>
<td>6.0</td>
<td>780</td>
</tr>
<tr>
<td>1.00</td>
<td>3.0</td>
<td>710</td>
</tr>
<tr>
<td>5.00</td>
<td>0.6</td>
<td>800</td>
</tr>
</tbody>
</table>

*Conditions:
Polymerisation Solution: 0.5 M 2,2'-bithiophene & 1.0 M NaClO₄ in acetonitrile
Working Electrode: Glassy carbon
Reference electrode: Ag/Ag⁺

Figure 2.14 Potentiodynamic polymerisation of 2,2'-bithiophene

Conditions:  
\[ E_{\text{initial}} = 0 \text{ mV} \quad E_{\text{lower}} = -1000 \text{ mV} \]
\[ E_{\text{upper}} = 800 \text{ mV} \quad \text{Scan rate} = 100 \text{ mV.s}^{-1} \]
Solution: 0.1 M 2,2'-bithiophene 0.15 M TBATFB in CH₃CN
To determine the potential range over which this polymer may be used in aqueous systems a C.V. of the polymer modified electrode in M NaCl was performed. This is
shown in Figure 2.15. From this figure it can be seen that as the upper potential applied to the polymer is increased to 1000 mV or greater, irreversible damage to the polymer occurs. This feature is evident in Figure 2.15(b) where a loss of electroactivity is seen on the second scan. By maintaining the upper potential limit to 800 mV the polymer does not undergo any noticeable irreversible oxidation, as seen in Figure 2.15(a).

2.3.2.2 Polymerisation of thiophenes onto RVC

The generation of poly(3-methylthiophene) on RVC has proven to be difficult, as potentiostatic polymerisation caused the polymer to form at the centre of the cartridge whereas potentiodynamic coating techniques tended to coat only the outer edges of the cartridge. The only way to produce some form of poly(3-methylthiophene) cartridges is to use potentiodynamic methods for an extended period, the cartridges are coated but the coating is uneven.

The only thiophene based polymer that has proven suitable for coating RVC is poly(2,2'-bithiophene). This is because polymerisation can be achieved at a constant current density. The polymers produced appear to coat the RVC cartridge evenly and are prepared at a potential that does not significantly damage the polymer during growth.

2.4 CONCLUSION

The preceding studies have confirmed that electrochemical synthesis of polypyrrole is readily achieved from both aqueous and acetonitrile solutions of pyrrole and an appropriate supporting electrolyte. It has also been shown that, provided galvanostatic polymerisation is used, RVC is readily coated with polypyrrole from either solution.

Studies investigating the effect of the anion present in the polymerisation solution have shown that the anion present in the polymerisation solution has a significant effect on the polymer morphology, the polymerisation process and the electrochemistry of the
resultant polymer. The incorporation of different counterions during polymerisation is a possible route to the preparation of chemically modified electrodes, however the utility of this approach is limited by the oxidation potential required for polymerisation. If this is greater than the oxidation potential of the counterion then polymerisation is not possible. If this is the case, an alternate route to the incorporation of the required functional group is through the preparation of a polymer with a readily exchangeable counterion. Derivatisation is then achieved by post synthesis ion exchange with an appropriate anionic reagent.

Studies of thiophene and 3-Methylthiophene based polymers have shown the disadvantage of using these polymers is the high oxidation potential required for polymerisation. This means that in most cases polymerisation can only be achieved by controlled potential techniques. This in turn limits the reproducability of the CMEs prepared by this technique. Also, the potential required for polymerisation causes irreversible damage to the polymer that is formed.

The only thiophene based monomer of those studied, found to be readily polymerised by galvanostatic techniques was 2,2'-bithiophene. The expected advantages of a higher positive potential limit were not realised when using this polymer as it had a positive potential limit of 800 mV (c.f. 700 mV for polypyrrole). A comparison of the preparation of CMEs with either thiophene or pyrrole based polymers has shown that pyrrole provides a more flexible route to electrode modification. This is primarily due to the fact that pyrrole is polymerised at low potentials and that polymerisation can be achieved from both aqueous and non-aqueous solutions.

Finally, this work has shown that whereas RVC cartridges may be coated by potentiostatic techniques, the most effective means of depositing conducting polymers onto the surface of the RVC cartridges are galvanostatic methods. As such the only two monomers studied that can be considered suitable for use in the derivatisation of RVC cartridges are pyrrole and 2,2'-bithiophene.
CHAPTER 3
DETERMINATION OF METHYLMERCURY USING CHEMICALLY MODIFIED ELECTRODES

3.1 INTRODUCTION

The impact of mercury on the environment and the determination of mercury in a variety of matrices is a topic that has been the focus of considerable attention in the past few decades [308, 309]. Whilst the determination of inorganic mercury compounds has received a great deal of attention it has been the detection and quantitation of organomercury compounds, particularly methylmercury, that has been the focus of a significant proportion of work. This is because methylmercury is by far the most toxic commonly occurring form of mercury [310].

Anthropogenic sources of methylmercury are rare [72], and much of the methylmercury present in contaminated sites has arisen from bacterial methylation of inorganic mercury [311]. It has been stated that acidic conditions favour this methylation reaction, thus lakes and waterways that are subject to both acid rain and mercury contamination are likely to have high levels of methylmercury. There have been reports of "pristine" lakes in Canada, Scandinavia and the U.S. having unacceptably high levels of methylmercury. Fish caught from these lakes have levels of methylmercury far in excess of the permissible limits [309]. The source of mercury in these lakes is thought to be industrial fallout which, when accompanied by acid rain, leads to the formation of methylmercury in the affected waterways.

The concern with organomercuries, primarily methylmercury, is the ease with which they enter the food chain through aquatic organisms to fish then higher animals, and
their persistence once there. Thus considerable effort has been spent in determining methylmercury levels in waters.

3.1.1 MERCURY AND METHYLMERCURY DETECTION

The determination and speciation of mercury compounds provides a challenging problem for the analyst. A wide range of methods have been used for both detection and speciation of mercury, with varying degrees of success. Cold vapour atomic absorption spectroscopy (CVAAS) has been used extensively for inorganic mercury analysis [71, 72, 76, 312, 313]. Modification of the mercury reduction step has allowed the determination of total mercury. The difference between total and inorganic mercury levels is subsequently attributed to organomercury compounds [71, 72]. A problem with this approach, however, is that organomercury usually accounts for a small percentage of the total mercury content and as such, errors in the organomercury measurement may be significant. Secondly, such an approach gives an indication of total organomercury content but gives no indication of species present. Derivatisation followed by solvent extraction and graphite furnace atomic absorption spectroscopy has also been used to quantify and speciate mercury [314], but it too suffers from the same shortcomings as the CVAAS approach.

A more suitable method appears to be the use of a chromatographic techniques for the separation and detection of organomercury compounds. Gas chromatography (GC) has been used to separate methyl, ethyl and phenyl mercury species, with detection being achieved by an electron capture detector [76, 314-316]. Greater selectivity and sensitivity in the detection step has been achieved using a mercury specific detector, microwave induced plasma emission spectroscopy (MIP). This detection system, first described by Lichte and Skogerboe [317], provides a sensitive interference free detection method that, when coupled with cold vapour generation, has a reported theoretical limit of detection (LOD) of $3 \times 10^{-17}\text{g}$ of mercury with a practical limit of detection of $10^{-14}\text{g}$ of mercury [317a]. The use of GC to separate the various mercury
species prior to introduction into the plasma has proven very useful and has been applied to the determination of methylmercury in fish and shellfish [313]. When preceded by preconcentration, derivatisation and headspace chromatography, the determination of methylmercury in water has been achieved by GC - MIP [72]. The detection limits quoted for this GC - MIP technique is in the sub picogram level [318].

There has been some concern expressed in the literature regarding the degradation of organomercury species at the elevated temperatures used for the GC separation [319 and references cited therein]. This degradation results in either the formation of new organomercury compounds or the breakdown of these compounds to mercury. To circumvent this problem some authors have investigated the use of high performance liquid chromatography (HPLC) for mercury speciation studies. Methyl, ethyl and phenyl mercury salts have been separated, as their dithiocarbamate complex, by reverse phase chromatography with UV absorbance detection at 254 nm [319-323]. The limit of detection of these methods is poor by comparison with the preceding methods and at best is in the high ppb levels [323].

The use of CVAAS detection following LC separation improves the LOD to the low ppb level [324, 325]. Cold vapour generation inductively coupled plasma atomic emission spectroscopy (ICPAES) has also been coupled with HPLC giving a LOD for inorganic, methyl, ethyl and phenyl mercury of 35, 37, 62 and 62 ng.mL⁻¹ respectively [326]. This approach was further improved by the use of ICP-mass spectrometry for mercury detection after chromatographic separation with a LOD for methylmercury of 1.2 ng.mL⁻¹ [327]. To achieve such sensitivity requires the modification of an extremely expensive and complicated instrument. However, similar LODs can be achieved at considerably less expense using electrochemical detection following the chromatographic separation.

MacCrehan and Durst [328] first demonstrated the suitability of "charge neutralisation reverse phase" chromatography for the separation of methyl, ethyl, phenyl and
inorganic mercury. In their work, detection was achieved by reductive differential pulse amperometry at a gold amalgamated mercury electrode (GAME). The limit of detection for this method was quoted as 2 ng.g\(^{-1}\) for methylmercury. Holak [325] adapted this method to determine methylmercury in fish, however, he used DPV at a hanging mercury drop electrode as the detection technique and was only able to achieve a 10 ng.g\(^{-1}\) detection limit.

Evans and McKee [329, 330] further optimised the method proposed by MacCrehan and Durst and were able to routinely achieve LODs of 1 - 2 ng.L\(^{-1}\) for methyl, ethyl, phenyl and inorganic mercury with an analysis time of less than 10 minutes.

Voltammetric methods have found some application in the determination of both mercury and methylmercury, however not normally simultaneously. Mercury has been determined at glassy carbon electrodes with the appropriate choice of supporting electrolyte [331-333]. The preferred electrode for the voltammetric determination of mercury appears to be gold [333-336]. When used with a matrix exchange step between preconcentration and determination, gold electrodes have exhibited superior sensitivity to glassy carbon [337]. Jagner et al. have also used gold electrodes for the determination of mercury (II) by flow potentiometric stripping analysis [338].

Modified electrodes, particularly modified carbon paste electrodes, have been investigated for inorganic mercury determination. Hernandez et al. [166] modified a carbon paste electrode with traces of zeolite. The modified electrode proved suitable for the determination of mercury within the concentration range from 0.11 to 2.2 \(\mu g.mL^{-1}\). Wang and Bonakdor used a carbon paste electrode modified with a crown ether to determine mercury [167]. The limit of detection for this method was 0.4 \(\mu g.mL^{-1}\). More recently carbon paste electrodes modified with diphenylcarbazone [160] and Dowex 50X8 cation exchange resin [154] have been used for mercury determination. The former electrode was used to determine mercury in acid solution with a LOD of 1 \(\mu g.mL^{-1}\) (10 minute preconcentration followed by matrix exchange.
prior to quantification), with the latter being used for the simultaneous determination of both copper and mercury, although the electrode sensitivity was poor (µg.mL⁻¹).

Tri-n-octylphosphine oxide (TOPO) has been used to form a TOPO modified gold film (on glassy carbon) electrode. The TOPO was immobilised in a PVC film on the gold film. The LOD for this method is 25 ng.L⁻¹.

Wallace et al. [201, 288, 302] have investigated the use of polypyrrole based modified electrodes for the determination of mercury. These authors found that both polypyrrole and a derivatised form of polypyrrole, poly(pyrrole-N-carbodithioate) were suitable for use as mercury sensors. Both sensors had a quoted limit of detection of 200 µg.L⁻¹, with the major difference being the method of mercury collection. Mercury is deposited onto the polypyrrole surface by electrodeposition, whereas it is trapped on the poly(pyrrole-N-carbodithioate) surface by a combination of electrodeposition and complexation through the dithiocarbamate functional groups present at the electrode surface. This sensor proved unsuitable for the detection of organomercury compounds [338a].

There have been few electrochemical studies aimed at determining methylmercury. Heaton and Laitinen have studied the voltammetric determination of methylmercury using polarographic methods [339], the most sensitive being differential pulse polarography. Ireland-Ripert et al. [340] have studied the voltammetric determination of methylmercury in the presence of mercury (II) ions. These workers use a gold film electrode and a double standard addition technique to detect methylmercury with a LOD of 2 x 10⁻⁸ mol.L⁻¹. Phase sensitive A.C. polarography has also been used giving a LOD of 10⁻⁷ mol.L⁻¹ [341].

3.1.2 AIM AND SCOPE OF THIS WORK

The application of voltammetric techniques to the determination of organomercury compounds, particularly methylmercury, is an area in which the use of chemically
modified electrodes may find application. Thus, this work was undertaken to determine the feasibility of such an approach. To achieve this, the electrochemical behaviour of organomercuries at various electrodes was studied.

The use of a dithiocarbamate modified electrode utilizing a polymer with a low background signal may be a suitable means of detecting methylmercury. Dithiocarbamates are known to form strong complexes with mercury salts [341a], a property that should ensure a reasonable degree of preconcentration of methylmercury at the sensor element. With this possibility in mind the electrochemistry of methylmercury dithiocarbamate was also investigated. The dithiocarbamate complex studied was that formed between methylmercury and ammonium pyrolidine dithiocarbamate.

Finally, using information gained from the previous studies the design and generation of a methylmercury sensor was considered and evaluated.

3.2 EXPERIMENTAL

3.2.1 REAGENTS AND SOLUTIONS

Mercury (II) standards (1000 μg.mL⁻¹) were prepared by dissolving the requisite amount of HgO in a minimum of nitric acid and diluting to volume. All working standards were made by serial dilution of this standard. Methylmercury and ethylmercury salts were obtained from Morton Thiokol (Danvers MA.) and phenylmercury acetate was obtained from Fluka. Organomercury stock solutions, 0.01 M, were prepared by dissolving the requisite amount of the salt in methanol. Working solutions were prepared on a daily basis from these stock solution. All stock solutions were refrigerated when not in use.
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Triton X100 (5x10^{-3}%) was added to all polarographic solutions as a maxima suppressor.

N-ethyltyramine was prepared in accordance with a method described previously by Imisides and Wallace [343].

Polymerisation solutions used were 0.1 M NET and 0.3 M NaOH in methanol. Solutions were stored under refrigeration until use.

3.2.2 EQUIPMENT

Voltammetric measurements were performed on either a BAS 100A electrochemical analyser (Bioanalytical Systems, West Lafayette), a BAS CV 27 voltamnograph or an ElectroLab system (Chapter 8). Polarographic and hanging mercury drop electrode (HMDE) experiments were performed with a PAR 174A connected to either a dropping mercury electrode (DME) or a model 303 static mercury drop electrode (used for all HMDE experiments).

3.2.3 PREPARATION OF THE GC/Hg'/pNET-[CS2] ELECTRODE

The glassy carbon electrode was first polished with Y alumina, rinsed with water, dried and polished on a dry hardened ashless (Whatman 542) filter paper. Final cleaning of the electrode surface was achieved by 5 minutes ultrasonic cleaning in distilled water.

Deposition of the mercury film was achieved by applying a constant potential of 200 mV to the electrode in a 10^{-2} M Hg^{2+} in 10% HNO_{3}. The solution was deoxygenated thoroughly prior to deposition and stirred thoroughly during deposition to ensure that the rate of deposition was not hindered by depletion of mercury at the electrode-solution interface.

1This electrode was developed in conjunction with Peter Teasdale at the University of Wollongong
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NET was polymerised potentiodynamically from a solution of 0.1 M NET and 0.3 M NaOH in methanol. The potential applied to the electrode was cycled between 400 mV and 2000 mV at 1 V.s\(^{-1}\) for 25 cycles.

The GC/Hg\(^{+}\)/pNET electrode was then placed in a stirred derivatisation solution, comprising of 50:10:10 V/V benzene:alkaline isopropyl alcohol:carbon disulphide for 24 hours. This treatment derivatises the 2° amine on NET to a dithiocarbamate functionality. The polymerisation and derivatisation of NET has been reported previously [343].

3.2.4 PREPARATION AND CHARACTERISATION OF METHYLMERCURY DITHIOCARBAMATE

Methylmercury dithiocarbamate was prepared by mixing 10 mL of 0.01M methylmercury chloride and 20 mL of 0.01 M ammonium pyrrolidine dithiocarbamate. A white precipitate formed almost immediately, however, the reaction mixture was left standing for a further 5 minutes after which the precipitate was filtered and dried at room temperature in an evacuated vessel. The product was then analysed by mass spectrometry and elemental analysis techniques.

3.3 RESULTS AND DISCUSSION

3.3.1 ORGANOMERCURY SENSING AT CONVENTIONAL ELECTRODES

The first step in developing an electrochemical sensor for methylmercury was to ascertain the electrochemical behaviour of methylmercury at a series of conventional electrodes. The first of these studies were designed to confirm the potential of the reduction responses for the individual mercury species at various electrodes. This was done in order to provide an understanding of the electrochemistry of the analyte at the electrodes to be used in subsequent investigations.
3.3.1.1 Methylmercury at a dropping mercury electrode

Initial studies involved investigating the electrochemical responses of methylmercury compounds at a dropping mercury electrode (DME). This type of electrode was chosen because it presents a continually renewed electrode surface to the sample, and as such is less prone to electrode fouling than other electrodes [289].

The voltammetry of methylmercury at a mercury electrode has been described previously [339, 342]. In this study we have sought to reinvestigate the voltammetric responses of methylmercury in order to facilitate a better comparison with the voltammetry of the methylmercury dithiocarbamate complexes.

A polarographic study of methylmercury in 0.1 M HClO₄ yields two well resolved reduction responses at -180 and -970 mV with a relative peak height ratio of 1:1. (Figure 3.1). The first of these peaks (a) has been attributed to the reduction of the methylmercury cation with the subsequent formation of the dimethylmercury species according to the following scheme [339]:

\[
\begin{align*}
CH_3Hg^+ + e^- & \rightleftharpoons CH_3Hg^- \\
2CH_3Hg^- & \rightleftharpoons (CH_3Hg)_2
\end{align*}
\]  

(3.1)

This reaction is reported to be reversible at high scan rates becoming irreversible at lower scan rates [339] due to:

\[
(CH_3Hg)_2 \rightleftharpoons \text{Slow} \quad Hg + (CH_3)_2Hg
\]  

(3.2)

The second peak (b) at -970 mV is thought to arise from the further reduction of the methylmercury radical, produced in the previous step, to inorganic mercury and methane. This is thought to proceed according to [339]:

\[
CH_3Hg^- + H^+ + e^- \rightleftharpoons CH_4 + Hg
\]  

(3.3)
A differential pulse voltammogram for the reduction of methylmercury at a DME is shown in Figure 3.2. The responses seen at -210 mV and -1010 mV correspond to the reduction reactions described by equations 3.1 and 3.3 respectively. It is also evident from this figure that, when considered in the light of the methyl mercury concentration present, these responses are far too insensitive for use in methylmercury detection.

The scans shown in Figures 3.1 & 3.2 were performed using 0.1 M HClO₄ as a supporting electrolyte, however, as many water samples have chloride present, it was decided that the reduction of methylmercury in M NaCl should be investigated. From this it was found that the reduction responses in M NaCl are less distinct and more drawn out than those seen for methylmercury in 0.1M HClO₄ (Figure 3.1). This would indicate that methylmercury is more difficult to reduce in NaCl than in HClO₄.

**Figure 3.1** Polarogram* of methylmercury

<table>
<thead>
<tr>
<th>Conditions:</th>
<th>Initial: 0 mV</th>
<th>Final: -1250 mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scan rate: 10 mV/s</td>
<td>Drop time: 1 s</td>
<td></td>
</tr>
<tr>
<td>Sample: 10⁻³ M methylmercury in 0.1 M HClO₄ with 5 x 10⁻³% triton X100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* All polarograms given in this work were prepared by plotting the maximum current vs potential
The addition of 0.01 M HClO₄ to the NaCl solution gives rise to a polarogram that is similar to those measured in 0.1 M HClO₄. Both reduction peaks in the 1 M NaCl/0.01 M HClO₄ supporting electrolyte are at a potential more negative than those recorded in 0.1 M HClO₄ indicating again that it is more difficult to reduce the methylmercury cation in the former solution compared with the latter. This change in reduction potential with pH and different supporting electrolyte has been reported by other workers [339, 341, 342]. Presumably, one cause of these differences is the stability of MeHgCl compared with MeHgClO₄. It should be noted, however, that in both solutions the reduction currents are similar (≈4.5 μA).

The NaCl/HClO₄ supporting electrolyte was used for all further polarographic studies of the organomercury compounds.

Whereas a DME, by virtue of the fact that the surface is constantly renewed, provides an excellent tool for initial investigative work it often impractical for routine analytical
work and definitely not suitable for use in portable instrumentation. In order to find a suitable sensing electrode the voltammetry of methylmercury was studied at several other conventional electrodes, namely a hanging mercury drop electrode (HMDE), a glassy carbon electrode and a mercury thin film electrode (MTFE).

3.3.1.2 The voltammetry of methylmercury at a HMDE

The linear sweep voltammetry (LSV) and differential pulse voltammetry (DPV) of methylmercury at a HMDE is shown in Figure 3.3. In both LSV and DPV scans the first reduction peak occurs at -480 mV, with the second reduction response appearing at -1200 mV. These peaks are thought to correspond with the formation of the methylmercury radical (equation 3.1) and the subsequent reduction of the radical to generate free mercury and methane (equation 3.3).

Figure 3.3 Voltammetric responses for the reduction of 10^{-3}M methylmercury (in M NaCl/ 0.01M HClO₄) at an HMDE using
a) Linear Sweep Voltammetry
b) Differential Pulse Voltammetry

Conditions: \( E_{\text{initial}} = 0 \text{ mV} \quad E_{\text{final}} = -1500 \text{ mV} \)
Scan rate = 10 mV.s\(^{-1}\) Drop time: a) 1 s b) 2 s
Modulation amplitude = 10 mV (DPV only)
3.3.1.3 Voltammetry at glassy carbon and MTF electrode

The reduction of methylmercury at glassy carbon was also studied. The responses observed for this compound are shown in Figure 3.4. The first reductive scan on Figure 3.4a has one significant peak at -1175 mV. This is due to the reduction of methylmercury to metallic mercury. The presence of which is confirmed by the oxidation peak at 170 mV. Cycling the potential applied to the electrode between 0 mV and various potentials down to -1500 mV indicates that the mercury oxidation response does not appear until the potential applied to the electrode is taken to -700 mV. At this potential a very small oxidation peak is seen on the reverse scan, with a magnitude of about 0.3 μA. As the potential applied to the electrode is made more negative the size of the mercury oxidation peak increases to ≈1.5 μA at a negative limit of -900 mV. It is not until the lower limit of the scan is decreased to a potential more negative than the potential at which the major reduction peak occurs (-1180 mV) that the mercury oxidation peak becomes significant. At a lower limit of -1500 mV the resultant mercury oxidation peak is about 25 μA. These data would suggest that the reduction peak at -1180 mV is due to the reduction of methylmercury to metallic mercury and that whilst some reduction of methylmercury to mercury may occur at -800 mV, this is not the major reaction occurring at this potential. Rather, as in the voltammetry of methylmercury at mercury, the broad reduction peak seen at ≈-800 mV may be due to the reduction of methylmercury to the methylmercury radical (equation 3.1). However, this was not confirmed.
An interesting feature of the voltammograms in Figure 3.4 is the difference between the first and subsequent reductive scans. The first scan shows a single major reduction peak at -1180 mV. This peak may be attributed to the reduction of
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methylmercury to mercury metal. The appearance of a significant oxidation peak at 200 mV on the oxidative scan due to the oxidation of mercury from the glassy carbon electrode, supports this suggestion.

The second and subsequent scans have major reduction peaks at 100 and -350 mV. The first of these peaks is due to the reduction of mercury ions produced on the oxidative scan and still within the vicinity of the electrode. The second peak is due to the reduction of methylmercury as described by equation 3.1. These data indicate that at a glassy carbon electrode the single electron reduction of methylmercury is not readily seen, although the broad reduction peak on scan (a) and centred about -820 mV may be due to this reaction. Once mercury is deposited on the surface of the electrode the reduction reactions that occur are essentially those that occur at a mercury-solution interface and as such, the single electron reduction response is evident on scan (b) (Figure 3.11).

It is also worth noting here that the reduction of methylmercury occurs at a less negative potential on the second scan, indicating that the methylmercury cation is more readily reduced at a mercury surface.

Thus the second and subsequent cycles at the glassy carbon electrode were essentially reduction at a mercury thin film electrode (MTFE). These responses appear to be more reproducible than those at a plain glassy carbon electrode. This was subsequently investigated and, whilst the response was more reproducible, it was still too insensitive to be suitable for use as an analytical signal.

3.3.2 VOLTAMMETRY OF METHYLMERCURY DITHIOCARBAMATE AT MERCURY BASED ELECTRODES

To better understand the electrochemical behaviour of methylmercury dithiocarbamate at mercury based electrodes, a HMDE and DME were used for studies of the voltammetry of both the free dithiocarbamates and the
methylmercury dithiocarbamate complex. Bond and co-workers (344-346) have studied the electrochemistry of various mercury dithiocarbamate complexes and postulate the two electron reduction of the dithiocarbamate complexes to mercury and the dithiocarbamate ligand according to:

\[ \text{Hg} [\text{R}_2\text{dtc}]_2 + 2e^- \rightarrow \text{Hg}^0 + 2[\text{R}_2\text{dtc}]^- \quad (3.4) \]

with mercury (I) intermediates, which are said to disproportionate as part of the overall reaction scheme. In their work these authors have restricted their studies to inorganic mercury dithiocarbamate complexes.

These have been a few voltammetric studies of the methylmercury cation but none reported for methylmercury dithiocarbamate complex.

3.3.2.1 Voltammetry of dithiocarbamates at mercury electrodes

This aspect of the investigations involved studying the voltammetry of the dithiocarbamate ligand to be used in this work. A differential pulse voltammogram for ammonium pyrrolidine dithiocarbamate (APDC), in M NaCl is shown in Figure 3.5

The reduction peak evident at -380 mV is not due to the reduction of the dithiocarbamate species alone, as these are not easily reduced. This was confirmed by running a cyclic voltammogram of the dithiocarbamate solution using a glassy carbon electrode. No responses were evident within the potential window 0 -1000 mV. Therefore, this reduction peak must be associated with either an impurity in the dithiocarbamate or the reduction of a species formed in the electrochemical cell. It is the later of these possibilities that appears to be occurring, as the dithiocarbamate salt used was A.R. grade and the peak persisted even after the dithiocarbamate was recrystallised twice from ethanol.
The most likely explanation for the cause of this peak is that it is associated with the electrochemical response of Hg(dtc)$_2$ formed at the HMDE. The presence of a similar peak has been reported by Randle et al. [347] in a study of the electrochemistry of a series of alkyl dithiocarbamates in aqueous solution. These authors attribute the peak to the desorption of mercury dithiocarbamates from the electrode surface.

It is quite feasible that the chemical and electrochemical conditions present when the potential is applied to the cell (i.e. an applied potential of 0 mV in $10^{-2}$ M H$^+$/$10^{-3}$ M dtc$^-$) would cause the formation of Hg(dtc)$_2$ according to:

$$2 \text{Hg} + 2 \text{[dtc}^-\text{]} \rightarrow 2 \text{Hgdtc} + 2 \text{e}^- \quad (3.5)$$

$$2 \text{Hgdtc} \rightarrow \text{Hg}^0 + \text{Hg(dtc)}_2 \quad (3.6)$$
Such reactions have been reported previously for mercury-dithiocarbamate interactions [347a].

The shape of the peak and the peak width at half height (=120 mV) suggest that this is not a surface effect but rather a slow reduction response, possibly the reduction of the dithiocarbamate complex in accordance with equation 3.5.

Although the exact cause of this response was not elucidated, its position and magnitude were determined to aid in the interpretation of voltammograms recorded in the presence of methylmercury and the dithiocarbamate.

### Voltammetry of methymercury-APDC complex at mercury electrodes

The methylmercury-pyrrolidine dithiocarbamate complex was prepared as described in the experimental section. Elemental analysis of the product is given in Table 3.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight percent</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>20.02</td>
<td>1.67</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.99</td>
<td>11.96</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.77</td>
<td>0.27</td>
</tr>
<tr>
<td>Sulphur</td>
<td>16.87</td>
<td>0.53</td>
</tr>
<tr>
<td>Mercury</td>
<td>50.06</td>
<td>0.25</td>
</tr>
</tbody>
</table>

From the results above, the molecular formula for the complex can be calculated as C₆H₄₇NS₂Hg. The ratio of mercury to sulphur implies the formation of a 1:1 complex between methylmercury and pyrrolidine dithiocarbamate. The hydrogen levels do not appear to be correct however, the result was not repeated as it was the ratio of Hg to S that was of interest as a result of this ratio the formula for the complex was determined to be C₆H₁₁NS₂Hg. The discrepancy in hydrogen levels between the molecular formula of the complex, as determined by elemental analysis, and that
expected is presumably due to the fact that at this level errors in the elemental analysis are significant and are amplified during the calculations.

To confirm that a voltammetric response due to the methylmercury dithiocarbamate complex could be detected, the complex was dissolved in a solvent containing supporting electrolyte and characterised. A differential pulse voltammogram for this complex dissolved in supporting electrolyte is shown in Figure 3.6. The result confirmed that a peak at -850 mV can be attributed to the MeHg(APDC) complex. Therefore, it was decided to evaluate the in-situ formation of this complex. The addition of 2 x 10^{-3} M ammonium pyrrolidine dithiocarbamate to a 10^{-3} M solution of CH₃HgCl in M NaCl/10^{-2} M HClO₄ causes the almost instantaneous precipitation of a white complex, methylmercury dithiocarbamate.

A differential pulse polarogram recorded on the supernatant 8 minutes after mixing, (Figure 3.7) shows reduction peaks at -320 mV, -460 mV and -800 mV. The responses at -320 mV and -460 mV may be attributed to the reduction of free methylmercury (c.f. Figure 3.3) and a mercury-APDC complex respectively (c.f. Figure 3.5). The peak at -800 mV appears to be due to the methylmercury dithiocarbamate complex. With time (Figure 3.7b) the peak at -320 mV completely disappears indicating no measurable amounts of free CH₃Hg⁺ in solution. This indicates that the reaction has gone to completion, a suggestion backed up by the observation that the peak at -800 mV no longer increases in size.

An interesting observation to come from these experiments was that, whereas with CH₃Hg⁺ it was difficult to achieve a reasonable reduction response for solutions less concentrated than 10^{-3} M (Figure 3.2), with APDC present the major portion of the complex precipitated. There was, however, a reasonable signal for the saturated solution of the MeHg(APDC) complex, the concentration of which was considerably less than 10^{-3} M. This would suggest that the use of dithiocarbamate complexes of methylmercury may be a sensitive technique for the determination of methylmercury.
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in solution. To this end a series of experiments were performed using APDC to determine trace MeHg in water.

**Figure 3.6** Differential pulse voltammogram of MeHg(APDC) in supporting electrolyte

Conditions: 
- \( E_{\text{initial}} = 0 \text{ mV} \)
- \( E_{\text{final}} = -1000 \text{ mV} \)
- Scan rate = 5 mV.s\(^{-1}\)
- Drop time = 1 s
- Modulation amplitude = 25 mV
- Electrode: HMDE
- Supporting Electrolyte: M NaCl/10\(^{-2}\) M HClO\(_4\)
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Even though the detection of MeHg(APDC) at an HMDE is more sensitive than the detection of MeHg+ at the same electrode, it was obvious that in order to achieve
useful detection limits a preconcentration step would be required prior to voltammetric
determination. Initial studies were aimed at investigating the feasibility of an
adsorptive stripping voltammetry approach to preconcentration. In this technique the
metal complexes of interest are accumulated at the electrode-solution interface by non-
electrolytic preconcentration. After sufficient accumulation the analyte is quantified by
the reduction or oxidation of the metal complex.

The first step in determining whether any adsorption responses may be present was to
investigate the effect of the initial potential on the analytical signal. Figure 3.8 shows
the effect of initial potential on the analytical peak height. From this figure it can be
seen that commencing a scan at -200 mV provides the greatest response.

![Figure 3.8 Effect of initial potential on peak height (MeHg APDC)](image)

Conditions: As in Figure 3.7b

To investigate the effect of accumulation potential on the analytical response, all scans
were commenced at -200 mV. Prior to each scan a 60 second accumulation step was
performed at various potentials, the relative responses for each accumulation potential
are shown in Table 3.2.
Using the optimum deposition potential of -400 mV the effect of starting the scan at -200 mV compared with -400 mV was again tested. The relative responses indicated that commencing the scan from -400 mV provided more sensitive response for the methylmercury-dithiocarbamate complex.

Thus, the conditions chosen for the determination of methylmercury by adsorptive stripping voltammetry are:

- **Reaction time**
  (for the reaction of the MeHg with the APDC): 15 minutes

- **Analytical waveform:** Differential pulse voltammetry

- **E_{dep}:** 400 mV
  **Scan rate:** 10 mV.s^{-1}

- **E_{initial} = -400 mV**
  **E_{final} = -1200 mV**

- **Step width: 1 second**
  **Modulation amplitude:** 25 mV

Using these conditions and an accumulation time of 60 seconds, a calibration curve for the MeHg response was constructed. As can be seen from Figure 3.9 the response is acceptable within the 50 - 500 ppb range.
This is a vast improvement on the responses for methylmercury determined at the same electrode. Using similar preconcentration conditions with no dithiocarbamate present the analytical response for 10 μg.mL⁻¹ methylmercury was 0.11 μA. Whereas, with the dithiocarbamate present, the response for 50 μg.L⁻¹ was 0.12 μA. This represents a 200 fold improvement in the limit of detection for methylmercury.

3.3.3.1 Interferences

A study of the effect of various potential interferences indicated that both copper(II) and lead ions can be expected to hinder the detection of methylmercury using this technique. In the dithiocarbamate solution the copper reduction response occurs at -740 mV and the lead reduction response at -800 mV. Both responses are broad and as such will be expected to overlap the methylmercury - dithiocarbamate response at -850 mV. Mercury gives a reduction response at approximately -500 mV.

Two other organomercury compounds, ethylmercury and phenylmercury were also examined as potential interferents.
The addition of $2 \times 10^{-3}$ M APDC to a $10^{-3}$ M solution of ethylmercury in M NaCl/10$^{-2}$ M HClO$_4$ was followed by the rapid formation of a heavy white precipitate. The voltammograms recorded for the supernatant solution, presumably saturated with the ethylmercury-pyrrolidine dithiocarbamate, exhibited significant variability with time. A voltammogram recorded after 30 minutes reaction time shows no significant peak attributable to the ethylmercury-pyrollidine dithiocarbamate complex.

A similar, if not more erratic behaviour was seen for phenylmercury under the same conditions.

### 3.3.4 Modified Electrodes for the Detection of Methylmercury

Given the suitability of dithiocarbamates for the preconcentration of methylmercury during the adsorptive stripping voltammetric procedure and the ease with which dithiocarbamate functionalised modified electrodes may be produced, the next stage in the development of the organomercury sensor is to transfer the complexation chemistry from the solution to the electrode surface.

#### 3.3.4.1 Glassy carbon/Hg$^+$/pNET-[CS$_2$]

The studies with polypyrrole based electrodes suggest that one of the requirements of a successful organomercury sensor would be a very low background signal. One group of polymers to possess this attribute are the tyramine based polymers, specifically poly-N-ethyltyramine. This polymer has been used previously for mercury detection [343]. In this case polymerisation followed by derivatisation, to form the dithiocarbamate functionalised polymer, was used to produce an electrode suitable for the determination of mercury. A further advantage of this type of polymer is that it has been used successfully in the production of a hybrid electrode, known as the dispersed metal electrode, which incorporates metallic mercury centres within the polymer matrix [348]. The combination of a mercury-polymer hybrid electrode with
Methymercury Sensing

a dithiocarbamate functionalised polymer as the polymer component could conceivably produce a sensor element that closely mimics the preconcentration and quantification techniques used in the adsorptive stripping approach.

The electrode preparation technique, described in the experimental section, is an adaptation and improvement of an electrode developed previously [349]. Whereas the original electrode was based on a platinum substrate, the electrode reported here was optimised for a glassy carbon substrate.

The first step in this study was to determine the optimum mercury film thickness. To do this mercury was deposited on glassy carbon electrodes at -200 mV from a vigorously stirred solution containing $10^{-2}$M Hg$^{2+}$. Deposition was carried out for 1, 2 and 4 minutes. The MTFE was then coated with poly-N-ethyltyramine by a potentiodynamic technique. A typical voltammogram for polymer growth is shown in Figure 3.10.

![Figure 3.10: Potentiodynamic growth of poly-N-ethyltyramine.](image)

**Conditions:**

- $E_{\text{initial}} = -400$ mV
- $E_{\text{lower}} = -400$ mV
- $E_{\text{upper}} = 2000$ mV
- Scan rate = 1000 m V.s$^{-1}$

**Solution:**

As described in experimental
The important feature of this voltammogram is the decreasing signal with subsequent scans indicates the electrode is being coated with a polymer layer of low conductivity.

The mercury-poly-N-ethyltyramine electrode was then derivatised for 24 hours as described in the experimental section. The resultant electrode consists of finely dispersed mercury drops surrounded by a dithiocarbamate functionalised polymer. This is shown schematically in Figure 3.11.

Layer of insulating polymer with mercury dispersed in it

Glassy carbon electrode

Glassy carbon

Figure 3.11 Schematic of dispersed mercury electrode

A comparison of the responses seen for a $10^{-4}$ M solution of methylmercury at the various derivatised electrodes indicates the electrode produced with one minute mercury deposition step exhibited no peaks for the $10^{-4}$ M solution. It did however give two poorly defined peaks for methylmercury reduction when the solution concentration was increased to $10^{-3}$ M. The electrode prepared with a four minute mercury deposition step had a large background response with no methylmercury responses evident.

The only electrode to give any reasonable response for methylmercury was that prepared with a two minute mercury deposition step during the electrode preparation.
From these results it is apparent that the level of mercury in the polymer is critical. Too little, and there is an insufficient number of sites to allow efficient reduction of the methylmercury trapped at the electrode, too much, and the background signal swamps the analytical signal.

The two minute mercury plating step was used in the preparation of the electrodes for all further investigations.

A cyclic voltammogram of the GC/Hg'/pNET-[CS2] in supporting electrolyte is shown in Figure 3.12. This figure shows the first and 15th cycles of the voltammogram.

![Cyclic voltammograms of composite electrode in supporting electrolyte.](image)

**Figure 3.12**

Conditions: \( E_{\text{initial}} = 0 \text{ mV} \quad E_{\text{upper}} = 0 \text{ mV} \quad E_{\text{lower}} = 1000 \text{ mV} \)

Scan rate = 100 mV s\(^{-1}\)

During the first cycle (Figure 3.12(a)) a large reduction peak is seen at -650 mV. The size of this peak gradually decreases until, by the 5th cycle (Figure 3.12(b)), it is insignificant.
The cause of this peak is unknown, but may be associated with the setting up of better charge paths within the polymer. This hypothesis is supported by the observation that with a freshly prepared electrode it is not possible to perform cyclic voltammograms with scan rates much greater than 100 mV.s\(^{-1}\). The response simply flattens out indicating that the potentiostat is incapable of applying a voltage sufficiently high enough to compensate for the internal resistance in the polymer. Whereas, after the electrode has been cycled in supporting electrolyte for a few scans, it is possible to perform cyclic voltammograms at higher scan rates, indicating the internal resistance of the polymer is significantly decreased during the conditioning step.

A cyclic voltammogram performed on a solution of 10\(^{-3}\)M methylmercury in supporting electrolyte shows a reduction response at approximately -450 mV, the magnitude of which changes with varying methylmercury concentration. Figure 3.13 shows the response obtained for a 2 x 10\(^{-3}\)M solution of methylmercury. The potential of this response is more in keeping with the single electron reduction of the methylmercury cation, as described in equation 3.1, rather than the reduction of a methylmercury-dithiocarbamate moiety.

![Cyclic voltammogram of a derivatised, composite electrode in 2 x 10\(^{-3}\)M CH\(_3\)Hg\(^+\)/supporting electrolyte](image)

**Figure 3.13** Cyclic voltammogram of a derivatised, composite electrode in 2 x 10\(^{-3}\)M CH\(_3\)Hg\(^+\)/supporting electrolyte

**Conditions:** As in Figure 3.12
Having determined the position of the methylmercury response there are a number of variables to be optimised in order to achieve the best analytical response possible.

3.3.4.1.1 Effect of Analytical Waveform

To optimise the analytical signal obtained both the voltammetric technique and the potential limits used in the determination were investigated. It was found that Osteryoung square wave stripping voltammetry (OSWSV) was the most appropriate technique to use. It gave a symmetrical well defined response with an acceptable analysis time. Linear sweep voltammetry was unsuccessful as the response was very broad. The response obtained with differential pulse voltammetry was well defined but the analysis time was too long. An OSWSV response for $10^{-3}$M methylmercury at a composite electrode is given in Figure 3.14.

![Figure 3.14 OSWSV scan of a derivatised, composite electrode in $10^{-3}$M CH$_3$Hg$^+$/supporting electrolyte](image)

Conditions:
- Initial $E = 0$ mV
- Final $E = -1200$ mV
- A.C. Amplitude = 25 mV
- Step potential = 4 mV
- Frequency = 15 Hz
The effect of the starting potential was determined and found to have little impact upon the analytical signal. This is illustrated in Table 3.3.

<table>
<thead>
<tr>
<th>Starting potential (mV)</th>
<th>Analytical response (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.39</td>
</tr>
<tr>
<td>-100</td>
<td>2.37</td>
</tr>
<tr>
<td>-200</td>
<td>2.43</td>
</tr>
<tr>
<td>-300</td>
<td>2.23</td>
</tr>
<tr>
<td>-400</td>
<td>--</td>
</tr>
</tbody>
</table>

* Analytical peak at -400 ± 10 mV

3.3.4.1.2 Effect of accumulation potential

Figure 3.15 shows the effect on the analytical signal of altering the accumulation potential prior to the commencement of the analytical scan. From this figure it can be seen that the optimum accumulation potential is within the window -200 mV to -400 mV.

![Figure 3.15](image)

*Figure 3.15 Effect of accumulation potential on the analytical response obtained for 10⁻³M CH₃Hg⁺*  

Conditions: as in Figure 3.14
To investigate this further, analyte accumulation at both -300 mV and -400 mV was conducted for a series of accumulation times and the responses compared. The results of this comparison are given in Table 3.4. From this table it can be seen that there is little difference between the responses obtained, with deposition at -400 mV giving a slightly larger signal at the shorter deposition times.

<table>
<thead>
<tr>
<th>Accumulation time (s)</th>
<th>Analytical response (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Accumulation at -300 mV</td>
</tr>
<tr>
<td>60</td>
<td>2.07</td>
</tr>
<tr>
<td>120</td>
<td>2.02</td>
</tr>
<tr>
<td>240</td>
<td>2.16</td>
</tr>
<tr>
<td>480</td>
<td>2.22</td>
</tr>
</tbody>
</table>

E_{initial} = 50 mV  E_{final} = -1200 mV  all other conditions as in Figure 3.21.

### 3.3.4.1.3 Optimum experimental conditions.

The data in the previous sections indicates that the optimum conditions for the detection of methylmercury are:

- **Waveform:** Osteryoung Square Wave Stripping Voltammetry
- **E_{initial}:** 50 mV
- **E_{final}:** -900 mV
- **E_{dep}:** -400 mV
- **t_{dep}:** 60 s

Using these conditions it is possible to detect 10^{-5}M CH$_3$Hg$^+$ with a the composite electrode. A voltammogram for a 10^{-5}M solution of methylmercury is shown in Figure 3.16.
Methylmercury Sensing

Figure 3.16 OSWS Voltammogram for 10^{-5}M (2.2ppm) CH$_3$Hg$^+$ at a composite electrode

Conditions: as in text.

In comparison, the voltammogram shown in Figure 3.17 is for the same methylmercury solution at a glassy carbon electrode. It can be seen that the peaks in this voltammogram would render this electrode unsuitable for the detection of the CH$_3$Hg$^+$ cation. The composite electrode provides a suitable substrate for the reduction of methylmercury with the polymer layer protecting the electrode surface from fouling.
It is evident from Figure 3.16 that the composite electrode does not possess a sufficient level of sensitivity to warrant further development. As a result of this no further work was carried out with this electrode. Therefore calibration and interference studies were not carried out.

3.6 CONCLUSIONS

The polarographic studies of methylmercury have shown that the reduction of the \( \text{CH}_3\text{Hg}^+ \) cation is favoured in acidic conditions. Studies of the reduction of methylmercury at stationary electrodes have also indicated that this reaction occurs more reproducibly at a mercury surface.

The use of the dithiocarbamate, ammonium pyrolidine dithiocarbamate, has been shown to increase the sensitivity of the methylmercury detection and forms the basis of an adsorptive stripping voltammetric technique for the determination of \( \text{CH}_3\text{Hg}^+ \) in
water. The technique is not suitable for the detection of either ethyl or phenyl mercury, although the choice of a different dithiocarbamate may improve this.

A modified electrode for the detection of methylmercury was considered. This was a composite electrode combining preconcentration at a dithiocarbamate functionalised polymer and detection at a mercury surface. This polymer proved to have inferior sensitivity when compared with the adsorptive stripping technique. However, the presence of the polymer film enhanced the methylmercury signal by virtue of the fact that it provided a barrier protecting the electrode from unwanted side reactions, providing a "cleaner" voltammogram. The potential of the CH$_3$Hg$^+$ reduction signal suggests that it is a single electron reduction of CH$_3$Hg$^+$ rather than the reduction of a methylmercury-dithiocarbamate species.

In summary, the detection of CH$_3$Hg$^+$ at a chemically modified electrode provides inferior detection to that achieved using an adsorptive stripping voltammetric approach at a HMDE.
CHAPTER 4
THE DETERMINATION OF GOLD USING CHEMICALLY MODIFIED ELECTRODES

4.1 INTRODUCTION

The preconcentration and determination of trace levels of gold remains an area of interest to those involved in either the processing of gold bearing minerals or the geochemical exploration for suitable ore bodies. Analysis of processing streams and plant effluent is essential to maximise the efficiency of the gold recovery processes [350, 351], whilst the analysis of groundwater is a useful tool in geochemical exploration [103, 139].

Instrumental techniques used for the determination of gold include: AAS [103, 352], HPLC [350 353], voltammetric methods [139, 156, 164, 351, 354-357] and instrumental neutron activation analysis (INAA) [83, 103, 358]. This is by no means an exhaustive list of techniques available, reviews and comparisons of suitable analytical techniques can be found in the literature [359, 360].

4.1.1 VOLTMETRIC DETERMINATION OF GOLD

Voltammetric methods, especially stripping voltammetry, are well suited to the determination of gold and as such have been investigated by a number of workers.

Simple polarographic determination of gold is not possible because gold is reduced at a potential more positive than the oxidation potential of mercury [361]. The appropriate choice of supporting electrolyte to form a more stable gold complex and effectively lower the reduction potential of gold, enabled the polarographic
determination of gold to be carried out [362], however this technique is too insensitive to be a viable method for the determination of trace levels of gold.

The stripping voltammetric determination of gold at carbon paste and graphite electrodes was investigated extensively during the 1960's and early 1970's [361, 363-368]. The use of very long deposition times with these electrodes enabled a limit of detection of 1 µg.L⁻¹ to be achieved [368]. However, the mechanical instability and lack of reproducibility of such electrodes have prevented them from coming into widespread use. Platinum electrodes have also found limited application in the determination of gold [369-371].

The advent of glassy carbon provided electroanalytical chemists with a very reproducible inert carbon based electrode and ASV techniques for gold, utilising the deposition of gold onto glassy carbon as a preconcentration step, were developed [351, 357, 372]. These techniques, especially when stripping was achieved using a pulsed voltammetric waveform, possessed excellent limits of detection [372]. However, a problem with the ASV determination of gold at glassy carbon is the interference caused by electroactive species commonly encountered with gold, these include Cu, Ag, Hg, Pt and Fe [357, 356]. This problem is usually overcome by including a solvent extraction step in the sample preparation protocol. [357].

An alternative approach reported involved using a modified electrode in the ASV determination of gold [373]. To achieve this a carbon paste electrode, modified with a chelating resin, was used for the non-electrolytic accumulation of gold(III). A medium exchange step followed the accumulation procedure after which the accumulated gold was reduced and subsequently determined by ASV. The method reported is essentially free of most common interferences [373].

Cathodic stripping voltammetry has found limited application in the determination of gold. Electrodes used in these studies have been either carbon paste [374, 375] or modified carbon paste electrodes [156, 159, 164, 376, 377]. The detection limits
achieved with the best of these electrodes has been in the high μg.L⁻¹ levels [156]. The effect of interferences varies between electrodes, with the presence of copper adversely affecting most determinations [156, 164, 159, 373].

4.1.2 POLY(4 VINYL PYRIDINE)

The use of poly (4-vinylpyridine) (PVP) for the modification of electrodes was first reported by Anson and Oyama [381] and later by a number of other workers [382-384].

The first report of the use of a PVP modified electrode in a sensor application was that of Cox and Kulesza [174]. In this work a PVP modified platinum electrode was used for the determination of anionic Cr(VI) species. The Cr(VI) was preconcentrated into the protonated PVP film and determined, after a matrix exchange procedure, by a reductive scan. During this scan the anionic Cr(VI) is reduced to a cationic Cr(III) species and subsequently expelled from the polymer.

This polymer possesses two properties that make it attractive as a potential sensing element for gold(III). Firstly, when protonated the polymer is capable of preconcentrating anions onto the polymer surface, presumably due to the presence of positively charged amine groups throughout the polymer. Secondly, whilst the polymer has a sufficient level of ionic conductivity to allow reduction or oxidation of species to occur at the polymer surface it does not show significant electrochemical responses over the potential range of interest.

4.1.3 AIM AND SCOPE OF THIS WORK

There are a number of analytical techniques suitable for the analysis of gold in aqueous samples, most of which are best suited to the analytical laboratory and would be difficult to adapt for use in the field if required. The only technique that has been
reported for the determination of gold in the field is a voltammetric one [139].
However, this technique is prone to interference in some applications.

Thus, it would appear that the voltammetric determination of gold could be improved
by the development of sensing elements that are less prone to the interferences
commonly associated with gold determination. A study of the interaction of gold with
electrochemically generated polymers may provide the necessary information to assist
in the development of a polymer based sensor for gold.

Here, as with the previous example, the judicious application of polymer modified
electrodes may provide a means of achieving this end. This work has therefore
focussed on investigating the interaction of gold with polymer modified electrodes as a
means of developing a sensor for the selective determination of gold.

4.2 EXPERIMENTAL

4.2.1 REAGENTS AND SOLUTIONS

All reagents used were analytical (A.R.) grade unless otherwise stated. Water used
was purified using a Milli-Q water purification system. Monomers used for the
electrochemically generated polymer were obtained from the Sigma Chemicals
Company and used as received. Gold solutions were prepared by serial dilution from
a 1000 mg.L\(^{-1}\) standard. This was prepared by dissolving 1g of gold metal (99.99%)
in a minimum of aqua regia and diluting to the required volume.

Supporting electrolyte was prepared by adding 10 mL of concentrated hydrochloric
cid and 20 mL of concentrated nitric acid to water and diluting to 1 litre.
4.2.2 INSTRUMENTATION

Cyclic voltammetry was performed using either a Bioanalytical Systems (BAS) (West Lafayette In.) CV-27 Voltammograph connected to a Houston Omnigraphic 2000 X-Y recorder or a BAS 100A Electrochemical Analyser. All other voltammetric measurements were performed using the BAS 100A Electrochemical Analyser. Glassy carbon disks (3 mm diameter) were supplied by either Chemtronics (Perth W.A.) or BAS.

Homemade platinum electrodes were prepared by sealing a 1-2 cm length of 0.5 mm platinum thermocouple wire into the end of a 1 mL pipette. Contact with the platinum was made by using wood's metal to join the platinum to a length of copper wire. The exposed platinum wire was trimmed to 1 cm length after fabrication.

Stripping voltammetry experiments were performed using a electrochemical cell supplied by Chemtronics. This unique cell design facilitates matrix exchange experiments and allows solution change without the electrode drying out [357]. A diagram of the cell is shown in Figure 4.1.
Control of the cell stirrer was achieved through a purpose built interface to connect it to the BAS 100A.

The preparation of specific electrodes used in this work is detailed below.

4.2.3 ELECTRODE MODIFICATION

4.2.3.1 Polypyrrole

Polypyrrole coated electrodes were prepared by the galvanostatic oxidation of pyrrole in a deoxygenated aqueous solution containing 0.5 M pyrrole and 1.0 M of the salt to be used during polymer preparation. Unless otherwise indicated, oxidation was achieved at a current density of 0.5 mA.cm⁻² for 6 minutes. After preparation all electrodes were washed thoroughly and used immediately.

4.2.3.2 Poly(2,2′bithiophene)

Poly(2,2′bithiophene) modified electrodes were prepared by the galvanostatic oxidation of 2,2′bithiophene from a deoxygenated solution of 0.5 M 2,2′bithiophene and 1.0 M concentration of a suitable salt, usually NaClO₄ or (C₄H₉)₄NBF₄ in acetonitrile. Oxidative conditions were identical to those used for the preparation of polypyrrole modified electrodes.

4.2.3.3 Chemisorbed poly(4-vinylpyridine) electrode

Poly(4-vinylpyridine) (Polyscience) was dissolved in methanol (A.R.) to give a 0.4% w/v solution of the polymer. A suitable aliquot of this polymer was placed on each glassy carbon electrode with a 5-50 μL pipette. The methanol was then allowed to evaporate at room temperature.

The polymer modified electrode was subsequently soaked for 10 minutes in a 0.1 M solution of H₂SO₄. This treatment both protonates the polymer and causes it to swell [174].
4.2.3.4 Electrochemically generated PVP

The polymer was synthesised by cycling a glassy carbon electrode between 0 and -2000 mV, in a solution of 1.0 mM divinylbenzene (Aldrich), 5 - 40 mM 4-vinylpyridine (Aldrich) in 60% N,N'-dimethylacetamide and 40% N/10 H₂SO₄. Typically, electrodes were scanned for 5 - 10 cycles.

4.3 RESULTS AND DISCUSSION

4.3.1 POLYPYRROLE

The ion exchange properties of polypyrrole have been discussed in chapter 2 of this work. Feasibly, this property could be used as a means of preconcentrating (AuCl₄)⁻ prior to voltammetric determination.

The following studies were designed to test the suitability of polypyrrole modified electrodes for this application and to investigate the effect of applied potential on the interaction of gold(III) with the polymers.

4.3.1.1 Voltammetry of gold at polypyrrole

Polymers used for this study were synthesised from a solution of 0.5M pyrrole and 1.0 M NaCl. Initial investigations involved studying the voltammetry of polypyrrole in M NaCl. Figure 4.2a shows a cyclic voltammogram of polypyrrole in M NaCl, Figure 4.2b shows a LSSV scan of the same electrode after 60 seconds accumulation at 700 mV. From these figures it is evident that there are no distinct reduction responses due to the polymer or supporting electrolyte over the voltage range scanned (0-700 mV). This observation held true for polypyrrole on both glassy carbon and platinum electrodes.
Figure 4.2

Voltammetric responses for polypyrrole in M NaCl

a) Cyclic voltammogram

b) Linear sweep stripping voltammogram

Conditions: Cyclic voltammetry
- $E_{\text{initial}} = 0 \text{ mV}$
- $E_{\text{upper}} = 700 \text{ mV}$
- $E_{\text{dep}} = 900 \text{ mV}$
- $E_{\text{final}} = 0 \text{ mV}$
- $t_{\text{dep}} = 60 \text{ s}$
- Scan rate = $100 \text{ mV.s}^{-1}$

A voltammogram for a polypyrrole coated platinum electrode, under the same experimental conditions, in a solution of 50 mg.L$^{-1}$ Au(III) in M NaCl shows a
distinct reduction response at 500 mV presumably due to the reduction of Au(III) to Au°. A LSSV scan from 700 - 0 mV, with 60 seconds preconcentration at 700 mV exhibits a large reduction peak at 490 mV, again presumably due to the reduction of gold(III) at the polymer electrode.

A similar series of experiments performed using polypyrrole coated glassy carbon electrodes yield slightly different results. There is no distinct gold reduction response seen on cyclic voltammograms recorded for polypyrrole modified glassy carbon electrodes in a 50 mg.L⁻¹ solution of Au(III) in M NaCl. A linear sweep stripping voltammogram using the same electrode/solution combination recorded after 60 seconds accumulation at 700 mV shows a distinct reduction response at 500 mV (Figure 4.3).

![Figure 4.3](image)

**Figure 4.3** LSSV response for 50mg.L⁻¹ Au(III) in M NaCl at a polypyrrole modified glassy carbon electrode

<table>
<thead>
<tr>
<th>Conditions:</th>
<th>LSSV</th>
<th>modified glassy carbon electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{initial}} = 700$ mV</td>
<td>$E_{\text{final}} = 0$ mV</td>
</tr>
<tr>
<td></td>
<td>$t_{\text{dep}} = 30$ s</td>
<td>$E_{\text{dep}} = 700$ mV</td>
</tr>
<tr>
<td></td>
<td>$\text{Scan rate} = 100$ mV.s⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

A series of experiments, performed to determine the interrelationship between accumulation potential and the reduction response, show that the magnitude of the
Reduction response increases as the accumulation potential is made more positive. These are shown in Table 4.1.

**Table 4.1** Effect of accumulation potential on analytical response for Au(III) at a PP/Cℓ electrode

<table>
<thead>
<tr>
<th>Accumulation potential (mV)</th>
<th>Response(a,b) (µA)</th>
<th>Au reduction potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>100</td>
<td>500</td>
</tr>
<tr>
<td>800</td>
<td>160</td>
<td>490</td>
</tr>
<tr>
<td>900</td>
<td>225</td>
<td>435</td>
</tr>
<tr>
<td>1000</td>
<td>response disappears</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Conditions: \(E_{\text{initial}} = 700\) mV, \(E_{\text{lower}} = 0\) mV, \(t_{\text{dep}} = 30\) s, \(\text{Scan rate} = 100\) mV.s\(^{-1}\)

\(b\) Sample: 50 mg.L\(^{-1}\) Au in M NaCl

This trend is evident up to an accumulation potential of 900 mV, after which the polymer is severely degraded and the gold reduction response is diminished and/or swamped by the polymer response.

With the increasing accumulation potential two phenomena occur. The first of these is an apparent increase in ion exchange capacity with increasing potential. This has the effect of increasing the amount of gold preconcentrated into the electrode which in turn increases the analytical signal. However, as the accumulation potential is increased the second phenomena begins to occur and the polymer is irreversibly damaged by "over oxidation" [378]. This causes the conductivity of the polymer to decrease. The resulting increase in iR drop across the polymer causes the potential of the gold reduction response to shift (Table 4.1) whilst making these responses broader and less distinct. This makes them more difficult to quantify.

Thus, the optimum analytical signal is obtained with an accumulation potential that maximises gold preconcentration whilst minimising polymer damage and therefore improving repeatability for subsequent determinations.
These results indicate that it is possible to accumulate gold(III) at these electrodes and that the application of a potential will enhance this accumulation process. It is also evident that, as the accumulation occurs at a potential more positive of that required to reduce the gold ions to metallic gold, accumulation must involve processes other than electrodeposition.

There are three possible modes of interaction available, being:

(i) Ion exchange, with the anions incorporated in the polymer being replaced by [AuCl₄]⁻ ions

(ii) Adsorption of the Au(III) onto the polymer surface. This may involve the interaction between protonated amine groups on the polymer and the [AuCl₄]⁻ anion.

(iii) A redox reaction between the polymer and the [AuCl₄]⁻ anion. Feasibly this could involve oxidation of the polypyrrole by the Au(III) ion with the concomitant reduction of Au(III) to Au⁰. This may be a possibility as Au(III) is a relatively strong oxidant (E₀ = 1.42 V vs SHE) and polypyrrole is readily oxidised.

However, the fact that the analytical response seen with these electrodes is most probably due to the reduction of gold from Au(III) to Au⁰ indicates that preconcentration of gold at polypyrrole involves trapping gold in the trivalent oxidation state (i.e. as AuCl₄⁻).

This observation suggest that option (III), discussed above, is not the mode of gold accumulation as any gold collected would be immobilised as Au⁰, not Au(III) and consequently not give rise to a reduction response. Thus, preconcentration of gold at polypyrrole must occur by either anion exchange, adsorption onto the polymer or possibly a combination of both mechanisms.

Having established that it is possible to preconcentrate gold(III) at polypyrrole and that an analytically useful signal could be obtained using polypyrrole modified electrodes.
the next phase of the studies was to determine the effect of polymer synthesis conditions on the analytical response for gold at polypyrrole.

4.3.1.2 The effect of polymer synthesis conditions on the voltammetry of Au(III) at polypyrrole

The previous voltammograms were recorded using polypyrrole synthesised from a solution containing the monomer and NaCl dissolved in water. The effect of the anion present in the synthesis solution on the subsequent voltammetric behaviour of the polymer formed was investigated and reported in Chapter 2 of this thesis. This work was subsequently extended to investigate the effect that these voltammetric differences between polymers may have on the voltammetry of gold(III) at polypyrrole electrodes.

To investigate this a series of polypyrrole polymers were produced incorporating chloride, nitrate, tetrafluoroborate, perchlorate, salicylate and dodecylsulphate(DS−) (0.01 M, Pyrrole 0.05 M) as the counterion in the polymer.

These polymers were subsequently studied to determine whether varying the anion incorporated during the polymerisation process caused any significant changes in the voltammetric response for gold(III) at the polypyrrole electrodes. To achieve this both the potential at which gold(III) was reduced and the magnitude of the reduction response were determined.

It can be seen from Table 4.2 that for a given set of experimental conditions, except in the case of polypyrrole/DS−, the variation in the potential of the gold(III) reduction response is minimal.
The reduction potential of gold at PP/DS\textsuperscript{−} is significantly lower than that at the other polypyrrole electrodes. This may be caused by the fact that polypyrrole/DS\textsuperscript{−} is a poor anion exchanger. The bulky DS\textsuperscript{−} anion is not readily released from the polymer and as such is not available for anion exchange. This anion is tightly bound within the polymer and it has been shown that PP/SDS takes up or expels cations to maintain charge neutrality when changing oxidation states [379]. As a result of the poor anion exchange capacity of PP/SDS it was not studied any further.

The effect of accumulation potential on peak height and potential was investigated. Figure 4.4 shows the effect of accumulation potential on the magnitude of the gold reduction response. The results for these anions show a wide variety of effects.
In the case of chloride the relationship is a linear one, with the increase in accumulation potential from 700 mV to 800 mV causing a similar increase in signal as increasing it from 800 mV to 900 mV. In both cases the reduction response was increased by 0.602 μA.mV⁻¹ increase in accumulation potential.

With the larger oxyanions NO₃⁻ and ClO₄⁻ the increase in accumulation potential from 700 mV to 800 mV cause a similar increase in reduction response as seen with the Cl⁻ anion. In this case the responses are increased by 0.515 μA.mV⁻¹ and 0.600 μA.mV⁻¹ respectively.

A further 100 mV increase in accumulation potential however, causes much more significant increase in the reduction response for gold(III). The response at PP/NO₃⁻ is increased by 0.960 μA.mV⁻¹ increase in accumulation potential and PP/ClO₄⁻ is increased by 1.10 μA.mV⁻¹ increase in accumulation potential. The reason for this dramatic increase in reduction response may be that at the more positive potentials the polymer is more porous, thus facilitating the ion exchange of the larger anions out of
the polymer. This effect would not be as significant for the smaller, more mobile, chloride anion.

The effect of accumulation potential upon the reduction response of gold(III) is most significant for the polymer incorporating the BF$_4^-$ anion. An increase in accumulation potential from 700 mV to 800 mV causes an increase in the reduction response of 0.794 μA.mV$^{-1}$. A further 100 mV increase in accumulation potential causes a further 1.65 μA.mV$^{-1}$ increase in the reduction response. These effects reflect the dependence of this ion exchange reaction on changes in polymer porosity, particularly for the bulky BF$_4^-$ anion.

In contrast to the significant effect that potential has on the accumulation of gold at PP/BF$_4^-$, increases in the accumulation applied to PP/salicylate cause only a small increase in the gold(III) reduction response. An increase in preconcentration potential from 700 mV to 800 mV causes a 0.25 μA.mV$^{-1}$ increase in the analytical response. A further 100 mV increase in accumulation potential causes an additional 0.21 μA.mV$^{-1}$ increase in response. The phenomenon is caused by the fact that the salicylate anion is quite bulky and as such will only exchange with difficulty (PP 105). The application of potential in this case does not significantly improve the ion-exchange reaction.

The effect of accumulation potential on the position of the gold reduction response was also investigated. The data, presented in Figure 4.9, shows a similar trend to that seen previously. The reduction potential becomes more cathodic as the accumulation potential becomes more anodic, again indicating that the polymer is being irreversibly damaged during the accumulation at higher potentials.
Thus, from the preceding data it would appear that the accumulation of gold(III) at polypyrrole electrodes is effected significantly by the anions incorporated into the polymer during polymerisation.

It was previously stated that accumulation of gold at polypyrrole may be due either to anion exchange into the polymer or to adsorption of the gold anions onto the polymer. Studies of the effect of the anion, present during electropolymerisation, on the analytical response have shown that any alteration in the anion exchange capacity of the polymer effects the gold analytical response. From this it can be concluded that the predominant mechanism of preconcentration is anion exchange of \((\text{AuCl}_4^-)\) into the polymer, for if adsorption was the primary preconcentration mechanism, change in polymer ion exchange capacity would have little or no effect on the analytical signal.

In the light of these data the mode of operation for this electrode may be postulated, equation 4.1 summarises this.
The anionic tetrachloroaurate is preconcentrated into the polymer by anion exchange at the potential used for accumulation. Following this the application of a negative going potential causes the gold(III) to be reduced to metallic gold at approximately 500 mV giving rise to the analytical signal.

Given the initial success with the voltammetry of gold at polypyrrole modified electrodes it was decided to investigate this further. The gold solutions used in this initial investigation were too concentrated to provide any useful indication of the limit of detection achievable with these electrodes.

Initially, calibration studies were performed with polymers prepared by galvanostatic oxidation at a current density of 0.5 mA.cm\(^{-2}\) for 6 minutes. These polymers have a nominal thickness of 0.75 μm.

The primary limitation to gold detection with these electrodes is the background signal due to the polymer itself. At the potential where gold(III) reduction occurs the polymer is still highly electroactive and gives rise to a significant reduction response.
As a result of this the detection of gold at concentrations less than 3 mg.L\(^{-1}\) was not possible. Coupled with this, the polymer background response changed significantly between determinations, causing unreliable analytical results. It was felt that this problem may be avoided if thin polymers were used. It can be seen from Table 4.3 that the analytical signal:background signal ratio was improved when thin polymers were used.

**Table 4.3**  
*Effect of film thickness on gold response at polypyrrole electrodes*

<table>
<thead>
<tr>
<th>Polymerisation time(^a)</th>
<th>Film thickness (theoretical)(^b)</th>
<th>Signal(^c) for 5 mg.L(^{-1}) Au ((\mu)A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 minutes</td>
<td>0.75 (\mu)m</td>
<td>51.8</td>
</tr>
<tr>
<td>3 minutes</td>
<td>0.375 (\mu)m</td>
<td>50.7</td>
</tr>
<tr>
<td>1 minutes</td>
<td>0.125 (\mu)m</td>
<td>30.2</td>
</tr>
<tr>
<td>0.5 minutes</td>
<td>0.063 (\mu)m</td>
<td>20.7</td>
</tr>
</tbody>
</table>

\(^{a}\) at 0.5 mA.cm\(^{-2}\)

\(^{b}\) assuming 100% electrochemical efficiency and film density of 1

\(^{c}\) Conditions: \(E_{\text{initial}} = 700\) mV \(E_{\text{final}} = 0\) mV \(E_{\text{dep}} = 900\) mV, \(t_{\text{dep}} = 60\) s

Scan rate = 100 mV.s\(^{-1}\)

The data presented in Table 4.3 indicates that thicker films give better signal. However, as the film becomes thicker the polymer background response becomes more significant and the gold(III) reduction response tends to broaden. This is shown in Figure 4.6. Thus, the best analytical signal is achieved with a very thin polymer, in this case 0.063 \(\mu\)m. With this polymer the limit of detection is, at best 1 mg.L\(^{-1}\). Coupled with this, the linear calibration region is extremely restricted. Figure 4.7 shows the calibration curve for a thin polymer. From this figure it is evident that polypyrrole based sensors do not possess sufficient sensitivity for this application.
Figure 4.6 A comparison of response for 5 mg L^{-1} gold(III) at different polymer thickness

a) 0.063 µm
b) 0.75 µm

Conditions: As in Table 4.3
The preceding investigations have shown it is possible to detect gold(III) with polypyrrole modified electrodes. However, the polymer background signal mitigates against achieving the desired LOD for gold with these electrodes.

It is possible, however, that other conducting polymers, capable of ion exchange, may be better suited to this application.

4.3.2 **POLY(2,2'BITHIOPHENE)**

As with the pyrrole based polymers, the possibility of the use of ion exchange accumulation of gold(III) at poly-2,2'bithiophene was investigated. The attraction of this polymer was its slightly higher positive potential limit over polypyrrole. Poly-2,2'bithiophene electrodes cycled in either M NaCl or 10% aqua regia solution exhibit no voltammetric responses over the potential range 0 to 800 mV. The addition of 50 mg.L$^{-1}$ Au(III) to the NaCl solution causes the appearance of a reduction peak at
470 mV and an oxidation peak at 850 mV, as shown in Figure 4.8a. The peak at 450 mV may be attributed to the reduction of the Au(III) ion to the metallic gold. The peak to peak separation of 400 mV is significantly greater than would be expected. This is primarily due to the difficulty with which gold is reduced.

The application of a preconcentration potential of 1100 mV for 60 seconds prior to a linear sweep scan from 1100 mV to 0 mV causes an increase in the magnitude of the gold(III) reduction peak at 400 mV. This data suggests that with these electrodes, as with those already discussed, the application of a positive potential causes accumulation of the tetrachloroaurate anion.

To verify this the effect of preconcentration potential on the gold(III) response was studied and it was found that, as with the other polymers studied, an increasingly positive accumulation potential resulted in a better analytical signal. This held true up to 900 mV after which the signal decreased with increasing accumulation potential. This is shown in Figure 4.19.
figure 4.8 Voltammetric responses for 50 mg.L⁻¹ Au(III) in M NaCl at a poly(2,2’bithiophene) modified electrode.

a) Cyclic Voltammogram

Conditions: Cyclic voltammetry
- E_{initial} = 1100 mV
- E_{upper} = 1100 mV
- E_{lower} = 0 mV
- Scan rate = 100 mV.s⁻¹

LSSV
- E_{initial} = 1100 mV
- E_{final} = 0 mV
- E_{dep} = 1100 mV
- Scan rate = 100 mV.s⁻¹
- t_{dep} = 60s

b) Linear Sweep Stripping Voltammogram

Electrode: Poly(2,2’Bithiophene) on platinum
Figure 4.9  Effect of accumulation potential on magnitude of gold(III) response at poly 2,2′bithiophene electrodes

Conditions:  
E_{initial} = 800 mV  
E_{final} = 0 mV  
t_{dep} = 60 sec  
Scan rate = 100 mV.s^{-1}  
Sample:  
10 mg.L^{-1} Au(III) in M NaCl  
Electrode:  
Poly(2,2′Bithiophene) on platinum

Figure 4.10 shows the effect of accumulation potential on the potential of the gold reduction peak and, as with the other polymers studied, the potential of this peak becomes more cathodic as the polymer is overoxidised during accumulation.

The fact that this polymer is more resistant to overoxidation than polypyrrole is seen by comparing the linear sweep stripping voltammogram recorded for each polymer at the optimum accumulation potential and at a potential more positive than the optimum. Whereas, with polypyrrole collection at 900 mV gives rise to the best analytical signal and collection at 1000 mV causes the signal to be so degraded it is unquantifiable, accumulation at poly 2,2′bithiophene is optimum at 900 mV with accumulation at 1200 mV causing some loss in response, but no significant degradation of the analytical signal. This is shown in Figures 4.11(a) and 4.11(b).
The limit of detection for gold(III), at these electrodes, was determined and using an electrode polymerised with BF$_4^-$ as the counterion, it was found that detection limits of 1 mg.L$^{-1}$ could be achieved. This is comparable with that achieved using polypyrrole with the added advantage of this polymer being the more positive potential limit available when using it.

The mechanism of gold preconcentration at polythiophene based electrodes is presumably the same as that seen at polypyrrole electrodes and involves the ion exchange accumulation of gold into the polymer.

Many gold bearing ores also contain significant amounts of copper. Therefore, the effect of copper interference upon the gold signal at this sensor was subsequently evaluated. It was found that copper causes a significant depression of the the gold analytical signal. Figure 4.12 shows this effect. As copper is potentially a major interference in the determination of gold this sensor, is unacceptable.
Figure 4.11  
Analytical response for gold(III) at poly 2,2'-bithiophene electrodes

a) Accumulation at 900 mV
b) Accumulation at 1200 mV

Conditions: As in Figure 4.9
Figure 4.12  Linear Sweep Stripping Voltammetric response for the reduction of gold(III) at a poly(2,2’s thiophene) electrode

a) 6 mg.L⁻¹ Au(III) in M NaCl
b) 6 mg.L⁻¹ Au(III) and 6 mg.L⁻¹ Cu²⁺ in M NaCl

Conditions:  $E_{\text{initial}} = 800 \text{ mV}$  $E_{\text{final}} = 0 \text{ mV}$
$\Delta t_{\text{dep}} = 60 \text{ sec}$  Scan rate = 50 mV.s⁻¹

From the data obtained for the polypyrrole and poly (2,2’thiophene) electrodes it would appear that, whilst conducting polymers are capable of preconcentrating the
anionic gold(III) species, the quantification of the gold reduction response is complicated by the polymer background response. As a result of this phenomenon these polymers are not suitable for use as gold sensors. However, in order to confirm this several other conducting polymers were generated and screened to determine both the magnitude and position of the gold(III) reduction response and the relative size of this response in comparison to the polymer background response.

4.3.3 CHEMISORBED POLY(4 VINYLPYRIDINE)

Initial studies involved investigating the voltammetric responses of the PVP modified electrode in both a supporting electrolyte and a solution of gold(III) in supporting electrolyte. Electrodes used in these initial studies were prepared using a technique similar to that described by Cox and Kulesza [174]. This involved dispensing a known volume of a 0.4% W/V solution of PVP in methanol, onto the electrode surface and allowing the methanol to evaporate to dryness. The electrode was then dipped into methanol 3 times, to remove any excess PVP, and allowed to dry. The dried polymer was then protonated by exposing the electrode to 0.1M HCl solution for 20 minutes.

Figure 4.13 shows the response obtained for a glassy carbon electrode (Figure 4.13a), a PVP modified electrode with no preconcentration prior to quantification (Figure 4.13b) and a PVP modified electrode with 4 minutes preconcentration, at no applied potential, prior to the reductive scan (Figure 4.13c). From this figure it can be seen that no gold(III) reduction response is obtained with an unmodified glassy carbon electrode. The presence of PVP on the electrode surface causes a very small gold(III) reduction peak to appear at 500 mV. The size of this peak increases dramatically if gold is accumulated at the electrode for several minutes prior to the reductive scan (4.19c), indicating that the preconcentration and quantification of gold(III) at these electrodes is feasible.
Gold Sensing

Reduction responses for gold(III) at

a) Unmodified glassy carbon electrode
b) PVP modified glassy carbon (no preconcentration)
c) PVP modified glassy carbon (4 minutes preconcentration)

Conditions:

- Initial = 1100 mV
- Final = 0 mV
- Scan rate = 100 mV.s⁻¹
- Sample: 10 mg.L⁻¹ Au(III) in M NaCl

Presumably this response is due to the reduction of gold accumulated at the polymer surface as a result of the preconcentration of AuCl₄⁻ at the protonated amine site on the polymer. This can be depicted schematically by the following equation:

\[
\text{Au}^0 + \text{C:C}^- \rightarrow \text{C:C}^- + \text{[AuCl}_4]^-
\]

Scan cathodic

(4.2)
The ability of the electrode to be used as a gold(III) sensor meant that it warranted further investigation, the first step of which was to optimise the electrode preparation technique. This involved using an alternative approach to electrode preparation. The technique used the procedure described previously but without the methanol dip step. The advantage of this technique is that it provides a more stringent control of the quantity of PVP on the electrode surface.

To evaluate any differences in the results obtained by this technique two electrodes were coated with equal amounts of PVP (11.3 μg.mm⁻²) and allowed to dry. One electrode was then subjected to the methanol rinse prior to protonation whereas the other was protonated directly. Both electrodes were then used for the determination of gold(III). The results for these determinations, given in Table 4.4, show that the non-rinsed electrode provides a better signal for gold(III).

Table 4.4  
Comparative responses for Au(III) at rinsed and non rinsed PVP electrodes

<table>
<thead>
<tr>
<th>Accumulation time (min)</th>
<th>Analytical Response (μA)(b)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rinse Electrode</td>
<td>Non-rinsed Electrode</td>
<td></td>
</tr>
<tr>
<td></td>
<td>No B/G correction</td>
<td>B/G Correction</td>
<td>No B/G correction</td>
</tr>
<tr>
<td>0</td>
<td>N.D</td>
<td>2.38</td>
<td>2.12</td>
</tr>
<tr>
<td>5</td>
<td>1.95</td>
<td>2.95</td>
<td>2.66</td>
</tr>
</tbody>
</table>

(a) Accumulation at no Eapp  
(b) Conditions:  
Waveform: Osteryoung square wave voltammetry (OSWV)  
Einitial = 1100 mV  
Efinal = 0 mV  
AC amplitude = 25 mV  
Frequency = 15Hz  
Step potential = 4 mV  
Sample : 5 mg.L⁻¹ Au (III) in M NaCl/ 1.5% aqua regia  
(c) Achieved by performing a blank determination of the polymer in supporting electrolyte only and subtracting this response from the analytical response after the determination.

As a consequence of these results the methanol rinse step was dispensed with for all subsequent studies.
4.3.3.1 Optimisation of analytical waveform

The choice of a suitable analytical waveform for the determination of gold(III) at PVP modified electrodes was also determined. Three techniques were evaluated, these were Osteryoung square wave stripping voltammetry (OSWSV), differential pulse stripping voltammetry (DPSV) and linear sweep stripping voltammetry (LSSV). In all cases the scans were preceded by 60 s accumulation at no applied potential. The responses obtained by each technique are shown in Figure 4.14. From this figure it can be seen that LSSV provides the most sensitive response for gold(III). As such, LSSV was the technique used in almost all of the subsequent work.
Comparison of responses for various potential waveforms

a) Osteryoung square wave stripping voltammetry
b) Differential pulse stripping voltammetry
c) Linear sweep stripping voltammetry

Conditions:

OSWSV: AC amplitude = 25 mV
DPSV: Scan rate = 10 mV.s⁻¹
pulse width = 50 ms;
LSSV: Scan rate = 500 mV.s⁻¹
All determinations 1 minute preconcentration at no Eapp

Sample: 10 mg.L⁻¹ Au(III) in M NaCl

Using LSSV the effect of scan rate upon the analytical response was determined and it was found that peak height was directly proportional to scan rate (Figure 4.15) indicative of a surface bound species undergoing a redox change [287].
The preceding scan rate studies were performed using the same electrode, regenerated between scans. Regeneration was achieved by scanning the electrode 20 times between the potential limits 1100 mV to 0 mV. This was done in a well stirred solution of 3% aqua regia. At the completion of the regeneration exercise a blank determination was performed to ensure that no gold response was evident.

During this regeneration the gold metal deposited on the electrode is reoxidised to $(\text{AuCl}_4)^-$ which is subsequently exchanged out of the polymer by the anions present in the regeneration solution. This is depicted in equation 4.3. Stirring is required to ensure that gold is rapidly depleted from the polymer/solution interface.

\[
\begin{align*}
\text{(AuCl}_4)^- + \text{Cl}^- & \rightarrow \text{(AuCl}_4)^2- \\
\text{(AuCl}_4)^2- + \text{Cl}^- & \rightarrow \text{(AuCl}_4)^- \\
\text{(AuCl}_4)^- + \text{Cl}^- & \rightarrow \text{(AuCl}_4)^2- \\
\text{Cl}^- & \rightarrow \text{Cl}^- \\
\text{Cl}^- & \rightarrow \text{Cl}^- \\
\end{align*}
\]  

(4.3)
Optimisation of analytical conditions for Chemisorbed PVP

The work described in the previous sections was performed using a starting potential of 1100 mV for the analytical determination. To further optimise the determination of gold(III) with the PVP electrodes the effect of altering the starting potential had on the resulting analytical response was determined.

A PVP electrode was used to determine gold(III) in solution, starting from various initial potentials. As with the previous study, the electrode was regenerated between determinations. The data obtained is given in Table 4.5 and shows that up to 1300 mV a more positive initial potential leads to a greater analytical signal. Starting potentials of 1400 mV or greater cause irreversible damage to the polymer, presumably due to oxidation of double bonds within the polymer backbone. This results in a significant change in the gold reduction potential at the PVP electrode and a difficulty in reproducibly determining the gold response. Reverting to a starting potential less than 1400 mV in subsequent determinations does not lead to a return of the original analytical signal. This indicates that the polymer has been irreversibly damaged.

These results indicate that starting the potential scans from 1300 mV will achieve the greatest sensitivity without causing significant damage to the polymer. Presumably the cause for this improvement in signal is that the gold(III) anion is attracted to the positively charged, protonated polymer, the more positive the charge the greater the attraction.

Subsequent studies showed that continual use of this starting potential caused a gradual degradation of the polymer with the concomitant loss of analytical signal. Therefore a starting potential of 1100 mV was used for all subsequent investigations.
4.3.3.3 Optimisation of electrode preparation

Even though the PVP electrodes studied gave an acceptable response it was possible that an increase in sensitivity could be achieved by optimising the polymer film build. Therefore the effect of polymer thickness on the analytical response and the linear response range for the electrode was studied. To investigate this, a series of PVP modified electrodes were prepared with varying polymer film thicknesses. These electrodes were then protonated in N/10 H₂SO₄ for 10 minutes and subsequently used for the determination of gold(III). The results obtained are shown in Table 4.6

Table 4.6 Effect of polymer coating on analytical response

<table>
<thead>
<tr>
<th>Surface concentration of PVP (µg/mm²)</th>
<th>Allquot (µL) of 4% w/v PVP solution</th>
<th>Film thickness (µm)</th>
<th>Analytical response (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>2.5</td>
<td>1.4</td>
<td>1.37</td>
</tr>
<tr>
<td>2.8</td>
<td>5.0</td>
<td>2.8</td>
<td>1.54</td>
</tr>
<tr>
<td>5.7</td>
<td>10.0</td>
<td>5.7</td>
<td>1.15</td>
</tr>
<tr>
<td>11.3</td>
<td>20.0</td>
<td>11.3</td>
<td>0.94</td>
</tr>
<tr>
<td>28.3</td>
<td>50.0</td>
<td>28.3</td>
<td>0.85</td>
</tr>
</tbody>
</table>

a Conditions: waveform: LSV
Eₐᵣₙᵢ₅ = 1100 mV; Eₐᵣₐₙ = 0 mV; Scan rate = 500 mV.s⁻¹
deposition time = 60s, no applied potential
b Sample: 1 mg.L⁻¹ Au(III) in 3% aqua regia
c Calculated assuming a protonated film density of 1 g.cm⁻³ [174]
These data indicate that increasing the amount of PVP added to the electrode surface increases the signal. This was presumably due to the increased number of anion exchange sites available. This effect held true up to a point, after which any increase in ion-exchange capacity was negated by increased resistance due to the polymer film. This increase in resistance was evidenced by the broad, drawn out gold chloride reduction responses which were observed using thicker coatings.

The trade-off here is between ion-exchange capacity and sensitivity. It was decided to use polymers prepared with a surface concentration of PVP within the range 2.8 - 11.3 µg/mm² (5 - 20 µL of solution) for the calibration studies.

### 4.3.3.4 Calibration studies

Using electrodes prepared as described previously, the dependence of analytical signal upon gold concentration was determined. As with previous studies it was necessary to cycle the electrodes in supporting electrolyte between scans to removed any gold bound to the electrode surface.

A calibration curve for gold(III) at a PVP electrode is shown in Figure 4.16. From this figure it can be seen that the analytical response is linear over the range 0-10 mg.L⁻¹ with a practical limit of detection of 1 mg.L⁻¹. While this LOD is still no low enough it may be improved by using thinner polymers or longer preconcentration times.
The calibration curve determined using a thinner polymer (2.8 μg.mm⁻² PVP) on glassy carbon is shown in Figure 4.17. This graph shows that the analytical signal flattens out at gold concentrations above 5 mg.L⁻¹, presumably due to saturation of the preconcentration sites on the polymer.

The analytical response is not linear over the 0-5 mg.L⁻¹ concentration range. However the calibration curve shows that it would be possible to quantify gold levels over this concentration range. The LOD for this electrode was approximately 0.2 mg.L⁻¹.
The effect of copper ions on the determination of gold was determined and it was found that, although the presence of Cu\(^{2+}\) in solution caused some suppression of the gold(III) reduction response it did not adversely affect the determination provided standard addition techniques were used. Table 4.7 lists the analytical response for gold(III) both with and without Cu\(^{2+}\) present.
4.3.4 **ELECTROCHEMICALLY GENERATED PVP (EC-PVP)**

The major problem with the PVP electrodes prepared as described in the preceding section is the modification technique used. In practice it was difficult to prepare reproducible electrodes using the chemisorption approach to electrode modification. Secondly, the adhesion of the modifier to the electrode surface was poor and as such the mechanical stability of the electrodes proved to be a problem.

Both of these problems, reproducibility and stability could be alleviated, if not totally removed, by the use of electrochemically generated polymers. Thus, it was decided to investigate the possibility of preparing a poly(4-vinylpyridine) modified electrode by electrochemical techniques.

### 4.3.4.1 Electrode preparation

The phenomenon of electrochemically initiated vinyl polymerisation was reported in the early 1950's [181]. Using this approach, initiators, electrochemically generated at the working electrode, react with the vinyl containing monomer and if conditions are right, a polymer will deposit on the working electrode [181]. Because the film itself is an insulator only very thin films are formed.

Initial studies were performed with a supporting electrolyte comprised of 60% N,N'-dimethylacetamide and 40% 0.2 M H$_2$SO$_4$. To this supporting electrolyte was added 5 mM 4-vinylpyridine and 1 mM divinylbenzene. A cyclic voltammogram recorded for this solution over the potential range 0 - 2000 mV is shown in Figure 4.18 (scans a-e).

---

**Table 4.7** Responses for 10mg.L$^{-1}$Au(III) at PVP modified electrodes

<table>
<thead>
<tr>
<th>No Cu$^{2+}$ (mg.L$^{-1}$)</th>
<th>Response($\mu$A) with $10mg.L^{-1}$ Cu$^{2+}$ present</th>
<th>With $20mg.L^{-1}$ Cu$^{2+}$ present</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8.47</td>
<td>7.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.26</td>
</tr>
</tbody>
</table>
From this figure it can be seen that on the first reductive scan (a) that a large reduction peak centred on -1500 mV is evident. This peak decreases in size with subsequent scans (b - c) as the electrode is coated with what appeared to be a poorly conducting polymer layer.

Figure 4.18  Cyclic voltammogram for the electropolymerisation of the 4-vinylpyridine/divinylbenzene mixture.

Conditions:  
E\text{initial} = 0 \text{ mV} \quad E\text{lower} = -2000 \text{ mV} \\
E\text{upper} = 0 \text{ mV} \quad \text{Scan rate} = 100 \text{ mV.s}^{-1}

A steady state voltammogram of the polymer coated electrode in 0.1 M HCl is shown in Figure 4.19. The shape and magnitude of the voltammetric response indicate that the glassy carbon electrode is coated with a surface layer of sorts and that this contaminant does not have any appreciable redox responses over the potential region investigated.
In order to ascertain which components of the polymerisation mixture were being reduced a series of cyclic voltammograms were recorded. The N,N'-dimethylacetamide:H₂SO₄ supporting electrolyte was found to exhibit only a change in baseline slope between -1000 mV and -1500 mV, presumably due to hydrogen evolution in the acidic solution. 4-vinylpyridine in the supporting electrolyte has a significant reduction peak at -1250 mV, however cycling the electrode potential past this limit for a number of scans does not result in the formation of a polymer on the electrode. This fact was confirmed by performing a cyclic voltammogram, of the electrode scanned in the 4-vinylpyridine, in M NaCl. No polymer response was evident at all. The addition of divinylbenzene to the polymerisation mixture causes the appearance of the peak centred around -1500 mV and the formation of the polymer on the electrode surface. Thus the polymerisation reaction would appear to involve the formation of a reactive species by the reduction of 4-vinylpyridine however the presence of divinylbenzene is required to achieve film formation.
4.3.4.2 Ion exchange properties

The modification scheme described above was sufficient to form a polymer on the electrode surface. What was not clear however, was whether or not this polymer was capable of ion exchange preconcentration.

To investigate this the electrode was cycled in a $10^{-5}$ M ferricyanide solution. It can be seen from Figure 4.20 that on the first scan no distinctive oxidation peak is seen, the first reductive cycle shows a significant Fe(III)/Fe(II) reduction peak after which both the reduction and oxidation peaks increase in size with continued cycling. This increase in peak size is caused by a gradual accumulation of ferricyanide/ferrocyanide in the polymer. The reduction-oxidation peak to peak separation of 49 mV is less than would be expected for a single electron transfer reaction in solution and is more in keeping with a redox reaction involving surface bound species, albeit with polymer iR drop contributing to the peak-peak separation. This non-zero peak-peak separation for Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ redox transitions at PVP modified electrodes has been reported previously [384]. These authors attribute this increase in $\Delta$Ep to slow electron transfer between the electrode and the redox centres in the polymer film as well as film or solution resistance effects.

Another indication that this response is not a solution response is the observation that a glassy carbon electrode cycled in the same solution under identical conditions does not exhibit any Fe(II)/Fe(III) redox responses.
Figure 4.20 Cyclic voltammogram of PVP modified electrode in 10⁻⁵M Fe(CN)₆⁴⁻.

Conditions:
- \( E_{\text{initial}} = 0 \text{ mV} \)
- \( E_{\text{upper}} = 700 \text{ mV} \)
- \( E_{\text{lower}} = 0 \text{ mV} \)
- Scan rate = 100 mV.s⁻¹

Sample:
- \( 10^{-5}\text{M K}_4\text{Fe(CN)}_6 \) in H₂O (no supporting electrolyte)

A cyclic voltammogram for an electrochemically generated PVP modified electrode in a 2 mg.L⁻¹ gold(III) solution is shown in Figure 4.21. From this figure it can be seen that a sharp, distinctive gold(III) reduction peak is evident at 450 mV.
From these data it would appear that the electrochemically generated PVP electrodes are suitable for gold accumulation and determination and warrant further investigation.

### 4.3.4.3 Gold determination - optimisation of potential waveform

The previous study with chemisorbed PVP, showed that the voltammetric stimulus used during quantification significantly affected the analytical result and that, contrary to expectations the pulsed techniques gave no improvement in signal to noise ratio.

Three voltammetric techniques were used to study the gold(III) reduction responses at the EC-PVP electrodes. The techniques used were linear sweep stripping voltammetry, Osteryoung square wave stripping voltammetry and differential pulse stripping voltammetry. In all cases the determinations were carried out with both 1 mg.L⁻¹ and 200 µg.L⁻¹ Au(III) solutions and included 60 seconds preconcentration at 1100 mV prior to the determination.

The results from these determinations are given in Table 4.8. From these data it may be seen that at both concentrations results obtained by LSSV (at 500 mV.s⁻¹) are superior to
those obtained by OSWSV and DPSV. The greater signal obtained by LSSV coupled with the "cleaner" background response (Figure 4.22) meant that LSSV was used for all subsequent studies.

Table 4.8  **Responses obtained with various voltammetric waveforms**

<table>
<thead>
<tr>
<th>Au(III) concentration (mg.L⁻¹)</th>
<th>LSSV</th>
<th>OSWSV</th>
<th>DPSV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>14</td>
<td>2.2</td>
<td>0.07</td>
</tr>
<tr>
<td>0.1</td>
<td>3.9</td>
<td>1.6</td>
<td>ND</td>
</tr>
</tbody>
</table>

Conditions: As in Figure 4.20 with accumulation at 1100 mV

The greater sensitivity of the linear sweep technique over the pulse techniques is contrary to expectations and may simply be a function of the higher scan rate used.

To investigate this a LSSV scan performed at 500 mV.s⁻¹ was compared with an OSWSV scan performed at the same scan rate. The response for 1 mg.L⁻¹ Au(III) determined by these scans was 11 μA and 5.5 μA respectively, indicating that it is not merely a scan rate effect. The increased signal observed with linear sweep techniques may be caused by a nonfaradaic component of the analytical response. This would be filtered out by pulse techniques.

An alternate explanation of this observation is that pulse techniques (especially square wave techniques) rely on the rapid reduction and oxidation of the analyte to achieve the enhancement of the analytical signal. This cycling of gold between the oxidised and reduced state is kinetically quite slow. This would adversely affect any potential enhancement analytical signal to be gained from using pulsed techniques.
Figure 4.22 Analytical responses for Au(III) at a glassy carbon electrode modified with EC-PVP

a) LSSV
b) OSWSV
c) DPSV

Conditions:
- \( E_{\text{initial}} = 1100 \text{ mV} \)
- \( E_{\text{final}} = 0 \text{ mV} \)
- \( t_{\text{dep}} = 60 \text{ sec} \)
- LSSV: Scan rate = 100 mV.s\(^{-1}\)
- OSWSV: AC amplitude = 25 mV, frequency = 15Hz, Step E = 4 mV
- DPSV: Scan rate = 10 mV.s\(^{-1}\), pulse width = 50 ms, pulse amplitude = 50 mV, pulse period = 1000 ms

Sample: 0.1 mg.L\(^{-1}\) Au(III) dilute aqua regia supporting electrolyte
4.3.4.4 Optimisation of analytical conditions

Both the scan starting potential and accumulation potential have had a considerable effect on the analytical signal obtained with the modifiers studied to date. Therefore it is to be expected that a similar effect may be experienced with EC-PVP modified electrodes.

This investigation was initially carried out by analysing a sample containing 250 \( \mu \text{g.L}^{-1} \) Au(III). The analytical procedure involved 60 seconds accumulation at the starting potential followed by a reductive scan to 0 mV at a scan rate of 500 mV.s\(^{-1}\). The electrode used for this study was regenerated between scans. The data listed in Table 4.9 indicates that the maximum analytical response can be obtained if accumulation occurs at 1200 mV. Accumulation or starting potentials greater than this cause irreversible damage to the polymers.

<table>
<thead>
<tr>
<th>Starting Potential</th>
<th>Peak Current (( \mu \text{A} ))</th>
<th>Peak Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1000</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>1100</td>
<td>2.31</td>
<td>496</td>
</tr>
<tr>
<td>1200</td>
<td>6.97</td>
<td>494</td>
</tr>
<tr>
<td>1300</td>
<td>Electrode damaged by applied potential</td>
<td></td>
</tr>
</tbody>
</table>

(a) Conditions: \( E_{\text{final}} = 0 \text{ mV} \) Scan rate = 500 mV.s\(^{-1}\)
(b) Sample: 250 \( \mu \text{g.L}^{-1} \) Au(III) in M NaCl

From these data the optimum accumulation potential was determined to be 1200 mV. However, it was later found that using this accumulation potential causes a slow degradation of the analytical response again indicating that the polymer is irreversibly oxidised at these potentials. Thus for all further studies the upper potential was limited to 1100 mV.

Using the potential window of 1100 mV to 0 mV for the analytical scan the effect of the deposition potential was also investigated. As with the starting potential the magnitude
of response increases as the deposition potential increases. The maximum response is obtained with a deposition potential of 1200 mV, however this causes slow degradation of the polymer and 1100 mV was the maximum deposition potential for all subsequent determinations.

The electrolyte matrix used for gold determination was also found to have a significant effect on the gold(III) reduction response. Table 4.10 lists some electrolytes studied and the results obtained. Aqua regia (3%) was chosen as the supporting electrolyte for gold determination as it provided the best analytical signal with the least level of background response.

Table 4.10  
Matrix Effects

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Blank response</th>
<th>Gold response $^{a,b}$ (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% Aqua regia</td>
<td>Sloped background</td>
<td>3.94</td>
</tr>
<tr>
<td>0.1 M HCl</td>
<td>Sloped background</td>
<td>7.99</td>
</tr>
<tr>
<td>0.1 M HClO$_4$</td>
<td>destroys polymer</td>
<td></td>
</tr>
</tbody>
</table>

(a) Conditions:  
$E_{\text{initial}} = 1100$ mV  
Scan rate = 500 mV.s$^{-1}$  
(b) Sample: 100 μg.L$^{-1}$ Au(III)

4.3.4.5  Optimisation of electrode preparation

Given that the optimum conditions determined provide the best analytical response for gold(III) there remains but one more parameter to be optimised, that is the preparation of electrodes. It is to be expected that there will be an optimum polymer thickness, above which iR drop across the film will cause a degradation of the analytical signal and below
which the ion exchange capacity of the polymer will either be too low to achieve a reasonable analytical signal or will saturate readily and possess a very limited linear range.

Table 4.11 lists the results obtained with polymerisation solutions containing varying amounts of 4-vinylpyridine. In all cases the electrodes were polymerised for 5 cycles (0 to -1500 mV and return) at 100 mV.s\(^{-1}\).

**Table 4.11**  
_The effect of varying 4-vinylpyridine concentration in the electropolymerisation solution on the magnitude of the Analytical response\(a, b\)_.

<table>
<thead>
<tr>
<th>4-vinylpyridine concentration (mM)(c)</th>
<th>Analytical Response (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>not detected</td>
</tr>
<tr>
<td>15</td>
<td>not detected</td>
</tr>
<tr>
<td>24</td>
<td>17.3</td>
</tr>
<tr>
<td>33</td>
<td>16.5</td>
</tr>
</tbody>
</table>

\(a\) Conditions:  
LSSV \(E_{\text{initial}} = 1100\) mV \(E_{\text{final}} = 0\) mV  
Scan rate = 500 mV.s\(^{-1}\) \(E_{\text{dep}} = 60\)s

\(b\) Sample: 250 μg.L\(^{-1}\) Au in M NaCl

\(c\) All electrodes were polymerised from a solution containing 1.0 mM divinylbenzene

Increasing the number of scans during the polymerisation step was also investigated and it was found that electrodes prepared with 10 cycles (0 to -1500 mV) were approximately 50% less sensitive than those prepared with only 5 cycles over the same potential range.

From these data it can be concluded that there is an optimum film thickness for gold determination and that this can be achieved by using a solution containing 24 mM 4-vinylpyridine, 1 mM divinylbenzene in a 60:40 N,N'-dimethylacetamide: 0.2 M H\(_2\)SO\(_4\) supporting electrolyte. The polymerisation is achieved by cycling the electrode for 5 complete cycles between the potential limits of 0 mV and 1500 mV at 100 mV .s\(^{-1}\). The actual thickness of the polymer formed has not been determined.
4.3.4.6 Calibration studies

Using the optimum analytical conditions and electrode preparation techniques described above calibration curves were prepared using gold(III) chloride as the analyte. The objective of this study was to determine both the limit of detection and response linearity for this system.

The analytical response for \((\text{AuCl}_4)^-\) was found to be linearly dependant upon gold(III) concentration up to 100 \(\mu\text{g.L}^{-1}\) after which a loss of linearity is evident. Presumably this is due to saturation of the available ion exchange sites on the polymer. Figure 4.23 shows the calibration curve obtained for gold(III) chloride.

![Calibration curve for \((\text{AuCl}_4)^-\) at a glassy carbon electrode modified with \(\text{EC PMP}\).](image)

**Figure 4.23** Calibration curve for \((\text{AuCl}_4)^-\) at a glassy carbon electrode modified with \(\text{EC PMP}\).

**Conditions:**
- LSV
- \(E_{\text{initial}} = 1100\text{ mV}\)
- \(E_{\text{final}} = 0\text{ mV}\)
- \(\text{Scan rate} = 500\text{ mV.s}^{-1}\)
- \(t_{\text{dep}} = 60\text{ s}\)
- \(E_{\text{dep}} = 1100\text{ mV}\)

**Sample:** \((\text{AuCl}_4)^-\) in 3% aqua regia solution

Using this electrode and the conditions described above a LOD of 5 \(\mu\text{g.L}^{-1}\) could be achieved.
The recovery of gold from gold bearing ores is usually achieved with the carbon in pulp extraction process. This process involves the dissolution of the gold into a cyanide solution with the formation of gold cyanide. Consequently, it was decided to investigate the electrochemistry of gold cyanide at a PVP modified electrode.

A cyclic voltammogram recorded for a 50 mg.L⁻¹ gold cyanide in NaN₃ (Figure 4.24a) shows a distinct gold reduction response at -500 mV, this can be attributed to the reduction of gold cyanide to metallic gold according to:

\[ \text{Au(CN)₂}^- + e^- \rightarrow \text{Au} + 2\text{CN}^- \]  \hspace{1cm} (4.4)

The reduction potential for gold cyanide is much lower than gold chloride indicating that this species is more difficult to reduce, and hence more stable than the chloro species. Also, the analytical response for the cyanide complex is less sensitive than that observed for the chloro complex.

This characteristic of the cyanide complex, coupled with the fact that any excess cyanide in solution can potentially impede gold preconcentration necessitates the acidification of the gold cyanide solution prior to analysis. This was achieved by the addition of aqua regia to convert the cyanide salt to a chloride salt with the concomitant evolution of HCN according to:

\[ \text{K(AuCN₂)} + 2\text{HCl} \rightarrow \text{K(AuCl₂)} + 2\text{HCN} \]  \hspace{1cm} (4.5)

A cyclic voltammogram of gold cyanide in M NaCl/3% aqua regia is shown in Figure 4.24b. The appearance of a new reduction peak at 375 mV indicates that a proportion of the gold cyanide has been converted to the chloro complex. However, the presence of a broad reduction peak at -500 mV suggests that there is still a significant level of gold cyanide present.
Quantification of the gold levels was achieved using acidified cyanide solution and the same experimental conditions as those employed for the determination of gold(III) chloride.

A LSSV scan of a gold cyanide sample treated in this manner is shown in Figure 4.25. The gold reduction potential has shifted by approximately 200 mV more cathodic than the \((\text{AuCl}_4)^-\) reduction response. This data may indicate that the species formed is not...
(AuCl)_2^- as expected, for this would have a reduction potential approximately 100 - 200 mV positive of the (AuCl_4^-) reduction potential. The fact that this gold complex is more difficult to reduce than the straight gold-chloride complex suggest that the species being reduced is not a simple gold chloro complex but rather an alternate species. For example, (Au(Cl)(OH))^- can exist in solutions of pH 3.2. This has a reduction potential significantly lower than either (AuCl_4^-) or (AuCl_2^-) \[385\] and may be the species being reduced here.

Using this technique a calibration curve for gold cyanide detection was prepared (Figure 4.26) and the response was determined to be linear over the gold concentration range 0 - 100 μg.L^-1 after which saturation of the polymer occurs. At this point the analytical response is limited by the available ion exchange sites in the polymer and not the gold concentration.
4.3.4.7 Copper interference

The most common interference in the ASV determination of gold is the presence of copper in the sample matrix. This is usually removed by a solvent extraction step prior to the gold analysis.

In acidic chloride media the gold is generally present as \((\text{AuCl}_4)^-\), the log \(\beta\) value for this species is 26 indicating that the equilibrium:

\[
\text{AuCl}_3 + \text{Cl}^- \rightleftharpoons (\text{AuCl}_4)^- \quad (4.6)
\]

lies very much to the right of the equation. Copper ions in chloride solution have four stepwise equilibrium constants for the reaction:

\[
\begin{align*}
\text{Cu}^{2+} + \text{Cl}^- & \rightleftharpoons (\text{CuCl})^+ \quad (4.7) \\
(\text{CuCl})^+ + \text{Cl}^- & \rightleftharpoons (\text{CuCl}_2) \quad (4.8)
\end{align*}
\]
\( (\text{CuCl}_2) + \text{Cl}^- \iff (\text{CuCl}_3)^- \) \hfill (4.9)
\( (\text{CuCl}_3)^- + \text{Cl}^- \iff (\text{CuCl}_4)^- \) \hfill (4.10)

The log \( B \) values for these reactions are 0.98, 0.69, 0.55 and 0.0 respectively, indicating that the favoured species in chloride media is the \( \text{Cu}^{2+} \) species.

The situation in cyanide media is somewhat different with the log \( B \) values for \((\text{AuCN}_2)^-\) and \((\text{AuCN}_4)^-\) being 38.3 and 56 respectively. For copper, the species \( \text{CuCN}_2, (\text{CuCN}_3)^- \) and \((\text{CuCN}_4)^2-\) have log \( B \) values of 24, 28.6 and 30.3. Thus, in a cyanide solution both anionic gold and copper species would be present.

This information suggests that with a judicious choice of supporting electrolyte (i.e. high \( \text{Cl}^- \) concentration) it should be possible to determine gold with little or no interference from copper.

A calibration curve was prepared using a series of gold standards in a matrix of 0.1M HCl containing 5 mg/L \( \text{Cu}^{2+} \). It was found that, in contrast to sample containing only gold, the analytical response was not linear. However, this deviation from linearity did not render the response unusable as the calibration curve (Figure 4.27) shows.

\[ \text{Figure 4.27} \quad \text{Calibration curve for Au(III) in the presence of 5 mg.L}^{-1} \text{ Cu}^{2+} \]

Conditions: As in Figure 4.25
Sample: Au(III) in 0.1M HCl with 5 mg.L\(^{-1}\) Cu\(^{2+}\)
The effect of cyanide in this solution was also investigated and it was found (Table 4.12) that the addition of 1 mg.L\(^{-1}\) CN\(^{-}\) to an acidified solution containing 100 µg.L\(^{-1}\) Au(III) caused a significant drop in the analytical response and a 62 mV cathodic shift in the gold reduction potential.

<table>
<thead>
<tr>
<th>Cyanide concentration (mg.L(^{-1}))</th>
<th>Response (µA)</th>
<th>Reduction potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.0</td>
<td>420</td>
</tr>
<tr>
<td>1</td>
<td>1.3</td>
<td>360</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>340</td>
</tr>
<tr>
<td>5</td>
<td>1.4</td>
<td>330</td>
</tr>
</tbody>
</table>

*Table 4.12  Effect of cyanide on gold reduction response\(^{a,b}\)*

\(^{a}\) Conditions: as in Figure 4.25

\(^{b}\) Sample 100µg.L\(^{-1}\) Au(III) in 0.5M HCl

The shift in reduction potential with the addition of cyanide is consistent with the formation of a new species in solution, a species more difficult to reduce than (AuCl\(_4\))\(^{-}\). By implication this species probably contains CN\(^{-}\).

The major shift in reduction potential and peak response suggests that the equilibrium is established immediately upon the addition of the first aliquot of CN\(^{-}\) and further additions of CN\(^{-}\) do little to alter this equilibrium. The probable scenario is that the excess cyanide merely reacts with the HCl and liberates HCN. The addition of copper to this solution also causes a significant decrease in the gold response. It would therefore appear that in order to achieve the maximum response for gold in a cyanide medium mere acidification is insufficient. Thus the cyanide needs to be destroyed by using either oxidative conditions or UV radiation to aid the degradation process.

The only other interferences to be investigated were Ag and Pt, both of which can exist as anionic chloro complexes in a high chloride media. Figure 4.28 shows a LSSV scan for a solution containing 100 µg.L\(^{-1}\) each of gold and platinum.
Responses were detected for both gold (456 mV) and platinum (168 mV). However the response for either metal was lower than that determined for each metal individually as both are competing for the same total number of ion exchange sites on the polymer. Silver gave no response at all.

4.4 CONCLUSION

The preceding studies have shown that there is a significant degree of interaction between the gold(III) anion and most of the conducting polymers studied. The mechanism of this interaction appears to be ion exchange of the gold chloro anion into the polymer. Although this interaction can be used to preconcentrate gold into the polymer. It is not possible to use conducting polymer based CMEs for gold sensing as the background response for the polymer swamps any analytical response present.

Secondly, the detection of gold(III) at poly(4-vinylpyridine) modified CMEs has been demonstrated to be viable. Presumably the interaction of gold with this polymer is
through the protonated amine groups present in the polymer structure. The preparation of these sensors may be achieved by two methods. The first involves the chemisorption approach whereby the polymer is dissolved in a suitable solvent, an aliquot of solution placed on the electrode and the solvent left to evaporate. The advantage of this approach is that electrode modification is simple and surface concentrations of PVP are easily altered. The disadvantage is that using this modification technique it is difficult to reproducibly modify electrodes. In terms of improved reproducibility a better approach to electrode modification is the use of electrochemically generated PVP. This has been shown to exhibit the appropriate ion exchange properties to make it suitable for use as a gold(III) sensor with the electrode preparation technique being more readily controlled and more reproducible.

Studies of potential interferences have shown that those species that form stable anionic complexes, in the supporting electrolyte being used for the gold determination, will interfere with the gold detection by virtue of the fact that they compete with the gold anion for the available ion exchange sites on the polymer electrode. A judicious choice of electrolyte conditions may minimise this effect.
CHAPTER 5
COLLECTION OF MERCURY AT CHEMICALLY MODIFIED RVC

5.1 INTRODUCTION

Chapter 3 of this thesis dealt with the use of chemically modified electrodes in the determination of methylmercury. The techniques used in this work rely on the chemical and electrochemical interaction of the analyte with the electrode modifier. It is entirely feasible that such reactions, provided they can be scaled up, could provide the basis of a solid phase adsorbent for the preconcentration of mercury species from aqueous systems.

5.1.1 SAMPLING OF MERCURY FROM AQUEOUS SYSTEMS

The stability of mercury compounds in aqueous samples has been studied by a number of workers [12, 13, 386]. To minimise losses of inorganic mercury it is suggested that the sample be adjusted to a low pH, high ionic strength oxidising environment and that all samples be stored in glass containers only [12].

Attempts to preconcentrate mercury from solution using solid phase extraction prior to quantification have used several different supports. Koshima and Hiroshi [88] have used activated carbon as the preconcentration medium. These authors claim 97% collection efficiency for inorganic mercury and 87% for methylmercury. Once collected the mercury was quantitatively determined by graphite furnace atomic absorption spectroscopy.
Preconcentration onto dithiocarbamate functionalised resins has been used by several authors [71, 72, 78, 79]. Minogawa et al. [71] used a commercial dithiocarbamate resin, Sumichelate Q10, for the collection of mercury from river water and fresh water samples. These authors report essentially quantitative collection of mercury over a wide pH range. Quantification of mercury, once collected, was achieved by cold vapour atomic absorption spectroscopy (CVAAS). A more recent study of this resin by Lansen et al. [72] has reported results that conflict with those presented previously. Whereas Minagawa found rapid, quantitative preconcentration of mercury over a wide pH range, the recent study reports rapid adsorption of 90% of the mercury present but states that 20 hours is required to achieve 97% removal. This study also found that pH was more critical than initially indicated with collection being optimum within the 4 - 10 pH region.

Using identical conditions to the previous study, Hansen found a 12.5% loss of mercury during sampling, compared with no losses seen on the initial studies. The reason for the discrepancies may be that the reagent blanks in the earlier study were of the same order of magnitude as the samples being analysed. Also the limit of detection quoted in the latter study (2 ng.L\(^{-1}\)) appears to be significantly lower than that achieved in the initial work.\(^1\)

Brown et al. [79, 78] have manufactured polyurethane disks loaded with diethylammonium diethyldithiocarbamate, these authors found that it was necessary to include a plasticiser (\(\alpha\)-dinonylphthalate) to the derivatisation mixture to achieve quantitative mercury retention at higher flow rates [79]. The mechanism of collection enhancement was not discussed in either paper. Quantitation is achieved by XRF, and it is interesting to note that these authors

\(^1\) These authors quote a 0.2 ngL\(^{-1}\) LOD for their method. This involves a 20 L to 30 mL preconcentration step which would imply a LOD for the determination step of \(\approx 133\) ngL\(^{-1}\).
report quantitative elution of the Hg dithiocarbamate complexes from the foam using acetone.

Other methods of mercury preconcentration include amalgamation onto silver or gold [387, 388] solvent extraction [312] and extraction onto sulphydryl cotton [76].

5.1.2 AIM AND SCOPE

It can be seen from the introductory information that, although there has been a great deal of activity in the field of mercury collection, there is still scope for improvement. Of particular interest here is the application of chemically modified electrodes to this application.

To achieve this requires the use of processes combining both an electrochemical and a chemical collection mechanism to enhance collection efficiencies. This can be achieved in either of two ways,

(i) Chemical step (eg. complexation) followed by an electrochemical process (eg. reduction of the mercury collected)

OR

(ii) Electrochemically enhanced chemical step, for example the application of a potential may enhance a complexation reaction, by altering the charge density at the point of interaction.

With the appropriate choice of electrode modifier it is possible to develop a sampling electrode with surface chemistry mimicking that found in conventional solid phase adsorbents. The analyte-electrode interactions may be further altered by the application of a potential to the electrode. In a manner analogous to the preconcentration step in a stripping voltammetric technique, the application of a preconcentration potential may change the electrode surface to favour analyte-electrode interactions. This may come about as a result of changes in polymer hydrophobicity, changes in charge density on functional
groups or simply changes in polymer morphology brought about by the application of a potential.

Therefore, this work has dealt with the modification of reticulated vitreous carbon (RVC) cartridges to provide polymer modified cartridges for use in the collection of mercury. The effect of applied potential on the polymer-analyte interactions has also been studied in order to ascertain whether this variable affects the collection efficiency at these electrodes.

5.2 EXPERIMENTAL

5.2.1 REAGENTS AND SOLUTIONS

All reagents used were A.R. grade unless otherwise specified. Mercury (II) standards (1000 mg.L\(^{-1}\)) were prepared by dissolving the requisite amount of HgO in a minimum of nitric acid and diluting to volume. All working standards were made by serial dilution of this standard.

Electrode modification solutions and techniques are described in chapter 2 of this thesis.

5.2.2 EQUIPMENT

Sampling experiments were performed using the sampler cell and controllers developed as part of this project. The general configuration used is shown in Figure 5.1.
Stationary cell collection experiments were performed in a dual compartment cell with potential control being supplied by a BAS CV 27 voltammograph. Stationary cell experiments were performed using the cell depicted in Figure 5.2.
Voltammetric measurements were performed on either a BAS 100A electrochemical analyser (Bioanalytical Systems, West Lafayette), a BAS CV 27 voltammograph or an ElectroLab system (Chapter 7).

5.2.3 CARTRIDGE MODIFICATION

Electrode modification was achieved by the techniques described in Chapter 2. Typically, electrodes were punched from a sheet of RVC using a laboratory cork borer. Once formed, the electrodes were boiled in concentrated nitric acid to remove all surface contamination after which they were rinsed with copious amounts of Milli Q water. Electrodes were stored in Milli Q water until derivatisation or use.

Prior to use RVC cartridges were sealed in a sleeve of heat-shrink teflon tubing (Unasco, Sydney, Australia). All tubing was soaked in concentrated nitric acid overnight and rinsed thoroughly with distilled water prior to use with the RVC.

The various electrodes used and expected collection mechanism are listed in Table 5.1.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Expected collection mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVC</td>
<td>Electrodeposition</td>
</tr>
<tr>
<td>PP/dtc</td>
<td>Complexation with the dithiocarbamate functional group</td>
</tr>
</tbody>
</table>
5.3 RESULTS AND DISCUSSION

5.3.1 Sampler Development

The development of an electrochemical preconcentration system required the combination of four components, being:

(i) The sample delivery system.
(ii) The sampling electrode.
(iii) The sampler cell.
(iv) The electrochemical controller.

A peristaltic pump has been used as the sample delivery device throughout this work. Items (ii) to (iv) were developed as part of this project. The development of the sampling hardware and electrode optimisation is detailed in reference 388. The final sampler cell design is shown in Figure 5.3.

![Figure 5.3 The final sampler cell design](image)

5.3.2 Collection at RVC

Initial studies of plain RVC as a collection medium involved determining the voltammetric behaviour of mercury at RVC. At higher scan rates a broad
Mercury sampling

A reduction peak is seen at \(-0\) mV. Oxidation peaks at \(380\) mV and \(540\) mV confirm that Hg has been deposited onto the RVC surface. A cyclic voltammogram recorded at a slower scan rate \(10\) mV.s\(^{-1}\) has a well defined mercury reduction response at \(-150\) mV, and the oxidation responses at \(350\) mV and \(516\) mV. The presence of 2 oxidation peaks for mercury has been reported previously [389]. In this work the peaks were attributed to the oxidation of mercury on mercury and mercury on glassy carbon. The fact that a well defined reduction response can only be seen at a slow scan rate would indicate that the rate of mercury reduction is slow or that cell resistance is high. However, given that this determination was carried out using \(M\) \(\text{NaNO}_3\) as the supporting electrolyte and a large area cylindrical Pt gauze electrode as the counter electrode it may be assumed that cell resistance is minimal. Also evident on this voltammogram is the cross over of the forward and reverse scans at \(-750\) mV. This voltammetric feature is commonly associated with the nucleation and growth of a metal deposit. Presumably in this case it is due to the further electrodeposition of mercury.

From these data it can be concluded that mercury could be collected onto RVC at a collection potential \(<150\) mV.

To study the effect of potential on mercury collection in a flowing cell, a series of samples were run through the sampler at different collection potentials. The deposition of mercury was greatest (95%) at \(-1000\) mV (Figure 5.4), although at this potential there were considerable quantities of oxygen evolved at the counter electrode. Presumably, this low potential is needed because of the effects of the cell iR drop.
Mercury sampling

Figure 5.4  
Collection efficiency of mercury (II) on RVC at various potentials

Sample: 10 mL of 1 μg.L⁻¹Hg²⁺ in M NaNO₃  
Flow rate: 1 mL.min⁻¹

Subsequent investigations used a sampling potential of -600 mV as this allowed mercury collection to proceed without the generation of oxygen at the auxiliary electrode. This was achieved with a slight reduction in sampling efficiency (decreased to ≈85%).

Using this sampling potential the effect of flow rate upon sampling efficiency was evaluated. It can be seen from Figure 5.5 that an increase in sample flow rate caused a significant decrease in sampling efficiency. This was presumably due to a combination of the slow rate of mercury reduction and the relatively short residence time of the sample in the preconcentration cell at the higher flow rates. Thus, plain RVC cartridges were deemed unsuitable for mercury collection.
Mercury sampling

Figure 5.5  Effect of flow rate upon sampling efficiency

Sample:  50 mL  0.2 μg.mL⁻¹ Hg²⁺ in M NaNO₃
Eapp:  -600 mV

5.3.3 COLLECTION AT POLYPYRROLE MODIFIED ELECTRODES

The preceding collection regimes rely on reduction to immobilise the mercury as such, no speciation data can be collected, thus it was considered that alternate collections mechanisms may be appropriate in some circumstances. To study this approach the collection of mercury at a variety of polymer modified electrodes was studies.

The synthesis of the polymer modified electrodes used in this work is detailed in Chapter 2. Based on the previous studies of mercury-dithiocarbamate interactions it was decided to investigate the use of polypyrrole modified RVC containing diethyldithiocarbamate anions within the polymer. The extremely high equilibrium constant for the mercury - dithiocarbamate complexes, [391] would also suggest that this is a valid approach. Throughout this study the dithiocarbamate derivatised cartridges used, were produced by the ion exchange derivatisation of polypyrrole chloride to produce polypyrrole with diethyldithiocarbamate anion (dtc) as the counterion in the polymer. This
reaction is thought to occur through the displacement of the chloride anion, incorporated into the polymer during synthesis, by the diethyldithiocarbamate anion from solution. This process may be depicted schematically by the following equation:

\[
\text{Scheme 1}
\]

Initial studies were aimed at investigating the voltammetry of Hg at polypyrrole/dtc electrodes in a stationary cell. This was followed by mercury collection in both stationary and flow through cells. A typical voltammogram of PP/dtc in M NaCl is shown in Figure 5.6.
Of particular interest to this study is the voltammetric behaviour of the polymer during the first negative going scan. From Figure 5.6 it can be seen that the
response at PP/dtc is extremely low, which, when considered in the light of other polypyrrole voltammograms, would imply that the polymer electroactivity is very low. At an applied potential of -700 mV a reduction response commences. This peak, centred around -850 mV can be attributed to the expulsion of dtc anions from the polymer, presumably due to the fact that, as a consequence of derivatisation, the mobile counterion incorporated during the polymerisation process is displaced by the less mobile diethyldithiocarbamate anion. The fact that the polymer conductivity returns as the polymer is cycled in M NaCl would tend to support this hypothesis. During the cycling (at highly negative potentials) the dithiocarbamate anion is expelled and replaced by a chloride anion. As this occurs the polymer electroactivity returns, as evidenced by the well separated positive and negative going scans on the cyclic voltammogram(Figure 5.6b).

The addition of mercury (II) ions (50 μg.mL\(^{-1}\)) to the solution causes some change to the cyclic voltammogram for PP/dtc. The most significant differences being the suppression of the dtc oxidation peak and the failure of the voltammogram to revert to the more typical shape.

The first of these differences is presumably due to the formation of the mercury dithiocarbamate complex, the oxidation potential of which is higher than that of the free dithiocarbamate. The second occurs because the mercury dithiocarbamate complex is less soluble than the free dithiocarbamate ligand and as such may impede any ion exchange with the chloride in solution. This in turn means that the mechanism by which conductivity increases is impeded, hence no significant change in the shape of the cyclic voltammogram.

What is interesting however, is the lack of any specific response due to either mercury or the mercury dithiocarbamate complex. The lack of a reduction response for the dithiocarbamate complex was particularly surprising however
it was felt that this may be the result of having insufficient mercury on the electrode. To test this hypothesis a PP/dtc electrode was soaked for 30 minutes in a 100 μg.mL⁻¹ mercury (II) solution, to ensure saturation of all available dithiocarbamate sites on the electrode, after which a cyclic voltammogram in M NaCl was recorded. This is shown in Figure 5.7.

![Cyclic voltammogram of a PP/dtc electrode in M NaCl after 30 minutes in 100 mg.L⁻¹ Hg²⁺ solution](image)

**Figure 5.7**  
*Cyclic voltammogram of a PP/dtc electrode in M NaCl after 30 minutes in 100 mg.L⁻¹ Hg²⁺ solution*

Conditions:  
- $E_{\text{initial}} = 0$ mV  
- $E_{\text{upper}} = 500$ mV  
- $E_{\text{lower}} = -1000$ mV  
- Scan rate 100 mV.s⁻¹

As with the previous test no distinct mercury response was seen. The CV was essentially the same as that recorded for PP/dtc in a mercury solution. The fact that the voltammogram does not rapidly interconvert to that for a more conductive polymer suggests that the mercury (II) is bound at the surface and inhibiting anion movement.
Despite the fact that no electrochemical response was seen for the mercury using the PP/dtc electrode it was decided that, given the known affinity of mercury for the dithiocarbamate group [391], this approach to mercury collection was worthy of further investigation in a stationary cell. The data in Figure 5.8 indicates the results obtained for the collection of mercury onto PP/dtc coated RVC electrodes in a stationary cell.

![Graph showing % Removal of mercury vs Applied potential (mV Vs Ag/AgCl)](image)

**Figure 5.8** Collection of Hg at PP/dtc in stationary cell

<table>
<thead>
<tr>
<th>Sample:</th>
<th>25 mL 100 µg.L⁻¹ Hg²⁺ in M NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 minute collection period</td>
</tr>
</tbody>
</table>

The collection time in this experiment was deliberately kept short to ensure that there would be less than 100% collection Hg²⁺ in all cases. This meant that differences in collection rate would be measurable. From this figure it is seen that adequate collection occurs within the potential region -300 to -700 mV. Using this data the collection work was continued using the flow
Mercury sampling

through cell. These studies showed that significant mercury removal could be achieved, even at -200 mV (Table 5.2)

<table>
<thead>
<tr>
<th>E_{app} (mV)</th>
<th>% removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>-150</td>
<td>85</td>
</tr>
<tr>
<td>-200</td>
<td>88</td>
</tr>
<tr>
<td>-500</td>
<td>46</td>
</tr>
<tr>
<td>-800</td>
<td>77</td>
</tr>
</tbody>
</table>

Table 5.2 Collection efficiency of PP/dtc

Sample: 60 μg.L^{-1} Hg in M NaCl
Flow rate: 1.0 mL.min^{-1}

This data indicated that it was entirely feasible to collect mercury at the PP/dtc cartridges, although lower flow rates would be needed to achieve quantitative removals.

A problem with PP/dtc electrodes is the leaching of small but significant quantities of the dithiocarbamate ligand from the cartridge into the sample solution, particularly at negative potentials. This phenomena has provided the basis for an on-line derivatisation electrode [380] but may cause two problems in the present application. The first is that loss of dithiocarbamate causes a decrease in cartridge capacity, the second is that the dithiocarbamate released may interfere with any subsequent analyses of cell effluent.

5.3.4 ELUTION OF MERCURY FROM CARTRIDGES

The elution of mercury from the preconcentration cartridges prior to analysis is an important step in the analytical process. During this step analyte may be lost or contaminants introduced to the system.

Elution of mercury from the RVC/Cu electrodes is readily achieved with electrochemical oxidation into 1:1 HCl prior to CVAAS analysis.
Elution of mercury from the PP/dtc cartridges is somewhat more difficult. Initial work with electrochemical oxidation into various acids was hampered by high reagent blanks. This was finally rectified and it was found that for all reagents used, blank levels were less than 10 μg.L⁻¹ (Table 5.3).

<table>
<thead>
<tr>
<th>Elution Potential (mV)</th>
<th>Eluting acid</th>
<th>[Hg] in 25 mL elution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1:1 H₂SO₄</td>
<td>&lt;10 ppb</td>
</tr>
<tr>
<td>+500</td>
<td>1:1 H₂SO₄</td>
<td>&lt;10 ppb</td>
</tr>
<tr>
<td>+1000</td>
<td>1:1 H₂SO₄</td>
<td>&lt;10 ppb</td>
</tr>
<tr>
<td>+500</td>
<td>1:1 HCl</td>
<td>&lt;10 ppb</td>
</tr>
<tr>
<td>+1000</td>
<td>HCl</td>
<td>&lt;10 ppb</td>
</tr>
</tbody>
</table>

Oxidative elution into 1:1 HCl was investigated first and it was found that recovery efficiency was quite variable and at the best only 80 - 90% efficient. Elution into 1:1 H₂SO₄ also proved to be problematic, suffering the same shortcomings as the previous method. The addition of a small amount of KMnO₄ to the 1:1 H₂SO₄ used for elution improved the recoveries such that they were generally in the 90 - 95% efficiency range when dealing with laboratory solutions. Presumably the permanganate aids in the oxidation of the dithiocarbamate ligand.

5.3.5 COLLECTION OF REAL SAMPLE

The application of the sampling electrode developed to the collection of mercury from an industrial effluent was considered.

For this work samples of effluent were obtained from ICI (Botany, Australia). Typically the effluent contained:
Mercury sampling

Hg: 50 µg.L⁻¹ (range >10 to < 100)

pH: ≈ 11

NaCl: 4 - 5%

Other constituents:
CaCO₃, CaSO₄, Ca(OH)₂, MgCO₃,
MgSO₄, Mg(OH)₂, Fe(OH)₃

various colloidal solids

organics: up to 300 mg.L⁻¹ of which
approximately 50 mg.L⁻¹ are
volatiles. Also high in surfactants
with some PVC powder present

NaOCl: up to 10 mg.L⁻¹

This effluent is high in organic interferents. These are known to affect electrodeposition [392] processes in an adverse manner. Thus the application of PP/dtc electrodes to this problem was investigated.

What was not evident however was the effect organics may have on collection with these cartridges and, given the previous success with collection synthetic samples it was decided to proceed to effluent samples, restricting the applied potential to a negative limit of -400 mV to minimise leaching of the dithiocarbamate anion. The results of this study are shown in Table 5.4.

These experiments show that there are components of the sample matrix which are adversely effecting the collection of mercury. This is in some ways quite surprising, as the formation constants for mercury dithiocarbamate complexes, even Hg(dtc)⁺, are quite high [341a]. It should be noted, however that these collection efficiencies are much better than those obtained with RVC (sampling standard solutions only) especially given that these studies were performed with non-acidified effluent. Presumably the formation of mercury dithiocarbamate complexes at the electrode is easier to achieve than the reduction of mercury in this media. The acidification of the samples prior to collection of mercury caused a significant drop in sampling efficiency (about 20 - 30% decrease).
This may be due to the instability of dithiocarbamate in acid solution causing a significant drop in the number of collection sites available on the electrodes.

### Table 5.4

<table>
<thead>
<tr>
<th>Sample Details</th>
<th>Applied Potential</th>
<th>% Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>125 μg.L⁻¹ Hg</td>
<td>0</td>
<td>&gt;92*</td>
</tr>
<tr>
<td>(25 mL sample)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>as above</td>
<td>-100</td>
<td>&gt;92*</td>
</tr>
<tr>
<td>as above</td>
<td>-100</td>
<td>84</td>
</tr>
<tr>
<td>as above</td>
<td>-200</td>
<td>&gt;92*</td>
</tr>
<tr>
<td>as above</td>
<td>-400</td>
<td>92</td>
</tr>
</tbody>
</table>

*i.e.: <10 μg.L⁻¹ Hg²⁺ in cell effluent*

### 5.4 CONCLUSIONS

The preceding studies have shown that the collection of mercury at unmodified RVC electrodes is far from satisfactory. The use of dithiocarbamate derivatised polypyrrole electrodes has also been studied. These electrodes have been shown to be suitable for mercury collection, particularly in solutions containing organic species that may interfere with electrodeposition of mercury onto an electrode.

To achieve quantitative or near quantitative collection of mercury requires sample flow rates of approximately 1 mL.min⁻¹. This may limit the applicability of this preconcentration method. These studies have also shown that the application of a preconcentration potential to the CME will alter the sampling efficiency of the electrodes studied. In the case of PP/dtc electrodes the optimum potential is less negative than that required for the collection of...
Mercury sampling.

mercury on an RVC electrode but sufficiently negative to reduce any mercury collected at the electrode.

Also, the application of the negative potential may increase the negative charge density at the dithiocarbamate groups and thus improve collection efficiency. The problem with applying the negative potential to the PP/dtc electrodes is that it causes a small but discernible amount of leaching of the dtc⁻ anion from the cartridge thus limiting the applicability of such a system. The use of dithiocarbamate functionalised polymers, prepared in a manner similar to that used in the preparation of the mercury sensor (chapter 3), may be suitable way to circumvent this problem.
CHAPTER 6
COLLECTION OF GOLD AT POLYPYRROLE MODIFIED RVC

6.1 INTRODUCTION

As was the case with mercury, an alternative to gold detection is to obtain samples from the appropriate collection point and transport these to a laboratory for treatment and analysis. This is not a problem if the sampling point and laboratory are relatively close to each other. However, particularly in the case of geochemical exploration, sampling point and analytical laboratory may be separated by thousands of kilometres [139].

In this case the transport of bulky liquid samples becomes a difficult and expensive exercise. A suitable solution to this problem is to collect the gold onto a small volume of solid phase adsorbent and transport this for analysis. The advantage of this is that whilst the gold is being collected onto the adsorbent it is also being preconcentrated thus making subsequent detection easier.

6.1.1 PRECONCENTRATION TECHNIQUES

The preconcentration of gold from aqueous samples has been achieved by a number of techniques. Solvent extraction of gold(III) into organic solvents has been used as the first step in the ASV determination of gold [351, 357] or as a matrix clean-up step prior to GFAAS determination [393]. Diethyldithiocarbamate (DDC) salts of nickel [358] and zinc [394] have been used in the solvent extraction of gold(III) from aqueous samples. According to Bajo and Wyttenback [358] if the mole ratio DDC/Au < 1 the complex Au
(DDC)Cl$_2$ is formed in chloride solution. Whereas if the ratio DDC/Au > 1 the complex Au(DDC)$_2$Cl is formed.

Collection of gold onto solid phase adsorbents has been investigated by a variety of authors. Brajter and Slonawska [395, 396] have used Cellex P, a cation exchange resin, to separate gold from platinum and rhodium prior to AAS determination. In this work an amine was added to the sample matrix to ensure the complex Au(Amine)Cl$_2^+$ is formed. This complex is then retained on the cation exchange resin.

Dithiocarbamate functionalised resins have also been used to preconcentrate gold prior to ICPAES determination [61]. Chen et al. [64] have studied the use of both dithiocarbamate resins and oxidised dithiocarbamate resins for the preconcentration of heavy metal ions. These workers found that both resin types preconcentrate gold. However, the capacity of the resins was quite low 0.5 - 0.6 meq ion/g compared with the capacity for heavy metals (e.g. Cu 3.8 - 4.2 meq ion/g). Thus, the technique may be suitable for the preconcentration of these metals, but not the separation of gold from the other metals in the matrix. Huang et al. [83] have also used an oxidised dithiocarbamate functionalised resin for the preconcentration of gold(III) prior to neutron activation analysis.

Myasoedova et al. [397] developed a series of derivatised resins collectively known at POLYORGs. The chelating groups on these resins contain one or any combination of the following functional groups, amine, hydroxyl, sulphonate, nitro, thiol, keto, thio, isonitrosoacetamide or carboxylic acid groups. POLYORGs have been shown to be suitable sorbents for noble metals, including gold.

In a similar manner Grote and Kettrup [101] developed a polystyrene resin functionalised with either S-bonded dithizone or dehydrodithizone. These resins are capable of selectively preconcentrating both gold and the platinum group metals from mixtures
containing base metals and salts. Appropriate control of the elution conditions allows the selective elution of the preconcentrated species.

Other workers have used tri-n-butylphosphate loaded polyurethane foam [398], unmodified polyurethane foam [399], 2,2'-dipyridyl-3-[(4-amino-5-mercapto)-1,2,4-triazolyl]hydrazone supported on silica gel [106] and silica gel modified with δ-aminopropyltriethoxysilane [91] for the preconcentration of gold(III) from water samples and the selective preconcentration of gold(III), from solutions containing Fe(III) and Cu (II) ions, respectively.

Finally, the simplest method of gold preconcentration reported involves the addition of activated charcoal to an acidified aqueous sample containing gold. The gold is preconcentrated onto the charcoal, after which the charcoal is filtered off and analysed by GFAAS, INAA or any other suitable technique [103].

6.1.2 AIM AND SCOPE OF THIS WORK

Although there are a variety of preconcentration techniques available for the enrichment of gold prior to analysis, most of these are best suited to the analytical laboratory and would be difficult to use in a field sampling application. This is primarily the domain of solid phase adsorbent, of which but a few have been reported for gold.

Thus it would appear that there is still scope for the investigation of alternate adsorbents for this application. A study of the interaction of gold with conducting polymers provides the necessary information to assist in the development of conducting polymer based sampling systems for gold.

Here, as with the previous example, the judicious application of polymer modified electrodes may provide a means of achieving this end. This work, has therefore, focused on investigating the interaction of gold with polymer modified electrodes as a means of developing a sampling element for the preconcentration of gold.
6.2 EXPERIMENTAL

6.2.1 REAGENTS AND SOLUTIONS

All reagents used were analytical (A.R.) grade unless otherwise stated. Water used was purified using a Milli-Q water purification system. Monomers used for the electrochemically generated polymer were obtained from the Sigma chemicals Company and used as received. Gold solutions were prepared by serial dilution from a 1000 mg.L\(^{-1}\) standard. This was prepared by dissolving 1g of gold metal (99.99%) in a minimum of aqua regia and diluting to the required volume.

6.2.2 INSTRUMENTATION

Cyclic voltammetry was performed on a Bioanalytical Systems (BAS) (West Lafayette In.) CV-27 Voltammograph connected to a Houston Omnigraphic 2000 X-Y recorder or a BAS 100A Electrochemical Analyser. Voltammetric measurements were also performed using the BAS 100A Electrochemical Analyser and where appropriate a chemtronics PDV 2000 portable electrochemical analyser.

Collection experiments were performed using the controller and cell described in the previous chapter.

6.2.3 CARTRIDGE MODIFICATION

Electrode modification was achieved by the techniques described in Chapter 2. Typically electrodes were punched from a sheet of RVC using a laboratory cork borer. Once formed, the electrodes were boiled in concentrated nitric acid to remove all surface contamination after which they were rinsed with copious amounts of Milli Q water. Electrodes were stored in Milli Q water until required for polymerisation.

The various electrodes used and expected collection mechanism are listed in Table 6.1.
### Table 6.1  Cartridges used for the collection of Gold

<table>
<thead>
<tr>
<th>Electrode designation</th>
<th>Expected collection mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/Cl⁻</td>
<td>ion exchange</td>
</tr>
<tr>
<td>PP/ClO₄⁻</td>
<td>ion exchange</td>
</tr>
<tr>
<td>PP/BF₄⁻</td>
<td>ion exchange</td>
</tr>
</tbody>
</table>

#### 6.2.4 Modification of RVC with Polypyrrole

Polypyrrole coated RVC electrodes were prepared by the galvanostatic oxidation of pyrrole in a deoxygenated aqueous solution containing 0.5 M pyrrole and 1.0 M of the salt to be used during polymer preparation. Oxidation was achieved at a current density of ≈0.2 mA.cm⁻² for 10 minutes (based on a RVC surface area of 65 cm².cm⁻³ [119, 120]).

After preparation all electrodes were washed thoroughly and stored in Milli Q water until they were needed for sampling experiments. All cartridges used in the sampling experiments were sealed in heat shrink teflon tubing as described in section 5.2.3 of this thesis.

#### 6.2.5 Analysis of Gold

Analysis of gold in solution was achieved using a chemtronics PDV2000 portable electrochemical analyser. The electrochemical method used in this device is anodic stripping voltammetry using a supporting electrolyte of dilute (3%) aqua regia.
6.3 RESULTS AND DISCUSSION

The interaction of gold with polypyrrole has been the major focus of this work and as such will be reported here. The effect of polymer synthesis conditions on this interaction has also been studied.

6.3.1 COLLECTION OF GOLD AT POLYPYRROLE MODIFIED RVC

The ion exchange properties of polypyrrole have been discussed in Chapter 2 and 4. The studies described below were designed to investigate whether this is a viable means of sampling gold (III), and whether the application of a potential could enhance the ion exchange reactions.

From the voltammetric data detailed in section 4.3 it would appear that it is possible to collect gold onto polypyrrole electrodes and that the optimum collection potential for gold (III) would be positive of the reduction potentials seen in the voltammograms, with the more positive potentials giving better preconcentration. What is not clear however, is whether or not 100% preconcentration can be achieved. For sensing purposes low, but reproducible, collection efficiencies are adequate. This is not the case for sampling where near total collection of the analyte is required.

Prior to attempting to collect gold onto polypyrrole modified cartridges it was essential to ascertain whether or not the gold had in fact been collected onto the polymer surface. To investigate this a polypyrrole coated glassy carbon electrode was placed in a solution (50 mg.L\(^{-1}\)) of gold in M NaCl and a preconcentration potential of 700 mV applied. Analysis of the electrode by electron probe micro analysis (EPMA) shows the presence of gold at the electrode surface. Figure 6.1 shows the spectrum obtained for a PP/Cl electrode after exposure, at 700 mV, to a 50 mg.L\(^{-1}\) solution of Au(III). These data confirm that gold is preconcentrated on the electrode surface. However it gives no information as to the mode of collection.
6.3.1.1 The effect of the anion present during synthesis on the collection of gold at polypyrrole

Voltammetric studies (chapter 4) indicate that the anion incorporated into the polymer has a significant effect on the magnitude of the interaction between the polymer and the (AuCl₄)⁻ anion.

To investigate this further polymers containing chloride, perchlorate and tetrafluoroborate as the anion incorporated during polymerisation were used for gold (III) collection. Figure 6.2 shows the collection efficiency of the polymers studied at various potentials.
In all cases the collection efficiency at the optimum potential was excellent, and for the 
ClO₄⁻ and BF₄⁻ anion it was not as affected by applied potential as the voltammetric 
behaviour (section 4.3.1.2) would lead one to expect. These data suggest that the primary 
mode of collection may not be ion exchange. For, if it was, the application of a positive 
applied potential, which have been shown to enhance anion exchange at polypyrrole 
(section 4.3.1.1) would be expected to enhance the collection of gold at these cartridges. 
The effect seen to date is either negligible, as evidenced here, or opposite to that expected. 

Collection at no applied potential was investigated and it was found that significant collection efficiency can be achieved without the application of an accumulation potential. However, the application of the appropriate potential causes an increase in sampling

* This was determined by passing a known amount of gold (III) solution through a polymer modified RVC cartridge and determining the amount of gold left in solution after it had been passed through the collection cartridge. This technique was used for all collection efficiency experiments.
Gold Sampling

efficiency. This may indicate that there is a redox reaction between the polymer and the gold, a subject investigated in section 6.3.1.2. This is shown in Table 6.2.

Table 6.2 Collection of gold (III) at polypyrrole (No Eapp).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>% Removal</th>
<th>At no Eapp</th>
<th>At most efficient Eapp</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/NaCl</td>
<td>89</td>
<td>89</td>
<td>(400 mV)</td>
</tr>
<tr>
<td>PP/NaClO4</td>
<td>83</td>
<td>99</td>
<td>(0 mV)</td>
</tr>
<tr>
<td>PP/NaBF4</td>
<td>92</td>
<td>99</td>
<td>(0 mV)</td>
</tr>
</tbody>
</table>

Conditions: As in Figure 6.2

From this table it can be seen that significant collection efficiency can be achieved without the application of an accumulation potential. The application of an appropriate potential generally causes this efficiency to increase. This data does show a slight trend here when comparing the collection efficiencies with applied potential. Polymers produced with larger anions show higher collection efficiencies for gold. This may indicate that the larger anions are more readily exchanged out of the polymer and that the AuCl₄⁻ is more readily exchanged into the polymer. This dependence of the ion exchange properties of polypyrrole on polymer synthesis conditions has been reported previously [399a].

In an attempt to collect [AuCl₄]⁻ by ion exchange only, the PP/NaCl cartridges were used to collect Au(III) at 450 mV. At this potential there is little gold reduction at the polymer and polymer damage is minimised whilst still allowing the ion exchange processes to occur. Using a single cartridge cell collection efficiencies varied within the range 70 - 90%. This degree of variability is too great. Therefore in an attempt to improve this the dual electrode cell was used utilising two PP/NaCl electrodes set at 450 mV.

The data in Table 6.3 suggests that it is possible to collect gold by anion exchange using the dual electrode configuration, indicating that a higher contact time between the sample and the polymer is needed to achieve efficient, quantitative collection.
The need for longer contact times was confirmed with the use of the packed bed cartridge to collect gold. Using this cartridge, which has a significantly greater surface area of polymer to contact with the solution, it was possible to quantitatively remove gold from solution without applying a potential to the electrode.

Table 6.3  % Removal of gold at 450 mV (onto polypyrrole coated RVC)

<table>
<thead>
<tr>
<th>Eapp</th>
<th>%Au removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>93</td>
</tr>
</tbody>
</table>

Conditions: As in Figure 6.2

6.3.1.2 Characterisation of gold-polypyrrole interaction

The observations so far, particularly the optimum collection potentials required, suggest that a preconcentration mechanism other than ion exchange may be responsible for the preconcentration of gold (III) onto polypyrrole. To investigate this a PP/Cl electrode was soaked overnight in 50 mg.L\(^{-1}\) Au (III) in M NaCl. The gold species at the electrode surface were then determined by XPS. Figure 6.5 shows the XPS spectrum for this electrode, the double peaks at 87.3 eV and 83.7 eV are typical of metallic gold [400]. Anionic gold species are expected to give a single peak at 87.5 eV.

These data indicate that the interaction of the polymer with gold involves the reduction of the gold (III) anion with the concomitant oxidation of the polymer to overoxidised polypyrrole by the gold anion. It does not however totally rule out ion exchange between gold(III) anions and chloride in the polymer as any signal due to ionic gold species would
be included under the peak identified at 87.3 eV. Possibly, the mode of interaction involves ion-exchange followed by the slow reduction of the gold accumulated.

That the polymer was oxidised by gold was further confirmed by measuring the potential of a polypyrrole electrode in gold (III) solutions. This data, shown in Table 6.4, shows that the potential at the electrode increases as the concentration of gold is increased.

![XPS spectrum at polypyrrole/Cl⁻ electrode that has been soaked in a solution containing 50 mg.L⁻¹ gold(III).](image)

Figure 6.6 shows the potential recorded at some polypyrrole coated RVC electrodes whilst collecting gold with no applied potential in the electrochemical sampler. In all cases the potential at the electrode gradually rises, indicating that oxidation is occurring. In contrast, similar potential measurements, recorded in M NaCl only, show no such increase in electrode potential with time.
Table 6.4  
Potential of Polypyrrole electrodes in gold (III) solutions

<table>
<thead>
<tr>
<th>Gold concentration (mg.L(^{-1}))</th>
<th>Electrode potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>240 mV</td>
</tr>
<tr>
<td>50</td>
<td>480 mV</td>
</tr>
<tr>
<td>100</td>
<td>650 mV</td>
</tr>
</tbody>
</table>

Reference electrode: Ag/AgCl  
Sample: All samples in M NaCl

---

Figure 6.6  
Chronopotentiograms of various polypyrrole electrodes in a 500 μg.L\(^{-1}\) Au(III) solution.  
a  PP/Cl\(^{-}\) in M NaCl  
b  PP/\(\text{BF}_4\)\(^{-}\) in gold solution  
c  PP/\(\text{Cl}_4\)  
d  PP/ClO\(_4\)  

Sample: 500 μg.L\(^{-1}\) Au(III) in M NaCl solution.
6.3.1.3 Elution and quantification

Oxidative elution, at +1000 mV, into M NaCl does not release the gold from the polymer.

The use of solvent extraction techniques, to remove any anionic gold species into ethylacetate, also fails to remove any gold from the polymer, even if the cartridge is soaked in the ethylacetate for up to 12 hours. This fact adds weight to the theory that the gold is primarily present on the surface as metallic gold and not the anionic gold (III) chloride.

Adequate elution of the gold has only been achieved by flushing the cartridges with aqua regia. The aqua regia solution is suitable for analysis by either GFAAS or electrochemical methods. Instrumental neutron activation analysis (INAA) has been successfully used to directly determine the quantity of gold on the polymer modified cartridges. The advantage of this technique is that the gold does not have to be eluted from the polymer prior to quantification. Figure 6.7 shows the mass of gold on a number of cartridges, as determined by INAA, and that expected. The expected mass of gold on the cartridges was calculated by determining the amount of gold left in a solution, of known initial concentration, after it had been passed through a polypyrrole modified RVC electrode. Elution of the gold from the surface of the polymer electrodes has proven to be a difficult task, presumably because most of the gold is present on the surface as Au°.
6.4 CONCLUSIONS

The preceding study demonstrates the feasibility of collecting Au(III) at polypyrrole modified RVC electrodes. The exact mode of collection is unclear but XPS data indicates that a proportion of the gold is present on the surface as Au° and not Au³⁺, indicating that a redox reaction between the polymer and gold has occurred. This theory is further supported by chronopotentiometric measurements of polypyrrole in Au(II) solution. These indicate that the polymer is gradually oxidised by the gold.

Elution techniques designed specifically to remove anionic gold species fail to remove gold from the polymer modified cartridges, again indicating that there is little anionic gold preconcentrated onto the electrodes.

The application of a preconcentration potential has been shown to improve the efficiency of gold collection. The optimum potentials determined are sufficient to reduce Au(III) to Au°. Thus, if preconcentration does involve an ion-exchange process, any gold preconcentrated would be readily reduced by the applied potential.
Gold Sampling

Contact time between the sample and the electrode has been shown to affect the preconcentration efficiency with long contact times giving more efficient and reproducible sampling. In a manner similar to that seen with the pyrrole based sensors, the anion present during polymerisation does affect the interaction. With the anions studied, polymers synthesised in the presence of large anions have better preconcentration efficiencies than those prepared with small anions. There are no trends evident when collecting gold at no applied potential. A tenuous link can be drawn between anion size and gold collection efficiency when collecting gold at applied potential, with polymers produced with larger anions providing the greatest preconcentration efficiency.

Finally, the difficulty with which gold is eluted from polypyrrole cartridges has meant that analysis is most easily achieved with INAA rather than electrochemical or spectrometric methods that require quantitative elution of the preconcentrated gold species.
CHAPTER 7
ELECTROLAB

7.1 INTRODUCTION

The further advancement of research in sensors based on chemically modified electrodes requires the development of new techniques for signal generation. This need arises from the fact that the interaction of many target molecules with CMEs cause changes at the electrode surface that are manifested, not as faradaic processes, but rather as non-faradaic signals. These signals may take the form of changes in resistance, capacitance or other changes at the electrode surface [401]. Such changes are not readily detected with conventional electrochemical instrumentation, particularly those utilising current sampled pulsed electrochemical techniques. These techniques have been developed with current sampling routines designed to effectively discriminate against the non-faradaic components of the electrochemical signal.

To allow the inclusion of such signals in the analytical response normally requires the modification of either the hardware or software or most conventional instruments. The challenge therefore is to develop an instrument that will permit the researcher to readily configure the electrochemical waveform in such a manner that it does not discriminate against the non-faradaic components of the analytical signal, as is the normal approach, but rather collects the data from them.

* The ElectroLab project was the combined effort of a number of people. Programming was carried out by Mr M. Knight et al. of Analogue Digital Instruments (ADI), New Zealand. Dr A.J. Hodgson provided a significant input into refining the user interface (screen designs) and testing the software. The author's contribution was the development and validation of the Design-A-Waveform. In particular ensuring that the definition of common voltammetric techniques could be achieved with this protocol and comparing the results obtained using Design-A-Waveform with those obtained with conventional instruments.
The increased flexibility available with computer based instruments, compared with their analog counterparts, would suggest that such an approach is feasible, however as yet most, if not all, computer based instruments have been configured to mimic hardware based systems.

Since the first report of a minicomputer controlled electrochemical system [402] there has been a great deal of activity in this area, particularly during the mid 1970's and early 1980's. This work was prompted by the prospect of both increased reproducibility and productivity from the ability to automate a particular experiment.

The computer based systems also included many innovative features such as averaging of multiple scans [403, 404, 405] background subtraction [403, 404, 405, 406], computer assisted optimisation of experiment [407, 408], resolution of overlapping responses [409] and the collection of data at extremely high data acquisition rates [410-412] facilitating rapid scan rate electrochemistry.

Many studies have concentrated on the hardware components of such systems. Ramaley et al. have reported the design of computer controlled potentiostats [413, 414], various waveform generators [411, 412] and an autoranging data acquisition system [415]. Others have reported potentiostats suitable for computer interfacing [416-418]. While some workers have designed software systems and interfaces suitable for use with commercially available potentiostats [405, 419, 420].

However, the majority of workers have designed total systems incorporating the potentiostat, the associated control lines for stirrers, dropping mercury electrodes, together with the data generation and acquisition software in one package.

There seems to have been as many different approaches to the computerisation of electrochemical experiments as there are authors of the various papers. At one extreme a programmable calculator [421] has been used to manipulate data collected on a dedicated
microprocessor unit whereas at the other minicomputers have been used to control electrochemical instruments [405].

It was the development of smaller more powerful computers that accelerated the computerisation of electrochemistry, and most other techniques.

Coken and Heimann [422] reported a system based around the Motorola 6800 microprocessor. Bond et al. have used a variety of systems in an extensive study of microprocessor controlled electrochemistry. They have performed cyclic differential pulse voltammetry on a system based on a Raytheon Data Systems RDS-500 computer [423]. A DEC PDP 11 was interfaced to a PAR 174 potentiostat in the development of a system to perform background current correction in differential pulse and alternating current polarography [423]. This instrument was also used for fast sweep differential pulse voltammetry at a dropping mercury electrode [410].

Anderson and Bond also coupled a Motorola 6800 microprocessor to a home made potentiostat and other peripheral devices to develop a system capable of performing digital AC polarography [424], differential pulse polarography and pseudoderivative normal pulse polarography [425]. A modified version of this unit was linked to a Sphere 6809 microcomputer and used to perform differential pulse stripping voltammetry with data collection in different time domains [426].

The microprocessor performs the data acquisition and control functions whilst the microcomputer is used for data manipulation, print out and display. The system was designed for use in clean laboratories and hazardous areas, where the microprocessor would be situated at the experiment and the microcomputer isolated in a normal office environment.

Other workers have also developed systems based on dedicated microprocessors [407, 427-429], personal computers [419, 420, 403, 430] and minicomputers [431]. Most of the programming for these systems was performed with high level languages (basic,
Fortran) although there has been one attempt to define a language that is specifically designed to run electrochemical experiments [432]. The program, ASYST, consists of a series of subroutines that may be configured to provide the control, stimulation and data acquisition cycles. Of particular interest in this package is the method of defining the voltammetric stimulus, by choosing the appropriate values for $\Delta E$, $T_p$, $T_b$, $E_p$ and $E$ (Figure 7.1) it is possible to select between staircase, differential pulse and square wave voltammetry.

![Figure 7.1](image)

*Figure 7.1 The voltammetric waveform definition parameters [from ref 432]*

Apart from the case listed above there has been no attempt to devise a generic approach to waveform definition, most workers have been content to simply write blocks of code to define each waveform used. Therefore if the researcher wished to investigate a new type of voltammetric stimulus it was necessary to write a new block of code defining the required waveform.

### 7.1.1 AIM AND SCOPE

The development of flexible computer based electrochemical systems requires the development of a new approach to waveform definition. To be successful this approach needs to be easy to use, have readily varied current sampling routines and provide a visual feedback of the waveform created, with the current sampling points indicated.
This chapter reports the development of a computer based electrochemical instrument, ElectroLab, that incorporates such a function. Specifically, the waveform definition protocol, known as Design a Waveform, will be the focus of this chapter. The flexibility of this technique will be demonstrated by way of evaluating a number of conventional voltammetric techniques defined with this waveform definition protocol.

7.2 EXPERIMENTAL

7.2.1 REAGENTS

All reagents used were analytical reagent (AR) grade unless otherwise stated. Wherever possible metal standards were prepared by dissolving pure metal (99.99% purity) in a minimum of concentrated acid and subsequently diluting the solution to the required volume. Alternatively, dry nitrate salts of the required metal were used. Mercury standards were prepared by dissolving mercury (II) oxide in concentrated nitric acid and diluting to the required volume.

7.2.2 HARDWARE COMPONENTS

The ElectroLab system consists of four major hardware components.

(i) The computer

(ii) The interface

(iii) The potentiostat

(iv) The cell stand

The choice of and development of these will be detailed in the results and discussion. Hanging mercury drop electrode experiments were performed with a PAR SMDE 303A electrode assembly connected to the ElectroLab with a purpose built interface.
7.3 RESULTS AND DISCUSSION

7.3.1 HARDWARE DEVELOPMENT

7.3.1.1 The computer

The computer chosen for development into the ElectroLab system was an Apple Macintosh, this was chosen because of the very efficient user interface. The Macintosh graphic user interface is widely accepted as being more efficient, more productive and easier to use than command driven interfaces. The combination of high resolution graphics, pull down menus, explicit menu item headings, dialogue boxes and menu command selection using a point and click mouse ensure that instrument operation is simplified.

7.3.1.2 The interface

Rather than develop a new interface for this project it was decided to use an existing system, the MacLab interface was chosen for modification.

This interface comprises of 1 output channel and 4 independent input channels, 2 of which are used in ElectroLab. The output channel is a 12 bit (40kHz) D/A convertor that supplies a zero to ±2000 mV signal to the potentiostat for control of the cell voltages.

The input channels on the interface are both 12 bit A/D convertor. One input is used to monitor current whilst the other is set aside for potential monitoring. The current monitoring channel has computer selected variable gain which, when coupled with the gain ranges available on the potentiostat (also computer selected), gives current sensitivities ranging from ±20nA to ±100mA in 1,2,5,10 increments. The actual configuration of the instrument to achieve the required current sensitivity is invisible to the operator. The setting is selected and the software configures the appropriate gain settings to achieve this.
The second input is used to monitor the potential of the working electrode. This is not needed for voltammetric work but the potentiostat circuit includes a galvanostat which will be used at a later stage in the instrument's development. The ability to monitor electrode potentials will be required to enable the recording of chronopotentiometric data.

7.3.1.3 The potentiostat

The potentiostat is a conventional 3 electrode configuration featuring computer selectable current sensitivity. These settings are software controlled to make the hardware set-up transparent to the user.

7.3.1.4 The cell stand

To complete the system a dedicated cell stand unit was developed. This unit houses the stirring and gas purging facilities as well as providing a means of reproducibly locating the electrodes.

All stirring and gas purging options can be operated under both manual or automatic control. However the hardware and software are configured such that during analysis automatic control overrides the manual control. The cell stand top was designed to facilitate the reproducible positioning of electrodes. To achieve this, all electrodes have a tapered sleeve fitted to the top of them. This sleeve then fits into machined tapers in the cell stand. Also, all electrodes (i.e. working, auxiliary and reference) have non-interchangeable couplings to prevent the accidental incorrect connection of electrode leads especially in a classroom setting. This was done to add a small degree of fool proofing to the system. The cell stand is only suitable for use with solid electrodes.

7.3.2 DESIGN A WAVEFORM

In Design a Waveform the voltammetric stimulus is considered to be composed of 4 distinct components, a voltage ramp, two superimposed pulses, and current sampling routines. The amplitude of the pulses may be increased, decreased or remain the same at
each voltage step in the base ramp. Thus to operate the system each parameter is defined individually and these are combined to form the voltammetric waveform desired. This approach, although new to the programming aspect, has been used for many years in the construction of analog instruments. With analog systems each component of the stimulus is generated separately and combined on the input side of the control operational amplifier [433]. Various voltage inputs are combined at the summing point (S) and the complex voltage ramp applied to the cell. The circuitry require to achieve this is shown in Figure 7.2.

![Circuit for an analog controlled potentiostat showing the summing point (S)](image)

*Figure 7.2*  
Circuit for an analog controlled potentiostat showing the summing point (S)

In a manner analogous with the hardware approach, to achieve the same effect with software it is also necessary to divide each waveform into its individual components. For example, differential pulse voltammetry can be considered to be a single pulse superimposed on each step of a staircase ramp, whereas square wave voltammetry requires both a positive and negative going pulse to be added to each step.
The best way to highlight the flexibility of this approach is to evaluate a series of waveforms that may be defined with the Design a Waveform dialogue. Prior to this the waveform set up techniques should be discussed.

7.3.2.1 Waveform set up

To simplify the operation of this technique an easy to use operator interface was developed. To activate this the operator selects Design a Waveform from the techniques menu at the top of the screen and is presented with the waveform set up dialogue as shown in Figure 7.3.

![Waveform Set Up Dialogue](image)

**Figure 7.3** The screen presented as the waveform set-up menu for Design a Waveform

Within this menu the base ramp parameters must be defined along with the pulses (maximum of two) to be superimposed upon each step in the ramp.

To activate each pulse the small box in the upper left hand corner of each pulse definition box is clicked and the appropriate parameters to define the pulse characteristics are entered. To aid in visualising the waveform created the *view* button is activated and a
graphical representation of three steps in the base ramp, with pulses superimposed, will be displayed on the screen.

The instrument may also be configured to perform stripping voltammetry with the waveform created this is achieved by activating the deposition dialogue. The required accumulation potential and time prior to the stripping ramp are entered into the appropriate dialogue boxes. It is also possible to apply a conditioning potential after the analysis, this is controlled by the "clean" dialogue box.

7.3.2.2 Current sampling

To efficiently use the flexibility inherent in the waveform definition parameters it is necessary to have a very flexible current sampling routine.

With ElectroLab it is possible to sample the current over four windows or periods within each step of the base ramp. Within each period the current sampling frequency is 10 kHz (1 sample every 100\(\mu s\)) and all samples taken over a particular period are averaged, with the average value stored against the potential of the base ramp at which it was sampled.

These current sampling periods are of variable width and may be positioned anywhere within the step width. To achieve this is a matter of simply activating the sampling button (Figure 7.3) and a sampling set-up dialogue (Figure 7.4) will be called up. Each period is activated by clicking in the small box to the left of the period number. To correctly define each sampling period the starting position and duration of each period must be specified, the only restrictions being that the periods must be defined in chronological order and must not overlap.

Again in order to aid with the set-up procedures a graphical representation of one step in the base waveform is shown, with any superimposed pulses shown by dotted lines. The current sampling periods are shown on this graphic as solid or hatched boxes with the sampling period numbers displayed above each period.
Once sampled, each of the four possible current value are stored independently and the individual voltammograms may be called up using the display menu. It is also possible to display differential voltammograms, plotting the difference in current ($\Delta i$) between any two current sampling periods versus the base ramp potential.

![Sampling Time](image)

*Figure 7.4 The current sampling dialogue (screen)*

7.3.3 CONSTRUCTING CONVENTIONAL VOLTAMMETRIC STIMULI USING DESIGN A WAVEFORM

The definition of a number of conventional waveforms is readily achieved with Design a Waveform. These will be illustrated in the following section.

7.3.3.1 Staircase voltammetry

With this technique only the base ramp is activated, the operator will define both the step width ($t$) and step heights ($\Delta E$) (Figure 7.5). This in turn dictates the coarseness of the
ElectroLab

ramp. Scan rate is a function of both step width and height. However, it was seen to be the most important of the three and as such in the ElectroLab system scan rate has been designated the "fixed variable". This allows the operator to manipulate either the step width or height with the other variable automatically altered to maintain the prescribed scan rate.

![Voltammetric waveform used in staircase voltammetry](image)

*Figure 7.5 Voltammetric waveform used in staircase voltammetry*

Current sampling in staircase voltammetry has been shown to be an important consideration [434]. In a comparison of voltammograms obtained by both linear scan voltammetry and staircase voltammetry Bilewicz et. al. [434] have shown that, in order to achieve a staircase voltammetric response comparable with the linear sweep counterpart, it is necessary to sample the current at one quarter of the step width (i.e. where \( t_s^* = t/4 \)). Figure 7.6 shows a staircase voltammogram recorded using Design a Waveform with the current sampled at \( t/4 \). Figure 7.7 shows a comparison of the responses determined at 4 different points on each step.

* \( t_s^* \) = current sampling point*
Figure 7.6  Staircase voltammogram* for the reduction of Pb²⁺ at an HMDE

Conditions  
E_{\text{initial}} = 0 \text{ mV}  \quad E_{\text{final}} = -1000 \text{ mV}  
Scan rate = 10 \text{ mV.s}^{-1}  
Current sampled at t/4 (20 ms current sampling window)  
Sample:  
5 \times 10^{-3} \text{M Pb}^{2+} \text{ in M HClO}_4

Ferrier et al have studied staircase voltammetry with varied current sampling times [435]. In this study they found that the analytical response for the reduction of an electrochemically reversible species was significantly effected by the position of the current sampling point. For a given scan rate \( i \propto t/t_\text{s} \), which effectively means the closer it is to the beginning of the step period, the higher the current. These authors also show that for an electrochemically irreversible reaction the position of the current sampling period has little effect on the analytical response and suggest that, by monitoring the current at several points within each step and comparing the responses recorded it should be possible to obtain a qualitative measure of the reversibility of a particular reaction.

To conduct this study the authors were required to build dedicated instrumentation with sophisticated current sampling circuitry. With the Design a Waveform it is possible to

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* The voltammograms shown in this chapter do not follow the sign convention used in previous chapters. The reduction responses are negative when using SCV, DPSV and only displayed in the positive direction with square wave voltammetry. Axes are also inverted when compared with previous figures. This occurs because the voltammograms included are screen dumps taken directly from voltammograms recorded with the ElectroLab software.
sample the current at 4 different sampling periods within each step. These periods are activated and varied by software control thus obviating the need for dedicated hardware. Figure 7.7 shows a voltammogram for the reduction of Pb$^{2+}$ illustrating the different responses at various current sampling times.

![Voltammogram](image)

**Figure 7.7** Staircase voltammogram for the reduction of the Pb$^{2+}$ showing the effect of varying the current sampling points at an HMDE

| Conditions |  
|------------|---|
| $E_{\text{initial}}$ | 0 mV |
| $E_{\text{final}}$ | -1000 mV |
| Scan rate | 10 mV.s$^{-1}$ |
| Current sampled at | $v/4$, $v/2$, $3v/2$ and for last 20 ms of each step (20 ms current sampling window) |
| Sample | 5x $10^{-3}$M Pb$^{2+}$ in M HClO$_4$ |

**7.3.3.2 Differential staircase voltammetry**

In contrast to staircase voltammetry, where only one current sampling point is taken for each step of the staircase waveform, differential staircase voltammetry [436, 437] requires two current samples to be taken during each step and the difference in current $\Delta i$ between these two values is plotted versus the potential of each step.
Figure 7.8 shows the waveform and current sampling points used in this technique. By sampling the current at two points within each step and plotting the difference in current, it is possible to effectively cancel out the charging current component [436].

Scholz et al. have reported two variants of this technique, with the first [436], the current was sampled twice at the end of each step as shown in Figure 7.8a. A problem with this approach is that a considerable component of the faradaic response will also be cancelled out.
The second approach reported by Scholz [437] involves sampling the current 20 ms after the step and again at 100 ms after the first sample is taken (Figure 7.8b). Using this approach the authors claim the achieve improvements in the signal/noise ratio that allow this technique to give a LOD equal to or slightly better than differential pulse voltammetry. Figure 7.9 shows a differential staircase voltammogram for the reduction of Pb\textsuperscript{2+} at a hanging mercury drop electrode.

Configuration of this technique with Design a Waveform is achieved by selecting the staircase waveform as in the previous example and then define two current sampling points on each step. The position and duration of each current sampling window is defined in the sampling dialogue and the display is readily configured to plot the difference between these points versus potential.

---

**Figure 7.9**

* Differential staircase voltammetric response for the reduction of Pb\textsuperscript{2+} at an HMDE

**Conditions**

- \( E_{\text{initial}} = 0 \text{ mV} \)
- \( E_{\text{final}} = -1000 \text{ mV} \)
- Scan rate = 10 mV.s\textsuperscript{-1}
- current sampled at 20 ms and 120 ms (20 ms current sampling window)

**Sample:** 5x 10\textsuperscript{-3} M Pb\textsuperscript{2+} in M HClO\textsubscript{4}
7.3.3.3 Differential pulse voltammetry

Differential Pulse Voltammetry (DPV) is easily defined with Design a Waveform. In this case is a single pulse of fixed amplitude superimposed on each step of a voltage ramp is required (Figure 7.10). To achieve this the ramp is selected as in the previous example and the pulse dialogue activated.

The desired pulse amplitude and width are entered along with the pulse starting time. This is the delay from the commencement of the step in the base ramp before the pulse is activated. This setting is chosen such that the pulse occurs at the end of each step in the ramp.

Current sampling windows are specified to ensure that the current is sampled before the imposition of the pulse and at the end of each pulse. The current differential is then displayed on the screen.
Figure 7.10  The component waveform and the composite differential pulse stimulus
Figure 7.11 shows a differential pulse voltammogram recorded for $5 \times 10^{-3} \text{ M Pb}^{2+}$ in M HClO$_4$. A comparison between this result and that obtained by DSCV (Figure 7.9) shows that for the solution studied the signal/noise ratio appears to be significantly better for the DPV technique.

![Graph showing a differential pulse voltammogram for the reduction of Pb$^{2+}$ at an HMDE.](image)

**Figure 7.11** A differential pulse voltammogram for the reduction of Pb$^{2+}$ at an HMDE.

**Conditions**
- $E_{\text{initial}} = 0 \text{ mV}$
- $E_{\text{final}} = -1000 \text{ mV}$
- Scan rate = 10 mV.s$^{-1}$
- Pulse width = 50 ms
- Pulse amplitude = 25 mV
- Pulse period = 200 ms
- (20 ms current sampling window)

**Sample:** $5 \times 10^{-3} \text{ M Pb}^{2+}$ in M HClO$_4$

The DPV technique has been varied by some workers, either to increase instrument sensitivity or to detect chemical interferences in the analytical process. Bond and Grabaric [410] developed a microprocessor based system to perform fast sweep differential pulse voltammetry. The technique required the imposition of 40 ms pulses with a 80 ms period between the commencement of each pulse, the effective scan rate used was 50 and 100 mV.s$^{-1}$.

In a similar study Yeakel et. al. [438] designed and built a digital signal generator for use with a PAR 174 electrochemical analyser that would adapt it for use in rapid scan DPV.
In this study scan rates of up to 500 mV.s\(^{-1}\) with pulse widths in the order of 17 ms or less and a pulse period of 20 - 50 ms [438].

Both techniques can be performed with Design a Waveform by simply entering the required values in the waveform set up menu. Figure 7.12 shows a rapid scan differential pulse voltammogram of Pb\(^{2+}\).

\[
\text{Figure 7.12} \quad \text{Rapid scan DPV response for the reduction of Pb}^{2+} \text{ at an HMDE}
\]

**Conditions**

- \(E_{\text{initial}} = 0 \text{ mV}\)
- \(E_{\text{final}} = -1000 \text{ mV}\)
- Scan rate = 100 mV.s\(^{-1}\)
- Pulse amplitude = 50 mV
- Pulse width = 40 ms
- Pulse period = 120 ms
- (20 ms current sampling window)

**Sample:**

- \(5 \times 10^{-3} \text{M Pb}^{2+} \text{ in M HClO}_4\)

Another modification of DPV reported by Bond et al was the collection of DPV data in different time domains i.e. at different delay periods after the imposition of the pulse. A comparison of the responses at these different periods provides an indication of whether the peak has been affected by any interferences [426]. The Design a Waveform dialogue allows the operator to sample the current several times across each pulse, although not as many as used by the above authors (5 samples), and display each point either individually or as a differential between any two points.
7.3.3.4 Square wave voltammetry

Square wave voltammetry (SWV) can be represented in two ways, either a base ramp with one pulse superimposed upon it or as a base ramp with two pulses superimposed upon it. With the former approach the pulse amplitude applied must by double the square wave amplitude and the base ramp must be offset, by a value equivalent to the amplitude of the square wave, to achieve the correct potential response.

Whereas with the latter approach the base ramp is simply defined (Figure 7.13a) and two pulses equal in magnitude, but of opposite polarity (Figure 7.13b&c) and with pulse width equal to half the width of each step in the base ramp, are applied. The resulting composite waveform is shown in Figure 7.13d.
To do this with the Design a Waveform dialogue requires a little thought as square wave parameters are usually reported as square wave amplitude, frequency and step height.
Whereas, with Design a Waveform the input parameters are scan rate, step height, step width, pulse amplitude, pulse width and pulse increment.

To set up SWV from Design a Waveform it is necessary to remember that

\[
\text{Scan rate} = \text{step height} \times \text{frequency}. 
\]

Therefore, the appropriate scan rate is calculated from the desired step height and frequency parameter. This is entered along with the step height required, the system automatically calculates and displays the appropriate step width. The pulse parameters are then set at:

- Pulse One with pulse duration half step width commencing at 0 ms. Pulse amplitude for pulse one is entered and the increment value is 0 mV.

- Pulse Two is set to commence at the end of pulse one for the same duration, however pulse amplitude is set in the opposite direction to pulse one.

The current sampling windows are set at the end of each pulse as described previously.

Figure 7.14 shows a square wave voltammogram for Pb\(^{2+}\) as recorded with Design a Waveform.

### 7.3.3.5 Normal pulse voltammetry

When considering normal pulse voltammetry (NPV) in the terms used in the Design a Waveform definition dialogue it can be considered as a base ramp of zero volts range with a superimposed incrementing pulse. However due to programming restrictions with the instrument it was not possible to define a ramp with a 0 volt range. Therefore another approach was taken.
Figure 7.14  
*A square wave voltammogram for the reduction of Pb$^{2+}$ at an HMDYE*

**Conditions**
- $E_{\text{initial}} = 0 \text{ mV}$
- $E_{\text{final}} = -1000 \text{ mV}$
- Scan rate = 30 mV.s$^{-1}$
- Step width = 66.7 ms
- Pulse width = 33.3 ms
- (10 ms current sampling window at end of each pulse)

**Sample:** $5 \times 10^{-3}$ M Pb$^{2+}$ in M HCIO$_4$

It is also possible to consider NPV as a coarse linear ramp onto which an incrementing pulse ramp of opposite polarity is superimposed. This is depicted in Figure 7.15

Using the Design a Waveform approach it is necessary to consider that the step width in the base ramp equates to the pulse period and the step height is the pulse amplitude (and increment) from NPV (Figure 7.15a). To complete the definition a pulse is superimposed on the ramp. This pulse commences at the end of the desired NPV pulse and has a duration of (step width - NPV pulse width). The height of this pulse is the same as the step height. Each increment is also 1 step height for each step of the base ramp (Figure 7.15b). This way it is possible to define a NPV waveform (Figure 7.15c) with the appropriate current windows being added after the waveform is defined. Figure 7.15 illustrates this approach.
Figure 7.15 The Design a Waveform approach to NPV

Figure 7.16 shows a normal pulse voltammogram for the reduction of Pb^{2+} as recorded with Design a Waveform.
In a variation of normal pulse polarography Bond and Anderson [ECW 004] describe a technique Variable-Amplitude Pseudoderivative Normal-Pulse Polarography. With this technique data points from pulses a fixed number of pulses apart (n = 1 to many) are subtracted from each other and plotted versus potential.

The data acquisition routines in ElectroLab collect and store each individual data point in a form that is compatible with any other Macintosh software. Therefore, whereas it is not possible to display a pseudoderivative voltammogram directly from the ElectroLab program, the raw data may be manipulated and plotted from any spreadsheet program.

### 7.3.4 SIMPLIFYING WAVEFORM DEFINITION DIALOGUES

Although it is possible to set up many analytical waveforms with the Design a Waveform menu, this is often a tedious procedure (see especially normal pulse and square wave voltammetry). Therefore the ElectroLab system has a series of preset techniques available. This is achieved by displaying a set-up dialogue in which the operator enters any parameters relevant to the technique chosen. The ElectroLab system
then uses these parameters to perform the appropriate calculations and set up the Design a Waveform parameters to perform the technique chosen.

The techniques available with preset dialogue are:

- Staircase Voltammetry
- Differential Pulse Voltammetry
- Square Wave Voltammetry
- Normal Pulse Voltammetry
- Cyclic Voltammetry

and the stripping variants of these.

For example when defining square wave voltammetry with Design-a-Waveform, once the initial and final potential have been set, it is necessary to define the scan rate, and step height to obtain the required frequency. From this the step width must be determined to calculate the pulse width. Two pulses, equal in duration and magnitude, but opposite in polarity must be sequentially superimposed on the base ramp to produce the required waveform. Once the waveform has been defined the current sampling dialogue must be activated and appropriate current sampling windows defined.

Using the preset dialogue it is only necessary to define initial potential, final potential, square wave frequency, base ramp step height and pulse amplitude. The template is then used to set all appropriate parameters in the Design a Waveform technique to implement the method required. A similar case applies for all techniques available on ElectroLab.
7.4 CONCLUSIONS

The Design a Waveform technique has been shown to be a versatile method for the definition of voltammetric stimuli. The combination of flexible pulse definition and current sampling protocol facilitate the use of a number of conventional and unusual voltammetric techniques.

The operation of the Design a Waveform technique has been simplified by using a combination of dialogue boxes and graphical feedback facilities in the waveform definition menu. The definition of the more conventional voltammetric stimuli has been further simplified by the inclusion of a number of preset techniques where the operator simply defined the voltammetric stimuli in terms normally used to specify the technique required (see square wave voltammetry example in 7.3.4).

The examples delineated in this chapter serve to illustrate the flexibility of this technique in defining voltammetric stimuli. The extension of the technique should allow a number of new methods to be developed.
CHAPTER 8
CONCLUSIONS

From the work described in this thesis there are a number of general conclusions that may be reached regarding the use of polymer modified electrodes in both sensing and sampling applications.

Studies designed to determine the most appropriate means of preparing polymer modified RVC electrodes have shown that this is best achieved by galvanostatic preparation techniques. This limits the range of monomers available for polymerisation onto this substrate. The modification of RVC has been achieved primarily using polypyrrole. The generation of a thiophene based polymer on RVC is best achieved using 2,2’ bithiophene as the starting monomer.

A second limitation on the generation of polymer modified electrodes in general is that associated with the incorporation of electroactive anions into the polymer when the monomer oxidation potential is greater than that required to oxidise the reagent. To circumvent this problem a technique has been devised whereby an easily exchangeable anion that is stable at the monomer oxidation potential is incorporated into the polymer. This anion is subsequently exchanged out of the polymer and replaced by the electroactive species that is required for polymer functionalisation. This technique has been used to produce electrodes for investigation in both sensing and sampling applications.

The development of a methylmercury sensor based around polymer modified electrodes has also been described. This sensor was based around a hybrid electrode prepared by the chemical derivatisation of a polymer film layed down over a thin mercury film. The rationale behind this electrode was the combination of preconcentration of the methylmercury compound with a dithiocarbamate functionality on the electrode surface with detection at a mercury film. The feasibility of using the approach in solution was
Conclusions

first demonstrated then the transfer of this technology to one electrode was attempted. The electrode prepared by this technique lacked the sensitivity to be suitable as a sensor in application requiring low limits of detection for methylmercury. Superior sensitivity was obtained using the adsorptive stripping voltammetric technique for methylmercury that was developed.

A number of polymers were investigated in an attempt to produce a polymer modified electrode for the determination of gold in aqueous samples. Polymers generated by both oxidative and reductive polymerisation were studied. The best sensor was that developed using poly-4-vinyl pyridine. This polymer is produced by reductive electropolymerisation techniques and has proven suitable for the determination of gold. The technique developed is capable of determining gold in the presence of copper, a common interferent in the voltammetric determination of gold. The reason that the polymer is suitable for this application is that it does not have an appreciable voltammetric signal in the region of interest yet possesses sufficient electrical conductivity to allow signal generation to occur. Accumulation at the polymer is achieved by ion exchange of the gold species onto the anion exchange sites present in the polymer.

Sampling with chemically modified RVC has been demonstrated and applied to the collection of mercury from industrial effluent.

RVC modified with a dithiocarbamate containing polypyrrole. This electrode, RVC modified with a dithiocarbamate containing polypyrrole, proved suitable for the collection of mercury from solution and was not affected as much by other organics in the sample. The interaction of the analyte with the sampling electrode was shown to be affected by the application of potential to the electrode. This has been shown to enhance the collection of mercury at these electrodes.
Conclusions

The collection of gold at polypyrrole modified RVC has been shown to be a feasible proposition. The interaction of the gold with the polymer has been shown to involve the reduction of gold at the polymer surface. As with the collection of mercury the collection of gold has been shown to be affected by the application of potential to the sampling electrode.

Both cases demonstrate the feasibility of using polymer modified RVC for the collection of analytes from solution. The technique should be suitable for wider application provided that suitable modifiers can be applied to the electrode surface.

The development of a controller and sampler cell for use with modified RVC electrodes has been demonstrated. The cell designed has proven suitable for use in situations requiring the application of a potential to the modified RVC. The controller has been designed to make it simple to use and suitable for field application. The combination of the controller, the sampler cell and the modified RVC electrodes with a small portable peristaltic pump make a device suitable for use in field sampling applications. Particularly, for the collection gold and mercury as described here. The limitation on the use of this device is that sampling must be carried out at flow rates no greater than 1mL.min⁻¹.

Finally, the development of an electrochemical workstation using a new way of defining the voltammetric waveform has been described. The technique, Design-A-waveform, is sufficiently flexible to be capable of performing most commonly used voltammetric techniques as well as having the flexibility to be used for new voltammetric waveforms. The variable current sampling routine available allow the operator to collect data at various positions within each stimulus and as such allow the collection of data not only due to faradaic processes but also due to the non-faradaic processes occurring at the electrode surface. This facility may prove useful in the development of sensing techniques based around polymer modified electrodes.