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The development of a chemically-modified mercury thin film electrode for electroanalysis

Mark David Imisides

University of Wollongong

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THE DEVELOPMENT OF
A CHEMICALLY-MODIFIED
MERCURY THIN FILM ELECTRODE
FOR ELECTROANALYSIS

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

Doctor of Philosophy

from
The University of Wollongong

by
Mark David Imisides, B.Sc.(Hons.)

Department of Chemistry June 1993
In Memoriam

This thesis is dedicated to the memory of two grand old ladies who did not live long enough to see it come to fruition:

Dora Stewart 1899-1992

Esther Mary Imisides 1905-1992

We will meet again.
...let us run with endurance the race that is set before us...

- Hebrews 12:1
It gets so dark before the dawn,
that's when it gets to me,
before the city symphony of taxi horns.
That's the way it always starts,
sitting here and waiting on the beating of my heart.

Last night I thought I heard my name.
Well it was too dark to see,
but it had to be,
the voice was just the same.
That's the way it always starts,
sitting here and waiting on the beating of my heart.

Now all the streets are dark and bare.
If you can live in this town,
and stick around,
you can live anywhere.
That's the way it always starts,
sitting here and waiting on the beating of my heart.

So tell me, why should it have to be this way?
Why can't it be all right?
Why can't I sleep at night?
Why should it have to be this way?
Why must there be this price to pay?

Mark Knopfler.
Soundtrack from “Local Hero.”
**PUBLICATIONS**

**Refereed Papers:**

1. "Deposition and electrochemical stripping of mercury ions on polypyrrole-based modified electrodes."
   M.D. Imisides and G.G. Wallace,

2. "Designing chemically modified electrodes for electroanalysis."
   M.D. Imisides, G.G. Wallace and E.A.I. Wilke.

3. "Metal ion uptake and voltammetry on a dithiocarbamate-containing polymer modified electrode."
   Imisides, M.D., O'Riordan, D.M.T., and Wallace, G.G.

4. "The use of electropolymerization to produce new sensing surfaces - a review emphasizing electrodeposition of heteroaromatic compounds."
   Imisides, M.D., John, R., Riley, P.J. and Wallace, G.G.
   *Electroanalysis*, 3(9), Nov '91

5. A new polymeric mercury thin film electrode.
   Imisides, M.D. and Wallace, G.G.
   *Electroanalysis*, 4, (1992) 97-105

6. "Use of authoring tools in the development of Instructional resources for scientific equipment."

7. "A computerised electrochemical system for teaching and analysis"
   *Chemistry in Australia*, Nov. 1991, 495-497

**Monograph:**

1. "Metal ion analysis using a polypyrrole-N-carbodithioate electrode."
   M.D. Imisides, D.M.T. O'Riordan and G.G. Wallace
   *Electrochemistry, Sensors and Analysis*;
   M.R. Smyth and J.G. Vos (Eds.) Elsevier (Amsterdam) 1987, 293-302
ABSTRACT

The purpose of this project was to develop a chemically-modified mercury thin film electrode (MTFE) for use in the determination of trace metals from aqueous solutions by anodic stripping voltammetry (ASV) in both quiescent and flowing solutions.

The CME (chemically-modified electrode) consists of a non-conducting polymer, poly-N-ethyltyramine (p-NET), coated onto a glassy carbon substrate, which was used with dithiocarbamate (dtc) groups grafted onto the polymeric amine groups. The complexing capabilities of the dithiocarbamate groups were used to provide a substrate for the formation of a chemically deposited mercury thin film electrode (MTFE) via complexation of mercuric ions at these sites. These results are presented in chapter 4, along with a comparison of the modified MTFE with the conventional MTFE.

The development and characterisation of the polymeric film itself is discussed in chapter 3.

To enable the performance of the electrode for ASV to be characterised, a study was carried out on the conventional MTFE, in which some previously unreported features of this electrode became apparent. These results are discussed in chapter 2.

Chapter 1 is devoted to a review of the current state of electroanalysis, with particular emphasis on both the current and potential electroanalytical applications of CMEs to anodic stripping voltammetry (ASV). This consists firstly of a study of electroanalysis based on conventional electrode materials, with particular emphasis on ASV, and thence the scope and applications of CMEs to this field.

Finally, to assist the characterisation of the (p-NET) modified MTFE, the application of this technology to a conducting polymer (polypyrrole) is discussed (chapter 5).
ABBREVIATIONS

AAS  Atomic Absorption Spectroscopy
AC   Alternating Current
A/D  Analogue to Digital (converter)
AdSV Adsorptive Stripping Voltammetry
ASV  Anodic Stripping Voltammetry
BAS 100A BioAnalytical Systems 100A Electrochemical Analyzer
BAS CV27 BioAnalytical Systems CV27 Voltammograph
CCD  Charge Coupled Device
CI   Chemical Ionisation
CME  Chemically Modified Electrode
CPE  Carbon Paste Electrode
CSV  Cathodic Stripping Voltammetry
CV   Cyclic Voltammetry
DC   Direct Current
DC18C6 Dicyclohexyl-18-Crown-6
DEDTC Diethyldithiocarbamate
DME  Dropping Mercury Electrode
DPV  Differential Pulse Voltammetry
dtc  dithiocarbamate
EI   Electron Ionisation
EMF  Electromotive Force
EPMA Electron-Probe Microanalysis
FAB  Fast Atom Bombardment (mass spectrometry)
FIA  Flow Injection Analysis
GC   Glassy Carbon
HMDE Hanging Drop Mercury-Electrode
HPLC  High-Pressure Liquid Chromatography
IC  Ion Chromatography
ISE  Ion-Selective Electrode
LSV  Linear Sweep Voltammetry
LTI  Low-Temperature Isotropic
MCMFE  Membrane-Coated Mercury Film Electrode
MTFE  Mercury Thin Film Electrode
NCTMFE  Nafion-Coated thin Mercury Film Electrode
NMR  Nuclear Magnetic Resonance
™PAD  ™Dionex (corporation) Pulsed Amperometric Detector
PAR  (EG&G) Princeton Applied Research
PDG  Potentiodynamic Growth
PED  ™Dionex (corporation) Pulsed Electrochemical Detector
PMPE  Polymethylene Polyphenyl Isocyanate
p-NET  Poly-N-ethyltyramine
PP  Polypyrrole
ppb  parts per billion (µg.L⁻¹)
ppm  parts per million (mg.L⁻¹)
PPO  Polyphenylene Oxide
PSG  Potentiostatic Growth
PVP  Polyvinyl Pyridine
RDE  Rotating Disc Electrode
RRDE  Rotating Ring-Disc Electrode
S/N  Signal-to-Noise
SCE  Saturated Calomel Electrode
SEM  Scanning Electron Microscope/Micrograph
SMDE  Static Mercury Drop Electrode
SQWV  Square Wave Electrode
StV  Staircase Voltammetry
tds  thiuram disulphide
TEAP  tetraethylammonium perchlorate
WIG  Wax-Impregnated Graphite
XPS  X-ray Photoelectron Spectroscopy
XRF  X-ray Fluorescence Spectroscopy
TABLE OF CONTENTS

Publications ................................................................. i
Abstract ............................................................................ ii
Abbreviations ................................................................. iii

Chapter 1:
General Introduction ......................................................... 1

1.1. Fundamentals of Electroanalysis .................................... 2
  1.1.1. Anodic Stripping Voltammetry (ASV) ....................... 4
  1.1.2. Cathodic Stripping Voltammetry (CSV) ................... 6
  1.1.3. Adsorptive Stripping Voltammetry (AdSV) ............... 6

1.2. Conventional Electrodes: ................................. 9
  1.2.1. Solid Electrodes .................................................. 9
    1.2.1.1. Metal Electrodes ............................................. 9
    1.2.1.2. Carbon Electrodes ........................................... 12
      1.2.1.2.1. Carbon Paste Electrodes (CPE): .................. 12
      1.2.1.2.2. Glassy Carbon Electrodes (GCE) ............... 13
    1.2.2. Mercury Electrodes ......................................... 17
      1.2.2.1. The Dropping Mercury Electrode (DME) .......... 18
      1.2.2.3. The Static Mercury Drop Electrode (SMDE) ....... 20
      1.2.2.4. The Mercury Thin Film Electrode (MTFE) ........ 21
        1.2.2.4.1. Film thickness ...................................... 24
        1.2.2.4.2. Morphology of mercury droplets ............... 27
        1.2.2.4.3. Other factors ....................................... 27

1.3. Chemically Modified Electrodes ............................... 29
  1.3.1. CMEs in AdSV ................................................. 29
    1.3.1.1. Requirements of CMEs for AdSV ..................... 29
    1.3.1.2. Applications ............................................. 30
      i. Carbon Paste Electrodes .................................... 31
      ii. Polymeric Electrodes ...................................... 31
  1.3.2. CMEs in ASV .................................................. 31
    1.3.1.2. Non-mercury-based CMEs for ASV ................... 32
    1.3.1.3. MTFE-based CMEs for ASV ............................ 34

1.4. Project Justification and Outline: ....................... 38

Chapter 2:
Studies on Conventional Electrode Substrates .................. 40

2.1. Introduction ......................................................... 41
2.2. Experimental ....................................................... 42
  2.2.1. Electrodes ................................................... 42
    2.2.1.1. Stationary electrode studies: ......................... 42
    2.2.1.2. Rotating electrode studies: .......................... 43
  2.2.2. Instrumentation ............................................. 43
Chapter 3: Nonconducting Polymer Electrode

3.1. Introduction ................................................................................................................. 108
   3.1.1. Selection of Complexing Agent ................................................................................. 109
      3.1.1.1. Dithiocarbamates in homogeneous systems .................................................. 109
      3.1.1.2. Dithiocarbamates in heterogeneous systems ............................................... 113
   3.1.2. Selection of Polymer Modifier ...................................................................................... 118
      3.1.2.1. PPO polymers - development ........................................................................... 119
      3.1.2.2. Polymerisation mechanism of PPO electrodes ................................................. 121
      3.1.2.3. Electroactivity of PPO polymeric electrodes .................................................. 124
   3.1.3. Design of the CME: .................................................................................................... 125

3.2. Experimental .................................................................................................................... 127
   3.2.1. Electrodes ................................................................................................................... 127
   3.2.2. Instrumentation ........................................................................................................... 128
   3.2.3. Solutions: .................................................................................................................. 128
   3.2.4. Electrochemical Cells and Glassware: ........................................................................ 129
   3.2.5. Experimental Procedures: ......................................................................................... 130
      3.2.5.1. Monomer synthesis: ......................................................................................... 130
      3.2.5.2. Polymerisation procedure: ............................................................................... 131
      3.2.5.3. Derivatisation procedure: ................................................................................. 133

3.3. Results and Discussion .................................................................................................... 134
   3.3.1. Monomer Characterisation: ....................................................................................... 134
   3.3.2. Polymerisation of N-ethyltyramine ............................................................................ 135
      3.3.2.1. Effect of dissolved oxygen during polymerisation ......................................... 136
   3.3.3. Electrochemical Activity ............................................................................................. 139
      3.3.3.1. Electroactivity of the polymeric electrode ....................................................... 139
      3.3.3.2. Electrochemistry of incorporated Species ......................................................... 148
      3.3.3.3. Effect on voltammetric background (vs GC) ..................................................... 155
      3.3.3.4. ASV Studies ....................................................................................................... 159
   3.3.4. Visual Characterisation ............................................................................................... 167
3.3.5. Chemical Derivatisation of p-NET .................................................. 168
  3.3.5.1. Optimisation of chemical procedure ........................................ 170
  3.3.5.2. Characterisation of derivatisation process ................................ 172
  3.3.5.3. Contamination problems ...................................................... 174
  3.3.5.4. Alternative derivatisation processes ........................................ 176

3.4. Conclusions: .................................................................................... 179

Chapter 4:
Development of a Chemically-Modified MTFE ........................................ 180

4.1. Introduction .................................................................................... 181

4.2. Experimental .................................................................................. 182
  4.2.1. Electrodes .................................................................................. 182
  4.2.2. Instrumentation .......................................................................... 183
  4.2.3. Solutions .................................................................................... 183
  4.2.4. Electrochemical Cells and Glassware ........................................ 184
  4.2.5. Experimental Procedures ......................................................... 184

4.3. Results and Discussion .................................................................. 187
  4.3.1. Selection of pH for Mercury Deposition ...................................... 187
  4.3.2. Oxidation States of Surface-bound Mercury .............................. 190
    4.3.2.1. Studies on GC-based p-NET-dtc electrode .......................... 191
    4.3.2.2. Studies on Pt-based p-NET-dtc electrode ........................... 201
  4.3.3. Analytical Performance ............................................................. 204
    4.3.3.1. Anodic stripping voltammetry ........................................... 204
    4.3.3.1.1. Stationary electrode studies ........................................ 204
    4.3.3.1.2. Studies at an RDE ....................................................... 209
  4.3.4. Mercury Film Digestion & Regeneration .................................... 217
  4.3.5. Visual Characterisation .............................................................. 223
  4.3.6. Long-term Stability ................................................................. 224

4.4. Comparison of Conventional and Chemically Modified MTFEs ....... 225
  4.4.1. Stationary Electrode: ................................................................. 225
  4.4.2. Rotating Electrode: ................................................................. 228
  4.4.3. High ν LSV: .............................................................................. 232

Chapter 5:
Studies With a Conducting Polymer (as an MTFE Substrate) ................. 237

5.1. Introduction .................................................................................... 237

5.2. Experimental .................................................................................. 239
  5.2.1. Electrodes .................................................................................. 239
  5.2.2. Instrumentation .......................................................................... 239
  5.2.3. Solutions .................................................................................... 240
  5.2.4. Electrochemical Cells and Glassware: ...................................... 240
  5.2.5. Experimental Procedures: ....................................................... 241

5.3. Results and Discussion .................................................................. 243
  5.3.1. Polypyrrole Characterisation: ................................................... 243
  5.3.2. Mercury-coated polypyrrole ..................................................... 245
5.3.3. Mercury-coated poly-(pyrrole-N-carbodithioate) ............... 245
5.3.4. Utility for ASV: ......................................................... 249
  5.3.4.1. Stationary solutions: ........................................... 249
  5.3.4.2. Flowing solutions: ............................................. 251
5.4. Conclusions: .................................................................. 253

Chapter 6:

Conclusions ........................................................................... 254

6.1. MTFE Studies ................................................................. 255
  6.1.1 Conventional MTFE ..................................................... 255
  6.1.2. Chemically-Modified MTFE ....................................... 256
6.2. Microelectrode Array ....................................................... 256
6.3. Future Work: ................................................................. 257

Bibliography ........................................................................... 259

Acknowledgements ................................................................ 273
Chapter 1:

General Introduction
1.1. FUNDAMENTALS OF ELECTROANALYSIS

Electroanalysis consists in the identification and quantification of a compound in solution (or air [1,2]) as a result of a signal generated by an oxidation, reduction, adsorption, desorption, incorporation or expulsion process occurring in the region bounded by the body of the electrode and the bulk of the analyte solution. The range of techniques employed to exploit those interactions is exhaustive and it is beyond the scope of this study to attempt to review them all. Essentially, however, the techniques may be grouped into three categories:

1. Potentiometry:

These techniques utilise a change of potential at an electrode crystal or membrane/solution interface as the analytical signal. Although these techniques are widely used on a routine basis, notably with ion selective electrodes (ISEs), the responses tend to be slow and prone to interferences, and have not been examined in this study.

2. Tensammetry:

Tensammetric signals, long viewed as sources of annoyance to the civilised electrochemist, have recently been examined as techniques for electroanalysis [3-6]. They consist of the sharp peaks produced in a voltammogram when a compound either adsorbs and desorbs, or reorients itself on the electrode surface. Although it seems certain that these techniques will continue to increase in popularity, particularly since they seem readily amenable to utilisation by CMEs, they do not presently occupy a great deal of space in the literature.

3. Amperometry/Voltammetry:

Amperometric and voltammetric techniques, in a general sense, refer to those techniques which rely upon the current generated by a Faradaic oxidation or reduction process as the analytical signal. These techniques are
classified depending on whether the applied potential is static (amperometry) or dynamic (voltammetry).

Amperometry finds its widest usage in electrochemical detectors for high pressure liquid chromatography (HPLC) and flow injection analysis (FIA) and, apart from a variety of titrimetric techniques, finds little usage for stationary solution analysis.

Voltammetry (polarography etc. included), on the other hand, represents the most widely used group of electroanalytical techniques, is used on a routine basis in many industries, and is the subject of a large amount of contemporary research, both applied and pure. The range of compounds amenable to determination by voltammetric methods is continually expanding and consists of metals, organics, oxyanions and halogens.

Voltammetric techniques may be divided into two groups, depending on whether they incorporate a preconcentration step or not.

i. **Bulk-diffusion techniques:**

These techniques incorporate no preconcentrating step, and rely on the diffusion of the electroactive species from the bulk of the solution, and its subsequent reduction or oxidation at the electrode, with the current generated by this process being the analytical signal. The most widely used bulk diffusion is cyclic voltammetry (CV) which is employed as a qualitative tool to elucidate electrodic kinetics and mechanisms, and is not routinely used for quantitative determinations.

Quantitative analysis is normally confined to renewable electrodes such as the DME and SMDE (sect. 1.2.2) which are used with the technique of DC polarography [7]. This technique suffers from poor sensitivity (normally confined to the ppm regime for electroactive heavy metals [8]), codeposition of metals (e.g. Pb,Tl), maxima (surface) and electrocapillary (change in surface tension of the mercury) effects.
ii. Preconcentrating techniques:

Those techniques that utilise a preconcentrating step include adsorptive stripping voltammetry (AdSV), cathodic stripping voltammetry (CSV) and anodic stripping voltammetry (ASV). Of these three techniques, CSV and ASV incorporate a Faradaic preconcentration step, whereas AdSV incorporates a non-Faradaic preconcentration step. The limitations of each technique, and the scope for the introduction of CMEs varies, and each is considered in turn.

1.1.1. ANODIC STRIPPING VOLTAMMETRY (ASV)

ASV consists of the reductive preconcentration of an analyte (usually metallic) at an electrode surface (under the influence of convection) for a preset time period followed by oxidative stripping, under the influence of an applied potential waveform, with the anodic current enabling quantification of the determinand.

Fundamentals of the technique are reviewed by Wang [9], and a number of excellent reviews discuss the use of this technique in various applications [10-13].

The process is summarised in figure 1.1

![Figure 1.1: Potential waveform for (linear sweep) anodic stripping voltammetry.](image-url)
This figure depicts the use of a mercury thin film electrode (MTFE) as the electrode from which the metals are stripped. This electrode, along with other electrodes which may be used in this application, is discussed in section 1.2.

The intrinsic usefulness of the technique lies in its inherent sensitivity, with determinations in the lower ppb regime being easily obtainable. There are two factors which mitigate against a wider usage of this technique than is currently observed both in the literature and in industry:

1. It is a requirement that the analyte metals have facile stripping (oxidative) kinetics from the substrate that is being employed (usually mercury), and as a consequence the number of metals that are determined by this technique is limited when compared to atomic spectroscopy.

The vast majority of routine ASV determinations concern one or more of zinc, cadmium, lead, or copper [8,11], both because they produce analytically useful stripping responses, and the environmental concern over these metals.

Other metals which have been determined by ASV are antimony [14,15], arsenic [14], gold [14,16], bismuth [15,17], cobalt [18], iron [19], gallium [20], mercury [21,22], indium [23,24], nickel [18,25], selenium [14,26], silver [27], tin [28], tellurium [29], and thallium [30,31].

2. ASV is a technique which is critically dependant upon the matrix of the analyte solution. In particular, the presence of surface-active organics has been shown to cause significant interference [18,32,33], and many real samples will contain compounds such as these, due to the presence of biota.
1.1.2. CATHODIC STRIPPING VOLTAMMETRY (CSV)

CSV is a technique in which the electrode is oxidised as part of the preconcentration step [7].

This material is usually mercury, and may be oxidised to either Hg\textsuperscript{I},

\[
2\text{Hg}^0 \rightarrow \text{Hg}_2\text{H}^+ + 2\text{e}^- \quad \text{eq. 1.1}
\]

\[
\text{Hg}_2\text{H}^+ + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 \quad \text{eq. 1.2}
\]

or Hg\textsuperscript{II},

\[
\text{Hg}^0 \rightarrow \text{Hg}^{2+} + 2\text{e}^- \quad \text{eq. 1.3}
\]

\[
\text{Hg}^{2+} + \text{Se}^{2-} \rightarrow \text{HgSe} \quad \text{eq. 1.4}
\]

The analytical step therefore consists of the reduction of the mercuric or mercurous ions back to the metal.

No CMEs which employ CSV have been reported, largely because it has not enjoyed wide usage as an analytical technique. A detailed discussion of CSV is beyond the scope of this project and will be considered no further.

1.1.3. ADSORPTIVE STRIPPING VOLTAMMETRY (ADSV)

The phenomenon of the adsorption of surface active compounds on electrodes used for voltammetry or polarography has long been a source of annoyance for electroanalytical chemists, who have had to endure erroneous results as a consequence of these processes interfering at either the preconcentration or stripping steps.
Although the potential analytical utility of this method was recognised as early as 1956 by Kalvoda who observed increases in the Faradaic responses after adsorptive accumulation of sulphur [34], poorly soluble inorganic compounds and alkaloids [35] and some benzophenones [36] at mercury electrodes, it was not until the last decade that work began in earnest in this area.

The concept of AdSV is based upon the principle that a hydrophobic substance, such as an organic compound or a metal complex, will preferentially adsorb onto a hydrophobic surface, such as an electrode, when it is dipped into an aqueous solution in which the hydrophobic analyte is present in trace amounts.

Depending on the nature of the adsorbate and adsorbent, however, a number of other factors may also exert an influence on the adsorption rate [37].

A fundamental difference between this process and that occurring during the cathodic Faradaic accumulation of ASV (sect 1.1.1) is that the adsorption process is governed by a number of thermodynamic factors, rather than the kinetic process induced by the cathodic ASV accumulation potential.

These factors include the solubility and hydrophobicity of the analyte, the hydrophobicity of the adsorbing surface, the (analyte) adsorption and diffusion coefficients, the degree of interaction of the adsorbate molecules on the surface of the electrode, and the bulk concentration of analyte.

These adsorption processes are formally accounted for by “adsorption isotherms”, each of which is a thermodynamic expression which makes varied assumptions concerning the factors which contribute to the process. The theory of some of the more widely accepted isotherms is beyond the scope of this project, and is dealt with elsewhere [38].

AdSV remains a peripheral technique which has not found widespread usage in either industry or applied research, and a review of speciation of trace metals in natural waters by Florence [8] in 1986 failed to even mention the method. There can be little doubt, however, that AdSV has enormous potential in this field, if only based upon the consideration that many complexing agents possess specificity for one oxidation state of a metal only, and a number of subsequent publications have demonstrated the utility of this technique in this context.
In particular, speciation of iron has been achieved with solochrome violet RS, due to the latter's preference for Fe\textsuperscript{III} over Fe\textsuperscript{II} [39]. In a slight variation of this approach, Van Den Berg [40] has used the AdSV responses of the copper-catechol complex to estimate the complexing capacities of natural waters for copper.

Zhang and Wollast [41] have successfully used AdSV for the determination of total cobalt and nickel in seawater, and reported, under the acidified conditions employed (pH 2), little or no interference from extraneous adsorbents.

The versatility of this technique has been further demonstrated by Wang & Mannino [42] who have utilised it for the speciation and determination of Fe\textsuperscript{III} in wine, a matrix which is more complex than seawater. This method employed solochrome violet RS as the chelating agent, and, due to the high concentrations of iron present, and the subsequent pre-analysis dilution, no significant interferences were reported.

A number of excellent reviews [37,43,44] describe the applications of this technique using conventional electrode materials (sect. 1.2).

AdSV represents the most utilised technique for CMEs designed for electroanalysis, and it is considered (as appropriate) in this context in section 1.3.1.
1.2. CONVENTIONAL ELECTRODES:

The term "conventional electrodes" is generally understood to refer to electrochemically active (i.e. facilitate interfacial charge transfer) metal or carbon electrodes, be they solid materials such as platinum, gold, palladium, glassy carbon, or tantalum, or liquid mercury. The most popular of these have been platinum, (glassy) carbon, gold and mercury [45].

1.2.1. SOLID ELECTRODES

The requirements for a solid electrode material are as follows:

1. inertness (chemical and electrochemical)
2. reproducibility
3. favourable redox kinetics for the processes of interest
4. a potential window which is suitable for the reactions of interest

Solid electrodes are of two types; metallic and carbon-based electrodes.

1.2.1.1. Metal Electrodes

In terms of satisfying the criteria listed above, platinum quickly became the metal of choice, since it was (or appeared to be) inert, and had excellent redox kinetics for most electrochemical processes. Gold, which also had excellent redox kinetics became unpopular due to its softness (particularly when used, for example, as a wire electrode), and its penchant for dissolving in mercury (when used as a substrate for an MTFE).

Platinum electrodes, however, turned out to not to be ideal as had been initially anticipated. In what has since become a landmark publication on the subject, Adams, in 1969, in his book "Solid Electrodes" [46], postulated the existence of three discrete oxide states of platinum, with accompanying variations in surface morphology and electrochemical reactivity, and which
change with applied potential. These conclusions were based on some earlier work by Anson [47,48] and Laitinen [49].

Other solid metallic electrodes suffer from similar problems, as Adams & Lee concluded in their work on the oxidation of platinum, gold and palladium electrodes[50]: “the rate of oxidation of the electrode surface is a complex function of the diffusion of the chemical species, the electrode surface condition and many other variables.”

In short, the existence of a chemically inert, reproducible metallic electrode has yet to be demonstrated.

A further complication with metallic electrodes arises from the fact that they are prone to fouling (irreversible contamination) by other metals when they are used as substrates for ASV [45]. When a metallic ion is reduced from solution, the metals so formed may be of finite solubility in the electrode material [9]. These problems have led to the introduction of carbon and graphite electrodes of various types.

Any metallic electrode will have as its useable negative potential limit (in aqueous solution) the reduction of hydrogen ions to hydrogen gas:

\[
2H^+ + 2e^- \rightarrow H_2 \quad \text{eq. 1.5}
\]

The potential at which this process occurs varies with the metal substrate and is a function of the heterogeneous reduction kinetics of the process. The kinetics of this process are determined by the \(d\)-shell character of the metal [51], with most of the noble metals displaying very low overpotentials.

Platinum and palladium, for example, in a .2M HCl/.6M KCl solution, and at a current density of 100 mA/cm\(^2\), will evolve hydrogen at -0.46V and -0.38V vs SCE respectively. [52]. Gold has a slightly more negative potential limit, evolving hydrogen at -0.61V vs SCE under the same conditions. [52].

The best of the noble metals in this regard is tantalum, which does not evolve hydrogen until -0.64V vs SCE [53], and does not suffer from any of the mechanical problems (softness) that gold does.
While there are clearly many instances where low overpotentials are desirable, the low hydrogen overpotential of these electrodes severely restricts the utility of these electrodes for the cathodic study of most metallic ions of interest, as many of these ions are reduced beyond the negative potential limit of the electrode.

In terms of the positive potential limit of solid metal electrodes, the situation is, if anything, more complex, and this has been studied by various workers [46-50,54-56].

The cause of this complexity is that long before the analyst actually sees bubbles coming off the electrode surface, he must contend with rising background currents due to the formation of metallic oxides and hydroxides, and adsorption or absorption of oxygen [46,49,54]. In the presence of a species which is undergoing oxidation at the electrode, this may not only result in a significant alteration of the mechanism of the oxidation process, but it can also obscure and distort the analytical signal.

The effective positive potential limit of the electrode is therefore critically dependant on the application for which the electrode is being employed. For example, the Pt-disc electrode employed in the \textsuperscript{TM}Dionex \textsuperscript{TM}PAD detector is dependant on the formation of an oxide film for its operation (\textsuperscript{TM}Dionex manual).

Other metals have particular factors which determine their effective positive potential limit. Palladium, for example, has been shown to be very porous to both hydrogen and oxygen gas [46]. Also, gold electrodes are limited by the potential at which the substrate oxidises to aurous ions [50].

Solid metallic electrodes are widely and successfully used as amperometric detectors in flowing systems, and a number of excellent reviews detail their usage in this context [57-61].
1.2.1.2. Carbon Electrodes

Of these, the two which have received the most attention are the carbon paste electrode (CPE) and the glassy carbon (GC) electrode.

1.2.1.2.1. Carbon Paste Electrodes (CPE):

The CPE consists of a recessed electrode into which is placed a paste made from carbon powder and an organic binding material. It was invented by Adams, in 1958 [62], and was reported to have lower background currents and greater reproducibility than other solid electrodes, although with a more limited potential range [63]. Buchali& Darlewski [63] examined several binding agents, including silicone oil, paraffin oil, bromonaphthalene, and Nujol (mineral oil), and concluded that the last of these performed the best overall.

The performance of CPEs has been more recently characterised by both DC [64] and AC [65] voltammetry, in which the effects of the binding agents on background currents, potential windows, and surface effects (oxidation of carbon) have been examined. Despite its advantages, however, and the intrinsic variability of the substrate binder, the CPE has to a large extent remained on the periphery of conventional electroanalysis, being shunned in favour of more mechanically stable substrates.

By designing an electrode in which the conducting medium (carbon) was mixed in with a substance of the analyst's choice, Adams was laying the platform for an electrode which would easily lend itself to modification by an extremely wide range of modifiers.

As a result of the ability to modify the binding material, the dominant mode of preconcentration employed with the CPE has been AdSV, and therefore a detailed study of this electrode lies beyond the scope of this review. Some salient preconcentration mechanisms and publications are, however, reviewed in section 1.3.1.
1.2.1.2.2. Glassy Carbon Electrodes (GCE):

Of the solid electrodes which have found application in electroanalysis, perhaps the most widely used is the glassy carbon electrode, both as a solid electrode and as a substrate for a mercury thin film electrode (MTFE). The MTFE is discussed in section 1.2.2.4.

First reported in 1962 by Yamada & Sato [66], glassy carbon is a hard, gas-impermeable substance formed by the controlled heating of a premodelled phenol-formaldehyde resin in an inert atmosphere [67]. Kawamura [67] examined the structure of glassy carbon with X-ray diffraction, and concluded that it is composed of "aromatic ribbon molecules which are oriented randomly and are tangled in a complicated manner."

Several materials are available which resemble glassy carbon, such as LTI (low temperature isotropic) pyrolitic graphite, but which have entirely different properties [67]. The properties of glassy carbon and pyrolytic graphite have been compared [68,69].

It is the restricted potential windows for metallic electrodes that have precipitated the popularity of glassy carbon as an electrode material. It has a greater range at both the negative and positive ends of the potential scale, due to its high hydrogen overpotential and its unwillingness to, like metallic electrodes, be oxidised at modest positive potentials.

Zittel & Miller [70] were the first to use glassy carbon as a substrate for electroanalysis, and they demonstrated its superior working potential range when compared to platinum. They examine its potential window for a number of acids and, twenty years on, Thornton & workers [71] are in reasonable agreement, although some discrepancies exist at the negative end of the scale.

Alder et al [72], in a more quantitative treatment of the subject, examined a range of conductive and semiconductive materials, and they defined the positive potential limit as the potential at which the current (due to oxidation of substrate or oxygen evolution) became equal to half the value of the anodic peak current for the oxidation of $10^{-3}M \text{ Fe(CN)}_6^{4-}$. Using this criterion, they defined the positive potential limit for glassy carbon as being 1.3V at pH 1.0, 1.4V at pH 4.2, and 0.95V at pH 10.0 (all potentials vs SCE).
Significant disagreement, however, exists in the literature regarding glassy carbon potential windows.

For example, despite the potential windows quoted by Zittel [70] and Thornton [71], anodic preconditioning of glassy carbon at 1.75-1.80V (vs SCE) is commonly reported [73-77]. This is difficult to rationalise if oxygen evolution does indeed commence at 1.4 to 1.5V (vs SCE) as, were this the case, a potential of 1.8V (vs SCE) would entail gross O₂ evolution. Gunasingham [78], however, reports that oxygen evolution does not commence until 1.8V (vs SCE), which, given the number of workers who pretreat their glassy carbon electrodes in this region, would seem to correspond to the consensus, although it is possible that oxygen evolution is part of the pretreatment procedure.

This type of discrepancy is not unexpected, however, since more than any other solid electrode, the electroactivity of the glassy carbon electrode, and therefore the overpotential for a process such as oxygen evolution, is a function of its history and pretreatment, be it mechanical, chemical, or electrochemical [79,80].

Adding to the difficulties surrounding the characterisation of the pretreatment procedure, and indeed of the electrode itself, is the fact that the glassy carbon, in its very substance, is highly inhomogeneous; individual
electrodes cut from the same rod may have vastly different voltammetric background responses and other electrochemical reactivities [81-83].

The negative potential limit for glassy carbon is more negative than any solid metallic electrode, with potentials of -1.2V vs SCE being readily attainable in neutral or weakly acidic media (e.g. acetate). In more strongly acidic media, the negative potential limit is closer to -0.8V (vs SCE) [70]. White [57], for example, reports a useable potential range of -1.3V to 1.5V (vs SCE).

Monien et al [84] examined a range of carbonaceous materials, including wax-impregnated graphite, wax-impregnated carbon, carbon paste, pyrolytic graphite and glassy carbon, and found that in terms of both the positive and negative potential limits, the glassy carbon had the broadest working range.

Since the limits of the potential windows are determined by the electrolytic decomposition of water, it may be seen that the use of a non-aqueous solvent can have the effect of significantly extending the working range of the electrode, as may be seen from figure 1.2. Given the constraint on the potential window imposed by the decomposition of water, the decomposition of the electrode itself at potentials beyond this range has received little attention.

The surface of the glassy carbon electrode has proven to be more difficult to characterise than those of metallic electrodes as, due to its polymeric nature, the analyst is faced with the possibility of the presence of a variety of hydrocarbon functional groups and their accompanying oxidation states. Various oxygen containing groups have been suggested [17,85,86] including a quinone/hydroquinone couple [87].

Pretreatment procedures:

The pretreatment procedures required to produce reproducibly low background currents have often been viewed as a black art [13], although, as noted by Batley [14], with care and appropriate maintenance techniques, this is readily achieved. The critical dependence of glassy carbon performance on pretreatment has not been appreciated by some authors, and the issue has been confused by, for example, the reporting of results on electrodes with unacceptably high background currents [88].
This explains the fact that there are as many pretreatment methods reported as there are papers on the subject.

In terms of mechanical pretreatment, an acceptable method is usually one that produces a smooth, scratch-free, mirror-like finish [89,90], and this is usually achieved with metallographic polishing equipment utilising diamond laps and/or alumina. With respect to this, it has been shown that the mechanical pretreatment procedure may influence the subsequent electrode performance [79].

Kamau [76], in a comprehensive review of glassy carbon pretreatment methods, attempts to wade through the mountain of literature on this subject, and concludes that electrode activation, and enhancement of redox kinetics, is brought about by the inclusion of a higher concentration of oxygen in the outer layers of the carbon [as he originally noted in an earlier publication [90]). He further notes that alumina pretreatment can enhance the redox kinetics of some processes, as a result of residual surface alumina enhancing electron transfer rates.

Once in its polished state, and providing that the only solid material that is allowed to come into contact with its surface is filter paper, current understanding has it that mechanical polishing should not be required for many years [24,32,91]

In terms of chemical/electrochemical pretreatment, both anodic and cathodic [66,73,92] techniques have been reported, but this is very much a function of the potential window in which electrode electroactivity is required. Other activation techniques include radiofrequency plasmas [93], lasers [75] chemical [94] and heat treatment [89,95], and AC techniques [80].

In other characterisation work, the background capacitance has been shown to be related to an increase in adsorption capacity for small, adsorbing, organic molecules (e.g. 1,2,4-trihydroxybenzene) [96], and the adsorbing capacity has been related to the rate of heterogeneous electron transfer [97,98].

For non-adsorbing compounds, however, no such relation between background capacitance and heterogeneous electron transfer kinetics was observed [99,100]. Engstrom [92] has suggested that the improvement of heterogeneous electron rate transfer kinetics is due to the introduction of quinone functionalities on the electrode surface.
Glassy carbon is not as chemically inert as metal electrodes, and degradation due to chemical attack by chlorine [8,101] and tetrafluoroborate [102] have been reported.

Glassy carbon electrodes, like metallic electrodes, are widely and successfully used as amperometric detectors in flowing solutions. They possess a number of advantages over metallic electrodes, as outlined above. A number of reviews discuss their usage [57-61].

1.2.2. MERCURY ELECTRODES

In contrast to solid electrodes, the analyst has the option of using mercury, which is a liquid at room temperature, as the electrode substrate. Mercury is itself oxidised slightly positive of 0V (vs SCE), and although this property is utilised for the technique of cathodic stripping voltammetry (CSV), it finds its greatest applicability as an electrode substrate for the reversible oxidation and reduction of metals in the negative potential region. In this context, it has some significant advantages over solid substrates:

• It possesses the ability to reversibly form amalgams with a range of metals simultaneously. This is a property which is utilised for ASV.

• It has a very high overpotential for the reduction of hydrogen ions to hydrogen gas.

• It presents the possibility of a constantly renewable surface. This eliminates the possibility of electrode poisoning by predeposited material.

• It is a more reproducible chemical surface. It does not have the dependence on the presence or absence of oxide layers and/or adsorbed or absorbed oxygen or hydrogen of a solid electrode. Furthermore, no mechanical pretreatment is either required or possible.

These properties have spawned a number of electrode configurations, each of which, according to the application, utilises one or more of the intrinsic advantages outlined above:
1.2.2.1. The Dropping Mercury Electrode (DME)

The DME consists of a mercury reservoir mounted over a capillary tube. The mercury is allowed to flow through the capillary into the analyte solution, where it forms as discrete droplets before dislodging either under the influence of gravity or with the aid of a mechanical knocker. Electrical contact is achieved by the immersion of a platinum contact into the mercury reservoir. Figure 1.3 illustrates a typical DME setup.

![Diagram of a dropping mercury electrode (DME)](image)

Figure 1.3: Schematic diagram of a dropping mercury electrode (DME).

This is the oldest of the mercury electrodes, and it predates the modern electroanalytical era. Its first reported usage is in 1871 by Varley, a co-worker of W. Thomson (Lord Kelvin) [103]. In this context it was used to study the connection between the surface and electrical energies of the mercury/solution interface.
The interfacial nature of DME studies continued up until 1922, when Heyrovsky first demonstrated a polarographic wave for oxygen reduction [104,105]. This heralded the beginning of the modern electroanalytical era, although it was not until the mid 1950's that DC polarography became a routine tool for trace metal analysis.

The interim period involved the development of instrumentation the automated DC polarograph was developed in 1924 [106] and a continued emphasis on the study of mercury/solution interfacial phenomena [107,108]. By 1930 the term "polarography" had been coined, deriving its name from the "ideally polarisable" mercury electrode.

For trace analysis, the inherent lack of a preconcentrating step has resulted in the DME being replaced by other mercury electrodes that allow this facility, and the DME has been largely confined to the teaching laboratory. Despite this, however, it is an electrode that has been used for the last thirty years in applications where ppm sensitivity is sufficient, and it is still used today in this context, with frequent reports in the literature of routine determinations of metal content in food products [109], die casting [110] acid baths [111,112], salt matrices [6], minerals [113], cement and steel [114], petrol [115], and nuclear fuels [116].

In addition, the DME has been used for the determination of a variety of organics, dyes and pharmaceuticals [117-124], as well as for complexation studies [125-127]. Finally, an indication of the ongoing interest in the DME is given by the continued development of the theory of this electrode [114,128-132].

A recent emphasis which has attracted some attention is the use of the DME in FIA and HPLC [129].

A problem with the DME in any context, be it in a stationary or flowing cell, is that the current changes as the surface area changes. This may be overcome by the use of electronic filters, or current sampling techniques [133]. The latter, however, requires more complex instrumentation, usually in league with a mechanical knocker (fig. 1.3), to facilitate synchronisation of the current sampling with the lifetime of the drop.

Conversely, however, the fact that the current changes as the drop grows may be used to advantage, as the techniques of chronoamperometry may be employed to study and characterise the \( i \) vs \( t \) curves of the individual drops. This technique has been successfully employed in flowing systems to monitor
imperfections in detector design[129], as well as to detect the presence of surfactants [134], and determine the highest possible flow rate for a given drop time [135].

In summary, the DME is continuing to be utilised in those applications where the analytes to be determined are not at trace level, and where the requirement for a renewable electrode surface is paramount.

1.2.2.2. The Hanging Mercury Drop Electrode (HMDE).

The HMDE consists simply of a drop of mercury suspended from a capillary, which acts as the working electrode. Unlike the DME, it possesses the advantage of convenience, as there are none of the problems associated with maintaining a flowing electrode (air bubbles may enter the capillary and sever electrical contact), although care must be taken to ensure a reproducible drop size.

It finds wide applicability, in conjunction with stripping techniques for the determination of metals such as lead, [24,136-140], copper, [136,137,139,141-144], cadmium, [136,137,139,140], zinc [136,137], indium [16,140], cobalt [41], nickel [41], gallium [20], uranium [144,145], platinum [146], selenium [26], molybdenum [147], and thallium [140], as well as a variety of organics [148,149]. In conjunction with these, it has attracted a significant amount of attention for speciation studies of metals in natural waters [41,44,141,142,150-155].

1.2.2.3. The Static Mercury Drop Electrode (SMDE)

A variation on the DME theme is the SMDE [156]. This is a similar arrangement to the DME, with the exception that the drop does not grow in a linear fashion under the influence of gravity, but is extruded by gas pressure. The fundamental difference is that the drop is extruded very quickly, and then remains static while the oxidation/reduction processes proceed at the surface. As a result of this, the potential is always applied to, and the current measured at, a stationary drop, and none of the charging current effects associated with the growing mercury drop are encountered.

Despite this significant advantage, however, the SMDE has not found wide applicability, due largely to its mechanical unreliability. Specifically, the
operation of the gas plunger may introduce gas bubbles into the capillary, thereby severing electrical contact [157]. Frequent silanisation and attention to detail is required to counter this problem[158].

First reported in 1979 [156], the SMDE has been used both as a DME, and as a highly reproducible HMDE [157]. As the former, it has been used for the determination of metals [126,158-160] and various organics, particularly pharmaceuticals [161,162]. As the latter, it has found similar applications for metal [126,138,150,163-165] and organic [166,167] determinations. As well as these applications a considerable amount of work has been done on the theoretical aspects of the electrode [129,158-161,168].

The SMDE has failed to find widespread use either in industry or for research.

1.2.2.4. The Mercury Thin Film Electrode (MTFE)

The MTFE is the most widely used electrode for ASV at trace and ultra-trace levels. It consists of a series of finely divided mercury droplets (<10μm [22]), ostensibly as a film, which are electrodeposited onto a solid substrate.

In an extensive study of the subject, Yoshida [169] examines the viability of a range of materials as substrates for MTFEs for ASV. His rationale is that glassy carbon is a poor substrate for mercury films purely because of the lack of mechanical stability of the latter, and he attempts to find a metal substrate that retains the property of having a high overpotential for hydrogen evolution, and which is able to mechanically stabilise the mercury film.

He groups the substrates according to the way they interact with the deposited mercury, and selects nickel as being the best, as it amalgamates the mercury into a true film, and with sufficient mercury, retains the property of a high overpotential for hydrogen evolution.

This study, however, does not address the critical aspect of reproducibility, and no mention is made of how a mercury film is reproducibly removed from the electrode surface, and the substrate returned to pristine condition.

Glassy carbon has been the electrode of choice for the vast majority of work involving MTFEs, for the following reasons:
Due to its non-metallic nature, its degree of interaction with the deposited mercury is extremely low [169], and the mercury is therefore reproducibly removed and redeposited without irreversible contamination of the electrode surface.

Glassy carbon has a high overpotential for hydrogen reduction (sect. 1.2.1.2.2). This is an important consideration since, as noted by Yoshida [169], electrodes such as glassy carbon, when coated with mercury, have a hydrogen overpotential which is largely determined by the electrochemical properties of the substrate.

The glassy carbon electrode surface is easily renewed (and maintained) by mechanical polishing with diamond laps and/or alumina (sect. 1.2.1.2.2), unlike the softer metallic substrates.

Despite this, however, metallic substrates such as silver [170-173], platinum [169,174,175], copper [169,176,177], gold [169], nickel [169], molybdenum [169], lead [169] and stainless steel [169], have also been used as substrates for MTFEs, although they have not found wide applicability. Also in this category is the wax-impregnated graphite (WIG) electrode [178-181].

The MTFE first rose to prominence in the early 70s, and represented an integral part of the general renaissance of electrochemical methods which occurred about that time. A number of publications around this period detail the early development work [22,24,182,183].

Since those early days, however, very little work has been devoted to a more rigid characterisation of the electrode per se, although it has continued to find wide applicability in a number of areas, most notably the analysis of marine [151,179,184-186] and other aquatic [30,150,186-188] samples, where the matrix and low level of determinands present problems for atomic spectroscopic methods. This hiatus in research is illustrated by the fact that, with respect to the physical morphology of the electrode, there has yet to be an update of Stulikova's landmark publication of 1973 [22], and this reference is cited in a number of modern publications [21,189-192]. There are two reasons for this situation:

1. The structure of the film is dependant on so many variables, notably the condition of the glassy carbon substrate (sect. 1.2.1.2.2) that it becomes difficult to draw general conclusions.
2. Physical characterisation of the MTFE is logistically difficult. The use of scanning electron microscopy to characterise the fine structure of the film necessitates drying of the film (removal of water) and this presents major problems with respect to the integrity of the data, particularly since the mercury itself is in the liquid state, and it possesses both finite volatility and surface tension (both at the glassy carbon and water interfaces).

Further, for any sort of in situ characterisation (by optical microscopy), an imaging system is required that can look through an optically flat cell, and a finite volume of water. This requires microscopes with special long focal-length objective lenses.

By far the most commonly determined metals at an MTFE with ASV are zinc, cadmium, lead and copper, with most ASV publications involving the analysis of one or more of these metals [15,179,193]. Other metals which have also been determined by ASV are antimony [15,24], bismuth [8,151], cobalt [18], indium [232,24], nickel [183], silver [27], tin [281], and thallium [30].

It is no part of this treatment to comprehensively detail all theoretical and practical aspects of the MTFE, as these have been dealt with in a number of excellent reviews [7,9,10,24,192,194-196], but rather to highlight some general principles, and some points where there is still confusion in the literature.

Although the MTFE (on a glassy carbon substrate) is generally acknowledged to be a series of fine droplets dispersed on the electrode surface [10,21 - see below], and is therefore not a true (unilamellar) film at all, references to its film-like nature are readily dispersed throughout the literature [8,13] with many references to determinable film "thicknesses." (vide infra). Perhaps the reason for this is that although it is not a true film, its behaviour closely approximates that of a true film [24].

Each aspect is now considered, and the extent to which these two aspects have been reconciled is examined.

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1 Mercury film is deposited in situ (Florence electrode).
2 Determination carried out in a flow system.
3 The authors do not say whether a HMDE or MTFE was used.
1.2.2.4.1. Film thickness

In terms of quantifying the thickness of the mercury film on a solid substrate, three approaches have been taken.

The first of these is that of Moros [197] who quantified the film thickness of an MTFE on a platinum substrate simply by mechanically removing the film from 10 electrodes (by rolling the surface with a piece of plastic tubing) and weighing the resulting mass of mercury. A gravimetric approach was also taken by Roe and Toni [198].

The second approach is that taken by De Vries [199] and De Vries & Van Dalen [200] in their landmark publications on MTFE theory, in which a mathematical model, based on Fick's second law of diffusion, is used. A similar approach has been taken by other authors [195,198,201].

A curious feature of this class of publication is that no form of independent assessment of film thickness has been attempted, even though in one case [195] experimental data is advanced in support of the theory. It is perhaps also interesting to note that De Vries & Van Dalen [200] cite the work of Moros [197], as evidence of the approximate thickness of an MTFE.

The third approach was that taken by Batley & Florence [24] who simply use coulometry to estimate film thickness, and Gunasingham [202] uses a similar approach.

They compare the simple coulometric relationship

\[ l = \frac{10^{-6}iWt}{\pi nFdr^2} \]  

\text{eq. 1.6}

where

\[ l = \text{average thickness of the mercury film} \]

\[ i = \text{limiting mercuric ion deposition current (mA)} \]

\[ W = \text{atomic weight of mercury} \]
t = deposition time (s)

n = stoichiometric electron number

d = density of mercury (13.6 g.cm\(^{-3}\))

r = radius of electrode surface in cm

with results obtained from the Roe and Toni equation [198],

\[
E_p = E_{1/2} + \frac{2.3RT}{nF} \log \frac{\delta ln F}{D_mRT} \tag{eq. 1.7}
\]

where

\begin{align*}
E_{1/2} & = \text{polarographic half wave potential} \\
D_m & = \text{diffusion coefficient of metal ion in solution (cm}^2\text{s}^{-1}) \\
d & = \text{diffusion layer thickness (cm)} \\
v & = \text{scan rate (V.s}^{-1}) \\
l & = \text{mercury film thickness (cm)}
\end{align*}

and find them to be in reasonable agreement

All of these models, however, assume an even, uniform film, and the concept of a calculable "film thickness" has enjoyed wide acceptability, despite the fact that at least in the case of glassy carbon, the film, certainly at the microscopic level, consists of a series of droplets, and is not a film at all [10,22,169,203].

These two concepts have never been reconciled quantitatively, either experimentally or theoretically, primarily because there has never been an experimental determination of the film thickness \textit{in-situ}. The tacit assumption that the coulometrically calculated film thickness refers to the "average film thickness" [204] is inadequate as it ignores the following:
1. The formation of insoluble Hg\textsuperscript{I} salts as part of the Hg\textsuperscript{II} → Hg\textsuperscript{0} process. Further, while ever Hg\textsuperscript{II} and Hg\textsuperscript{0} are present, disproportionation will occur [205] as:

\[ \text{Hg}^{2+} + \text{Hg}^0 \rightleftharpoons \text{Hg}_2^{2+} \quad \text{eq. 1.8} \]

These are significant considerations, as most Hg\textsuperscript{I} salts are insoluble. For this reason, it has been suggested that where coulometric considerations are important, one should "eschew mercury two" [206].

2. Not all the mercury metal that initially forms stays on the surface. This is discussed in chapter 2.

3. The size and distribution of the mercury drops are determined by the [Hg\textsuperscript{2+}], E\textsubscript{dep}, and degree and type of glassy carbon pretreatment [22,191] and not simply the charge density. Furthermore, since the performance of the electrode is a function of drop size and mercury surface area [10,21,192 - \textit{vide infra}] and not just "film thickness," it may be seen that the coulometric "thickness" of the electrode has little bearing on its subsequent performance.

From these considerations it may be seen that a simple interpretation of electrode performance in terms of a coulometric "film thickness" is palpably inadequate.

In fairness to these authors, however, it should be noted that the assumption of the De Vries and Van Dalen model [1018] of an even, uniform film, was made at a time when most of the experimental work on MTFEs had been done on metal coated films [197,198,207-210], in which case, at least for metals such as nickel, copper, gold [169], and iridium [10], the assumption is valid.

It is, however, plainly a mistake to extend this model, and the accompanying theory, to the treatment of glassy carbon.
1.2.2.4.2. Morphology of mercury droplets

The difficulties involved with characterising a series of finely divided mercury droplets have been outlined in section 1.2.2.4.

The only serious attempt to characterise the mercury film in terms of size and distribution has been that of Stulikova [22], and this paper, as has been noted, has been oft cited in this context. There are however, some faults in the interpretation of his data which have led to some systematic errors.

In particular, the author provides no details of the electrode and camera setup, although he does mention that the electrodes are dried prior to being photographed. This in itself would introduce errors [211], as mercury, being a liquid, is dependent upon its surface interaction with its environment for its shape, and since it forms a non-wetting and mechanically unstable film on glassy carbon [191], it must be concluded that the medium with which the bulk of the surface area comes into contact will play a significant role in determining its structure.

In particular, the drying of a mercury film results in significant deformation of the film, with coalescing of drops and the exposure of glassy carbon substrate (as Stulikova himself notes).

The general conclusions, however, of this paper, are not called into question, as the drying effect could be expected to exert a uniform influence on all films examined. The actual morphology presented, and the drop sizes quoted, however, should be regarded with extreme caution.

1.2.2.4.3. Other factors

The misunderstandings concerning the nature of the film and the lack of work that has been devoted to characterising it, combined with the intrinsic irreproducibility of the glassy carbon substrate, have paved the way for some significant disagreements concerning the nature of the MTFE.

For example, it has been reported that electrode redox processes are both dependent [151,192,212] and independent [182,183] of "film thickness", with Stojek and Kublik reporting thickness dependent shifts in the stripping potential [195]. It has been reported that mercuric ions may not be
electrodeposited below $7.5 \times 10^{-7} M$ [213], whereas Mann [82] determines Hg$^{2+}$ by this method on a routine basis at concentrations down to $2.5 \times 10^{-8} M$ (5 ppb).

The stability of the MTFE has also been the subject of some conjecture, with Mlakar & Lovric [192] suggesting that the electrode be held at -0.1V between scans to avoid electrode degradation, while other workers suggest that it is stable for 2-8 hours [211], a day [13,30], or 20-40 days in neutral or weakly acidic media [7]. None of these authors suggest mechanisms to account for the observed (or proposed) film degradation.

The only parameter that has been used to characterise mercury film degradation by these workers is loss of analytical performance. While this is clearly a highly pragmatic approach, from the point of view of electroanalysis, it yields little information about the real nature of the degradation, particularly since, as has been noted, the relationship between performance and morphology/structure is itself not understood.

The mechanical stability of the MTFE is also a point on which contradictions abound. The very formation of non-wetting droplets on a surface necessarily implies poor mechanical stability [169], and yet the electrode has been successfully used in flowing systems [59,212,214,215], including the use of wall-jet electrodes [202,216-218], and any number of ASV determinations using an RDE.

The question that needs to be addressed is:

Is the mercury film electrode mechanically unstable or is it not? If it is mechanically unstable, then may its utility in high convection systems be explained by the fact that it is able to undergo a significant degree of (uncharacterised) mechanical degradation, and yet still be able to function adequately as an analytical system, and that the discrepancies in the literature are a consequence of ostensibly similar systems that have undergone differing degrees of (unknown) degradation, such that their is little connection between theoretical film parameters and actual film parameters?

This question is the subject of the experimental study in chapter 2.
1.3. CHEMICALLY MODIFIED ELECTRODES

The need to extend the range and/or performance of electrochemical stripping methodology has spawned a number of approaches to chemical modification of electrode surfaces. While most of these have been targeted at AdSV, due to its non-Faradaic accumulation mechanism, a number of approaches to modification of electrode surfaces for ASV have also been taken.

Each technique is considered in turn.

1.3.1. CMES IN AdSV

The scope for CME’s in AdSV is immense. The non-specific and poorly defined nature of adsorption processes at conventional electrodes provides the analyst with a mandate to design electrodes which will either selectively adsorb a specific analyte, or selectively exclude a specific interferent.

1.3.1.1. Requirements of CMEs for AdSV

The requirements for a CME that is to be used for AdSV, are as follows:

1. Selectivity:

The electrode must possess the ability to either selectively bind an analyte, or selectively exclude an interferent, from a complicated matrix.

2. Sensitivity:

Although in some cases, sensitivity has been targeted as the primary function of a CME, it is not usually a major consideration, owing to the intrinsic sensitivity of electrochemical methods.

3. Capacity:

In order to be analytically useful, the CME must possess a capacity sufficient to enable it to maintain linearity over a suitable concentration range of analyte.
4. Reuseability/Stability:

To enable the electrode to be a viable proposition for multiple analyses, it must be either stable for a long period, or capable of regeneration. This is a common problem with many CMEs as, with the unending quest to achieve specific binding (of some sort) of analyte to substrate, very often very little thought is given as to how the analyte may be reversibly removed.

There are essentially three approaches that have been taken to facilitate the reversible removal of the analyte:

(i) A complexing group may be used which is specific for one oxidation state of the metal only. Such an approach was reported by Abruna [219] who used an electrode containing a complexing group (2,9-dimethylsulphonated bathophenanthroline), for which the cupric ion is complexed much more strongly than the cuprous ion. Reduction of the bound copper results in the complex releasing its copper to return to the uncomplexed state, ready for the next determination.

(ii) Another approach involves the use of a CME system that relies upon cation/anion incorporation into a (usually polymeric) modifier as a counterion of some sort. The analytical signal, and the simultaneous regeneration of the CME may then simply consist in the expulsion of the cation/anion by a reversal of the electrostatic or electronic conditions in the surface film that led to its initial incorporation. Examples of these electrodes are examined subsequently.

(iii) The electrode need not require regeneration if it is easy and cheap enough to manufacture. The advent of disposable electrodes (sensors) is an exciting new area of electroanalytical chemistry that has been rendered possible by conducting polymer technology and improved surface coating technologies.

1.3.1.2. Applications

There are essentially two types of substrate that have been employed as CMEs with AdSV: carbon paste electrodes (CPEs) and polymeric electrodes.

CPEs are generally considered to be on the periphery of CME technology, as evinced by the fact that a number of CME review articles fail to even mention them [220-222]. Indeed, in this context, Bond [10] says “In a broader sense, one can
include paste electrodes and solid graphite electrodes containing additives in this class of electrode.”

This reluctance to classify CPEs as *bona fide* CMEs probably stems from the fact that, at a microscopic level, they are composite electrodes, rather than discrete substrates which have been subjected to a specific surface modifying process. In terms, however, of the broad definition of CMEs as “deliberate control of the molecular structure at the surface, aimed to tailor the electrode to meet specific applications” [223], and certainly at a macroscopic level, the CPE must be classified as a CME.

A detailed study of the many and varied preconcentration schemes employed for AdSV with CMEs is beyond the scope of this project, and selected references only are given. The references are grouped according to the accumulation mechanisms that they employ.

**i. Carbon Paste Electrodes:**

CPEs have preconcentrated metallic ions by ion exchange [224-226], complexation [227-229] and bioaccumulation [230,231], and organic species by selective extraction into the binding material [232,233].

**ii. Polymeric Electrodes:**

Polymeric electrodes have preconcentrated metallic ions by complexation [234-236], metallic complexes by ion exchange (as cations [237-239] and anions [240-242]) and complexation [243-245], organics by extraction into a hydrophobic layer [149,246,247], organometallics by covalent binding [248], and non-electroactive organics by tensammetry [43] and signal suppression [249].

**1.3.2. CMES IN ASV**

Unlike AdSV, the technique of ASV relies on an externally applied EMF to induce reductive preconcentration of an analyte at the electrode surface. Whatever role the modifier plays, therefore, an accumulation mechanism need not be one of them. As a consequence of this, the analyst has been able to turn his attention to chemical modifiers with highly specific properties such as
permselectivity, or other methods of interferent exclusion, whether the interferents be adsorbing organics, or co-depositing inorganics.

Although ASV predominantly employs mercury based electrodes, the chemical modification of a solid electrode may circumvent this requirement, and CMEs for ASV, both with and without mercury, have been reported.

Each is considered in turn.

1.3.1.2. Non-mercury based CMEs for ASV

One advantage of mercury based electrodes, as has been noted, apart from their ability to reversibly form amalgams with many metals of interest, are their high overpotential for mercury reduction. Any CME, then, that seeks to work in the negative potential domain (i.e. $< -0.7V$ vs Ag/AgCl) must address this problem. Such was the approach taken by Miwa and workers [250], who used a silanising procedure to coat a glassy carbon electrode with the group:

![Functional group on silanised glassy carbon electrode surface](image)

They used this electrode for the ASV determination of copper, and apart from an increased hydrogen overpotential, report advantages in the area of electrode reproducibility and interferent exclusion.

Reproducibility is an intrinsic problem both with glassy carbon (vide supra) and mercury film electrodes, and the modifier reported by these workers improves on this aspect and obviates the need for pretreatment between scans by presenting to the solution a more reproducible interface. The electrode was used up to 100 times without the need for electrode treatment. Further, whereas antimony and bismuth would interfere in an ASV determination of copper by conventional means, no interference is reported in this work despite the presence of these metals in up to a 12 times molar excess. No explanations are given for these phenomena.
Dong & Wang have designed CMEs for the ASV determination of silver [251] and lead [252], for which the emphasis is on lowering the already low ASV detection limits for these metals. The system they use to achieve this is a ™Nafion/DC18C6 (dicyclohexyl-18-crown-6) composite, and they report detection limits of $2 \times 10^{-9}M$ for lead, and an astonishing $2 \times 10^{-12}M$ for silver.

Their explanation of the mechanism for these processes suggests that the DC18C6 moiety complexes with the metal of interest, forming a large cation. The ion exchange properties of the ™Nafion sulphonate groups attract the cation, at which point the metal ion is reduced at the electrode surface and the DC18C6 is regenerated. It will be noted that it is in cases such as this that the distinction between AdSV and ASV becomes a little clouded, as this electrode employs both accumulation mechanisms.

Liu et al [253] report on a Schiff-base-modified ™Nafion film electrode for the ASV determination of mercuric ions. Although it seems clear that the Schiff-base complexes the mercury at some stage during the Faradaic accumulation procedure, its specific role with regard to the reduction of the mercury has not been elucidated.

The electrode shows good selectivity for mercury over a number of other ions, and proves resilient to interference from non-ionic and anionic surfactants (sect. 1.1.1), although significant interference is caused by cationic surfactants, as would be expected given the strong ion-exchanging properties of the ™Nafion sulphonate groups.

The intrinsic complexity of a system that relies upon Faradaic accumulation in the presence of a chemical modifier, whatever the role of the modifier may be, is no doubt a reason for the lack of publications in this area. That is, since the analyte is accumulated cathodically, the role played by the modifier, if the performance of the conventional system is to be enhanced, must be either to assist the Faradaic accumulation process (by complexation etc.) or to exclude specific interferents from the electrode surface, and there are, therefore, two processes occurring simultaneously at the accumulation step.

For the case of a mercury-based thin-film electrode, however, the modifier has the opportunity of assuming another role, namely, the modification of the mercury film, with a concomitant enhancement of its intrinsically favourable properties as a substrate for stripping analysis.
1.3.1.3. Mercury Thin Film based CMEs for ASV

MTFEs are, in general, poorly understood, as is outlined in chapter 2. In general they are operationally defined, rather than being physically characterised by some independent method, and amongst their most diagnostic operational parameters is their susceptibility to interference from surface active agents (sect 1.1.1), be they proteins in blood or urine, humic or fulvic acids in marine samples, or detergents from industrial outfalls. Consequently, the major thrust of chemical modifications of MTFEs to date has been directed towards eliminating this problem.

Smart & Stewart [254,255] addressed the surfactant-interference problem by attaching dialysis membranes (Spectra/Por 6 cellulose) to the surface of the electrode prior to plating the mercury film. The dialysis membrane acts as a permselective barrier to high molecular weight organics and is thus able to minimise interferences, although the porosity of the electrode to ionic transport does demonstrate pH dependence [254].

These workers examined the effects on the modified MTFE of eight surfactants, chosen to model ionic, non-ionic, complexing and polysaccharide compounds and concluded that “the dialysis membrane provided a protective barrier on the MCMFE [membrane covered mercury film electrode] and eliminated the influence of the surfactants in each case.” [255]. This work, however, only demonstrated the utility of this approach for cadmium, and its applicability to other metals has yet to be demonstrated.

Further, the ten minute membrane equilibration period in the mercury solution is on the same time scale as an individual experiment and represents a disadvantage unless the stability of the electrode is such that it allows multiple determinations over a long period of time. No mention of this aspect (stability) is made by the authors, although, given the susceptibility of the membrane to attack by cellulytic microorganisms, and the fact that only small changes on the electrode surface are required to profoundly influence the electrode performance (vide infra) it is difficult to envisage an electrode life any longer than a couple of days.

Wang [256] used a cellulose acetate film as the permselective film and, in contrast to the previous approach, coated the modifier on top of the mercury film, rather than underneath it. Treatment of the cellulose film with KOH attacks the surface and creates diffusion channels through which analyte ions
can diffuse to the underlying mercury film. Porosity of the film may be varied by the time frame of this treatment. The response of the electrode in the presence of gelatine, agar, and dodecyl sodium sulphate is examined, and its resilience to interference from these compounds is demonstrated.

As with the dialysis membrane, however, the resistance of the film can hinder the electrochemical processes at the electrode, and this is demonstrated by the shifting and broadening of the copper peak. Also, as with the dialysis membrane electrode, the electrode preparation time represents a significant inconvenience, in this case being greater than two hours. No data on long term electrode stability is presented.

Florence & workers [257] attempted to improve on the mass transport limiting properties of these films by introducing a ™Nafion coated thin mercury film electrode (NCTMFE). In an extremely thorough investigation of the electrode’s properties, aspects such as film (™Nafion) thickness, extent and region of mercury coverage, pH dependence, matrix effects, ™Nafion ion exchange properties, excitation waveform effects, transport properties and surfactant interference are examined [257].

This study [257] consists of an examination of six surfactants with respect to the ASV stripping signal: Triton X-100 (non-ionic), sodium dodecyl sulphate (anionic), n-dodecylpyridinium chloride (cationic), gelatin (a colloidal protein), a protein standard solution (albumin and globulin in the weight ratio 5:3), and 1-octanol (long chained alcohol). The extent of interference (peak depression) for the cadmium stripping peaks was far less than that observed at a conventional MTFE, although interference was observed with some surfactants, and occurred in the order cationic > non-ionic > anionic, which is the order that would be expected given the cationic ion exchange properties of the perfluorosulphonate ™Nafion functionalities.

They later applied this electrode to the ASV analysis of body fluids [258], and reported superior performance characteristics when compared to the dialysis membrane and cellulose acetate modified MTFEs. These advantages essentially consist of smaller shifts in stripping potentials, and enhancement of sensitivity when compared to conventional MTFEs, and these effects are attributed to the thinness of the ™Nafion films when compared to the others.

Another significant advantage of the NCTMFE over the previously reported modified MTFEs is the shorter electrode preparation time, the only
significant increase over a conventional MTFE being the time taken for the dip coated polymer solution (1:1 ethanol/water) to dry. Like the previous MTFEs, however, no significant increase in film stability (with respect to the conventional MTFE) was reported, with a lifetime of "at least one working day" being quoted [258].

Perhaps the greatest drawback of this electrode is its poor reproducibility, a legacy of its dip coated genesis [259]. The solvent evaporates from the periphery of the electrode towards the centre, thus creating an uneven polymeric distribution [260], and the possibility of non-reproducible coatings.

Cassidy and workers [261] utilise polystyrene as the permselective polymer for their mercury film electrode, but take the process one step further by attempting to stabilise the mercury via complexation to incorporated zeolite A particles. Electrode stability up to four weeks is reported, provided the mercury (II) is maintained in its oxidised form.

No data is given on the stability of the mercury film once in its metallic state, or the possibility of mercury oxidation and recomplexation. Once again, reproducibility is a problem with this film, and, given the lack of data regarding the stability of the electrode once in use, the five day zeolite/mercury equilibration step represents a significant inconvenience.

The concept of stabilising the mercury film by complexation of its mercuric ions does, however, represent a significant advance, at least in conceptual terms, despite the apparent non-reversibility of this process with this electrode.

The same authors report on an electrode which is similar in concept, and consists of mercuric ions dip coated onto a glassy carbon substrate in a PVP matrix [262]. The main advantage of this electrode over the zeolite electrode is the much shorter preparation time. Data are reported for cadmium and lead, with copper once again being a problem. Similar stability and stability conditions are reported as for the zeolite electrode, with three weeks electrode stability with the mercury in its oxidised state.

Permselectivity of this electrode is demonstrated by the resilience of its stripping signal to the addition of gelatin.

Despite the lack of long term stability data on these electrodes, an interesting concept is introduced: the stabilisation of the mercury film itself.
This contrasts with the permselective approach which consists not so much in modification of the film as simply protection of a conventional film. The latter approach is fraught with difficulties, however, as the presence of a modifying film on the intrinsically irreproducible mercury film can only add to problems with reproducibility.

The former approach shows some promise, however, particularly if it can result in the retention of the positive qualities of the MTFE, while eliminating or minimising its undesirable qualities. Such an approach, as Cassidy has demonstrated [261,262] may consist of chemical stabilisation of mercuric ions on the electrode surface, since mercuric ions readily form complexes with a number of functional groups.

The obvious advantage of this approach is that the stability of the electrode is not dependent on the poor mechanical interaction of mercury metal with the electrode surface, but may be conditioned on a much more specific chemical interaction with a specific surface-bound complexing group. This project reports the development of an MTFE based upon this concept.
1.4. PROJECT JUSTIFICATION AND OUTLINE:

The conventional MTFE may be summarised as follows:

- It is a highly sensitive electrode which, when employed with ASV, is capable of determining electroactive metals in the trace regime (lower ppb).

- The specific growth parameters ($E_{\text{app}}$ and $[\text{Hg}^{2+}]$) which determine its performance have never been rigidly characterised, and significant disagreement occurs in the literature concerning substrate pretreatment and MTFE stability.

- It is mechanically unstable, and has received little attention in flow-detection applications.

This project seeks to address the limitations of the conventional MTFE by utilising a system whereby the mercury is stabilised by (reversible) complexation to surface-bound dithiocarbamate groups (as $\text{Hg}^{II}$) and insertion (as $\text{Hg}^{0}$) into the pores of a self-assembling microelectrode array (*vide infra*).

That is, not only is the mercuric ion initially stabilised (by complexation with the dithiocarbamate groups) on the as-formed electrode, as with Cassidy's system [261,267], but it is capable of returning to this state subsequent to its reduction to the metal and use as an MTFE. This is addressed in chapter 4.

This electrode is a multilayered device with three discrete surfaces; the glassy carbon, the polymer coating, and the mercury film. To enable it to be fully characterised, it must be studied at each level.

The analytical parameters that were selected for the characterisation of the electrodes used throughout this project were their ASV responses to cadmium, lead and copper, as these three metals have very different interactions with mercury (sect. 2.3.2.1) and therefore may be expected to behave differently when being stripped from a mercury amalgam.

As an addendum to this study, it was necessary to examine the stripping responses of these three metals at the uncoated GC substrate. The reason for this is that since some of the mercury films examined in this study were vanishingly thin (invisible to the naked eye), it is therefore reasonable to
assume that some degree of metallic deposition on the glassy carbon substrate will take place concurrently with the deposition into the amalgam. In order for these responses to be distinguished from each other it is therefore necessary to examine the stripping responses of the three metals in question at the uncoated GC electrode.

As well as this, it became necessary to characterise the performance and physical morphology of the conventional MTFE. It was never the author's intention to conduct a study of this nature, but the inadequacy of the literature on this topic rendered it necessary. In particular, such a study was required in this case to assist with the subsequent characterisation of the chemically-modified MTFE.

This requirement stems from the fact that throughout the lifetime of the modified electrode the mercury may exist in up to three discrete oxidation states, depending on the previously applied waveform(s). To enable, therefore, the surface oxidation states of the mercury on the modified electrode to be assigned, it is necessary to know the influence of the amount of elemental mercury on the electrode surface on its analytical performance.

The characterisation of the analytical performance of the conventional MTFE (and the glassy carbon) are discussed in chapter 2.

Chapters 3 and 4 discuss the development of the chemically modified electrode, with chapter 3 discussing the generation and characterisation of the polymer coating, and chapter 4 describing the generation of the MTFE. Chapter 4 then examines the analytical performance of the electrode, in both stationary and flowing solutions, after which a comparison is made with the performance of the conventional MTFE.

Chapter 5 describes some complementary work in which a conducting polymer (polypyrrole) was derivatised with dithiocarbamate and also used as the basis for an MTFE.
Chapter 2:

Studies on Conventional Electrode Substrates
2.1. INTRODUCTION

This chapter lays the basis for the later characterisation of the polymer-coated electrode. It does this firstly by characterising the glassy carbon electrodes used as substrates throughout this project, and secondly by characterising (in qualitative terms) the ASV performance, morphology and stability of the conventional (GC-based) MTFE.

This is facilitated firstly by an examination of the background responses of each of the glassy carbon electrodes used, and secondly by examining the ASV stripping responses of Cd$^{2+}$, Pb$^{2+}$, and Cu$^{2+}$ at both the uncoated and mercury-coated glassy carbon electrodes.

Mercury thin films of varying relative thicknesses were examined and the characteristics of the stripping responses for each of the three metals evaluated in these terms. The electrode surfaces were also examined in situ with optical microscopy, and the mechanical stability of the films under various conditions was evaluated.

Studies were carried out with both stationary and rotating electrodes.

The specific parameters that are examined in each case are delineated in the appropriate section.
2.2. EXPERIMENTAL

2.2.1. ELECTRODES:

The cell and electrode assemblies used for the stationary and rotating electrodes were different, and each is described in turn.

2.2.1.1. Stationary electrode studies:

Working Electrodes:

Three glassy carbon working electrodes, ostensibly identical, were used throughout this study. They were standard glassy carbon electrodes (55 x 6mm, carbon electrode diameter 3mm) model MF 2012, as supplied with the Bioanalytical Systems 100A Electrochemical Analyser (BAS 100A).

All electrodes were metallographically polished prior to use with 6, 3 and 1μ diamond paste polishing pads on a Buehler Metaserv.

Counter Electrode:

The counter electrode used was a platinum gauze of approximate dimensions 1 x 2 cm bent into a U-shape around the working electrode.

Reference Electrode:

The reference electrode was a BAS MF2020 Ag/AgCl single junction reference electrode, and was used in conjunction with a fritless salt bridge made in the laboratory.
2.2.1.2. Rotating electrode studies:

Working Electrode:

The working electrode employed was an EG&G Princeton Applied Research Model 636 Rotating Ring Disc Electrode with a 5.5 mm diameter glassy carbon disc as the electroactive surface.

Counter Electrode:

The counter electrode employed was a platinum sheet electrode of dimensions 1cm x 1cm which was spot welded to a platinum wire and sealed in a glass B12 electrode mounting assembly.

Reference Electrode:

The reference electrode employed was a Metrohm 6.0718.000 double junction Ag/AgCl (3M KCl) reference electrode assembly.

2.2.2. INSTRUMENTATION

Electrochemical Instrumentation:

Three instruments were used throughout the course of this project:

Bioanalytical Systems CV 27 Voltammograph:

This is a simple instrument which produces an analogue linear sweep waveform only, and is essentially designed for cyclic voltammetry. No pulsed waveforms are available. Since the signal feeds into a mechanical chart recorder, high sweep rates (>200mV.s⁻¹) are not available, although a number of analogue-to-digital devices are available for signal digitisation. These instruments are widely used in research environments.
Bioanalytical Systems 100A Voltammetric Analyzer:

This is a software-driven instrument with digital excitation waveforms and data processing. As well as LSV, a large number of pulsed and differential waveforms are available. This instrument is considered state-of-the-art, and is widely used in electroanalytical research laboratories.

ElectroLab™:

This instrument was designed and developed at the University of Wollongong, and is the newest of the three instruments used. Like the BAS 100A it employs digital excitation waveforms and data processing. Although it does not possess the large number of default waveforms that the BAS 100A does, it possesses greater flexibility, and the ability to design customised excitation and current sampling programs.

Optical Imaging Systems:

Two microscope assemblies were used throughout this project:

Nikon Epiphot Inverted Metallurgical Microscope:

This instrument (fig 2.1) was used in conjunction with a purpose-built electrochemical cell for dynamic studies at the electrode surface. This was made possible by the fact that it was fitted with special long working distance objective lenses to provide high resolution images of electrode surfaces under water.

These images were displayed on a TV monitor via a Charge Coupled Device (CCD) TV camera, and were stored digitally using an Imaging Technology PC Vision frame grabber. The apparatus also provided a permanent record of data by storing the images from the monitor on a VHS video tape, or still photographs on 35mm film taken directly from the microscope image. Both the video recorder and the 35mm camera were used throughout this study, and although most of the images presented are from the 35mm camera, dynamic phenomena which were observed with the former device are discussed where appropriate.
Figure 2.1: Schematic diagram of Nikon Epiphor Inverted Metallurgical Microscope and electrochemical cell. Cell employs a Pt sheet and Ag/AgCl reference electrode with Luggin capillary.

*Leitz Orthoplan Geological MPV2 Microscope:*

This microscope was a conventional arrangement (not inverted) and was used for quantitative estimations of mercury drop sizes and electrode surface coverage. The mercury films were grown in the Metrohm electrochemical cell, and the working electrode was subsequently removed (ensuring that the surface remained covered with a film of water) and placed on the microscope stage. The photographs were taken with a film of water sandwiched between the lens and the electrode surface.

**2.2.3. SOLUTIONS:**

*Electrolyte solutions:*

NaNO₃ solutions were made from A.R. grade salts and were used without further purification.

The 0.2M acetate buffer used throughout this project was prepared by adding 3 parts by volume of 0.20M acetic acid to 7 parts by volume of 0.20M
sodium acetate, such that the resulting solution had a pH of 5.00. All reagents used were A.R. grade and the water was Milli-Q type 1 grade.

**Metal standards:**

Pb(NO₃)₂, Cd(CH₃COO)₂·2H₂O, and Cu(CH₃COO)₂·H₂O (ex BDH) were used for the lead, cadmium and copper standards respectively. All standards solutions were modified with 1% HNO₃ and stored in high-density polyethylene (HDPE) bottles. All reagents used were A.R. grade and were used without further purification. Water was Milli-Q type 1 grade.

**Mercury Plating Solutions:**

Mercury plating solutions of concentrations of 10 ppm Hg²⁺, 100 ppm Hg²⁺, and 1000 ppm Hg²⁺ were made by solubilisation of A.R. grade HgO (ex BDH) in a minimum volume of conc. acetic acid, and subsequent dilution to pH 5.00 with the acetate buffer.

**2.2.4. ELECTROCHEMICAL CELLS AND GLASSWARE**

The cell employed in conjunction with either of the rotating electrode assemblies was a standard Metrohm electrochemical cell. 20.00mL was used as the nominal solution volume throughout.

The cell assembly for the stationary electrode work was made in the laboratory, and consisted of a magnetic stirrer with stepwise speed settings, and an electrode and cell holder assembly as depicted in figure 2.2. 10.00 mL was the nominal solution volume used throughout.
2.2.5. EXPERIMENTAL PROCEDURES

Electrode Pretreatment:

The pretreatment procedure employed for all the GC electrodes used consisted of the removal of the visible Hg film (if present) with Whatman #542 filter paper, followed by polishing for 10s on a LECO flocked twill polishing pad with .05μ alumina slurry, and ultrasonication for 30s.

Selection of Excitation Waveform:

The waveform that was used for the majority of work throughout this project was, ostensibly, Linear Sweep Voltammetry (LSV). The LSV waveforms of the BAS100A, CV 27 and ElectroLab™ are compared subsequently. There are three reasons for choosing LSV as the waveform to be employed throughout this project:

i. LSV is fast, when employed at high sweep rates, and produces results quickly. This is an obvious advantage when doing multiple determinations.

ii. LSV is a simple waveform. If ASV is going to find its way into the marketplace, it must do so at a competitive instrumental cost. Clearly, the
more simple the waveform employed, the more simple are the electronics required, and therefore the cheaper the instrument. This project was therefore directed at developing an electrode which performed under these conditions.

iii. LSV provides adequate sensitivity when used with an MTTE at high scan rates. High scan rates are rendered feasible due to the small volume of mercury employed and the concomitantly small size of the droplets, the latter having the effect of rendering diffusional processes in the mercury negligible.

It has yet to be demonstrated that there exists a pulsed waveform which can compete with LSV at an MTTE, on the basis of limit of detection, under these conditions (this is not the case with the HMDE or the SMDE). Further consideration is given to the possibility of very high LSV sweep rates at the MTTE in chapter 4.

For those voltammograms run on the BAS CV 27, the waveform is true linear sweep, as it is an analogue instrument. For the ElectroLab™ and the BAS 100A, however, the situation is a little more complex, as these are both digital instruments, and the waveform can only ever approximate a true analogue ramp.

In reality, these instruments use Staircase Voltammetry (StV). This waveform has received some attention in the literature [263-266], with Osteryoung et. al devoting some attention to comparing the analogue and digital waveforms [264,266,267]. As a result of these studies they suggest that for StV to best approximate LSV the current should be sampled at 0.75τ, where τ is the period of the potential step.

The designers of the BAS100A seem to give this very little credence, as the programmed LSV waveform for this instrument follows the following scheme [268]:

"The potential waveform generator creates 0.1 mV steps. We sample the current every mV (until we reach 17000 mV/s where we sample less often due to speed limitations of the A/D). At scan rates less than 500mV/s, on every tenth step the current is sampled 16 times in a 1 ms period and the 16 points are averaged. At scan rates greater than 500mV/s, the current is sampled instantaneously (sampling time less than 1 ms) on every tenth step. I don't know the precise point on the waveform when the current is sampled. Since the step is so small, I don't think there is any observable difference between LSV obtained with the 100A and that with an analog waveform generator."
The ElectroLab™ used a more conventional approach, with a minimum \( \tau \) of 2 ms., and the current being sampled at 0.25\( \tau \) for a period of 250 \( \mu \)s. While this is also at odds with the theory of Osteryoung et. al. [266], studies revealed that it made little, if any, difference[81], and a close approximation to the analogue waveform was achieved.

The minimum step width of 2 ms determined the effective upper limit of \( v \) for the ElectroLab™, as a potential scan of 1000 mV at a sweep rate of 1000 mV.s\(^{-1}\) resulted in a voltammogram comprising 500 data points. While this number of points could be considered adequate, it is clear that sweep rates much greater than this could produce voltammograms with poor resolution. As a consequence of this, the standard sweep rate employed throughout this project was 1000 mV.s\(^{-1}\) despite the fact that the modified electrode system will perform adequately at sweep rates well above this (sect. 4.4.3).

**Voltammetric Parameters:**

All ASV determinations were performed with \( E_{dep} = -1000 \text{ mV}, \ t_{dep} = 60 \text{s} \), with a cleaning step of 5s at the upper potential limit (200 - 400 mV). The magnetic stirring flea (12 x 4.5mm) was set at the maximum rate of 500 rpm (stationary electrode) and \( \Theta \) was set at 3000 rpm (RDE) Stirring was carried out during the deposition and cleaning steps, but not during the stripping step. A rest period of 2s during which the stirrer (or RDE) was shut off, was employed between the deposition and stripping steps. Sweep rate for all ASV determinations was 1000 mV/s, with \( \Delta E \) (step height of staircase waveform) set at 2mV, and \( \tau \) (period of step) set at 2 ms.

**Mercury Plating Parameters:**

Mercury deposition times of 1, 5 and 10 minutes at -1000 mV were employed. Subsequent to deposition, the film was stripped to 200 mV and cleaned for 5s to remove any codeposited metals in the film. After this, the electrode holder, containing all electrodes, was raised from solution and the electrodes rinsed with water. A drop of water was kept covering the mercury electrode at all times. The solution was then replaced by the analyte solution.
Deoxygenation:

Deoxygenated and nondeoxygenated solutions were examined for the mercury plating step. All ASV determinations were carried out in deoxygenated solutions. Where employed, deoxygenated consisted of bubbling "high purity" nitrogen (ex CIG, Australia) through the solution for six minutes. When checked against blank solutions, it transpired that the level of contaminants introduced into the solution by this process was negligible.

Experimental Procedure (stationary electrode):

All permutations of deoxygenation or otherwise of plating solution, the concentration ranges of mercury plating solution and mercury deposition times were studied. All analyte solutions were deoxygenated prior to determination. Owing to the intrinsic lack of reproducibility of a stationary electrode with a stirrer as compared to an RDE, the following precautions were taken:

1. The cell holder was machined such that the electrodes were fixed in exactly the same position, both laterally and vertically.

2. Two cells were used only; one for all mercury plating, and one for all stripping. Each cell had a dedicated stirring flea which was not changed throughout.

3. Each determination was carried out at least in triplicate, and until triply reproducible results (within 5%) were achieved.

Experimental Procedure (RDE):

All permutations of deoxygenation or otherwise of plating solution, the concentration ranges of mercury plating solution and mercury deposition times were studied. All analyte solutions were deoxygenated prior to determination. The film was deposited for the appropriate time with the electrode rotating at 3000 rpm, followed by a stripping sweep to 200 mV to bring about any morphological conditioning which may be the cause of irreproducible stripping behaviour on the first ASV sweep of a newly grown film [24].
The electrode tip was then removed from the electrode assembly, ensuring that a drop of water remained on the surface of the electrode, and clamped onto the microscope stand such that the drop of water formed a film between the surface of the electrode and a microscope slide placed on the stand. The gap between the electrode surface and the microscope slide was typically about 1 mm. Throughout this procedure, the surface of the electrode was at no stage exposed to air.
2.3. RESULTS AND DISCUSSION

2.3.1. GLASSY CARBON CHARACTERISATION

The myriad of pretreatments suggested in the literature for glassy carbon substrates of, no doubt, varying compositions and electroactivities, forms the basis for Kramer et. al's suggestion [151] that the electrodes should be individually characterised and optimised for each individual experimental system. This procedure was employed for these studies.

2.3.1.1. Pretreatment Procedures

The specific pretreatment that is of concern with this study is that which will best prepare the electrode surface to act as a substrate for a mercury film. In particular, it is of interest to consider the pretreatment required (including removal of a previous mercury film) to ensure reproducible mercury films on a given electrode.

The fact that the surface of the glassy carbon electrode should be mechanically smooth prior to growth of a mercury film is universally acknowledged (although the author has yet to find a published reason for this) and a number of mechanical polishing procedures have been reported (chapter 1), typically involving the use of diamond laps and/or alumina.

Once in its pristine state, however, and assuming that the electrode is to be used for MTFEs the literature is strangely silent with respect to how the electrode should be maintained in this state between films, or how the mercury film is to be removed prior to the plating of a new film, although for other applications a significant number of excellent reviews have been published (chapter 1).

Most authors make no mention of how they remove their mercury films and maintain their electrodes. Those that do have suggested that the film be removed by tissue [192,269], filter paper [24], or alumina [193], with one author even suggesting that the electrode may be polished "too well" [13].
The first of these approaches (tissue) was not examined, as, since some tissues contain surfactants, it is a probable source of electrode fouling [206]. As well as this, tissues are not designed for laboratory use, and one could reasonably expect significant inhomogeneities of composition between different brands or types.

At a macroscopic level, there is no obvious difference between filter paper and alumina treatments, as mercury films grown after either treatment will yield a visibly uniform grey film. These studies, however, revealed a significant difference at the microscopic level.

Figure 2.3 shows the surface of an MTFE after the previous mercury film had been removed by wiping with a Whatman 541 filter paper for a few seconds.

![Figure 2.3: Optical micrograph of a MTFE-coated glassy carbon electrode which had the previous film removed by wiping the electrode with a Whatman 541 filter paper. Film as shown was grown from a 100ppm Hg²⁺ solution for 3 minutes at a stationary electrode. The grey material is the mercury and the black background is the glassy carbon. Scale: 1 cm = 100 μm.](image)

The streaky nature of the growth suggests that the redeposited mercury has preferentially grown onto residual mercury microdroplets remaining behind after the removal of the previous film with the filter paper. If however, the electrode was rubbed with the filter paper (circular motion) for a longer
period of time (1 minute), homogeneous film growth resulted during the subsequent electrodeposition.

It may be seen from this that while filter paper will remove a mercury film from a glassy carbon substrate [24], it requires a substantial amount of polishing before this is achieved.

This is an important finding, as a single wipe of a GC/MTFE with a filter paper will remove all mercury that is visible to the naked eye, and in the absence of the data here presented, one may conclude that efficient removal had been achieved. Indeed, the film presented in figure 2.3 appeared, to the naked eye, to be uniform, and provided no indication of the inhomogeneity present at the microscopic level.

This finding is hardly surprising, given that the mercury removal procedure is dependent on the mechanical dislodgement of individual drops brought about by two flat surfaces coming into contact with each other, and no specific chemical or physical interaction (adsorption or absorption) could be expected between the mercury and the filter paper.

The effect of polishing with alumina (followed by ultrasonication) was to produce an even, uniform film with none of the defects present in figure 2.3 (sect. 2.2.3.2).

The reason for the increased efficiency of removal of the mercury and therefore uniformity of the subsequent film, arises from the greater abrasive properties of the alumina, which actually removes part of the surface of the carbon electrode [270-273].

This becomes clear if figure 2.4 is examined. After repeated voltammetric cycling in a blank solution (>100 cycles), the electrode exhibited a rather sluggish redox couple with $\Delta E_p = 350 \text{mV}$ and $b_{1/2}$ values which were greater than $300 \text{mV}$ (fig 2.4 - dashed line). When the electrode was removed from solution and polished on both moistened and dry filter papers, no change was observed in the redox couple, but when it was polished with alumina/flocked twill, the responses were seen to diminish greatly in magnitude (fig 2.4 - solid line).

The exact nature of the surface group responsible for the observed redox couple is unclear, although given that functionalities such as carboxyls [274,275], quinones/hydroquinones [276,277], phenols [278,279], peroxides [280]
and others [281] have been reported, it is not difficult to envisage, with the repeated cycling, one of these groups exhibiting a redox couple.

\[ E \text{ (V vs Ag/AgCl)} \]

**Figure 2.4:** GC electrode before (shaded line) and after (solid line) polishing with alumina. Electrode cycled in deoxygenated 0.2 M acetate buffer (pH 5.0).

The salient point is, however, that whatever the functional group responsible for the responses, the alumina treatment has effectually removed it, and returned the electrode to its pristine state.

The superiority of regular maintenance with alumina over filter paper reported in this work is consistent with the conclusions of Hu *et al.* [282], Kamau [76,90] and Rusling [283], who conclude that degradation of the electrode surface occurs with the passage of time, by either oxidation of the surface or the adsorption of impurities, and that electrode activity is restored by polishing with alumina. Kamau [191], reported reproducible electrode reactivity over a seven month period using this procedure.

As a consequence of these studies, therefore, the glassy carbon electrodes used throughout these studies were polished with alumina on a routine basis between experiments. This procedure was necessary even in the absence of a deposit on the electrode surface, as it has been shown that degradation of glassy carbon electroactivity occurs by storage in air, solution, or nitrogen-soaked electrolyte [90].
2.3.1.2. Voltammetric background

Given the inhomogeneity of glassy carbon, each of the three glassy carbon electrodes used was characterised with respect to background current. No specific attempt was made to assess electroactivity by the reporting of hexacyanoferrate (II/III) heterogeneous transfer coefficients [284,285], as this does not necessarily bear any relation to the electroactivity of a subsequently-coated mercury film.

The parameter that is of major concern with MTFEs that are used in conjunction with LSV is the slope of the background current which is recorded during the stripping voltammogram, as it affects the signal-to-noise ratio and, as a consequence, the sensitivity and limit of detection of the electrode.

The background current of each glassy carbon electrode was assessed as the slope of the voltammogram produced by an LSV scan from -1000 to 0 mV in a blank NaN03 (pH 6.0) solution and both acetate (pH 5.0) and borate (pH 8.0) buffers. Since the voltammograms often had steeply sloping sections at either end (fig. 2.7), the linear section from -700 to -200mV was used to measure the slope of the voltammogram. Each value is the average of five determinations and is expressed in units of µA.V⁻¹. Results are presented below in tabular form:

Table 2.1: Slope of voltammograms recorded in blank solutions for BAS electrode #1. All values expressed in µA.V⁻¹. Each data point is an average of five determinations. Voltammograms recorded between -1000mV and 0mV; slope measured between -700mV and -200mV.

<table>
<thead>
<tr>
<th>Electrode 1:</th>
<th>Sweep Rate (mV.s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0.1M borax</td>
<td>0.17</td>
</tr>
<tr>
<td>0.1M NaN03</td>
<td>0.28</td>
</tr>
<tr>
<td>1.0M NaN03</td>
<td>0.24</td>
</tr>
<tr>
<td>0.2M Ac/HAc</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Table 2.2: Slope of voltammograms recorded in blank solutions for BAS electrode #2. All values expressed in μA.V⁻¹. Each data point is an average of five determinations. Voltammograms recorded between -1000mV and 0mV; slope measured between -700mV and -200mV.

<table>
<thead>
<tr>
<th>Electrode 2:</th>
<th>Sweep Rate (mV.s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0.1M borax</td>
<td>0.63</td>
</tr>
<tr>
<td>0.1M NaNO₃</td>
<td>0.62</td>
</tr>
<tr>
<td>1.0M NaNO₃</td>
<td>0.27</td>
</tr>
<tr>
<td>0.2M Ac/HAc</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Table 2.3: Slope of voltammograms recorded in blank solutions for BAS electrode #3. All values expressed in μA.V⁻¹. Each data point is an average of five determinations. Voltammograms recorded between -1000mV and 0mV; slope measured between -700mV and -200mV.

<table>
<thead>
<tr>
<th>Electrode 3:</th>
<th>Sweep Rate (mV.s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0.1M borax</td>
<td>2.1</td>
</tr>
<tr>
<td>0.1M NaNO₃</td>
<td>2.5</td>
</tr>
<tr>
<td>1.0M NaNO₃</td>
<td>1.9</td>
</tr>
<tr>
<td>0.2M Ac/HAc</td>
<td>2.6</td>
</tr>
</tbody>
</table>

From these tables it is clear that electrode #1 has the lowest overall background slope, as this is the case with each of the electrolyte solutions examined, with electrode #3 having the highest overall background currents.
Although the behaviour of electrodes 1 and 2 did not vary significantly with the electrolyte used, it is interesting to note that that of electrode #3 did, with significantly lower background currents observed with the acetate electrolyte.

The fact that the presence of a different electrolyte had such a dramatic effect on the background, and the presence of significant inter-electrode variability, clearly illustrates the inhomogeneity of three ostensibly identical electrodes, all of which have had the same mechanical pretreatment. Specifically, it suggests differing surface functionalities, as both the Faradaic and non-Faradaic background will be altered by variations in this regime.

The Faradaic contribution arises from inter-electrode variations in the overpotential for hydrogen reduction, although this was only a contributor for electrode #3 (fig. 2.5), where a residual current from this process was still evident at -700mV.

The non-Faradaic background is the charging current, and the reason for the differing properties of these three electrodes may be appreciated if the expression for the charging current generated at an electrode surface under the influence of a ramping potential is considered.

![Graph showing linear sweep voltammograms of electrode #1 (shaded line) and electrode #3 (solid line) in 0.1M NaNO3.](image)

**Figure 2.5.** Linear sweep voltammograms of electrode #1 (shaded line) and electrode #3 (solid line) in 0.1M NaNO3.
This expression assumes that the electrode interface consists of a monolayer of adsorbed ions which acts as a capacitor when a potential is applied at the electrode surface.

The expression is given by equation 2.1 [287]:

$$i_c = \nu C_d + \left[ \left( \frac{E_i}{R_s} - \nu C_d \right) \exp \left( \frac{-t}{R_s C_d} \right) \right]$$

where

$\nu$ = sweep rate

$i_c$ = charging current

$C_d$ = capacitance of double layer

$E_i$ = potential step

$R_s$ = solution resistance

$t$ = time

The first part of this expression ($\nu C_d$) refers to the contribution of the potential ramp to the charging current, whereas the remainder of the expression refers to the charging current produced upon the initial application of the potential (this current quickly decays to zero).

From this it may be seen that, provided the value of $C_d$ remains constant, so too will the current. On a voltammogram this would manifest as a flat (but finite) background (fig. 2.6).

The fact that this behaviour is seldom seen on voltammograms makes it clear that the model of an ideal capacitor is inadequate. This is not unreasonable, since one of the plates (of the capacitor) in this model is composed of adsorbed ions, which could reasonably be expected to move under the strong electric field induced at the charging interface. This would bring about a concomitant change in the value of $C_d$ and therefore produce the sloping backgrounds observed on these and other voltammograms.
The obvious corollary to this is that if the surfaces of the electrodes were either morphologically different, or composed of different types (or surface densities) of functional groups, the mobility of the adsorbed ions would be affected, thereby inducing differently shaped background (charging) currents.

From these data it seems that electrode #1 is the most desirable of the three, as it possesses the dual properties of low background current and high overpotential for hydrogen evolution. Consequently, except where noted, it was used for all stationary electrode work.

2.3.1.3. Potential Window

Throughout the course of this project, the glassy carbon electrode was to be polarised at potentials ranging from -1000mV (ASV [vs Ag/AgCl]) to 2000mV (polymerisation [vs Ag/Ag^+]), and as a consequence, the potential range over which these particular electrodes were stable was a factor which required investigation.

Along with aspects of the glassy carbon electrode such as mechanical and electrochemical pretreatment, the factors which cause its performance to break down at extreme potentials have not been investigated in detail. For most workers, the potential windows in which experimentation is carried out is well within the range in which the glassy carbon is known to be stable, and so this topic receives little attention. The history of the study of the potential window of glassy carbon is reviewed in chapter 1.
The subsequent study focuses on the positive potential limit of the electrode. This study is required to assist in the characterisation of the subsequent polymer coating, since it is generated at high potentials (2000 mV vs Ag/Ag⁺) and any moisture present in the (methanolic) solvent (typically about 0.1%) from which the polymer is grown (sect. 3.2) will be electroactive in this region. In particular, the identification of any incorporated species will be rendered possible by identification of aqueous redox processes in this regime.

These studies also provide a basis for the physical characterisation of the polymer coating (chapter 3) with respect to the accessibility of solvent molecules to the electroactive glassy carbon substrate.

The negative potential limit of the electrode is of trivial significance as, at no stage throughout the project, was -1.0V exceeded, at which point hydrogen evolution is not excessive and, in any case, the electrode suffers no degradation as it does with the oxidative process.

Studies were carried out in acetate solution (since that is the matrix that was used for the ASV determinations) and NaN₃.

**Acetate Solution:**

When set at an upper potential limit of 1800mV, the electrode, after about ten cycles in the deoxygenated acetate buffer solution settled down to a stable background response as shown in figure 2.7.

The tailing offscale at the positive end corresponds to oxygen evolution as suggested by Gunasingham [78]. The electrode, upon visual examination, showed no signs of any degradation, and retained its smooth, mirror-like appearance.

Upon cycling out to 2000mV, however, a dramatic change occurred in the voltammetric response, with a number of oxidation and reduction peaks occurring (fig. 2.8).
**Figure 2.7**: Cyclic voltammogram of GC electrode in 0.2M acetate buffer (pH 5.0). Three successive cycles shown.

**Figure 2.8**: Cyclic voltammogram of GC electrode in 0.2M acetate buffer (pH 5.0). Cycles 1, 2, 4, 9, 23, 41, 61, 92, 111, 142 shown.
With subsequent cycling to 1800 mV, the second cathodic peak at -210 mV was replaced by a single, large peak at the potential of the initial peak, which was stable to 10 repeated cycles, whereas the anodic peak at 1500 mV gradually diminished over this period (fig. 2.9).

**Figure 2.9:** As for fig. 2.8 after the upper E limit had been reduced to 1800mV. Shaded responses are reproduced from fig. 2.8 and represent (a) the initial peak produced upon cycling to 2000mV and (b) the peak produced upon multiple cycling to 2000 mV.

Inspection of the electrode after these cycles revealed the presence of a uniform, dull, blue film, which could not be removed by mechanical polishing on a moistened, Whatman #542 filter paper. Vigorous and prolonged polishing (2-3 mins) with .05μ alumina resulted in some degree of electrode restoration, with smooth, shiny regions being interspersed with a series of apparently deep scratches.

The origin of these scratches probably arises from hard, graphitic oxide [288] degradation products which were dislodged by the polishing process. In any case, these electrodes required complete polishing with the 6, 3 and 1μ polishing pads as described previously (sect. 2.2.4) to restore the smooth finish.
The reproducible reduction response observed for the degraded surface is not surprising, since Dodson and Jennings [288] have reported that “the oxidised surface of the vitreous (glassy) carbon is no longer inert.”

The salient point to come from this is that even though the electrode was clearly in a degraded state after cycling to 2000 mV, it remained voltammetrically stable when the upper limit was once again set at 1800 mV. Further, it is clear that the degradation experienced at 2000 mV may be directly attributed in some way, to the evolution of oxygen, since,

1. the potential of a glassy carbon electrode may be extended well beyond this region, without degradation, by the use of nonaqueous solvents [71],

2. oxygen evolution is the degradation mechanism that is reported by Dodson and Jennings [288], and

3. the evolution of oxygen was clearly responsible for the very large currents at 2000 mV.

**NaNO₃ solution:**

The degradation process in nitrate solution was qualitatively the same as that which was observed for the acetate solution, with the electrode exhibiting voltammetric stability up to 1800 mV (fig. 2.10), beyond which degradation occurred.

These data, then, concur with that of Gunasingham and Fleet [78], in suggesting an aqueous upper potential limit of 1800 mV for the glassy carbon electrode. Although Gunasingham and Fleet [78] use a SCE in their work, the difference (20 mV) between this and the Ag/AgCl reference electrode is considered negligible with respect to these conclusions.
2.3.1.4. Performance for ASV

"Given the ideal characteristics of mercury for trace metal analysis, solid electrodes are generally used only when there is no other alternative" - Wang [9].

Glassy carbon is generally not considered as a substrate for ASV of cadmium, lead, or copper and is only used for metals that oxidise at more positive potentials than mercury, such as silver, gold, or mercury itself (*vide infra*). In this context the study of glassy carbon as a substrate for ASV of cadmium, lead and copper was carried out purely to assess the background responses for these metals, as outlined in section 2.1.

Cadmium, lead and copper were individually examined, as well as all three together to identify and characterise any intermetallic effects that may have occurred. Results for the three metals are considered, initially, individually, and subsequent to this, collectively. The concentration range studied was 20 ppb to 1000 ppb.
Cadmium:

The most notable feature of this study was a sharp tailing of the response at the negative end of the voltammogram, which commenced with the first addition (20 ppb) of Cd\(^{2+}\) (fig 2.11 - shaded line). This response contrasted sharply with the electrolyte background response (fig 2.11 - solid line).

At higher concentrations (>150 ppb) a small oxidation peak appeared (fig 2.12) at -650 mV, and this response yielded the calibration curve shown in figure 2.15.

![Graph showing ASV responses before and after addition of Cd\(^{2+}\) to acetate buffer electrolyte.](image_url)

**Figure 2.11:** ASV responses before (solid line) and after (shaded line) addition of 20 ppb Cd\(^{2+}\) to acetate buffer electrolyte.
Lead:

The stripping response for lead was quite well defined with values for $b_{1/2}$ of about 60-70 mV (fig 2.13). As well as the well-defined response, there was none of the tailing of the response at negative potentials as was observed for cadmium. The calibration curve for this response is shown in figure 2.15.

Clearly, the kinetics of both the deposition and stripping of lead from glassy carbon are quite favourable, with no specific anomalies, double peaks or background effects manifesting. It cannot, however, compete with the GC-based MTFE (vide infra) for this application, as far as limit of detection, sensitivity and definition ($b_{1/2}$) of response are concerned (sect. 2.3.2). Also, the bare glassy carbon could be expected to suffer from problems with electrochemical reproducibility when used as an analytical substrate on a more routine basis.
Figure 2.13: ASV response of 250ppb Pb$^{2+}$ at GC electrode in acetate buffer (pH 5.0).

Copper:

Deposition was carried out at -500mV to circumvent the possibility of cadmium codeposition and intermetallic interference. Up until the electrode became saturated, at 200ppb, the copper stripping response was the most sensitive of the three metals studied (180µA/ppm for Cu$^{2+}$ vs 102µA/ppb for Pb$^{2+}$ and 28µA/ppm for Cd$^{2+}$). A calibration curve for all three metals is shown in figure 2.15.

The stripping peak was rather broad ($b_{1/2} = 100$ mV), although it remained symmetrical and yielded a linear response up until its saturation point, beyond which it developed a shoulder and ceased to increase in magnitude (fig. 2.14). A $b_{1/2}$ of 100mV would be expected if the copper was being stripped into a chloride medium, but since the medium in this case is acetate, it can only be due to the unfavourable kinetics associated with stripping from the solid substrate.
The saturation phenomenon (and further broadening of the peak) is no doubt due to the formation of multiple layers of copper on the electrode surface [289-291].

![Graph](image)

**Figure 2.14:** ASV response for GC electrode in 200ppb (shaded line) and 600ppb (solid line) Cu$^{2+}$ solutions. $E_{dep} = -1000\text{mV}$, $t_{dep} = 60s$. $v = 1000\text{mv.s}^{-1}$.

![Graph](image)

**Figure 2.15:** Calibration curves for Cu$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$ when stripped from a glassy carbon electrode in 0.2M acetate buffer (pH = 5.0).
Multielement Deposition:

When simultaneous additions of Cd\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) were made to the acetate buffer, two features were evident in the subsequent stripping responses. The first of these was the tailing at the negative end of the potential scale which was due to the stripping of the cadmium (fig. 2.16).

The second feature of note was that despite the presence of all three metals, the only one that manifested a tangible stripping response was copper, with the lead response being nothing more than a small, broad hump (fig. 2.16).

The salient feature of this voltammogram is the magnitude of the copper response in figure 2.16. It did not plateau as it did when it was the only metal present (fig. 2.15), but continued to increase. When compared directly with the response due to the single metal (fig. 2.17), it became apparent that the two responses were comparable up to about the saturation point of the latter.

![Figure 2.16: Stripping response for 250 ppb Cd\(^{2+}\), Pb\(^{2+}\),Cu\(^{2+}\) in acetate buffer (pH 5.0)](image)

While the electrodeposited cadmium could be expected to co-strip with the copper [292], this factor alone does not account for the magnitude of
the response, even if one assumes that the lead is also co-stripping with the copper.

![Graph showing calibration curves for ASV of Cu²⁺ at a glassy carbon electrode in the presence and absence of Cd²⁺ and Pb²⁺.](image)

**Figure 2.17:** Comparison of calibration curves for ASV of Cu²⁺ at a glassy carbon electrode in the presence and absence of Cd²⁺ and Pb²⁺.

This may be seen if the magnitude of the copper stripping response is compared with the additive stripping responses for each of Cd²⁺, Pb²⁺, and Cu²⁺ (fig. 2.18). The fact that the copper response does not saturate in the presence of the other two metals, and that the response is greater than that of the three metals combined, suggests that the microstructures formed on the electrode surface when all three metals are present are more amenable to the stripping process.

This is further supported by the observation that the copper stripping response under these circumstances (fig. 2.16) exhibits none of the tailing at the positive end of the stripping peaks which was observed in figure 2.14.

The complete absence of a mercury film has the obvious result of producing surface intermetallic formation of the most gross form. In particular, the intermetallic that forms between cadmium and copper is well documented [9,293-296], the observable effects being suppression of the cadmium signal and enhancement of the copper signal, and it is clear that these data show a striking and significant increase in the sensitivity of the copper response in the presence of the cadmium.
Figure 2.18: ASV response for Cu$^{2+}$ in the presence of Cd$^{2+}$ and Pb$^{2+}$ compared with the added response for each of these three metals when present alone.

It is interesting to note that, although there has never been a lead intermetallic reported, to the author's knowledge, for a mercury-based electrode, the absence of a tangible lead response in the presence of the cadmium and copper suggests such a phenomenon (possibly Cu/Pb - sect. 2.3.2.1), no doubt induced by the extreme conditions of no mercury being present.

2.3.2. CHARACTERISATION OF THE GC/MTFE

In order to attempt to draw a comparison between the conventional MTFE and the chemically-modified MTFE, the conventional MTFE was characterised with respect to

1. ASV performance, and

2. visual appearance (microscopic)

To target the first of these, a stationary electrode was used in preference to a rotating electrode. This was because it avoided the possibility of any mercury film degradation effects brought about by the electrode rotation, and
produced results which were ostensibly a direct function of the mass ("thickness") of the film.

A rotating electrode was used to characterise the film visually, as this enabled a direct qualitative measure to be made of the mechanical stability of the film.

Each aspect is examined in turn.

2.3.2.1. Stationary Electrode studies: ASV Performance

The rationale behind the selection of cadmium, lead and copper as tools to assist in the characterisation of the MTFE becomes clear if the interaction of these metals with mercury is considered.

Electrochemically deposited metallic films on electrode surfaces comprising two or more metals may be classified into four groups. Neiman [295] summarises them as follows:-

"First, there are systems where components do not interact on the electrode surface at all; elements forming binary and more complex systems of this type comprise d-elements of Group II of the Periodic Table (Zn, Cd, Hg), p-elements of Groups III and IV (In, Tl, Sn, Pb) and bismuth, electrodeposited in various combinations on carbonaceous electrodes.

Secondly, there are systems where components interact to form solid solutions during the electrolysis; among the elements forming deposits of this type, there are the d-elements of Group I of the Periodic System (Cu, Ag, Au) deposited with each other and also with Pb, Tl or Hg (metals of period VI).

Thirdly, there are systems where components form intermetallic or chemical compounds during the electrolysis stage so that the stripping currents cannot serve as analytical signals in ASV. Systems of this group can be formed by simultaneous electrodeposition of d-elements of Group I with p-elements of Group II (Zn, Cd), p-elements of Groups III (Ga, In) and IV (Ge, Sn) and also with metals of the iron subgroup.

In the fourth type, components forming binary systems interact during electrolysis to produce electrochemically active compounds, the stripping currents of which in the working potential range of the electrode can serve as analytical signals in ASV. Binary systems of this group are produced by simultaneous electrodeposition of As, Se, Te and metals of the platinum subgroup with metals such as Pb, Sn, Hg, Cd, Au, Ag and Cu."
From this it may be seen that cadmium and lead belong to group one, and no unfavourable effects are to be expected as a result of either of these electrodes being deposited into a mercury film.

Copper, however, belongs to group two and clearly interacts with the mercury in a different and more profound manner than do the lead and cadmium. Interestingly, copper also forms a "solid solution" with lead, although, as no unfavourable copper/lead interactions for ASV have been reported, it is reasonable to assume that the effect with the mercury is far greater, either intrinsically or as a result of the greater amount of mercury present with an MTFE. This does, however, explain the codeposition of these two metals (Cu and Pb) which was observed in section 2.3.1.4.

The interaction of copper with both cadmium and zinc as described in the third grouping, accounts for the well documented zinc/copper and cadmium/copper intermetallic interferences in ASV [170,293,294,297,298].

Since cadmium, lead and copper, have very different properties with respect to their interaction with mercury, therefore, it is reasonable to expect that optimum mercury film parameters with respect to sensitivity and definition of stripping peaks (kinetics of oxidation process) are different for each of the three metals. The most obvious difference between the three metals is their solubility in mercury, with the cadmium and lead (5.0 and 1.2% solubility by weight respectively) being far more soluble than copper (1 $\times$ 10$^{-3}$ % by weight [9]).

Further to this, the type of "solubility" varies, although again it is cadmium and lead which differ significantly from copper [295,299]. A study, however, of the relative ASV responses of these three metals as mercury film parameters are varied has never been carried out, and such is the purpose of this study, both for this reason above, and to enable the author to characterise the ASV performance, with respect to comparative mercury film parameters of the chemically modified MTFE presented in chapter 3.

The parameters examined were:

1. Effect of deoxygenation of the mercury plating solution,
2. Influence of concentration of mercury in plating solution, and
3. Dependence of mercury film plating time.

All permutations of the above three variables were examined. The comparison consists of the analysis of a 10 ppb solution of Cd\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\), with the performance being evaluated with respect to the magnitude and/or shape of the stripping response, as well as any substrate effects.

The deoxygenation of the mercury plating solution is of particular interest as it has never been the subject of a specific study, with deoxygenation of mercury plating solutions being *de rigeur* for ASV. Clearly, if deoxygenation of the plating solution is not required, the analytical procedure is simplified somewhat.

Stripping currents are presented in tabular form (tables 2.4–2.6), and are grouped according to the concentration of the mercury plating solution. Key results are discussed subsequently, along with representative voltammograms.

**Table 2.4:** Stripping currents for films grown from 10 ppm Hg\(^{2+}\). All currents are in μA and represent the averaged value from triplicate scans. The terms “deox” and “nondeox” refer to the mercury plating solution.

<table>
<thead>
<tr>
<th>plating time (min)</th>
<th>Cd nondeox</th>
<th>Cd deox</th>
<th>Pb nondeox</th>
<th>Pb deox</th>
<th>Cu nondeox</th>
<th>Cu deox</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>4.6</td>
<td>3.4</td>
<td>26.6</td>
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</tr>
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</tbody>
</table>
Table 2.5: Stripping currents for films grown from 100ppm Hg\textsuperscript{2+}. All currents are in µA and represent the averaged value from triplicate scans. The terms “deox” and “nondeox” refer to the mercury plating solution.

<table>
<thead>
<tr>
<th>plating time (min)</th>
<th>Cd</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>nondeox</td>
<td>deox</td>
<td>nondeox</td>
<td>deox</td>
</tr>
<tr>
<td>1</td>
<td>17.6</td>
<td>17.9</td>
<td>8.0</td>
</tr>
<tr>
<td>5</td>
<td>17.1</td>
<td>20.9</td>
<td>9.9</td>
</tr>
<tr>
<td>10</td>
<td>16.5</td>
<td>4.3</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 2.6 Stripping currents for films grown from 1000ppm Hg\textsuperscript{2+}. All currents are in µA and represent the averaged value from triplicate scans. The terms “deox” and “nondeox” refer to the mercury plating solution.

<table>
<thead>
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</thead>
<tbody>
<tr>
<td>nondeox</td>
<td>deox</td>
<td>nondeox</td>
<td>deox</td>
</tr>
<tr>
<td>1</td>
<td>4.3</td>
<td>3.7</td>
<td>2.3</td>
</tr>
<tr>
<td>5</td>
<td>4.1</td>
<td>3.4</td>
<td>2.2</td>
</tr>
<tr>
<td>10</td>
<td>4.2</td>
<td>3.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

2.3.2.1.1. Effect of Deoxygenation

Deoxygenation is routinely carried out on both the mercury plating solution and the analyte solution for most electrochemical processes. There seems little point in "reinventing the wheel" by examining the latter aspect as,
apart from the enhancement of lead responses reported by Batley [24] when ASV is performed in neutral or basic media, non-deoxygenation of the analyte solution is generally understood to produce deleterious effects as a result of sloping baselines and unfavourable metal hydroxide formation. [9].

The effect of deoxygenation on the mercury plating solution, however, did warrant investigation, as alluded to previously, and is examined subsequently.

Deoxygenation of aqueous solutions on which electroanalysis is to be performed in the negative potential region is standard procedure as, being present at up to $10^{-3} \text{M}$ at room temperature and pressure, it undergoes reduction in acidic media as follows:

\begin{align*}
\text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow \text{H}_2\text{O}_2 \quad \text{eq. 2.2} \\
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow 2\text{H}_2\text{O} \quad \text{eq. 2.3}
\end{align*}

and in neutral or basic media as

\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 2e^- & \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \quad \text{eq. 2.4} \\
\text{H}_2\text{O}_2 + 2e^- & \rightarrow 2\text{OH}^- \quad \text{eq. 2.5}
\end{align*}

These reactions result in, at the very least, an increased background current, as well as the possibility of the $\text{OH}^-$ or $\text{O}_2$ species causing either localised precipitation of metals in the vicinity of the electrode, or oxidation of metals from the amalgam respectively [9].

It is interesting, however, that despite the fact that none of these processes present a specific problem when depositing a mercury film for electroanalysis, the concept of using a non-deoxygenated mercury solution,
and the intrinsic time saving it represents has, with one exception [300], never been considered in the literature; this is despite the wide applicability that the MTFE has found in flowing systems [202,212,216,301,302], and the intrinsic inconvenience of deoxygenating under these conditions.

In the one case where a non-deoxygenated mercury solution has been used for plating a mercury film [303], it has been done purely for the sake of convenience, and no comment is made with respect to the effect that this is expected to have on the analytical response.

Despite the silence of the literature on this topic, it is interesting to note that the manufacturer of a commercially-available portable voltammetric analyser, the PDV 2000 (manufactured by Chemtronics Ltd. - Western Australia) recommends a mercury deposition procedure which does not include deoxygenation.

This approach concurs with the results of this study, which make it clear that, at least within the constraints of the chosen parameters, the mercury film grown from the non-deoxygenated mercury solution is of comparable quality to those grown from a deoxygenated solution (table 2.1) with, for the 10 ppm films, a slight enhancement of the lead response.

The most likely cause of the enhancement of the lead response (table 2.1) is the presence of hydroxide groups (either adsorbed onto, or absorbed into the mercury film) as a reduction product of dissolved oxygen during the mercury deposition step. This effect did not manifest, to any extent, for the more massive films (100 ppm and 1000 ppm), the likely explanation being that for the 10 ppm films, the ratio of hydroxide ions to mercury at the electrode surface would be greater during the deposition step, thus resulting in increasing adsorption or absorption.

While electrochemically-generated hydroxide is primarily a product of oxygen reduction only in neutral or basic media (eq. 2.4), it could be expected to make at least a partial contribution at pH 5.0. Electrochemically-generated hydroxide has been previously shown to result in an enhanced lead response [24].

Another likely contributor to the observed differences between the deoxygenated and non-deoxygenated film centres around the removal of mercury from the surface of the electrode as it plates. This is most likely due to the chemical oxidation of Hg⁰ to HgII by either the O₂ or H₂O₂. That this
accounts for the differences observed between the two film types becomes clear if the background responses of the voltammograms are examined.

Figures 2.19 and 2.20 show the comparative responses recorded for 1 minute deposition from a *10 and 100 ppm Hg films respectively, both with and without deoxygenation.

![Graph showing comparative responses](image)

Figure 2.19: ASV of 10ppb Cd\(^{2+}\), Pb\(^{2+}\), Cu\(^{2+}\) at a mercury film grown from de-oxygenated (shaded line) and non-deoxygenated (solid line) 10 ppm Hg\(^{2+}\) in acetate buffer (pH 5.0) for 60s.

The tailing of the background responses on the voltammograms (at negative potentials) in figures 2.18 and 2.19 is highly diagnostic in nature as it is indicative of cadmium depositing on the glassy carbon substrate (sect. 2.3.1.4).

This is supported by visual inspection of the MTFEs (sect. 2.3.2.3) which revealed, at best, a very pale smear of grey (mercury) against a black background, and hence the coverage, by the mercury, of only a small percentage of the substrate, with a large percentage of the glassy carbon

\* In the interest of brevity, a shortened format is used throughout this thesis to describe the growth conditions of the mercury films. For example a "deoxygenated 1 minute, 10 ppm Hg film" refers to a mercury film which was grown from a deoxygenated 10ppm mercury solution for a period of 1 minute. Also, for example, a "deoxygenated film" refers to a film grown from a deoxygenated mercury solution.
surface being available for the cathodic deposition of electroactive metals. Batley [24] has noted the propensity of cadmium to deposit onto exposed glassy carbon substrate with very thin MTFEs.

Further, the tailing effect is more pronounced for the deoxygenated 10 ppm Hg film (fig. 2.19) than for the deoxygenated 100 ppm Hg film (fig. 2.20), with no difference being observed between the 10 and 100 ppm non-deoxygenated films. This is reasonable since the 100 ppm Hg film may be expected to have a greater amount of mercury present on the surface.

This effect was seen, for the deoxygenated 10 ppm Hg films, with both the 5 minute and 10 minute films, although it diminished as the deposition time increased. For the 100 ppm Hg films, however, it was only observed for the 1 minute film (fig. 2.20), and was not evident for the 5 and 10 minute films, despite the fact that for these films a significant amount of glassy carbon substrate was still visible.

The presence of significant areas of exposed substrate (for the 100 ppm Hg films) with the absence of the characteristic substrate deposition effects (tailing of voltammogram) need not, however, be seen as a means of contradicting the explanation that has been advanced concerning substrate
effects (Cd deposition). This is because the amalgam-forming capability of mercury makes it a more favourable substrate for deposition of cadmium than the glassy carbon, and the cadmium will only deposit on the glassy carbon substrate when its solubility in the mercury has been exceeded, as may be reasonably expected to be the case for the 1 minute films.

With respect to this, Wang has observed "When the solubility of the metal in mercury is exceeded, a surface coating of a metal precipitate can be observed, resulting in drastic changes in the nature of the electrode, irreproducible results, and lower hydrogen overvoltage" [304].

No substrate deposition effects were observed for any of the 1000 ppm Hg films.

2.3.2.1.2. Film thickness

It is reasonable to expect that a mercury film grown for a longer period from a more concentrated mercury solution will be thicker than that grown for a shorter period from a more dilute mercury solution. Given the intrinsic inapplicability of the term “thickness” for a surface deposit consisting of a series of droplets, however, the films are henceforth considered in terms of the relative mass of mercury present on the electrode surface. The linearity or otherwise of this relationship with respect to the mass of mercury present and the actual thickness of the film, or the tendency of the film thickness to plateau after a period of time has, as outlined in section 1.1.2.4, never been examined.

Although this study falls short of quantitatively establishing such a relationship, some valuable qualitative relationships have been forthcoming. The most notable of these is that the film seems to consist of two discrete phases which are dependent on the amount of mercury present on the electrode.

The first phase, which manifested for all of the 10 ppm Hg films and for all of the 100 ppm Hg films (table 2.1), with the exception of the deoxygenated 10 minute, (100ppm) film, was highly sensitive, giving well formed stripping peaks for all of the metals examined, and showing variations in both the background current and size of the stripping peaks with variations in the film deposition conditions.
Figures 2.21 and 2.22 illustrate the effect of mercury deposition time for these films. Figure 2.21 shows the stripping responses obtained with films grown from 10 ppm Hg solutions, and figure 2.22 shows those obtained at films grown from 100 ppm Hg solutions, with in each case a 5 minute film being compared with a 10 minute film.

![Graph showing ASV of Cd²⁺, Pb²⁺, Cu²⁺ at a mercury film grown from a non-deoxygenated 10 ppm Hg²⁺ solution for 5 minutes (solid line) and 10 minutes (shaded line) in acetate buffer (pH 5.0).]

Figure 2.21: ASV of 10ppb Cd²⁺, Pb²⁺, Cu²⁺ at a mercury film grown from a non-deoxygenated 10 ppm Hg²⁺ solution for 5 minutes (solid line) and 10 minutes (shaded line) in acetate buffer (pH 5.0).

From these figures (and table 2.1) it may be seen that copper produces an enhanced response at less massive films, whereas cadmium and lead produce enhanced responses at the more massive films. It may also be seen that the magnitude of the variation with film deposition conditions is greater for copper than for lead and cadmium. That is, the increase in surface mercury brought about by the increased deposition time in figure 2.21 resulted in a diminution in the copper response, without a tangible change in either the cadmium or lead responses.

Conversely, for the films grown from the more concentrated solution (fig. 2.22), where the films could be assumed to be more massive, no difference in the copper response could be seen between the 5 and 10 minute films, where the magnitude of the response seems to have plateaued, whereas the cadmium and lead responses experienced the greatest relative variance in their
responses for the thicker (100ppm) films, although the relative variance was at no stage as great as that observed for the copper (fig. 2.21).

![Graph showing ASV of 10ppb Cd^{2+}, Pb^{2+}, Cu^{2+} at a mercury film grown from a deoxygenated 100 ppm Hg^{2+} solution for 5 minutes (solid line) and 10 minutes (shaded line) in acetate buffer (pH 5.0).]

**Figure 2.22:** ASV of 10ppb Cd^{2+}, Pb^{2+}, Cu^{2+} at a mercury film grown from a deoxygenated 100 ppm Hg^{2+} solution for 5 minutes (solid line) and 10 minutes (shaded line) in acetate buffer (pH 5.0).

The reasons for the observed dependencies on the mercury film parameters for each of the three metals are considered in turn.

**Copper:**

The fact that the copper response essentially showed an inverse dependence on film thickness with respect to sensitivity may be explained in terms of its interaction with mercury. Since copper forms a "solid solution" [295] with the mercury, its concentration in the mercury would be expected to decrease as the film thickness increased. The exception was the 1 minute 10 ppm Hg film, where a double peak was observed, and this may be explained by it exceeding its rather low solubility (10^{-3}\%) in the small amount of mercury present, and depositing as a solid film on the electrode surface.
Lead:

The lead response generally increased with increasing surface mercury. This phenomenon has been reported by Florence [305] for an in-situ mercury film (Florence electrode).

The dependence of the lead response on the amount of surface mercury has never been accounted for, and is essentially viewed as an empirical phenomenon, particularly in the light of the tacit and widely accepted assumption that the magnitude of stripping peaks are a simple function of their "concentration" in the amalgam [9,24].

Indeed, this hypothesis has never been pursued with respect to the fact there is clearly a profound and fundamental difference between "concentration" as understood in an aqueous or non-aqueous solvent, and "concentration" as understood in a mercury amalgam, particularly since, as noted by Neiman et al [295], the type of interaction of different metals in binary, or other systems, on an electrode surface varies.

Regarding the observed dependence of the lead stripping response on the amount of surface mercury, however, the classifications of Neiman et al [295] may be invoked to provide the basis for a possible explanation. According to this classification, lead and mercury "do not interact on the electrode surface at all." [295] Consequently, if lead reduction may be assumed to be enhanced at a mercury substrate with respect to glassy carbon (a widely accepted principle for any of the electroanalytically determinable metals), then with respect to the mercury film, the only function performed by a greater amount of surface mercury (with a larger surface area), would be to allow the deposition of a greater amount of lead on the electrode surface in a given time.

For the stripping step, then, since they do not interact at all, the oxidation of the lead would occur entirely independently of the amount of mercury present and by virtue simply of the greater amount of lead present, may be expected to give a larger stripping response. This is clearly a fundamentally different process from the copper as, at the stripping step, the copper would have to come "out of solution" before it could actually oxidise.
Cadmium:

Cadmium follows the same general trend with respect to its dependence on film thickness as lead, although the exact nature of the dependence is a little more difficult to assign. This is because although the magnitude of the response increases with increasing mercury deposition time for a given mercury plating solution, the 5 minute 10 ppm Hg film produced a greater response than did the 5 minute 100 ppm Hg film.

Since cadmium falls into the same category as lead with respect to its interaction with mercury [295], the same general trend as lead, with respect to its dependence on surface mercury, may be expected.

Batley & Florence [24] noted that there was a relationship between the magnitude of mercury present and the magnitude of the cadmium stripping peak, although they were unable to account for it. They did, however, suggest that in the presence of lead, the lead may preferentially deposit into the mercury. Were this the case, one would expect the cadmium response pattern to be quite complex, as it would be dependent on both the quantity of mercury present and the concentration of lead.

These observations, however, applied only to a certain point, beyond which the nature of the film changed dramatically. This “second phase” manifested for all the 1000 ppm Hg films, as well as the deoxygenated 10 minute 100 ppm Hg film, and resulted in a film of poor sensitivity with little or no variation in the size of the peaks as the film parameters varied (table 2.1). The fact that this effect manifested for the deoxygenated 10 minute 100 ppm Hg film, but not for the non-deoxygenated 10 minute 100 ppm Hg film further confirms the mercury-removing effects of solution oxygen.

The nature of the transition from first phase to second phase behaviour is difficult to characterise, as it suggests a fundamental change in the film structure. This phenomenon is further considered when the film is characterised visually (sect. 2.3.2.3).

The likely cause of the lack of variance in the ASV responses for these second phase films is that, when depositing from a 1000 ppm Hg$^{2+}$ solution, the amount of surface mercury reaches saturation very quickly, and a film which
is deposited for 10 minutes has no more mercury present than one which is deposited for 1 minute. This process is characterised visually in the subsequent section.

2.3.2.3. Rotating Electrode Studies: Visual Characterisation

A rotating electrode was used to characterise the MTFE visually, due to both its ubiquity in the literature, and the fact that any mechanical degradation effects due to the electrode rotation could be observed.

The purpose of this study was to mimic the work of Stulikova [22], with the exception that the film would be examined in solution, without exposure of the mercury droplets to air. The experimental procedures used to achieve this goal are outlined in section 2.2.4.

Whereas, however, Stulikova [22] held deposition time and [Hg$^{2+}$] constant and varied the deposition potential, the purpose of this study was to examine the effect of varying the deposition time and [Hg$^{2+}$]. Films grown at both rotating and stationary electrodes were examined, to enable the convective effect of the electrode rotation to be examined. When rotated, the rotation rate was kept constant, as for Stulikova's [22] work, at 3000 rpm, as this seems to be a popular electrode rotation rate for many workers [186,211,192,306].

The matrix for the Hg$^{2+}$ deposition which was employed for this study was acetate, rather than dilute HNO$_3$ (0.1M), as used by Stulikova [22]. The choice of dilute acid as a deposition matrix by Stulikova [22] is puzzling, as the subsequent films are unstable under these conditions [7], and, at an $E_{dep}$ of -1000 mV (or -1200 mV, which is the negative limit he examines) this will involve a significant amount of hydrogen evolution, which would interfere with any sort of coulometric measurement, and could cause mechanical interference with the film formation.

A possible reason for this choice of deposition matrix is the reported dependence of mercury stripping peaks on the pH of the solution from which they are deposited [22,306,307] with better defined peaks being obtained at pH<2 (although one of these authors suggests that perhaps the important factor is the pH of the solution into which the mercury is stripped [306]).

In any case, the fact that 0.1M HNO$_3$ was used as the deposition matrix, instead of acetate, which is by far the most common deposition matrix
[24,30,177,308,309], affords greater evidence for the assertion that the data presented by Stulikova [22] bears little relevance to the majority of MTFEs as used today.

Finally, the effect of deoxygenation of the plating solution was examined with respect to mercury film morphology.

The parameters which were studied were:

1. Mercuric ion concentration: 10, 100 and 1000 ppm ($5 \times 10^{-5} M$, $5 \times 10^{-4}$, $5 \times 10^{-3} M$).
2. Deposition time: 1, 3 and 5 minutes.
3. Effect of deoxygenation of plating solution.
4. Effect of subsequent rotation on a film which had been grown on a non-rotated electrode.
5. Effect of rotation during mercury deposition.

2.3.2.3.1. Effect of Mercury Concentration

10 ppm Hg film:

The diluteness of this solution, combined with the absence of convection, resulted in negligible amounts of mercury being deposited on the stationary electrode at deposition times up to five minutes.

Mercury was, however, seen to deposit on the electrode when the electrode was rotated during deposition as a very fine, uniform film (fig. 2.23). The drops appeared to range in size from about 0.5 - 1.0 μ, with an average size of about 0.7 μ. The only observable difference between the films grown for 300s and 60s was less surface coverage with the latter, with more of the GC substrate being visible.

100 ppm Hg films:

An interesting, deposition-time-dependent trend was observed for the 100 ppm films grown at the stationary electrode for $E_{dep} = 1,3$ and 5 minutes, as shown in figures 2.24, 2.25 and 2.26 respectively.
Figure 2.23: Mercury film grown from 10 ppm Hg\textsuperscript{2+} at a rotated GC electrode. $E_{\text{dep}} = -1000\text{mV}$, $t_{\text{dep}} = 300\text{s}$. Scale: 1 cm = 5 \mu m.

Figure 2.24: Mercury film grown from 100 ppm Hg\textsuperscript{2+} at a stationary GC electrode. $E_{\text{dep}} = -1000\text{mV}$, $t_{\text{dep}} = 60\text{s}$. Scale: 1 cm = 5 \mu m.

\footnote{It will be noted that this and many subsequent images have a number of artefacts appearing as dark blotches. These are a result of dust trapped within the lens assembly. As well as this, a number of white "water marks" are present from the original negatives.}
The 1 minute film (fig 2.24) consisted of large, widely dispersed droplets, of approximate average size 1-2μ, with a surface coverage of about 5-10 %. The 3 minute film (fig 2.25) showed a greater surface coverage (about 20%) with a larger variance in drop sizes (a substantial number of drops were either < 1μ or > 2μ). The trend of increasing variance in drop sizes was reversed for the 5 minute film (fig. 2.26) with most drop sizes being about 1μ, and the surface coverage increasing to 30-35 %.

The explanation for these data centres around the mechanical instability of the mercury films on the carbon substrate, and to enable the dynamics of this system to be characterised, the process was duplicated in-situ.

This process consisted of the mercury film being grown at a stationary glassy carbon electrode and watched with the Nikon (inverted) microscope. The observed sequence of events was as follows:

Initially, as the potential was applied a smaller number of larger drops were seen to form. These drops grew quickly and began dislodging, due to
their mass. As quickly as they dislodged, other drops grew quickly in their place, indicating the presence of highly active electrochemical “hotspots.” As this process continued, a finer, more uniform film was seen to gradually form between these “hotspots,” and as it increased the rate of growth and dislodgement began to slow, presumably due to the fact that the thermodynamic advantage enjoyed by these more favourable carbon sites had now been substantially narrowed by the presence of finely divided mercury nucleation sites at which incoming mercuric ions would readily undergo reduction.

Figure 2.26: Mercury film grown from 100ppm Hg²⁺ at a stationary GC electrode. E_{dep} = -1000mV, t_{dep} = 300s. Scale: 1cm = 5μm.

After a further period of time, the growth and dislodgement of the larger drops ceased entirely as the “hotspots” became covered with mercury, until eventually dislodgement of drops recommenced at random sites as the film became too thick to sustain further growth. Since the dislodgement of mercury drops, even in the absence of a rotating electrode, occurs so readily in mercury solutions in the normal concentration range used for MTFE plating, it may be seen that mercury thickness data based on coulometric considerations must be given very little credence.
Mercury films grown at the rotating electrode were highly uniform in nature, up until the onset of inertial depletion (*vide infra*). The absence of the larger drops may be attributed to the transport kinetics for the rotated electrode swamping the tendency of the mercury to deposit at a fewer number of thermodynamically favourable sites. Figures 2.27, 2.28 and 2.29 show the mercury films grown for 1, 3 and 5 minutes respectively at the rotating electrode.

Figure 2.27: Mercury film grown from 100ppm Hg$^{2+}$ at a rotated GC electrode. \(E_{\text{dep}} = -1000\text{mV}, t_{\text{dep}} = 60\text{s}\). Scale: 1cm = 5μm.
Figure 2.28: Mercury film grown from 100ppm Hg$^{2+}$ at a rotated GC electrode. $E_{dep} = -1000\text{mV}$. $t_{dep} = 180\text{s}$. Scale: 1cm = 5μm.

Figure 2.29: Mercury film grown from 100ppm Hg$^{2+}$ at a rotated GC electrode. $E_{dep} = -1000\text{mV}$. $t_{dep} = 300\text{s}$. Scale: 1cm = 5μm.
The 1 minute film (fig. 2.27) is extremely fine in nature, with quantification of either individual droplet sizes or surface coverage not being possible, other than to say that most of the droplets are <1μ. The average droplet size increased with deposition time, at about 0.8-1.0μ (40-45 % surface coverage) for the 3 minute film (fig. 2.28), and 1.0-1.2μ (45-50% surface coverage) with the 5 minute film (fig. 2.29).

It is interesting to note that the photographic contrast increased as the deposition time increased (figure 2.27 vs 2.28 vs 2.29), which suggests that the droplets are becoming more massive as the deposition time increases. This is an obvious result of the passage of a greater amount of charge, and the increased mass of the droplets eventually results in inertial degradation of the film, as is seen in figures 2.30 and 2.31.

Figure 2.30: Mercury film grown from 100ppm Hg²⁺ at a rotated GC electrode. E_{dep} = -1000mV. t_{dep} = 300s. Film grown at Metrohm RDE, for which the centre of rotation was offset by = 0.5mm. Scale: 3cm = 500μm.

The noteworthy feature of these figures is that whereas the centre of the film is undisturbed (figs. 2.29 and 2.30), mechanical degradation commences with increased angular velocity (as displacement from the centre of rotation increases).
Figure 2.31 focuses on the region in which the inertial degradation is beginning, and clearly evident are faults which arise from mercury droplets cutting a swathe through the film.

![Figure 2.31: Mercury film grown from 100ppm Hg2+ at a rotated GC electrode. E_{dep} = -1000mV. t_{dep} = 180s. Film grown at Metrohm RDE. Scale: 3cm = 100μm.](image)

This appears to suggest a mechanism whereby, under the influence of the centripetal acceleration of the electrode, adjacent drops coalesce, by virtue of their inertia. As the drops coalesce their mass increases and the larger drop, now with even greater inertia, cuts a swathe through the film, gathering in size as it goes. The fate of some of these droplets when they reach the edge of the electrode is indeed interesting, and is shown in figure 2.32.

Clearly evident is a ring of droplets around the periphery of the electrode (on the teflon), and corresponding uncoated circular or semi-circular regions on the very edge of the glassy carbon. This image (which was typical) suggests that the mercury actually has greater adherence to the teflon than it does to the glassy carbon, since the transition from the glassy carbon to the teflon could not be made until the droplet had gathered sufficient mass (and therefore inertia). Further, having made the transition to the teflon, its friction was enough to stop its movement, despite its massive size (up to 20μ) and the increased angular velocity on the edge of the electrode.
Figure 2.32: Mercury film grown from 100ppm Hg$^{2+}$ at a rotated GC electrode. $E_{\text{dep}} = -1000$ mV. $t_{\text{dep}} = 300$ s. Edge of electrode shown. Scale: 1 cm = 18 $\mu$m.

1000 ppm Hg films:

The films grown at the stationary electrode followed the same qualitative trend as for the 100ppm films with the exception that, as would be expected, surface saturation was achieved more quickly.

Figure 2.33 shows the 1 minute film, with the electrochemical "hotspots" being clearly limned against the grey background of the fine, more uniform film.

An interesting feature of this figure is the presence of a localised mercury-depleted region around each of the "hotspots." This phenomenon suggests that the nucleated mercury centre is a substantially more favourable deposition site than the surrounding glassy carbon, and has a correspondingly substantial diffusion region.

The 3 minute (figure 2.34) and 5 minute films were identical, and showed an even, uniform coating with no evidence of any preferential deposition sites.
Figure 2.33: Mercury film grown from 1000ppm Hg$^{2+}$ at a rotated GC electrode. $E_{\text{dep}} = -1000\text{mV}$. $t_{\text{dep}} = 60\text{s}$. Scale: 1cm = 5$\mu$m.

Figure 2.34: Mercury film grown from 1000ppm Hg$^{2+}$ at a stationary GC electrode. $E_{\text{dep}} = -1000\text{mV}$. $t_{\text{dep}} = 180\text{s}$. Scale: 1cm = 5$\mu$m.
When viewed in three dimensions, through the microscope, the droplets appeared rather massive in nature. The consequence of this was that the point of focus which was selected was a little arbitrary since, as one focussed through the film, different parts of the drops came into focus. The films grown at rotating electrodes manifested the same mechanical degradation effects observed for the 100 ppm films but to a greater degree (figures 2.35 and 2.36). Whereas the 100ppm films consisted of a central undisturbed region beyond which spiralling commenced, the 1000ppm films had no region of undisturbed film. The spiral extended almost from the rotational centre of the electrode, an inalienable function of the greatly increased rate of mercury deposition brought about by the tenfold increase in mercuric ion concentration with respect to the 100 ppm films.

Figures 2.35 and 2.36 show the same image photographed under different lighting conditions. Figure 2.35 was captured in the absence of any special filters, and shows clearly the individual droplets, thus facilitating size calculations. Figure 2.36 was captured with a polarising filter in the light path, and the resultant figure achieves a high contrast between the mercury and the glassy carbon background, thus highlighting the spiralling effect of the mercury.

If the centre of the spiral is examined (fig 2.35), a region is seen where the film consists of drops with a large size variance (up to 5μ). These features are most likely an effect of minimal inertia, due to the low angular velocity, at the rotation centre, along with a significant vertical solution hydrodynamic effect brought about by the development of a vortex at the rotation centre; the latter effect tending to push the film onto the electrode, rather than sweep it off.

The only significant differences between the 1 minute rotated film and the 3 and 5 minute films is that for the latter two there was a less discrete cutoff between the central region and the outer spiral, with the central region being more uniform, no doubt a consequence of the equilibrium between the vortex and inertia effects having more time to each equilibrium.
Figure 2.35: 1 minute deposition at -1000mV from a 1000 ppm Hg$^{2+}$ solution in 0.2M acetate buffer (pH 5.0) at a rotated GC electrode. Scale: 1cm = 15μm.

Figure 2.36: As for figure 2.35, with a polarising filter
Bubble Defects:

One of the features of the MTFE which detracts from its inter-electrode reproducibility is the possibility of bubbles adsorbing to the surface during the deposition process. Both stationary and rotating electrodes are prone to this effect. Figure 2.37 illustrates this effect for the stationary electrode.

The remarkable feature of this electrode is the well-defined strata of mercury layers visible at the periphery of the circle. These strata most likely relate to the mercury that was able to squeeze underneath the non-wetting air bubble, up to the point at which it contacted the carbon surface. It is worthy of note that the size of the bubbles observed on stationary electrodes could be up to 1 or 2mm in diameter, and these were larger than were observed on any of the rotated electrode films.

![Figure 2.37: Bubble adsorbed onto stationary electrode (1000ppm Hg^{2+}, 3min). Scale: 1cm = 20\mu m.](image)

If the corresponding defect at a rotated film is examined, it may be seen that air adsorbs quite strongly to the glassy carbon (figure 2.38). This bubble was displaced from the centre of rotation by about 0.5mm, and remained adsorbed to the electrode surface despite the substantial rotation rate of the electrode (3000rpm), and the presence of solution hydrodynamics in its vicinity.
This latter effect is particularly noteworthy, as the bubble halted the propagation of some mercury droplets, while causing others to stream around it. The presence of the bubble faults in MTFEs has, to the author’s knowledge, never been either reported or considered in the literature.

![Image of bubble adsorbed onto MTFE grown from 100ppm Hg²⁺ for 3 minutes.](image)

**Figure 2.38:** Bubble adsorbed onto MTFE grown from 100ppm Hg²⁺ for 3 minutes. \( \omega = 3000 \text{ rpm} \). Image is a 5x magnification of fig. 2.30. Scale: 3cm = 100μm.

### 2.3.2.3.2. MTFE stability to rotation

The previous study has established the fact that the morphologies of the films grown at stationary and rotating electrodes are markedly different. It is of interest, consequently, to examine the stabilities of these films to subsequent rotation, such as they would experience during a ASV experiment.

To examine this effect, a mercury film which was grown at a stationary electrode for 3 minutes from 100ppm Hg²⁺ was stirred for 1 minute at 3000 rpm. This electrode is shown in fig 2.39. The stirring removed most of the visible mercury, with the only remaining visible mercury being some streaks in a spiral pattern, presumably left behind by larger drops as they were flung from the electrode surface.
Figure 2.39: As for figure 2.31 after stirring electrode for 1 minute at 3000 rpm. Scale: 1cm = 5μm.

Of particular interest is the fact that previous work has shown that an MTFE such as this (grown at a stationary electrode and rotated subsequently) will produce useable stripping responses [211]. Despite the visible lack of mercury on the surface, however, this result is not surprising, as the results produced by the MTFEs grown from the 10ppm Hg^{2+} solutions in this study (sect. 2.3.2.1) showed that an electrode on which mercury is completely invisible to the naked eye, and barely visible under a microscope, is still capable of being used for ASV.

This does, however, perhaps explain the irreproducibility and confusion that prevails with respect to MTFEs, as people simplistically apply coulometry to film thickness calculations without appreciating the number of assumptions that are implicit in these calculations.

The electrode that was grown at a rotated electrode displayed somewhat greater stability upon subsequent stirring than did the film grown from the nonrotated electrode. An electrode was grown from a rotated 1000 ppm Hg^{2+} solution for 3 minutes, and used for two stripping determinations for a minute each at 3000 rpm. No visual differences were apparent in the mercury film before and after the ASV determinations.
2.3.2.3.3 Drying of film:

As noted previously, the most cited study of the physical morphology of the MTFE [22] examined the film after subsequent drying of the electrode. The effect of this process has never been studied in the literature. Consideration is now given to this effect.

The first observation to be made is that there is little observable difference when viewed with the naked eye. When viewed microscopically, however, a profound difference is observed, as is shown in figure 2.40.

This figure shows the interfacial region of a mercury film on which the drop of water on the electrode (subsequent to growth) had contracted part of the way across the surface. The process of examining the film microscopically resulted in the remaining water being spread across the electrode surface, such that the image was captured under water.

Figure 2.40: Mercury film grown from 100ppm Hg\textsuperscript{2+} at a rotated GC electrode. E_{dep} = -1000mV. t_{dep} = 180s. Electrode surface has been partially exposed to air (subsequent to mercury film deposition): the interfacial region is shown. Scale: 1cm = 15\mu m.
The uniform grey region of the image in the lower left corner of the photograph is the undisturbed film, the broad zone extending from the upper left to the lower right is the meniscal (interfacial) region, and the section to the upper right is the part of the electrode that has been exposed to the air.

The obvious effect of the drying of the electrode is to cause the drops to coalesce, thereby exposing substantial amounts of underlying substrate. In particular, the generally sparse distribution of droplets in the upper right corner of figure 2.40 was more typical of the dried section of the electrode, as is illustrated in figure 2.41. This figure may be seen to bear a striking resemblance to the images produced by Stulikova [22].

Of further note is the effect that the drying process had on the surface coverage of the electrode by the mercury. Using Stulikova's figures of 30 droplets of average size $0.7 \mu m$ per $2.07 \times 10^{-4} \text{ mm}^2$ surface area (for $E_{dep} = -1000 \text{ mV}$), one arrives at an approximate coverage of about 5%.

![Figure 2.41: Mercury film grown from 100ppm Hg$^{2+}$ at a rotated GC electrode. $E_{dep} = -1000 \text{ mV}$. $t_{dep} = 180s$. Electrode surface has been exposed to air subsequent to film growth. Scale: 1cm = 5\mu m.]

\[1\] It is difficult to see how Stulikova [22] arrives at an average droplet size of 0.7\mu m, as this would correspond to a photographic diameter of 0.35mm at the quoted magnification of 500x, and the average size of the droplets in his images is demonstrably larger than this.
This corresponds approximately with the degree of surface coverage obtained by performing similar calculations for the film in figure 2.41. In contrast, however, the surface coverage obtained under similar experimental conditions when the film is not allowed to dry is about 50% (fig.2.29).

These studies, therefore, place serious doubts on the validity of Stulikova's [22] data for aqueous mercury films.
2.4. CONCLUSIONS

A number of conclusions regarding the GC and GC/MTFE electrodes may be drawn from the ASV and visual microscopic studies pursued in this chapter:

1. The GC/MTFE is capable of being used for ASV with an amount of mercury on the surface which is invisible to the naked eye.

2. The sensitivities (with ASV) of cadmium, lead and copper are far less on the glassy carbon substrate than they are on the GC/MTFE.

3. For mercury films grown at stationary electrodes, two discrete phases manifest, dependant on the amount of mercury on the electrode surface. The thinner films, termed “first phase”, are highly sensitive, and the thicker films, termed “second phase” have relatively lower sensitivity.

4. Up until the formation of the second phase films, cadmium and lead produce stripping responses which generally increase with increasing surface mercury, whereas the copper response manifests an inverse relationship.

5. Cadmium deposition on the glassy carbon substrate is characterised by the catalysis of hydrogen reduction evidenced by gross tailing offscale at the negative end of the stripping voltammogram at potentials more positive than -1000mV.

6. For thicker mercury films (those which may be seen with the naked eye) not all the mercury that is deposited on the electrode surface remains there, with it being partially removed either by gravity or by the centripetal acceleration of a rotating electrode.

7. For all GC/MTFEs (examined in this study) a significant percentage of the glassy carbon substrate is exposed (at least 50%). For thinner films, this is due to the fact that there has not been enough mercury deposited to cover the surface, whereas with thicker films this is due to mercury which has been removed from the electrode surface by electrode rotation, gravitation, or the presence of adsorbed bubble defects in the film.
This result is not surprising, as mercury does not wet glassy carbon [295] and can therefore never form a true unilamellar film.

8. As a consequence of the mechanical instability of mercury, the quantity of mercury on the electrode surface may not be reliably quantified by coulometry, although this is more likely to be more valid for very thin films.

9. The changes induced by the departure of elemental mercury result in variations in film morphology.

10. The quantitative data advanced by Stulikova in the most oft-cited study of mercury film morphology [22] is seriously and fundamentally flawed, although his conclusions (dependance of droplet size on \( E_{\text{dep}} \)) seem to be correct in qualitative terms.

Further consideration is given to these data and conclusions when the GC/MTFE is compared with the chemically modified MTFE in Chapter 4.
Chapter 3:

Development of Nonconducting Polymer Electrode
3.1. INTRODUCTION

Chapter 2 established the following facts concerning the conventional GC/MTFE:

1. The mercury need not be visible to the naked eye for the electrode to function adequately as a substrate for ASV.

2. Thicker mercury films are prone to mechanical degradation as a result of the electrode rotation process.

3. The mercury film is irreproducible, largely as a result of the irreproducibility of the electroactivity of the glassy carbon substrate and the possibility of defects caused by adsorbed gas bubbles.

As a consequence of these limitations, this project sought to develop a high-performance MTFE, with significant advances in at least some of the areas outlined above. The goal that was identified was to produce an electrode that contained a monolayer coating of mercury that was reproducible, and stable both chemically and mechanically.

In order to achieve the requirement of a reproducible, stable monolayer coating, electrochemical deposition was abandoned in favour of complexation as a means of binding the mercury to the electrode surface. The reasons for this are:

- electrochemical deposition, at the microscopic level, is intrinsically non-uniform, as nucleation and deposition occur preferentially in localised regions of high electrochemical activity.

- mercury may deposit on predeposited mercury, to render the presence of a monolayer impossible.

The advantages, conversely, offered by complexation are:

+ once a site is complexed, no further mercury will deposit. This will result in a mercury coating that will conform exactly to the morphology of the underlying complexing groups.
the mechanical stability of the film will be enhanced by the presence of much smaller mercury drops (once the complexed mercury has been reduced).

if the (metallic) mercury film may be reversibly returned to its complexed state between analyses, it will result in an enhancement of the chemical stability of the film.

3.1.1. SELECTION OF COMPLEXING AGENT

The ligand that was selected to bind the mercury to the electrode surface was the dithiocarbamate species, due to the fact that it forms an extremely stable chelate with the mercuric ion, much more so than with any other metal [310]. A review of its properties must be undertaken at two levels:

1. The chemical and electrochemical properties of the ligand and its metal complexes are considered with respect to relative stability constants, pKa, chemical stability, oxidation/reduction processes, and the effect of substituents. This study will focus on the properties of dithiocarbamates in homogeneous systems.

2. Since this project involves an electrode consisting of dithiocarbamate functionalities immobilised on an electrode surface, the extent to which these homogeneous dithiocarbamate properties apply to a heterogeneous system is examined.

The properties of dithiocarbamates in homogeneous and heterogeneous systems are examined in turn.

3.1.1.1. Dithiocarbamates in homogeneous systems

A number of excellent and comprehensive reviews have been devoted to the study of dithiocarbamates [310-317]. It is no part of this study to comprehensively review all aspects of the chemistry of dithiocarbamates, but rather to highlight the aspects that are relevant to this project. These are factors such as their relative affinities for the metals examined in this study, the effect of pH on both the complexing capacity of the ligand and its chemical
stability, and the conditions under which it may dimerise to form the thiuramdisulphide (tds).

Further, the electrochemical responses of both the free and the complexed ligand will be examined.

Dithiocarbamate is a 1,1-dithioacid with a pKa that is dependant on the amine from which it is derived. For an amine of the form R₂NH, where R = alkyl groups from C₁ to C₄, the pKa ranges from 3.7 to 5.2 [318,319]. The pKa of the diethyldithiocarbamate species (DEDTC) that would most closely mimic the electron density of the dtc-derivatised NET, is 4.0 [318,319].

Soni and Trivedi [320] report results of 7.5 and 8.4 for DEDTC (for pKα₁ and pKα₂, which refer to the deprotonation of the nitrogen atom and sulphur atoms respectively), but since these values are significantly at variance with both the reported data for this compound [318,319], and the general constituent trend, it may be assumed to be in error.

The deprotonated form of the dithiocarbamate interacts strongly with metal (or metalloidal) ions to form compounds where, with a few exceptions, both of the sulphur atoms are bound to the metal ion.

The dithiocarbamate group possesses a highly noteworthy property; the ability to stabilise metal ions in unusually high oxidation states. So profound is this effect that Williams et al.[315] question the validity of the concept of a formal metallic oxidation state, as, in many complexes the "formal oxidation numbers have little correlation with the charge distribution in the molecule" [315].

The special features of the dithiocarbamate ligand can be appreciated if it is compared to the more general case of a 1,1-dithioacid:

\[
\begin{align*}
\text{R} & \quad \text{C} = \text{S} \\
& \quad \text{S} \\
\text{1,1-dithioacid}
\end{align*}
\]

**Figure 3.1** : Generalised structure of a 1,1-dithioacid
The 1,1-dithioacid possesses both δ-donor and π-acceptor properties. The possibility of the ligand to stabilise a particular oxidation state of a metal is dependant on the balance between the δ and π effects being such that the charge on the metal centre may be levelled, or stabilised. With the 1,1-dithioacids, the magnitude of the δ and π effects are about the same, and the ligand therefore has no special charge-stabilising properties. The special feature of the dithiocarbamate ligand is an additional π-electron flow from the nitrogen atom to the sulphur atoms via a planar delocalised π-orbital system:

![Figure 3.2: Resonance structures of a dithiocarbamate based on a secondary amine.](image)

The result of this is a strong electron donation effect that results in a high electron density on the metal centre, and a strong stabilisation of a higher formal oxidation state.

The consequence of this property of dithiocarbamates is that the most stable metal complexes formed are those of the higher oxidation states, and in some cases this has resulted in previously unreported formal oxidation states of the central metal (eg. Cu^{III} [315]).

Quite apart from the redox chemistry of the various metal dithiocarbamate complexes with which this study is concerned, it is incumbent to examine the redox properties of the free dithiocarbamate ligand.

Such a study was undertaken by Scrimager and De Hayes [321], and was a direct result of the ambiguity surrounding formal oxidation states of metals in dithiocarbamate complexes. Their study was an attempt to isolate the electrochemical responses of the free ligand, in an attempt to better characterise the electrochemical responses of the complexed species. Their study identified a number of oxidation and reduction products.

Of specific interest was that the dithiocarbamate (DEDTC) was reversibly oxidised to thiuram disulphide at .05 V (at a Pt electrode vs SCE in acetonitrile)
and reduced back to the dithiocarbamate at -1.85 V. A number of higher oxidation products were identified, but they are of no interest to the present study.

Of the metallic complexes which this ligand forms, the one that is of most interest to the present study is the mercury complex. Mercury (II) complexes are the most stable complexes of dithiocarbamate that have been reported: the Hg(dtc)₂ complex has a stability constant of $10^{39.1}$.[310]

An interesting feature of Hgᴵᴵ-dtc compounds is that they may be formed at mercury electrodes, since oxidation of the mercury electrode occurs before that of the free dithiocarbamate complex. This process consists, initially, of the oxidation of the mercury to Hg¹, which process is quickly followed by disproportionation to Hg⁰ and Hgᴵᴵ [322,323].

\[
2\text{Hg} + 2[\text{dtc}^-] \rightleftharpoons 2\text{Hg(dtc)} + 2e^- \quad \text{eq. 3.1}
\]
\[
2\text{Hg(dtc)} \rightleftharpoons \text{Hg} + \text{Hg(dtc)}_2 \quad \text{eq. 3.2}
\]

Two crystal structures for mercury (II)-diethylthiocarbamate have been reported. The α-form [324] is described as a “distorted tetragonal pyramid,” with the β form [324,325] on the other hand being described as “linear.” In this latter form, which has been described by two x-ray studies [324,325], the bond lengths of the two sulphurs in each dithiocarbamate molecule are dissimilar, with one being much shorter (2.397Å). As well as this, the C-S bond distance shows an inverse relationship with the Hg-S bond distance.

The electrochemistry of Hgᴵᴵ-dtc complexes, as with those of other group 2b elements (Znᴵᴵ, Cdᴵᴵ) is centred on the ligand, and oxidation of the complex either chemically or electrochemically, results in oxidation of the dithiocarbamate group to thiuramdisulphide (fig. 3.3)
This process has been observed electrochemically at Pt electrodes [317], and with halogens as chemical oxidants [326-328].

Other metals have a metal-based redox response. The copper-dtc complex [329], for example, is able to participate in redox processes in which the central metal may assume formal oxidation states of I, II or III, while the properties of other complexes, such as the lead complex, are unknown.

While this information is of fundamental interest to this study, it is of greater interest to determine the extent to which these processes are applicable to heterogeneous systems, since this is the system that was studied throughout this project.

3.1.1.2. Dithiocarbamates in heterogeneous systems

The strong complexing properties of dithiocarbamates have made them very attractive for the selective removal of many metals from solution for various applications.

This is particularly interesting as, despite the fact that dithiocarbamates are widely used in analytical chemistry, heterogeneous systems are few, and far between. This is illustrated by the fact that a recent comprehensive review on the subject of “the analytical chemistry of dithiocarbamate complexes” [316] fails to make mention of heterogeneous systems.

All work in this area has been confined to the use of dtc-containing resins to selectively preconcentrate metals from solution, prior to subsequent acid digestion of the metals and determination by spectroscopic methods. The most prolific worker in this area has been Barnes, who, along with various co-workers has used this technique to preconcentrate a variety of metals from matrices such as urine, coal slurries, fuel oil, seawater, and various biological samples [330-335]. Dithiocarbamates have also been used in speciation studies [332,334].
The typical approach is to complex the metals at the appropriate pH and, having done so for a preset period of time, digest the complexes with concentrated acid for subsequent atomic spectroscopic determination. An interesting variation to this approach was that taken by Leyden & Luttrell [336] and Dingman et al. [337] who, having preconcentrated the metals on the resin surface, determined them directly with XRF. Wing & Rayford [338] employ an approach whereby soluble metal dithiocarbamates are flocculated from industrial effluents with a cationic polymer before being digested and determined spectroscopically.

The pH at which dithiocarbamates complex metals is typically within the range 4 to 9, with the reported optimum [333] for Hg$^{2+}$, Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ at pH 5.0. The lower pH limit stems from the fact that the dithiocarbamic acids will only form metal complexes in their deprotonated form, and the pKa of most dithiocarbamic acids is about 4.0 [318,319].

The resins from which these dithiocarbamate groups are functionalised are varied. The most popular resin is that which was first used by Siggia [337], and later by Hackett and Siggia [339], and Barnes et al. [330-335], and which consisted of polyethyleneimine (PEI 18-1800 molecular weight) and polymethylenepolyphenyl isocyanate (PMPI) which were reacted in an 8:1 molar ratio. The derivatisation procedure varied significantly, however, as discussed in section 3.3.5.

An alternative substrate for the binding of dithiocarbamate groups is afforded by the attachment of secondary amine groups to surfaces by silylation. This approach was successfully employed by Leyden & Luttrell [336] on silica, and by Hercules [340] on fibreglass.

The use of a heterogeneous dithiocarbamate system for the binding of metals from solution introduces two special considerations.

The first of these respects the ability of the ligands to orient themselves around the incoming metal atom with both the appropriate symmetry and stoichiometry. For example, for Cu$^{2+}$ to bind to the ligands in the same manner in which it does in the homogeneous system, it must contact the resin surface at a point at which there are two dithiocarbamate groups in the same plane and separated by 5 or 6 Å. For the Cd$^{2+}$, Pb$^{2+}$, or Hg$^{2+}$, the situation is more complex, as the metal must bind at a site at which adjacent
Dithiocarbamate groups are oriented at about 90° to each other (to enable them to form their characteristic tetrahedral or distorted tetrahedral structures).

This phenomenon was noted by Dingman et al. [337], whose dithiocarbamate resin displayed an affinity for metallic ions in the order Ag⁺ > Hg²⁺ > Cu²⁺ > Sb³⁺ > Pb²⁺ > Cd²⁺ > Ni²⁺ > Zn²⁺ > Co²⁺, which is at variance with the literary order [310] of Hg²⁺ > Ag⁺ > Cu²⁺ > Ni²⁺ > Co²⁺ > Pb²⁺ > Cd²⁺ > Zn²⁺, for M(dtc)₂ complexes in solution (M = metal).

They suggested that the steric limitations imposed by the heterogeneous system may have led to a greater proportion of 1:1 metal-dtc complexes than would be present in a homogeneous system. This hypothesis is supported by the fact that the monovalent Ag⁺ ion occurs higher in the order (it is normally below Hg²⁺; Hg²⁺ is known to displace it from an Ag-dtc complex [341]) than it otherwise would (in a homogenous system), whereas the trivalent Sb³⁺ occurs lower in the order than one might expect on the basis of its theoretical affinity for sulphur ligands, due to the fact that the heterogeneous system would require three ligands to favourably position the metal on the solid substrate.

It is difficult to draw this conclusion unequivocally, however, as a complex stability series has never been reported for 1:1 metal-dtc complexes.

The second special consideration introduced by the use of a heterogeneous dithiocarbamate system refers to the stability of this species under acidic conditions.

This process, for homogeneous systems, has been characterised in some detail by Bode [342] and by Zahradnik and Zuman [318]. The decomposition of a dithiocarbamate under acidic conditions may be represented as a two-step process:

![Figure 3.4: Acidic decomposition of secondary amine-based dithiocarbamate](image-url)
Where pH > pKa of the dithiocarbamic acid the rate of decomposition proceeds according to

\[ V = -k[H^+]C_{dtc}K_a^{-1} \]  

 eq. 3.3

where \( V \) = reaction velocity and \( k \) = rate constant for the decomposition process. When pH < pKa, the rate of decomposition is independent of pH and proceeds according to

\[ V = -kC_{dtc} \]  

 eq. 3.4

This terminology simply translates to the fact that where the pH is above the pKa of the dithiocarbamic acid, the initial protonation is the rate-determining step, whereas below this pH the dithiocarbamate is in form II (fig. 3.4) and the rate of decomposition is now determined by the rate of the second reaction.

A range of primary amines ranging from C = 1 to C = 7 were studied [318] and compared with a range of secondary amines, either where \( R_1 \) and \( R_2 \) were linear alkanes, or where the amine formed part of an aliphatic ring structure. The results established conclusively, even taking into account the estimation involved in the determination of the decomposition rate constant for the secondary amines, that the pH-independent decomposition of the dipolar ion (II) for the secondary amine occurs at a much greater rate (about two orders of magnitude) than the primary amines.

The reasons for this are twofold. Firstly, if the protonation equilibrium is considered in figure 3.4, it may be seen that the electron donating effect (positive induction) of the aliphatic R group is magnified when there are two of them (2° amine), resulting in a stabilisation of the intermediate (II), and a concomitant shift of this equilibrium to the right. Secondly, having formed the intermediate (II), the presence of the two bulky R groups will, for the case of the secondary amine, result in a significant degree of steric crowding, and a concomitant weakening of the C-N bond.
The critical step, it may be seen, is the initial protonation of the amine group. When this proceeds readily, as it does in a homogeneous system (typical pKₐ in the region of 2 to 4 [318]), the decomposition proceeds very quickly, and the end result is that a dithiocarbamate based on a secondary amine decomposes, in acidic media, more quickly than does that which is based on a primary amine.

For heterogeneous systems, however, since the dithiocarbamate group is immobilised on a solid substrate, it is not as readily accessible to solution protons, and the entire decomposition process hinges upon the ease with which the amine group is protonated. The steric bulk of the secondary amines hinders this step more profoundly than is the case for the primary amines, and the consequence of this is that, for heterogeneous systems, dithiocarbamates based on secondary amines are more stable to acidic attacks than are those based on primary amines.

This is confirmed by the fact that, with one exception [336], dithiocarbamates based on secondary amines are used exclusively for the heterogeneous studies [330-337,339,340]. This is in spite of the fact that few authors seem to be aware of the rationale behind this approach, as there is only one passing reference [336] to the superior stability of secondary dithiocarbamates, in the solid phase, with respect to primary dithiocarbamates.

Indeed, it is interesting to note that whereas most workers target the pH range 4-9 for most metals [330] (with pH 5 being determined as the optimum pH for Cd²⁺, Cu²⁺, Hg²⁺ and Pb²⁺ [333]), there has been some work carried out at much lower pH.

Barnes and Lenna [333], for example, complex selenium and tin at pH 1. Leyden and Luttrell complex Cu²⁺, Ag⁺, and Hg²⁺ at “pH<2” and Hackett and Siggia [339] report that Cu²⁺, Pb²⁺ and Cd²⁺ are complexed at “very low pH”, and advise their readers to avoid pH of <1 due to the instability of the dithiocarbamate. If these pH were even approached in the homogeneous systems, the decomposition reaction would be well into the pH-independent range [318, 342] and rapid decomposition would ensue.

Finally, the digestion media employed for the heterogeneous metal complexes considered in this review are exclusively concentrated acids, and not, as would be sufficient for the homogeneous systems dilute acids. The
digestion solutions used are hot $8M \text{HNO}_3$ [339], 1:1 hot $\text{HNO}_3/\text{H}_2\text{SO}_4$ [333,334], $c\text{HNO}_3$ [335] and $c\text{HNO}_3/30\% \text{H}_2\text{O}_2$ [332,330].

Dithiocarbamates formed from secondary amines, then, possess a significantly greater degree of stability to acidic attack in a heterogeneous system than they do in a homogeneous system. The extent to which the enhanced solid-phase stability of the secondary dithiocarbamates impinge on this project are considered in chapter 4.

3.1.2. SELECTION OF POLYMER MODIFIER

The principal requirement of the polymer required to act as substrate for this study, was that it have free secondary amine groups available for subsequent derivatisation to the dithiocarbamate.

One polymer that has been successfully employed in this regard is polypyrrole. It was, however, considered unsuitable as a substrate for ASV, since its conducting properties result in a very high background current (both Faradaic and non-Faradaic) when used with fast-scan LSV (chapter 5).

The polymer that was selected for this task was N-ethyltyramine (fig. 3.5), since it comes from a class of polymer that has been shown to be able to form very thin, reactive films on electrode surfaces (sect. 3.1.2.1).

![Formula](attachment:formula.png)

Figure 3.5: N-ethyltyramine
This polymer belongs to the general class of polyphenylene oxide (PPO) polymers, and consideration is now given to the development and applications of this type of polymer.

### 3.1.2.1. PPO polymers - development.

The use of non-conducting polymers to modify electrode surfaces is not without precedent. Non-conducting polymers have been used as flow amperometric detectors [343], mediators for enhanced polymerisation of other conducting polymers [344], redox buffers for conducting polymers [345], for assessing redox mechanisms and kinetics of surface-bound metal complexes [241,242,245,346-348], catalysis of otherwise irreversible electrode processes [347,349-352], elucidation of polymer conduction mechanisms [347,353-355] and mimicking of solid state electronic properties [356].

A detailed consideration of this class of CME is, however, beyond the scope of this work, owing to their essentially non-analytical applications, and will not be pursued further.

The general formula for the monomeric precursors of PPO polymers is:

![General formula for the polyphenylene oxide (PPO) monomeric precursor.](image)

**Figure 3.6**: General formula for the polyphenylene oxide (PPO) monomeric precursor.

Substitution may be at either the ortho, meta or para groups, with polymerisation taking place through an ether linkage with the phenolic oxygen and a benzyl carbon at one of the unsubstituted sites of an adjacent monomer molecule.
Although the first electrochemically generated PPO polymers were reported in 1972 [356] work on these polymers did not begin in earnest until 1977 [357]. The rationale of the early work [357] was to form an insulating film for the purpose of pacifying the metal surface against corrosion. Since these polymers, as formed, are non-conjugated, they are insulating (conductivity of about $10^{-13} \, \Omega$ [358]) and since they will therefore not grow on themselves, this results in an even, uniform, adherent polymeric layer on the electrode surface.

Further work [359] emphasised the possibility of including reactive or catalytic functionalities as the substituents on the phenol ring, and a range of hydroxymethyl-substituted phenols as well as some disubstituted phenols, were examined. In this paper the authors advance the possibility of a polymer film that is of a porous nature, and make the following suggestion:

“It thus seems likely that this new procedure for obtaining reactive films where the implantation of carbonyl functional groups can be monitored presents numerous advantages over chemical surface treatment procedures for which the functional groups are distributed at random” [359].

These polymers are further referred to as a “new family” [359] of reactive polymers and it is concluded that “their good adherence on metal surfaces also makes it possible to conceive a more general approach to functionalised electrodes.”

Further work [360] extended the range of phenolic functional groups to amino and anilino functionalities. The amine-containing phenol, tyramine, was chemically derivatised with ferrocene after polymerisation, by which means two vital characteristics of this class of CME were elucidated.
1. The possibility of further functionalisation of the polymeric functional groups was demonstrated.

2. The subsequent electroactivity of the ferrocene groups demonstrated the fact that the insulating nature of the polymer was not a barrier to electroactivity, despite the fact that the ferrocene groups, being attached to the polymeric side chain, do not enjoy intimate contact with the electrode surface.

   This latter feature is of particular note, as the immobilised ferrocene on this electrode [360] displayed an extraordinary stability to repeated cycling, and far more so than that observed when it was immobilised by other means. The implications of this phenomenon for the electroactivity of the polymer-coated electrode are discussed in section 3.3.3.1.

   The use of p-NET as an analytical substrate has not been previously reported in the literature, although Pham et. al. [361] attempted to use a polytyramine electrode to complex Cu$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Fe$^{2+}$ and Zn$^{2+}$. These workers only achieved moderate success, however, with the solution metal concentrations (10$^{-1}$M) required for complexation at the free amine and ethereal oxygen being far greater than that which could be put to any analytical use.

   Their work did, however, demonstrate the feasibility of forming three-dimensional metallic chelates on an electrode surface.

### 3.1.2.2. Polymerisation mechanism of PPO electrodes

The most fundamental property of any electrochemically generated polymer is that it be insoluble in the solvent in which its monomeric precursor is solvated. This criterion is ably met by the use of alcoholic solvents, as the phenolic monomers are readily solvated in these media, whereas the polymers are not, and subsequently deposit on the electrode surface.

Pham et al [357] suggest that the solution should be strongly basic and deoxygenated for optimum film growth. Both these considerations are connected with the formation of soluble quinones in preference to the polymeric product. The role of the OH$^-$ (the base of choice for this work) may be understood if the reaction mechanism is considered:
The formation of III is represented [357] as the initiation step, with the propagation step consisting of the addition of III to IV. The presence of the strongly basic conditions is also required for further propagation of the polymer [357].

The role played by solution oxygen is likewise critical. For an ortho-substituted phenylene oxide, this will result in the oxidation of the initial phenoxy radical to hydroquinone:

\[
2 \text{II} + \text{O}_2 \rightarrow 2 \text{VII}
\]

Figure 3.8: Oxidation of phenylene oxide.

Figure 3.9: Reaction of ortho-substituted phenylene oxide with solubilised oxygen.

For a para-substituted monomer, the most likely product of this process is an orthoquinone:
Figure 3.10: Oxidation of phenoxy radical to an orthoquinone by solution oxygen.

Although the specific example studied by these workers [357] was 2,6-xylenol ($R_1 = R_2 = CH_3$), their studies, along with those of others [361], suggest that the repeating unit of the p-NET is:

\[
\begin{align*}
R &= CH_2-CH_2-NH-CH_2-CH_3 \\
\end{align*}
\]

![Repeating unit of poly-N-ethyltyramine](image)

**Figure 3.11:** Repeating unit of poly-N-ethyltyramine

The polymerisation process is initiated by the application of a positive potential at an electrode immersed in a strongly basic, alcoholic solution of the monomer. As the polymer propagates and becomes insoluble it deposits on the electrode surface as a thin, adherent film. Although, in principle, any electrochemical waveform could be used for this process, the only waveform that has been reported to date is cyclic voltammetry, with the upper potentials lying in the range $1.5V$ [359] vs Ag/Ag$^+$ to $2.0V$ [361] vs SCE.

The reason for the choice of cyclic voltammetry as the polymerisation waveform lies in the highly diagnostic nature of the voltammogram recorded during the growth of the polymer. The fact that the polymer is of an insulating nature results in passivation of the electrode surface, as further monomer is inhibited from coming into contact with the electrode substrate. The
voltammogram recorded during this process therefore yields, on the first sweep, broad oxidation responses characteristic of the oxidation of the monomer and oligomers, with the second and subsequent sweeps being essentially flat, due to the insulating coating on the electrode.

The thickness of the PPO film [357,359-361] was found to vary with the number of cycles, upper E limit and substrate (Fe,Cu,Pt,Ni), with, in one case, ferrocene used as a redox catalyst [359] to promote film thickness and electroactivity. A detailed study of these parameters was not carried out in the course of this project.

The conditions that were selected for the p-NET synthesis were identical to those used for the most recent of the voltammetric polytyramine studies [361] and consisted of ten successive cycles from 0.0v to 2.0V (vs SCE) from a 0.1M solution of the monomer in 0.3M NaOH in methanol.

A non-aqueous reference electrode was used throughout this work (Ag/Ag+, .001M AgClO4), as the volume of monomer solution used is very small (=2mL), and any water that was introduced from an aqueous reference electrode may have resulted in oxygen evolution at the anode, with consequent generation of quinone/hydroquinones and resultant interferences from the polymerisation processes these compounds would produce.

3.1.2.3. Electroactivity of PPO polymeric electrodes

That PPO coatings may permit passage of charge to the underlying substrate becomes apparent from the work of Pham et al [360], in which a ferrocene group that was grafted onto a polytyramine substrate displayed a normal redox couple.

In the absence of any mechanism to account for any tangible polymeric conductivity, one is left with a model based on the passage of current, through pores in the polymer, to the substrate. Such a model has been suggested and interpreted for these polymers [362], as well as for other film-coated electrodes [363-365].

Although no specific mention of pore size or distribution is made for the case of the p-PPO electrodes, a mathematical model is developed nonetheless [362]. The model treats the polymer film as a "film" rather than a "membrane", thus obviating the need for a partition equilibrium between the liquid phase
and the inner part of the film. The case of hydrophilic membranes is dealt with elsewhere [366,367].

Pham's study [362] is confined to the reaction of bulk solutes at the electrode surface and incorporates no consideration of surface-bound reactants. His study considers both reversible and irreversible reactions, and the manner in which the kinetics of these processes are influenced by the various permutations of slow or fast diffusion kinetics from either the bulk solution or through the film.

He also considers the mechanism of conduction of an electrochemically active species that is attached to the surface (either by complexation or covalent bonding) of a non-conducting, polymeric, electrode film [360,361,368]. In each case, the conduction, and electroactivity of the films is interpreted in terms of conducting sites dispersed throughout the polymer, by either ionic migration or electron hopping. These studies include incorporated species such as ferrocene [360] and Cu$^{2+}$ and Co$^{2+}$ [361].

Anson [369] has also considered conduction mechanisms for (inert) polymers reliant on electron hopping for their conductivity.

Where the polymer has no electrochemically active species incorporated into its structure, however, and the polymer coating may be assumed to be totally inert, a model is required which accounts for the passage of charge to the underlying substrate. This is considered further in section 3.3.3.1.

### 3.1.3. DESIGN OF THE CME:

Having selected both the polymer and the complexing agent to be used for this study, the final step in the process consisted simply in their union. This process was consummated by a chemical derivatisation step, and is outlined in sect. 3.3.5.

Following the electrochemical polymerisation process, the polymer was chemically derivatised to graft dithiocarbamate groups onto the amine groups. This step was followed by deposition of mercury onto the dithiocarbamate groups for the formation of an MTFE.
Various methodological parameters were examined at each step (including two polymerisation methods), and the rationale and scope of each of these are considered in the appropriate sections.

The steps involved in the overall design, therefore, of the CME that was studied are outlined below:

```
Monomer Synthesis
    ↓
Polymerisation
    ↓
Derivatisation
    ↓
Mercury Deposition
    ↓
Electroanalysis
```

- Potentiodynamic
- Potentiostatic
3.2. EXPERIMENTAL

3.2.1. ELECTRODES

Working Electrodes:

Both glassy carbon and platinum electrodes were used. The glassy carbon electrodes used were, for the stationary electrode work, the BAS glassy carbon electrodes as described in section 2.2.1, and for the rotating electrode work, the Metrohm 628 Rotating Disc Electrode as also described in section 2.2.1.

The platinum wire electrodes used were made in the laboratory, and consisted of a platinum wire (0.5 mm diameter, ex Johnson Matthey) being sealed in a narrow (soda) glass tube. A copper wire, that had previously been spot-welded to the platinum wire, protruded from the opposite end of the electrode and acted as the conducting support to which the instrument was connected. The length of platinum wire protruding from the sealed end of the electrode was typically about 1 cm.

Counter Electrodes:

The counter electrode used for the polymerisation procedure was a Pt sheet electrode of approximate dimensions 1x1 cm. The sheet was spot-welded to a 0.5 mm platinum wire that was sealed in a pyrex tube with a B12 fitting (to ensure an airtight fit in the electrochemical cell).

The counter electrodes used for the aqueous systems (with both stationary and rotating working electrodes) are as described in section 2.2.1.

Reference Electrodes:

The non-aqueous reference electrode was a double junction system comprising a Metrohm 6.0724.140 Ag/Ag+ non-aqueous internal electrode (0.001 M AgClO₄ internal solution) with a Metrohm 6.0711.100 salt bridge. The
solvent employed was acetonitrile (A.R. grade ex Mallinckrodt), and the salt used in the salt bridge was 0.1 \textit{M} \text{NaClO}_4.

Aqueous reference electrodes were as described in section 2.2.1.

3.2.2. INSTRUMENTATION

All electrochemical instrumentation used is as described in section 2.2.2.

\textit{NMR}:

\textsuperscript{1}H NMR spectra were acquired at 400 MHz on a Varian Unity 400 Nuclear Magnetic Resonance spectrometer, operating in the pulse Fourier transform mode at ambient temperature (22\textdegree C). Typical acquisition parameters were 32 scans over a sweep width of 4500 Hz and 32000 data points. Samples were dissolved in CDCl\textsubscript{3}.

\textit{Mass Spectrometry}:

The mass spectra were recorded on a VG 1212 Quadrupole mass spectrometer in both CI and EI modes. For the fast atom bombardment (FAB) mass spectra, the beam of fast xenon atoms was produced by charge exchange in a saddle field ion gun (2 mA and 8 kV) and focussed on the FAB target.

3.2.3. SOLUTIONS:

\textbf{Electrolyte Solutions:}

Acetate buffer and sodium nitrate solutions used were as described in section 2.2.3. Methanol electrolyte solution was 0.3\textit{M} in NaOH. NaOH was "Baker Analyzed." All electrodes as described previously. The 0.3\textit{M} NaClO\textsubscript{4}/MeOH solution was made from AR grade NaClO\textsubscript{4} ex BDH.

\textbf{Monomer Solution:}

The monomer solution was 0.1\textit{M} N-ethyltyramine (NET), 0.3\textit{M} NaOH in methanol. The NET was synthesised (\textit{vide infra}), the NaOH was "Baker
Analyzed” and the methanol was A.R. grade ex Mallinckrodt. The ferricyanide solution $0.1M$ in Fe($\text{CN})_6^{3-}$ and was made from its sodium salt.

**Derivatisation Solutions:**

**Solution 1:** 39.2 mL A.R. grade benzene (ex BDH) and 7.9 mL of each of A.R. grade carbon disulphide and 2-propanol were mixed together to make a volume of 55 mL. To this was added 1 pellet of “Baker-Analyzed” NaOH.

**Solution 2:** Neat CS$_2$ (A.R. Grade ex BDH) was added to the derivatisation vessel along with one grain of “Baker Analyzed” NaOH.

**Solution 3:** Carbon disulphide (A.R Grade ex BDH) and 2-propanol (A.R. Grade ex BDH) were added to the derivatisation vessel in a 1:1 volumetric ratio along with a pellet of “Baker Analyzed” NaOH. The single pellet, however, dissolved and further NaOH was required before saturation was achieved.

**Solution 4:** A small volume of A.R Grade CS$_2$ (about 1% by volume) was added to a .04$M$ aqueous solution of NaOH (Baker Analyzed).

**3.2.4. ELECTROCHEMICAL CELLS AND GLASSWARE:**

The electrochemical cells used for the stationary and rotating electrode work are as described in section 2.2.2.

The cell used to grow the polymer was a laboratory-built cell and is seen in figure 3.13. The cell was designed to enable the polymer to be grown from a very small volume of solution (about 2 mL) so as to minimise the monomer requirement.

The vessels used for the derivatisation of the electrodes were 100 mL erlenmeyer flasks with B12 quickfit necks. The glassy carbon electrodes were suspended from the top of the flasks by laboratory-made nylon holders such that air-tight seals were formed. This was important from the point of view of the highly volatile solvents employed.

Each derivatisation vessel was dedicated to a particular electrode, and never contained anything except the derivatisation solution to be employed for that particular electrode. Each cell also contained a dedicated stirring flea.
3.2.5. EXPERIMENTAL PROCEDURES:

3.2.5.1. Monomer Synthesis:

Synthesis of Diacetyltyramine Intermediate. To a mix of 15g tyramine and 150mL acetic anhydride, 0.5g of sodium acetate was added at 0°C. This was warmed to room temperature and stirred for 24 h. Water (250 mL) followed by 500 mL of saturated sodium bicarbonate were added dropwise over a period of 5-6 h. The solution was extracted with chloroform (washed 2 x with H₂O, 2 x with saturated NaCl, and again with H₂O). It was dried with MgSO₄, evaporated, and then recrystallised from ethanol. A yield of 87% was obtained.

Synthesis of N-ethyltyramine. To 6 g of LiAlH₄ under N₂ was added 250 mL dry THF (sodium dried and distilled from LiAlH₄) at 0°C. To this mix was added 10 g of O,N-diacetylttyramine in 200 mL dry THF dropwise at 0°C, before stirring at room temperature for 1 hr and refluxing for 72 h. The resulting
mix was cooled to 0°C and hydrolysed. It was then filtered through celite and dried with MgSO₄. A yield of 85% was obtained.

The synthetic pathway is shown in figure 3.13:

Figure 3.13: Synthetic pathway for poly-N-ethyltyramine synthesis.

3.2.5.2. Polymerisation Procedure:

The solutions and polymerisation conditions employed were identical to those employed by Pham et al. [361], with the exceptions that the monomer was N-ethyltyramine (instead of tyramine) and the reference electrode employed was an Ag/Ag⁺ system (0.001M AgClO₄). The latter was employed (instead of an aqueous reference electrode) to prevent the catalytic formation of quinones (figure 3.10) by the generation of oxygen at the anode.

Voltammetric Parameters:

The polymer was grown both potentiodynamically and potentiostatically. The voltammetric parameters employed for the potentiodynamic growth are recorded below:

Initial E = 0 mV

Final E = 0 mV
Upper E = 2000 mV
Lower E = 0 mV
Number of cycles = 10
Sweep rate = 50 mV.s\(^{-1}\)
Waveform = Cyclic Voltammetry

The potentiostatic method consisted of polarisation of the working electrode at 1.5V (vs Ag/Ag\(^+\)) for a period of ten minutes.

**Procedure:**

The monomer solution (2mL) was placed in the cell along with the counter electrode and degassed with N\(_2\) for 10 mins. While this was proceeding, the glassy carbon working electrode was treated in the following manner:

1. **The surface was polished on a methanol-moistened filter paper to remove any traces of polymer from previous work.**
2. After rinsing, the electrode was polished on a flocked twill (ex Leco) polishing pad with a .05\(\mu\) alumina slurry for 5 or 10 seconds.
3. **The electrode was then placed in an ultrasonic bath for 30 seconds, after rinsing, in Milli-Q water.**
4. **After the ultrasonication, the electrode was rinsed with water, then methanol, after which it was placed in the polymerisation vessel.**

After this, the reference electrode assembly was placed in the polymerisation vessel, and degassing continued for about a minute prior to the application of the potential waveform. The reference electrode assembly was placed in the vessel last so as to minimise contamination of the frit of the salt bridge by the monomer. After this, the potentiodynamic waveform was initiated.
3.2.5.3. Derivatisation Procedure:

The appropriate derivatisation solution was added to the derivatisation vessel, the solution was stirred gently, and the electrode allowed to derivatise for a period of 24 hours. To ensure reproducible stirring, dedicated and identical derivatisation vessels and stirring fleas were used for each electrode, and stirring was carried out on a laboratory-made stirrer with preset stirring speeds. The same preset stirring speed was used for all derivatisations.

Characterisation of derivatised product:

Since the derivatised polymer is immobilised on the electrode surface, it is intrinsically difficult to characterise directly. Consequently, the approach that was taken was to derivatise the monomer, and isolate it for subsequent characterisation by NMR and mass spectrometry.

A methylation step was inserted in the process to protect the dithiocarbamate group from being decomposed at the acidification step of the extraction procedure.

The method that was employed was:

1. Allow a small volume of monomer solution to evaporate in an empty derivatisation vessel.
2. Add derivatising solution to vessel and stir for 24 hours.
3. Add Iodomethane (Gold label ex Aldrich) in 5 x molar excess and allow to react for 1 hour.
4. Acidify (to pH 4-5) with dilute HCl.
5. Extract into CH₂Cl₂ (A.R. Grade ex BDH).
6. Dry with Na₂SO₄ and MgSO₄ and filter.
7. Redissolve in CH₂Cl₂
8. Extract with 10% cold NaOH
9. Repeat steps 4-6
10. Characterise with NMR and Mass spec.

Steps 7-9 were employed to remove any unwanted neutral organic species.
3.3. RESULTS AND DISCUSSION

The development and characterisation of this electrode involved the initial characterisation of the monomer, followed by characterisation of the polymerisation process and the investigation and characterisation of the derivatisation process. Each is considered in turn.

3.3.1. MONOMER CHARACTERISATION:

The structure of the N-ethyltyramine was confirmed by NMR (fig 3.14). The data accompanying figure 3.14 is given below:

\[ \text{\textsuperscript{1}H NMR (COCl\textsubscript{3}) \delta 6.96 (d, J = 6.8Hz, 2H, ArH); 6.69 (d, J = 6.8 Hz, 2H, ArH); 2.91 (t, 2H); 2.78 (m, 4H); 1.16 (t, J = 6.8Hz, 3H, \text{CH}_3) } \]

Figure 3.14: NMR of N-ethyltyramine. Instrumental parameters as outlined above.

These spectra confirm the presence of the N-ethyltyramine molecule, with the peak assignments as indicated below:
3.3.2. POLYMERISATION OF N-ETHYLTYRAMINE

PPO-type polymers have been synthesised almost exclusively under potentiodynamic [357,360,361,368,370,] conditions, although one case of a galvanostatically generated polymer has been reported [371]. As a consequence of this, and given its self-diagnostic properties (shape of the CV curve during polymerisation), the potentiodynamic technique was selected as the method to be used for the bulk of the work in this project.

An alternative method that was investigated was potentiostatic polymerisation, and this technique is examined in section 3.3.3.1.

The potentiodynamic polymerisation technique used throughout this project was not varied from that of Pham et al [361]. The reason for this is that the system employed by Pham [361] has been well characterised with respect to polymer thickness, mechanism of growth and stoichiometry. This was used as a basis for the further characterisation of the polymer-coated electrode with respect to its electrochemical properties, both during and after polymerisation.

The parameters that were investigated were the effect of the choice of substrate material, the effect of dissolved oxygen on the polymerisation process, and the electrochemical activity of the polymer-coated substrate.
3.3.2.1. Effect of dissolved oxygen during polymerisation:

The effect of solubilised oxygen in the monomer solution on the polymerisation process was examined. As suggested in section 3.6.1, the potential effect of dissolved oxygen during the polymerisation process is to react with the free radical monomeric or oligomeric intermediates to produce quinones or hydroquinones, and therefore either halt the propagation of the polymer chain or promote crosslinking.

The effect of dissolved oxygen on the polymerisation voltammogram is seen if the response in the absence of dissolved oxygen (fig. 3.16) is compared with the response produced if the deoxygenation step is omitted (fig. 3.17).

For a deoxygenated solution, the only sweep (of the 10) that produces a tangible response is the first one (fig 3.16), with two broad oxidation responses appearing in the region 400-800 mV (vs Ag/Ag⁺). The remaining nine sweeps produce very small responses in the same region, and but for a broad oxidation at \( E_p > 1700 \) mV, are essentially featureless.

The voltammetric responses produced in the presence of solubilised oxygen are strikingly different, as may be seen from figure 3.17. Of particular note is the fact that with the latter, an oscillating trend was observed, with significant differences being observed between the even (fig 3.17a) and odd (fig. 3.17b) numbered scans. In particular, the odd-numbered scans (fig. 3.17b) manifested an oxidation peak at about 1.2V, whereas the even-numbered scans did not (fig 3.17a). The fact that this peak only manifested on every second cycle is singularly curious, and it followed a similarly oscillating trend for the peak at 1.6V, although this was less pronounced.
Figure 3.16: Cyclic voltammograms recorded during growth of p-NET at a glassy carbon electrode from a deoxygenated monomer solution (.3M NET, .1M NaOH/MeOH). All other conditions as described in "experimental."

Figure 3.17a: Cyclic voltammograms recorded during growth of p-NET at a glassy carbon electrode from a non-deoxygenated monomer solution (.3M NET, .1M NaOH/MeOH). All other conditions as described in “experimental” Cycles 1,3,5,7,9 are shown.
Figure 3.17b: Cyclic voltammograms recorded during growth of p-NET at a glassy carbon electrode from a non-deoxygenated monomer solution (.3M NET, .1M NaOH/MeOH). All other conditions as described in "experimental" Cycles 2,4,6,8,10 are shown.

The cause of this phenomenon, which was reproducible, and which has not been observed by the author either otherwise experimentally, or in the literature, is not immediately obvious. Subsequent studies, however, revealed that a polymer so grown performed poorly with respect to subsequent derivatisation and mercury complexation.

The most likely explanation for this effect is that the presence of the quinones and hydroquinones during the polymerisation process altered the structure of the polymer in such a manner as to render the secondary amine sites, or a sufficient number of them, unavailable for derivatisation to the dithiocarbamate functionality.

As a consequence of this, deoxygenation of the monomeric solution was employed for all subsequent work.
3.3.3. ELECTROCHEMICAL ACTIVITY

A discussion of the electrochemical activity of the p-NET-modified electrode centres not on the polymer itself, since it is nonconducting, but, in a more general sense, on the region bounded by the bulk of the electrode substrate and the bulk of the solution.

Four specific aspects of the electrochemical reactivity of this system are considered.

1. The reactivity of a bulk solution analyte at the electrode surface. This is used to characterise the mechanism of charge transfer in terms of accessibility of analyte to the substrate.

2. The reactivity of solvent or electrolyte oxidation products that are incorporated into the polymer film during synthesis.

3. The effect of the polymeric coating on the voltammetric background when employed in linear sweep mode (sect. 2.3.1.2).

4. The reactivity of a surface-bound analyte at the electrode surface (ASV).

Each aspect is considered in turn.

3.3.3.1. Electroactivity of the polymeric electrode

Studies were carried out at both bare and polymer-coated electrodes in the presence of $\text{K}_3\text{Fe(CN)}_6$, a compound with facile electrodic oxidation and reduction kinetics.

Cyclic voltammetry was selected as the waveform to be employed for this study. The reason for this is that it enables the magnitude and shape of the oxidation and reduction responses to be monitored, and the dependance of these parameters on sweep rate may be employed to yield information about diffusional processes occurring at the electrode surface, and therefore the mechanism by which charge is transported across the polymer film to the underlying substrate.

When cycled at the bare glassy carbon electrode, responses were produced, at the various sweep rates, as shown in figure 3.18.
Figure 3.18: CV at a glassy carbon electrode in deoxygenated 0.1M K₃Fe(CN)₆³⁻. Sweep rates as indicated.

A sigmoidal response is seen for a sweep rate of 1mV.s⁻¹, beyond which peak-shaped responses characteristic of analyte depletion at the electrode surface are observed. When compared with the polymer-coated electrode, some interesting features manifest.

As outlined in section 3.2.5.2, two polymerisation methods were employed for the generation of the p-NET film, potentiodynamic generation (PDG) and potentiostatic generation (PSG). The properties of each of these polymers were examined.

The PDG polymer yielded the response shown in figure 3.19. The response is sigmoidal, and independent of scan rate, up to 5 mV.s⁻¹, beyond which depletion effects set in. The fact that the electroactive area of the electrode is very much less than its geometric area, due to the polymer film, is apparent if the current scales of figures 3.18 and 3.19 are compared.

The response of the PSG polymer is shown in figure 3.20. The most noteworthy feature of these responses is the fact that the sigmoidal-shaped response, and non-dependance on scan rate, persisted up to 2000 mV.s⁻¹, with the first sign of a peak-shaped response not manifesting until 4000 mV.s⁻¹ (fig 3.20.)
As well as this, a direct comparison with the PDG polymer made it clear that the PSG polymer had a greater electroactive surface area, by virtue of its greater voltammetric response at the same scan rate (fig 3.21).

**Figure 3.19**: CV at a p-NET coated (PDG) glassy carbon electrode. Solution conditions as for figure 3.15.
Figure 3.20: CV of a 0.1\text{M} \text{Fe(CN)}_6^{3-} solution at 2000 mV.s\textsuperscript{-1} (solid line) and 4000 mV.s\textsuperscript{-1} (shaded line).

Figure 3.21: CV of a 0.1\text{M} \text{Fe(CN)}_6^{3-} solution at 20 mV.s\textsuperscript{-1} for PSG (solid line) and PDG (shaded line) polymers.
These data suggest that the polymer-coated electrode behaves as a microelectrode array, with the observed electroactivity occurring as a result of the analyte gaining access to the electrode substrate via a series of faults, or micropores, in the polymeric coating.

Consideration is now given to this model.

A microelectrode array consists of series of microdisc electrodes separated by an insulating material, the “microdiscs” being simply the isolated microscopic regions of the substrate not completely covered by the film. A detailed description of the theory of microelectrode arrays, or microelectrodes in general, is beyond the scope of this study, and a number of excellent reviews are available [364,372-375]. A brief description, however, of some of their salient features will be undertaken.

A microelectrode array may be depicted as in figure 3.22.

![Diagram of a microelectrode array](image)

**Figure 3.22:** Diagram of a microelectrode array. $r$ = radius of microdisc electrode. $s$ = separation between microdiscs

For the reaction of solubilised analyte species at the electrode surface under the influence of a ramping potential waveform, three limiting cases are possible.

1. When the scan rate is sufficiently low, and the time scale of the experiment sufficiently long, diffusion regions from adjacent microdiscs overlap, and the combined diffusion layer takes on a planar shape, resulting in linear diffusion, as with a macroelectrode.
Under such conditions, the current is determined by the geometric area of the electrode (that is, including the area between the microdiscs that is either covered with an insulating film, or constituted of a non-conducting material), and is identical to that of a macroelectrode of the same area. The voltammetric responses are peak-shaped, as with a macroelectrode. This “total overlap” behaviour occurs at large r, small s and low v (large t).

2. At higher v, and therefore a shorter time at the electroactive potential, the material in the immediate vicinity of the electrode is quickly depleted, and the diffusion layer takes on a hemispherical shape (fig 3.23)

The consequence of this is “steady state” diffusion (often termed “radial” diffusion). That is, since the electrode is drawing on a hemispherical-shaped diffusion layer of ever increasing surface area, it is able to supply analyte to its active surface at a constant rate (flux). The resultant voltammogram takes on a sigmoidal (or near-sigmoidal) shape.

![Figure 3.23: Hemispherical diffusion at a microdisc electrode](image)

The relationship between current and electrode surface area follows a complex relationship [364], and is given by:

\[
\frac{i}{\pi r^2} = \frac{nF D c^0}{(\pi D t)^{1/2}} \left[ .9979 + 1.7947 \frac{(D t)^{1/2}}{r} + .4944 \frac{(D t)^{1/2}}{r} \exp\left(-.7246 \frac{r}{(D t)^{1/2}}\right) \right]
\]  

eq. 3.5
This behaviour persists while ever diffusion regions from adjacent microdiscs do not overlap, and therefore breaks down at very low $\nu$ (large $t$).

3. At higher scan rates ($\nu$), the diffusion layer extends linearly from the electrode surface. The reason for this is that on the time scale of the experiment, radial diffusion does not have time to develop. The voltammograms so produced conform to the theory for semi-infinite linear diffusion, with a normal peak-shaped response.

This limiting case has been designated “linear active” [376]. The magnitude of the response is proportional to the active electrode area (i.e. the total area of the microdiscs). This limiting case occurs at high $\nu$ and therefore small $t$ (where $t = \text{time taken for an individual scan}$), large $\tau$, and is independent of $s$.

From an examination of these three limiting cases, it is clear that the most desirable scenario is the “steady state” situation, as it is here that the electrode is behaving as an array, with the best definition of response, and non-dependance on the sweep rate. A consideration of the factors contributing to each of these cases make it clear that a small value for “$r$” will discriminate against both the “linear active” and “total overlap” cases, and extend the range of the intermediate “steady state” case. To this end it becomes clear that microelectrode array (steady state) behaviour is promoted by having the ratio of $s$ to $r$ as large as possible (a typical value is 6 [377,378]), with a judicious choice of $\nu$.

For the case of the p-NET electrodes, “total overlap” behaviour, as reported by Whiteley et. al [376] was not observed down to 1 mV.s$^{-1}$, for either the PSG or PDG polymers. The fact that the “total overlap” scenario does not manifest suggests that the micropores in the polymer film are well separated as, in the considerably long timeframe of the voltammetric sweep, their diffusion layers never overlap.

For the PDG polymer, the data suggests that the size of the pores are large by microelectrode standards, as linear diffusion sets in at about 10mV.s$^{-1}$ (fig. 3.21), with the characteristic loss of the sigmoidal current response, and a peak current response ($i \propto \nu^{1/2}$), which indicates the presence of semi-infinite linear diffusion (fig. 3.24).

Conversely, with the PSG polymer, the high sweep rates required to induce linear diffusion (4V.s$^{-1}$) make it clear that the size of its micropores are
much smaller than those of the PDG polymer film; this electrode, therefore, behaves a great deal more like a microelectrode array than the PDG polymer.

![Plot of i vs \(v^{1/2}\) for potentiodynamically generated polymer when cycled in 0.1M Fe(CN)\(_6\)\(^{3-}\). Oxidation response shown.](image)

Figure 3.24: Plot of \(i\) vs \(v^{1/2}\) for potentiodynamically generated polymer when cycled in 0.1M Fe(CN)\(_6\)\(^{3-}\). Oxidation response shown.

The significance of this result may be appreciated if the present state of microelectrode array technology is considered.

There are two types of microelectrode arrays that have been reported in the literature. The first type consists of a bundle of individually conducting microelectrodes (carbon fibres) being sealed in an insulating material (epoxy) [379,412,413], and the second type consists of a conventional macroelectrode having coated onto it a layer of an insulating material that contains microscopic faults through which charge, or charged species, may diffuse to the electrode surface.

The development of array electrodes of the first type (microfibres sealed in epoxy) are of no relevance to this work, and will not be examined. Arrays of the second type, however, are of significant interest, as they operate by the same mechanism as the PPO electrode under consideration.

The first reported instance of partially blocked surfaces being considered as microelectrode arrays was in 1983, by Amatore et al [363]. This work did not
consider a specific chemical system, but developed theory based on a
generalised model.

Sabatani and Rubinstein [365] reported a “self assembling” monolayer-based ultramicroelectrode array based upon the adsorption of octadecyl derivatives with trichlorosilane or mercaptan head groups onto gold film electrodes. The reported “self-assembling” properties of the electrode stem from the densely packed molecules arranging themselves in a preferred orientation on the electrode surface as a result of the amphiphilicity or otherwise of the molecules’ functional groups.

Thus, it is seen that insulating coatings on conducting substrates present three attractive possibilities to the analyst:

1. The formation of a microelectrode array.
2. The incorporation of chemically specific catalysts or complexing groups.
3. The utilisation of these properties to carry out electroanalytical processes without interference from the Faradaic and non-Faradaic background currents associated with conducting polymers when likewise employed.

A further class of microelectrode array generated from the partial blocking of an electrode surface is a membrane-covered electrode that has had carbon paste (or some other conducting material) deposited into the pores, either mechanically or electrochemically, but these devices are beyond the scope of this study [376,381,382].

The significance of the microelectrode array properties of the potentiostatically-generated p-NET electrode may be appreciated if it is compared to those of Israel & Sabatani [383,365]. Although both types of electrodes may be classified as “self-assembling,” the salient difference is that the p-NET electrode is generated from an actual polymerisation process, and not simply an adsorptive process. The presence of the polymer could therefore be expected to result in enhanced chemical and mechanical stability.

Also, since its formation (the polymer) is dependant on kinetic factors (applied E) and not thermodynamic (adsorptive) processes, it could be expected to be more reproducible, particularly since these studies have established that the polymeric coating has the effect of damping any inter-electrode surface variability on the glassy carbon substrates.
 Despite the fact, however, that the PSG polymer performed better, as a microelectrode array, than the PDG polymer, subsequent studies revealed that its performance as a substrate for the mercury film that was subsequently developed in this project was inferior to that of the PDG polymer. This issue is addressed in chapter 4.

3.3.3.2. Electrochemistry of Incorporated Species

Some of the aspects of the voltammetric responses of the p-NET electrode are explainable in terms of the species that are incorporated into the polymer during its synthesis. To characterise this process, the voltammetric behaviour of the glassy carbon electrode in the presence of the matrix electrolyte (of the monomer solution) was considered.

The potential window of the methanol was first studied by examining the voltammetric behaviour of a NaClO$_4$/MeOH solution in the range 0.0 to 2.0 V (vs Ag/Ag$^+$). The NaClO$_4$ is known to not be voltammetrically active in this range, and any redox processes must therefore be solvent-based.

The result of this was a flat background with an oxidation response beginning at about 1.7 V, due to the oxidation of the methanol (fig. 3.25 - trace a). The situation is markedly different if hydroxide is used as the anion instead of perchlorate (fig. 3.25 - trace b).

Clearly, the hydroxide ion is undergoing oxidation commencing at 0.6 V, as:

$$4\text{OH}^- \longrightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \quad \text{eq. 3.6}$$

If this hydroxide oxidation response is compared with the voltammetric response in the presence of the monomer, the efficacy with which the polymeric coating shields the electrode surface from solution species becomes apparent (fig. 3.26).

In the absence of the monomer (fig 3.26 - trace a), the oxidation of the OH$^-$ reaches a maximum current of $>4$ mA (before depletion effects set in), whereas when the monomer is present in solution (fig 3.26 - trace b), and the
sweep therefore generates a polymer coating, the current in the same voltammetric regime is limited to <1 mA.

$$i \text{(mA)}$$

$$E (V \text{vs Ag/Ag}^+)$$

Figure 3.25: Cyclic voltammograms recorded at a glassy carbon electrode in (a) 0.3M NaClO$_4$/MeOH and (b) 0.3M NaOH/MeOH. Scan rate 50 mV.s$^{-1}$. Solutions deoxygenated for 10 minutes prior to scans.

In real terms the current due to the oxidation of the OH$^-$ in the latter case may be even less than this, as there is no way of knowing how much of the broad oxidation peak observed between 1.0 and 2.0V is due to this process and how much is due to the oxidation of the monomer. It is reasonable, however, to assume that the OH$^-$ oxidation is a major contributor, as the two curves are similarly shaped in this region, and this response continues to manifest when the initial monomer oxidation responses (at 400-800mV) do not.

The voltammetric response of the polymerisation process could not be examined in the absence of hydroxide, as strongly basic conditions are required for the propagation of the polymer during synthesis (sect. 3.1.2.2). Further, these data suggest that a substantial film forms well before 0.8V, as it is at this potential that the response at the naked electrode exceeds that at the polymer-coated electrode.
Figure 3.26: CV recorded at a glassy carbon electrode in (a) .3mNaOH/MeOH and (b) 0.1M NET, 0.3M NaOH/MeOH

The oxidation of the monomer at the electrode surface at the same time as oxidation of the solubilised hydroxide may be expected to result in the incorporation of a significant amount of oxygen in the polymeric matrix, and this effect was observed. Figure 3.27 shows the voltammogram recorded at a p-NET electrode in a blank solution immediately after polymerisation.

The broad reduction peak observed on the initial negative potential sweep occurs at exactly the same potential, and is of the same shape as that observed at a glassy carbon electrode in a non-deoxygenated solution (fig 3.28).

The presence of the reduction peak in a deoxygenated solution, and its disappearance on the second scan strongly suggests the presence of incorporated oxygen as an oxidative product of the methanolic hydroxide matrix of the monomer solution. Further, the magnitude of the initial reduction response, which is of about the same magnitude as in figure 3.10, suggests that significant levels of oxygen were incorporated.
Figure 3.27: CV recorded at a pNET electrode in deoxygenated 0.2M acetate buffer (pH 5.0) immediately after polymerisation. Initial scan in positive direction. Scans 1 and 2 labelled.

Figure 3.28: CV of a glassy carbon electrode in a non-deoxygenated 0.2M acetate solution (pH 5.0). First scan negative.
The disappearance of the response on the second scan (fig 3.27) may be attributed to the fact that most of the hydroxide produced by reduction of the incorporated oxygen (that which is accessible to the solution) will be stripped from the polymer by the acetate buffer matrix (pH 5.0).

A further interesting feature of figure 3.27 is the small, broad oxidation peak that manifested at 800 mV on the second positive potential sweep. The fact that it did not manifest on the first sweep implies that it is the oxidation of a reduced product of the first negative sweep.

This oxidation response is due to residual OH\textsuperscript{-} from the initial reductive sweep that is immobilised in regions of the polymer from which it does not have ready access to the solution. That this is the case is implied by the fact that it occurs at about the same potential as the OH\textsuperscript{-} oxidation in the monomer matrix solution (figure 3.25), even taking into account the 40 mV discrepancy between the reference electrodes.

Removal of this residual OH\textsuperscript{-} proved to be a difficult proposition. Although the reductive response had disappeared with the second sweep, the oxidative response persisted with repeated cycling (the absence of a visible reduction response may be interpreted in terms of the "irreversibility" of the oxygen reduction reaction and the fact that very low levels are present in the polymer matrix). This may be expected, as the OH\textsuperscript{-} may well be stabilised in the polymer matrix by ion-pair association with protonated amine groups of the polymer backbone.

Two strategies were, however, successfully employed to facilitate the OH\textsuperscript{-} removal. The Nernstian equilibrium between these two species is:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 2e^- \rightleftharpoons 4\text{OH}^- \quad E^\circ = 401 \text{ mV} \quad \text{eq. 3.7} \]

Removal of the OH\textsuperscript{-} may be facilitated by removal of the oxygen, according to Le Chatelier's principle. At the rest potential of the polymer (~300 mV), however, the equilibrium lies very much to the right, and the lowering of the [O\textsubscript{2}] produced by immersing the electrode in a deoxygenated solution is not sufficient to exert any significant influence on the equilibrium
This effect was observed; immersion of the electrode in a deoxygenated blank solution for one hour produced no change in the oxidation response.

To effect this change, then, the equilibrium must be shifted to the left either electrochemically, or with the use of a stronger deoxygenating agent than nitrogen. The former approach consisted of holding the potential of the polymer at 1000 mV for 5 minutes while the solution was purged. This resulted in an increase in the $[O_2]$ by oxidation of the $OH^-$, as equation 3.7 was shifted to the left, and, as a consequence, significant removal of $OH^-$ from the polymer (fig 3.29).

The second approach consisted of soaking the electrode in a blank solution containing excess ascorbic acid for 60s. The resultant voltammogram is shown in figure 3.30.

The highly anaerobic conditions produced by the ascorbic acid resulted in a high degree of removal of oxygen from the polymer, as evinced by the loss of the oxidation peak at 800 mV. Also of interest is the flatter background in the negative potential region, indicating that a residual oxygen reduction response was apparent prior to the ascorbic acid treatment. The incorporation of the oxygen into the polymer was reversible, as an electrode that was left to stand overnight in a non-deoxygenated solution manifested both the oxidation and reduction peaks currently under discussion.

It will be noted that both figure 3.29 and 3.30 manifest the redox couple around 200 mV that is discussed in section 2.3.1.1.

To demonstrate this phenomenon more overtly, however, three cycles from -1000 to 2000 mV were performed in the acetate blank with the final scan finishing at 2000 mV. The electrode was then removed from the solution, placed in a nitrogen-purged acetate solution and cycled immediately (fig 3.31), with a large and obvious oxygen reduction response manifesting.

The clear conclusion to be drawn from this and the previous voltammograms, therefore, is that oxygen is incorporated into the p-NET as an anodic product of $OH^-$ oxidation during the polymerisation procedure, and that, although the bulk of it is easily removed by nitrogen purging and voltammetric cycling, elimination of all electroactive traces of these species requires the application of specific processes.
Figure 3.29: CV of p-NET electrode in deoxygenated 0.2M acetate buffer (pH 5.0) before (solid line) and after (shaded line) polarisation of the electrode at 1000 mV for 5 minutes.

Figure 3.30: CV of p-NET electrode in deoxygenated 0.2M acetate buffer (pH 5.0) before (solid line) and after (shaded line) immersion of the electrode in an acetate buffer (0.2M, pH = 5.0) containing excess ascorbic acid.
Effect on voltammetric background (vs GC)

The three BAS glassy carbon electrodes used throughout this study were characterised, with respect to their voltammetric backgrounds, in section 2.3.1. Before the polymer coating on these electrodes could be further modified for use as substrates for ASV, it was incumbent to determine the effect that it had on the voltammetric background, as it is a clear requirement of the modifying film that it not introduce significant background currents. As in section 2.3.1, this was determined by conducting linear sweeps and measuring the slope of the resulting background (charging) current.

All parameters and solutions examined were identical to those examined for the conventional electrode (sect. 2.3.1), so that a direct comparison could be drawn. The results are presented in tabular form in table 3.1.
Table 3.1: Comparison of slope of background currents for glassy carbon electrode #1, in various solutions. All results are in μA.V⁻¹.

**Electrode 1:**

<table>
<thead>
<tr>
<th>Sweep Rate (mV.s⁻¹)</th>
<th>10</th>
<th>10²</th>
<th>10³</th>
<th>10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>borax (pH 8.0)</td>
<td>0.09</td>
<td>0.68</td>
<td>4.8</td>
<td>34</td>
</tr>
<tr>
<td>0.1M NaNO₃</td>
<td>0.02</td>
<td>0.53</td>
<td>4.2</td>
<td>28</td>
</tr>
<tr>
<td>1.0M NaNO₃</td>
<td>0.07</td>
<td>0.61</td>
<td>4.3</td>
<td>28</td>
</tr>
<tr>
<td>0.2M Ac⁻/HAc</td>
<td>0.28</td>
<td>1.5</td>
<td>5.8</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 3.2: Comparison of slope of background currents for glassy carbon electrode #2, in various solutions. All results are in μA.V⁻¹.

**Electrode 2:**

<table>
<thead>
<tr>
<th>Sweep Rate (mV.s⁻¹)</th>
<th>10</th>
<th>10²</th>
<th>10³</th>
<th>10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>borax (pH 8.0)</td>
<td>0.32</td>
<td>1.2</td>
<td>9.4</td>
<td>39</td>
</tr>
<tr>
<td>0.1M NaNO₃</td>
<td>0.40</td>
<td>1.6</td>
<td>6.8</td>
<td>31</td>
</tr>
<tr>
<td>1.0M NaNO₃</td>
<td>0.32</td>
<td>2.0</td>
<td>12</td>
<td>28</td>
</tr>
<tr>
<td>0.2M Ac⁻/HAc</td>
<td>0.76</td>
<td>3.5</td>
<td>14</td>
<td>56</td>
</tr>
</tbody>
</table>
Table 3.3: Comparison of slope of background currents for glassy carbon electrode #3, in various solutions. All results are in μA.V⁻¹.

**Electrode 3:**

<table>
<thead>
<tr>
<th>Sweep Rate (mV.s⁻¹)</th>
<th>10</th>
<th>10²</th>
<th>10³</th>
<th>10⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>borax (pH 8.0)</td>
<td>1.9</td>
<td>9.7</td>
<td>36</td>
<td>37</td>
</tr>
<tr>
<td>0.1M NaNO₃</td>
<td>1.6</td>
<td>8.7</td>
<td>35</td>
<td>111</td>
</tr>
<tr>
<td>1.0M NaNO₃</td>
<td>1.7</td>
<td>11</td>
<td>51</td>
<td>150</td>
</tr>
<tr>
<td>0.2M Ac/HAc</td>
<td>0.2</td>
<td>0.9</td>
<td>5.5</td>
<td>40</td>
</tr>
</tbody>
</table>

An analysis of the data in table 3.1 reveals a number of salient features:

1. In general, the polymer-coated electrodes had lower background currents than the uncoated electrodes at the lower sweep rates. In some cases, the polymer-coated electrode also had lower background currents at the higher sweep rates, although a more typical result was that the background currents of the polymer-coated electrodes would exceed that of the uncoated electrodes at the higher sweep rates (fig. 3.32).

2. The polymer coating increased the inter-electrode reproducibility of the background currents. This may be seen if figure 3.33 (uncoated) is compared with figure 3.34 (polymer-coated).

That is, the difference between the coated and uncoated electrodes was greatest for the glassy carbon electrode with the lowest background currents (#1) and least for the electrodes (#3) with the highest background current. With electrode #3, the polymer-coated electrode has lower background currents with all solutions and sweep rates, whereas for electrode #1 the polymer-coated electrode had lower background currents only at the very lowest sweep rates.
Figure 3.32: Double log plot of slope of background currents of bare and polymer-coated BAS#2 GC electrode in $M$ NaNO$_3$.

Figure 3.33: Double log plot of slope of background currents vs sweep rate at uncoated GC electrodes #1, 2 and 3 in 0.2$M$ acetate buffer.
The cause of the increase in the inter-electrode variability occasioned by the polymer coating is likely to be due to the simple fact that most of the electrode is covered by a polymer. That is, the inter-electrode variability produced by the varying surface chemical compositions of the glassy carbon electrodes (chapter 2) is swamped because these surface functionalities are now covered with a polymer, and the adsorbing ions that produce the capacitance current (with a ramping potential) are limited, in their interaction with the surface, to regions of the electrode (polymer) surface where faults and micropores occur (sect. 3.3.3.1).

3.3.3.4. ASV Studies

The p-NET electrode, like the bare glassy carbon electrode, is not to be given serious consideration as a substrate for ASV, as it possesses none of the desirable amalgam-forming properties of mercury electrodes (chapter 1). For the sake of completeness, however, with respect to an examination of the effect of a surface-bound, electroactive species at the p-NET electrode, and to provide a basis for comparison with the mercury-coated p-NET, such a study was undertaken.
The ASV was, as in chapter 2, performed with Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ in solutions containing both each metal individually, and all metals simultaneously. Each is examined in turn.

**Cadmium:**

As with the bare electrode, the polymer-coated electrode manifested gross catalytic hydrogen reduction in the presence of trace levels of electrodeposited cadmium (20ppb). Its stripping response, however, was manifestly different, as is seen in figure 3.35. At a [Cd$^{2+}$] at which the bare electrode manifested a tangible response (fig 3.35 - solid line), the response at the polymer-coated electrode appeared as nothing more than a shoulder, which at higher concentrations grew into a small peak (fig. 3.36).

![Figure 3.35: Comparative stripping responses of 500ppb Cd$^{2+}$ at an uncoated (solid line) and polymer-coated (shaded line) GC electrode.](image)
Lead:

The stripping responses of the lead at the polymeric electrode were smaller and broader than those at the uncoated electrode. Figure 3.37 shows the stripping response at the polymeric electrode for a 500ppb solution, and figure 3.38 compares the calibration curves obtained at the uncoated and polymeric electrodes.
Figure 3.37: Stripping response of 500ppb Pb$^{2+}$ at a p-NET coated GC electrode.

Figure 3.38: Comparative calibration curves for Pb$^{2+}$ when stripped at uncoated and p-NET-coated GC electrodes.
Copper:

The stripping response at the polymeric electrode, while being less sensitive initially than that at the uncoated electrode, did not plateau at higher concentrations, as was the case with the latter. The respective calibration curves of the two electrodes are compared in figure 3.39.

As well as this, the stripping response at the polymeric electrode, although relatively broad ($b_{1/2} > 100\text{mV}$), did not suffer from any of the gross broadening (and tailing of response) effects as occurred with the uncoated electrode (fig. 2.11). The stripping response at the polymeric electrode is shown in figure 3.40.

![Graph showing comparative calibration curves for Cu$^{2+}$ stripping responses at uncoated and p-NET-coated GC electrodes.](image)

**Figure 3.39:** Comparative calibration curves for Cu$^{2+}$ stripping responses at uncoated and p-NET-coated GC electrodes.
Multielement deposition:

As with the multielemental codeposition at the uncoated electrode, the only metal that produced a tangible stripping peak at the polymeric electrode was copper, with the voltammograms also displaying the tailing at negative potentials that is characteristic of cadmium deposition.

The magnitude of the copper peak at the polymeric electrode (with multielement deposition) was smaller than that at the uncoated electrode, as shown by the comparative calibration curves in figure 3.41.

An interesting observation with the polymeric electrode was that the catalytic hydrogen response diminished as the level of deposited metal increased. This is illustrated in figure 3.42, where the responses for the two electrodes are compared (at 500ppb mixed metal concentration).
Figure 3.41: Comparative calibration curves for Cu$^{2+}$ stripping responses at uncoated and p-NET-coated GC electrodes in the presence of equal concentrations (mass/vol) of Cd$^{2+}$ and Pb$^{2+}$.

Figure 3.42: Comparative stripping responses at uncoated (solid line) and p-NET-coated GC (shaded line) electrodes for 500ppb Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$. 
These data are consistent with the microelectrode-array model for the polymeric film. The fact that cadmium requires high concentrations to produce a tangible stripping response (on the glassy-carbon) suggests that its oxidative kinetics at glassy carbon are poor, and that the process is not facilitated until sufficient cadmium has deposited on the electrode surface for multiple layers to form, such that the cadmium strips from, effectively, a cadmium electrode.

Such a comprehensive coating is not required for the catalytic hydrogen reduction process, since the reduction of hydrogen at cadmium (or indeed at most solid metallic substrates) is highly facile with respect to glassy carbon, and the concomitant thermodynamic advantage will result in hydrogen preferentially undergoing reaction at isolated cadmium nucleation centres on the carbon surface.

Clearly, therefore, the deposition of metallic cadmium in the polymeric micropores will facilitate the hydrogen reduction process, while inhibiting the formation of discrete cadmium films on the electrode surface.

The stripping of lead at the glassy carbon electrode is a more facile process than that of the cadmium, as evinced by the fact that it produces a well-defined stripping response (fig. 2.13). As a consequence of this, the presence of the polymeric film serves only to limit the amount of lead that may deposit, and the observed loss of sensitivity is the result.

Copper, unlike cadmium, is a metal where the presence of multiple metallic layers is not required to produce a stripping response, and where these layers present a palpable problem when present, with the onset of both plateauing and broadening of the stripping response (fig. 2.14). This explains the absence of the plateauing effect in figure 3.39 for the polymeric electrode since, as with the cadmium, these layers do not have the opportunity to form on the electrode surface.

It is interesting to note that the discrepancy in sensitivity between the electrodes, at the lower concentrations, is more pronounced with the copper than with the lead, although the mechanism of the effect (limited amount of material deposited in the polymeric micropores) is likely to be the same.

Notably, all three metals examined, (Cd, Pb and Cu) are solids in their reduced state, and their behaviour is interpreted in these terms. In particular, the polymer film was seen to inhibit the deposition of these metals, as might
reasonably be expected given that most of the electrode surface is covered with a polymer film.

The effect of the polymer film on the electroactivity of the (liquid) mercury that is deposited on the electrode surface to form the MTFE, is discussed in chapter 4.

3.3.4. VISUAL CHARACTERISATION

The polymer film forms on the electrode as a pale orange coating which is only clearly visible when coated onto a platinum substrate, and it is difficult to see against the black background of the glassy carbon.

When viewed microscopically, the film was smooth and featureless, following the contours of the underlying substrate (fig 3.43).

Figure 3.43: Microscopic image of p-NET/GC electrode. Microscopic details in section 2.2.2. The small, black marks are artefacts produced by the photographic assembly. Scale: 1cm = 10μm.
Attempts to view the polymer film with SEM resulted in the polymer film cracking and peeling from the surface as a result of the high vacuum employed, and the fact that it was coated onto the less adherent platinum.

3.3.5. CHEMICAL DERIVATISATION OF P-NET

For a secondary amine such as p-NET to be derivatised to the dithiocarbamate, three things are simultaneously required of the derivatising solution:

1. The presence of CS$_2$ as the group to be added to the polymer.
2. The presence of a strong base to deprotonate the amine group.
3. The presence of a solvent capable of solubilising both these species.

The mechanism for this reaction is given in figure 3.44.

O’Riordan and Wallace [384] were the first workers to examine the addition of a dithiocarbamate group to the amine functionality of p-NET, and in an attempt to satisfy the three criteria outlined above, three solutions were examined:

**Solution 1:**
- 50 mL benzene
- 10 mL carbon disulphide
- 10 mL 0.3M NaOH in MeOH
- 10 mL 2-propanol

**Solution 2:**
- 50 mL benzene
- 10 mL carbon disulphide
- 10 mL saturated NaOH in benzene
- 10 mL ethanol

**Solution 3:**
- 50 mL benzene
- 10 mL carbon disulphide
- 10 mL 0.3M NaOH in 2-propanol
Figure 3.44: reaction mechanism for derivatisation of poly-N-ethyltyramine to poly-N-ethyl-N-dithiocarbamatotyramine.
Of the three solutions, solution 2 was inhomogenous, solution 1 resulted in the removal of the polymer from the electrode surface, and solution 3 was found to perform the derivatisation adequately. This is in agreement with the work of O'Riordan and Wallace [384], who used this solution to derivatise their p-NET electrode to a dithiocarbamate.

O'Riordan and Wallace [384] attributed the removal of the polymer with solution 1 to it dissolving in the solution. Since, however, the polymer is clearly insoluble in methanol (since this is its very mechanism of polymerisation), a more likely explanation involves the poor mechanical adhesion of the polymer to the platinum substrates that were used for this study. This is confirmed by the fact that solution 1 was investigated with a p-NET coated glassy carbon electrode, and the polymer remained on the electrode surface after the derivatisation step, despite the fact that the mercuric deposition step was not successful (chapter 4).

The author investigated other approaches to derivatisation (with dithiocarbamate) other than these three, although none were successful (in terms of their ability to heterogeneously complex mercury - see chapter 4). Consequently, solution 3 was the one that was used throughout this work for all characterisation and metal deposition studies. Some optimisation of the procedure employed by O'Riordan [384] was, however, required, and is examined subsequently.

3.3.5.1. Optimisation of Chemical Procedure

The techniques outlined by O'Riordan and Wallace [384] consisted of each of the solutions being prepared separately before being added in the order: benzene, carbon disulphide, NaOH/2-propanol. The difficulty with this technique centred on the solubility of the NaOH in the as-made solution.

Specifically, when the NaOH/2-propanol solution was added to the colourless mixture of the C₆H₆/CS₂ two things happened immediately:

1. A fine precipitate of NaOH formed. Owing to the fact that the solution was stirred during this step and throughout the subsequent derivatisation, the solution retained a translucent consistency throughout the procedure.
2. A yellow colour formed in solution. This is due to the formation of a xanthate by the process:

\[
\begin{align*}
\text{HO}^+: & \quad \xrightarrow{\text{CS}_2} \quad \text{S} = \text{S}^- \quad \text{HO}^+ \\
\text{CH}_3\text{HCH}_3 & \quad \quad \quad \text{C} \quad \quad \quad \text{O}^- \quad \quad \text{CH}_3\text{HCH}_3
\end{align*}
\]

\[\text{NaOH} \rightarrow \text{S} = \text{S}^- \quad \text{Na}^+
\]

---

**Figure 3.45**: Formation of xanthate in solution

The electrodes produced by this process had poor reproducibility, as characterised by their mercury chelating properties. Further, the derivatisation solutions themselves had poor reproducibility, despite the fact that the volumes were dispensed by burettes. A precipitate did not always form, and when it did not, the intensity of the yellow colour of the solution varied significantly. This could be attributed to varying concentrations of the NaOH in the 2-propanol.

Since the 2-propanol/NaOH solution was not stable upon storage in either glass (etching of surface) or plastic (formation of an unidentified brown substance in solution), it had to be freshly made before each derivatisation. As the concentration of the NaOH never quite reaches 0.3M in the 2-propanol, and to avoid contamination problems introduced by the weighing of exact amounts, saturated NaOH in 2-propanol was used in its place. The problem arose from the fact that the rate of solubilisation of the NaOH in the 2-propanol was extremely slow, and sometimes the concentration had not reached saturation point after substantial periods (30 minutes) of stirring or ultrasonication.

The irreproducibility therefore arose from the fact that the deprotonation of the polymeric amine group took place at different rates (as the [OH⁻] varied) and that the solid NaOH particulates in solution attacked the electrode surface, or in some way interfered with the derivatisation procedure.

A simple solution to this problem involved the addition of the three neat solvents to the derivatisation vessel followed by the addition of a single grain of
NaOH. Under the mild convection conditions employed for this procedure, this had the effect that very few NaOH particulates developed, and those that did stayed close to the bottom of the vessel and well away from the electrode surface. This procedure served the purpose of maximising the \([OH^-]\) at a reproducible level due to the saturation conditions, without introducing an excessive number of particulates into the solution.

3.3.5.2. Characterisation of derivatisation process

Direct characterisation of the derivatised polymeric surface was rendered difficult by the fact that it was in the solid state. In particular, it was incumbent to prove that the species present on the electrode surface was, in fact, dithiocarbamate, and not some other sulphur-containing species. This rendered characterisation techniques such as EPMA and XPS of little use, as the surface had to be characterised \textit{in-situ}, in the absence of either polymeric drying effects or O$_2$ oxidising effects.

As a consequence of this, the method that was used involved the derivatisation and subsequent characterisation of the monomer (in solution). In this form it lent itself to characterisation by both NMR and mass spectrometry.

Details of the experimental procedure employed are given in the experimental section. The reaction scheme is as set out in figure 3.46.

The NMR resonances recorded were $\delta$ 7.1(m,2H), 6.8 (m,2H), 5.8(m,3H), 2.9 (q,2H), 2.5(s,3H), 1.2 (t,3H). These resonances confirm the structure of V.

Mass spectra were recorded in both negative and positive chemical ionisation modes, with isobutane reagent gas. A sample result is given in figure 3.47.
Figure 3.46: Reaction pathway for formation of derivatised N-ethyltyramine adduct
3.3.5.3. Contamination Problems

Of all the steps in the synthesis of the p-NET electrode, both prior and subsequent to this step, the derivatisation step was that which was most prone to the introduction of unwanted contaminants to the system. The reason for this stems from the fact that the dithiocarbamate groups grafted onto the electrode form extremely stable complexes with Hg$^{2+}$, Ag$^{+}$ and Cu$^{2+}$, and moreover, they have 24 hours to do it. It may be seen, therefore, that impurities present at trace, or even ultra-trace, levels could introduce significant problems.

This was ably demonstrated by early attempts to successfully synthesise this electrode, for which very little mercury was seen to deposit subsequent to the derivatisation step. A systematic investigation of the possible sources of contamination revealed that the problem lay with the A.R. grade NaOH that was used. This is not surprising, as an assay of this compound (BDH-A.R. Grade) lists the concentration of copper as $5 \times 10^{-4}$%.
This translates to a level of about 9 ppb Cu\(^{2+}\) in the derivatisation solution. Over a period of 24 hours it is therefore reasonable to suggest that a significant proportion of the copper ions will be complexed by the dithiocarbamate groups.

Of all the heavy metals present, the one that is of most concern is copper, since it occurs abundantly at trace levels in many systems, and in this case is the third most strongly complexing metal with dithiocarbamate (log K=28.8 [385]), behind Hg\(^{2+}\) and Ag\(^{+}\). The Hg\(^{2+}\) is clearly not a problem, as it is the metal that will ultimately be complexed to the surface anyway, and Ag\(^{+}\) does not occur, even at trace levels, as a contaminant in most systems.

To examine the electrode surface with respect to possible copper contamination, Fast Atom Bombardment Mass Spectrometry (FAB/MS) was employed, and the spectrum is seen in figure 3.48.

The M and M+2 peaks at m/z = 63 and 65 respectively are characteristic of copper and confirm the presence of copper on the electrode surface. A further problem introduced by copper is that the complex that it forms with the dithiocarbamate is sufficiently stable that it will not be displaced by Hg\(^{2+}\). This means that an electrode so contaminated has been irreversibly poisoned.

This problem was solved by using "Baker Analyzed" NaOH in the derivatising solution. Although the "Baker Analyzed" NaOH actually has twice the level of copper of the BDH product, it has a great deal more mercury present, translating to concentrations in the final solution of 20 and 200ppb respectively. As a consequence of this, it may be expected that whenever dithiocarbamate sites do become available for metal complexation, the mercury will bind in preference to the copper by virtue both of its greater concentration and its greater affinity for the ligand.

This reagent was successfully employed throughout the remainder of this study.
3.3.5.4. Alternative Derivatisation Processes

The obvious problem with the derivatisation process previously described is that it takes 24 hours, which clearly mitigates against the quick manufacture of the electrode. In an attempt to alleviate this problem, three alternative derivatisation methods were examined.

It should be noted that an inalienable difficulty with this study arose from the fact that the system was heterogeneous, and many well established organic reaction mechanisms that are reliant upon mechanisms facilitated by homogenous reactants may be totally inapplicable. As a consequence of this, the mechanistic rationalisation of the derivatisation processes used in this project must be approached with some caution.

The three alternative derivatisation processes studied and the results obtained thereby are presented:

1. This method was based on a review by Kitson [314] where, for a homogeneous system, a secondary amine was reacted with CS₂ added to an aqueous solution of NaOH, with the proposed mechanism being
When this procedure was employed in this study, the solution took on an orange/brown colour after a few minutes. After the derivatisation period, the electrode showed no propensity whatever to chelate metals. If dithiocarbamate groups were therefore grafted onto the electrode surface by this method, then their orientation or stoichiometry was such that the metal complexes that were subsequently formed were not electroactive.

2. The second method that was employed was a modification of the standard method and consisted simply of the elimination of benzene from the derivatisation solution. The rationale behind this process was an attempt to speed up the derivatisation process by ensuring higher concentrations, in the derivatising mixture, of CS₂ and NaOH.

This solution formed a much more intense yellow colour than that of the standard derivatisation solution, a direct consequence of the higher concentration of xanthate in solution. This electrode did display evidence of the presence of surface dithiocarbamate groups (mercury complexation), but the method was rejected as an alternative to the standard method for two reasons:

(i). The mercury film electrode subsequently formed on this electrode had inferior sensitivity to that formed by the standard method.

(ii). The process still took 24 hours of derivatisation to reach this stage (its performance was monitored after 3 and 18 hours) and does not therefore represent an improvement in terms of time considerations.

3. The third procedure consisted of a further simplification of method #2, in that the 2-propanol was eliminated from the reaction mixture.

No yellow colour, as had formed in the solutions in which the 2-propanol was present, was observed in this solution, owing to the absence of the xanthate. No evidence (mercury deposition studies) of surface dithiocarbamate groups was seen for this electrode.
It is worth noting, with respect to the grafting of the dithiocarbamate groups onto the electrode surface, that the mere presence of these groups is not sufficient for the case at hand. To possess analytical utility for the polymeric electrode under consideration, the dithiocarbamate groups must, firstly, be available to the solution to facilitate metal complexation and, secondly, must bind the metals in a form such that they are electroactive. This applies with respect to both the effect of the derivatising process on the complexing capabilities of the electrode and the morphology and/or electroactivity of the underlying polymeric substrate.

None of the alternative methods examined were able to bind mercury in a more analytically useful form, and were therefore pursued no further.
3.4. CONCLUSIONS:

These studies have established that electrochemically synthesized poly-N-ethyltyramine will deposit on an electrode as a thin, transparent film. Its microscopic structure consists of a series of holes, or faults, in the polymer coating that enable it, when synthesized potentiostatically, to exhibit the electrochemical characteristics of a microelectrode array. In this respect it is the first reported example of a self-assembling microelectrode array that is generated in-situ.

During synthesis the polymer coats, and passivates, the electrode surface very quickly, and incorporates oxygen (as the product of hydroxide oxidation) into its structure as part of this process.

The polymer may be subsequently derivatised, at the amine groups, to form dithiocarbamate functionalities.
Chapter 4:

Development of a Chemically-Modified Mercury Thin Film Electrode
4.1. INTRODUCTION

Chapter 3 outlined the development and characterisation of a dtc-derivatised poly-N-ethyltyramine electrode (fig. 3.45). This chapter details the deposition of Hg$^{2+}$ onto this substrate and its subsequent use as an MTFE for ASV in both stationary and flowing solutions.

ASV in stationary solutions is examined both with stationary and rotating electrode systems. The stationary electrode studies were required to allow the conclusions gleaned from chapter 2 to be employed; namely, the relationships between relative film thicknesses and performance of the MTFE for each of cadmium, lead and copper.

The studies at the RDE were carried out in order to assess the performance of the p-NET-MTFE under conditions of high convection (as opposed to the low convection stationary electrode system). Also, the RDE is by far the most common electrode to be employed as an MTFE substrate in the literature.

The experimental tools which were used throughout this study were potentiometry and voltammetry. The potentiometry was used to monitor the potential of the electrode prior to, and immediately after, the voltammetric scans, and the voltammetric scans were used to induce changes in the oxidation states of the mercury, with the production of the accompanying anodic and cathodic current responses.

The p-NET-MTFE is characterised with respect to both its performance and stability, and it also examined visually with optical microscopy.
4.2. EXPERIMENTAL

4.2.1. ELECTRODES

Working Electrodes:

Electrodes used for stationary electrode studies were the BAS glassy carbon electrodes as described in chapter 2. The glassy carbon electrode used for the rotating electrode work was the Metrohm 636 assembly as described in chapter 2.

The platinum wire working electrode was made in the laboratory, and consisted of a platinum wire sealed in glass, the exposed wire being of diameter 0.5 mm and length about 8 mm (approximate surface area = .14cm²).

The polymer modified electrodes used were glassy carbon electrodes coated with poly-N-ethyl-N-dithiocarbamatotyramine as described in chapter 3. All polymer-modified MTFEs utilised a potentiodynamically-synthesised polymeric substrate, as is also described in chapter 3.

The working electrode used for the flowing solution studies was a glassy carbon electrode as part of a ™DIONEX electrochemical flow cell.

Counter Electrode:

The counter electrodes used for the stationary and rotating electrode studies, and for the polymerisation, were identical to those described in chapter 3.

Reference Electrode:

The reference electrodes for the stationary and rotating electrode studies, and for the non-aqueous work, were identical to those described in chapter 3.
4.2.2. INSTRUMENTATION

Electrochemical Instrumentation:

The electrochemical instruments used for all voltammetric studies were a BioAnalytical Systems 100A Electrochemical Analyser and a ™ElectroLab. The potentiometer used throughout this study was a Hewlett-Packard 3468A multimeter with an input impedance of $10^{10}$ Ω.

Optical Imaging System:

The optical imaging system used was that which is described in chapter 2.

Atomic Absorption Spectrometer:

The atomic spectrometer used for the mercury solution analyses was a Varian SpectrAA-20 with a VGA-76 vapour-generation accessory.

4.2.3. SOLUTIONS

Electrolyte:

The acetate buffer (pH 5.0) used is described in chapter 2. The “Chemtronics” electrolyte was made up according to the recipe in the instruction manual for the PDV 2000 Portable Digital Voltammeter (Chemtronics Ltd. - Western Australia), and was comprised as follows: 117.0g NaCl, 35.0g Ascorbic Acid, 7.7g NaOH in 500 mL type 1 Milli-Q water.

Mercury Plating Solutions:

The mercury plating solutions used were identical to those used and described in chapter 2.
4.2.4. ELECTROCHEMICAL CELLS AND GLASSWARE

Electrochemical Cells:

The cells used for the stationary and rotating electrode studies, and for the polymerisation procedures, were identical to those described in chapter 2. The cell used for synthesising the polymer on the flow-cell electrode was a large watchglass. The procedure is described.

The flow cell that was used was a \textsuperscript{TM}DIONEX flow cell.

4.2.5. EXPERIMENTAL PROCEDURES

Electrode Pretreatment:

Pretreatment procedures for the glassy carbon electrodes consisted of alumina polishing and subsequent ultrasonication, as described in chapter 2.

Polymerisation Procedures:

Polymerisation and derivatisation procedures were identical to those described in chapter 3, with the exception of the polymerisation of the \textsuperscript{TM}DIONEX flow-cell.

The logistics of this process were very complex, due to the size and shape of the cell and the arrangement of the electrodes therein. The electrodes, which are imbedded in the upper half of the Kel-F body of the cell, cannot be exposed to the monomer solution by the normal arrangement, as the body of the cell will not fit in any of the glass electrochemical cells normally used for this process. Further, the use of a very large electrochemical cell introduced logistics problems of its own, as this would require large volumes of the monomer solution, which due to its non-availability commercially, was at a premium.

To circumvent these problems, a special cell was used to simultaneously provide a large surface area and low solution volume. The arrangement is illustrated in figure 4.1.
Derivatisation Procedure:

For the BAS and Metrohm glassy carbon electrodes, the electrodes were suspended from customised nylon electrode holders into 100mL erlenmeyer flasks for 24 hours, with gentle stirring. The arrangement was such that it was airtight. This was a consideration both from the point of view of the volatility of the CS$_2$ as well as the possibility of trace contaminants entering the system.

For the ™DIONEX flow cell, alligator clips were attached to the electrode connection points, and the cell suspended from the top of a sealed quickfit glass jar such that only the lower electrode surfaces were immersed in the solution. The alligator clips were attached to bundles of carbon fibre, and the carbon fibres jammed in position by the lid of the flask.

Figure 4.1: Experimental setup for the polymerisation procedure with the ™DIONEX flow cell.
Mercury Deposition Procedure:

This consisted of removal of the polymer electrode from the derivatisation solution, rinsing with copious amounts of, firstly, 2-propanol and, secondly, water, before immersion in a stirred 100ppm Hg$^{2+}$ solution (in the acetate buffer) for a period of at least 20 minutes.

Voltammetric Conditions:

Individual potential windows and waveform parameters are described in the appropriate sections. Unless stated otherwise, however, the voltammetric scan rate employed for all (LSV) determinations was 1000 mV.s$^{-1}$. Where the ™ElectroLab was used, the step width, height, and sampling points were identical to those employed in chapter 2.
4.3. RESULTS AND DISCUSSION

The mercury, unlike a conventional MTFE, is deposited chemically, with no applied potential, and is bound to the surface by complexation with the surface dithiocarbamate groups. For the p-NET-dtc-MTFE to be fully characterised, it is necessary to determine the oxidation state of the surface-bound mercury initially, during, and after use for ASV, as well as the physical appearance of the as-formed mercury film and the performance of the electrode for ASV. These parameters are considered in turn.

Prior to this, however, attention is given to the deposition conditions, particularly with respect to pH, in order to justify the conditions that were selected for this electrode.

4.3.1. SELECTION OF pH FOR MERCURY DEPOSITION

The work of Barnes et al [332,334,337,339] has established that the pH range over which the metallic ions may be deposited at a surface-bound dithiocarbamate functionality is quite broad, essentially encompassing the pH range 4-10. For the purposes of this study, it was therefore necessary to select an optimum pH within this range at which to deposit the Hg$^{2+}$.

At high pH the mercury forms a Hg(OH)$_2$ complex. This complex, although soluble, has a pH-dependent stability constant that is given by the expression [386].

$$\log \left( \frac{[\text{Hg(OH)}_2]}{\text{Hg}^{2+}} \right) = -6.09 + 2\text{pH}$$  \hspace{1cm} \text{eq. 4.1}

This means that from about pH 3.04 the Hg(OH)$_2$ complex is the predominant solution species.

This does not present a problem in terms of the complexation process at the dithiocarbamate site, as the stability constant for the Hg$^{II}$-dtc complex is
many orders of magnitude higher (10^{39.1}[310]) than that of the hydroxide complex, and the complexation of the free Hg^{2+} will result in the Hg(OH)_2 dissociating.

At high pH, despite lower concentrations of free mercuric ion, the dithiocarbamate complexation will still dominate, and the upper pH limit must be set by factors other than the dithiocarbamate complexation process, such as, for example, the formation of colloidal metal hydroxides.

At low pH, two considerations influence the process. The first of these concerns the acidic digestion of the dithiocarbamate group. As was seen, however, in section 3.1.1.2, the heterogeneous secondary dithiocarbamate species is stable to quite low pH, and although this has never been specifically studied, pH of 1 or 2 seem not to present a problem.

The second, and more profound, consideration respects the ability of the dithiocarbamate species to complex the mercury. Since it is the conjugate base of the dithiocarbamic acid that complexes the metal, it is apparent that it must be in its deprotonated form:

\[
R-C=S \quad \text{↔} \quad R-C=S^- + H^+ \quad K_a = ?
\]

**Figure 4.2: Dissociation of 1,1-dithiolate**

The salient feature of figure 4.2 is that part of the R group is the amine function and, as Zahradnik & Zuman [318] have pointed out, this group is more basic than the thio group, and it is the amine that is protonated in the protonated form of the dithiocarbamic acid (although Bode [342] tries to rationalise the two).

In this case, however, with the heterogeneous system, and as has been strongly implied by the stability of these systems to acidic attack, the amine function is sterically blocked, and under these circumstances it is reasonable
to assume that the thio group will become the dominant acid/base functionality.

Given this consideration, and that all the reported values [310] for acidity constants of dithiocarbamic acids are for homogeneous systems, it becomes difficult to predict the $K_a$ values for the thio acid functionality (hence the question mark in figure 4.2), other than to say that it will be greater than that of a similar thio acid compound (i.e. not a dithiocarbamate) due to the inductive effect of the adjacent nitrogen.

As well as this, it becomes difficult to predict the effect of the heterogeneous immobilisation of the acid group on its acid-base properties.

In terms of the p-NET, the reported compound that most closely resembles it (in terms of electronic density on the functional group) is diethyldithiocarbamate, which has a reported p$K_a$ of 4.0 [310]. This figure may reasonably be assumed to be within one pH unit of the true p$K_a$ of the immobilised thioacid, taking into account the quantitative difficulties outlined above.

Initial experimental work was carried out at pH 4.0, with mixed results. When mercury deposition was carried out at this pH, the results were highly irreproducible. On some occasions the polymer adequately complexed the mercury, whereas on other occasions it gave no indications whatever of having complexed mercury, and all states between these two extremes were variously observed.

The irreproducible results at pH 4.0 may be understood if this was, in fact, very close to the p$K_a$ of the thioacid, as small fluctuations of pH may have resulted in large fluctuations in the number of thioacid sites in the deprotonated state. As a consequence of this, the pH that was selected for the mercury deposition was 5.0, which is within the pH range that is commonly used for the deposition of this metal, and other metals, at dithiocarbamate sites in heterogeneous systems [330,332,334,335,337,339,387].

This pH simultaneously achieves complete deprotonation of the thioacid sites, while maximising the favourability of the dithiocarbamate complexation process over the hydroxide complexing process. Further, no extraneous insoluble metallic hydroxides are present at this pH.
4.3.2. OXIDATION STATES OF SURFACE-BOUND MERCURY

Mercury(II)-dtc complexes are the most stable dithiocarbamate complexes known, and the only form in which mercury binds to dithiocarbamate [310,388-390].

In this case, however, the complex is bound to an electrode that is exposed to externally applied electrical potentials spanning quite a large range in both positive and negative directions. It is, consequently, of interest to examine the changes in oxidation state or states induced in the Hg\textsuperscript{II}-dtc complex by these applied potentials. For example, are the redox processes confined exclusively to the mercury, or does the dithiocarbamate participate in ligand-based redox couples, as is the case with homogeneous mercury dithiocarbamates [317]?

The electrochemical responses of both the free and complexed ligand (in solution) have been examined as reviewed in section 3.1.1. The electrode under consideration, however, introduces the special consideration that it is a heterogeneous system, and has therefore not, to date, been the subject of an electrochemical study, as the only heterogeneous systems that have been reported are resin-based chromatographic systems (sect. 3.1.1.2).

One possibility, in terms of surface redox processes at this electrode, is the formation of a thiuramdisulphide (tds) from adjacent dithiocarbamate groups with the application of an oxidising potential:

\[
2 \text{R}_2\text{NC} \overset{\text{ox}}{\rightarrow} \text{R}_2\text{NC} - \text{S} = \text{S} - \text{CNR}_2 + 2e^-
\]

**Figure 4.3:** Oxidation of dithiocarbamate to thiuramdisulphide

This was examined voltammetrically in this study.

The open circuit potential of the p-NET-dtc electrode in the deoxygenated 0.2\textit{M} acetate buffer solution (pH 5.0) was 120mV vs Ag/AgCl. The electrode
was scanned positive from this point in an attempt to induce the oxidation of the dithiocarbamate to the thiuramdisulphide. Up to the point at which O\textsubscript{2} evolution commenced (1.8V), no oxidation processes were seen.

A negative scan likewise failed to produce any reduction responses prior to H\textsubscript{2} evolution (-1.4V), and an electrode that had been treated in this manner showed no less a tendency to deposit Hg\textsuperscript{2+} than one that had not been so treated.

From this it may be seen that in the potential range available in aqueous solutions with this electrode (-1.4V to 1.8V), no redox processes may be induced at the surface-bound dithiocarbamate sites. This is not unreasonable since the oxidation or reduction of these sites necessitates a dynamic mobility which the surface-bound groups would be unlikely to possess.

From figure 4.3 it may be seen that the formation of the thiuramdisulphide bridge requires the presence of adjacent dithiocarbamate groups [321] with sufficient flexibility and proximity to enable the adjacent sulphurs to form covalent bonds. Although the orientation of the polymeric chains on the surface of this electrode is unknown, it is apparent that these criteria are not easily fulfilled in a heterogeneous system.

Any redox processes observed for this electrode must therefore be a function of the oxidation or reduction of the complexed mercury, and this subject is now considered. Studies were carried out on both glassy carbon and Pt-based electrodes. The latter substrate was used because of its highly facile kinetics for most electrochemical processes of interest.

4.3.2.1. Studies on GC-based p-NET-dtc electrode

The manner in which the mercury attaches itself to the surface of the electrode becomes clear if the following data are considered.

The p-NET-dtc electrode, when placed in a deoxygenated acetate buffer at pH 5.0, equilibrates at a potential of 120mV (after about 30 seconds). When this solution is spiked with Hg\textsuperscript{II} to a concentration of 100 ppm, the potential immediately begins drifting in a positive direction until it plateaus at 368mV after about 18 minutes (fig. 4.4).
Figure 4.4: E vs t curve for open-circuit potential at p-NET-dtc electrode after spike with Hg$^{2+}$ to 100ppm.

When the potential is scanned from this point, in a positive direction (fig. 4.5), a small oxidation response is seen at the onset of the potential. A subsequent cyclic voltammogram on the same electrode yields the response as shown in figure 4.6.

Figure 4.5: Linear sweep voltammogram of p-NET-dtc-Hg electrode after potentiometric equilibration at 368mV in 100ppm Hg$^{2+}$ (ac. buffer).
The response in figure 4.5 rather resembles the latter part of a voltammetric (oxidation) peak. That this is what it actually is, rather than charging current occasioned by the initial application of the potential, is apparent from the fact that the electrode was swept positive from its thermodynamic potential, and there was therefore no potential step involved in the initial application of the potential.

This oxidation response may be attributed to the oxidation of small amounts of metallic mercury that have deposited in the microscopic faults in the polymer surface. That metallic mercury deposits on the electrode surface becomes apparent if the following data is considered.

A \textsuperscript{TM}Dionex twin glassy carbon cell had a p-NET film grown and subsequently derivatised on one of the electrodes. The electrode was then shorted against the other glassy carbon electrode, and the assembly placed in the 100 ppm Hg\textsuperscript{2+} (ac. buffer) solution (fig. 4.7)
This process was allowed to proceed overnight before the cell was removed and the electrodes examined. After this period, the bare glassy carbon electrode was observed to have an even, uniform mercury film on it. This therefore provides direct evidence for a galvanic couple formed by the mercuric ions and something in or on the derivatised surface. This phenomenon has been observed with conducting polymers, and is discussed in chapter 5.

Clearly, therefore, with the case of a single p-NET-dtc electrode, the reduced mercury has no option but to deposit on the parts of the substrate that are exposed by the faults in the polymeric film. This could be expected to result in a microarray-type MTFE, with very small, highly dispersed mercury centres.

This mechanism provides an explanation for why the PDG polymer is a superior MTFE substrate to the PSG polymer (vide infra). In section 3.3.3.1 it was demonstrated that the PSG polymer behaves more like a true microarray than the PDG polymer. That is, the holes in the polymer surface are smaller for the former than for the latter, and while this is a clear advantage in terms of the bulk diffusion properties of the electrode (microarray behaviour), it may be seen to be a disadvantage in terms of the formation of an MTFE, as it may not be able to sustain enough mercury to allow it to display amalgamating properties with electrodeposited analyte metals.
A comparison of the magnitudes of the oxidation responses in figures 4.6 and 4.5 makes it clear that the majority of the mercury on the electrode surface is in a complexed state. This can only be a Hg\textsuperscript{II} complex, since Hg\textsuperscript{I} does not form a complex with dithiocarbamate (sect. 3.1.1.1).

As well as this, the Hg\textsuperscript{I} oxidation state is an extremely rare, unstable, and generally insoluble form of the mercury. Where it is present in appreciable amounts it will quickly disproportionate to Hg\textsuperscript{0} and Hg\textsuperscript{II} [296].

\[
\text{Hg}_2^{2+} \rightleftharpoons \text{Hg}^{2+} + \text{Hg}^{0} \quad \text{eq. 4.2}
\]

This has resulted in, with the exception of the SCE, Hg\textsuperscript{I} being almost unheard of in the literature. This is not surprising, however, if one considers the three standard reduction potentials for mercury:

\[
\begin{align*}
\text{Hg}^{2+} + 2e^- & \rightleftharpoons \text{Hg} \quad E^0 = 0.851 \text{ V} \quad \text{eq. 4.3} \\
2\text{Hg}^{2+} + 2e^- & \rightleftharpoons \text{Hg}_2^{2+} \quad E^0 = 0.905 \text{ V} \quad \text{eq. 4.4} \\
\text{Hg}_2^{2+} + 2e^- & \rightleftharpoons 2\text{Hg} \quad E^0 = 0.799 \text{ V} \quad \text{eq. 4.5}
\end{align*}
\]

All three processes span, under standard conditions, a mere 100 mV, resulting in a very narrow potential range in which the Hg\textsuperscript{I} species is stable, and will be found in an appreciable concentration.

The broad and drawn-out nature of the reduction response in figure 4.6 may be attributed to the dependence of this reaction on the preceding dissociation process in eq. 4.6 (CE mechanism).

\[
\text{Hg(dtc)}_2 \rightleftharpoons 2\text{ dtc}^- + \text{Hg}^{2+} \quad \text{eq. 4.6}
\]
As well as accounting for the sluggish nature of the reduction responses at this electrode, equation 4.6 may also be used to explain the highly reversible oxidation response observed in figure 4.6., as the willingness of the dithiocarbamate groups to stabilise the Hg\textsuperscript{II} species will assist the kinetics of the oxidation process (EC mechanism).

The CV (fig. 4.6) indicates a broad reduction response extending from about 0.0V to -0.5V. The effect that the process had on the oxidation state of the surface-bound mercury was monitored potentiometrically. To facilitate this, on three consecutive linear sweeps the electrode potential was swept, to 0.0, -0.5 and 1.0 volts respectively, with the open circuit potential monitored between each sweep.

After the sweep to 0.0V, the potential time curve yielded the profile shown in figure 4.8.

![E vs t curve for open-circuit potential at p-NET-dtc-Hg electrode after a sweep to 0V (at 5mV s\textsuperscript{-1}). Potentiostat disconnected after sweep.](image)

**Figure 4.8:** E vs t curve for open-circuit potential at p-NET-dtc-Hg electrode after a sweep to 0V (at 5mV s\textsuperscript{-1}). Potentiostat disconnected after sweep.

This curve is identical, within 10mV, to that of figure 4.4, indicating that the oxidation state of the surface-bound mercury has not changed. This is not unexpected, as the voltammetric data (fig. 4.6) suggests that the reduction process is only in its infancy at 0.0 V, and perhaps the 10mV shift that is seen is a consequence of the onset of this process, and the reduction, to Hg\textsuperscript{0}, of a small proportion of the surface Hg\textsuperscript{II} groups.
When the potential is scanned down to -0.5V (at 5mV.s⁻¹) the open circuit potential observed when the potentiostat is disconnected is shown in figure 4.9.

![Figure 4.9: Open-circuit E vs t profile immediately following a sweep to -500mV. Potentiostat disconnected after sweep.](image)

The potential of this system stabilised, at least within the time frame of the experiment (3 hours) at 348 mV. It took some time for this potential to develop (110 mins), and this may be attributed to the net reduction of complexed Hg²⁺ to Hg⁰ brought about by the applied potential, and the subsequent slow reoxidation to Hg²⁺ by the scheme:

$$2\text{Hg} \rightleftharpoons \text{Hg}_2^{2+} + 2e^- \quad \text{eq. 4.7}$$

$$\text{Hg}_2^{2+} \rightleftharpoons 2\text{Hg}^{2+} + 2e^- \quad \text{eq. 4.8}$$

$$2\text{Hg}^{2+} + 4\text{dtc}^- \rightleftharpoons 2\text{Hg(dt)c}_2 \quad \text{eq. 4.9}$$

The identity of the oxidant for this process is likely to be the species that experienced a net oxidation at the anode during the application of the potential.
Since the system has now moved away from its thermodynamic potential (as a result of the applied potential) it will seek to return to that potential provided a favourable kinetic pathway is available. The stabilisation of the Hg$^{II}$ afforded by complexation with the dithiocarbamate provides just such a pathway. The fact that the electrode potential eventually returned to something very close to its thermodynamic potential suggests that this process was quite efficient.

Application of a potential of -1.0V with subsequent disconnection of the potentiostat yielded the potential vs time curve as shown in figure 4.10.

The reduction of the electrode potential that was observed in this case was more profound than when it had been polarised at 0.0 and -0.5 V respectively with, after two hours, the electrode potential failing to reach 300 mV, and still showing no signs of plateauing.

![Figure 4.10](image)

**Figure 4.10:** As for figure 4.8 with the exception that the electrode potential was swept to -1.0 V prior to the potentiostat being disconnected.

This may be explained by the same mechanism as was advanced for the sweep to -0.5 V, with the applied potential resulting in the reduction of surface-bound Hg$^{II}$ species to Hg$^{0}$. Under open circuit conditions, the complexing capacity of the dithiocarbamate species results in a net oxidation of those mercury atoms in the immediate vicinity of the dithiocarbamate sites, with the remainder remaining in their metallic form.
This process may be appreciated if consideration is given to the physical form of the polymer. With the electrode surface consisting of a polymeric film with faults (filled with metallic mercury) that permit passage of charge to the underlying substrate (sect. 3.3.3.1), it is reasonable to suppose that reduced (liquid) mercury will migrate towards the preexisting mercury droplets under the influence of an applied (reducing) potential. Whereas the Hg\(^0\) would initially (upon reduction) form as small nucleation centres from the complexed Hg\(^{II}\), the longer the electrode spends at more negative potentials, the more likely it is that the metallic mercury will migrate away from the dithiocarbamate sites and towards these polymeric faults, coalescing in the process (the surface tension of mercury decreases with more negative potentials).

As a consequence of this, in a given timeframe the electrode polarised at -1.0V is less likely to return to its thermodynamic potential than one that is polarised at less negative potentials, and this effect was seen in these studies (fig. 4.10 vs fig. 4.9).

It is, of course, possible that the electrode that was polarised at -1.0 V would also have returned to its initial potential given enough time, since after two hours the potential had still not plateaued, and since this is the thermodynamic potential of the system. In all likelihood, however, this may not have eventuated prior to the solution all evaporating.

Interestingly, the initial (thermodynamic) potential of this electrode was restored by immersing it in the original 100 ppm Hg\(^{2+}\) solution, and allowing it to equilibrate overnight. The likely mechanism of this process is twofold. Firstly, the Hg\(^{II}\) would readily complex at the free dithiocarbamate sites, and secondly, it would utilise a disproportionation reaction to remove excess metallic mercury from the electrode surface as:

\[
\text{Hg}^{2+} + \text{Hg}^0 \rightleftharpoons \text{Hg}_2^{2+} \quad \text{eq. 4.10}
\]

The solution excess of Hg\(^{II}\) would shift this equilibrium to the right.

Electrochemically deposited mercury was also capable of producing a tangible reduction response upon repeated cycling in a blank solution. Figure
4.11 shows a redox couple produced by the repeated cycling of a p-NET-dtc electrode that had previously had Hg\textsuperscript{II} deposited chemically, followed by subsequent cycling at negative potentials in the presence of solvated mercuric ion.

After 15 cycles, the oxidation peak had diminished to a minimum, and the reduction peak had all but disappeared, such that the only mercury remaining on the electrode surface was that which was complexed to the dithiocarbamate sites.

This was demonstrated by polarisation of the electrode at 700mV for 5 minutes, after which the voltammogram shown in figure 4.12 was produced.

\textbf{Figure 4.11}: Cyclic voltammetry of p-NET-dtc electrode (in 0.1M NaNO\textsubscript{3}10ppm Hg\textsuperscript{2+}) with both chemically and electrochemically deposited mercury on the surface.

It is interesting to note that no reduction response was seen for this electrode at the sweep rate employed (100mV.s\textsuperscript{-1}). This may be attributed to the sluggish nature of the reduction process for the complexed mercury, as noted previously, and that very slow sweep rates are required to produce a visible voltammetric response for the process (fig. 4.6).

The enhancement of the oxidation response seen after the polarisation at 700mV is a likely result of the return of the film to its microdroplet state (as a
result of the subsequent reduction of the complexed mercury), as the previous repeated cycling to negative potentials would have had the effect of causing the mercury droplets to coalesce, thereby compromising the ideality of the stripping signal.

4.3.2.2. Studies on Pt-based p-NET-dtc electrode

While the GC-based electrode was studied because it forms the basis for the MTFE used in this project, it was the platinum-based electrode that was the more diagnostic of the two. This is most likely due to the fact that it is a highly electroactive electrode surface, with most electrochemical processes behaving more "reversibly" than at carbon electrodes.

An interesting feature of the processes occurring at the Pt-based p-NET-dtc-Hg electrode surface is revealed if figure 4.12 is examined.

![Graph](image)

**Figure 4.12:** As for fig. 4.11 after polarisation at 700mV for 5 minutes. Initial scan direction positive.

The mercury was, in this case, electrodeposited, and not chelated chemically, as has been the standard procedure for the dithiocarbamate electrode used throughout this study. This was achieved by polarisation of the
electrode at -1.0 V in a 10 ppm Hg\textsuperscript{2+} solution. Any mercury that may have initially complexed as Hg\textsuperscript{II} would be quickly reduced to Hg\textsuperscript{0}.

The purpose of this was to leave the dithiocarbamate sites uncomplexed so that they would be free to uptake Hg\textsuperscript{II} generated by the voltammetric oxidation of the metallic mercury. This was further facilitated by the use of a mercury solution in an acetate buffer of pH 4.0, at which pH the rate of Hg\textsuperscript{II} complexation is poor (sect. 3.1.1) The consequence of this deposition procedure was that two peaks appeared when the electrode was scanned from 0 to 1000 mV (fig. 4.13) in a blank solution.

The first of these peaks is due to the oxidation of the Hg\textsuperscript{0} to Hg\textsuperscript{II}, as the $b_{1/2}$ for this peak is about 40 mV, which is close to the theoretical $96/n$ mV value for $b_{1/2}$ (where $n = 2$).

The second peak, with a $b_{1/2}$ of less than 20 mV, can only be due to either an adsorption/desorption process or a nucleation/growth process, the obvious choice in this case being the former, since this is exactly what is expected for this system: the Hg\textsuperscript{0} is oxidised to Hg\textsuperscript{II} and is immediately complexed by the free dithiocarbamate groups.
Further, coulometric data suggests that this is an adsorption process corresponding to approximate monolayer adsorption. Integration of the second (smaller) peak in figure 4.13 yields a charge of about 70 μC.cm$^{-2}$ (taking into account the electrode surface area of 0.14cm$^2$), which is of the same order of magnitude as the more typical value of 200 μC cm$^{-2}$ [206]. The implication of this is that only a portion of the geometric surface area of the electrode is covered with dithiocarbamate functionalities.

Further evidence for this second peak corresponding to a Hg$^{II}$ adsorption process stems from the observation that despite the fact that the deposition time for the mercury was varied, and this was accompanied by concomitant changes in the magnitude of the oxidation peak, the second peak stayed exactly the same size (within 3%). This is what would be expected from an adsorption process, as the magnitude of this peak would be a function of the surface area of the dithiocarbamate sites, which will remain constant.

Despite this, however, two difficulties arise:

1. If previous data (fig. 4.6) suggest that the mercury complexation takes some minutes, how is it that a sharp voltammetric response indicative of rapid and instantaneous adsorption is observed?

The likely reason for this lies in the localised concentration of Hg$^{II}$ at the point of adsorption. For the process described by figure 4.6, the concentration of Hg$^{II}$ at the electrode surface is never any higher than 100 ppm, and actually drops below this value once complexation commences and the solution becomes depleted in the vicinity of the electrode.

For the process occurring in figure 4.13, however, the electrode complexes the mercury immediately after the electrochemical oxidation of Hg$^{0}$ to Hg$^{II}$, at which point the localised concentration of Hg$^{II}$ at the electrode surface would be very high, and significantly greater than that of the bulk 100 ppm solution. This may be seen to result in the very fast adsorption (complexation) process observed.

2. The second question to be addressed refers to why the adsorption peak does not manifest for the dtc-based mercury film where the mercury had only been complexed chemically.

The explanation for this phenomenon is, once again, the localised concentration of mercury available at the dithiocarbamate site. The dtc-based
mercury film would only deposit that amount of mercury that complexed with
the dithiocarbamate groups, whereas the micropore-based (electrochemically
deposited) mercury film would have an amount of mercury present that would
be dependant upon the electrochemical deposition time and potential, and this
would be expected to be a greater amount.

This results in the electrochemically deposited film having a much
higher localised concentration of Hg\textsuperscript{II} at the dithiocarbamate sites, subsequent
to oxidation, than the chemically deposited film, and hence the rapid and
highly diagnostic adsorption process.

4.3.3. ANALYTICAL PERFORMANCE

The performance of the p-NET-dtc-Hg electrode as a substrate for
electroanalysis was monitored using anodic stripping voltammetry (ASV) and
electrochemical detection with ion chromatography (IC). Each is considered in
turn.

4.3.3.1. Anodic Stripping Voltammetry

The three metals that were chosen for the characterisation of the ASV
performance of this electrode were cadmium, lead and copper. These three
metals were chosen to permit a direct comparison between the performance of
this electrode and that of the conventional MTFE, as described in Chapter 2.

4.3.3.1.1. Stationary Electrode Studies

As established in chapter 2, the ASV response for copper has an inverse
relationship to mercury film thickness, whereas lead and cadmium have a
direct relationship. Of these latter two, the more diagnostic is cadmium as,
unlike lead, it will not produce a stripping response in the absence of mercury
on the polymeric substrate. As a consequence, the magnitude of the copper
response may be utilised as an indicator of relative film thinness, whereas the
cadmium response may be used as an indicator of relative film thickness.

To produce, therefore, an electrode with good sensitivity for both the
copper and cadmium, a judicious choice of deposition conditions is required.
The stripping response at such an electrode is shown in figure 4.14.
Some features of this voltammogram are particularly noteworthy. The \( b_{1/2} \) values for cadmium and copper are both significantly less than the theoretical value of 96/n mV, at 44 and 65 mV respectively (\( n=1 \) for copper as it is being stripped into a chloride medium). Further, the sensitivity of the electrode is very high considering it is a stationary electrode in a low convection system (stirring bar) with a short accumulation time. As well as this, the scan rate (5000 mV/s) is beyond the normal regime of conventional MTFEs, as significant kinetic peak broadening would occur under these circumstances. This aspect is further considered when a comparison is made with the conventional MTFE in section 4.4.

![Figure 4.14](image)

**Figure 4.14:** ASV of 7 ppb Cd\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) in "Chemtronics" electrolyte at stationary electrode. Hg\(^{2+}\) deposited chemically for 20 minutes from 100 ppm Hg\(^{2+}\) (pH 5.0). \( v = 5 \text{V.s}^{-1} \)

These data suggest that the electrode is composed of a very finely divided series of very small mercury droplets dispersed across the electrode surface in a microarray arrangement.

The high sensitivity, however, occurs at the expense of capacity, as such an electrode possesses a very short linear range for cadmium. Typically, such an electrode will tolerate no more than 30 or 40 ppb cadmium before
suppression of the signal begins occurring, along with a concomitant enhancement of the copper signal. The performance characteristics, however, of such an electrode may be reversed by altering the amount of mercury present on the electrode surface. This effect may be illustrated if figure 4.15 is considered.

Figure 4.15 shows a very thin film electrode after the addition of only 10 ppb Cd to the blank solution. Lead and copper are present at background levels only (~5ppb). The cadmium addition, although it did result in an enhancement of the cadmium, resulted in a much greater enhancement of the copper peak (fig. 4.16), and, to a lesser extent, the lead peak. This is a direct consequence of the extremely small amount of mercury on the surface of the electrode (5 min Hg$^{2+}$ deposition), and this result was typical.

To illustrate the effect further, the electrode was polarised at 1000 mV for 60s to remove whatever mercury was not present in the immediate vicinity of the dithiocarbamate groups. The minuscule amount of mercury remaining behind gave, as expected, extremely small cadmium and lead peaks, but a significant copper peak (figure 4.17).

![Graph](image)

**Figure 4.15**: p-NET-dtc-Hg electrode that has had Hg$^{2+}$ complexed for 5 minutes from a 100ppm Hg$^{2+}$ solution (pH5.0). Solution is 10 ppb Cd$^{2+}$ in "Chemtronics" electrolyte (background levels of Pb$^{2+}$ and Cu$^{2+}$)
Figure 4.16: As for figure 3.15 with the addition of a further 10 ppb Cd$^{2+}$.

Figure 4.17: As for figure 4.16 after electrode had been polarised at 1000 mV for 60s.
The effect of a thicker mercury film on its stripping responses was ably illustrated by the result of allowing this electrode to uptake mercury from a 100ppm Hg$^{2+}$ solution for 2 days (figure 4.18).

**Figure 4.18**: As for figure 4.17 after the electrode had been allowed to uptake Hg$^{2+}$ for 2 days.

When the identical solution to figure 4.17 was analysed (20 ppb Cd, background levels of lead and copper from the same blank solution) a large and well-defined cadmium peak manifested, whereas the copper peak, as is its wont for thicker films, was broad and ill-defined (chap. 2). The lead peak also manifested an increase in magnitude due to its propensity for thicker films (chap. 2).

Further additions of Cd$^{2+}$ to the solution resulted in a steadily increasing cadmium response, which when determined with subsequent experiments, remained linear in the range 10-700 ppb.
4.3.3.1.2. Studies at an RDE

The p-NET-dtc-MTFE was examined at a rotating disc electrode (RDE) to study its performance in a high convection system.

The most transient response of the three metals studied was that of copper, which is not surprising since, according to the classification of Neiman [295], it is the only one of the three metals that chemically interacts with the mercury. As a result of this, the sensitivity of the electrode varied greatly according to the state of the mercury film, as the following data shows.

For this electrode, the Hg$^{2+}$ was chemically deposited (onto the p-NET-dtc) for a period of 5 minutes. It was then subjected to multiple scans to determine the viability of this electrode for multiple analyses, and the procedures that were required to keep it in a pristine state between scans.

The specific parameter that was studied was that of the "cleaning" step, as this forms an integral part of the waveform selection for multiple ASV determinations. With a conventional MTFE, the "clean" step consists of holding the potential of the electrode at a potential that is more positive than the last metal stripped for a few seconds at the end of the stripping scan, and serves to ensure that all analyte metals are quantitatively removed from the mercury film.

This step is most critical when one of the analyte metals is copper, as, depending on the choice of solution electrolyte, the mercury can strip at a potential quite close to that of copper, and a judicious choice of cleaning potential is required to ensure both that the copper is removed and that the mercury film does not get oxidised. Cleaning potentials for such a system typically lie in the range -100 to 100mV. For a conventional MTFE, an adequate time period for the cleaning step is usually of the order of about five seconds.

With the p-NET-dtc-Hg electrode, however, the cleaning potential assumes a second, more important role, in addition to the "cleaning" process. For an acetate system, the last trace of the copper oxidation signal has disappeared by about -50mV, suggesting that a cleaning potential of 0 mV for about five seconds would be adequate to the task. For the p-NET-dtc-Hg
electrode, however, this is not the case, and this becomes clear if the following data are considered.

In the absence of a cleaning step, and even scanning as positive as 200mV, degradation of the copper response was seen with subsequent scans (fig. 4.19).

![Graph](image)

4.19: p-NET-dtc-Hg electrode in 10 ppb Cd^{2+}, Pb^{2+}, Cu^{2+}, in 0.2M acetate buffer (pH 5.0). Deposition time 60s. No clean step. Solid line is original voltammogram, and shaded line is voltammogram recorded after five consecutive voltammograms without a clean step.

Interestingly, the degradation of the copper response was accompanied by an enhancement of the cadmium and lead peaks. This provides clear evidence for a change of morphology of the mercury film on the surface of the electrode, as it is behaving as though more mercury were present when, clearly, this is not the case.

This effect was able to be reversed, however, if an appropriate "cleaning" procedure was employed (fig. 4.20).
Figure 4.20: Effect of clean step on restoration of voltammetric response. All solutions and conditions as in figure 4.19, with the exception that clean steps of 5s at 100mV (scan 1), 5s at 200mV (scan 2), and 30s at 200mV (scan 3) were employed.

Figure 4.20 illustrates how this step may be carried out, by demonstrating the effect of the choice of the cleaning procedure on the copper response. This electrode had previously manifested well-defined responses for all three metals prior to a series of seven scans without a cleaning step, after which figure 4.20 (scan 1) was recorded.

If the clean step consists of polarisation at 100 mV for 5 sec (scan 1), no reversal (enhancement) of electrode response is seen on the subsequent scan (scan 2). When it is polarised at 200 mV for 5 seconds (scan 2), partial restoration of the copper response is seen (scan 3), and when it is polarised at 200 mV for 30 seconds (scan 3), full restoration of response is seen (scan 4).

The explanation of this concerns the mobility of the mercury on the surface of the electrode. The degradation of copper response that is observed is a function of the time that the electrode spends with -1.0 V applied to it, and the restoration of the response is a result of the amount of time that the electrode spends at positive potentials. There is, for example, a clear and reproducible difference between those voltammograms recorded immediately after polarisation at 200 mV for 5 seconds and 30 seconds (fig. 4.21).
Figure 4.21: Graph of current values for consecutive ASV responses at p-NET-dtc-Hg electrode for the solution in fig. 4.19 with different clean steps: scans 1-5 were recorded after the previous voltammogram had used a clean potential of 100mV for 5s, scans 6-8 at 200mV for 5s and scans 9-11 at 200mV for 30s.

It is seen, therefore, that it was not the mere application of the 200mV potential that regenerated the copper response, but the application of 200 mV for 30 seconds. That is, were the only function of the clean step to induce an oxidative process, as with the conventional MTFE, the 5s clean would be sufficient to the task. The fact that a 30s clean is required to fully restore the response suggests that the relative times that the electrode spends at the various potentials play a crucial role in determining the film morphology.

The likely explanation of this phenomenon concerns the surface mobility of the mercury on the surface of the electrode. With the application of the negative potentials, the mercury (sect. 4.3.2) will move from the sites of dithiocarbamate deposition to the more electroactive micropores, probably coalescing as they do so. This would result in a greater amount of electroactive mercury, and hence the suppression of the copper response.
As the electrode spends more time at positive potentials (without the mercury metal being oxidised), the energetic (Nernstian) driving force that is forcing the equilibrium

$$Hg^{2+} + 2e^- \rightleftharpoons Hg^0$$  \hspace{1cm} eq. 4.11

to the right diminishes, and the complexing capacity of the dithiocarbamate groups draws the equilibrium to the left.

While the applied potential does not directly induce a Faradaic oxidation of the $Hg^0$, therefore, it does result in a net migration of the mercury metal away from the electroactive micropores, and towards the less electroactive dithiocarbamate sites. This results in a decrease in the amount of electroactive mercury on the electrode surface, and hence an enhancement of the copper signal.

The net effect of this is to shift the reversible (open circuit) potential of the electrode to more positive potentials. This is the same effect as was observed in section 4.3.1 for immersion of the reduced electrode in $Hg^{2+}$ solution for a period of time. For this reason, storage of unused electrodes in $Hg^{2+}$ solutions could be expected to return the electrodes to their pristine (i.e. as complexed initially) state and promote longevity. This issue is addressed in section 4.3.5.

It will be noted that the effect of the cleaning procedure on the lead and cadmium responses was not as profound as that for the copper (fig. 4.21). This phenomenon was noted for the very thinnest of the conventional MTFEs examined (chapter 2).

The fact that the kinetics and/or intra-film diffusion processes occurring during the stripping step influence the copper oxidation response, but not that of either cadmium or lead (as discussed in chapter 2) is seen by the presence of some degree of non-ideality (irreversibility) in the copper peak as its magnitude increases in figure 4.20 ($\Delta E_{ox}$ and slight peak asymmetry). These effects were also observed with the copper response at the conventional MTFE, but have never been observed (by the author, or to the author's knowledge, in the literature) with either the conventional or chemically-modified mercury films for either cadmium or lead.
4.3.3.2. Flow systems

The utility of the p-NET-dtc-Hg for ASV in a flow system was assessed. This consisted of the p-NET-dtc-Hg being deposited on the glassy carbon electrode (as described in section 4.2.4), and used for flow injection analysis (FIA) with a ™Dionex flow system. The electrochemical detector that was used was a ™Dionex ™PAD (pulsed amperometric detector) set up to operate in ASV mode.

Unlike conventional ASV, this did not consist in ramping the potential, but rather in pulsing the potential between oxidising and reducing potentials. This was achieved by setting the ™PAD to pulse according to the following scheme:

\[
\begin{align*}
E_1 &= 200 \text{ mV} & \tau &= 60 \text{ ms} \\
E_2 &= 0 \text{ mV} & \tau &= 0 \text{ ms} \\
E_3 &= -1000 \text{ mV} & \tau &= 240 \text{ ms}
\end{align*}
\]

The potential pulses to each of the three preset potentials in turn, with the current being sampled for the last 50 ms of \(E_1\). Since \(E_2\) is set to \(\tau = 0\), the resultant excitation waveform consists of accumulation at -1000 mV for 240 ms, followed by stripping at 200mV, with the anodic current being sampled in the last 50 ms of the stripping (\(E_1\)) pulse.

The p-NET-dtc-Hg film, when used in this capacity, was both highly sensitive and highly stable. Figure 4.22 shows the responses recorded for Cd\(^{2+}\), Pb\(^{2+}\) and Cu\(^{2+}\) at 500ppb and 1ppm.

The electrode showed linearity of response for all three metals in the range 500ppb to 10ppm.

The stability of this electrode was demonstrated by allowing the system to run, with potentials applied, over a twelve hour period. The calibration curves recorded for Cu\(^{2+}\) before and after this period are shown in figure 4.23.

An attempt to use a conventional MTFE in this system resulted in a randomly drifting baseline, as shown in figure 4.24. The likely cause of this phenomenon is changes occurring in the morphology of the mercury film induced by the flowing solution.
Figure 4.22: ASV responses of Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ recorded at a p-NET-dtc-Hg-coated glassy carbon electrode in a Dionex flow cell. Concentrations of metals as indicated. Eluant = 0.2 M acetate buffer (pH 5.0). Flow rate = 0.5 mL.min$^{-1}$.

Figure 4.23: ASV calibration curves for Cu$^{2+}$ recorded before and after continuous running of Dionex flow system over a twelve hour period (with PAD potentials applied) at a p-NET-dtc-Hg-coated glassy carbon electrode in a Dionex flow cell. Eluant = 0.2 M acetate buffer (pH 5.0). Flow rate = 0.5 mL.min$^{-1}$. 
While these results demonstrate the viability of the p-NET-dtc-Hg electrode as a flow detection system, considerable scope remains for optimisation of the system, for the following reasons:

1. The shape and construction of the electrode assembly presented considerable difficulties from a logistics point of view. In particular, it was incumbent to ensure that at no stage throughout the synthesis or derivatisation steps the solution came into contact with the copper electrode lugs on the top of the cell. As well as this, assembly of the cell had to be carried out in a manner in which no mechanical degradation of the electrode occurred by incorrect locating of the cell gasket.

The consequence of these phenomena was an element of inter-electrode irreproducibility. It is anticipated that the development of dedicated hardware would minimise these problems.

2. The ™PAD has inflexible current sampling, in that the width and period may not be varied. Further, it samples at one potential only and is therefore incapable of subtractive data processing. The ™Dionex corporation has recently released the ™PED (pulsed electrochemical detector), and it is

Figure 4.24: Baseline current recorded with a ™PAD ™Dionex flow system over a two hour period at a Hg-coated glassy carbon electrode (3 minutes at -1000mV from 100ppm mercuric ion solution) in a ™Dionex flow cell. Eluant = 0.2 $M$ acetate buffer (pH 5.0). Flow rate = 0.5 mL.min$^{-1}$. 
envisaged that the increased flexibility afforded by this instrument would pave the way for significant optimisation of the ASV process employed in this study.

4.3.4. MERCURY FILM DIGESTION & REGENERATION

A series of studies on the p-NET-dtc-Hg electrode in strongly acidic conditions were undertaken. The goal of these experiments was to quantify the amount of mercury present on the electrode surface (by digestion of the film), as well as to test the ability of the electrode surface to be subsequently regenerated. The stability of the heterogeneous dithiocarbamate under these conditions was also assessed.

The amount of mercury present on the surface of the p-NET-dtc-Hg electrode was examined as a two-step procedure.

In the first step, a voltammetric scan was run up to 0.7 V, resulting in oxidation of whatever surface mercury was oxidisable. The second step consisted of digesting the film overnight in 10% HNO₃, to remove the mercury that had been retained by the dithiocarbamate sites. Subsequent to this step, the electrode was rederivatised, had mercury redeposited, and its ASV properties assessed before the entire process was duplicated. By this procedure, the electrode was capable of being rederivatised and regenerated. The results are presented in table 4.1.

The initial observation to be made from these data is that the regenerated electrode is fundamentally different from the original CME. This is seen from the fact that the mercury deposited on the electrode surface after acid digestion and rederivatisation was substantially less than that which was present originally, and seemed to plateau after the second derivatisation.

For a film for which the mercury had been deposited for 2 min, the mercury liberated (table 4.1) by the electrochemical oxidation step, at the stationary electrode, was about 0.40 μg. That which was liberated after acid digestion corresponded to about 1.1 μg. If the chemical deposition time was allowed to proceed for a much greater period of time (30 min), a concomitant increase in the amount of mercury on the surface is observed. For such an electrode, the mercury liberated by the electrochemical oxidation was 7.7 μg, and that liberated by the acid digestion was 3.7 μg.
It will be seen that, within the experimental error of the hydride generation AAS method used, the ratios of the mercury liberated at each of the two steps is about the same. If anything, the amount of mercury retained after the first step is a little higher, proportionally, at the thicker film than it is at the thinner film. This is to be expected, since as the Hg⁰ was oxidised to Hg²⁺, the localised concentration of Hg²⁺ in the vicinity of the dithiocarbamate groups would be higher, thereby promoting a modicum of re-complexation at these sites.

As suggested in section 4.3.2, the mercury deposits on the electrode surface both in its ionic form, by complexation, and in its metallic form, by reduction. Consideration is now given to the reducing agent responsible for this latter process.

As discussed in section 4.3.2, the only thing stopping the oxidation of adjacent dithiocarbamate functionalities to thiuramdisulphides (tds), either under the influence of an applied potential, or in the presence of mercuric ion, is their heterogeneity, and the physical restraints that are therefore placed on

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**Table 4.1:** Amount of mercury (μg) on surface of p-NET-dtc-Hg electrodes after electrochemical oxidation and overnight digestion in M HNO₃. Triplicate rederivatisations and digestions were performed.

<table>
<thead>
<tr>
<th>Hg(μg)</th>
<th>Initial Electrode</th>
<th>First Rederivatisation</th>
<th>Second Rederivatisation</th>
<th>Third Rederivatisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidisable Hg</td>
<td>0.4</td>
<td>0.4</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Acid-digested Hg</td>
<td>1.1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total Hg</td>
<td>1.5</td>
<td>0.5</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>
such a process. The derivatisation mixture, however, contains a xanthate (fig. 3.46), which will easily oxidise to a dimer:

\[
\begin{align*}
\text{S} & \equiv \text{C} \quad \text{S}^- \text{Na}^+ \\
\text{O}^{-} & \quad \text{C} \quad \text{H}_3 \text{C} \quad \text{H}_3
\end{align*}
\]

\[
\begin{align*}
\text{S} & \equiv \text{C} \quad \text{S} \quad \text{S} \quad \text{C} \quad \text{S} \\
\text{O}^{-} & \quad \text{C} \quad \text{H}_3 \text{C} \quad \text{H}_3 \quad \text{C} \quad \text{H}_3
\end{align*}
\]

Figure 4.24: Oxidation of isopropyl xanthate to its disulphide dimer

That this is the actual species that is responsible for the reduction of the mercury is suggested by two considerations:

1. It is a thermodynamically viable process. The chemical oxidation of dithiocarbamate to thiuramdisulphide by mild oxidising agents such as iodine has been demonstrated [326,327], and mercury is a stronger oxidising agent than iodine \( E_{\text{Hg}^{\text{II}}}^{0} > E_{\text{I}_2}^{0} \).

2. The rederivatised electrodes will successfully redeposit \( \text{Hg}^{0} \) despite the fact that they will not redeposit \( \text{Hg}^{\text{II}} \). Table 4.1 indicates that after the second rederivatisation of the electrode, all the mercury that is subsequently deposited (chemically) is removed from the electrode surface by polarisation of the electrode at positive potentials. This implies the absence of dithiocarbamate groups on the electrode. In other words, although dithiocarbamate groups were not successfully grafted onto the electrode surface, it still deposited \( \text{Hg}^{0} \) chemically. The only possible way that this could be done was by chemical reduction by something in the derivatisation mixture.

The mercury deposition process at the p-NET-dtc electrode, therefore, involves two unconnected processes; the chemical reduction of \( \text{Hg}^{\text{II}} \) to \( \text{Hg}^{0} \) by an adsorbed or occluded component of the derivatisation mixture (xanthate) and the complexation of \( \text{Hg}^{\text{II}} \) by surface-bound dithiocarbamate groups, with the bulk of the mercury being in the complexed state. Further consideration is given to this subject when the conducting polymer is discussed in chapter 5.
The analytical properties of these rederivatised electrodes were different to those of the original film, implying a mercury film with fundamentally different morphology and/or deployment on the polymer substrate. This is illustrated in figure 4.25.

Clearly, if the mercury film of the regenerated electrode were fundamentally the same as that of the original electrode, it would be expected to produce an enhanced copper response, and diminished cadmium and lead responses, by virtue of the diminished amount of mercury present. The opposite, however, is manifestly the case, as attempts to isolate the copper response, by deposition at a less negative potential, followed by subsequent deposition of the cadmium and lead, resulted in gross film degradation (fig. 4.26).

Figure 4.25: ASV of 10ppb Cd\(^{2+}\), 20ppb Pb\(^{2+}\), 10ppb Cu\(^{2+}\) in acetate buffer (pH 5.0) at pristine (solid line) and acid digested and rederivatised (shaded line) p-NET-dtc-Hg electrode.
Figure 4.26: Acid digested and rederivatised p-NET-dtc-Hg electrode. Solution as for figure 4.25. Shaded line is Cu$^{2+}$ response after isolation of response by accumulation at -500 mV, and solid line is subsequent ASV response for $E_{dep} = -1000$mV.

The degradation phenomenon may be attributed to the copper having exceeded its rather low solubility in the mercury ($5 \times 10^{-3}\%$), and depositing in the solid phase on the polymer surface, thereby inhibiting the subsequent deposition and stripping of the cadmium and lead. The solid copper remained behind after the initial scan due to the absence of a clean step. The fact that the voltammogram tailed off at the negative end is indicative of the deposition of solid cadmium on either the copper or the polymeric substrate.

The fact that the acid digestion of the p-NET-dtc-Hg electrode resulted in a fundamentally different polymeric surface is indicated by the fact that it was not possible to re-graft dithiocarbamate sites onto it. The nature of this effect is unknown, although it noteworthy that the initial p-NET-dtc-Hg electrode displayed extraordinary stability to the acidic attack as, after 1 hour in the 10% HNO$_3$ (1M) digestion mixture, mercury was still present on the surface of the electrode.

This is indicated by both its ability to produce ASV responses for cadmium and lead, and the presence of a mercury stripping response (fig. 4.27)
This extraordinary stability may be attributed to the steric impediment imposed upon the protonation of the secondary amine group by the heterogeneity of the system (sect. 3.1.1.2).

No systematic study was undertaken of the ability of the p-NET-dtc-Hg electrode to perform ASV in acidic media, but it is envisaged that this electrode would be more stable, under these conditions, than a conventional MTFE.
4.3.5. VISUAL CHARACTERISATION

To characterise the system, high resolution optical microscopy was used. The electrode that had mercury deposited from the 100 ppm Hg$^{2+}$/acetate buffer (pH 5.0) for 30 minutes developed a fine, uniform grey film. When viewed microscopically, however, little detail was visible due to a lack of contrast with the polymeric substrate. When the electrode surface was allowed to dry, however, and again viewed microscopically, the mercury droplets were visible (fig. 4.28), presumably due to the agglomeration that occurs under these circumstances (sect. 2.3.2.3.3).

It appears that one of the major reasons for the virgin mercury film being microscopically invisible (prior to drying) is that it has a greater propensity to wet the polymeric surface (unlike glassy carbon [169]), due to the hydrophobic polymer surface. The obvious consequence of this is that the mercury has a greater adherence to the polymeric substrate than to glassy carbon, and therefore possesses greater mechanical stability.

Figure 4.28: Optical micrograph of p-NET-dtc-Hg electrode that had been allowed to dry. Electrode surface rewet prior to recording of micrograph. Scale: 1cm = 15μm.
4.3.6. LONG-TERM STABILITY

While the 24 hour period required to synthesise the p-NET-dtc-Hg electrode may be considered to be a logistical disadvantage, it is compensated for by the fact that the electrode is stable for an extremely long period of time when stored in a mercury solution. This is both due to its self-regenerating properties (sect. 4.3.1), and the fact that the Hg^{II}-dtc is highly stable.

When stored in a mercuric solution, the electrode was stable over a period of many months, and for at least one month when stored in water. This creates the attractive possibility of an MTFE that may be synthesised in the laboratory and used in a remote location. Stability of a conventional MTFE over this period has never been reported.
4.4. COMPARISON OF CONVENTIONAL AND CHEMICALLY MODIFIED MERCURY THIN FILM ELECTRODES

These studies have demonstrated the intrinsic variability of the MTFE, in that it may be engineered to perform better for some metals than for others, with large variations in the amount, and morphology, of mercury on the surface. A comparison, therefore, between the conventional and chemically-modified electrodes must target specific and well-defined performance parameters.

With respect to the stationary electrode system, the comparison is, essentially, of a qualitative nature, and confined to a comparison of the relative amounts of mercury present on electrodes of similar sensitivity. For the RDE, the study is more comprehensive, and consists of a study of comparative sensitivity, precision and linear range.

4.4.1. STATIONARY ELECTRODE:

To enable a significant comparison to be drawn between the conventional and chemically-modified electrodes, it is imperative that there be a judicious choice of parameters to be compared. For example, there seems little point in directly comparing electrodes with similar amounts of mercury on the surface, as the physical nature of the films is very different, and even the thinnest of conventional MTFEs has a great deal more mercury on the surface than the polymer-modified CME.

As well as this, the absence of a reliable means of quantifying the amount of surface mercury in-situ, renders such a comparison highly impractical. As a consequence of this, the approach that was taken was to generate a conventional MTFE with the same sensitivity as that of the CME, and then to compare the surface mercury levels of these two electrodes.

The voltammograms produced by conventional and modified electrodes of approximately similar sensitivity are shown in figure 4.29. Both electrodes are of the thicker variety (greater amount of mercury) and are therefore more
specific for the cadmium and lead, and less so for the copper, as evinced by the lack of a copper response.

![Graph](image.png)

**Figure 4.29:** ASV of 6ppb Cd²⁺, Pb²⁺, Cu²⁺ in 0.2M acetate buffer (pH 5.0) deposition time = 60s. Shaded line: conventional MTFE ($E_{dep}$ for Hg²⁺ = 180s from 100 ppm Hg²⁺ in acetate buffer - pH 5.0) at stationary electrode in stirred solution. Solid line: p-NET-dtc-Hg electrode with Hg²⁺ deposited for 20 min from 100 ppm solution (acetate buffer - pH 5.0) with no applied potential.

Although the sensitivity of these electrodes are about the same, it is interesting to note that a significant shift is evident in the stripping potentials of the two metals. This, along with the fact that the $b_{1/2}$ values for the modified electrodes are slightly smaller (41 and 34mV vs 45 and 47mV), suggest that the kinetics of the stripping process at the modified electrode are faster than those of the conventional electrode. This should result in the modified electrode being able to be used at greater sweep rates without experiencing significant peak broadening.

Mechanistically, this shift is due to diffusion of the analyte metals from the centre of the mercury drops to the periphery that, although a negligible contribution at lower scan rates, becomes significant on the time scale of a sweep rate of 1000 mV s⁻¹. This effect is more pronounced at the conventional MTFE simply by virtue of the fact that the drops are larger. The effect for cadmium and lead, it should be noted, is fundamentally different from the
case with copper, where more significant $\Delta E_p$ are observed (sect. 2.3.2.1) due to the latter's more intimate interaction with the mercury, with concomitantly greater dependance on intra-film diffusion processes.

At thinner, more copper-specific films, the $\Delta E_p$ for the cadmium and lead is less pronounced, as is seen in figure 4.30.

![Graph](image)

**Figure 4.30**: ASV of 10 ppb Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$ in 0.2M acetate buffer (pH 5.0). $t_{dep} = 60s$. Solid line: conventional MTFE grown from 10ppm Hg$^{2+}$ (pH 5.0) for 60s. Shaded line: p-NET-dtc-Hg electrode. Mercury deposition for 300s from 100 ppm Hg$^{2+}$ (pH 5.0)

In this case, the cadmium and lead peaks have shifted negative by about 10 or 20 mV (for the conventional film) with respect to the thicker film of figure 4.29. Of note is the fact that the presence of the copper response on the modified film has brought about a positive potential shift of the cadmium and lead peaks (fig. 4.28). This phenomenon suggests that the deposition and stripping of copper introduces an element of non-ideality to the film, although the exact nature of this effect is unclear.

It is also worthy of note, in figure 4.30, that the modified film has outperformed the conventional film for all three metals. (This figure represents an analysis performed in the same solution). Clearly, as suggested previously, there is more to characterising the behaviour of mercury film electrodes than
merely accounting for the amount of mercury present. This is clear if the amount of mercury present on each of the two electrodes is examined.

The modified electrode, as was described previously had 0.4μg mercury that was oxidisable from the electrode surface, and a further 1.1μg that was removed by acid digestion. The conventional electrode, conversely, had 6.1μg of oxidisable mercury, and 0.5μg of acid-digestible mercury.

These data suggest that a great deal of the mercury on a conventional MTFE is inactive or, at the very least, that it has lower surface area to mass ratio than that of the modified film. This is not unexpected, given the highly dispersed, microscopic nature of the mercury drops on the modified film.

4.4.2. ROTATING ELECTRODE:

The rotating electrode system was used to obtain a quantitative comparison of the ASV performance of the modified and conventional films for cadmium, lead and copper. The mercury film conditions that were selected for the conventional film were deposition from a deoxygenated 100 ppm Hg2+ solution (pH 5.0) for 1 minute. These conditions were selected so as to produce a film that would produce useable copper responses. The p-NET-dtc-Hg electrode had Hg2+ deposited for 5 minutes. Calibration curves for the two electrodes used may seen in figure 4.31.
Figure 4.31: Calibration curves for Cd\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) at the conventional MTFE electrode (a, c, e) and the modified electrode (b, d, f). Conditions as described in "experimental" section.
The comparative properties of the two electrodes may be summarised:

1. The conventional MTFE displayed greater sensitivity than the modified film. This may be seen if the following data for comparative sensitivities are examined.

   **Table 4.2:** Comparative sensitivities of conventional and chemically-modified (p-NET-dtc) MTFEs.

<table>
<thead>
<tr>
<th>Slope of calibration curve μA/ppb</th>
<th>Cd</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional film</td>
<td>.94</td>
<td>.58</td>
<td>2.5</td>
</tr>
<tr>
<td>Modified film</td>
<td>.09</td>
<td>.16</td>
<td>.23</td>
</tr>
</tbody>
</table>

   The signal to noise ratio for both electrodes was, however, about the same, resulting in similar limits of detection. The reason for the greater currents at the conventional electrode is simply due to the fact that it has a greater electroactive surface area (macroelectrode) than the modified electrode (microelectrode array - type behaviour).

2. The conventional electrode had a wider linear range than the modified electrode, as the calibration curves were approximately linear up to 2 ppm, at which stage significant departure from linearity became evident. The modified electrode was only linear up to about 100 ppb, an order of magnitude less, and this may be attributed to the greater capacity of the conventional film, which exists as a simple function of the greater amount of mercury present.

3. The modified film displayed greater precision, which may be seen from the correlation coefficients of the calibration curves\(^1\), and this result was typical. In particular, the copper response was highly irreproducible at the conventional electrode. While duplicate determinations on a solution typically

---

\(^1\) A polynomial fit was used for graphs d and f (fig. 4.31) because of the precise fit obtained with this type of fit. The nature of the curves suggests that although the precision of the stripping responses was high, there was a gradual shift in the deployment of mercury on the surface (inducing gradual variations in the stripping dependancies) brought about by inadequate attention to the "clean" step. This phenomenon is discussed in section 4.3.2.
yielded reproducible results for cadmium and lead (within 2%), it often took as many as four or five determinations before duplicity of response was seen for the copper.

The cause of this phenomenon may be connected with an alteration of the morphology of the mercury film on a microscopic scale as the metals are deposited and stripped. The non-wetting nature of mercury films on glassy carbon, and the fact that the surface tension of mercury is known to vary with $E_{\text{app}}$ render this a tangible possibility. In particular, the intimate interaction of copper with the mercury may be instrumental in inducing such a change in the amalgamated state by altering the electrocapillary curve of the latter.

The modified film, conversely, has a polymeric substrate that has a greater affinity for the hydrophobic mercury (i.e. it wets the surface), and mercury morphology changes are less likely to occur as a consequence.

In summary, therefore, both the conventional and modified mercury film electrodes are capable of determining cadmium, lead and copper in the lower ppb range. The modified film possesses greater reproducibility than the conventional film, and both electrodes have similar S/N ratios at a given concentration (when employed at a sweep rate of 1000mV.s$^{-1}$).

Were instrumentation available, however, that could scan reliably at very high sweep rates (> 20V.s$^{-1}$), the modified film could be reasonably expected to outperform the conventional film, due to its faster stripping kinetics for the metals studied. The fact that it is composed of a greater number of very finely divided droplets of mercury means that the kinetic diffusion of oxidising species to the individual droplet surfaces is very fast, and very high sweep rates may be employed without broadening of the signal, although it is the very fineness of the drops that reduces its linear range with respect to the conventional film. Further consideration is given to the use of high sweep rates in section 4.4.3.

The most salient of the advantages of the modified film over the conventional MTFE is its superior mechanical stability, that enables its use, in flowing systems, on a routine basis. As well as this, it advances the possibility of the use of an MTFE in other high convection systems (such as the wall-jet configuration) which have hitherto been considered beyond the realm of the MTFE.
4.4.3. HIGH \( \nu \) LSV:

The performance of the polymer-modified MTFE developed in this project has introduced the possibility of high \( \nu \) LSV. This approach has not received the attention in the literature that it deserves, even for the conventional film, despite the fact that electrochemical theory predicts that it will produce a significant enhancement of stripping response [199,200].

Consideration is now given to this theory and the implications for both conventional and chemically-modified MTFEs.

The expression for the peak Faradaic current produced by the stripping (oxidation) of an oxidiseable substance from a “thin film” (sect. 1.1.2.4) immobilised on an electrode surface under the influence of a linearly ramping potential is given by:

\[
   i_p = \frac{n^2F^2\nu l A C_M}{2.7RT}
\]

where

- \( i_p \) = peak current
- \( \nu \) = sweep rate
- \( l \) = nominal film thickness
- \( A \) = electrode surface area
- \( C_M \) = concentration of the analyte metal in the film

All other terms have their usual meaning. This equation simplifies to the well known voltammetric relationship:

\[
i_p \propto \nu
\]
Thus, while ever the electrode displays "thin film" behaviour, an increase in the sweep rate will produce a concomitant increase in the magnitude of the stripping response.

Conversely, the effect that the sweep rate has on the charging current with a ramping potential may be seen if equation 2.1 is examined:

\[ i_c = \nu C_d + \left[ \left( \frac{E_i}{R_s} - \nu C_d \right) \exp \left( -\frac{t}{R_s C_d} \right) \right] \]  

This equation (as discussed in sect. 2.3.1.2) is based on a model in which the electrode is part of an RC circuit, with the working electrode behaving as an ideal capacitor. The theory is based on the Helmholtz model, which has a monolayer of ions "specifically adsorbed" to the electrode surface, and forming the second plate of the capacitor (along with the electrode surface).

The consequence of this is that for a given value of \( \nu \) (the bracketed term quickly becomes negligible - sect 2.3.1.2), the charging current, under the influence of the ramping potential, will maintain a constant value, and this would manifest on a voltammetric scan as a flat, although non-zero, baseline.

On this basis, therefore, according to the theoretical models that have been considered, the effect of increasing the sweep rate for ASV will be to produce an enhanced Faradaic (stripping) response superimposed on an increasing, but nonetheless flat, charging current response.

This model has, however, a simplifying assumption built into it that mitigates against its rigid application, and that is that the electrode/doublelayer interface behaves as an ideal capacitor. Anyone who has used voltammetric methods, however, knows that this assumption is inapplicable, as flat baselines with LSV, particularly at high sweep rates, are never observed, and it is largely this phenomenon that has spawned the various pulsed and differential waveforms that are currently in use.

As discussed in section 2.3.1.2, the fact that real linear sweep voltammograms produce sloping baselines implies that the value of \( C_d \) does not remain constant, and therefore that the nature of the doublelayer is actually changing as the sweep progresses.
The sloping LSV background, therefore, admits to no simple theory to enable its effect to be characterised, and leaves the option open of its effect being less profound than the direct proportionality observed for the Faradaic process. Were this the case, therefore, the sensitivity of the MTFE would increase with increasing $v$, and the upper limit of $v$ would be set by either the onset of semi-infinite linear diffusion in the mercury film, or instrumental limitations.

While, as has been noted, the polymer-modified electrode will outperform the conventional MTFE with respect to the first of these limiting factors, it is apparent that the second of these factors has limited the performance of the conventional MTFE, as a result of the limitations of the instruments that have been employed in this context.

To reliably accumulate the analytical signal (for LSV) at sweep rates any greater than about 200mV.s$^{-1}$, computerised instrumentation must be used, as mechanical chart recorders have difficulty maintaining resolution at these speeds. It is, however, only in the last decade or so that computerised current accumulation has become readily available, and many workers [391-393] are still using mechanical chart recorders for signal accumulation.

As well as this, for those who do use electronic data accumulation, it seems not to have occurred to them that high $v$ LSV has been rendered possible by these devices. Indeed, voltammetry was routinely performed at 1000mV.s$^{-1}$ throughout this project with the conventional MTFE, and this is, to the author's knowledge, without precedent in the literature (on GC-based MTFEs), with most workers not sweeping at rates beyond 100mV.s$^{-1}$ [24,394,395]. Indeed, with an MTFE, neither DPV nor SQWV can compete with high $v$ LSV on the basis of sensitivity, and the use of pulsed, differential waveforms is rendered obsolete.

In summary, therefore, the onset of kinetic peak broadening with the conventional MTFE limits sweep rates to about 1000mV.s$^{-1}$, (sect. 4.4.1) whereas no such effects were observed for the polymer-modified film at sweep rates up to 34V.s$^{-1}$ (fig. 4.32).
Figure 4.32: ASV of 1 ppb Cd\textsuperscript{2+} and Cu\textsuperscript{2+} (Pb\textsuperscript{2+} present at a background level of \( \approx 5 \text{ppb} \)) in 0.2M acetate buffer (pH 5.0). \( t_{\text{dep}} = 120s \). \( v = 34V.s^{-1} \).

This therefore introduces the possibility of an electrode that may be used at sweep rates that are normally considered to be in the domain of microelectrodes (>50mV.s\(^{-1}\)), with concomitant enhancement of sensitivity.
Chapter 5:

Studies with a Conducting Polymer (as an MTFE substrate)
5.1. INTRODUCTION

Given the poor adherence of mercury to the highly polished glassy carbon electrode surface, an alternative approach to the formation of an MTFE that was investigated was that of coating the electrode surface with a conducting polymer. The monomer that was selected for this purpose was pyrrole, for four reasons:

1. The polymer is easily coated onto the electrode surface *in-situ* by electrochemical oxidation of the monomer, and the use of galvanostatic conditions facilitates rigorous control of the polymeric charge density (and therefore thickness), and obviates the requirement for a reference electrode.

2. Since it is a secondary amine, it may be derivatised to a dithiocarbamate, as described in section 3.3.2.

3. The porous nature of the polymer [396] may be expected to enhance the mechanical adhesion of the mercury.

4. It is one of the most studied of the conducting polymers, and a large body of literature is available[222,397-399].

Polypyrrole, in its present form as a conducting, adherent, electrode coating, was first reported by Diaz in 1980 [400]. Since that time, it has been investigated for both its mechanical [401,402] and chemical properties [403,404], the latter being of interest from an analytical point of view due to the ability of the polymer to incorporate chemically-active species of interest (usually an anion).

This latter property stems from the manner in which the electrode is synthesised, which may be represented as in figure 5.1.

Various parameters such as choice of solvent, solution electrolyte (both ions play a role), substrate, positioning of electrodes in cell, and rate of polymerisation (galvanostatic current density) influence the form and properties of the as-grown polymer. A number of excellent reviews detail some of the specifics of the effects of these, and other, variables [405-407].
The dtc-derivatised polypyrrole was first reported by O’Riordan [384], and was used to chemically preconcentrate a number of metals prior to stripping analysis, including Cu$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Mn$^{2+}$, although not all of these metals produced useful stripping peaks.

The postulated mechanism for the derivatisation process is similar to that of the p-NET (chapter 3) and consists simply in the initial removal of the amine hydrogen, followed by addition of the CS$_2$ species (section 3.3.2).

This study, therefore, considered both the derivatised and non-derivatised electrodes with respect to their ability to act as substrates for MTFEs, and a number of aspects are examined in this regard, as outlined in section 5.3.
5.2. EXPERIMENTAL

5.2.1. ELECTRODES

Working Electrode:

The working electrode was a platinum wire electrode as described in section 3.2.1.

Counter Electrode:

The counter electrode used was a platinum gauze assembly as described in section 3.2.1.

Reference Electrode:

The reference electrode used for the aqueous work was a Ag/AgCl double-junction assembly as described in section 3.2.1.

The reference electrode used for the nonaqueous work was an Ag/Ag⁺ double-junction reference electrode as described in section 3.2.1.

5.2.2. INSTRUMENTATION:

A Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat in conjunction with a PAR Model 175 function generator, a PAR 178 electrometer probe, and a PAR Model 179 coulometer were employed for the polymer synthesis, and were used in conjunction with a Houston Instrument Omnigraphic 2000 chart recorder. Voltammetry was carried out on the BAS 100A.

The FAB mass spectrometer employed was a model MM1212 from VG Analytical. Cold vapour Mercury analyses were performed using an Instrument Laboratory 551 AA/AE Spectrophotometer with a Varian model 65 cold vapour generation unit.

The SEMs were recorded on a Hitachi 450 Scanning Electron Microscope.
5.2.3. SOLUTIONS:

All chemicals used were AR grade purity unless otherwise stated. Pyrrole was Purum ex Fluka and carbon disulfide was obtained from BDH. The pyrrole was distilled before use. AR grade benzene and 2-propanol were obtained from Ajax. HPLC grade acetonitrile was obtained from Mallinckrodt.

Metal stock solutions were prepared by dissolving appropriate salts in triply distilled water. The mercury stock solution was prepared from AR grade HgO ex Merck.

The solution from which the polypyrrole was grown was 0.1M in pyrrole and 0.5M in tetraethylammonium perchlorate (TEAP) with the addition of 1% (v/v) water. Due to the instability of this solution to UV oxidation it was prepared immediately prior to use.

The derivatisation solution was based upon the work of O'Riordan and Wallace and was constituted as follows: 50mL of AR grade benzene was added to the derivatisation vessel followed by 10mL AR grade carbon disulphide, 10mL AR grade methanol and 10mL 0.3M NaOH (Baker Analyzed) in AR grade 2-propanol.

The saturated Zn(NO)₃ solution was made from A.R. grade Zn(NO)₃ ex BDH.

5.2.4. ELECTROCHEMICAL CELLS AND GLASSWARE:

The electrochemical cell employed for the aqueous work was a Metrohm electrochemical cell as described in section 3.2.1.

A specially modified dual counter electrode electrochemical cell (fig. 5.2) was employed for the polymer plating. This cell minimised overpotential problems by ensuring, firstly, a high ratio of counter electrode surface area to working electrode surface area, and secondly, proximity of electrode surfaces to each other, thereby ensuring uniform polymer growth.
5.2.5. **EXPERIMENTAL PROCEDURES:**

**Electrode Pretreatment:**

The electrode pretreatment procedure that was employed was a three-step procedure:

1. The electrode was coated with an oxide film by immersion in chromic acid, followed by rinsing in $10M \text{ HNO}_3$.

2. The electrode surface was stripped of the oxide by cathodic electrolysis ($E_{\text{app}} = 0.18V$ vs Ag/AgCl until no further current decay).

3. The electrode surface was stripped of adsorbed hydrogen by anodic electrolysis ($E_{\text{app}} = 0.07V$ vs Ag/AgCl until no further current decay).

This procedure results in a platinised platinum surface as described by Adams [46].
Polypyrrole film formation:

The polymer was formed by electropolymerisation at a current density of 0.5 mA.cm\(^{-2}\). The polymer was grown for 60s, resulting in a nominal thickness of 0.75μm. The relationship between charge density and polymer thickness has been characterised by Diaz [408].

Preparation of poly (pyrrole-N-carbodiimide) electrode:

Dithiocarbamate groups were grafted on to the polymer surface by immersion of the as-grown polypyrrole in the derivatisation vessel for a period of 48 hours (O'Riordan & Wallace).
5.3 RESULTS AND DISCUSSION

In terms of the ability of the polypyrrole electrode (derivatised or underivatised) to act as an MTFE substrate, a number of aspects required examination:

1. Characterisation of the uncoated polypyrrole electrode. This was performed both voltammetrically and with electron microscopy.

2. Characterisation of the mercury-coated electrodes. This was also studied voltammetrically and with electron microscopy.

3. Characterisation of the performance of the electrodes as an MTFE.

5.3.1. POLYPYRROLE CHARACTERISATION:

Polypyrrole forms on the electrode surface as a dull, black film. An SEM of the electrode surface (fig. 5.3) revealed an uneven morphology, which would be expected given the ability of the polymer to grow on itself (due to its conducting nature), unlike the non-conducting p-NET.

Due to the ability of the polymer to grow upon itself, very thin films are difficult to grow uniformly, as incoming monomer will not automatically seek an uncovered (active) site, as it will for a non-conducting (polymeric) electrode. Insufficient attention to the pretreatment procedure will therefore result in patchy and uneven growth, and this may be monitored visually.

The very thinnest polypyrrole films are, however, transparent in nature, gradually becoming more opaque as they thicken. The point at which opacity is achieved is about 0.75μm, and this was therefore the nominal thickness that was selected for this study.

The polymer is weakly adsorbed to the platinum substrate, and it may easily be wiped off with a tissue when wet. When dry it adheres to the substrate considerably more strongly.

When cycled in a blank electrolyte solution, polypyrrole produces a characteristic voltammogram, as shown in figure 5.4.
**Figure 5.3**: SEM of a polypyrrole coated Pt wire electrode. Synthetic conditions: galvanostatic growth with $i_d = 0.5 \text{ mA.cm}^{-2}$, $t_{dep} = 60\text{s}$, from an acetonitrilic solution of $0.1M$ pyrrole in $0.5M$ TEAP. Diameter of wire $= 0.5\text{mm}$.

**Figure 5.4**: Cyclic voltammogram of polypyrrole-coated Pt wire electrode in $0.1M$ NaNO$_3$. Polymeric synthesis conditions as in section 5.2.
The large oxidation peak at -200mV is due to the oxidation of the polymeric backbone, resulting in the formation of (cationic) bipolarons, and the incorporation of the solution anion [409,410]. The reduction peak at -600mV is due to the reejection of the incorporated anion, the reduction of the polymeric backbone, and the return of the electrode to its nonconducting state.

No differences in either the voltammetric behaviour or the visual appearance were observed between the derivatised and underivatised electrodes.

5.3.2. MERCURY-COATED POLYPYRROLE.

The polypyrrole electrode deposited mercury electrochemically, as with a conventional electrode material. Its stripping responses are discussed by the author elsewhere [411].

SEM imaging of the surface indicated the presence of small mercury beads (fig. 5.5) wedged in the surface undulations of the electrode.

5.3.3. MERCURY-COATED POLY-(PYRROLE-N-CARBODITHIOATE)

The poly(pyrrole-N-carbodithioate) electrode (polypyrrole-dtc) was successfully used to deposit mercury from solution, both chemically and electrochemically.

Mercury was deposited electrochemically and the deposition rate compared both with polypyrrole and bare platinum. This was done by monitoring of the concentration of mercury deposition solutions using cold vapour AAS. The results are presented in table 5.1.
Figure 5.5: SEM of a polypyrrole-coated platinum electrode after electrochemical deposition of mercury at -100mV from a 1ppm Hg$^{2+}$ solution for 20 minutes. Scale: 1cm = 10μm.

Table 5.1: [Hg$^{2+}$] in solution after indicated time. $E_{\text{app}} = -0.1V$ vs Ag/AgCl, deposition time = 20 min (stirred solution). [Hg$^{2+}$] determined using cold vapour AAS.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Platinum (ppm)</th>
<th>Polypyrrole (ppm)</th>
<th>Poly(pyrrole-N-carbodithioate) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.00</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>5</td>
<td>2.77</td>
<td>2.78</td>
<td>2.16</td>
</tr>
<tr>
<td>10</td>
<td>2.40</td>
<td>2.22</td>
<td>2.14</td>
</tr>
<tr>
<td>15</td>
<td>2.38</td>
<td>2.10</td>
<td>2.14</td>
</tr>
<tr>
<td>20</td>
<td>2.38</td>
<td>2.10</td>
<td>2.14</td>
</tr>
</tbody>
</table>
These results indicated that the coated electrodes removed more mercury ions from solution more rapidly than a bare platinum electrode. As a result, the stripping responses obtained with this modified platinum substrate were much larger in magnitude [411].

To ascertain if this was simply a surface area phenomenon, linear sweep voltammograms of a standard $K_3Fe(CN)_6$ oxidation response were recorded at platinum and polypyrrole-platinum electrodes. The limiting currents obtained were identical, indicating that the electroactive surface areas must be similar. Consequently, the polypyrrole must facilitate either the mercury trapping process or enhance the oxidation kinetics in some way. The latter is highly likely, as solid metallic electrodes are poor substrates for mercury stripping due to their interaction with the mercury [169].

With polypyrrole-dtc electrode the mercury is removed from solution at a greater rate than the polypyrrole at the potentials investigated. This would suggest that the polypyrrole-dtc uptakes via complexation with the sulphur groups as well as by electrodeposition. Note that particularly in the early stages of deposition the rate of removal is markedly greater.

It is likely that at more negative potentials (than -100 mV) the relative rates of deposition of the derivatised and non-derivatised electrodes would be similar, as the Fermi-level overlap between the donor (electrode) and acceptor (Hg$^{2+}$) orbitals would be greater, thereby inducing a greater rate of electrochemical reduction, with a concomitant discrimination against the complexation process, which could be expected to proceed at an essentially constant rate.

As well as this, any Hg$^{II}$ that did complex to the dithiocarbamate sites would be quickly reduced to the metal. At a potential of -100 mV, however, there could be expected to be an appreciable population of Hg$^{II}$-dtc complexes on the electrode surface.

When used to deposit mercury chemically (without the application of a potential), the polypyrrole-dtc electrode developed a uniform and finely-divided mercury film that was clearly visible to the naked eye.

When examined at a microscopic level with SEM, it became apparent that the derivatised electrode had a greater number of smaller mercury droplets, thereby confirming the fact that it had a greater number of deposition sites than the non-derivatised polymer (fig. 5.6).
A further noteworthy feature of the polymer surface at the microscopic level is the degree of surface unevenness. Although the mercury may not be expected to adhere to the polymeric substrate to any greater degree than the glassy carbon, it is clear that the surface unevenness provides more scope for mechanical stabilisation of the individual droplets, by allowing them to sit in the crevices and pores.

The formation of the metallic mercury film by a galvanic couple at or within the surface of the derivatised polymer is not without precedent, as this is what was seen in chapter 4 with the p-NET-dtc electrode. With the case of the p-NET-dtc, however, the mercury was forced to deposit in the polymeric faults, where the substrate is exposed. Because the polypyrrole-dtc is conducting, however, this requirement is obviated, and the mercury is free to deposit on the polymeric substrate. The consequence of this is that a visibly greater amount of mercury is deposited.
The reducing agent, as with the p-NET-dtc, is likely to be the xanthate generated during the derivatisation (sect 5.2.5). The difference between this and the p-NET-dtc electrode is that polypyrrole is a highly porous polymer [396] and a greater amount of the derivatising mixture (and therefore the xanthate) is likely to be adsorbed onto and into the electrode surface.

An interesting observation in this context is that the mercury film is not seen to (chemically) deposit unless the electrode is air-dried prior to immersion in the mercury solution. That is, while ever a liquid coating is visible on the polypyrrole between the derivatisation and deposition solutions, even if the liquid coating is the solvent that is used to rinse the derivatisation solution from the electrode surface (2-propanol, followed by water), the mercury will not deposit.

A likely explanation for this phenomenon is that both the benzene and carbon disulphide used in the derivatisation mixture could be expected to adsorb quite strongly to the hydrophobic polymer surface, and unless they are removed by evaporation (leaving behind the xanthate), they could act as an insulating film that would prevent the formation of the galvanic couple necessary for the deposition of the mercury.

5.3.4. UTILITY FOR ASV:

The polymer-based MTFEs were studied in both stationary and flowing solutions. Each is considered in turn.

5.3.4.1. Stationary Solutions:

From the point of view of ASV with a polymeric MTFE, there is little to choose between the derivatised and underivatised electrodes. While one might expect that the polypyrrole-dtc might outperform the polypyrrole electrode due to its more finely divided mercury film, this turns out to be a minor consideration.

In particular, the major difficulty with the polypyrrole electrodes is the presence of the polymeric background current, which has contributions from both charging and Faradaic (if one commences a positive scan any more negative than about -800mV) processes. If LSV is used as the analytical waveform, this limits the sweep rate to about 50mV.s⁻¹, as the metallic
oxidation responses are swamped by the polymeric background at higher \( u \). These electrodes are therefore not conducive to high sensitivity or low limits of detection.

An example of a stripping response with LSV is given in figure 5.7

![Graph](image)

**Figure 5.7:** LSV stripping response for 100 ppb Cd\(^{2+}\) and Pb\(^{2+}\) (in “Chemtronics” electrolyte) at a polypyrrole-MTFE.

The use of pulsed waveforms was investigated in an attempt to discriminate against the background response, although without a great deal of success. Differential pulse voltammetry did result in an enhanced response, although the degree of enhancement (of the sensitivity) observed was not great, and given the low sweep rates required for DPV (<10 mV.s\(^{-1}\)) and the time required for each analysis, it is questionable as to whether it is the preferred method.

Square wave voltammetry gave no enhancement of the mercury response, but did result in a flat background over the potential range investigated.

When considering alternative waveforms, it must be borne in mind that the polymeric coating does more than simply contribute a charging current, as would be the case for a conventional electrode. The polymeric coating, as well
as doing this, is also providing the conduction by which Faradaic processes may be both induced and observed. If kinetic hindrances occur with the conduction process, as a function of the ramping potential, then the result will be overpotential effects and broadening of stripping peaks. This was observed for LSV at sweep rates much greater than 50mV.s⁻¹.

It is, therefore, reasonable to expect that pulsed waveforms, except for those that operate on a long timescale (such as low v DPV), will not significantly outperform the linear waveform, owing to the sharp changes in potentials that accompany the potential steps with these waveforms.

5.3.4.2. Flowing Solutions:

The mechanical stabilisation afforded by the presence of the polymeric substrate advanced the possibility of the polypyrrole electrodes being used as MTFE substrates for amperometric detection in flowing solutions.

Both the polypyrrole and polypyrrole-dtc performed adequately in this regard. Figure 5.8 shows the result obtained at a polypyrrole-Hg electrode when used with pulsed amperometric detection, and figure 5.9 shows the result obtained with the polypyrrole-dtc-Hg electrode under potentiostatic conditions.

![Figure 5.8: Pulsed amperometric detection of 250ppb Cd²⁺, Pb²⁺, Cu²⁺ at a Pt-polypyrrole-Hg electrode. Conditions as described. Analysis performed by the Dionex corporation](image)
Figure 5.9: Potentiostatic cathodic amperometric detection of 100 ppm Pb$^{2+}$ at a polypyrrole-dtc-Hg electrode. $E_{\text{app}} = -1.2$ V.
5.4. CONCLUSIONS:

Polypyrrole and polypyrrole-dtc electrodes were shown to result in substantial mechanical stabilisation of a mercury film that had been deposited either chemically or electrochemically.

The polypyrrole-dtc electrode demonstrated its ability to chemically deposit a metallic mercury film, as with the p-NET-dtc electrode in chapter 4.

The mercury-coated polypyrrole electrodes were shown to be suitable as substrates for use as electrochemical detectors in flow systems.
Chapter 6:

Conclusions and Future Work
This thesis describes the development of a chemically modified mercury thin film electrode (MTFE) and an in-situ, self-assembling microelectrode array. Each is considered in turn.

6.1. MTFE STUDIES

These studies involved both the development and characterisation of a chemically-modified MTFE, as well as some studies at the conventional MTFE.

6.1.1 CONVENTIONAL MTFE

These studies, which were necessitated by the lack of information on this subject in the literature, were successful in establishing some qualitative relationships between film parameters and performance. In particular, it was established that cadmium and lead have stripping responses that increase with increasing film thickness, whereas copper has an inverse relationship.

It was also established that the amount of mercury required for an MTFE to work (in the lower ppb range) is extremely small, and cannot be observed on the electrode surface with the naked eye. A less sensitive “second phase” film was also seen to form with greater surface coverage.

As well as this, some previously unreported physical features of the mercury film were reported, notably those of “bubble faults” and the development of centripetally-induced spiral patterns (at a rotating electrode) on the electrode surface with increased film coverage.

Finally, the degree of surface coverage of the glassy carbon substrate with the mercury film was assessed under different conditions, and particular attention was given to the deleterious effect of drying on the morphology of the mercury film, and the relevance of these considerations to the scientific literature on MTFEs.
6.1.2. CHEMICALLY-MODIFIED MTFE

Dithiocarbamate-modified secondary amine polymers, both conducting and non-conducting, were studied as substrates for MTFEs. The conducting polymer, polypyrrole, while affording increased mechanical stability for the mercury film, was unsuitable for ASV when used with a steeply ramping potential, due to the large polymeric background currents. It was, however, successfully used as an amperometric detector in a flow system, and provided qualitative information regarding the formation of the mercury film at the derivatised surface that was utilised in the study of the nonconducting polymer.

The nonconducting polymer, poly (N-ethyl-N-dithiocarbamatotyramine), was successfully used as a substrate for the formation of a MTFE. It consists of a very finely divided mercury film deposited in microscopic faults in the polymeric coating, with mercuric ions complexed at the surface-immobilised dithiocarbamate groups. Although of comparable sensitivity to the conventional MTFE, it represents a significant advance in the areas of reproducibility and chemical and mechanical stability.

As well as this, because of the extremely small size of the mercury drops, it introduces the possibility of enhanced sensitivity due to the use of LSV at sweep rates normally considered to be in the microelectrode realm (>100V.s⁻¹).

The mercury-coated glassy carbon MTFE is the first generation MTFE, and, despite its high sensitivity, is essentially unstable, inefficient, irreproducible, and poorly understood. The polymer-modified MTFE described in this project represents the first of a new generation of MTFEs which are stable, efficient, and reproducible, and will assist ASV to take its rightful place as an analytical tool in both industry and the academic sphere.

6.2. MICROELECTRODE ARRAY

This thesis also describes the development and characterisation of an in-situ, self-assembling microelectrode array. The ease with which this device is synthesised, compared to the microelectrode arrays extant in the literature, advances the possibility of electrochemically-generated polymers
revolutionising this technology. The p-NET array, as well as possessing the considerable advantage of ease of manufacture, also represents a significant advance over the surfactant-based self-assembling arrays in terms of chemical stability, as it exists on the electrode surface as a discreet polymeric film.

As a consequence of this, it is envisaged that self-assembling microelectrode array systems will dominate microelectrode array research at the expense of the more complex microfibre systems, and will form the basis for the next generation of high-performance electrochemical sensors.

6.3. FUTURE WORK:

There is significant scope for optimisation of this electrode, given that this project has successfully demonstrated the viability of the concept. Areas that are subject to examination in this regard are:

1. The ethyl substituent on the N-ethyltyramine could be substituted with an alkane of a different chain length. This may well alter the morphology of the polymer, the size of the micropores, and hence its electrochemical properties in general.

2. The derivatisation step, despite the fact that alternatives were investigated throughout this project, requires optimisation. An organic reaction process that could graft dithiocarbamate groups onto the polymer in less than 24 hours would significantly shorten the most time-consuming step of the chemical modification process.

3. The polymerisation process requires optimisation. It may well be that a polymerisation process employing a different waveform to the potentiodynamic waveform used throughout this project, or cycling over a different potential range, or at a different sweep rate, or for greater or fewer scans, will result in an electrode with improved properties.

Further to these, a comprehensive understanding of this electrode system requires an in-situ method for the characterisation of the microscopic mercury droplets present on the electrode surface, at all stages of the voltammetric process. Such technology does not, to the author's knowledge, yet exist.
A further possibility to come from these studies is technology based on the ability to grow mercury films chemically on polymeric substrates. In particular, this technology is well poised to revolutionise LCEC technology. The use of polypyrrole beads as stationary phases in these systems has been demonstrated (411), and as a result of these studies it should now be possible to synthesise a column with mercury-coated polymeric beads. Numerous possibilities are introduced by this concept, including the ability to separate cations by successive deposition/stripping cycles, as well as selective preconcentration.
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