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MEASUREMENT OF HALIDES IN PHOTOGRAPHIC EMULSIONS

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Ph.D.

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MEASUREMENT OF HALIDES IN PHOTOGRAPHIC EMULSIONS

by

Stephen Edwards

A thesis submitted for the degree of Doctor of Philosophy of the University of Luton

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Measurement of halides in photographic emulsions

ABSTRACT

Conventional Ag/AgX electrodes, responsive to halide X, cannot be used to monitor the addition of a second halide Y since such additions result in a slow chemical conversion of the macroscopic halide coating AgX to AgY. This is a serious problem in the manufacture of photographic emulsions that frequently contain more than one silver halide. The thesis describes a new electrochemical measurement technique with the ability to make appropriate determinations in solutions of mixed halides. In the new technique (termed "clean/coat/measure"), silver electrodes were prepared "in situ" by applying square wave pulses to the electrode. First the previous halide layer was removed, then the electrode was coated in situ with a new layer of silver halide and this was used to measure the open circuit potential before the cycle was repeated. In this way the halide coating reflected the composition of the measurement solution. Existing commercial instrumentation was inappropriate for the proposed measurement sequence. Thus, a range of instrument hardware and software was designed and built by the author and used to study the influences of a multitude of parameters on the measurement performance.

1. A stable and accurate measurement system was designed and fabricated allowing the potentials of eight electrodes to be measured simultaneously in grounded solutions. Data was collected and stored on a PC using custom written software. Calibration curves for conventional silver/silver chloride, bromide and iodide electrodes were obtained over a range of concentrations and temperatures. Silver/silver halides electrodes with small surface areas (<9 mm^2) and thin halide coatings (<1 nm thick) were studied to ensure that such electrodes performed as conventional large, thickly coated electrodes. Calibration curves showed no deterioration of response due to small surface areas and, over short time scales (<2 min), no deterioration due to thin layers.

2. A laboratory instrument was designed and built to apply potential pulses, control a rotating disc electrode (RDE) and collect data. The system allowed both controlled potential pulses to be applied to the electrodes and open circuit

potentiometric measurements to be made. Measurements of potential and current were collected at a rate of 10,000 measurements per second. The system used custom software running on a PC to control the instrumentation and to store data on the PC. Using this instrumentation a RDE was used to study the new "clean/coat/measure" pulsed technique. Results from the RDE study indicated that an electrode capable of sensing halide could be produced by this technique if an applied potential pulse with sufficient charge was applied. This minimum charge (11×10^{-5} C cm^{-2}) produced a coating thickness approximately equivalent to a monolayer. The study also indicated that the technique was independent of the speed of rotation of the silver electrode and was successful over a wide range of conditions of pulse time, applied potential and cycle times for solutions of potassium bromide in the range 0.001 to 0.05 M. The technique also successfully measured the addition of potassium iodide to a solution of potassium bromide while conventional thickly coated electrodes did not.

3. Two further instrumentation systems were designed and built to be used in a grounded stainless steel emulsion making vessel, one to apply controlled potential pulses and one to apply constant current pulses. Using these instruments and the conditions found for the RDE, static cylindrical electrodes in stirred solutions were investigated using both controlled potential and constant current square wave pulses of between 50 and 500 ms. Both potential step and current step techniques successfully measured the halide concentration of solutions of potassium chloride and bromide (0.001 to 0.5 M) and potassium iodide (0.0001 to 0.5 M). Both methods were also shown to be able to successfully monitor the addition of iodide to bromide and chloride solutions.

With respect to future work, modifications to the instrumentation are proposed, including the replacement of the PC by an on-board microprocessor, the design of a multi-channel system and use of intelligent software to determine the optimum potential or current to apply. Areas of work required to be carried out before the system could be used in a production environment are given.

LIST OF CONTENTS

Abstract	II
List of Contents	IV
List of Figures	XII
List of Plates	XIX
List of Tables	XX
Acknowledgements	XXIII
Declaration	XXIV
Glossary	XXV

Chapter 1 Introduction 1

1.1. Aims of the Project and structure of the thesis 1

1.1.1. Aims and Objectives 1

1.1.2. Structure of the thesis 2

1.2. Manufacture of photographic "emulsions" 3

1.2.1. Raw materials 4

1.2.1.1. Gelatin 4

1.2.1.2. Silver nitrate 4

1.2.1.3. Sodium chloride, sodium bromide and potassium bromide 4

1.2.2. Precipitation 4

1.2.2.1. Single run 6

1.2.2.2. Double Run 6

1.2.3. Emulsion grain size 6

1.2.4. Grain growth (ripening) 7

1.2.5. Measurement of the VAG or halide ions with silver halide electrodes 8

1.2.6. VAG control 9

1.2.7. Computer controlled emulsion making 11

1.3. Problems with the current measurement systems 11

1.4. Proposed Research Work 13

Chapter 2 Theoretical Considerations 16

2.1. Introduction 16

2.2. Process A, plating or oxidation 18

2.2.1. Potential step theory 18

2.2.2. The coating process 19

2.2.3. Diffusion theory 25

2.2.4. Rotation Disc Electrode 26

2.2.5. Current profile of an applied potential coating pulse 28

2.2.6. Potential profile of an applied constant current pulse 29

2.3. Process B, potential measurement 29

2.3.1. Equilibrium potential 30

2.3.2. Solubility Product 30

2.3.3. Activity coefficients 31

2.3.4. Junction potential 33

2.3.5. Thermal coefficient of standard potential, $(dE^0/dT)_{thermal}$ 33

2.3.6. Theoretical values for the measured cell 34

2.3.7. Selectivity to other halides 34

2.4. Process C, reduction of silver halide 36

2.4.1. Current profile for controlled potential stripping 36

2.4.2. Potential profile for constant current stripping pulse 37

Chapter 3 Potentiometric measurements at equilibrium 39

3.1. Introduction 39

3.2. Equipment and instrumentation 40

3.2.1. Electronic instrumentation 41

3.2.1.1. Potentiometric measurement circuits 41

3.2.1.2. Front-end interface module 42

3.2.1.3. Analogue Devices RTI850 card 44

3.2.1.4. RTI 850 software library 46

3.2.1.5. Software program 47

3.2.1.6. Equipment for electrochemical coating of silver 47

electrodes
3.2.2. Electrochemical cell 48
3.2.2.1. Reference Electrode 48
3.2.2.2. Standard Silver Electrode 49
3.3. Electrode preparation methods 50
3.3.1. Electrochemical preparation 50
3.3.2. Chemical preparation 52
3.3.3. Comparison of preparation techniques 53
3.3.4. Experimental procedure 53
3.3.5. Results 54
3.3.6. Discussion 55
3.4. Equilibrium cell potentials measurements 55
3.4.1. Measured equilibrium potential of a silver/silver halide electrode with variation of halide ion concentration 55
3.4.1.1. Measurement procedure 55
3.4.1.2. Chloride Results 57
3.4.1.3. Bromide Results 58
3.4.1.4. Iodide Results 59
3.4.1.5. Discussion 60
3.4.2. Measured equilibrium potential of a silver/silver bromide electrode with variation of temperature 63
3.4.2.1. Measurement procedure 63
3.4.2.2. Results 65
3.4.2.3. Discussion 67
3.5. Effect of electrode surface area on measured equilibrium potential 69
3.5.1. Electrode fabrication 69
3.5.2. Measurement procedure 70
3.5.3. Results 71
3.5.4. Discussion 72
3.6. Effects of depositing thin layers of silver bromide 73
3.6.1. Measurement procedures 73

3.6.2. Results 73
3.6.3. Discussion 74
3.7. Summary 75

Chapter 4 Investigations using a rotating disc electrode 78
4.1. Introduction 78
4.2. Equipment and instrumentation 79
4.2.1. Analogue Devices RTI815 and RTI850 PC cards 80
4.2.1.1. RTI800 software functions 80
4.2.1.2. RTI 850 Card 81
4.2.1.3. RTI 815 Card 81
4.2.2. Pulse controller 82
4.2.3. Rotation Disc Electrode 84
4.2.4. Measurement cell 85
4.2.4.1. Reference Electrode 84
4.2.5. Software 86
4.3. Experimental methods and details 90
4.3.1. Experimental procedures 90
4.3.2. Materials 90
4.3.3. Experimental details 91
4.3.3.1. CV of potassium bromide and potassium iodide solutions 91
4.3.3.2. Initial investigation using the rotating disc electrode (RDE) 91
4.3.3.3. Investigation of the stripping pulse current 92
4.3.3.4. Investigation of the coating pulse 95
4.3.3.5. Investigation of the stripping and coating pulse while varying the bromide concentration 97
4.3.3.6. Investigations of the open circuit potential. 97
4.3.3.7. Investigations on varying bromide concentration 99
4.3.3.8. Investigations with mixed bromide and iodide halide present 100

4.4. Results and Discussion 102
4.4.1. CV of potassium bromide and potassium iodide solutions 103
4.4.2. Initial investigation using the rotating disc electrode (RDE) 102
4.4.3. Results from experiments to investigate the stripping pulse 107
4.4.3.1. Coating pulse duration 107
4.4.3.2. Applied stripping potential 110
4.4.3.3. Stripping pulse rotation speed 112
4.4.3.4. Discussion 114
4.4.4. Investigations of the coating pulse 115
4.4.4.1. Effect of adding a delay time and varying the rotation speed 116
4.4.4.2. Effect of varying delay time on coating current 117
4.4.4.3. Effect of coating potential on coating current 122
4.4.4.4. The effect of coating pulse duration on coating current 124 125
4.4.4.5. Effect of number of cycles 125
4.4.4.6. Discussion 133
4.4.5. Investigations of the stripping and coating current while varying the bromide concentration 133
4.4.5.1. Results and Discussion 136
4.4.6. Factors effecting the open circuit potential 136
4.4.6.1. Variation of silver electrode rotation speed 137
4.4.6.2. Variation of applied stripping potential 138
4.4.6.3. Variation of applied coating potential 140
4.4.6.4. Variation of coating pulse duration 142
4.4.6.5. Effect of the number of cycles on the open circuit potential
4.4.6.6. Discussion – Approach to the steady state open circuit potential 142
4.4.7. The effect of bromide on the clean/coat/measure cycle 144
4.4.7.1. Discussion 147
4.4.8. Results from experiments with bromide and iodide present 148

4.4.8.1. Effect of adding iodide to a bromide solution 148
4.4.8.2. Discussion 152
4.5. Summary 153

Chapter 5 Experiments in "clean-coat" technique using cylindrical electrodes in stirred solutions with a controlled potential 156

5.1. Introduction 156
5.2. Equipment and instrumentation 157
5.2.1. Analogue Devices RTI 800 Series Cards. 158
5.2.2. RTI800 software functions 158
5.2.3. Programmed potential pulse controller 158
5.2.4. Electrodes 160
5.2.5. Software 161
5.3. Experimental methods and details 164
5.3.1. Experimental procedures 166
5.3.1.1. Cyclic Voltammetry 166
5.3.1.2. Variation of pulse duration 166
5.3.1.3. VAG value point versus time after pulse 167
5.3.1.4. Variation of applied potential during coating pulse 168
5.3.1.5. Effect of bromide concentration on CCM VAG 168
5.3.1.6. Variation of ionic strength on stripping and coating current 169
5.3.1.7. Calibration of an optimised system in potassium chloride, bromide and iodide solutions 169
5.3.1.8. Effect of addition of other halide ions 171
5.4. Results and Discussion 172
5.4.1. Experiments with a controlled stripping and coating potential 172
5.4.1.1. Cyclic Voltammetry 172
5.4.1.2. Variation of pulse duration 173
5.4.1.3. VAG value point versus time after pulse 176
5.4.1.4. Variation of applied potential during coating pulse 178

5.4.4.5. Effect of bromide concentration on CCM VAG 180
5.4.4.6. Variation of ionic strength on stripping and coating current 184
5.4.4.7. Calibration curves for potassium chloride, bromide and iodide using an optimised system 182
5.4.4.8. Effect of addition of other halide ions 184
5.4.4.9. Discussions 185
5.5. Summary 190

Chapter 6 Experiments in "clean/coat/measure" technique using cylindrical electrodes in stirred solutions with a constant current. 192

6.4. Introduction 192
6.2. Equipment and instrumentation 193
6.2.1. Analogue Devices RTI815 and RTI850 PC cards. 193
6.2.2. RTI800 software functions. 193
6.2.3. Constant current pulse controller 193
6.2.4. Electrodes 194
6.2.5. Software 195
6.3. Experimental methods and details 195
6.3.1. Experimental procedures: Constant current experiments 196
6.3.1.1. Variation of pulse duration 196
6.3.4.2. Variation of constant current value 197
6.3.1.3. Effect of bromide concentration 197
6.3.4.4. Effect of addition of other halide ions 198
6.4. Results and Discussion 200
6.4.1. Experimental results using a constant current 200
6.4.1.1. Effect of pulse duration 200
6.4.4.2. Effect of variation of stripping and coating constant current 204
6.4.4.3. Effect of halide concentration on final potential 202
6.4.4.4. Effect of addition of other halide ions 203
6.4.4.5. Discussion 209

6.5. Summary 214

Chapter 7 Conclusion 216

7.1. Introduction 216

7.2. Measurement of steady state potential using silver halide electrodes 217

7.3. Rotating disc silver electrode 218

7.4. Stripping and coating under controlled potential in stirred solutions 220

7.5. Use of constant current stripping and coating pulses 221

7.6. Selectivity to interfering halide ions 221

7.7. Applicability to emulsion manufacturing 222

7.8. Instrumentation 223

7.9. Completion of aims and objectives 223

7.10. Future work 224

References 225

Appendices A1

Appendix I A1

Appendix II A7

Appendix III A10

LIST OF FIGURES

Chapter 1

1.1 VAG versus grain shape 10

1.2 Schematic of "clean/coat/measure" cycle 15

Chapter 2

2.1 Clean/coat/measure cycle 16

2.2 Coating of silver halide 19

2.3 Diffusion model of electrode-solution interface 23

2.4 Model Voltammogram for a solution of chloride, bromide and iodide 25

2.5 Rotating disc electrode 26

2.6 Diffusion layer thickness as a function of the rotation speed 27

2.7 Model of current profile for a +500 mV applied potential coating pulse 29

2.8 Activity coefficients for potassium bromide at various concentrations and temperatures 33

2.9 Stripping of the AgCl layer 36

2.10 Modelled current profile for controlled potential stripping pulse 37

2.11 Sands model of chronopotentiometry 38

Chapter 3

3.1 Experimental set-up comprising IBM PC, data collection hardware, reference bridge and measurement cell. 40

3.2 Simple potentiomtric measurement circuit 41

3.3 Differential measurement circuit utilising a solution ground. 42

3.4 Circuit diagram showing high impedance amplifiers on reference and silver electrode channels and differential circuit. 43

3.5 Analogue Devices RTI 850 PC card 45

3.6 Reference electrode in salt bridge. 49

3.7 Massive silver electrode 50

3.8 Electrode coating station 52

3.9 Equilibrium potential, measured after 2 minutes, for a silver/silver 57

chloride electrode in potassium chloride test solutions at 40 °C.
3.10 Equilibrium potential, measured after 2 minutes, for a silver/silver bromide electrode in potassium bromide test solutions at 40 °C. 58
3.11 Equilibrium potential, measured after 2 minutes, for a silver/silver iodide electrode in potassium iodide test solutions at 40 °C. 59
3.12 Difference between measured equilibrium potential and theoretical calculated value at 40 °C for silver/silver chloride electrode 60
3.13 Equilibrium potential of silver/silver chloride electrodes at various temperatures and chloride concentrations 65
3.14 Equilibrium potential of silver/silver bromide electrodes at various temperatures and bromide concentrations 66
3.15 Equilibrium potential of silver/silver iodide electrodes at various temperatures and iodide concentrations 67
3.16 Difference between theoretical and observed potential values for silver chloride (top), silver bromide (middle) and silver iodide (bottom) electrode at 25, 40 and 60 °C 68
3.17 Equilibrium potential for Silver bromide electrodes of various surface areas 71
3.18 Difference between theoretical and measured equilibrium potential with variation of surface area. 72
3.19 Variation of potential measured over 5 minutes for electrodes coated at a current density of 5 mA cm^{-2} for coating times between 10 ms and 100 seconds in 0.1 M (top) and 0.001 M KBr (bottom) 74

Chapter 4

4.1 The full "clean/coat/measurement" cycle 78
4.2 Experimental set-up showing rotating disc electrode and control units 79
4.3 Simple Potentiostat circuit 82
4.4 Pulse controller 83
4.5 Hydrogel reference electrode with potassium nitrate fill solution 85
4.6 Software flow diagram of program A 87

4.7	Timing diagram of complete cycle showing the applied potential and rotating speed.	88
4.8	Software flow diagram of program B	89
4.9	Cyclic voltammogram showing the formation of silver bromide at the rotating silver disc electrode with subsequent stripping at negative applied potentials	102
4.10	Cyclic voltammogram showing the formation of both silver bromide and silver iodide at the rotating silver disc electrode with subsequent stripping of the halides during reverse scan	102
4.11	Full current (top) and voltage cycle (bottom) – (hundredth cycle in a series of cycles).	104
4.12	Effect of rotation speed on the stripping and coating currents with no delay between the two processes	105
4.13	Plot of coating pulse current measured at 25 ms and 75 ms after the start of the pulse versus the square root of the RDE rotation speed	106
4.14	Plot of charge calculated from stripping and coating curves at varying rotation speeds.	106
4.15	Effect of varying the coating pulse time and hence the amount of silver bromide converted on the stripping pulse currents.	108
4.16	Plot of coating pulse time against total charge consumed during the oxidation process	109
4.17	Current and Voltage curves showing silver electrode at ground potential for a few milliseconds after the coating pulse potential has been switched off.	109
4.18	Value of the charge passed for the coating pulse compared against the stripping pulses	110
4.19	Effect of varying the stripping potential while keeping constant the amount of silver bromide converted during the coating process constant	111
4.20	Plot of total charge drawn for the stripping and coating pulse at all applied stripping potentials.	111
4.21	Coating current curves at 16 Hz coating pulse rotation speed and 1 to	112

36 Hz stripping rotation speed with a 5 s delay.
4.22 Stripping current curves at 16 Hz coating pulse rotation speed and 1 to 36 Hz stripping rotation speed with a 5 s delay 113
4.23 Coating current curves at 1, 16 and 36 Hz coating pulse rotation speed with 1 to 36 Hz stripping rotation speed and a 5 s delay 116
4.24 Plot of potential and current with delay added between stripping and coating pulses 117
4.25 Coating current plot showing the three distinct sections 118
4.26 Coating pulse current versus time for section 2 (left) and section 3 (right) for various delays at 1 Hz (top) and 36 Hz (bottom) rotation speed. 119
4.27 Coating pulse current versus time for section 2 (left) and section 3 (right) for 10 ms (top) 5800 ms (bottom) delays at various rotation speeds. 121
4.28 Plot of coating pulse currents for various applied potentials with a 10 ms delay between the stripping and coating pulses 122
4.29 Relationship between duration of section 2 and applied coating potential (top) and plot of charge against applied coating potential (bottom). 123
4.30 Plot of coating pulse currents for various coating pulse durations with a 300 ms delay between the stripping and coating pulses. 124
4.31 Coating pulse currents for cycle 10 and cycle 15000 of a four hour run. 125
4.32 Diagram of solid silver, diffusion layer and bulk solution for 1 and 36 Hz rotation speed 126
4.33 Diagram of solid silver, diffusion layer and bulk solution for 1 and 36 Hz rotation speed with delay between stripping and coating pulses 128
4.34 Stripping (top) and Coating (bottom) current curves for varying bromide concentrations 134
4.35 Open circuit potential for various silver electrode rotation speeds. 136
4.36 The measured potential for various stripping pulse applied potential 137

4.37 The effect of the variation of applied coating potential on measured open circuit potential 139
4.38 The effect of the variation of applied coating potential on measured open circuit potential 140
4.39 The effect of the variation of coating pulse duration on measured open circuit potential. 141
4.40 Open circuit potential for cycle 10 and cycle 15000 of a four-hour run. 142
4.41 Varying Bromide concentration by addition 145
4.42 Variation of potassium bromide concentration on measured open circuit potential. 146
4.43 Varying Bromide concentration by addition with theoretical values marked for each concentration 146
4.44 Effect of adding iodide to a bromide solution 144
4.45 Effect of adding iodide to a bromide solution 151

Chapter 5

5.1 Simple potentiostat circuit 159
5.2 Circuit for applying potential to silver electrode in grounded vessels 160
5.3 Hydrogel reference electrode 161
5.4 Clean/coat/measure timing cycle 163
5.5 Clean/coat/measure program flow chart 164
5.6 CV of potassium bromide in potassium nitrate using PAR174 potentiostat (top) and potential pulse controller module 172
5.7 Variation of stripping and coating pulse duration 50 ms (top) 200 ms (bottom) on cycle current and potential 174
5.8 Variation of concentration and stripping and coating pulse duration on final potential 175
5.9 VAG measured at various points after the coating pulse 176
5.10 Average VAG measurements plotted against time after coating pulse 177
5.11 Variation of coating potential on cycle current and potential 178
5.12 Effect of changing the applied coating potential on measured VAG 179

5.13 Effect of bromide on measured currents and potentials. 180
5.14 Effect of ionic strength on measured current and potential profiles 182
5.15 Calibration curves for chloride (top), bromide (middle) and iodide (bottom). 183
5.16 Electrode potential changes due to the addition of concentrated bromide to an initial solution of potassium bromide/nitrate 184
5.17 Electrode potential changes as iodide was added to a bromide solution. 185

Chapter 6

6.1. Circuit for applying a constant current to the silver electrode 194
6.2. Measured potentials during and after constant current stripping and coating 200
6.3. Potential profiles for stripping and coating pulses at various constant currents 201
6.4. Open circuit potentials of solutions of potassium bromide with various concentrations 202
6.5. Open circuit potentials of solutions of potassium bromide with various concentrations 203
6.6. Potential profiles for standard solutions of chloride, bromide and iodide. 203
6.7. Response of CCM and conventional coated electrodes to the addition of potassium iodide to a potassium chloride solution 204
6.8. Measured potentials during the cycle immediately before and after the addition of potassium iodide to a solution of potassium chloride 206
6.9. Response of CCM and conventional coated electrodes to the addition of potassium iodide to a potassium bromide solution 207
6.10. Measured potentials during the cycle immediately before and after the addition of potassium iodide to a solution of potassium bromide 208
6.11. Response of CCM and conventional AgCl coated electrodes to the addition of potassium iodide to a potassium chloride solution 208
6.12. Oxidation wave of silver-silver bromide 212

6.13. Conversion of silver chloride to silver iodide 212
6.14. Conversion of silver bromide coating to silver iodide 213

LIST OF PLATES

Chapter 4

4.1 Photograph of experimental set-up 80

4.2 Pulse controller module 84

4.3 Rotating disc electrode 84

LIST OF TABLES

Chapter 1

1.1 Types of emulsions, properties and uses 5

Chapter 2

2.1 Parameters used to model voltammogram 24

Chapter 3

3.1 Composition of chemical coating solution 53

3.2 Results from chemically coated silver bromide electrodes 54

3.3 Results from electro-chemically coated silver bromide electrodes 54

3.4 Measured potentials for a silver/silver chloride electrode in potassium chloride test solutions at 40 °C 57

3.5 Measured potentials for a silver/silver bromide electrode in potassium bromide test solutions at 40 °C 58

3.6 Measured potentials for a silver/silver iodide electrode in potassium bromide test solutions at 40 °C 59

3.7 Gradients of trend lines for measured and theoretical values 61

3.8 Measured equilibrium potential of a silver/silver chloride electrode with variation of temperature 65

3.9 Measured equilibrium potential of a silver/silver bromide electrode with variation of 66

3.10 Equilibrium potential of silver/silver iodide electrodes at various temperatures and iodide concentrations temperature 67

3.11 Silver electrodes fabricated with surface areas and coating currents. 70

3.12 Equilibrium potentials for silver bromide electrodes with various surface areas. 71

3.13 Thickness of silver bromide coating calculated from the charge passed and the density of silver bromide. 75

Chapter 4

4.1 Conditions used in experiment to investigate electrode rotation speed 92

4.2	Stripping pulse experimental details	94
4.3	Coating pulse experimental details	96
4.4	Conditions used to study the variation of bromide concentration on stripping and coating current curves.	97
4.5	The effect of rotation speed (W_{SP}), stripping potential (E_{SP}), delay time (t_D), coating potential (E_{CP}) and coating pulse duration (t_{CP}) on open circuit equilibrium potential measurement	98
4.6	Experimental conditions to determine the effect of bromide concentrations on open circuit potential	100
4.7	Effect of addition of iodide to bromide solution on open circuit potential	101
4.8	Optimised conditions	155

Chapter 5

5.1	Conditions used to investigate the effect of stripping and coating pulse duration	167
5.2	Conditions used for the investigation of the CCM VAG potential time after coating pulse	167
5.3	Conditions used to determine the effect of coating potential on CCM VAG	168
5.4	Conditions used to determine effect of concentration on CCM VAG	168
5.5	Conditions used to test effect of ionic strength	169
5.6	Optimised conditions for controlled potential system	169
5.7	Conditions used for calibration curves	170
5.8	Condition used for the addition of concentrated potassium bromide	171
5.9	Conditions used for the addition of a solution of potassium iodide to a potassium bromide solution.	171
5.10	Mean and standard deviation of VAG measurements	177
5.11	Average measured coating charge at 50 ms and 200 ms pulse durations in four bromide concentrations. Conditions given in Table 5.1	186
5.12	Standard operating conditions	188

Chapter 6

6.1. Conditions used to investigate stripping and coating pulse duration. 197

6.2. Conditions used to investigate stripping and coating constant current 197

6.3. Conditions used to investigate effect of bromide concentration.

6.4. Concentration of comparison standards 199

6.5. Conditions used in emulsion simulation test 199

6.6. Additions and timings of simulated emulsion tests 199

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My family - Liz, Abbi and Alice - who allowed me to lock myself in my office for six months, and more .....

Declaration

I declare that this thesis is my own, unaided work. It is being submitted for the degree of Philosophy at the University of Luton. It has not been submitted for any degree or examination in any other University.

Stephen John Edwards



February 2003

Glossary

symbol	description	units
a_i	activity of species i	mol dm^{-3}
A	surface area	cm^2
A_C	Debye Huckel constant	
A_M	Debye Huckel constant	
(aq)	aqueous phase	
B_C	Debye Huckel constant	
B_M	Debye Huckel constant	
β	Debye Huckel constant	
C	capacitance	F cm^{-2}
c_b	concentration in bulk	mol cm^{-3}
c_i	concentration of species i	mol cm^{-3}
C_s	concentration at electrode surface	mol cm^{-3}
CV	cyclic voltammogram	
D_i	diffusion coefficient of species i	$cm^2 s^{-1}$
d	distance	cm
δ	diffusion distance	cm
E	potential	V
E_{ref}	reference electrode potential	V
E_{app}	applied potential	V
E_{eq}	equilibrium potential	V
$E^0_{Ag/AgX}$	standard potential of Ag/AgX couple	V
E_T	theoretical potential	V
E_m	measured potential	V
E_{CP}	coating pulse potential	V
E_j	junction potentail	V
E_{SP}	stripping pulse potential	V
E_{WE}	potential of working electrode	V
ε	dielectric constant of water	
ε_0	permititivity of free space	F cm^{-1}
F	Faraday constant	C mol^{-1}
[i]	concentration of species i	mol dm^{-3}
I	current	A
I_C	ionic strength	mol dm^{-3}
I_{limit}	limiting current	A
I_{CP}	coating pulse current	A
I_{SP}	stripping pulse current	A
j_i	flux of species i	mol cm^{-2} s^{-1}
k	Boltzman constant	JK^{-1}
$\overleftarrow{k}, \vec{k}$	rate constant	cm s^{-1}
K_{spAgX}	solubility product of AgX	mol^2 dm^{-6}
$K^{pot}_{X,Y}$	selectivity coefficient of X over Y	
n	number of electrons	
N_A	Avogadro constant	mol^{-1}

η	overpotential	V
η_s	viscosity of fluids	Pas
ρ	density	g cm^{-3}
Q	charge	C
R	resistance	ohm
R	Gas constant	J K^{-1} mol^{-1}
s_i	ionic distance of i	cm
STDEV	standard deviation	
(s)	solid phase	
ν	kinematic viscosity	cm s^{-1}
T	absolute temperature	°K
θ	temperature (centigrade)	°C
τ	transition time	s
t_{CP}	duration of coating pulse	s
t_D	delay time	s
t_{SP}	duration of stripping pulse	s
t_m	time of potential measurement (VAG)	s
$t_{measure}$	duration of measurement collection	s
μ_i	chemical potential of species i	J mol^{-1}
W	angular velocity	Hz
VAG	potential of measurement cell	V
W_{CP}	rotation speed during coating pulse	Hz
W_{SP}	rotation speed during stripping pulse	Hz
γ	activity coefficient	
z	charge number of an ion	

Chapter 1. Introduction

This project was undertaken to understand better the measurement of the silver or halide ion activity in a solution of mixed halide ions containing a silver halide precipitate. In the photographic industry silver and halide ion activities are measured routinely by potentiometry in order to control the precipitation process during the manufacture of photographic products. The potential difference measurement method uses a silver halide coated silver metal electrode as an indicator electrode. This coated electrode is responsive to the halide ions. This is accomplished easily in solutions of only one halide ion; however, when two or more halide ions are present, both the interfering effect of the extra halides and the conversion of the halide in the coated layer by the extra halides make measurement with conventional silver/halide electrodes troublesome. This project, based on a recent patent (Edwards and Sandifer, 1995), describes and investigates a technique where the halide coating on a silver substrate is repeatedly renewed by applying cleaning and coating electrical pulses just prior to a potentiometric measurement. This "clean/coat/measure" technique will be more fully described later in this chapter.

1.1 Aims of the project and structure of the thesis

1.1.1 Aims and objectives

The aim of the project was primarily to investigate and optimise a new method for the determination of the free halide in a silver halide photographic "emulsion" based on the technique of repeatedly recoating the silver electrode immediately before measurement in the sample solution described in the above patent. This was sub-divided into four main objectives:

a) to study current methods of producing silver/silver halide electrodes and to investigate effects of size, preparative techniques, concentration and coating thickness on the steady state potential;

b) to study the new clean/coat/measure technique using precision laboratory equipment and a rotating disc electrode to discover the dependant parameters and the limits of the system;

c) to design and fabricate a system for use in a "real" emulsion situation and to test this over a wide range of parameters; and

d) to propose a system and conditions for trials in a process environment.

1.1.2 Structure of the thesis

This chapter describes the aims of the project, gives an introduction to photographic emulsion making, and gives a brief technical description of the proposed technique.

Chapter 2 documents the theory necessary to understand the techniques and processes studied and derives equations used to calculate the theoretical values for the steady state potential of the silver halide electrode.

Chapter 3 describes the equipment and associated software designed, built and used to study the potential of silver electrodes. It also details the investigations of the steady state potential of conventional silver halide coated electrodes and compares different methods of preparation, effects of concentration, electrode surface area and coating thickness. Results are given along with the difference from theoretical values.

In Chapter 4 an explanation of the new proposed technique is given along with the design of the laboratory equipment built for this project. Experimental results of the studies to determine the various conditions that affect the measured steady state potential and the processes of the technique are shown. Conclusions on these results and the proposed optimised conditions are discussed.

Chapter 5 describes the controlled potential method using a small cylindrical electrode in stirred solutions instead of the rotating disc electrode. It gives results obtained using this system under various conditions and in a variety of samples.

Chapter 6 describes the clean/coat/measure technique using constant current pulses instead of controlled potential pulses. Results of experiments in single halide as well as mixed halide samples are given.

Chapter 7 includes a final discussion and gives the conclusions of the investigation. It also proposes a measurement system and gives an outline of what future research work might usefully be undertaken.

1.2 Introduction to the manufacture of photographic "emulsions"

Photographic emulsion is a dispersion of small grains of light sensitive silver halide in a dilute gelatin solution (5-10% w/v). The process of making an emulsion has the basic steps:

1. The formation of silver halide micro-crystals in a gelatin solution ("precipitation").

2. Grain growth to achieve the desired grain size ("ripening").

3. Washing the emulsion to remove the by-products of the precipitation stage or in some cases of the grain growth stage ("washing").

4. Chemical sensitisation - usually with a heat treatment to increase the emulsion speed ("finishing").

5. Spectral sensitisation to impart emulsion sensitivity to specific areas of the light spectrum ("finishing").

Some of these steps are sometimes combined or even omitted, depending on the characteristics required of the final emulsion.

1.2.1 Raw materials

1.2.1.1 Gelatin

To produce a fine dispersion of silver halide grains, it is necessary to have a means of keeping the grains separated and in suspension throughout the production cycle, otherwise the emulsion will coagulate into an amorphous mass at the bottom of the manufacturing vessel. Early in the development of photographic emulsions, it was found that gelatin not only fulfilled this role but had the added advantage of setting when chilled making the coating of glass plates straight forward. Further advantages became obvious when the emulsions needed to be washed and finished, because natural impurities in the gelatin actually helped to sensitise the early emulsions to visible light. The gelatin used in the photographic industry is mainly extracted from cattle bones or pig skin.

1.2.1.2 Silver nitrate

The silver nitrate used in emulsion making is produced by dissolving bars of pure silver bullion in concentrated nitric acid. This produces a solution of silver nitrate, which is further processed by slowly evaporating water to yield pure crystalline silver nitrate.

1.2.1.3 Sodium chloride, sodium bromide and potassium bromide

Sodium chloride is mined or processed from sea-water. The bromide salts are made by the reaction of bromine with either sodium or potassium hydroxide. The reaction produces a mixture of the respective bromide and bromate, the latter being converted to bromide by the action of either formaldehyde or hydrazine.

1.2.2 Precipitation

Silver nitrate is very soluble in water but silver chloride, bromide or iodide are virtually insoluble. Therefore if a solution of soluble halide is added to a solution of silver nitrate, solid silver halide is formed which is held in suspension by the

gelatin solution. The crystal grains normally have a lattice structure consisting of an array of alternating silver atoms and halide atoms in a cubic structure. Other crystal shapes are possible by changing the environment in which the precipitation takes place and by the presence of different halides. Photographic emulsions are made either from silver nitrate and a single halide salt or from silver nitrate and a mixture of halide salts. These mixed halide emulsions find use in specialised applications, Table 1.1.

Not only is the halide mix important to the type of use of a given emulsion but probably more important is the effect of the grain size and shape. Chloride and chloro-bromide emulsions have historically been regarded as small-grain, slow speed, high contrast emulsions. Bromide and bromo-iodide emulsions are regarded as large-grained, fast, lower contrast emulsions. However this is more due to the historical modes of preparation than the inherent properties of the different emulsions.

Emulsion Type	Properties	Uses
Silver chloride	Most soluble of silver halide emulsions. Easy to reduce to silver metal (easily developed) Low sensitivity to visible light.	Graphic products.
Silver chloride/silver bromide (chloro-bromide emulsions)	Highly soluble Easy to reduce to silver metal (easily developed).	Paper products.
Silver bromide	Lower solubility and slower development rate, but higher natural sensitivity to blue light.	Rarely used except in instant films.
Silver bromide/silver iodide (bromo-iodide emulsions)	Lowest solubility, low development rate.	
Silver iodide	Not very easy to develop and not very light sensitive.	Very rarely used.

Table 1.1 Types of emulsions, properties and uses.

There are two common processes for the manufacture of photographic emulsions : the single-run and the double-run types.

1.2.2.1 Single run

All the halide is present in the manufacturing vessel or kettle at the start of the make, and the silver nitrate solution is added slowly under controlled conditions to form the emulsion. In this type of process there is a high concentration of halide present in the kettle at the start which decreases as the run proceeds. The excess halide creates an ideal grain growth environment and causes the nuclei formed near the start of the process to grow while new nuclei are still being formed in the kettle. If the run time is very short then the grains do not have very long in which to grow before the silver run is complete and so small grain size emulsions with a fairly narrow grain size spread are produced. However, if the silver run is very long then there is ample time for grain growth to take place and the resulting emulsions tend to have a wide spread of grain sizes producing a fast but low contrast emulsion ideal for most camera films where wide exposure latitudes are needed.

1.2.2.2 Double-run

At the start of the process in this method, either there is only gelatin solution present or there is gelatin solution with a low concentration of a halide. Silver nitrate and the halide solutions are run into the manufacturing vessel at the same time to form the emulsion. This, the most commonly used method of precipitation, normally involves the control of the silver ion concentration by potentiometry and produces a more uniform emulsion. This control is called "VAG control" where the VAG value is the potentiometric difference obtained from a silver electrode or silver halide electrode and reference electrode. This will be explained further in section 1.5

1.2.3 Emulsion grain size

The size and shape of the grains have a direct effect on the photographic speed of the final emulsion. Clearly, for a given level of light exposure, more light will fall

on a larger grain than a small one. This means that the larger grains are more sensitive to light than small ones, and so are regarded as being photographically faster.

The main factors that affect the grain size are –

- solubility of the silver halide in the kettle
- addition rate of the silver and halide salts
- runtime.

As the solubility of the various halides in the emulsion decreases in the order chloride to bromide to bromo-iodide, the grain size produced falls respectively. This can be seen if we consider what happens during the runs. At the start of the runs, only nuclei (very small grains) are formed, and this continues for about the first 1.5 to 2 minutes for a single-run emulsion or 10 to 15 seconds for a double-run emulsion after which time a grain growth stage is entered. The number of grains formed during the nucleation depends on the solubility of the particular silver halide in the gelatin solution

A low solubility silver halide such as AgBr/I will tend to form nuclei more easily than a high solubility silver halide such as AgCl, because less AgBr/I is able to stay dissolved in the solution than AgCl. The size and number of grains therefore depends on the type of silver halide being formed in the vessel.

1.2.4 Grain growth (ripening)

After the nucleation stage of the runs, a grain growth stage is entered, during which time the number of grains in the kettle decreases. This growth stage is often referred to as "Ostwald ripening" during which time the small grains, which are more soluble than larger ones, dissolve preferentially to form a supersaturated solution which reprecipitates out the silver halide on the surface of the larger

grains, causing them to grow. During this stage in a double-run emulsion, the rate of formation of nuclei is balanced by the rate at which they are redissolved to precipitate out again on the surface of larger grains. Any factors that increase the solubility of the small grains in the vessel will increase the rate of grain growth and hence the final emulsion grain size. The most common ways to increase grain growth are:

- increase kettle temperature.
- increase free halide concentration
- addition of grain solvents, e.g. ammonia, thioethers.

1.2.5 Measurement of the VAG or halide ions with silver halide electrodes

Currently there are two potentiometric methods suitable for the measurement of the silver/halide equilibrium ion activity in a process control environment where the halide ion is in excess. Both of these measurements yield a potential defined as the VAG. The first method used is based on the principle that a silver electrode will respond to the silver ion activity. The Nernst equation defines the relationship:

$$E_{Ag/Ag^+} = E^0{}_{Ag/Ag^+} + \frac{RT}{nF} \ln a_{Ag^+} \qquad 1.1$$

In silver halide emulsions the activities of silver and halide ions are frequently determined by the equilibrium constant. The silver electrode should theoretically respond to changes in halide ion because, due to the silver halide solubility product, changes in the bromide ion activity cause changes in the silver ion activity. However in silver halide emulsions with a high excess of halide ion, the silver ion activity is relatively small and a bare silver electrode will respond to changes in halide activity relatively slowly. This method is considered unsuitable to measure or control the halide activity because a fast response is needed for

control and because before precipitation takes place at the start of the process there may be no silver ions present, leading to a fluctuating, non-meaningful start potential.

A second technique uses a silver electrode that has been coated with the silver halide of interest. The silver ion activity at the electrode surface is, therefore, directly affected by changes in the halide ion activity in the bulk solution as defined by the solubility product of the silver halide, K_{sp}.

$$K_{sp} = a_{Ag^+} a_{Br^-} \qquad 1.2$$

Equation 1.1 only defines part of the measured cell potential, the other half cell, usually a reference electrode and the junction potential between the various reference and reference bridge solutions also contribute to the measured potential difference. Thus measured potential or VAG is given by:

$$\mathrm{VAG} = E_m = E^{\circ}_{Ag/Ag^+} - E_{ref} + E_{junction} \qquad 1.3$$

Calculations defining the activity coefficient and solubility product and hence the "theoretical" measured values are given in Chapter 2.

1.2.6 VAG control

In most emulsions the VAG and hence halide ion concentration is controlled at a fixed value equal to the start concentration or controlled in a number of step changes to facilitate the growth of more complex crystal grains. In a VAG controlled double-run emulsion, the emulsion becomes saturated with silver halide very quickly. In only 10 seconds no more grains are formed. The VAG in the kettle at the start of the runs will determine the number of grains formed and hence the final grain size. A lower VAG (higher halide concentration) will tend to make the grains more soluble in the manufacturing vessel, which in turn leads to more ripening and a larger grain size. However, at a constant VAG this gives rise to a very narrow grain size distribution.

In recent years, the drive towards making faster emulsions for both camera and industrial uses has made the shape of the emulsion grain very important. The major factor determining the basic emulsion speed is the diameter of the grain. This can be increased in conventional ways by grain growth as already described but more recently a method has been developed to make very large diameter grains by growing them along specific crystal faces by very tight control of the emulsions. These are called "T-grain" emulsions, and have been successful not only for their speed but because they are so thin. The result is that in many cases, each T-grain actually contains less silver than a conventional emulsion and yet has many times its cross-sectional area and photographic speed. Fig. 1.1 shows the relationship between the VAG and the shape of the grains formed from silver bromide emulsions. In this example, as the concentration of the bromide in the emulsion increases and the VAG gets lower, the grain shape moves from cubic to cube-octahedral to octahedral and on towards T-grain shape. The shaded areas represent VAG regions where the shapes are intermediate. Some of the VAG ranges for forming a particular grain shape are very narrow, especially in the case of T-grains. It is therefore important to be able to measure the VAG accurately during the VAG controlled run.

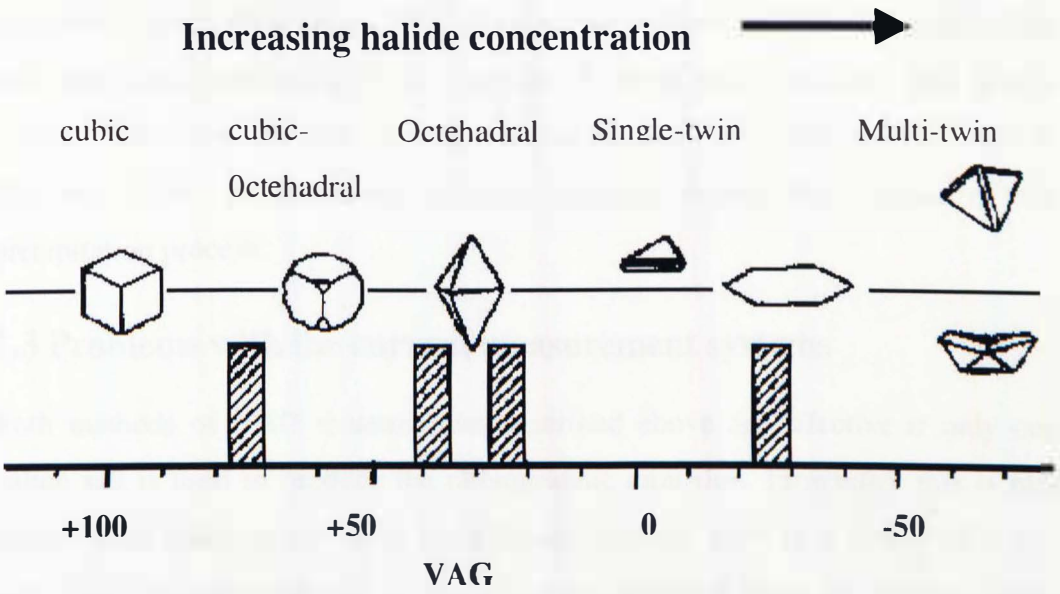


Figure 1.1 VAG versus grain shape (Lane, 1989)

1.2.7 Computer controlled emulsion making

The previous sections have demonstrated that the key factor in the production of reproducible emulsion is the accurate control of the emulsion manufacturing environment throughout the process cycle. The introduction of computer control into emulsion manufacturing allowed this to be done quickly and reliably. The critical parameters that tend to be put under computer control are:

- silver flow
- salts flow
- kettle VAG
- kettle temperature, and
- stirrer speed.

The silver nitrate, salt, and gelatin solutions are prepared separately from the manufacturing vessel in small preparation kettles. Before the start of the process, the gelatin solution is added to the manufacturing vessel and the pH and VAG adjusted to given start values. The silver nitrate and salt solutions are then added with their flows controlled by the computer. In most cases the silver flow is kept constant while the salt flow is controlled to maintain the VAG control point so that the halide concentration is kept constant during each phase of the precipitation process.

1.3 Problems with the current measurement systems

Both methods of VAG measurement described above are effective if only one halide salt is used to produce the photographic emulsion. In practice this is rare and in most cases two or even three halide salts are used in a variety of ways. Salts may be added together or sequentially to produce layers of different silver halide on the grains. In most cases in the emulsion process the more soluble silver

halide salt (silver chloride/silver bromide) is precipitated first by adding silver and halides salts together to a halide rich environment to form small seed grains. A second halide is then added which partially dissolves the grain and forms a shell of less soluble silver halide (silver bromide/silver iodide) on the grain. The second halide may be added as a fixed volume or run in for a short time after which the first halide salt is continued to be added along with the silver salt. After all of the second halide is precipitated the solution then again becomes rich in the first halide and precipitation of that halide then continues. Thus, for example, the solution starts at a high chloride concentration, changes to a high bromide concentration and then changes back to a high chloride concentration. To measure and control at the start of the process when there is only chloride salt present the electrode has to be sensitive to chloride. A chloride coated silver electrode is used to measure the VAG because a bare silver electrode would not be sensitive to chloride ions without silver ions being present. This electrode responds well until the bromide salt solution is added and the chloride coating begins to dissolve. At this point the VAG should step more negative to reflect the addition of bromide and the corresponding reduction in free silver ions. However, the electrode continues to respond to the silver ions in equilibrium with the chloride in the silver chloride electrode coating. Gradually a layer of silver bromide replaces the coating and the VAG begins to fall to more negative values as the electrode becomes more sensitive to bromide ions. This process may take up to 15 minutes in which time the control computer must be suspended. At the end of the bromide precipitation the bromide concentration then drops and the chloride ion concentration becomes dominant. At this time the electrode is coated with bromide and will not respond to changes in chloride concentration. As the silver bromide layer is much more insoluble than a silver chloride layer the replacement process would take many hours longer than the manufacturing process. For this reason the VAG control can no longer be used.

The changing of halide precipitant during the process causes this kind of problem for most cases. Procedures using thinly coated electrodes and two or three different halide coated silver electrodes have been tried to overcome this problem

but because electrodes will only change relatively quickly when going from a more soluble silver halide to a less soluble silver halide and will only change slowly going from a less soluble silver halide to a more soluble silver halide, the problem is only partially solved. Bare silver electrodes have also been used alongside halide coated electrodes. The silver halide electrodes are needed to measure the starting solution, which is silver ion free, and where the bare silver electrode would only respond to silver ions. Although this will work in practice, preparation of the bare silver surface is difficult and large differences in the silver electrode half-cell potential are seen.

For the reasons above it is very difficult to measure a reproducible VAG in a mixed halide emulsion and hence control during their processing becomes impossible. Generally a single electrode of one halide layer type is used and the VAG is assumed to be reproducible in similar process batches. The control values are therefore only arrived at by experimental measurements, which can take many hours of expensive production testing. These values are dependant on the vessel size and geometry making scale-up from research batches impossible.

1.4 Proposed Research Work

Prior to the start of this research project, work had been carried out on a new technique to measure the activity of halide ions in a mixed halide solution. This work concentrated on the cleaning and more importantly the coating of the silver electrode surface in situ in the environment that it would be required to measure. Earlier work at Kodak (Lin, 1989) had proposed an "in situ" technique where the silver electrode was coated just after the halide salt had been changed. This was not taken up by the manufacturing departments due to the sudden change in measured potential of the electrode after this "in situ" coating had taken place which adversely affected the process control (although this new measured reading was more accurate and stable). However later work, which led to a patent (Edwards and Sandifer, 1995), used a technique of continuously cleaning, coating

and measuring the silver electrode in a cyclic manner throughout the duration of the emulsion manufacturing process thus avoiding the sudden potential jump experienced with the former method.

The research reported here further investigated the "clean/coat/measure" technique concentrating on the underlying theoretical considerations. Work covered the design of necessary electronic circuitry and software programs, the halide response and analysis of silver electrodes cleaned and coated by both programmed voltage and constant current.

Two techniques were investigated to determine the feasibility of this approach. The first approach used a technique whereby a cleaning voltage is applied to the silver electrode followed by a coating voltage, for a fixed duration. This is followed by an equilibrium period and then potentiometric measurement. This cycle was repeated at varying rates from 10 Hz to 0.1 Hz (Fig. 1.2). In this case the voltages applied and measured are referenced to a standard reference electrode The second technique used a single cycle a.c. constant current square wave pulse of fixed amplitude and duration followed by a period for equilibrium and measurement of the silver electrode potential (Fig. 1.2.). This cycle was repeated as in the above method. Both these techniques renewed the silver electrode surface such that the surface halide coating reflected the halide ion present in the solution at that time. In both cases due to the measurement being used as a process control signal for the emulsion manufacturing process, measurement cycle rates were desired to be in the range of 3 to 10 Hz.

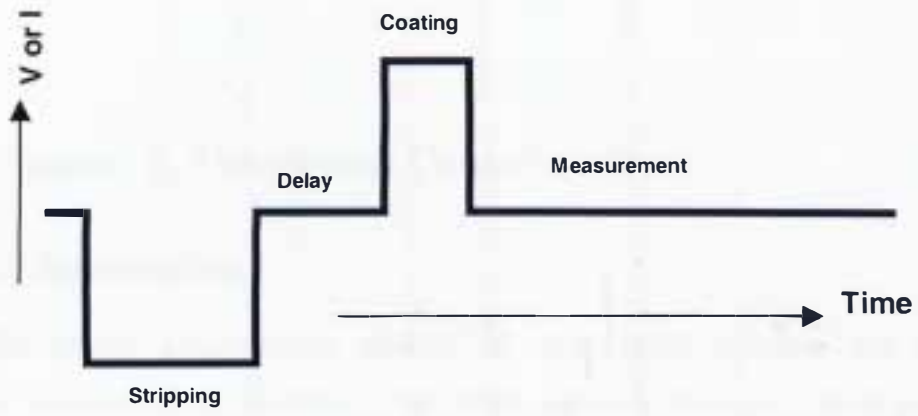


Figure 1.2 Schematic of "clean/coat/measure" cycle

Initially work was carried out to investigate the equilibrium potential obtained from a conventional potentiometric measurement system and to compare these results with the best theoretical calculations available from the literature. A computer program was written to generate VAG values for pure halide solutions at various temperatures, concentrations and ionic strengths.

The second part of this project was divided into two sections. Work in the research laboratory concentrated on using a rotating disc silver electrode to gain a better understanding of some of the underlying processes involved in the measurement. While in the development laboratory, measurement systems using cylindrical electrodes in stationary and stirred solutions in stainless steel prototype emulsion manufacturing vessels was investigated.

The electrodes studied were smaller than those conventionally used in emulsion manufacturing, so size of the silver electrode surface area was studied to determine the importance of this with respect to measured potential and linearity of slope. The thickness of the silver halide layer was also examined to determine whether the short coating period required by the "clean/coat/measure" technique, also affected electrode performance.

Chapter 2. Theoretical Considerations

2.1 Introduction

The project concerned a method of continuously cleaning and coating a silver/silver halide electrode in the sample solution. The cycle can be divided into four steps each with clearly defined processes. Figure 2.1 shows graphically these processes. Each step will be discussed along with the relevant theory underlying each process.

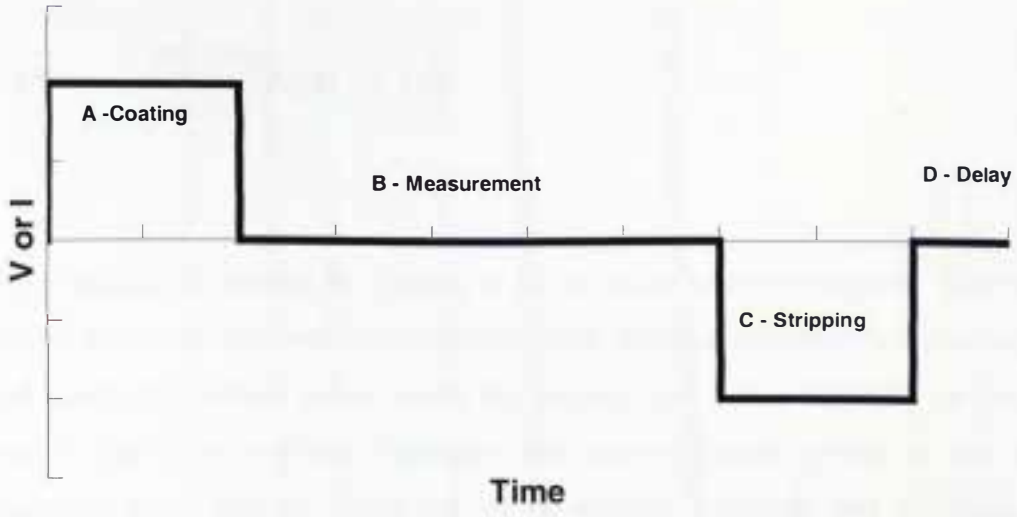


Figure 2.1 Clean/coat/measure cycle

Process A is the coating of silver metal with a thin layer of silver halide by oxidation of the silver electrode surface so as to precipitate silver halide using the halide salt in the bulk solution. During process B the electrodes are switched to

open circuit and the electrode potential of the silver halide electrode measured using a high impedance amplifier. Process C involves the stripping or conversion of the silver/silver halide electrode back to a metallic silver electrode by reduction of the silver halide layer. Process D is the delay between reduction of the silver halide to bare silver and the recoating of the bare silver with silver halide to allow reaction products to diffuse into the bulk. Process D may or may not be present.

The reduction and oxidation of the silver/silver halide system can be described by the following reaction equations.

$$AgCl(s) + e^- \underset{\text{coating}}{\overset{\text{stripping}}{\rightleftharpoons}} Ag(s) + Cl^-(aq) \qquad 2.1$$

$$AgBr(s) + e^- \underset{\text{coating}}{\overset{\text{stripping}}{\rightleftharpoons}} Ag(s) + Br^-(aq) \qquad 2.2$$

$$AgI(s) + e^- \underset{\text{coating}}{\overset{\text{stripping}}{\rightleftharpoons}} Ag(s) + I^-(aq) \qquad 2.3$$

Two methods to achieve the plating of silver halide were investigated. The first used a three electrode cell with counter, silver working and reference electrodes and controlled voltage pulses while the second used a two electrode cell with counter and silver working electrodes and constant current pulses to coat the electrode. Both methods used the silver working electrode and a reference electrode to measure the final potential.

The processes involved in the technique will be examined separately. The process starts with the silver electrode being coated with a layer of silver halide. The electrode is then used to make an estimate of the steady-state potential as the potential at the silver halide interface relaxes towards its equilibrium value.

Finally the coating is stripped off and the electrode cleaned ready for the next coating and measurement cycle.

2.2 Process A, plating or oxidation

This process can be divided into two sub-processes, an initial phase where the current flowing is mainly capacitance due to the step change of the potential or current and a secondary phase where the current flowing is mainly Faradaic.

2.2.1 Potential step theory

The metal electrode-solution interface behaves as a simple metal plate capacitor with the charge, Q defined as

$$Q = CE \qquad 2.4$$

where C = capacitance and E = potential across the interface.

At a given potential, a charge will exist on the metal electrode, Q_m, with an equivalent opposite charge Q_s in the solution. The signs of the charge will depend on the potential across the interface.

$$Q_m = -Q_s \qquad 2.5$$

The distribution of charge across the interface is the *electric double layer*. The double layer capacitance is in the order of 10 – 40 μF and is dependant on the potential.

If the potential across the interface is changed by a step in the applied potential, ΔE, then current is drawn to charge the interface to a new value. The current as a function of time, t, is defined as

$$I = \frac{\Delta E}{R} e^{-t/RC} \qquad 2.6$$

For a potential step an exponential decay current is observed with time constant, $\tau = RC$. A typical resistance for the systems used in this project was in the order of 100 Ω, with a capacitance of 20 μF the current will decay to 37% in ≈2 ms.

For a step change in current, ΔI, the potential changes linearly as

$$E = \Delta I\left(R + t/C\right) \qquad 2.7$$

2.2.2 The coating process

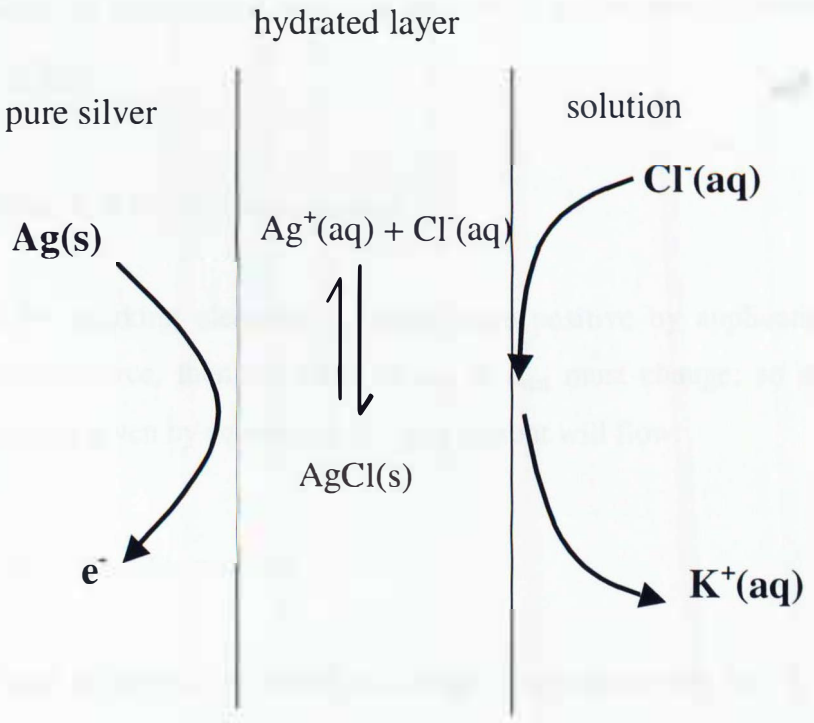


Figure 2.2 Coating of silver halide

This step is an anodic process and can be described as

$$Ag(s) + Cl^{-}(aq) \rightarrow AgCl(s) + e \qquad 2.8$$

or more generally as

$$Ag(s) + X^{-}(aq) \rightarrow AgX(s) + e \qquad 2.9$$

When no current flows the potential of the cell will move towards a steady state value indicating that the cell is at equilibrium. The potential at the working electrode, E_{WE}, is defined by the Nernst equation to be

$$E_{WE} = \overset{r}{E}_{WE} + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \qquad 2.10$$

While no total current flows the forward, $\overset{-}{I}$ and reverse, $\overset{f}{I}$ currents are

$$\vec{I} = \overleftarrow{I} = I_o \qquad 2.11$$

where I_o is the exchange current

If the working electrode is made more positive by application of an external driving force, then the ratio of a_{ox} to a_{red} must change; so as to maintain the balance given by equation 2.10, thus current will flow:

$I = \overset{-}{I} + \overset{f}{I}$ and is positive 2.12

These equations are based on simple thermodynamics but in fact these partial currents are also dependent on the kinetics of the electron transfer process. The partial currents are dependant on the concentration of oxidants/reductants and rate constants defined by

$$\vec{I} = nF\vec{k}a_{ox} \qquad 2.13$$

$$\overleftarrow{I} = nF\overleftarrow{k}a_{red} \qquad 2.14$$

These rate constant are however dependant on the applied potential:

$$\vec{k} = \vec{k}_0 \exp\left(\frac{-\alpha_C nF}{RT}E\right) \qquad 2.15$$

and

$$\overleftarrow{k} = \overleftarrow{k}_0 \exp\left(\frac{-\alpha_A nF}{RT}E\right) \qquad 2.16$$

$$a_A + a_C = 1 \qquad 2.17$$

if η = overpotential

where

$$\eta = E_{app} - E_{eq} \qquad 2.18$$

at η = o

$$\vec{I} = \overleftarrow{I} = I_0 \qquad 2.19$$

and

$$I = \vec{I} + \overleftarrow{I} \qquad 2.20$$

Substituting equations 2.13 and 2.14 into equation 2.20 gives

$$I = I_0\left[\exp\left(\frac{\alpha_A nF}{RT}\eta\right) - \exp\left(\frac{\alpha_C nF}{RT}\eta\right)\right] \qquad 2.21$$

Equation 2.21 is known as the Butler-Volmer equation.

For the silver electrode at equilibrium the potential is given by the Nernst equation

$$E_{\text{Ag Electrode}} = E^{0}_{\text{Ag/Ag}^{+}} + \frac{RT}{nF}\ln\left[\frac{a_{\text{Ag}^{+}}}{a_{\text{Ag(s)}}}\right] \qquad 2.22$$

where $E^{0}_{\text{Ag/Ag}^{+}}$ is the standard potential of the silver/silver halide half cell This value has been reported (Bates, 1956, 1957, 1973; Covington, 1995; Harned, 1933, 1935, 1937; Lingane, 1937). In the case of the silver electrode the activity of silver is taken as 1. If the applied potential becomes more positive, then current flows and the anodic process in equation 2.9 takes place. In the presence of halide ions the activity of the silver ion and hence the equilibrium potential is modified by the solubility product of silver halide.

$$K_{\text{spAgX}} = a_{\text{Ag}^{+}} \times \quad a_{\text{X}^{-}} \qquad 2.23$$

$$E_{\text{Ag}} = E^{0}_{\text{Ag/Ag}^{+}} - \frac{RT}{nF}\ln\left[\frac{a_{\text{X}^{-}}}{K_{\text{spAgX}}}\right] \qquad 2.24$$

or

$$E_{\text{Ag}} = E^{0}_{\text{Ag/Ag}^{+}} - \frac{RT}{nF}\left\{\ln\left[a_{\text{X}^{-}}\right] - \ln\left[K_{\text{spAgX}}\right]\right\} \qquad 2.25$$

Thus,

$$E_{\text{Ag}} = E^{0}_{\text{Ag/AgX}} - \frac{RT}{nF}\ln\left(a_{\text{X}^{-}}\right) \qquad 2.26$$

where

$$E^0_{Ag/AgX} = E^0_{Ag/Ag^+} + \frac{RT}{nF} \ln K_{spAgX} \qquad 2.27$$

Assuming a double layer model with a stagnant layer of thickness, d and bulk and surface concentrations, c_b and c_s (Figure 2.3; Bard, 1980).

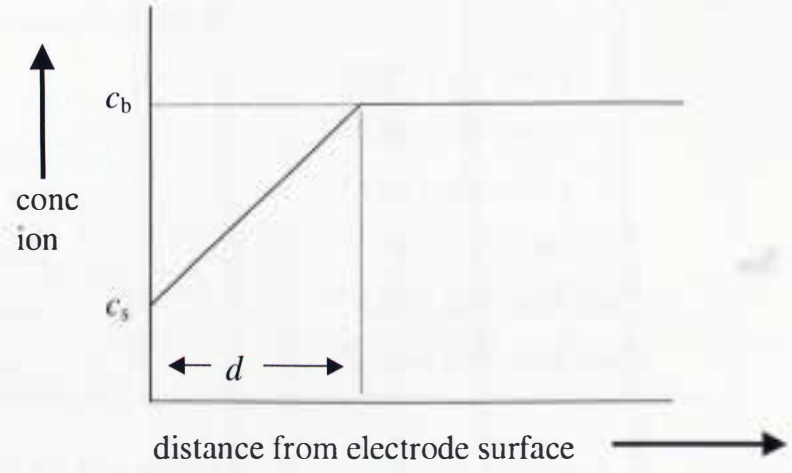


Figure 2.3 Diffusion model of electrode-solution interface

The current flowing can be calculated from

$$i = -\frac{nFA}{d} D_i (c_s - c_b) \qquad 2.28$$

Substituting concentration instead of activity into the Nernst equation and rearranging gives the concentration at the electrode surface, c_s, as,

$$c_s = c_b e^{-(E_{app} - E^0_{Ag/AgX})nF/RT} \qquad 2.29$$

For a solution of mixed halides the total current is

$$I = -\frac{nFAc}{d}\sum D_i(c_s - c_b) \qquad 2.30$$

Figure 2.4 shows the current modelled for applied potentials from -0.4 to 0.75 V for a solution of chloride, bromide and iodide at three concentrations. Parameters used in the calculation are given below.

Parameter	**Value**
Electrode surface area	0.3 cm^2
Diffusion thickness layer, *d*	0.002 cm
Diffusion coefficient	
D_{Cl^-}	*2.03 × 10^{-5} cm^2 s^{-1}
D_{Br^-}	*2.08 × 10^{-5} cm^2s^{-1}
D_{I^-}	*2.05 × 10^{-5} cm^2s^{-1}
K_{spAgCl}	+1.78 × 10^{-10} mol^2 dm^{-6}
K_{spAgBr}	+4.27 × 10^{-13} mol^2 dm^{-6}
K_{spAgI}	+8.30 × 10^{-17} mol^2 dm^{-6}

Table 2.1 Parameters used to model voltammogram

*(Dionex Inc. 1981)

+(James, 1977)

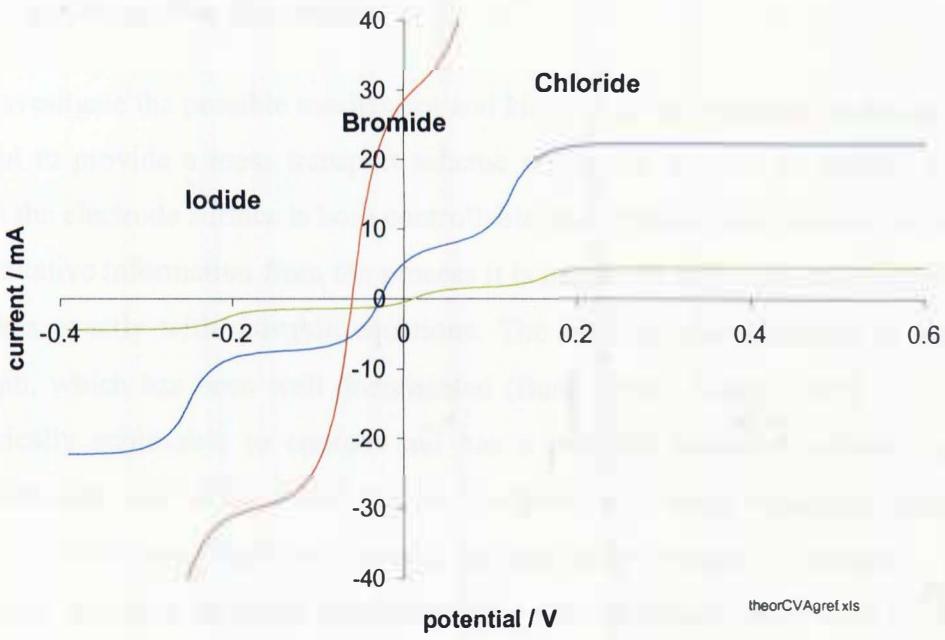


Figure 2.4 Model Voltammogram for a solution of chloride, bromide and iodide at a concentration of 0.1 M (—), 0.025 M (—) and 0.005 M (—). Potential values are plotted versus a saturated silver/silver chloride reference electrode

The potential where the current shows the steepest gradient is defined by the equilibrium potential at the particular concentration for the particular halide. The plateau regions of the curves are where the current is limited by the diffusion of bromide to the electrode surface.

2.2.3 Diffusion theory

The sum of the chemical and electrical energies of a species in solution is defined as its electrochemical potential, μ_i. When a system is at equilibrium this potential must be constant throughout the system. If it is not, the species i gradually diffuses from parts of high electrochemical potential to lower parts in the system until the system is at equilibrium. The flux of the species i, j_i is defined as the quantity of matter which flows across a plane of unit area in unit time. The flux is determined by the concentration and potential gradient in the system.

The flux in terms of concentration gradient is defined by

$$j_i = D_i \left(\partial c_i / \partial x\right) \qquad 2.31$$

2.2.4 Rotating Disc Electrode

To investigate the possible mechanism and kinetics of the proposed technique it is useful to provide a mass transport scheme where the transfer of species to and from the electrode surface is both controllable and reproducible. In order to obtain quantitative information from the process it is necessary to be able to describe this process exactly with solvable equations. The rotating disc electrode is such a system, which has been well documented (Bard, 1980; Prater, 1970). It is both practically achievable to operate and has a material transport scheme that is reproducible, well defined and can be described with exact equations. Rotating disc electrodes are simple to construct and are easily operated to achieve a wide variation of mass transport conditions. The disc electrode must only have the planar face of the electrode exposed to the solution; the remainder of the electrode must be well sheathed in an insulating layer.

If a rotating disc electrode is rotated in a sufficiently large volume of solution, a well defined flow pattern is obtained. Figure 2.5 shows a diagram of the flow pattern. As the electrode rotates, solution is drawn up to the planar surface of the disc and then is thrown outwards in a horizontal direction back into the bulk of the solution. The rotating disc electrodes acts as a pump, pumping solution across the face of the electrode in a well defined manner.

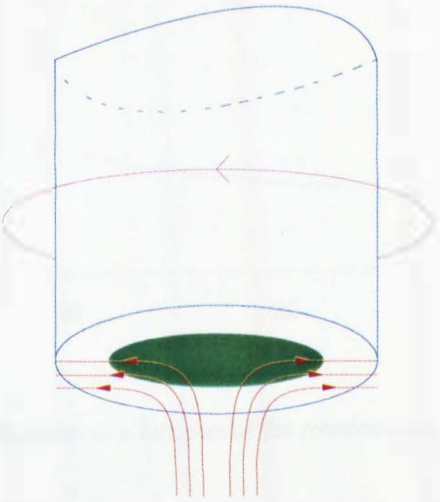


Figure 2.5 Rotating disc electrode

The current at a rotating disc electrode is limited by the diffusion of reactive species to the electrode surface. This limiting current can be calculated from:

$$I_{\text{lim}} = 1.554nFAD^{2/3}\nu^{-1/6}\mathrm{W}^{1/2}c_{\text{b}} \qquad 2.32$$

where W is the angular speed in Hz^{-1} and υ is the kinetic viscosity given by

$$\nu = \frac{\eta_s}{\rho} \qquad 2.33$$

The diffusion layer thickness, δ, can be calculated from

$$\delta = \frac{0.64\nu^{1/6}D^{1/2}}{\mathrm{W}^{1/2}} \qquad 2.34$$

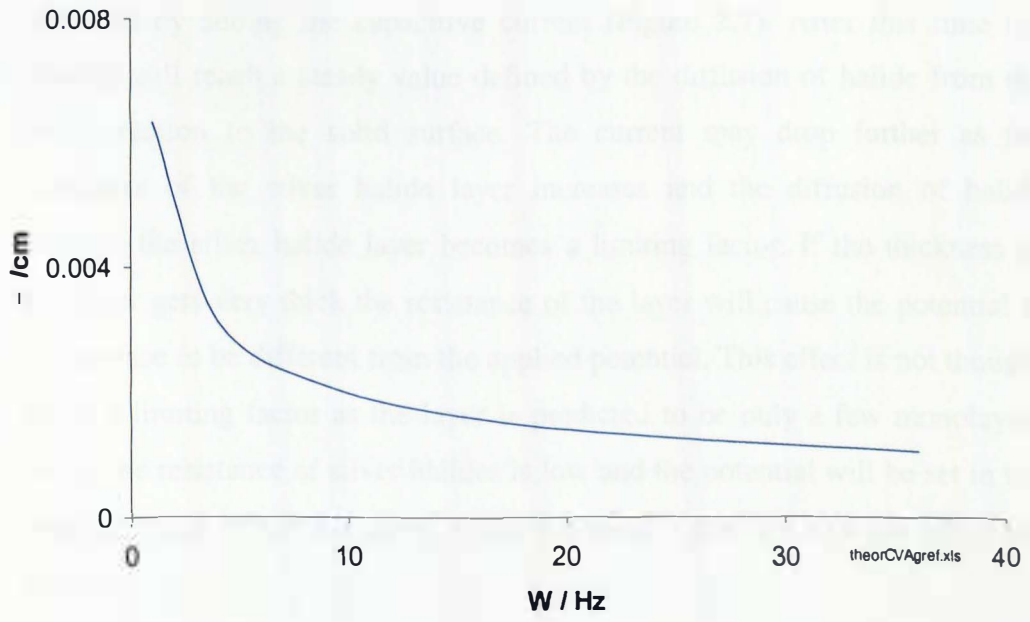


Figure 2.6 Diffusion layer thickness as a function of the rotation speed

2.2.5 Current profile of an applied potential coating pulse

If a coating pulse with an applied potential more positive than the equilibrium potential of the system is applied in a step, a current pulse will be observed. In the first ms the current will be mainly defined by the capacitive charging of the electrode-solution interface. The initial current will also be limited by the current capacity of the amplifier in the potentiostat. The capacitive current will drop logarithmically as defined by equation 2.6. The faradaic current will initially be high as the surface concentration of the halide ions equals the bulk concentration. As the silver metal is oxidised and silver halide is formed the current will decrease with time until the diffusion of the halide ion through the diffusion layer equals the rate of oxidation at the electrode surface. An approximate profile can be plotted assuming the current decays according to the Cottrell equation (Equation 2.35). The time taken for the diffusion layer to build up is found from the "drunken sailor" solution (Equation 2.36) and the limiting current at that time by equation 2.32. The total current can be obtained by adding the capacitive current (Figure 2.7). After this time the current will reach a steady value defined by the diffusion of halide from the bulk solution to the solid surface. The current may drop further as the thickness of the silver halide layer increases and the diffusion of halide through the silver halide layer becomes a limiting factor. If the thickness of the layer gets very thick the résistance of the layer will cause the potential at the surface to be different from the applied potential. This effect is not thought to be a limiting factor as the layer is predicted to be only a few monolayers thick, the resistance of silver halides is low and the potential will be set in the plateau region of the *E-I* curve where a drop of a few mV will not affect the current.

$$I(t) = \frac{nFAD^{0.5}c_b}{\pi^{0.5}t^{0.5}} \qquad 2.35$$

$$l = \sqrt{Dt} \qquad 2.36$$

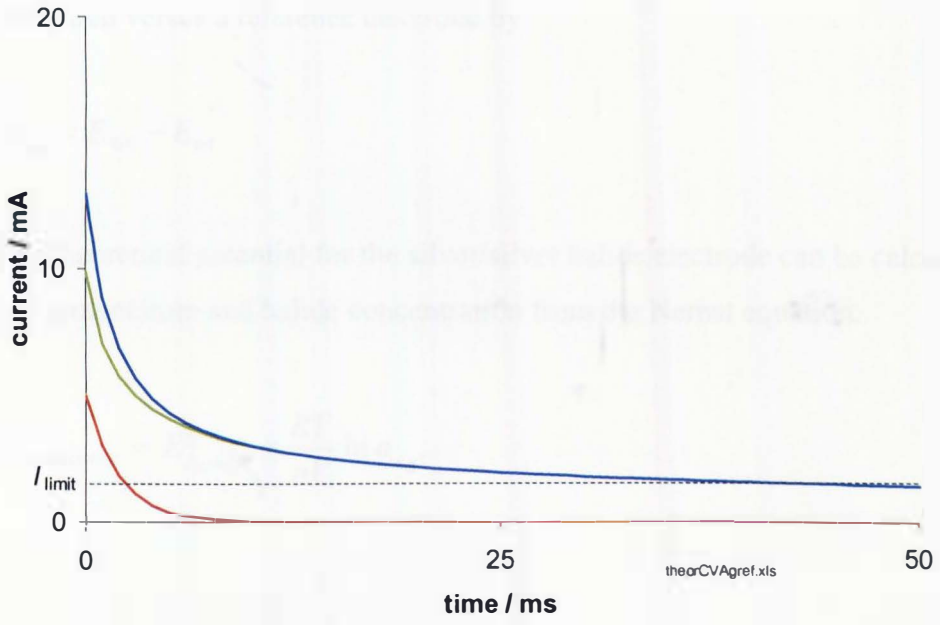


Figure 2.7 Model of current profile for a +500 mV applied potential coating pulse.
(—) Capacitive current,(—) Faradaic current,(—) total current.

2.2.6 Potential profile of an applied constant current coating pulse

If a constant current coating pulse is applied to the system, the potential of the working electrode will rise to the potential defined in equation 2.27 where the silver metal is oxidised and converted to silver halide. During this initial period the interface will charge. Once at this coating potential it will remain constant until the current is switched off. A slight rise in potential may be observed as the resistance of the silver halide layer increases.

2.3 Process B, potentiometric measurement

The potentiometric measurement process can be divided into an initial period where the potential is changing due to diffusion of ions from the liquid layer adjacent to the electrode surface back to the bulk and a steady period where the measured potential moves towards the equilibrium value.

2.3.1 Equilibrium potential

The equilibrium cell potential for a silver electrode in aqueous silver ions is measured versus a reference electrode by

$$E_{\text{cell}} = E_{\text{WE}} - E_{\text{ref}} \qquad 2.37$$

The theoretical potential for the silver/silver halide electrode can be calculated at any temperature and halide concentration from the Nernst equation.

$$E_{\text{Ag electrode}} = E^{0}_{\text{Ag/Ag}^{+}} + \frac{RT}{nF} \ln a_{\text{Ag}^{+}} \qquad 2.38$$

or

$$E_{\text{Ag Electrode}} = E^{0}_{\text{Ag/Ag}^{+}} + \frac{RT}{nF}\left[\ln a_{\text{Br}^{-}} - \ln K_{\text{spAgBr}}\right] \qquad 2.39$$

The standard potential, $E^{0}_{\text{Ag/Ag}^{+}}$, is also dependant on temperature therefore a temperature coefficient of this standard potential is required before any useful calculations can be performed. This is covered later in this chapter, section 2.3.5.

2.3.2 Solubility Product

The solubility of the silver halides in water increases with increasing temperature. Empirical equations to calculate the solubility products of silver chloride, silver bromide and silver iodide have been reported (James, 1977) as.

$$pK_{\text{spAgCl}} = 10.830 - 4.79 \times 10^{-2}\,\theta + 2.03 \times 10^{-4}\,\theta^{2} - 4.33 \times 10^{-7}\,\theta^{3} \qquad 2.40$$

$$pK_{\text{spAgBr}} = 13.702 - 6.17 \times 10^{-2}\,\theta + 2.57 \times 10^{-4}\,\theta^{2} - 5.58 \times 10^{-7}\,\theta^{3} \qquad 2.41$$

$$pK_{\text{spAgI}} = 17.873 - 7.85 \times 10^{-2}\,\theta + 2.65 \times 10^{-4}\,\theta^{2} \qquad 2.42$$

Where θ is the temperature in centigrade.

Workers in Kodak (Lin, 1981) have reported simpler equation based on electrochemical measurements of the silver halide system, which are quicker to compute and give values within acceptable limits.

$$pK_{spAgCl} = -12.126 + 5868.6/\theta + 0.015953\,\theta \qquad 2.43$$

$$pK_{spAgBr} = -10.034 + 4663.6/\theta + 0.013887\,\theta \qquad 2.44$$

$$pK_{spAgI} = -12.275 + 7124.8/\theta + 0.014951\,\theta \qquad 2.45$$

2.3.3 Activity coefficients

The activity of a simple bromide solution can be derived from the concentration of bromide ions and the activity coefficient as defined in equation 2.45.

$$a_{Br^-} = c_{Br^-} \times \gamma_{Br^-} \qquad 2.46$$

The activity coefficient at a particular ionic strength, I_C can be derived from the Debye-Huckel equation 2.46 (Guugenheim, 1955; Robinson, 1968):

$$\ln \gamma_{-}^{+} = \frac{z^2 A_M I_C^{0.5}}{1 + B_M s_i I_C^{0.5}} \qquad 2.47$$

or the extended Debye-Huckel equation for high ionic strengths (Robbins, 1973)

$$\ln \gamma_{-}^{+} = \frac{z^2 A_M I_S^{0.5}}{1 + B_M s_i I_S^{0.5}} + \beta . I_C \qquad 2.48$$

Where

z = charge on ions

s_i = ionic distance (radius of the positive ion plus radius of negative ion)

A_M, B_M, A_C and β are constants.

$$A_M = A_C d_O^{0.5} \qquad 2.49$$

$$A_C = \left(\frac{2\pi N}{1000}\right)^{\frac{1}{2}} \frac{e^3}{2.3025 * (4\pi\varepsilon_0)^{\frac{3}{2}} * k^{\frac{3}{2}}} \left(\frac{1}{T^{\frac{3}{2}} \varepsilon^{\frac{3}{2}}}\right) \qquad 2.50$$

$$B_M = B_C d_O^{0.5} \qquad 2.51$$

$$B_C = \left(\frac{8\pi N}{1000}\right)^{\frac{1}{2}} \frac{e}{(kT\varepsilon)^{\frac{1}{2}} (4\pi\varepsilon_0)^{\frac{1}{2}}} \qquad 2.52$$

where

ε is the permeability of water

ε_0 is the permeability of a vacuum

d_0 is the density of the solvent, water

e is the charge on the electron

k is the Boltzman constant

Values for the activity coefficients for solutions of chloride, bromide and iodide at temperatures between 20 and 60 °C have been calculated. (see Appendix I). Figure 2.8 shows activity coefficients for potassium bromide at 20, 40 and 60 °C.

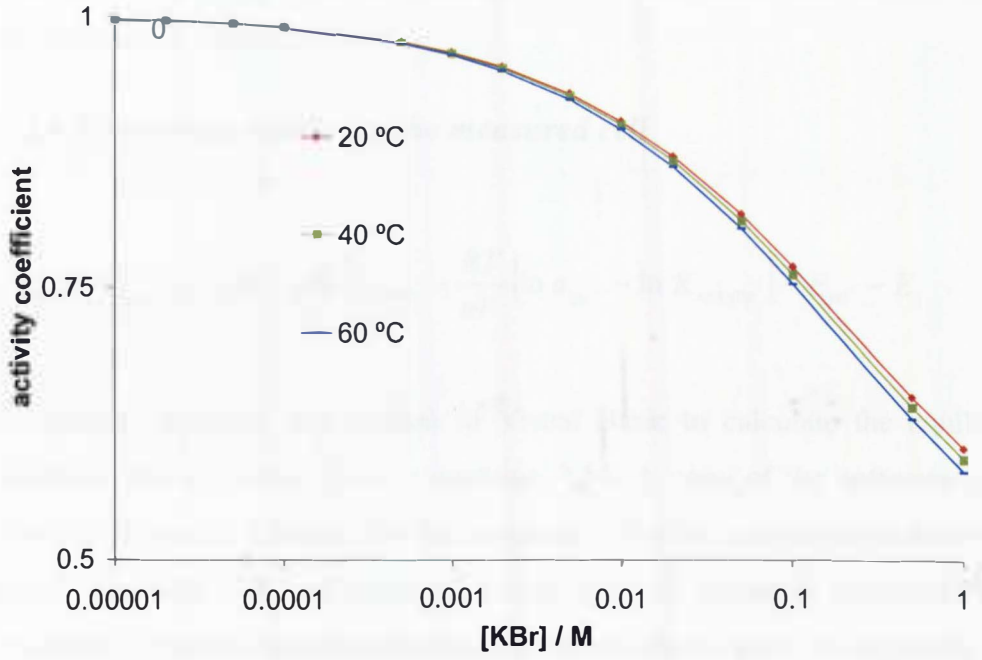


Figure 2.8 Activity coefficients for potassium bromide at various concentrations and temperatures.

2.3.4 Junction potential

When two solutions of different composition or concentration contact one another at an interface a junction potential is developed. The Henderson equation (Henderson, 1908) was used to calculate the junction potentials between the sample solution and the reference bridge solutions and between the various bridge solutions in the reference electrode.

$$E_j = -\frac{RT}{F} \frac{\sum^{Sample} z_i m_i c_i - \sum^{ref} z_i m_i c_i}{\sum^{Sample} z_i^2 m_i c_i - \sum^{ref} z_i^2 m_i c_i} \ln \frac{\sum^{sample} z_i^2 m_i c_i}{\sum^{ref} z_i^2 m_i c_i} \qquad 2.53$$

Where z_i is the charge on the ion, m_i is the mobility and c_i is the concentration of the ion.

2.3.5 Thermal coefficient of standard potential, ($dE^0/dT)_{thermal}$

Several values for the thermal coefficient of the standard potential of the silver electrode $(dE^0/dT)_{thermal}$, have been reported (deBerthune, 1957; Covington, 1995; Mattock, 1961; Owen, 1938). Values range from 0.09 mV $°C^{-1}$ to 0.3 mV $°C^{-1}$. Measurements made on a thermal silver/silver bromide cell prior to the start of

this project gave a value of 0.09 mV $^{o}C^{-1}$. This value was chosen for the theoretical calculation.

2.3.6 Theoretical values for the measured cell

$$E_{Ag} = E^{0}_{Ag/Ag^{+}} + \left(dE^{0} / dT\right)_{thermal} - \frac{RT}{nF}\left[\ln a_{Br^{-}} - \ln K_{spAgBr}\right] - E_{ref} - E_{j} \qquad 2.54$$

A software program was written in Visual Basic to calculate the equilibrium potential and all values used in equation 2.54. A copy of the software code is given in Appendix I.Values for the potential of the cell comprising a silver/silver halide electrode and a reference electrode in a salt bridge in potassium halide solutions of various concentrations and temperatures are given in Appendix Table A1.1 – A1.3. These values were used to verify and calibrate the experimental systems used in this project.

2.3.7 Selectivity to other halides

The selectivity of ion selective electrodes to interfering ions is well documented (Moody, 1971) and an exhaustive theoretical study with respective to silver halide electrodes is given by Buck (1978). Attempts have been made to empirically determine the selectivity coefficients for silver/silver halide electrodes in mixed halide solutions. Klasens (1977) used a method based on the Nicolsky equation (Nicolsky, 1937),

$$E = E^{0}_{Ag/AgX} - \frac{RT}{F}\ln(a_{X^{-}} + K^{pot}_{X,Y}a_{Y^{-}}) \qquad 2.55$$

Where a_X and a_Y are activities of halides X and Y and $K^{pot}_{X,Y}a_{Y^{-}}$ is the selectivity coefficient. This assumed that when the silver/silver halide was immersed in the mixed halide solution the surface became coated with a mixed AgX solid phase (Buck, 1968), which is in thermodynamic equilibrium with both halides as defined by

$$X^-(s) + Y^-(aq) \longrightarrow X^-(aq) + Y^-(s) \qquad 2.56$$

The selectivity coefficient is equal to the ratio of the solubility products.

$$K^{pot}_{X,Y} = K_{spAgX} / K_{spAgY} \qquad 2.57$$

Buck (1968; 1974) derived equations for the interference of iodide ions on a chloride membrane electrode assuming that the heterogeneous, ion-exchange equilibrium in established between the silver chloride and silver iodide solid phase. Sandifer (1981) reported that this mixed phase did not occur and that the composition of the solid phase changes abruptly from one composition to another. This implies that the halide electrode will respond to one halide until the composition of the halides in solution forces the solid silver halide phase to chemically convert to the other silver halide whereupon it will respond to that halide. In the previous reported work (Sandifer, 1981 and Klasens, 1977), the solid silver halide phase was in the form of a pressed silver halide pellet or a single crystal of silver halide between 0.1 and 1 mm thick. In the clean/coat/measure technique the silver halide is present as a very thin layer in the order of a few monolayers thick. This will allow the chemical conversion process to take place relatively quickly.

2.4 Process C, reduction of silver halide

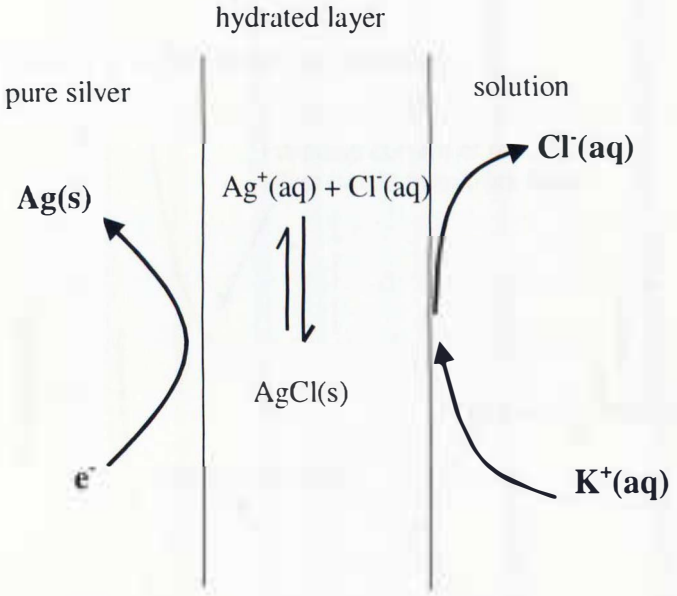


Figure 2.9 Stripping of the AgCl layer

2.4.1 Current profile for controlled potential stripping pulse

The reduction of the silver halide layer on the surface of the electrode can be shown to be the sum of several processes occurring simultaneously. In the case of a controlled potential stripping pulse the current profile is similar to the coating pulse. Initially there is a capacitive current due to the charging of the electrode interface and a faradaic current as the diffusion layer is formed. There is also a steady current defined by the diffusion of bromide away from or counter ion towards the electrode surface. However in the case of the stripping pulse there is a finite amount of silver halide to reduce after which time the current will drop to zero. The stripping pulse is therefore the sum of the capacitive and faradaic current, which decreasing rapidly at the start, a steady period where the faradaic current is limited by either the diffusion of bromide through the solid layer or through the aqueous diffusion layer and a final phase as the monolayer of silver halide is reduced and the current decreases to zero. The final period can be modelled as a modified electrolysis or titration curve curve using the equation below (Bard, 1980). Figure 2.10 shows the sum of these currents.

$$I(t) = I(0)\exp(-pt) \qquad 2.58$$

Where p is a first order rate constant

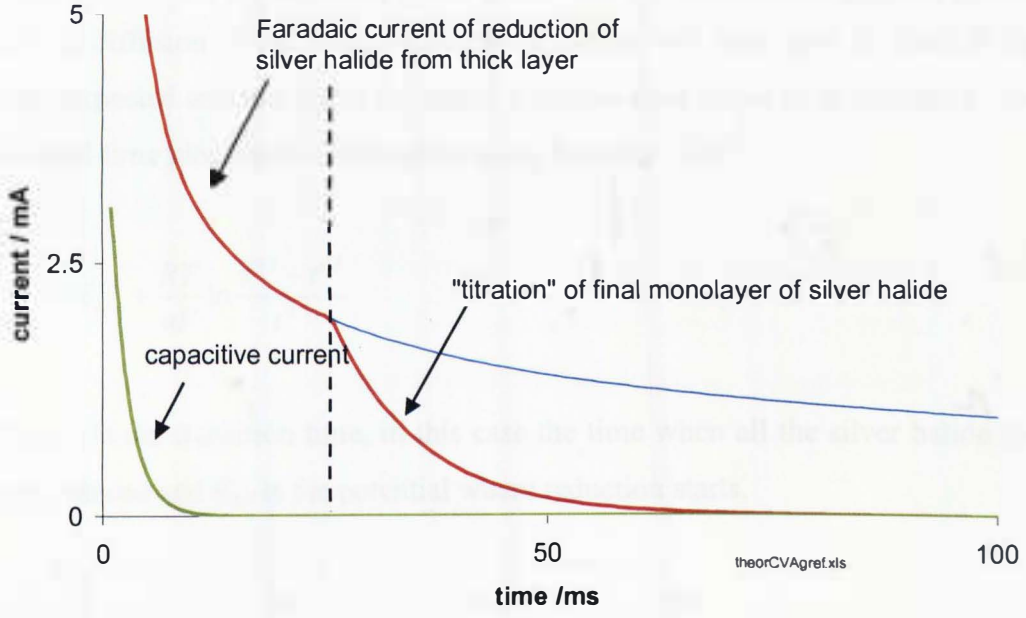


Figure 2.10 Modelled current profile for controlled potential stripping pulse (—) Capacitive current, (—) Faradaic current and (—) total current.

2.4.2 Potential profile for constant current stripping pulse

In the case of the constant current stripping pulse the profile follows a process analogous to chronopotentiometry except that the oxidised form is a solid instead of dissolved in the solution. As the negative current pulse is applied the potential changes from the equilibrium potential to a more negative value as the electrode interface is charged. The potential decreases until it reaches the potential when the silver halide in reduced to silver metal and bromide ions. The potential then decreases slowly as the silver halide layer is reduced. When no more silver halide is present the potential then moves to a potential when the second halide layer is reduced or if none is present, moves to the reduction potential of water or the limit of the constant current circuit. For chronopotentiometry controlled by diffusion the Sands equation (Equation 2.59) gives a good approximation to the potential profile.

$$I\tau^{0.5} = \frac{nFD^{0.5}\pi^{0.5}c}{2} \qquad 2.59$$

In this case where the stripping of the silver halide is determined by other factors such as diffusion in the solid phase this equation will only give an idea of the shape expected and not allow the actual potential-time curve to be modelled. The potential-time plot can be obtained by using Equation 2.60

$$E(t) = E_{\tau/4} + \frac{RT}{nF}\ln\frac{\tau^{0.5} - t^{0.5}}{t^{0.5}} \qquad 2.60$$

where τ is the transition time, in this case the time when all the silver halide has been reduced and $E_{\tau/4}$ is the potential where reduction starts.

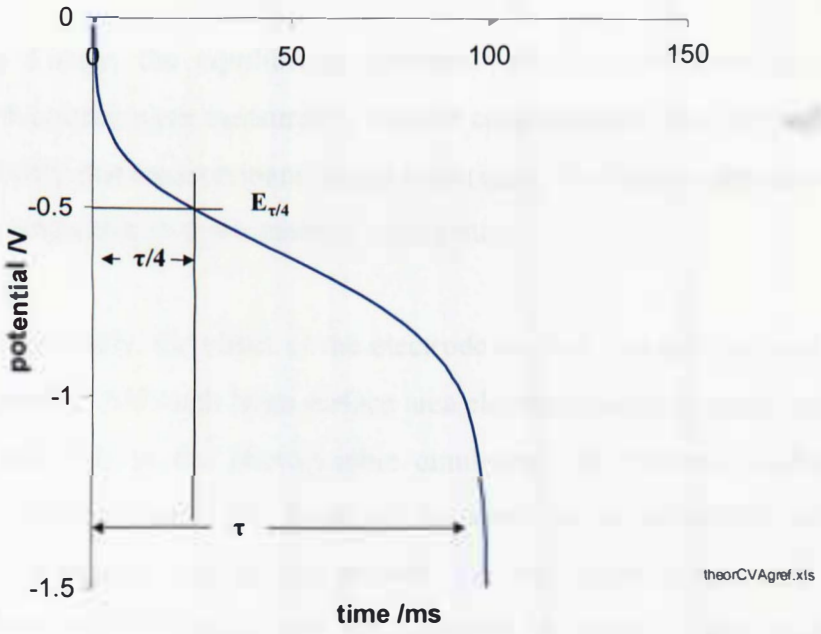


Figure 2.11 Sands model of chronopotentiometry.

Chapter 3 Potentiometric measurements at equilibrium

3.1 Introduction

As discussed in Chapter 1, the technique investigated was a continuous method of cleaning, coating and measurement of the potential of a silver halide electrode. Before investigating the process in detail, it was important to determine whether the potential measured was as predicted by theory and to determine what external factors would affect this measured potential.

The results of three experiments are reported in this chapter:

- Firstly, the equilibrium potentials of chloride, bromide and iodide silver electrodes were measured at various concentrations and temperatures. This was to verify that measurements made when using the clean/coat/measure technique were comparable to those made at steady-state;

- Secondly, the effect of the electrode surface area on electrode performance was studied. Although large surface area electrodes were normally used to measure the potentials in the photographic emulsions, the currents needed to coat similar electrodes were too great to be used in an industrial environment where inflammable liquids are present. As the clean/coat/measure technique being investigated required that the electrode be coated in situ in the manufacturing vessel it was necessary to use small surface area silver electrodes to reduce the required current;

- Thirdly, experiments were performed to determine if the amount of silver halide coated onto the surface of the electrode affected the sensitivity of the electrode to halide ions by electrochemically coating the electrode for short times.

All of the experiments were carried out at 40 °C except where temperature effects were being measured. This temperature is used in the photographic manufacturing process to maintain the gelatine solution in a liquid state, and it was easier to control and maintain solutions at 40 °C than at temperatures closer to room temperature.

Although there are many ways in the literature described to prepare silver halide electrodes (Briggs, 1952; Ives, 1961; Lai, 1951) only two techniques were investigated. Data is included to show the comparison between these two methods.

3.2 Equipment and instrumentation

As these type of measurements are particular to Kodak Ltd., all of the equipment was either fabricated for this project or was manufactured specially for use within Kodak Ltd. All software was written in Microsoft QuickBASIC 4.0 specifically for the investigation. The silver and reference electrode system used were not commercially available but were fabricated particularly for this measurement. The experimental set-up is shown in Fig 3.1

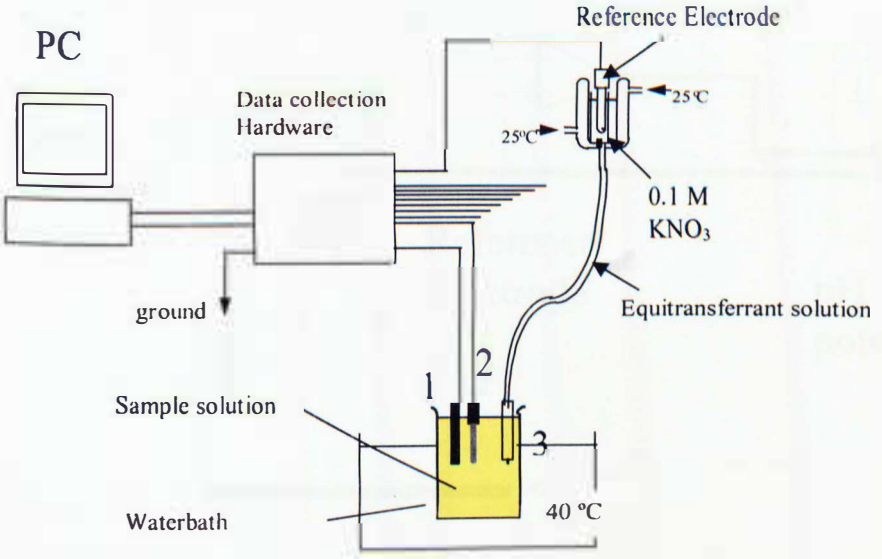


Fig 3.1 Experimental set-up comprising IBM PC, data collection hardware, reference bridge and measurement cell. (1. Solution ground, 2. Silver electrode, 3. Reference junction)

3.2.1 Electronic instrumentation

To facilitate data acquisition, a data logger was developed using a purpose built front-end interface module and a Compaq 486 PC with an Analogue Devices ADC card. Software using Microsoft QuickBASIC Version 4.0 was used to collect and store data and drive the ADC card.

3.2.1.1. Potentiometric measurement circuits

The simplest potentiometric measurement circuit (Figure. 3.2), found in a standard pH meter was used to successfully measure the equilibrium potential difference between a silver halide and a reference electrode in the laboratory environment. However, in an environment where the solution to be measured was in contact with grounded metal, at a different potential from the meter ground, errors in the measured value could arise due to current flowing through the reference electrode. Using meters with isolated power supplies or battery power units could avoid such ground loops. A second problem encountered was that due to the high input impedance of the indicator amplifier; high levels of ac noise present caused offsets in the measured value. The offset was often dependant on the type and make of instrumentation used to make the measurements.

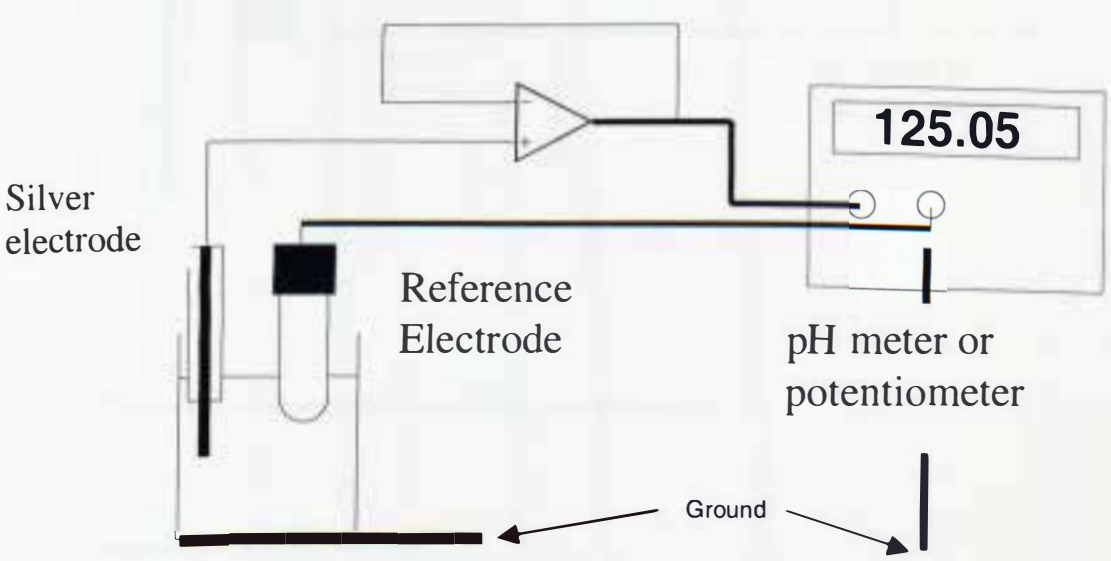


Fig. 3.2 Simple potentiomtric measurement circuit

In an industrial or electrically noisy environment, a better circuit using a differential amplification method and a solution ground electrode is often used (Figure. 3.3). This circuit measures the potential of each half-cell with reference to the ground (either the solution ground electrode or the stainless steel vessel holding the solution) using high input impedance amplifiers. A differential amplifier measures and amplifies the difference between them. This differential mode circuit (Clayton, 1982) has the advantage that it can reject a.c. noise present on both half-cells and gives a cleaner signal in industrial environments. For this circuit to be effective all parts of the solution ground electrode, grounded vessel and process equipment must be connected and at the same potential. Ground loops are not as serious a problem as with the simple potentiometer as both electrodes are effectively isolated from the ground by the high input amplifiers, but should still be avoided.

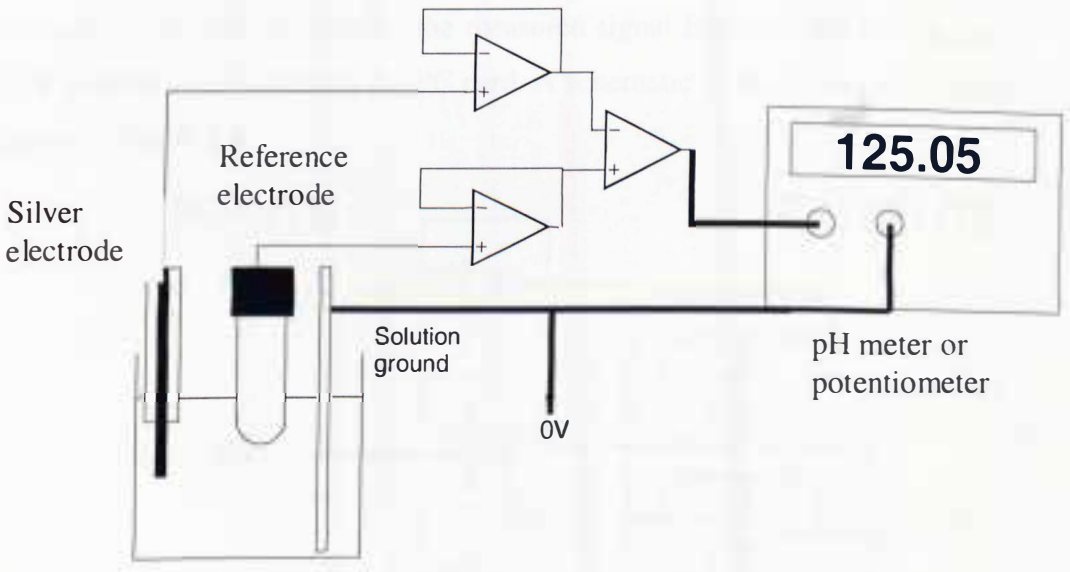


Figure 3.3 Differential measurement circuit utilising a solution ground.

3.2.1.2 Front-end interface module

As research into the manufacture of photographic emulsions is carried out in stainless steel vessels it was decided that the system and instrumentation developed should be capable of being used in these earthed stainless steel vessels.

A front-end interface module was designed with the differential circuit described in 3.2.1.1 and built by the author to interface directly with the PC data collection card allowing potential measurements to be stored directly on the PC hard drive for later analysis.

It was also necessary to use this type of circuit because the non-commercial reference electrodes used in the photographic industry have a high resistance. This required a second high input impedance amplifier on the reference electrode input of the circuit.

The interface used all eight channels of the analogue to digital PC card to collect eight channels of data simultaneously allowing more electrodes to be investigated at one time. This was achieved by using two circuit boards each with four differential circuits for the 4 channels. Each channel incorporated a ×20 differential amplifier to amplify the measured signal from +/- 500 mV to the +/- 10 V needed for the input to the PC card. A schematic of the differential design is shown in Figure 3.4.

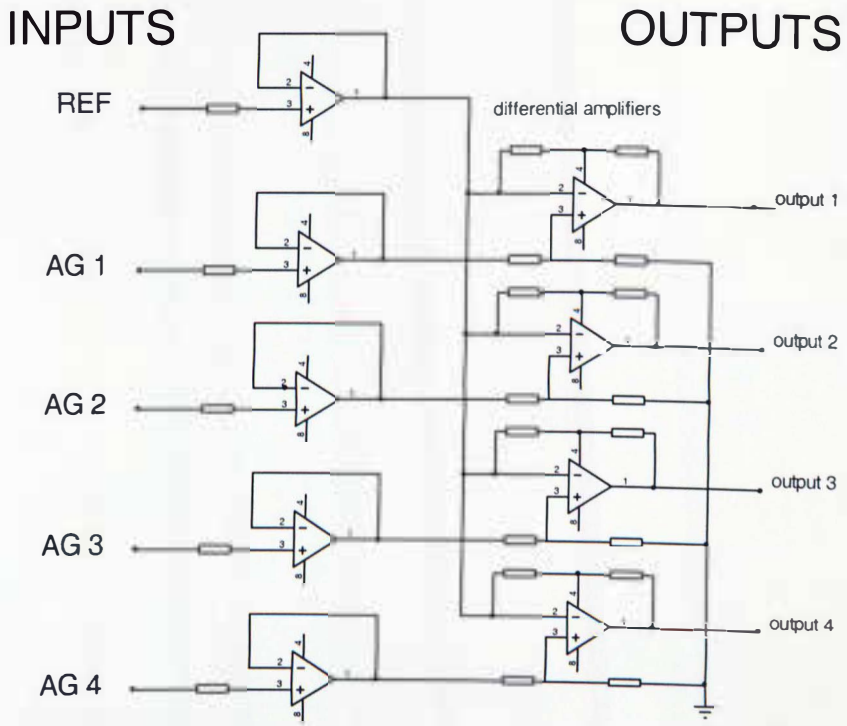


Figure. 3.4 Circuit diagram showing high impedance amplifiers on reference and silver electrode channels and differential circuit.

3.2.1.3 Analogue Devices RTI850 card

The Analogue Devices RTI850 PC card is a high-resolution data acquisition card that plugs into one of the expansion slots of an IBM PC AT type computer. The board contains eight differential input channels that acquire signals in the range +/- 10 volts. The RTI 850 card can acquire data from a single channel or can be programmed to scan data from all eight channels a number of times. Data can either be stored on board or passed to the PC. The board contains one high-resolution 16-bit analogue to digital converter and timing functions that allow collection of data at preset intervals without intervention from the PC. Although the RTI850 can operate at a 50 kHz sample rate if on-board memory is used, in the work reported here there was no on board memory installed and the maximum sample rate of 10 kHz was limited by the speed of the PC data bus. Software controlled the timing and order of channel sampling as well as the total number of samples collected. A schematic of the board is shown in Figure 3.5.

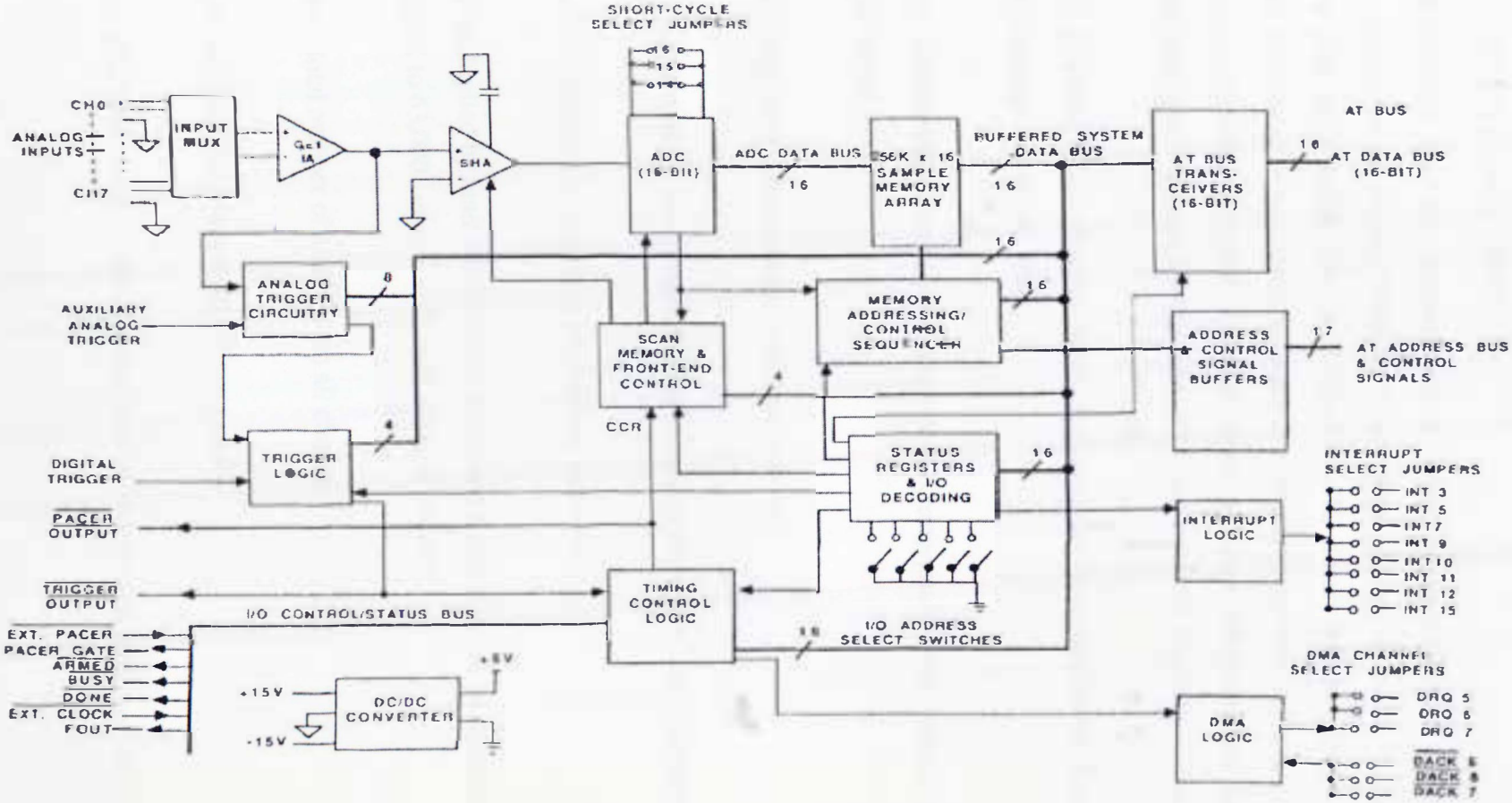


Figure. 3.5 Analogue Devices RTI 850 PC card

3.2.1.4 RTI 850 software library

The RTI850 PC card was supplied with a library of sub-routines or functions to allow the hardware on the board to be accessed. It was necessary to link this library with the standard Microsoft QuickBASIC library and to compile a new library to use when running the software in either development mode or as a fully compiled executable program. Although there were over fifty functions and sub-routines only four were used in the data collection software program. These were:

CALL INITIALIZE Initialises boards and looks for errors and faults. Returns an errors message to indicate fault;

CALL CSCAN850(*lchan,board,chanarray(x),range,mult,rcount,erstat*) sets up RTI850 board where,

lchan= logical or virtual channel assigned to board,

board= RTI 850 assigned board number in case of more than one RTI850 board,

chanarray(x) where x = number of channels to be read,

range multiplied by *mult* = time interval between measurements in microseconds, (*range* =1 to 63,000 *mult* = 1,10, 100, 1000 or 10,000),

rcount = total number of readings on all channels,

erstat = variable that holds status or error code;

CALL CSCAN(*array(y),erstat*) starts data collections and indicates array to store values;

CALL CHECK stops data collection and transfers data to array.

The functions were declared at the start of the program and then called when required. These library functions eliminated the need to write complex code to control the RTI850 data collection card.

3.2.1.5 Software program

A simple software program was written to collect data from 1 to 8 channels at a preset sampling rate. For each data point required, the signal was sampled a number of times over 4 cycles of the ac mains frequency to avoid aliasing of the final value. In the software used for the equilibrium measurements data was collected at intervals of one second or above. The channels were sampled sequentially with 125 μs between measurements. In this way 40 data points were collected for each of the channels in an 80 ms period. The 40 points were averaged to give the one second value. By this means the precision of the measurement system could be reduced to 16 μV. The measured values were stored on a file on the hard disc of the PC after each reading. The data was then protected if for any reason the PC crashed due to power failure or surges.

The software allowed input of number of channels, experiment length, interval between measurements, experiment title and file name. The software added time and date to the header of the file. The data was stored as text in a DOS type file structure. The software program was designed to allow the data file to be imported directly into a number of commercial software packages. These included Microsoft EXCEL, Lotus 1-2-3 and Bio-optronics V-Calc. Data analysis and graph preparation was carried out using one of these packages.

3.2.1.6 Equipment for electrochemical coating of silver electrodes

An eight channel microprocessor controlled constant current device and coating cell were fabricated to allow electrodes to be prepared in bulk. The instrument used a single constant current circuit and an Intel 8048 microprocessor and a multiplexer to time each coating and switch to the next channel. The current was altered from 0.1 to 50 mA by adjusting an internal variable resistor in the constant

current circuit. The coating time was software adjusted by re-programming the microprocessor to give coating pulses from 10 ms to 10 minutes.

3.2.2 Electrochemical cell

The cell comprises of the silver halide electrode, a solution ground electrode, a reference bridge and a reference electrode.

3.2.1.1 Reference electrode

For this project a specially designed reference half-cell was used to minimise the effect of junction potentials. It was based on a standard commercial silver/silver chloride reference electrode (Corning 476029) immersed in a double junction salt bridge solution (Figure 3.1).

It is not possible to immerse a commercial reference electrode directly into solutions containing silver ion as chloride ions leaking out from the internal fill reference solution cause precipitation of silver chloride in the junction material. This causes the flow to be blocked and drifting of the reference potential. Calculations (Chapter 2) showed that it should have been possible to insert a concentrated equitransferrant sodium/potassium nitrate solution between the equitransferrant potassium chloride fill solution and the sample without causing a junction potential. In practise large junction potentials are seen to arise between the two concentrated solutions. This was avoided by placing a dilute potassium nitrate solution between the two concentrated salt solutions. Any junction potentials caused between the concentrated and dilute solutions were balanced out. In practise this double junction system agreed well with the theoretical value calculated in chapter 2. The particular concentrations used are described in previous literature (Lin, 1989) and were chosen to minimise the junction potential.

A further improvement was found by maintaining the reference electrode at 25 °C by incorporating a water jacket around the upper chamber. This stabilised the reference electrode and protected it from any sudden changes in the sample temperature. The junction materials used were chosen to best suit their surroundings. The first junction was the standard ceramic junction incorporated in

the commercial Corning 476029 electrode. The second junction, between the dilute potassium nitrate and the equitransferrent salt solution was a small ceramic junction fired into a glass capillary specially contracted by Russell pH Ltd for the project. The third junction, the bridge sample junction, used a cotton-wool material to maintain a high flow rate.

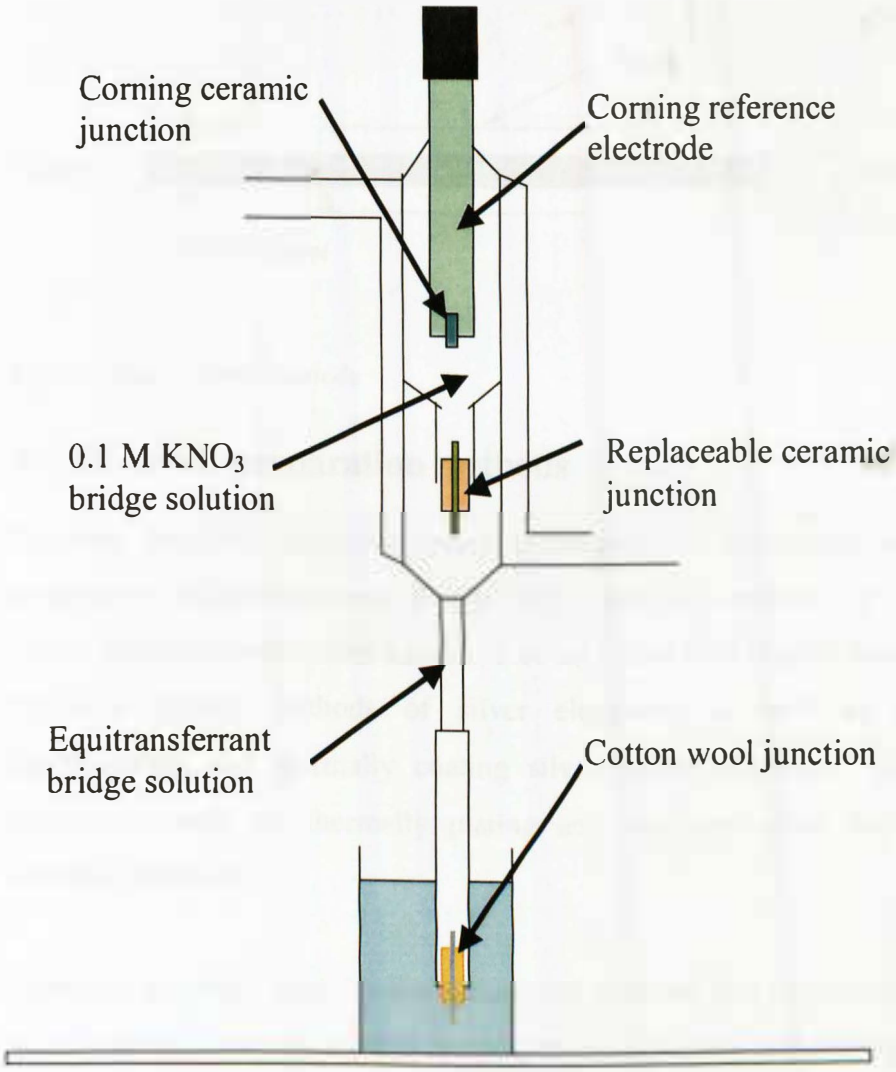


Fig. 3.6 Reference electrode in salt bridge.

3.2.1.2 Standard silver electrode

A standard "massive" silver electrode fabricated internally by Kodak Ltd was used for these equilibrium potential difference measurements. These electrodes

were made from a 6.25 mm rod of 99.99% pure silver encased in an epoxy body with 30 mm of the rod exposed to the solution (Figure 3.3). The surface area of each electrode was 619.7 mm^2. New electrodes were obtained for all experiments ensuring that electrodes were only used with the same halide except where the effect of mixing the halides was being investigated. Preparation of these electrodes and the method a coating the silver halide layer is discussed later.

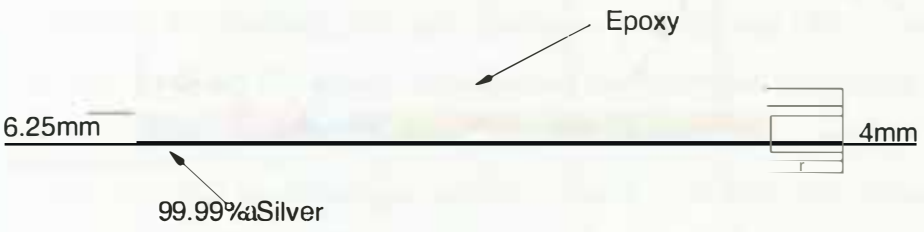


Fig. 3.7 Massive silver electrode

3.3 Electrode preparation methods

Previous literature describes many techniques for preparing and coating a silver/silver halide electrode. Briggs (1952) sets out methods for electroplating silver metal electrodes with halides, Ives and Janz (1961) give details of several chemical plating methods of silver electrodes as well as methods for electroplating and thermally coating silver halide electrodes. Galster (1991) reports methods for thermally plating and oxidising silver halide reference electrode elements.

However, previous work by the author (not reported here) found two techniques to be superior. The first used an electrochemical cleaning and coating technique to deposit a layer of silver halide, while the second used a mechanical polishing and chemical solution to coat a silver halide layer.

3.3.1 Electrochemical preparation

In this method the electrodes were first cleaned of any old silver halide coating by applying a negative potential to the silver rod in a 2 % solution of either

potassium nitrate or a potassium salt of the relevant halide. Any residual coating was easily wiped clean with a paper towel. The electrodes were either polished with a paper towel or with a polishing paste containing 1 μm aluminium silicate particles. The electrodes were first rinsed in acetone and then in water. It was important that the electrodes were recoated with halide quickly before the surface was tarnished with silver sulphide. The electrodes were placed in a fresh solution of 2 % potassium halide salt and a positive potential applied. It was found that a two-electrode cell using constant current was both more reliable and more robust in a factory environment than using a program potential and a three-electrode cell. Previous work by the author (not reported here) showed the voltage applied to maintain the constant current did not fall by an appreciable amount during the coating and that no advantage could be gained by coating the electrodes under programmed applied voltage. It was found that the most reliable coating of these silver electrodes required a current of 30 mA for four minutes.

An eight channel microprocessor controlled constant current device and coating cell was fabricated to allow electrodes to be prepared in bulk (3.2.1.6). To avoid current being drawn unevenly from one electrode, the electrodes were coated one at a time in a cycle rather than in parallel. The eight electrodes were arranged evenly around a platinum counter electrode in a 500 ml cell with a 30 mm gap between electrode and counter. During the coating the solution was stirred from beneath with a large magnetic stirrer. Electrochemical coating was carried out at 20 °C. At the end of the coating time the electrodes were removed and rinsed in demineralised water for 10 minutes. Before use the electrodes were soaked in water for at least one hour.

For later experiments where the duration of the coating process was varied the microprocessor was re-programmed for each experiment.

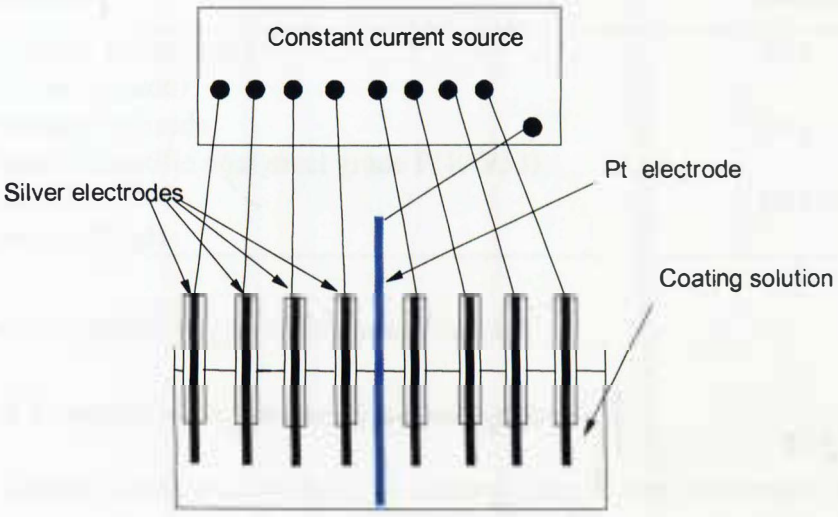


Fig. 3.8 Electrode coating station.

3.3.2 Chemical preparation

Various methods of chemically coating silver halide electrodes have been used and documented in Kodak Ltd. A variety of solutions were investigated. Chemical coating has the advantage that the coating thickness and speed of coating does not depend on area but only on the concentration of chemicals, the time in the coating solution and the temperature of the coating solution. Electrodes of different sizes could be coated in the same solution. In this project one type of coating solution, based on potassium ferricyanide and potassium halide, previously investigated by the author and optimised to give the best performance, was used (Table 3.1). Electrodes were cleaned and polished as in the electrochemical coating method and then immersed in the stirred coating solution for 10 minutes. The electrodes were subsequently removed and rinsed in running demineralised water for 10 minutes. As in the case for electrochemical coating before use the electrodes were left soaking in water for at least 1 hour.

Chemical	Amount
potassium ferricyanide (analytical grade)	20 g
potassium bromide ((Fisher Scientific analytical grade P/400/53)	20 g
water (demineralised)	1000 ml

Table 3.1 Composition of chemical coating solution

3.3.3 Comparison of preparation techniques

To compare these two methods of coating sixteen, new electrodes were obtained and polished with 1 μm polishing paste. For the purpose of this experiment silver bromide coated electrodes were evaluated in three concentrations of potassium bromide. Eight electrodes were immersed in the bromide chemical coating solution and eight electrochemically coated. The electrodes were then rinsed and soaked ready for use.

3.3.4 Experimental procedure

Test solutions containing bromide ions were prepared by dissolving 11.9 g potassium bromide (Fisher Scientific analytical grade P/400/53) in 1000 ml demineralised water to give a 0.1 molar concentration. This solution was diluted by pipette and volumetric flask to give a 0.001 molar and 0.0001 molar test solutions. 500 ml glass beakers were filled with each solution, placed in the 40 °C water bath and left for 30 minutes to reach equilibrium. Eight electrodes, four of each type plus the bridge junction, a temperature sensor and a platinum ground electrode were then lowered into the first test solution and the potential measured every second for two minutes. The electrodes were first tested in the 0.1 M bromide test solution followed by rinsing in demineralised water and dabbing dry. This procedure was repeated in the 0.001 Mt and 0.0001 M solutions in the same way. This order was then reversed back to the 0.1 M bromide. This was repeated for the other eight electrodes, four chemically and four electrochemically coated. The value for the equilibrium potential was taken from the average reading over the last 10 seconds of the 2 minutes. The results of this comparison are given in Table 3.2 and Table 3.3

3.3.5 Results

	[potassium bromide] / M					
Electrode no.	0.1	0.001	0.0001	0.0001	0.001	0.1
c1	-48.1	69.1	130.5	130.9	69.7	-48.5
c2	-49.3	68.6	129.9	130.2	69.1	-49.1
c3	-47.8	69.4	131.2	131.6	70.1	-47.2
c4	-50.1	67.3	129.4	129.9	68	-49.5
c5	-51.7	65.2	127.1	129	66.2	-50.9
c6	-46.9	70.1	131.5	131.5	70.3	-46.9
c7	-52.4	64.2	130.2	130.9	67.3	-52.4
c8	-49.6	67.5	128.6	129.1	68.6	-49.8
mean	-49.49	67.68	129.80	130.39	68.66	-49.29
STD	1.90	2.07	1.43	1.01	1.43	1.82

Table 3.2 Equilibrium potentials (mV) from chemically coated silver bromide electrodes

	[potassium bromide] / M					
Electrode no.	0.1	0.001	0.0001	0.0001	0.001	0.1
e1	-50.4	66.8	128.7	128.1	67.2	-49.3
e2	-49.7	68.1	129.3	130.1	68.6	-48.9
e3	-51.2	66	127.6	128.4	66.4	-50.9
e4	-50.7	66.7	128.4	128.3	66.2	-50.1
e5	-49.8	68.2	129.6	129.9	67.3	-48.1
e6	-51.2	65.9	127.8	128.1	66.1	-51.1
e7	-49.7	67.8	127.1	126.9	67.4	-48.9
e8	-51.6	66	127.1	127.5	66.8	-50.5
mean	-50.54	66.94	128.20	128.41	67.00	-49.85
STD	0.76	0.97	0.96	1.09	0.82	1.18

Table 3.3 Equilibrium potentials (mV) from electro-chemically coated silver bromide electrodes

3.3.6 Discussion

The results of the comparison between the electrochemically and chemically coated electrodes showed that the electrochemically coated electrodes gave a smaller mean bias from the theoretical value calculated in Chapter 2. The mean bias was obtained by calculating the differences between the means for all electrodes at each concentration and the theoretical value at that concentration. The mean of these differences then gave the mean bias. The mean bias value obtained was 0.44 mV for the electrochemically coated electrodes and 1.61 mV for the chemically coated electrodes. However, this observation could have been caused by the half-cell potential of the reference electrode, as it is difficult to obtain reference electrodes with the absolute theoretical potential. More importantly, the standard deviation of the electrochemically coated electrodes was lower than the chemically coated electrodes. It was also observed that the chemical coating procedure was much more sensitive to the stirring conditions. If the stirring was not vigorous enough electrodes did not coat in a uniform way with light areas of coating clearly visible at the end of the time. Therefore, all further work investigating the comparison of measured potential of silver/silver halide electrodes with theoretical values was continued using electrochemically coated electrodes.

3.4 Equilibrium cell potentials measurements

3.4.1 Measured equilibrium potential of a silver/silver halide electrode with variation of halide ion concentration

Comparison of the measured potentials and theoretically calculated values of silver/silver halide electrodes in solutions of halide ion in ideal laboratory conditions were carried out in various concentrations to determine the limit of sensitivity to the respective halide ion. This data was used later in the research work to compare the value obtained by the new "clean/coat/measure" technique.

3.4.1.1 Experimental procedure

The measurement of the equilibrium potential for silver chloride, bromide and iodide electrodes was carried out using the equipment described in 3.2. Eight

electrodes were fabricated for each halide and only tested in that halide ion to prevent contamination. For each experiment eight new silver electrodes were prepared and electrochemically coated with the silver halide layer required.

A concentrated 0.1 M solution of the halide ion being investigated was prepared using potassium chloride (Fisher Scientific analytical grade), potassium bromide (Fisher Scientific analytical grade P/400/53) or potassium iodide (Fisher Scientific analytical grade P/5840/53) in demineralised water. The solutions were diluted by pipette and volumetric flask to obtain the final test solutions (Table 3.5, 3.6, 3.7). 500 ml of each test solution was placed in a stainless steel vessel located in a 40 °C water bath for 30 minutes or until the temperature in the solution had reached 40 °C. The eight silver electrodes plus the reference junction, a platinum ground electrode and a temperature sensor were immersed in the test solution. To prevent the electrode assembly cooling down the initial test solution the electrodes were first held in a beaker of demineralised water at 40 °C. The potential was measured using the front-end interface module with data being collected every second for two minutes. The raw data and the average reading over the last 10 s were stored on file for analysis. The solutions were tested from most concentrated to least concentrated. This procedure was repeated 8 times with fresh solutions and electrodes being prepared each time. The results of one electrode are given with the theoretical values calculated in chapter 2. The data for chloride, bromide and iodide from all eight electrodes is given in Appendix II.

3.4.1.2 Chloride results

[chloride] / M	Activity/ M	E_T/mV	E_m /mV
1	0.53930000	46.60	40.1
0.5	0.29985000	61.99	56.7
0.1	0.07448000	98.99	97.5
0.05	0.03999000	115.65	115.1
0.02	0.01719800	138.33	138.6
0.01	0.00895400	155.91	154.5
0.005	0.00461450	173.77	173
0.002	0.00189880	197.72	197.7
0.001	0.00096350	216.02	213.1
0.0005	0.00048695	234.43	231.1
0.0001	0.00009881	277.46	264.5

Table 3.4 Measured potentials for a silver/silver chloride electrode in potassium chloride test solutions at 40 °C

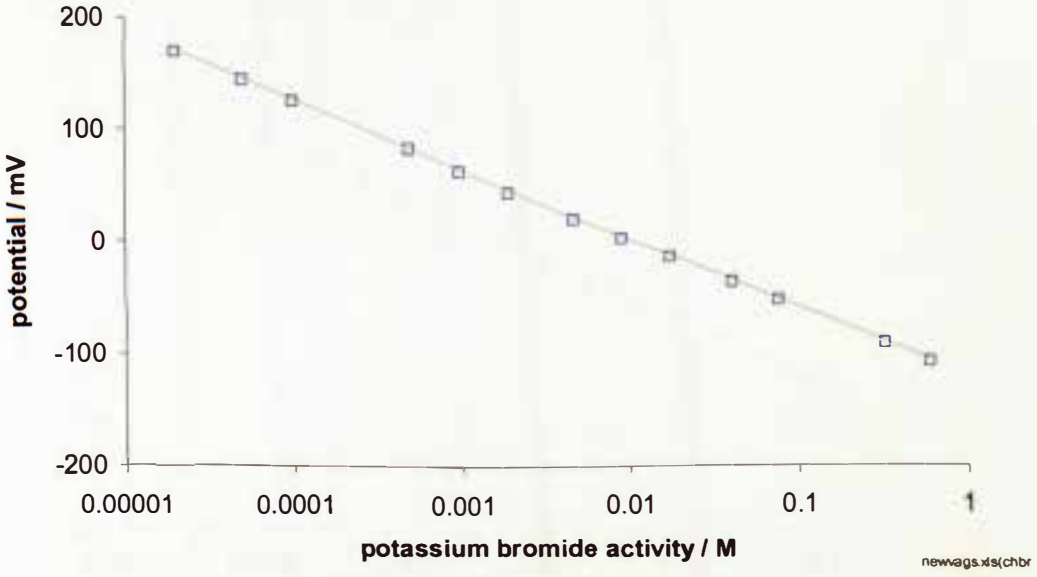


Figure. 3.9 Equilibrium potential, measured after 2 minutes, for a silver/silver chloride electrode in potassium chloride test solutions at 40 °C.(□) Conventional coated electrode;(—) Theoretical value.

3.4.1.3 Bromide results

[bromide] / M	Activity /M	E_Tt/mV	E_m /mV
1	0.59130000	-105.16	-107.9
0.5	0.31970000	-89.01	-91
0.1	0.07615000	-50.89	-52.1
0.05	0.04051000	-33.97	-35.7
0.02	0.01730200	-11.10	-12.7
0.01	0.00898300	6.55	4.9
0.005	0.00462250	24.45	22.8
0.002	0.00190020	48.42	46.7
0.001	0.00096390	66.73	64.9
0.0005	0.00048705	85.15	84.7
0.0001	0.00009881	128.19	126.4
0.00005	0.00004958	146.80	145
0.00002	0.00001989	171.44	169.3

Table 3.5 Measured potentials for a silver/silver bromide electrode in potassium bromide test solutions at 40 °C

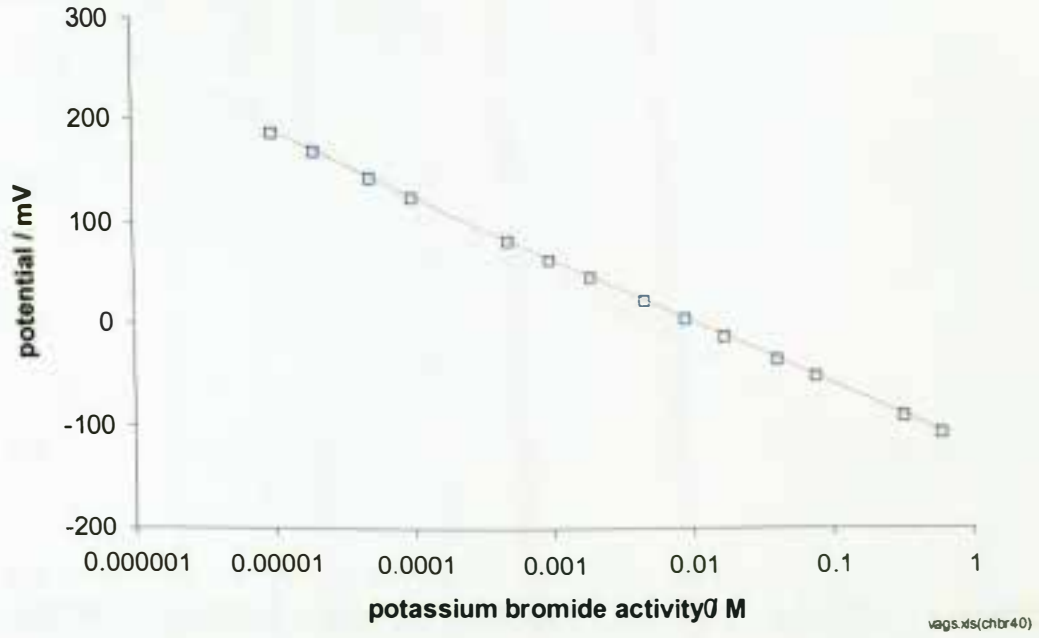


Figure. 3.10 Equilibrium potential, measured after 2 minutes, for a silver/silver bromide electrode in potassium bromide test solutions at 40 °C. (□) Conventional coated electrode; (—) Theoretical value.

3.4.1.4 Iodide results

[iodide] / M	Activity /M	E_T/mV	E_m /mV
1	0.60040000	-326.07	-307
0.5	0.32320000	-309.80	-300.1
0.1	0.07646000	-271.49	-270.9
0.05	0.04061000	-254.53	-253.9
0.02	0.01732200	-231.63	-230.1
0.01	0.00898800	-213.97	-213.4
0.005	0.00462450	-196.05	-195.8
0.002	0.00190060	-172.07	-173.4
0.001	0.00096400	-153.76	-156.2
0.0005	0.00048705	-135.35	-137.1
0.0001	0.00009881	-92.31	-92.9
0.00005	0.00004958	-73.70	-74
0.00002	0.00001989	-49.06	-52.6
0.00001	0.00000996	-30.40	-35.8

Table 3.6 Measured potentials for a silver/silver iodide electrode in potassium bromide test solutions at 40 °C.

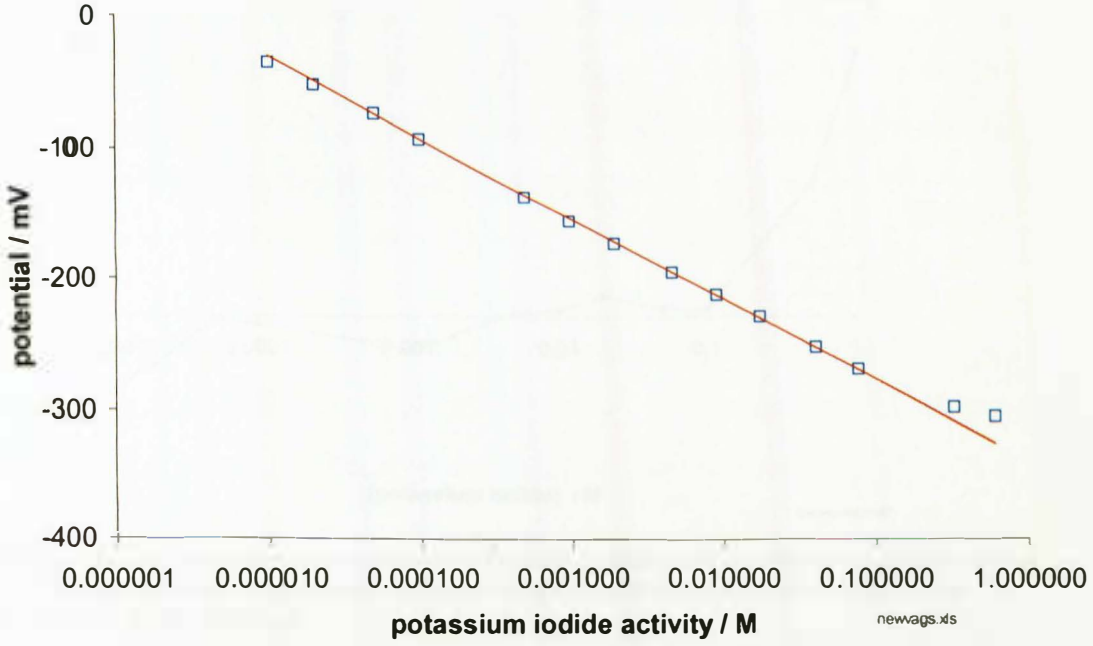
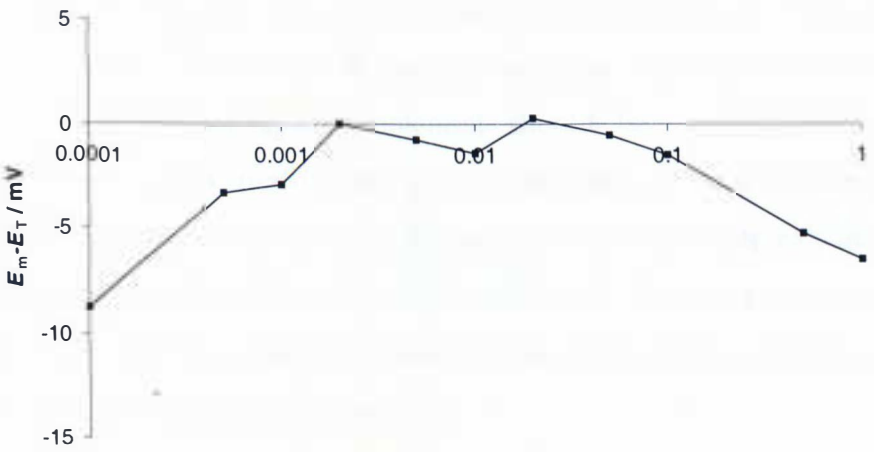
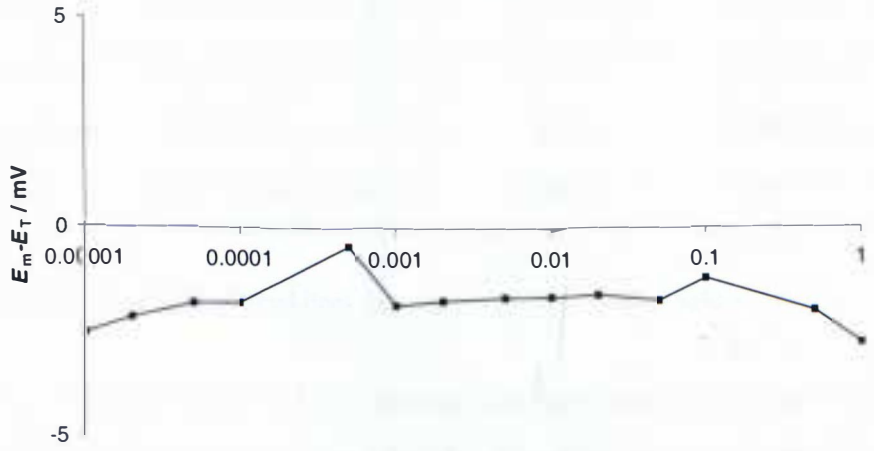


Figure 3.11 Equilibrium potential, measured after 2 minutes, for a silver/silver iodide electrode in potassium iodide test solutions at 40 °C.(□) Conventional coated electrode;(—) Theoretical value.

3.4.1.5 Discussion





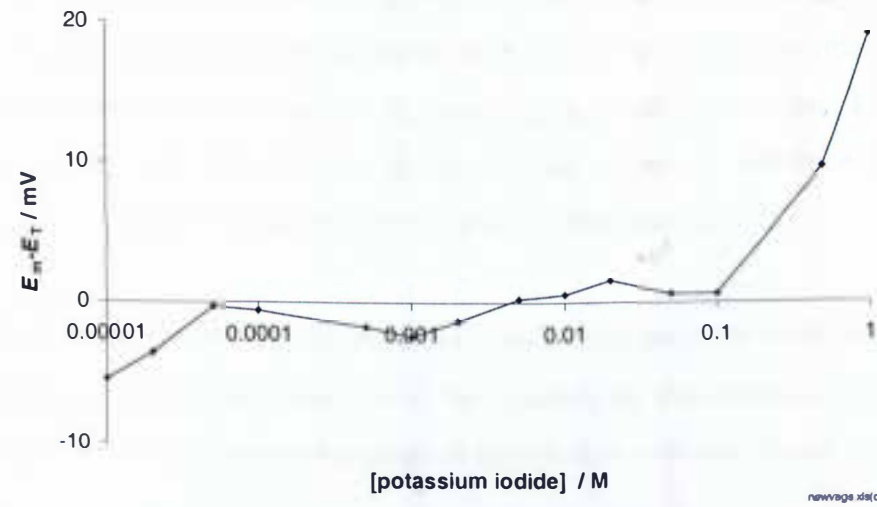


Figure 3.12 Difference between measured equilibrium potential and theoretical calculated value at 40 °C for silver/silver chloride electrode (top), silver/silver bromide electrode (middle) and silver/silver iodide (bottom).

The equilibrium potential measurements for the silver/silver chloride, silver/silver bromide and silver/silver iodide coated electrodes were in good agreement with the calculated values. The theoretical nernstian slope for calibration lines where activity is plotted against potential should be $-26.977\ln a_X$. However the theoretical values used for this project take into account the change in junction potential at each concentration. Equations for the trendline calculated in EXCEL for the measured and theoretical values for each calibration curve are given below. The difference between the measured and the theoretical values were calculated for each concentration (Figure 3.12)

Halide	Measured line equation	Std Err ($R^{2)}$	Theoretical line equation
chloride	$-26.755\ln(a_{Cl^-}) + 28.767$	0.9986	$-26.855\ln(a_{Cl^-}) + 29.473$
bromide	$-26.901\ln(a_{Br^-}) - 121.74$	1.0000	$-26.902\ln(a_{Br^-}) - 119.97$
iodide	$25.577\ln(a_{I^-}) - 331.32$	0.9978	$-26.894\ln(a_{I^-}) - 340.46$

Table 3.7 Gradients of trend lines for measured and theoretical values

The plots in Figure 3.12 indicated that there was a systematic offset in all the solutions for the potassium bromide. The difficulty of obtaining and maintaining of reference system with the correct theoretical half-cell potential can explain this. The particular reference electrode used for the bromide experiments was not the same system as that used for the chloride and iodide solutions. Differences of a few millivolts in commercial silver/silver chloride reference electrodes are common and are within the specification of the electrode.

In all three halides the values for the equilibrium potential were most inaccurate at high concentrations. This could be because of inaccuracies in the theoretical values or due to chemical changes at high halide concentrations:

- It was shown in Chapter 2 that at low concentrations the activity coefficient approaches 1 so that concentration equals the activity. At concentrations above 0.1 M the activity coefficient decreases causing the

calculated activity of the solution and hence the calculated equilibrium potential to be more sensitive to the value of constants used in the original calculation. Although the values for chloride and bromide at high concentration show good agreement with calculated values, the values observed for the silver iodide electrode at high concentrations are almost 20 mV more positive than the theoretical values.

- It has also been reported (Ives, 1961) that at high halide concentrations complex silver halide compounds are formed. The solubility product is altered by the presence of these silver halide complexes. These changes in solubility have a direct effect on the calculated equilibrium potential; however, insufficient data is available to determine new calculated values for the equilibrium potential.

At concentrations between the lowest test solutions and 0.1 M the electrodes were in very good agreement with the calculated values if an average offset was subtracted from all values due to the reference electrode bias. For a silver chloride coated electrode the best values were obtained over a two-decade concentration range of between 0.001 and 0.1 M chloride. For a silver bromide electrode the electrode responded with near theoretical values over a four-decade concentration range between 0.00005 and 0.5 M. Due to the deviation at high concentrations the silver iodide coated electrode was only observed to give comparable values over a three decades of concentration from 0.001 to 0.1 M

At the lowest concentrations none of the halide electrodes responded with the calculated Nerstian slope of 62.13 mV per decade concentration. For a silver chloride coated electrode the limit of detection can be calculated from the solubility constant at a particular temperature. At 40 °C the pK_{spAgCl} was calculated to be 9.2 giving a limit of detection of 2.5×10^{-5} M for chloride ions. The lowest concentration of test sample measured was 1×10^{-4} M. However as this is only four times the concentration of the detection limit it would be expected that the electrode would not responded in a Nernstian way at this concentration. Similarly

for bromide, the pK_{spAgBr} at 40 °C was calculated to be 11.61 giving a detection limit of 1.56×10^{-6} M. In this case, where a better agreement with the calculated value was found, the lowest concentration of sample tested was 1×10^{-5} M, ten times the detection limit. In the case of iodide the detection limit well below the lowest concentration tested. The pK_{spAgI} was calculated to be 15.1 giving a detection limit of 2×10^{-8} M, a thousand times lower than the lowest concentration of iodide tested.

This agrees well with published data (Bishop, 1963; Morf, 1974) which gives detection limits and calibration curves for chloride, bromide and iodide electrodes.

3.4.2 Measured equilibrium potential of a silver/silver bromide and silver/silver chloride electrode with variation of temperature

In the manufacture of photographic emulsions the temperature of the process can vary from 40 to 80 °C. It was therefore important to determine whether the equilibrium potential measurements carried out with the equipment developed and used in this project gave results comparable with the theoretical values predicted from the calculations in Chapter 2. Solutions of bromide were measured at six temperatures and solutions of chloride and iodide measured at three temperatures. Due to the extensive time required to carry out this experiment, not all solutions of chloride and iodide were tested at all the temperatures.

3.4.2.1 Measurement procedure

Eight halide coated electrodes were fabricated using the electrochemical coating technique described in 3.3.1. Electrodes were marked for chloride, bromide or iodide and kept separate to reduce contamination. Test solutions of chloride, bromide and iodide were prepared as previously described in 3.4.1.1. from 0.00001 to 1 M for bromide and iodide and from 0.0001 to 1 M for chloride. 500 ml of the solutions were placed in a stainless steel vessel situated in a water bath at the required temperature for 30 minutes before any measurements were made. The electrodes were held at the temperature of measurement by immersing in a vessel of demineralised water in the water bath. After 30 minutes the eight electrodes plus the reference junction and a platinum ground electrode were

immersed in the test solution. The solutions were measured from high to low concentration with a thorough rinsing in demineralised water held at the temperature of measurement between each measurement. The potential was measured using the differential interface module connected to the PC with data being collected every second for two minutes. The raw data and the average reading over the last 10 s were stored on file for analysis. All bromide test solutions were measured at 25, 40 and 60 °C with three 0.001, 0.01 and 0.1 M being measured at 20, 30 and 50 °C. The chloride test solutions were measured at 25, 40 and 60 °C.

All iodide solutions were measured at 40 °C and five at 25 and 60 °C. The mean potential value of all eight electrodes for each test solution at each temperature was calculated. (Tables 3.8 – 3.10, Figures 3.13 – 3.15).

3.4.2.2 Results

	Test solution temperature/ °C		
[chloride] /M	**25**	**40**	**60**
1	35.6	40.1	41.5
0.5	51.2	56.7	60.1
0.1	90.1	97.5	101.2
0.05	107.1	115.1	119.5
0.02	128.7	138.6	143.6
0.01	144.5	154.5	162.3
0.005	161.9	173	181.6
0.002	184.9	197.7	206
0.001	200.9	213.1	226.6
0.0005	217.5	231.1	244.3
0.0001	256.8	268.7	284.5

Table 3.8 Measured equilibrium potential of a silver/silver chloride electrode with variation of temperature

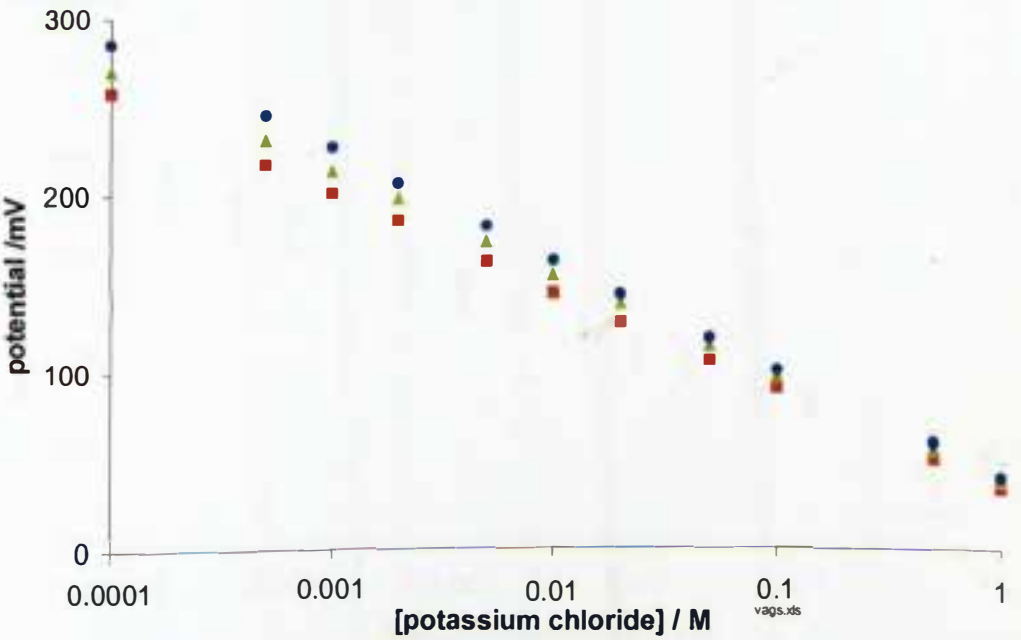


Figure 3.13 Equilibrium potential of silver/silver chloride electrodes at various temperatures and chloride concentrations. (■) 25 °C; (▲) 40 °C; (●) 60 °C.

	Test solution temperature / °C					
[bromide] /M	**20**	**25**	**30**	**40**	**50**	**60**
1		-114.7		-107.9		-104.1
0.5		-98.8		-91		-85.2
0.1	-65.8	-62.5	-60.8	-52.1	-52	-45.3
0.05		-45.9		-35.7		-27.1
0.02		-23.9		-12.7		-3
0.01	-11.3	-6.8	-6	4.9	7.6	15.5
0.005		10.1		22.8		34.2
0.002		32.8		46.7		60.3
0.001	44.7	50.2	52.5	64.9	69.1	80
0.0005		67.8		84.7		99.4
0.0001		107.8		126.4		144.2
0.00005		126		145		164.6
0.00002		148.7		169.3		190.1
0.00001		166.3		187.6		209.1

Table 3.9 Measured equilibrium potential of a silver/silver bromide electrode with variation of temperature

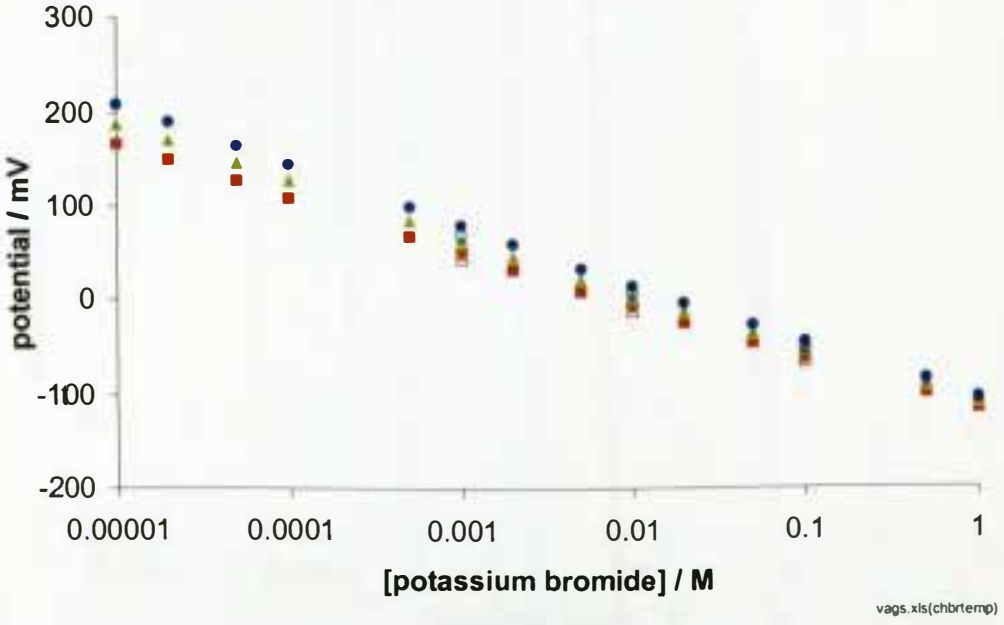


Figure 3.14 Equilibrium potential of silver/silver bromide electrodes at various temperatures and bromide concentrations. (□) 20 °C; (■) 25 °C; (△) 30 °C; (▲) 40 °C;(○) 50 °C; (●) 60 °C.

	Temperature/ °C		
[iodide]/ M	**25**	**40**	**60**
1		-307	
0.5		-300.1	
0.1	-277.3	-270.9	-262.8
0.05		-253.9	
0.02		-230.1	
0.01	-228.5	-213.4	-200.3
0.005		-195.8	
0.002		-173.4	
0.001	-174.9	-156.2	-136
0.0005		-137.1	
0.0001	-118.1	-92.9	-70.1
0.00005		-74	
0.00002		-52.6	
0.00001	-54.7	-35.8	-5.1

Table 3.10 Equilibrium potential of silver/silver iodide electrodes at various temperatures and iodide concentrations

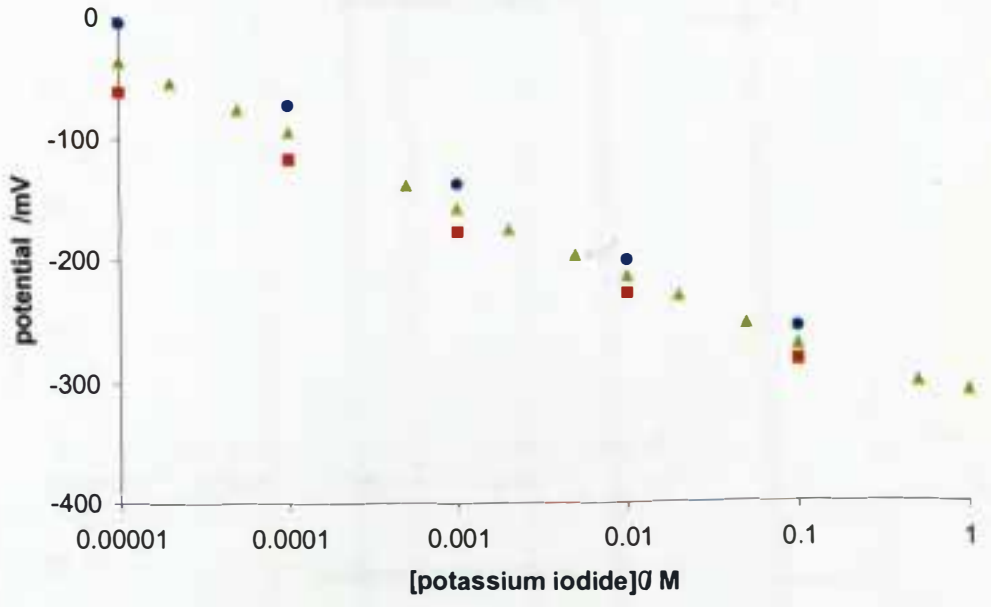


Figure 3.15 Equilibrium potential of silver/silver iodide electrodes at various temperatures and iodide concentrations. . (■) 25 °C; (▲) 40 °C; (●) 60 °C.

3.4.3 Discussion

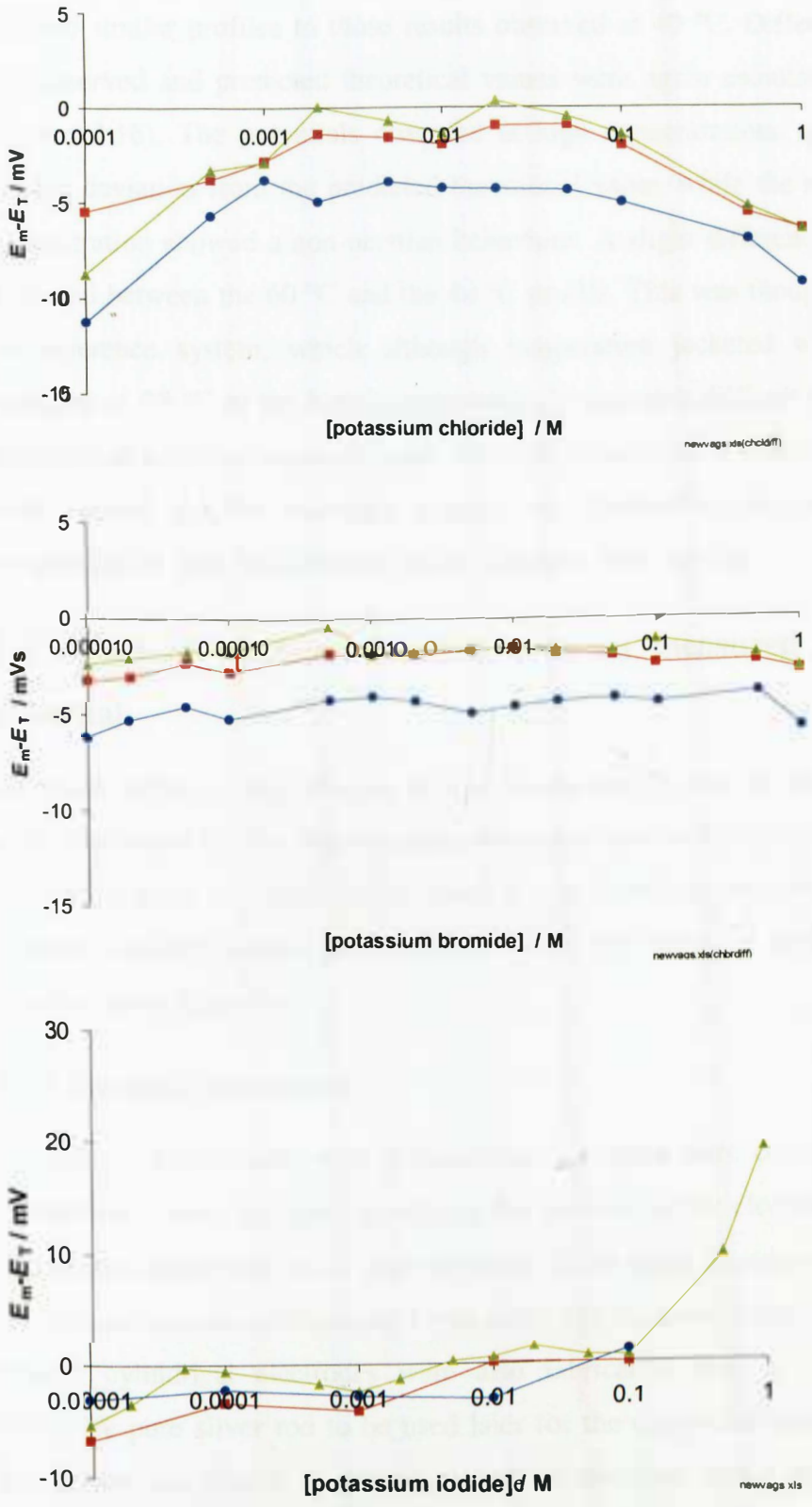


Figure 3.16 Difference between theoretical and observed potential values for silver chloride (top), silver bromide (middle) and silver iodide (bottom) electrodes at (■) 25 °C, (▲) 40 °C and (●) 60 °C.

The observed potentials for the silver chloride, silver bromide and silver iodide electrodes in solutions of varying concentration at temperatures of 20 – 60 °C showed similar profiles to those results observed at 40 °C. Differences between the observed and predicted theoretical values were again calculated and plotted (Figure 3.16). The potentials observed at high concentrations again showed a similar deviation from the predicted theoretical value, while the response at low concentration showed a non-nerstian behaviour. A slight difference in offset was observed between the 60 °C and the 40 °C profile. This was thought to be due to the reference system, which although temperature jacketed was difficult to maintain at 25 °C at the high temperatures. It was also difficult to maintain the reference at a precise constant value since after each time a series of experiments were carried out the reference system was dismantled for storage at room temperature to stop the different bridge solutions from mixing.

3.5 Effect of electrode surface area on measured equilibrium potential

As stated earlier in this chapter, it was impractical to use the standard massive silver electrodes for the clean/coat/measure experiments due to the large currents required to coat the silver halide layer. It was therefore necessary to determine whether a smaller surface area electrode would give the same performance as the massive silver electrodes.

3.5.1 Electrode fabrication

A number of electrodes with different surface areas were constructed for this experiment. These included modifying the massive silver electrodes to produce two shorter electrodes and a disc electrode of the same diameter and fabricating two smaller disc electrodes using 1 mm and 2 mm diameter silver rod.

Smaller cylindrical electrodes were also fabricated from a 2 mm diameter 99.9999% pure silver rod to be used later for the clean/coat/measure technique. The design was similar to the massive silver electrode accept that the length of exposed silver was reduced to 2 mm. Table 3.11 shows the surface areas of these electrodes

Electrode Type	Dimensions			Coating current
	Dia. / mm	Len.t/ mm	Area / mm^2	/mA
Massive cylinder	6.25	30	620	30
Massive cylinder	6.25	12	266	13
Massive cylinder	6.25	6	148	7
Flat disk	6.25	0	30.7	1.5
Flat disk	2	0	3.1	0.15
Flat disk	1	0	0.8	0.04
CCM electrode	2	1	9.4	0.5

Table 3.11 Silver electrodes fabricated with surface areas and coating currents.

3.5.2 Measurement procedure

The electrodes were prepared for coating as with the massive silver electrode. The electrodes were coated for the standard 4 minutes in the same coating solution and at the same current density as used previously. Actual currents used are shown in Table 3.11. The method used to determine the equilibrium potentials was as described in section 3.4.1.1.

3.5.3 Results

[bromide]	Electrode surface area / mm^2						
	E_T	620	266	148	30.7	3.1	0.8	9.4
0.1	-50.89	-47.4	-50.3	-50.2	-49	-48.7	-47.1	-50.1
0.05	-33.97	-29.6	-32.4	-32	-32	-31	-29.4	-33.2
0.01	6.55	11.6	8.7	9	7.7	10.2	11.8	7.1
0.005	24.45	28.1	26.8	26.4	26.2	27.3	29.4	26.1
0.002	48.42	52.7	50.4	50	50.1	51.2	53.5	48.9
0.001	66.73	72.27	69.3	69.6	65.2	69.3	72.7	68
0.0005	85.15	89.1	87.3	86.7	87	88	90.2	86.1
0.0001	128.19	133	129.5	129.6	130.1	131.2	133.4	129.2
0.00005	146.80	150.4	148.4	148.5	148	149.2	151	147.6
0.00002	171.44	173	171.3	171.5	171.3	172.9	173.2	169.6
0.00001	190.10	190	189	189.5	187.9	190.9	190.7	186

Table 3.12 Equilibrium potentials for silver bromide electrodes with various surface areas.

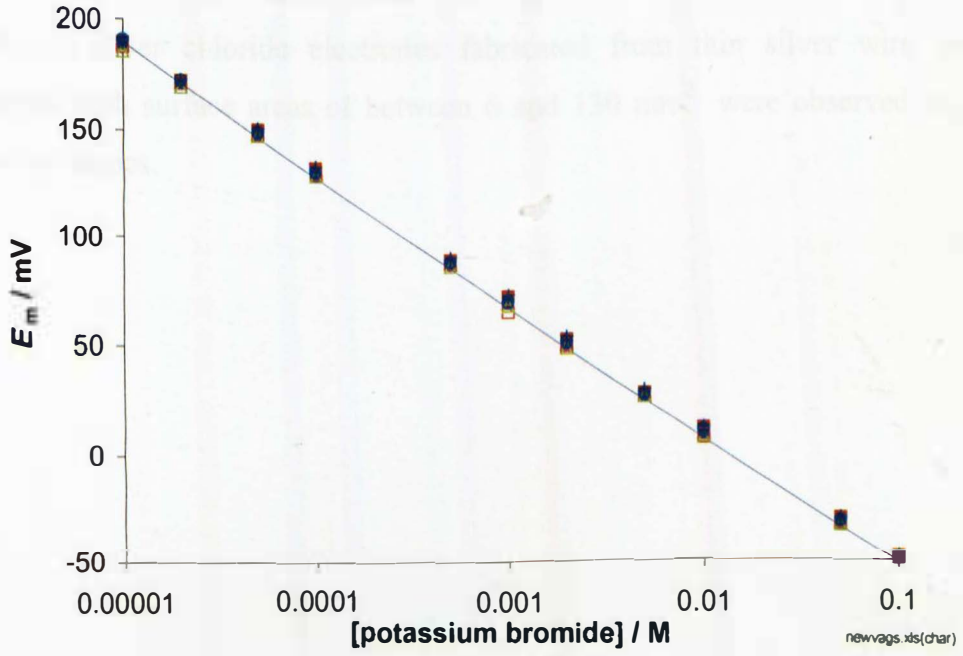


Fig. 3.17 Equilibrium potential for Silver bromide electrodes of various surface areas.
Area /mm^2 :(■) 620; (▲) 266; (●) 148; (□) 30.7; (△) 9.4; (○) 3.1; (+) 0.8.

3.5.4 Discussion

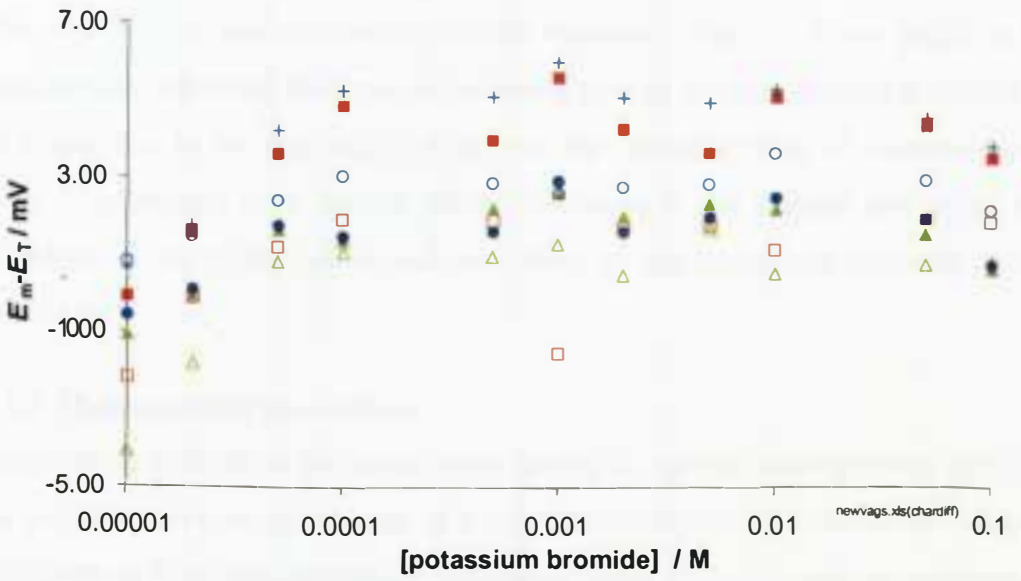


Figure 3.18 Difference between theoretical and measured equilibrium potential with variation of surface area. Area /mm^2 :(■) 620; (▲) 266; (●) 148; (□) 30.7; (\) 9.4; (○) 3.1; (+) 0.8.

The results observed for electrodes of different surface area were similar to the values for the massive silver electrode and similar to the previous experimental data from the study of the massive silver electrode in solutions of potassium bromide at various concentrations (Figure 3.12). No effect was observed with variation of electrode surface area. This agrees with data published (Watson, 1969) on silver chloride electrodes fabricated from thin silver wire where electrode with surface areas of between 6 and 130 mm^2 were observed to give nernstian slopes.

3.6 Effects of depositing thin layers of silver bromide

The new "clean/coat/measure" technique requires a layer of silver halide to be deposited on the silver electrode in as short a time as possible and for that layer to be responsive to the particular halide over the complete range of concentrations used. Experiments were carried out to determine if the amount and hence the thickness of the silver halide had any effect on the range and response of the electrode.

3.6.1 Measurement procedures

Seven small cylindrical electrodes were coated at various coating times from 10 ms to 100 s at a constant current of 0.5 mA in a 2% potassium bromide solution. The purpose built microprocessor electrode coater (3.2.1.6.) was reprogrammed between changes of coating time.

As the thin coatings were thought to be susceptible to sulphide contamination, within a few seconds of being coated, the electrodes were quickly rinse in demineralised water and placed in the test solutions. The equilibrium potential was then measured for five minutes in two test solutions (0.001 M and 0.1 M potassium bromide) using the eight channel PC based potentiometer. A new coating was prepared for each test solution.

3.6.2 Results

The potential of the seven electrodes was recorded every second over a 5 minute period. The potential values for each coating time in the two test solutions is shown below (Figure 3.19).

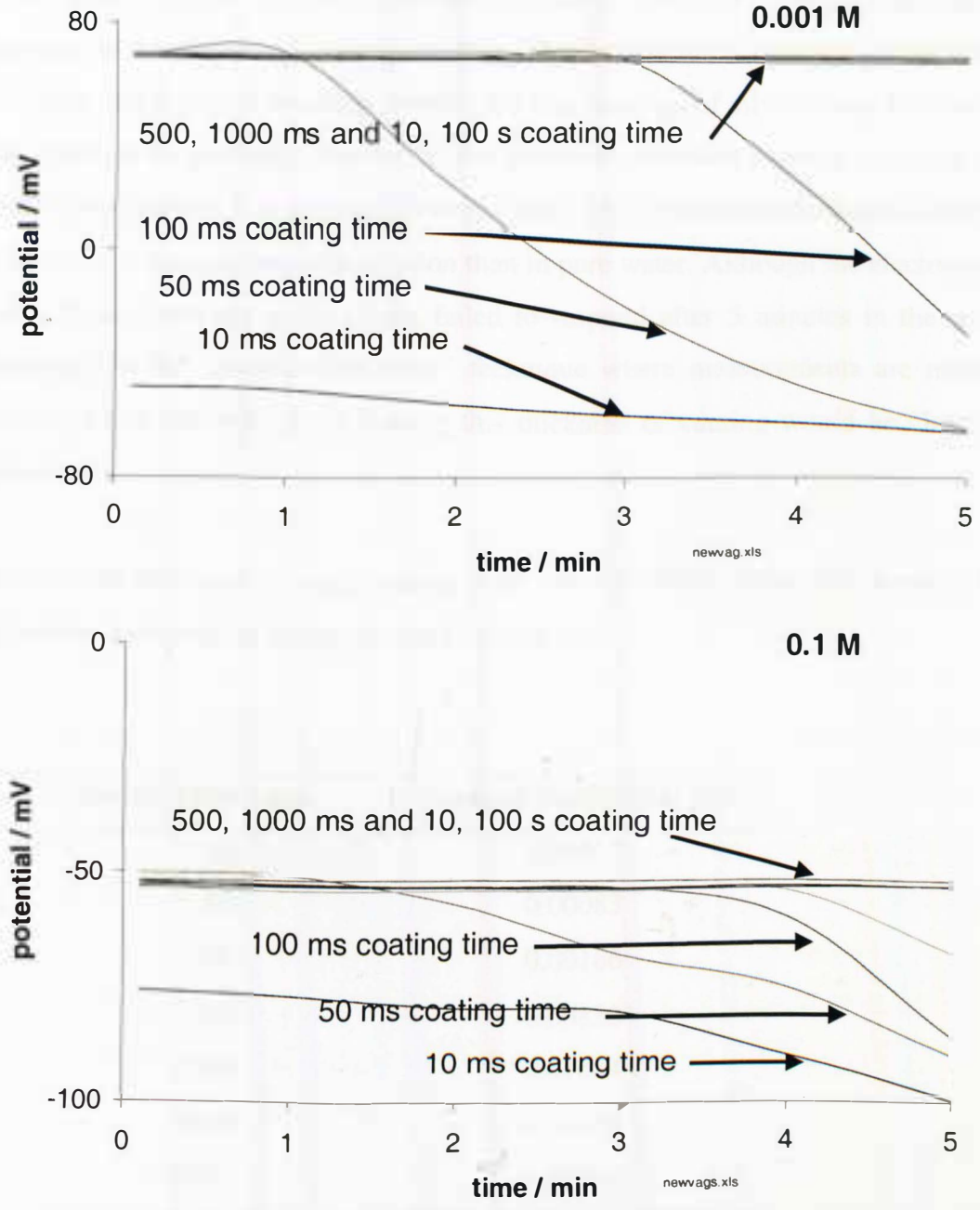


Figure 3.19 Variation of potential measured over 5 minutes for electrodes coated at a current density of 5 mA cm^{-2} for coating times between 10 ms and 100 seconds in 0.1 M (top) and 0.001 M KBr (bottom).

3.6.3 Discussions

In both solutions the electrode with a 10 ms coating showed no response to bromide giving similar behaviour to that of a polished bare silver electrode. The electrodes with a coating of 50 and 100 ms initially responded to bromide concentration but gradually drifted to more negative values after 2-3 minutes. Electrodes with greater than 1000 ms coating times responded to bromide, giving

comparable values to the conventional silver bromide coated electrodes previously described and maintaining this value for the full 5 minutes. As the test solution had no silver bromide present, the thin coatings of silver bromide would be expected to gradually dissolve in the potassium bromide solution to reveal a bare silver surface. It is reported (Ives and Janz, 1961) that silver bromide is more soluble in potassium bromide solution than in pure water. Although the electrodes with 50 and 100 ms coating time failed to respond after 5 minutes in the test solution, in the "clean/coat/measure" technique where measurements are made within a few seconds of the coating this thickness of coating would be clearly adequate.

The actual thickness of each coating time was calculated using the density of silver bromide and the charge passed (Table 3.13).

Coating time / ms	Coating thickness/ μm
10	0.00017
50	0.00083
100	0.00166
500	0.00832
1000	0.01664
10000	0.16639
100000	1.66394

Table 3.13 Thickness of silver bromide coating calculated from the charge passed and the density of silver bromide.

3.7 Summary

Two methods of preparing silver halide electrodes were investigated. The first, described by many previous workers used an electrochemical method to deposit a coating of silver halide onto a polished silver surface by passing a current through the electrode in a solution of the respective halide ions. It was reported (Gerischer,1955) that a current density of 3 – 18 mA cm^{-3} produced uniform

coatings, whereas current densities below this produced coatings of irregular thickness. The current density used during this investigation was 5 mA cm^{-2}.

The chemical method of preparation was reported by previous workers and optimised by the author in previous work. This method had the advantage that the thickness of coating was dependent on the concentration of reactants in the coating solution and the coating times but not on the surface area of the electrode. This allowed electrodes of different surface area to be coated with a similar coating thickness without the need to alter the constant current circuit in the multicoater equipment. However, results indicated that this method did not achieve electrodes of as precise potentials as the first method. This was in part due to the difficulty of maintaining a constantly stirred coating solution that is needed in the chemical method to obtain electrodes of uniform coating thickness.

The silver halide electrodes prepared for the measurement of chloride, bromide and iodide gave near theoretical responses in solutions of varying concentration. However, in concentrations above 0.1 M halide ion for all three silver halide electrodes, the observed values deviated from the theoretical values calculated in Chapter 2. This was thought to be due to either silver halide complexation changing the solubility product or errors in the constants used to calculate the activity coefficient, particularly at high concentrations.

For silver chloride and bromide coated electrodes in concentrations from 0.1 M down to 10 times higher than the theoretical detection limit, calculated from the solubility product, the electrodes gave potential values in good agreement with those calculated in Chapter 2. For silver iodide coated electrodes concentrations near the detection limited were not tested. However the electrode gave comparable potential values from 0.1 down to 0.00005 M iodide.

At concentration levels below ten times the detection limit for the silver chloride and bromide electrode, and at concentration below 0.00005 M for the silver iodide electrode, the slope of the electrode response was observed to decrease and

deviate from the predicted values. In all of the photographic emulsions investigated, the level of all three halide ion concentrations was higher than this level. In most cases the concentration was also below 0.5 M.

The observed differences between measured and theoretical values of equilibrium potential at a variety of temperatures showed a similar profile to the plots at 40 ºC. There were deviations from the expected potentials at both high and low concentration for all the halides – but within a wide middle range there was good agreement with potentials predicted from theory.

Investigations carried out to study the effect of the surface area of the coated electrode on potential showed that over the range of the areas studied (0.8 to 600 mm^2) no significant difference was observed.

Experiments to investigate the thickness of the silver halide layer coated and the thickness that was required to produce a silver halide electrode with a useable response confirmed that very thin coating would give comparable equilibrium potential values to the conventional thick coating. Silver halide layers of thicker than 83.2×10^{-10} m (coating time greater than 500 ms) responded to bromide ions at two concentrations giving stable potentials for over five minutes. Layers of thickness from 8.3 to 83.2×10^{-10} m (coating time between 50 and 500 ms) were observed to respond to bromide and to maintain this potential for two minutes. Layers of 1.7×10^{-10} m (coating time less than 50 ms) did not respond to bromide ions but gave behaviour consistent with a bare silver electrode This confirmed that silver halide layers coated in the 50 - 500 ms time period required for the "clean/coat/measure" technique would give responsive halide electrodes.

Chapter 4 Investigations using a rotating disc electrode

4.1 Introduction

In this part of the project the clean/coat/measure pulse technique described in Chapter 1 was investigated using a silver rotating disc electrode (RDE). The schematic for one cycle of the technique is shown in Figure 4.1. Each complete cycle comprises a cleaning or stripping pulse (A), a delay (B), a coating pulse (C) and a measurement step (D). Step D also acts as a delay before the start of the next cycle. The steady state potential value (VAG) was taken during the measurement step. To optimise the method to achieve VAG results similar to those using silver halide coated electrodes, it was necessary to understand how each step affected the final measured potential.

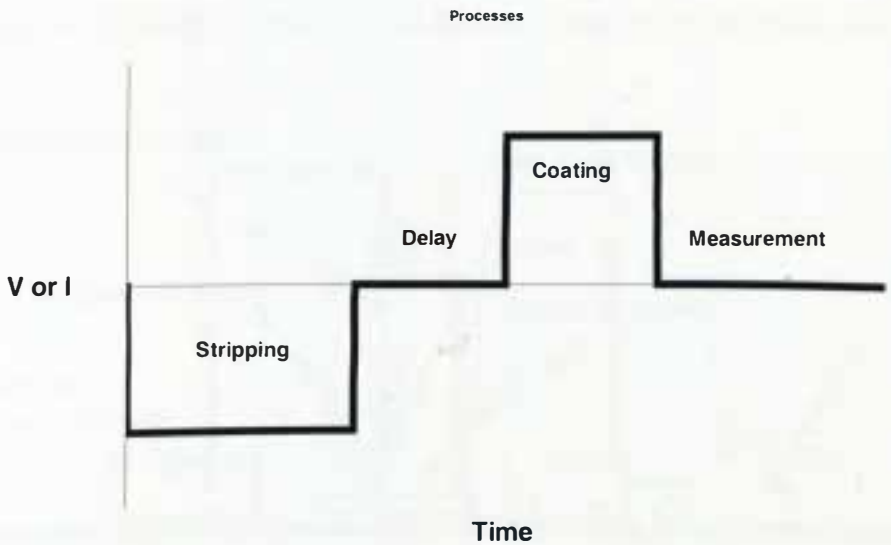


Figure 4.1 The full "clean/coat/measurement" cycle

Experiments were carried out to study both the reduction of the silver halide layer (stripping or cleaning process) and the oxidation of the silver surface to silver halide (coating process). Variations of pulse times, pulse potentials, delays and rotation speeds were carried out to investigate possible mechanisms. To minimise the number of experiments, initial investigations were carried out on a single concentration of potassium bromide using a silver bromide electrode. Final experiments investigated the effects of bromide concentration and the effect of iodide on the measurement technique.

The RDE was useful because it allowed good mass transport control. A silver rotating disc electrode had previously been reported to determine the diffusion coefficients of anions (Shimizu, 1981). Due to the need to both apply pulses to the electrode and measure the steady state potential a purpose built pulse potentiostat controller and potentiometer was designed and fabricated.

4.2 Equipment and instrumentation

The experimental set-up was similar to that used for the previous experiments in that an IBM 486 PC with Analogue Devices PC cards was used as a data logger, interfaced to the measurement cell via the pulse controller. The experiments were carried out at room temperature in a glass cell, purpose designed for the silver rotating disc electrode. Figure 4.2 and Plate 4.ϕ show the experiment set-up.

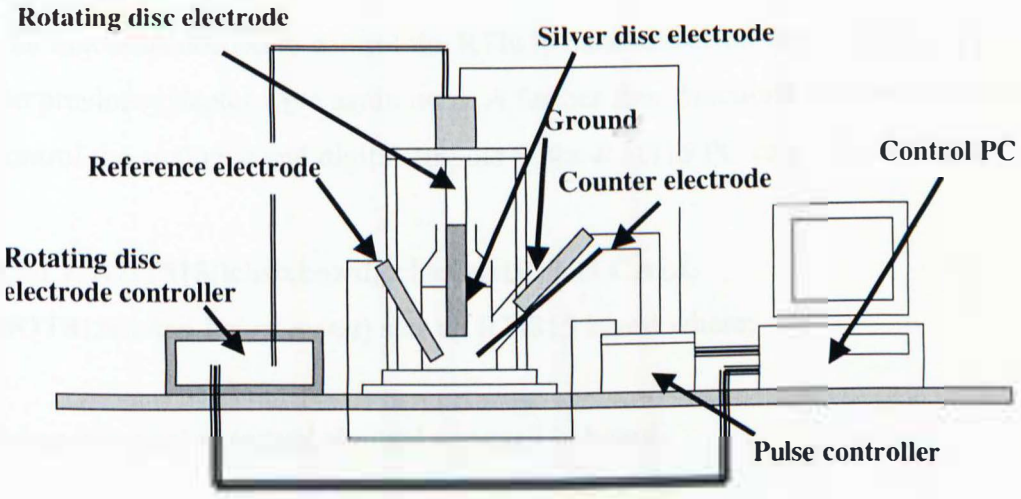


Fig. 4.2 Experimental set-up showing rotating disc electrode and control units

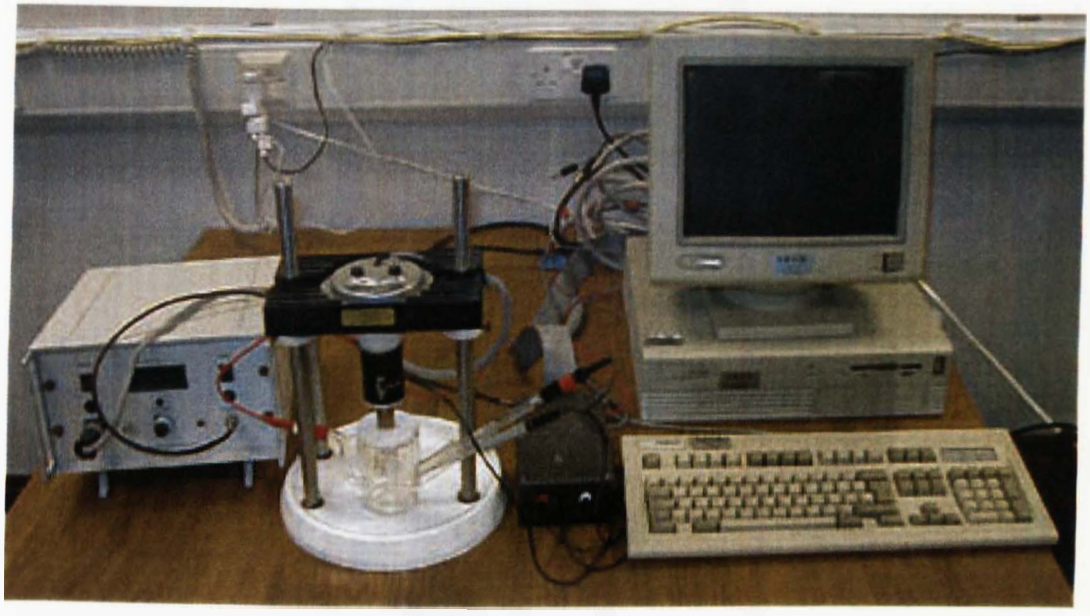


Plate 4.1 Photograph of experimental set-up

4.2.1 Analogue Devices RTI 800 series cards.

Two PC cards were used for all measurements and control, a high speed analogue 16-bit, eight channel analogue to digital card (RTI 850) and a combined analogue to digital card with two 12-bit digital to analogue channels and 16 input/output lines (RTI 815). The second card also had eight 12-bit analogue input channels but these were not used.

4.2.1.1 RTI800 software functions

The functions needed to control the RTI850 data collection card and described in the previous chapter were again used. A further four functions were necessary to control the analogue and digital outputs of the RTI815 PC card. These were:

CALL AOT815(lchan,board,pchan,erstat) and **CALL DOT815**(*lchan,board,erstat*) sets up RTI815 board where;

lchan = logical or virtual channel assigned to board,

board= RTI 850 assigned board number in case of more than one RTI850 board,

pchan = analogue channel (0 or 1),

erstat = variable that holds status or error code;

CALLAOT(*lchan,valueout,erstat*) outputs an analogue value;

CALL DOT815(*lchan,valueout,erstat*) outputs byte on the I/O port.

4.2.1.2. RTI 850 Card

As previously described (Chapter 3) except that here only four channels were used and at higher collection speeds.

4.2.1.3 RTI 815 Card

The Analogue Devices RTI815 is a multifunctional analogue/digital input/output PC card. This also fits the long expansion slots of a IBM or compatible PC .The board has two 12-bit digital to analogue converters capable of a +/- 10 V output, a sixteen channel digital input/output bus and an eight channel 12-bit analogue to digital converter. Only the analogue and digital outputs were used. A new RTI library of functions was created by linking the RTI850 and RTI815 libraries with the QuickBASIC library. This new library included functions to control both cards. Major errors occurred during this operation causing the library not to function correctly. This problem was caused by identical function names in the libraries of the Microsoft and Analog Devices software. A fix was obtained which renamed certain functions within the libraries allowing a workable combined library of functions to be used.

4.2.2 Pulse controller

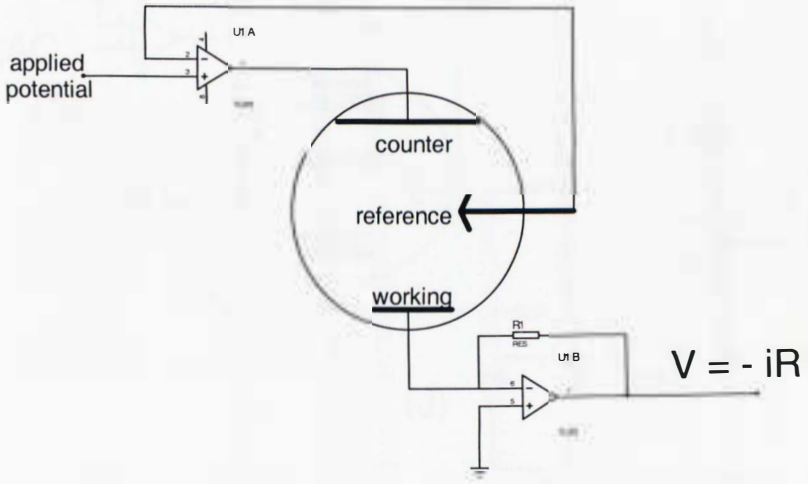


Fig 4.3 Simple potentiostat circuit

A simple potentiostat circuit (Figure 4.3), described in many electrochemical textbooks, (Greef, 1985), was used as the basis for the pulse controller (Figure 4.4) with the required potential output from the RTI815 PC card (A) being applied to the counter electrode via an operational amplifier (B) with inverted input connected to a feedback loop from the reference electrode. The current drawn by the silver electrode was measured with a second operational amplifier(C) with non-inverted input held at ground and the feedback from the output via the measurement resistor (D) connected to the inverted input. The current drawn was given by –V/R, where V is the output voltage from amplifier C and R is the feedback resistor D.

In addition two high impedance amplifiers (E & F) measured the potential of the reference and silver electrode versus a solution ground electrode connected to the instrument ground (0 volts) and a differential amplifier (G) then gave the potential difference of the cell. This differential amplifier had a fixed gain of ×10 which

giving +/- 10 volts output required by the RTI850 PC card from a cell potential of +/- 1000 mV.

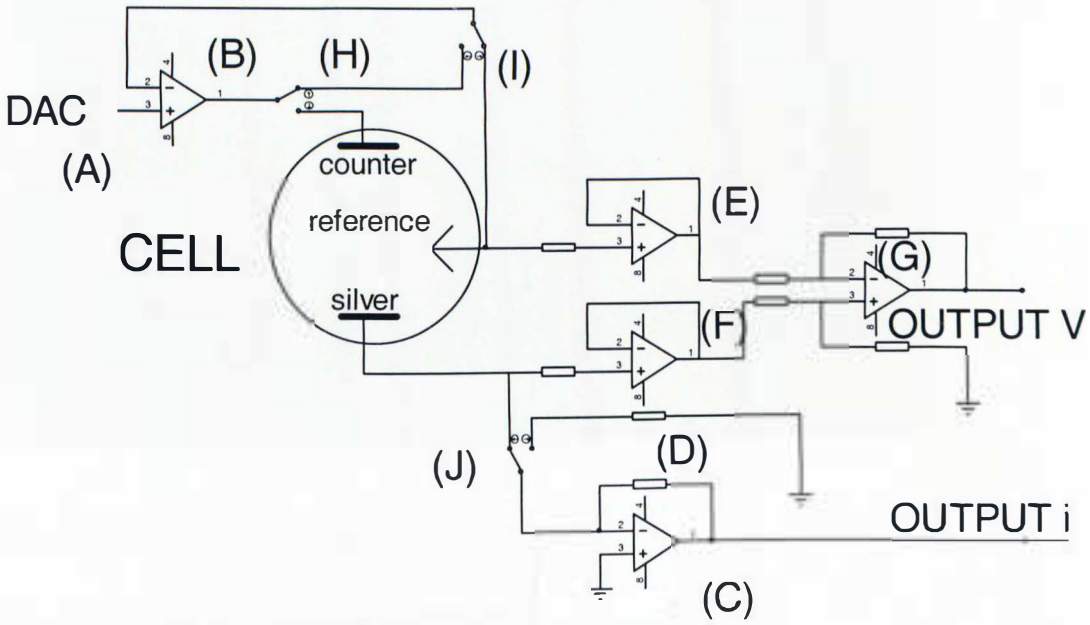


Figure 4.4 Pulse controller

Three fast acting relays (H, I & J), with minimum contact bounce, isolated the measurement circuit from the potentiostat circuit during the open circuit measurement cycle. These three relays were controlled from a single output line from the RTI815 PC card. To reduce noise to a minimum the circuit was fabricated as a printed circuit board and housed in a conductive plastic case. Leads going to and from the box were screened. Power was supplied from a low noise bench power supply. Plate 4.2 shows a photograph of the pulse controller.

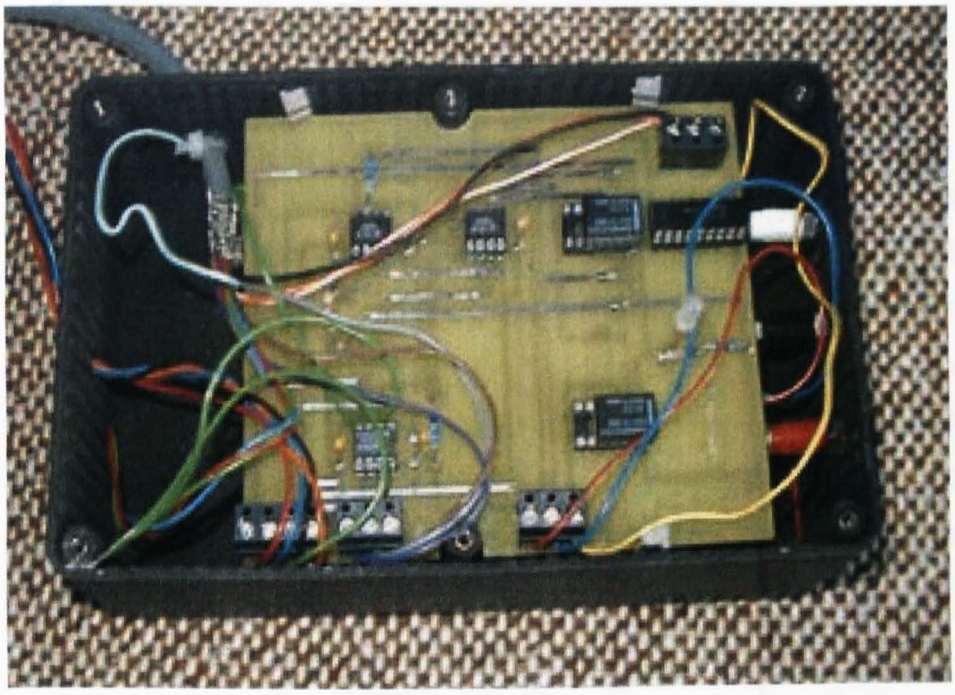


Plate 4.2 Pulse controller module.

4.2.3 Rotating disc electrode (RDE)

A rotating disc electrode was fabricated using a 6 mm 99.99% silver rod in an insulating PTFE sheath. The surface area of the exposed silver was 28.3 mm^2.

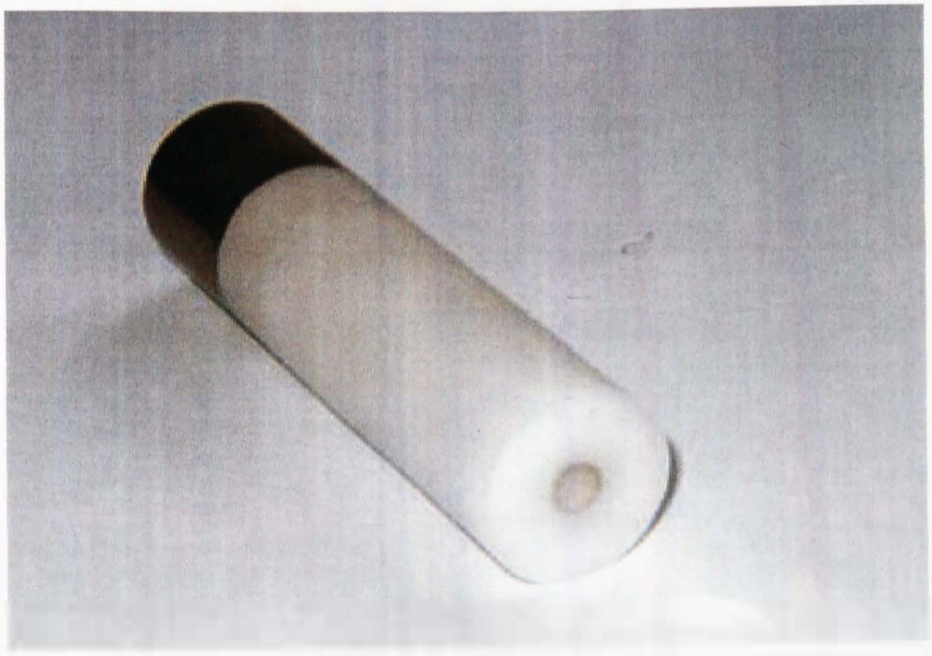


Plate 4.3 Rotating disc electrode

4.2.4 Measurement cell

4.2.4.1 Reference electrode

A special hydrogel reference electrode with potassium nitrate salt bridge solution incorporated into the hydrogel chamber was designed by the author (Edwards et al, 1990) and fabricated by Russell pH Ltd. (Figure 4.5). The need for a bridge junction system as described in Chapter 3 was not necessary because all the rotating disc electrode experiments were carried out at 25 °C. The electrode could be dipped directly into the 25 °C solution. The new reference electrode was more robust, more stable and needed less maintenance than a salt bridge system but due to the complex effect of the salt hydrogel, it was not possible to calculate the theoretical half-cell potential. It was also found that although the free flowing cotton wick junction of the triple junction system was generally unaffected by flow in the sample, on occasions the wick junction appeared to block and give large junctions potentials dependant on the stirring speed. The hydrogel electrode had an open hole junction with the hydrogel in direct contact with the sample solution. This junction appeared to be insensitive to flow conditions so was ideal for use in the rotating disc electrode cell.

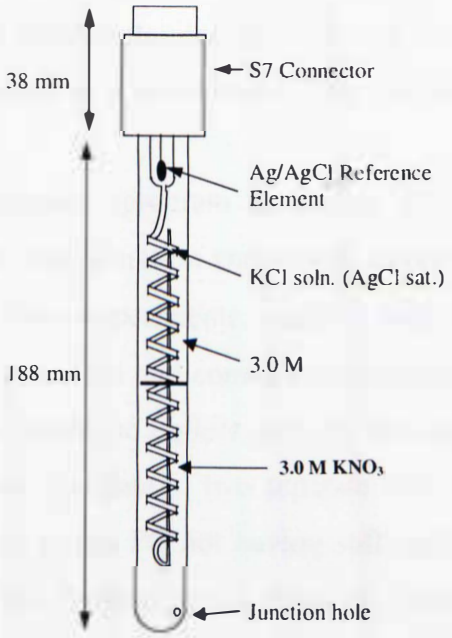


Figure 4.5 Hydrogel reference electrode with potassium nitrate fill solution.

4.2.5 Software

The software program was written in QuickBASIC V4.0 using functions from the compiled RTI 800 series library (program A, Figure 4.6). The RTI850 board was run at a sampling speed of 10 kHz, the fastest sampling rate possible. Although this board will function at a higher rate of 50 kHz, this required on board memory, which was not present on the particular boards used. Both output analogue channels of the RTI815 board were used, one for the potentiostat and one to control the speed of the rotating disc. One bit of the digital output was used to control the relays. Experiment details and control parameters were entered at the start of the program and saved with the data on each file. Control parameters were rotation speed, the delay before the stripping cycle started, the stripping pulse time and potential, the delay between pulses and the coating pulse time and potential. A timing diagram for the program is shown in Figure 4.7. Initially the analogue board was set-up to collect the measured potential and current output from the pulse controller module using two channels at a rate of 5000 points per channel per second. Later a third channel was added by using a second pulse module to measure a conventional silver halide electrode in the same solution. Output from the program at the end of each cycle was written to the hard disc in text format as a data file (XXX.dat). Each file contained one second of measured data formatted as 5000 lines of text each containing the time and the channel data. These files could be easily imported to a spreadsheet program such as Microsoft Excel for analysis.

A more complex program (program B, Figure 4.8) was developed for later experiments with the pulse duration and timing controlled separately and a delay time added. In these later experiments, where a large delay between pulses was used, two files were produced and combined for data analysis. The QuickBASIC control program was altered to collect data for the one second after the start of each pulse and to store the data in two separate files, which were combined for analysis. This was due to the PC not having sufficient RAM to store more than 10,000 data points. The rotation speed could be changed after the end of each pulse and the start of the delay to allow the electrode to reach the required speed before the start of the next pulse.

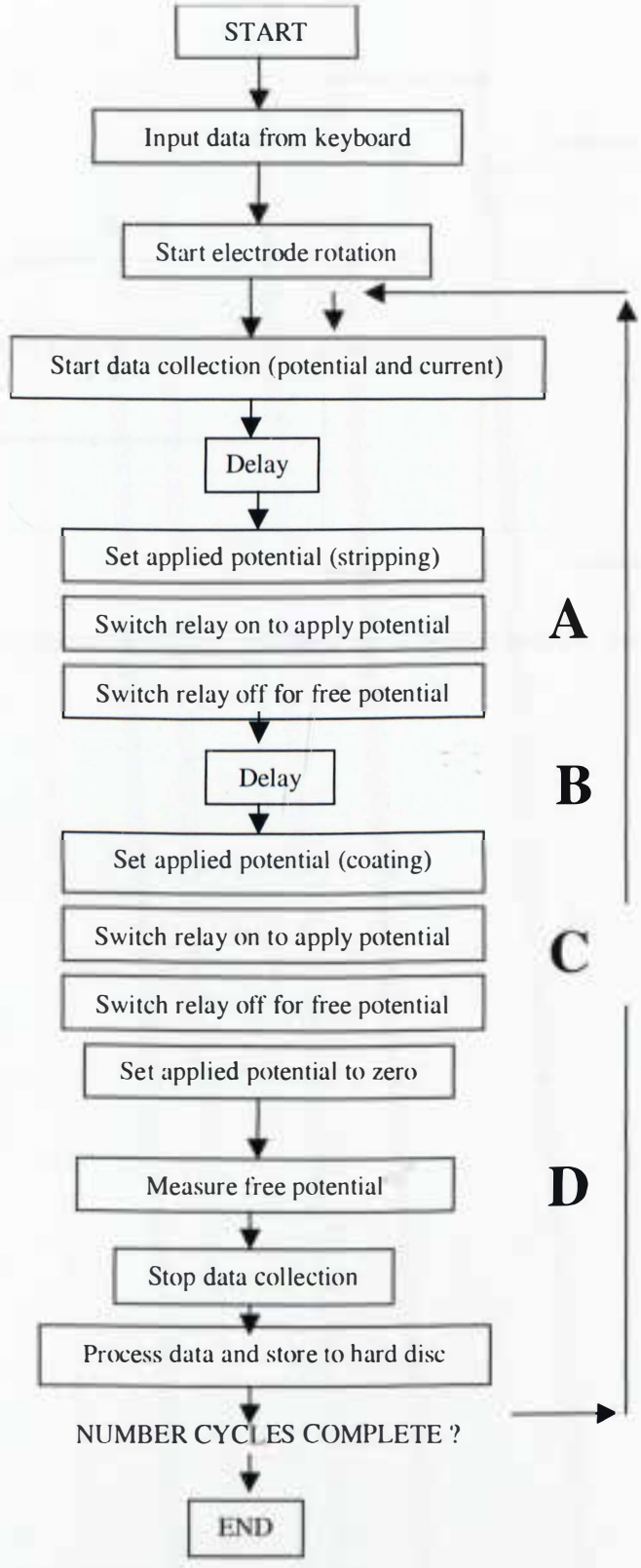


Figure 4.6 Software flow diagram of program A

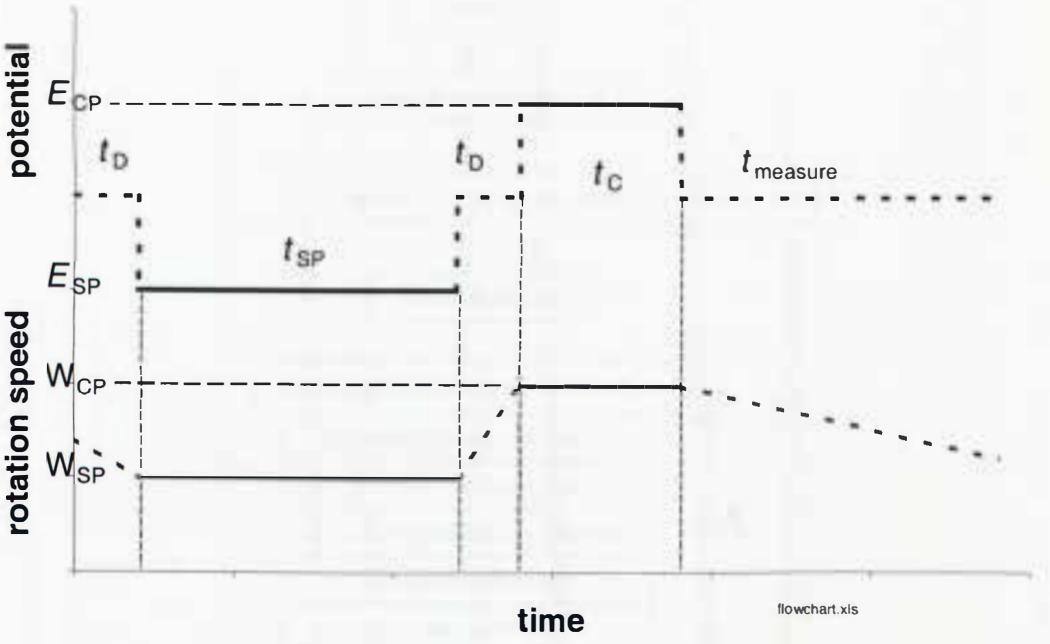


Figure 4.7 Timing diagram of complete cycle showing the applied potential and rotating speed.

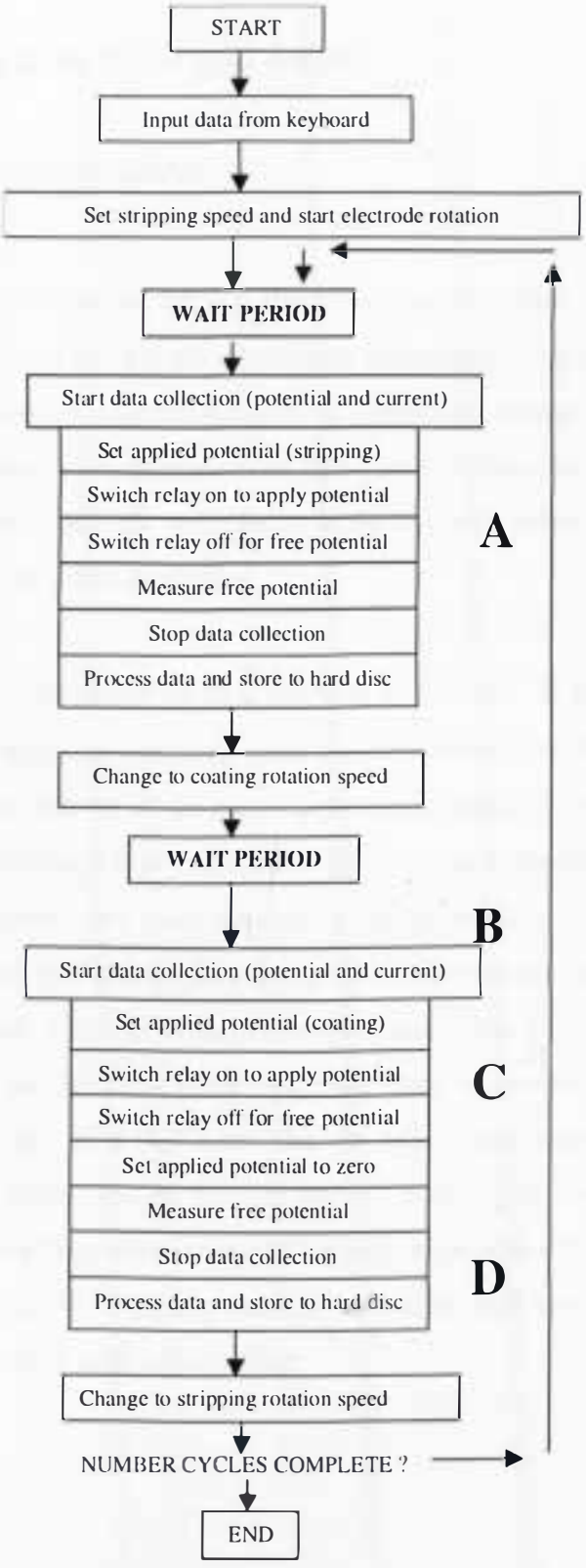


Figure 4.8 Software flow diagram of program B

4.3 Experimental methods and details

4.3.1 Experimental procedures

At the start of each experimental run the silver disc electrode was polished with diamond paste to clean off any silver sulphide tarnishing. The reference electrode was transferred from its storage solution of potassium nitrate and placed in the side arm of the glass measurement vessel along with a platinum counter electrode. The solution ground electrode was placed in the opposite side arm. All electrodes were connected to the pulse controller.

Experiments were carried out using a solution of 5×10^{-3} M potassium bromide with 5×10^{-2} M potassium nitrate to raise the ionic strength to the level necessary to carry the current. 100 ml of the test solution was placed in the glass vessel and the rotating disc electrode lowered so that 10 mm was immersed in the solution. The rotating disc power unit was switched on (at this point no rotation occurred as the analogue control line was held a zero by the pulse controller program).
The control program was started and the experiment name and control parameters keyed in. At the end of each pulse cycle the data in memory was transferred automatically to disc as a XXX.dat file. In most experiments the data files contained 10,000 points for each cycle and as many cycles were performed, a large number of data files were produced for each experiment. Data files collected were copied from the PC to backup discs at the end of each day for security and to keep the PC disc free of unnecessary files.

4.3.2 Materials

Test solutions were prepared using analytical grade potassium bromide (Fisher Scientific P/400/53), analytical grade potassium iodide (Fisher Scientific P/5840/53) and analytical grade potassium nitrate (Fisher Scientific P/6120/53) in

water prepared using a reverse osmosis unit with ion exchange polishing (Elgastat, Elga).

The rotating disc silver electrode was polished using 15, 5 and 1 μm abrasive paper and 1.0 μm polishing paste (Buehler or Metadi diamond compound).

4.3.3 Experimental details

4.3.3.1 CV of potassium bromide and potassium iodide solutions

Initial experiments were carried out to investigate the applied potential required to oxidise the silver metal electrode to silver bromide and to reduce the silver bromide coating back to silver metal. A cyclic voltamogram was run using an ECO Chemie Autolab 10 using the RDE in the experimental set-up described in section 4.2 with a 5×10^{-3} molar solution of potassium bromide in 5×10^{-2} molar potassium nitrate. A second voltamogram was run using 5×10^{-3} molar solution of potassium bromide and 5×10^{-3} molar solution of potassium iodide in 5×10^{-2} molar potassium nitrate.

4.3.3.2 Initial investigation using the rotating disc electrode (RDE)

Initial experiments were carried out to test the system and to determine a standard test solution and experimental conditions to use through the study. A potassium bromide concentration of 0.005 M was chosen for several reasons. Firstly, this is in the mid range of concentrations used in the photographic emulsion process, being about ten times more concentrated than the lowest used concentration. Secondly, results of the open circuit potential measurement of this concentration gave good reliable results when using conventional coated electrodes. Thirdly, preliminary results using this technique showed that this concentration gave clear, measurable current curves well above the noise level of the system.

Using this test solution an initial set of experiments was carried to study whether and to what extent the speed of the RDE affected the technique. The RDE speed was kept constant throughout the whole of each 5 min run. All of the processes

(strip, coat and measure) were carried out at the same rotation speed. Seven experiments were carried out with identical conditions but with the speed of the rotating disc ranging from 0 to 36 Hz (Exp. set Feb28e51-57).

The stripping pulse was set at an applied potential of –400 mV for 200 ms followed by a coating pulse of +400 mV for 100 ms with no delay and no disconnection of the circuit between these pulses. The stripping pulse time was set at twice the coating pulse time to ensure all of the silver bromide converted on the electrode had been removed. Other conditions are shown in Table 4.1

Parameter	**Symbol**	**Feb28e51-57**
Stripping pulse duration /ms	t_{SP}	200
Stripping pulse potential /mV	E_{SP}	-400
Stripping pulse rotation speed /Hz	W_{SP}	0 – 36
Coating pulse duration /ms	t_{CP}	100
Coating pulse potential /mV	E_{CP}	+400
Coating pulse rotation speed /Hz	$= W_{CP}$	$=_t W_{SP}$
Delay between stripping and coating pulses /ms	t_D	0

Table 4.1 Conditions used in experiment to investigate electrode rotation speed

4.3.3.3 Investigation of the stripping pulse current

To study the stripping pulse it was first necessary to determine whether the stripping current was directly proportional to the amount of silver bromide converted from silver metal in the coating process. To investigate the relationship between the amount of silver bromide produced by the coating pulse and the current drawn during the stripping pulse when the silver bromide was converted back to silver metal, a set of experiments (Exp. set Ma20e1-7) was carried out. The coating pulse time and hence the amount of silver converted to silver bromide was varied but all other conditions were unchanged. The rotation speed was kept constant at 9 Hz. Seven experiments were performed, the first with a zero coating time and the others varying from 2 to 60 ms.

A further set of experiments (Ma20e8-12) was carried out to determine if the efficiency or proportion of charge drawn during the stripping process was affected by the applied potential used during the stripping pulse. The amount of silver converted to silver halide was kept constant by keeping coating conditions constant. Potentials of -100, -200, -400, -500, -600 and -700 mV were applied to the RDE during the stripping pulse.

To study the processes that were occurring at the electrode surface during the stripping pulse, the flow over the surface of the electrode was changed by varying the rotation speed of the RDE. To study the effects of the rotation speed on the stripping current it was necessary to place a delay between the stripping and coating pulses so that the rotation speed of the electrode could be changed during the cycle (My22e1-7). This allowed coating speeds and coating conditions to be kept constant while varying rotation speeds during the stripping pulse. A new QuickBASIC program, Program B (section 5.2) was written which used a 2 s wait period. An initial group of experiments was run with a constant RDE speed of 10 Hz during the coating pulse and with RDE speeds from 0 to 36 Hz during the stripping pulse. The 2 s wait period between the pulses was used to allow the RDE to change to the new speed and for the solution flow to come to equilibrium. Data was collected from the start of the stripping pulse for 1 s and then stored. After the 2 s delay the data collection was restarted for a further 1 s and the coating pulse initiated. This data was stored and the cycle started after a further 2 s delay. The complete strip/coat/measure cycle was therefore 6 s in duration with a 2800 ms delay between the stripping and the coating pulses. The experiment was repeated using a 20 Hz speed during the coating pulse. During the delay the applied potential was disconnected. A repeat of this experiment was carried out using a 5 s wait period and RDE rotation speeds of 1, 9 and 36 Hz during the coating pulse (Jun20e1-21).

Experimental conditions for the stripping pulse investigation are shown in Table 4.2

	Effect on stripping pulse of variation in silver bromide coated during pulse	**Effect on stripping pulse of variation in stripping applied potential**	**Effect on stripping pulse of variation in stripping pulse RDE speed with 2800 ms delay**	**Effect on stripping pulse of variation in stripping pulse RDE speed with 5800 ms delay**
t_{SP}/ms	200	200	200	200
E_{SP}/mV	- 400	-100, -200, -400, -500, -600, -700	- 400	- 400
W_{SP} /Hz	9	9	0,1,4,9,16,25,36	0,1,4,9,16,25,36
t_{CP}/ms	0,02,05, 10,020,040,060	20	100	100
E_{CP}/mV	+ 400	+ 400	+ 400	+0400
W_{CP}/Hz	9	9	10,020	1, 16, 36
t_{DC}/ms	0	0	2800	5800
Exp set no.	Ma20e1-7	Ma20e8-12	My22e1-7	Jun20e1-21

Table 4.2 Stripping pulse experimental details

4.3.3.4 Investigation of the coating pulse

To investigate the effect of a delay on the coating pulse current a series of experiments were conducted where the delay between the pulses was varied between 10 ms and 5800 ms and the coating and stripping RDE speeds kept constant at 1 Hz (Jun25e1-21). A minimum of 10 ms was necessary to allow the applied potential to be disconnected and reconnected. This series of experiments was repeated at 9 and 36 Hz RDE rotation speed.

To study the affect of both the RDE rotation speed and the applied coating pulse potential on the coating pulse profile a series of experiment were run with coating pulse potentials varying from 0 to +800 mV at three different RDE rotation speeds with a 10 ms delay between the pulses (Jul3e1-27). This set of experiments was repeated with a 420 ms delay between the pulses (Jul18e1-16).

To investigate the affect of both the coating pulse applied potential and the coating pulse duration on the coating current profile a series of experiments were performed using 12 different coating pulse durations and two coating pulse applied potentials (Jul28e15-27).

Finally, the effect of continuously running the technique was investigated by completing 15000 cycles in a four hour period and recording current/potential for cycle number 10 and 15000 (Jul28e28).

	Effect on coating pulse of adding a delay between coating and stripping pulses	**Effect on coating pulse of delay time between pulses**	**Effect on coating pulse of variation of coating applied potential with 10 and 420 ms delay**	**Effect on coating pulse of duration of coating pulse with +400 and +800 mV applied potential**	**Effect on coating pulse of number of cycles completed**
t_{SP} /ms	200	200	200	200	200
E_{SP} /mV	- 400	- 400	- 400	-400	-400
W_{SP} /Hz	0,1,4,9,16,25,36	1, 9, 36	1, 9, 36	9	9
t_{CP} /ms	100	100	100	5, 10, 15, 20, 30, 40, 50, 60, 70, 80 , 90, 100	100
E_{CP} /mV	+400	+ 400	+0, 200, 400, 600, 800	+400, +800	+400
W_{CP} /Hz	1,16,36	= W_{SP}	= W_{SP}	9	9
t_D /ms	5000	10, 100, 420, 800, 1800, 2800, 5800	10, 420	300	300
Exp set no.	Jun20e1-21	Jun25e1-21	Jul3e1-27, Jul18e1-16	Jul28e1-14	Jul28e28

Table 4.3 Coating pulse experimental details

4.3.3.5 Investigations of the stripping and coating current while varying the bromide concentration

To determine how the concentration of bromide ion affected the stripping and coating steps, five concentrations of potassium bromide were used with all conditions kept constant. (Table 4.4)

Parameter	**Symbol**	**Aug9e1-5**
[Br^-] /M	c_{Br^-}	5×10^{-4} – 1.3×10^{-2}
Stripping pulse duration /ms	t_{SP}	200
Stripping pulse potential /mV	E_{SP}	-400
Stripping pulse rotation speed /Hz	W_{SP}	9
Coating pulse duration /ms	t_{CP}	100
Coating pulse potential /mV	E_{CP}	+400
Coating pulse rotation speed /Hz	W_{CP}	9
Delay between stripping and coating pulses /ms	t_D	250

Table 4.4 Conditions used to study the variation of bromide concentration on stripping and coating current curves.

4.3.3.6 Investigations of the open circuit equilibrium potential.

The main purpose of this analytical technique was to measure the open circuit potential of the silver electrode after coating with the halide salt. To determine the optimum settings for the technique, experiments were carried out to investigate the effect of stripping potential, delay time between stripping and coating pulses, coating pulse potential and coating pulse duration on the measured open circuit potential. The effect of rotation speed was also investigated to determine the possible effect of stirring speed when the technique was used in a production system. Experimental conditions are shown in Table 4.5.

	Effect on open circuit potential of variation in RDE speed	Effect on open circuit potential of variation of stripping applied potential	Effect on open circuit potential of variation of coating pulse applied potential with 10 ms delay	Effect on open circuit potential of variation of coating pulse applied potential with 420 ms delay	Effect on open circuit potential of variation of coating pulse duration with E_{CP} = +400 mV	Effect on open circuit potential of variation of coating pulse duration with E_{CP} = +800 mV
t_{SP} /ms	200	200	200	200	200	200
E_{SP} mV	-400	-200 to -700	-400	-400	-400	-400
W_{SP} /Hz	0 – 36	9	1, 9, 36	1, 9, 36	9	9
t_{CP} /ms	100	20	100	100	5 - 100	5 - 100
E_{CP} /mV	+400	+ 400	+0, 200, 400, 600, 800	+0, 200, 400, 600, 800	+400	+800
W_{CP} /Hz	0 – 36	9	1,9,36	1,9,36	9	9
t_D /ms	0	0	10	420	300	300
Exp set no.	Feb28e51-57	Ma20e8-12	Jul3e1-21	Jul18e1-16	Jul28e1-14	Jul28e15-27

Table 4.5 The effect of rotation speed (W_{SP}), stripping potential (E_{SP}), delay time (t_D), coating potential (E_{CP}) and coating pulse duration (t_{CP}) on open circuit equilibrium potential measurement.

4.3.3.7 Investigation on varying bromide concentration

Experiments were carried out to study the effect of changing the bromide concentration on the difference between the measured potential and the theoretical potential from Chapter 3 and the time taken to reach a steady potential after the coating pulse. The first was carried out by the addition of varying amounts of a concentrated bromide solution (0.1 M KBr) to an 80 ml sample of a weak bromide solution (0.0005 M KBr) to determine the effect of changing the bromide concentration during the experiment. In this case the current and potential cycle was recorded two minutes after each addition to study the time taken for the open circuit potential to reach a steady potential after the coating pulse had ended.

The second set of experiments used the technique to measure the open circuit potential of seven separate solutions of varying bromide concentration. Each solution was prepared with the bromide concentration shown in Table 4.6 and with a 0.05 M potassium nitrate concentration. A new modified program was written with the cycle repeated every 5 s instead of 1 s and the open circuit potential measured at 0.5, 1, 2, 3, and 4 s. The experiment was carried out for five minutes with each cycle being recorded.

Parameter	Aug12e1-21	Aug9e1-5	Sep27e3red
t_{SP} /ms	200	200	200
E_{SP} mV	-400	-400	-400
W_{SP} /Hz	9	9	9
t_{CP} /ms	100	100	100
E_{CP} /mV	+400	+400	+400
W_{CP} /Hz	9	9	9
$t_{D}d$ms	250	250	250
[Br^-] /M	Continuous by addition	Samples	Continuous by addition
	0.0005	0.0005, 0.001	0.0005
	0.001	0.002, 0.005	0.00125
	0.0033	0.01, 0.02	0.0036
	0.013	0.05	0.015

Table 4.6 Experimental conditions to determine the effect of bromide concentrations on open circuit potential

The third experiment was similar to the first in that a concentrated bromide solution was added to a weak bromide sample. However, in this experiment only the open circuit potential was recorded at 0.5, 1, 2, 3, and 4 s after the start of the cycle and not the current and potential over the full cycle. These values were recorded for all cycles throughout the time of the experiment.

4.3.3.8 Investigations with mixed bromide and iodide halide ion present

Two experiments were carried out to study the effect of adding potassium iodide to a potassium bromide solution. As with the previous experiment only the open circuit potential was recorded at 0.5, 1, 2, 3 and 4 s after the start of the cycle. These values were recorded for all cycles throughout the time of the experiment.

Parameter	Sep27e4red	Oct3e1
t_{SP} /ms	200	200
E_{SP} mV	-400	-400
W_{SP} /Hz	9	9
t_{CP} /ms	100	100
E_{CP} /mV	+400	+400
W_{CP} /Hz	9	9
t_{D} /ms	250	250
$[Br^-]$ /M		
Step 1 (only bromide present)	0.0005	0.005
Step 2 (with bromide addition)	0.001	No add. 2
$[I^-]_d$/M		
Step 3 (with iodide addition)	0.0006	0.005

Table 4.7 Effect of addition of iodide to bromide solution on open circuit potential

4.4 Results and Discussion

4.4.1 Cyclic voltammetry of potassium bromide and potassium iodide solutions

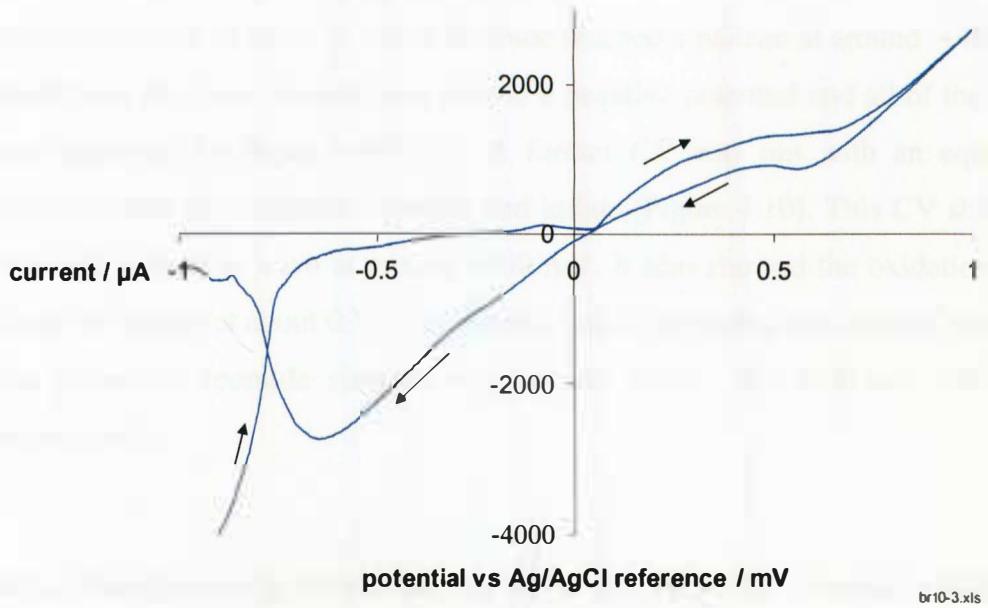


Figure 4.9 Cyclic voltammogram showing the formation of silver bromide at the rotating silver disc electrode with subsequent stripping at negative applied potentials. [KBr]/M=0.005; [KNO_3]/M=0.05.

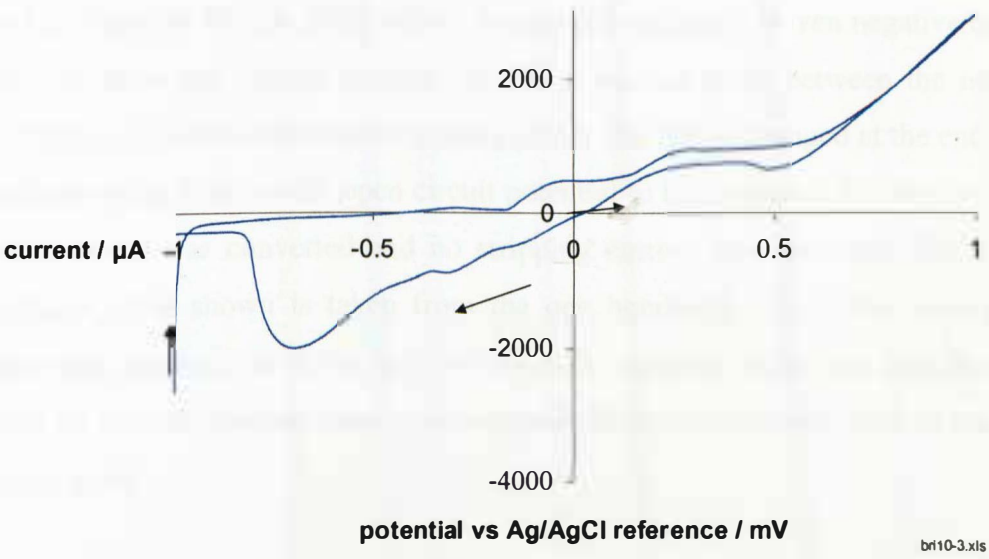


Figure 4.10 Cyclic voltammogram showing the formation of both silver bromide and silver iodide at the rotating silver disc electrode with subsequent stripping of the halides during reverse scan. [KI]/M=0.005; [KBr]/M=0.005; [KNO_3]/M=0.05.

A cyclic voltamogram was run using an ECO Chemie Autolab 10 and the silver rotating disc electrode in the experimental set-up described in section 4.2 with a 5 $\times 10^{-3}$ molar solution of potassium bromide in 5 $\times 10^{-2}$ molar potassium nitrate. The current-voltage curve is shown in Figure 4.10. It can be seen that the oxidation of silver metal to silver bromide reached a plateau at around +400 mV. Reduction of silver bromide was seen at a negative potential and all of the halide was removed by about –600 mV. A further CV was run with an equimolar concentration of potassium bromide and iodide (Figure 4.10). This CV showed a bromide reduction wave at around –300 mV. It also showed the oxidation wave for silver iodide at about 0 V. The potential of the stripping and coating pulses for the potassium bromide samples was initially set at –400 mV and +400 mV, respectively.

4.4.2 Initial investigation using the silver rotating disc electrode (RDE)

The full current and voltage curve of one cycle from an experiment from the initial investigation of the system using a mid-range potassium bromide concentration diluted in the lowest potassium nitrate solution is shown (Figure 4.11). Note the 100 ms delay before the applied voltage is driven negative to –400 mV to allow the system to stabilise. There was no delay between the negative stripping pulse and the positive coating pulse. The relays changed at the end of the coating pulse to allow the open circuit potential to be measured. On the first cycle no bromide was converted and no stripping current was observed. The current voltage curve shown is taken from the one hundredth cycle. The open circuit potential measured at the point just before the stripping pulse was approximately 700 ms after the coating pulse was switched off and initially was used as the VAG value point.

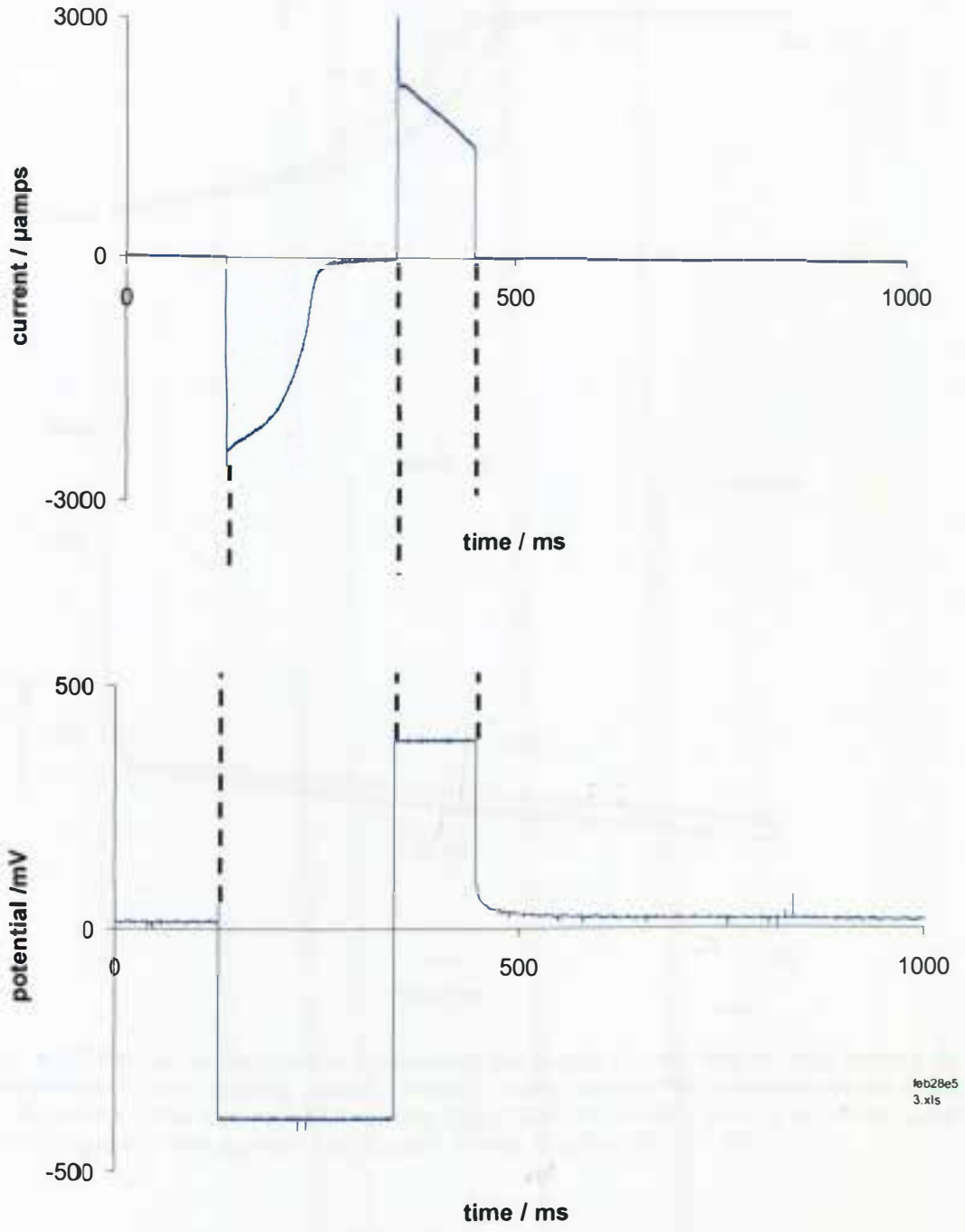


Figure 4.11 Full current (top) and voltage cycle (bottom) – (hundredth cycle in a series of cycles). [KBr] /M = 0.005; [KNO_3] /M = 0.005; t_{SP} /ms = 200; E_{SP}/mV = -400; t_{CP}/ms = 100; E_{CP} /mV = +400; W_{SP}, W_{CP} /Hz = 4.

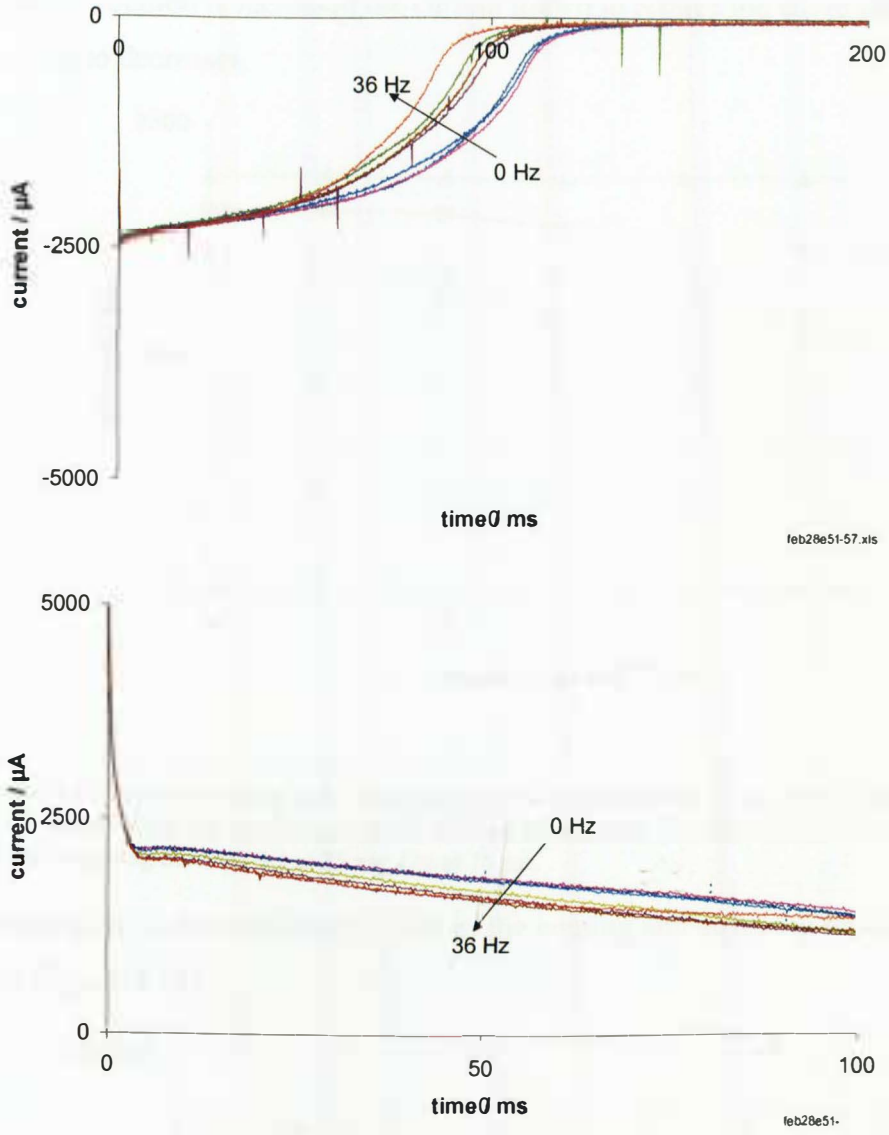


Fig. 4.12 Effect of rotation speed on the stripping and coating currents with no delay between the two processes. (Top) Stripping currents. (Bottom) Coating currents. The arrows indicate the trends as the rotation speed were varied between the limits. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; W_{SP},W_{CP} /Hz = 0…36.

Figure 4.12 shows the sections of the current curves for the stripping and coating pulse cycles for all silver electrode rotation speeds. Values for the coating current 25 and 75 ms after the start of the pulses were measured. Fig 4.13 shows a plot of current taken 25 and 75 ms after the start of the pulses against the square root of the rotation speed. The current is seen to decrease slightly as the speed of rotation increases. This implies that as the speed increases less silver bromide is formed on the silver metal surface. Analysis of the stripping curves indicates that as the

speed of rotation is increased the current drawn to reduce the silver halide to silver metal also decreases.

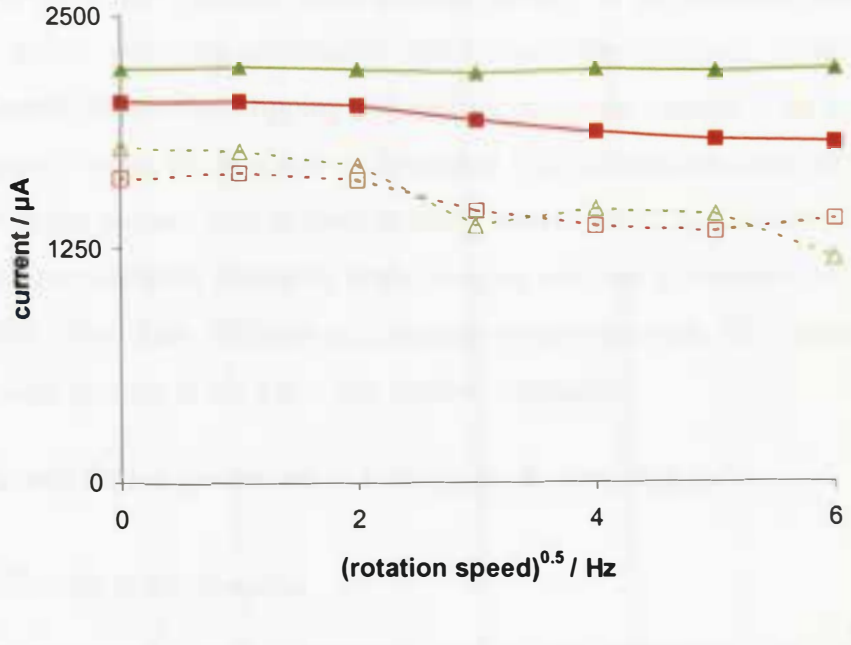


Figure 4.13 Plot of stripping and coating pulse current measured at 25 ms and 75 ms after the start of the pulse versus the square root of the RDE rotation speed. Coating current (■) at 25 ms; (□) at 75 ms; Stripping current (▲) at 25 ms; (△) at 75 ms.

Calculation of the total charge used in the coating and stripping process confirms this (Figure 4.14).

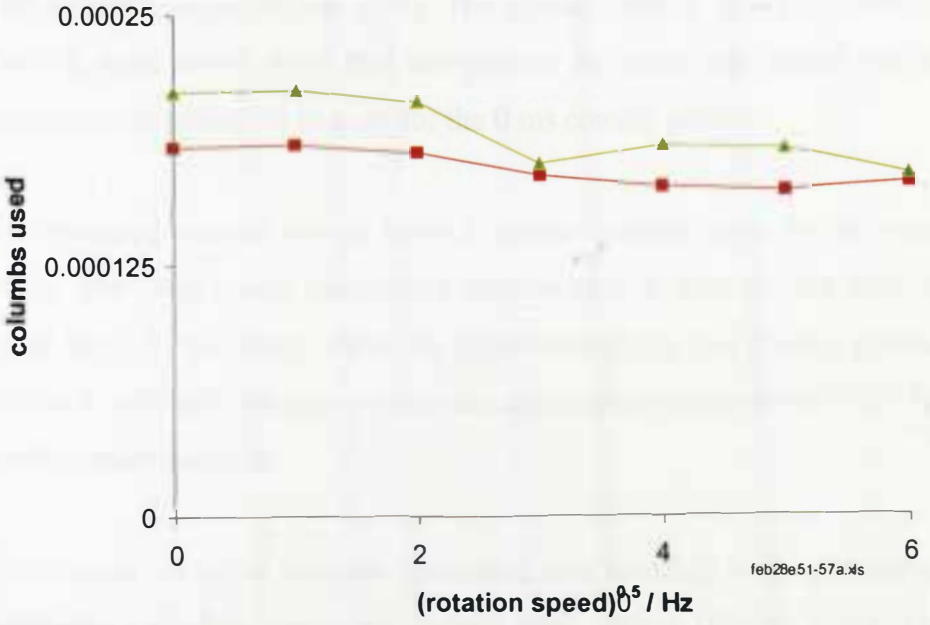


Figure 4.14 Plot of charge calculated from stripping (▲) and coating (■) curves at varying rotation speeds.

From the initial experimental data it can be seen that increasing the speed of rotation of the RDE does not increase the current of the stripping or coating pulse as would have been expected if the reaction process at the electrode surface were limited by the diffusion of bromide ions towards the electrode. In the first few milliseconds of both the stripping and coating pulses the current is the same for all RDE speeds. After the first few milliseconds a slight but consistent decrease can be seen in the current with respect to RDE speeds. From this initial study it was clear that the electrode processes were complex and that the currents were limited by factors other than diffusion of bromide to the electrode. To investigate this further each process of the cycle was studied separately.

4.4.3 Results from experiments to investigate the stripping pulse

4.4.3.1 Coating pulse duration

The first experiment in this series was designed to determine how the stripping current was affected by the amount of silver bromide converted from silver metal and deposited onto the electrode surface during the coating pulse. The coating pulse time was varied from 0 ms to 60 ms while all other conditions were kept constant. The results from experimental set Ma20e1-7 were plotted for the coating and stripping steps (Figure 4.15). The plotted coating current curves for various coating pulse times show that the process for each experiment was similar. A slight current pulse can be seen for the 0 ms coating pulse.

The stripping current curves show a similar shaped curve for all coating pulse times. The point where the current reaches zero is seen to vary with the coating pulse time. In this case, where the applied stripping and coating potentials are –400 and +400 mV the time to strip the electrode is approximately the same as the coating pulse duration.

The amount of silver bromide converted was assumed to be proportional to the coulombs calculated from the current-time curves (Figure 4.16). Figure 4.16 shows the relationship between the coating pulse time and the calculated coulombs.

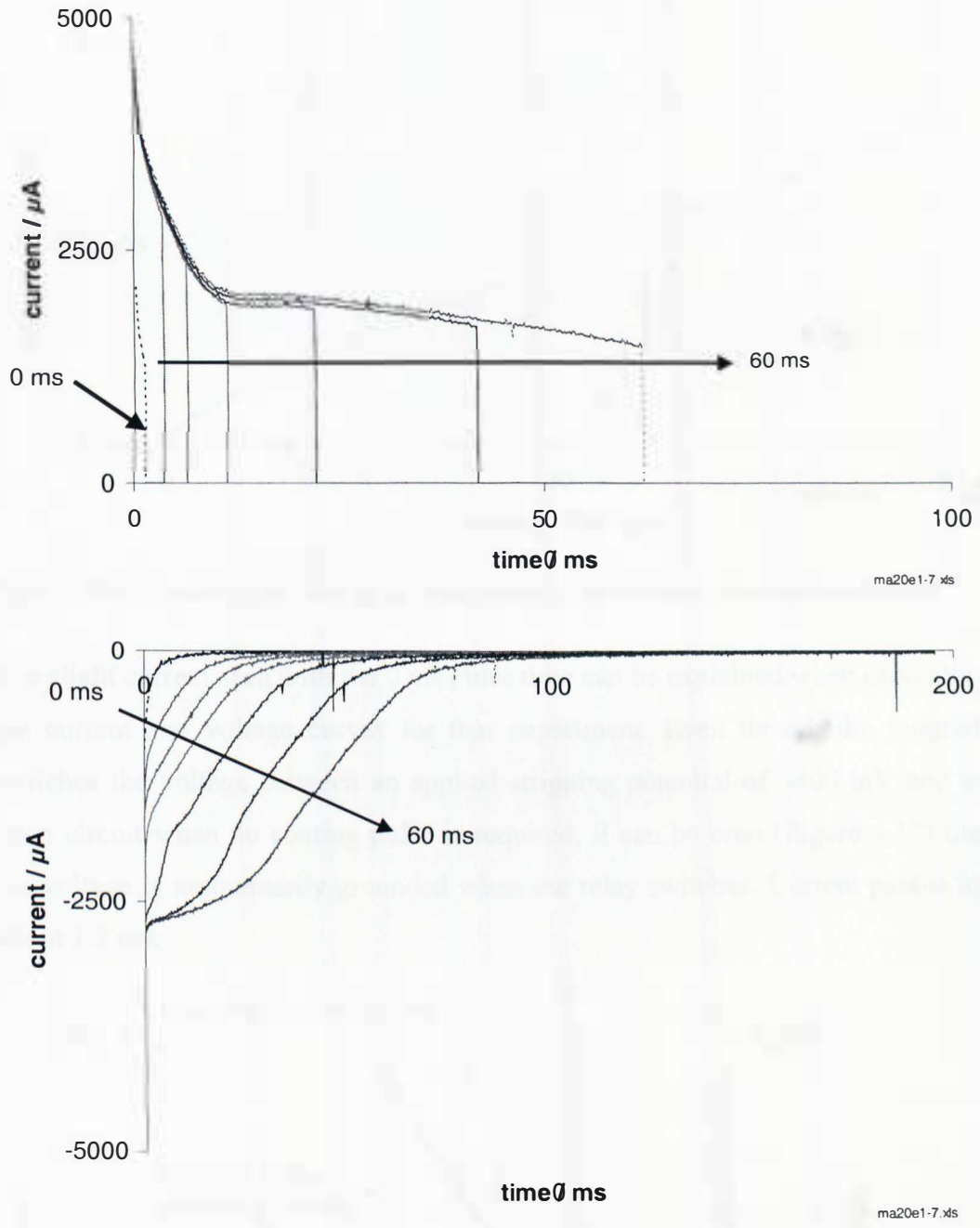


Fig 4.15 Effect of varying the coating pulse time and hence the amount of silver bromide converted on the stripping pulse currents. (Top) Coating currents. (Bottom) Stripping currents. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 0...60; E_{CP} /mV = +400; $W_{SP} = W_{CP}$ /Hz = 9.

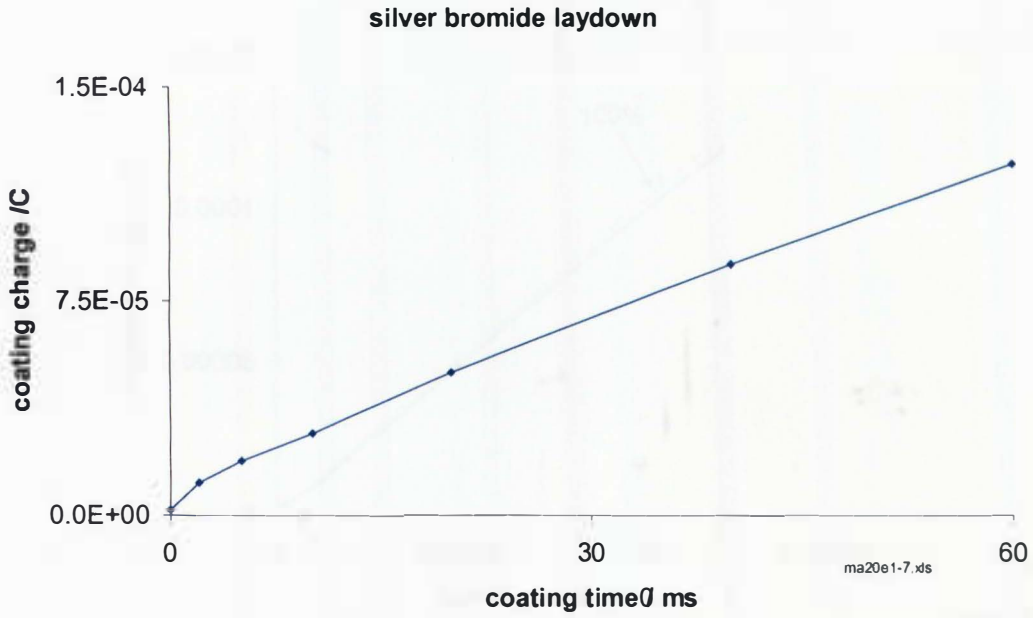


Fig 4.16 Plot of coating pulse time against total charge consumed during the oxidation process

The slight current seen with the 0 ms pulse time can be explained when expanding the current and voltage curves for that experiment. Even though the program switches the voltage between an applied stripping potential of –400 mV and an open circuit when no coating pulse is required, it can be seen (Figure 4.17) that the voltage is momentarily grounded when the relay switches. Current passes for about 1.2 ms.

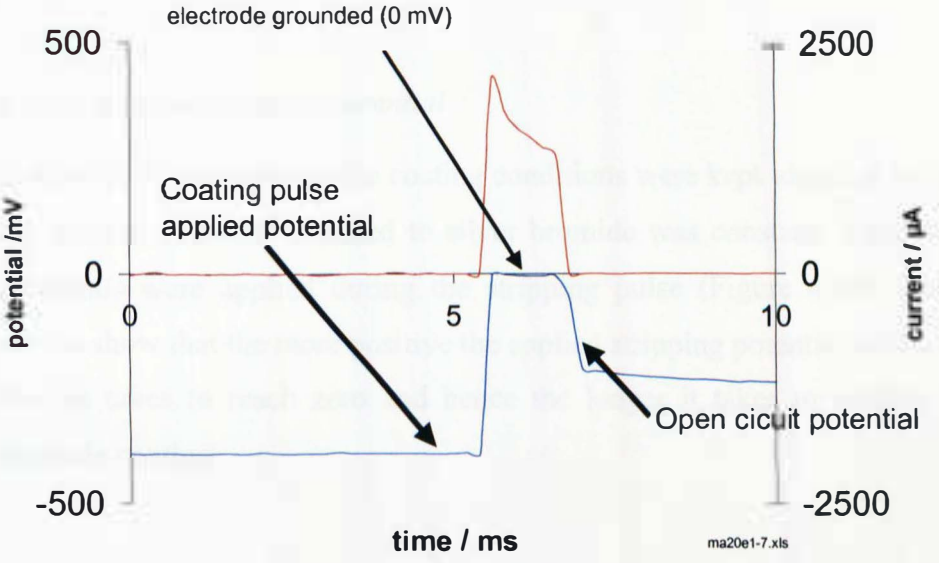


Figure 4.17 Expanded current (—) and voltage (—) curves showing the CCM silver electrode at ground potential for a few milliseconds after the coating pulse potential has been switched off.

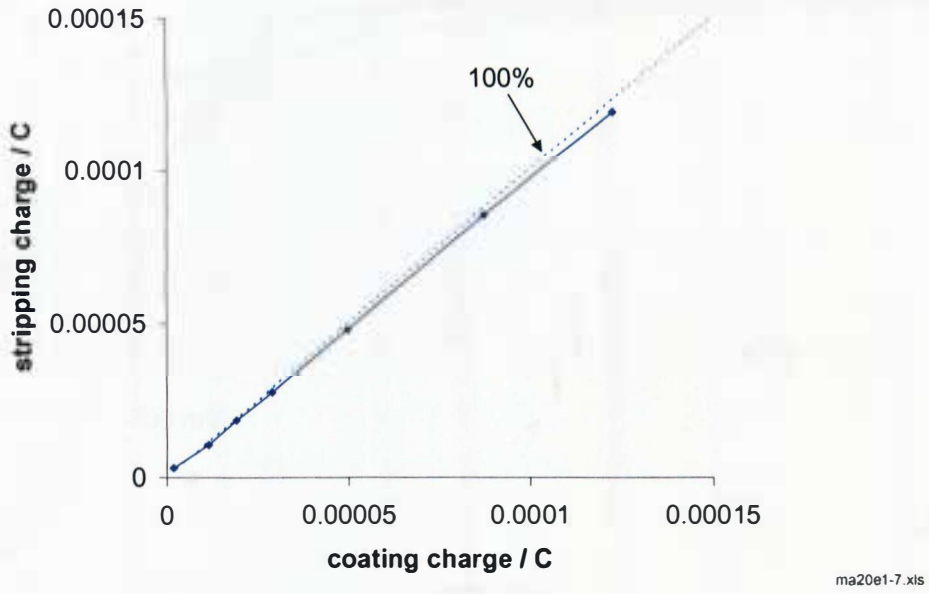


Figure 4.18 Value of the charge passed for the coating pulse compared against the stripping pulses (original data shown in Figure 4.15).

The value of the charge passed at all coating pulse durations was approximately the same for the coating and stripping processes (Figure 4.18). The slight difference can be attributed to either the plating process is inefficient – some of the charge is used for processes other than the bromide coating process, or some of the solid silver bromide is lost into solution before the stripping process takes place.

4.4.3.2 Applied stripping potential

In this set of experiments the coating conditions were kept identical to ensure that the amount of silver oxidised to silver bromide was constant. Various stripping potentials were applied during the stripping pulse (Figure 4.19). The currents curves show that the more positive the applied stripping potential is, the longer the current takes to reach zero and hence the longer it takes to remove the silver bromide coating.

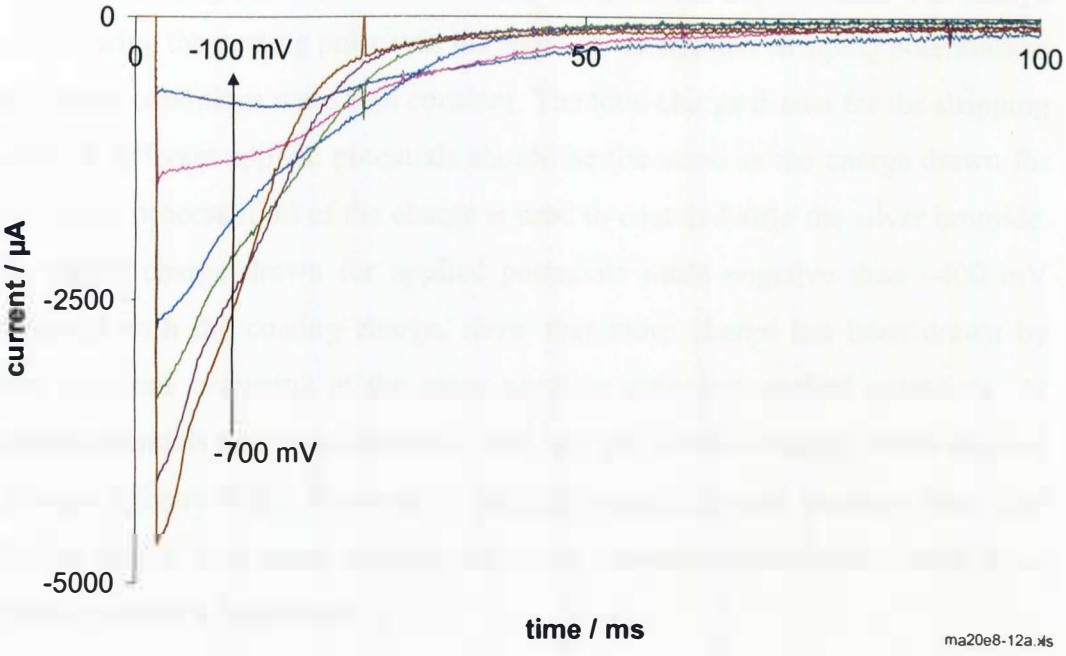


Fig 4.19 Effect of varying the stripping potential while keeping constant the amount of silver bromide converted during the coating process constant. The arrow indicates the trend as the applied stripping potential is reduced. . [KBr] /M = 0.005; [KNO_3] /M = 0.05;t_{SP} /mse= 200; E_{SP} /mV = -100…-700; t_{CP} /ms = 20; E_{CP} /mV = +400; W_{SP},W_{CP} /Hz = 9.

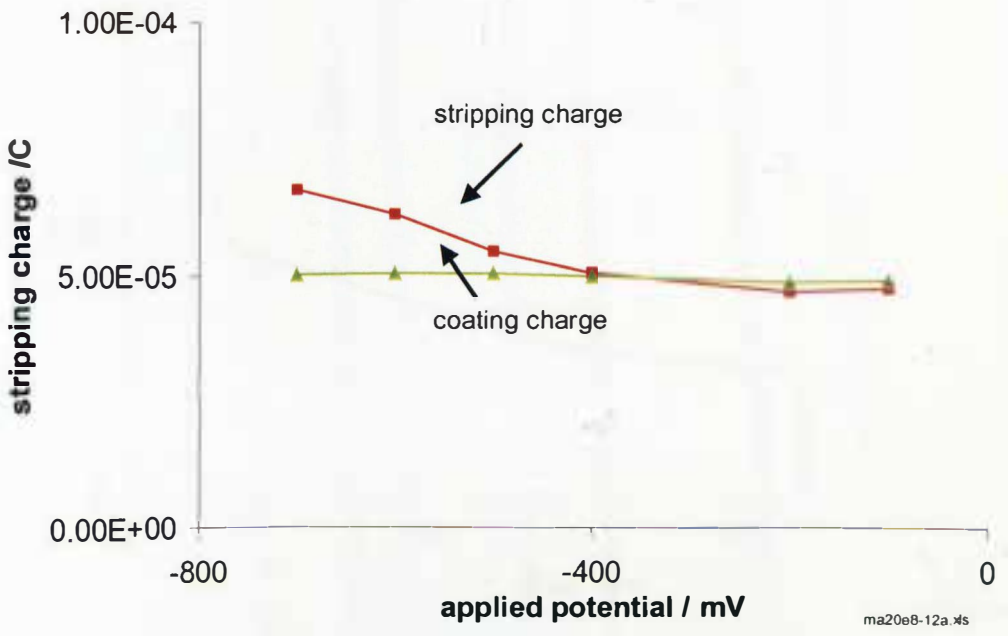


Fig. 4.20 Plot of total charge drawn for the stripping (■) and coating (▲) pulse at all applied stripping potentials.

The total charge drawn during the stripping process for all values of applied stripping potential are plotted (Figure 4.20). The charge passed in coulombs for the stripping pulse at a –400 mV applied potential was similar to that obtained for

the 20 ms coating pulse duration value in the previous experiments. The charge passed during the coating pulse was the same for all applied stripping potentials as the coating conditions were kept constant. The total charge drawn for the stripping pulses at different applied potentials should be the same as the charge drawn for the coating process if all of the charge is used to coat and strip the silver bromide. The higher charge drawn for applied potentials more negative than –400 mV compared with the coating charge, show that more charge has been drawn by other reactions occurring at the more negative stripping applied potentials. At applied potentials more positive than –400 mV the value of charge drawn reached a plateau (Figure 4.20). However at applied potentials more positive than -300 mV the longer time taken to strip the silver bromide would make using these applied potentials impractical.

4.4.3.3 Stripping pulse rotation speed

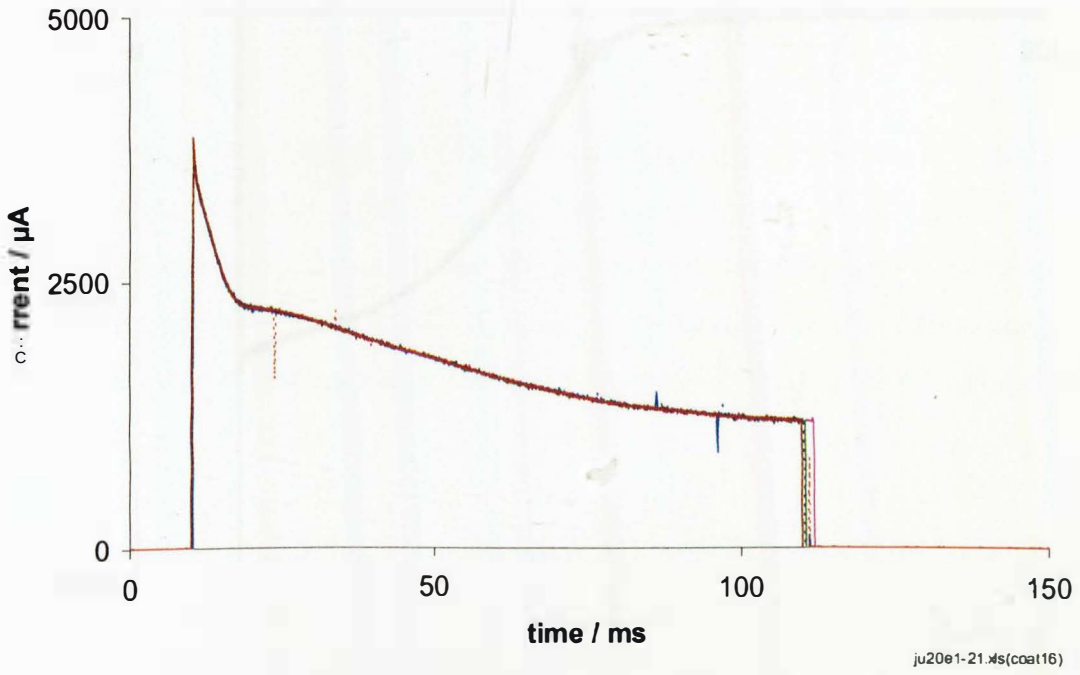


Fig. 4.21 Coating current curves at 16 Hz coating pulse rotation speed and 1 to 36 Hz stripping rotation speed with a 5 s delay. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /mse= 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_{D}= 5s; W_{SP} /Hz = 1....36; W_{CP} /Hz = 16.

In this set of experiments the rotation speeds of the silver electrode during the coating pulse were set at 1, 16 and 36 Hz with the silver electrode rotation speed during the stripping pulse set at 0, 1, 4, 9, 16, 25 and 36 Hz for each coating speed. A five second delay was added to allow the electrode speed to come to equilibrium. For each set where the coating pulse rotation speed was the same, the amount of silver bromide converted on the electrode should be the same for all value of stripping pulse rotation speed if all of the silver bromide was reconverted back before the end of the pulse. A plot of coating pulse current with coating pulse rotation speed constant at 16 Hz and for all values of stripping pulse rotation speed (Figure 4.21) shows that the current curves are identical. Similar results can be shown for the 1 and 36 Hz coating pulse rotation speeds. This confirms that the amounts of silver bromide converted were the same for all cases with the same coating pulse rotation speed.

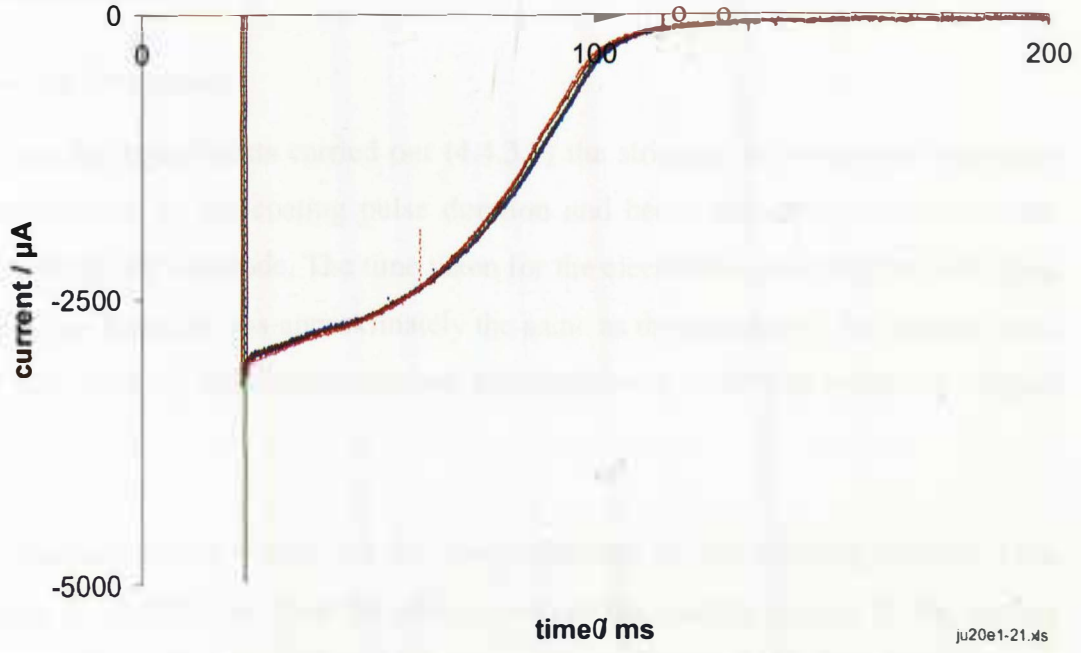


Fig. 4.22 Stripping current curves at 16 Hz coating pulse rotation speed and 1 to 36 Hz stripping rotation speed with a 5 s delay. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /s = 5; W_{SP} / Hz = 1....36; W_{CP} / Hz = 16.

Plots of the stripping pulse currents for the same set of experiments (Figure 4.22) show that not only is the total charge drawn during the stripping pulse the same,

as would have been expected from earlier experiments, but that the rate of stripping for all values of stripping pulse rotation speed is the same. This indicates that the rotation speed of the electrode during the stripping pulse has no effect on the reduction of the silver bromide during the stripping process.

For each of the three sets of experiments with the 1, 16 and 36 Hz coating rotation speeds an increase in the coating current with increased rotation speed was observed. It would be expected that with an increase in coating currents, more silver bromide would be converted and the stripping pulse currents would increase. This was found to be true. This again confirmed that the stripping current was independent of the silver electrode rotation speed during the stripping pulse.

Experiments with a shorter delay of two seconds between the stripping and coating pulses but at only two coating pulse rotation speed (10 and 20 Hz) showed similar results.

4.4.3.4 Discussion

From the experiments carried out (4.4.3.1) the stripping pulse current is directly proportional to the coating pulse duration and hence amount of silver bromide coated on the electrode. The time taken for the electrode to be completely stripped of silver bromide was approximately the same as the duration of the coating pulse if the stripping and coating applied potentials were –400 and +400 mV (Figure 4.15).

Experiments have shown that the charge required for the stripping process is the same or slightly less than the charge used in the coating process if the applied stripping potential is –400 mV or more positive (Figure 4.18). The slightly lower stripping charges indicated that some of the silver bromide layer may be dissolving in the solution before the stripping pulse occurs. At applied potential more positive than –400 mV the time required to complete the stripping process becomes much longer (Figure 4.19). The total length of the stripping pulse does

not affect the process although it must be sufficient for the current to return to zero to strip the entire electrode surface during the pulse.

At applied stripping potentials more negative than –400 mV the charge drawn for the stripping pulse is greater than the coating charge indicating that other electrochemical processes are seen to be taking place (Figure 4.20). Applied stripping potentials more negative than –400 mV still appear to strip the electrode efficiently.

Experiments with a fixed coating rotation speed of 16 Hz and varying stripping pulse rotation speed showed that the stripping current curves for all stripping pulse speeds were identical implying that the stripping process was unaffected by the stripping rotation speed. This indicated that the stripping process was not limited by diffusion of bromide ions through the diffusion layer into the bulk solution but must be limited by either the diffusion of bromide ions through the solid silver bromide or by a process occurring at the silver/silver bromide interface

This experiment was repeated at 1 and 36 Hz coating pulse speed with similar results. These experiments at coating speeds of 1 and 36 Hz confirmed that the stripping process was unaffected by variation in the stripping rotation speed. The coating current increased with coating pulse speed for the three speeds of 1, 16 and 36 Hz (Figure 4.23) and hence the stripping current also increased because more silver bromide was coated on the electrode surface. This result is at variance with the initial experiments where the coating current decreased slightly with coating pulse rotation speed. This was thought to be due to the inclusion of a delay time between the stripping and coating pulses. This is discussed later in the section dealing with coating currents.

4.4.4 Investigations of the coating pulse

The purpose of the coating pulse was to convert the silver metal electrode into a silver halide coated electrode, which would be selective to a particular halide ion.

From the results of 4.4.3 it was shown that the entire previous silver halide layer could be removed during the stripping process. If the halide ions in the sample solution were changed to another halide, a fresh layer of that silver halide will immediately allow the electrode to sense that new ion. It has already been shown from the studies on silver electrodes at equilibrium (3.6.1) that the coating duration and the amount of silver bromide coated greatly affect the value of the measured open circuit potential of the silver halide electrode.

4.4.4.1 Effect of adding a delay time and varying the rotation speed

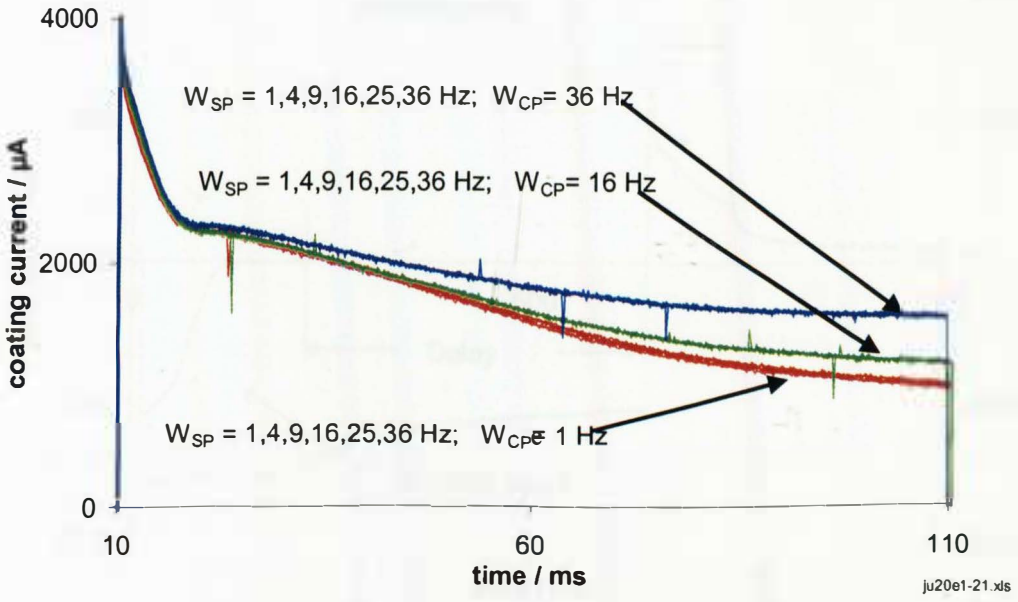


Fig. 4.23 Coating current curves at 1, 16 and 36 Hz coating pulse rotation speed with 1 to 36 Hz stripping rotation speed and a 5 s delay. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /mse= 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} / mV = +400; t_D /s = 5; W_{SP} /Hz = 1....36; W_{CP} /Hz = 1, 16 and 36.

To investigate the processes involved in this step it was necessary to study the effect of changing the mass transport or flow of material to the electrode surface with the RDE. In the previous section (4.4.2) it was seen that with no delay between the stripping and coating pulses the coating current was inversely affected by the rotation speed (Figure 4.12). However, when a 5 s delay was inserted between the pulses, then the coating current was seen to increase with increasing RDE speed. Figures 4.23 shows the coating current curves at three coating pulse rotation speeds (1, 16 and 36 Hz) and seven stripping pulse rotation speeds (0, 1, 4, 9, 16, 25 and 36 Hz). In 4.4.2 it was seen that the coating current

decreased with increasing speed, however, in this experiment although the current was similar for the first milliseconds, the coating pulse currents after that time showed a slight but consistent increase with increasing speed of coating rotation. The only difference between the experimental conditions was that in the first experiment, where a slight negative effect in coating current was observed no delay between stripping and coating pulse was present, while in this experiment a 5 s delay between the pulses was added.

4.4.4.2 Effect of varying delay time on coating current

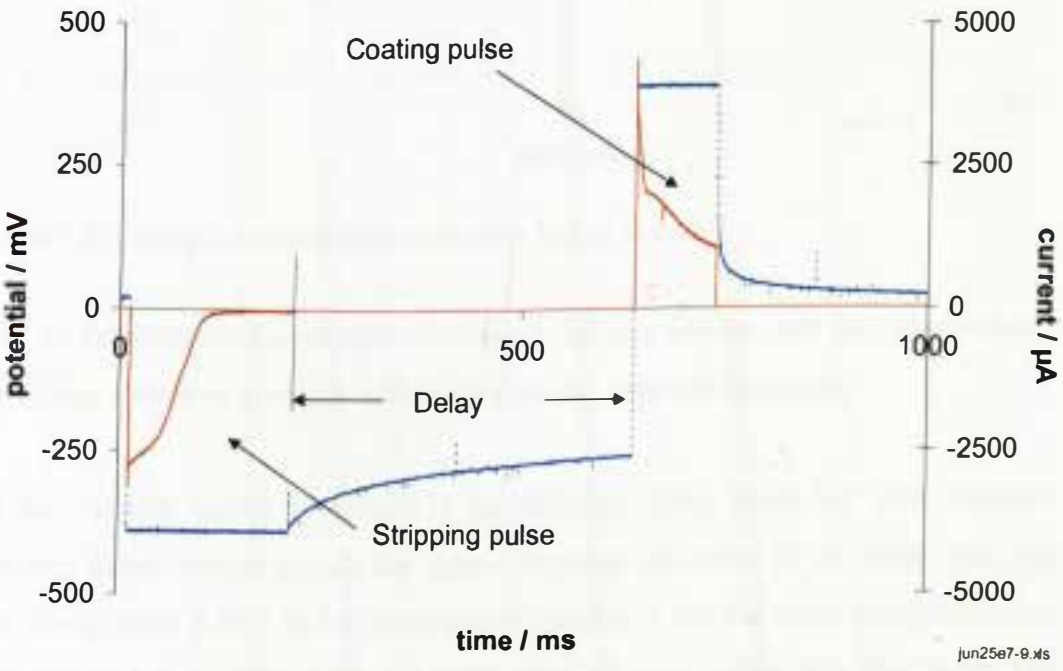


Figure 4.24 Plot of the measured potentials (—) and current (—) with a delay added between stripping and coating pulses.

To study the effect of delay time, experiments were carried out with delay times varying between 10 and 5800 ms and coating pulse rotation speeds of 1, 9 and 36 Hz. When studying these current curves it is helpful to subdivide the plot into three sections (Figure 4.25). The first period of 1 – 2 ms is where the current fell rapidly to a value of 3000 to 5000 µA. In the second section of the current curve, which lasted 8 to 10 ms, the currents fell linearly and more slowly to about fifty percent of the initial value, and the third section where the current was either constant or fell very slowly.

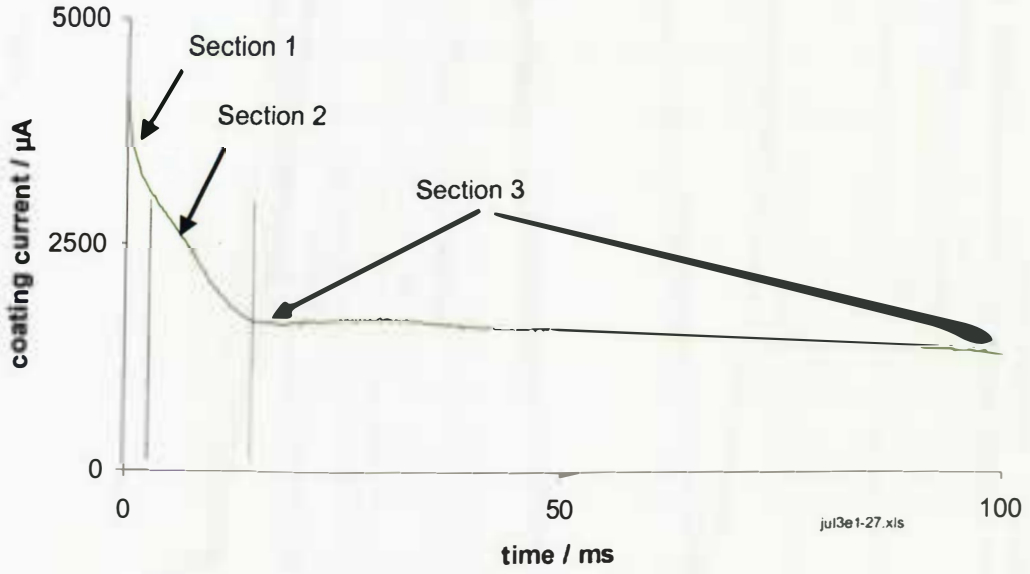


Figure 4.25 Coating current plot showing the three distinct sections

For all experiments the current in section 1 fell at a rate too fast for the electronic sampling system to give any information on the shape of the curve.

If the currents curves in section 2 for different delay times but with constant coating pulse rotation speeds are plotted together the effect of the delay time can be seen (Figure 4.26). At the low rotation speed of 1 Hz the shape and gradient of the curves are unaffected by the delay times (Figure 4.26a) but the curves are offset to give lower current values for the longer delay times. At the higher rotation speed of 36 Hz the shorter the delay, the steeper is the gradient of the current curve (Figure 4.26c). However, final current at the end of section 2 is the same for all delay times.

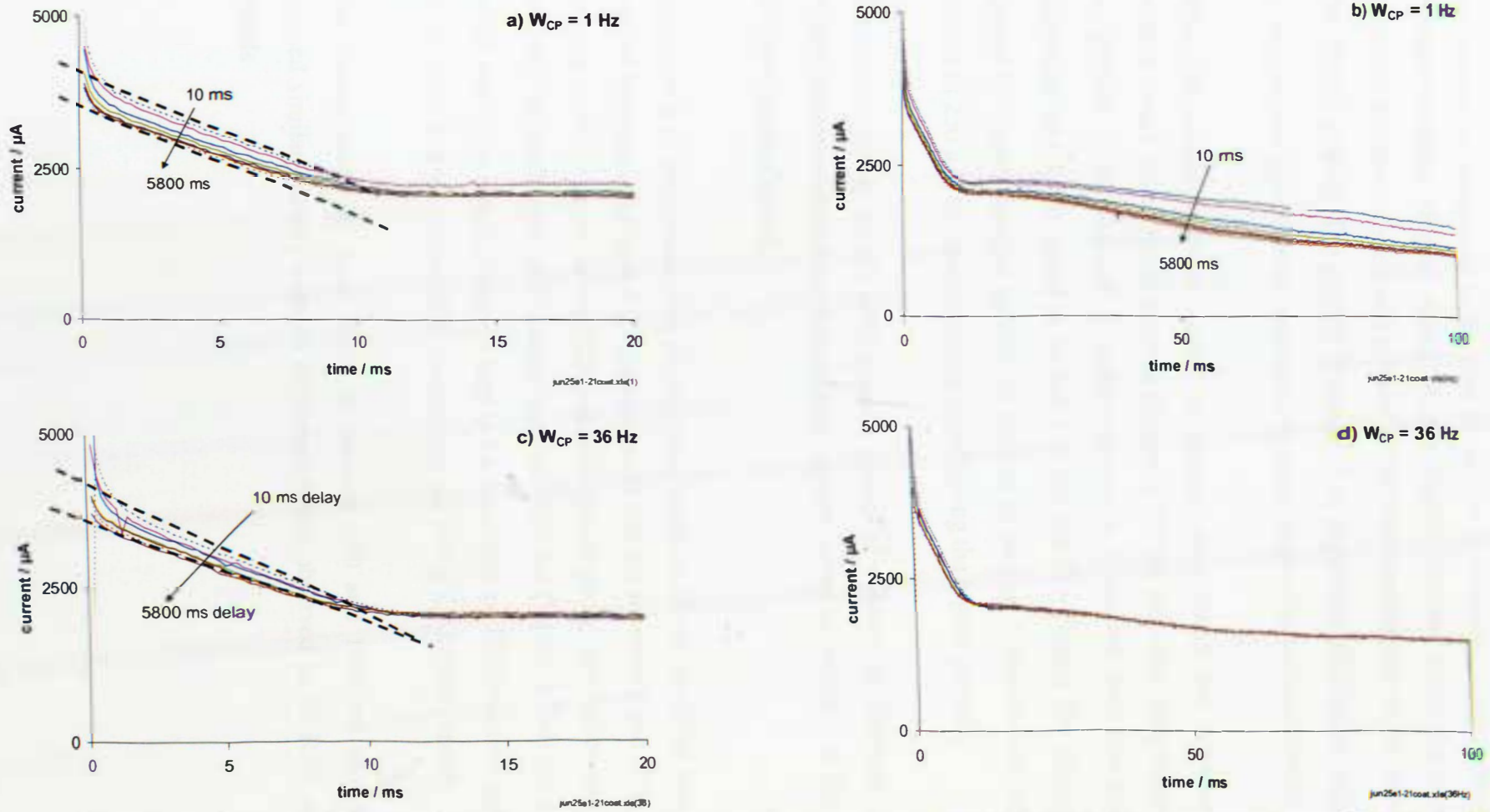


Figure 4.26 Coating pulse current versus time for section 2 (left) and section 3 (right) for various delays at 1 Hz (top) and 36 Hz (bottom) rotation speed. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP}/mV = -400; t_{CP} /ms = 100; E_{CP}/mV = +400; t_D/ms=10..5800; W_{SP} = W_{CP}/Hz = 1, 36.

Section 3 of the current plots at the low rotation speed show that the current offset with respect to delay time at the start of section 3, increases as the coating pulse process continues (Figure 4.26c). At the higher rotation speed the current is similar at the start of section 3 (Figure 4.26d) and continues to be so throughout the coating process. The current in section 3 is negatively effected by delay time at low rotation speeds but is unaffected by delay time at high rotation speed.

When the coating current curves for similar delay times but different RDE rotation speed were plotted together (Figure 4.27) the plots for delay times of 10 ms (Figure 4.27a) showed a similar current at 2 ms but with the gradients dependant on rotation speed in section 2 of the plot (2 – 10 ms) The gradient was greater for higher rotation speeds. At the end of section 2 there was an offset in current of 250 μA, the lower rotation speed giving the higher currents.

The current curves for all RDE rotation speeds at a delays of 5800 ms (Figure 4.26b) showed no difference between the current curves in section 2 of the plot at different rotation speeds.

In section 3 of the current plots for the delay times of 10 ms the offset seen at the start of this section (Figure 4.27c) increases to 400 μA between 1 and 36 Hz RDE rotation speed with the lower RDE rotation speeds giving the higher current. In section 3 of the curves with a delay time of 5800 ms (Figure 4.27d) the current, which starts at a similar value, is seen to be dependant on RDE rotation speed but in this case with the higher RDE rotation speeds giving the higher current.

The current plots for delay times of between 500 and 1800 ms (not shown) showed similar profiles with no difference being observed at all RDE rotation speeds

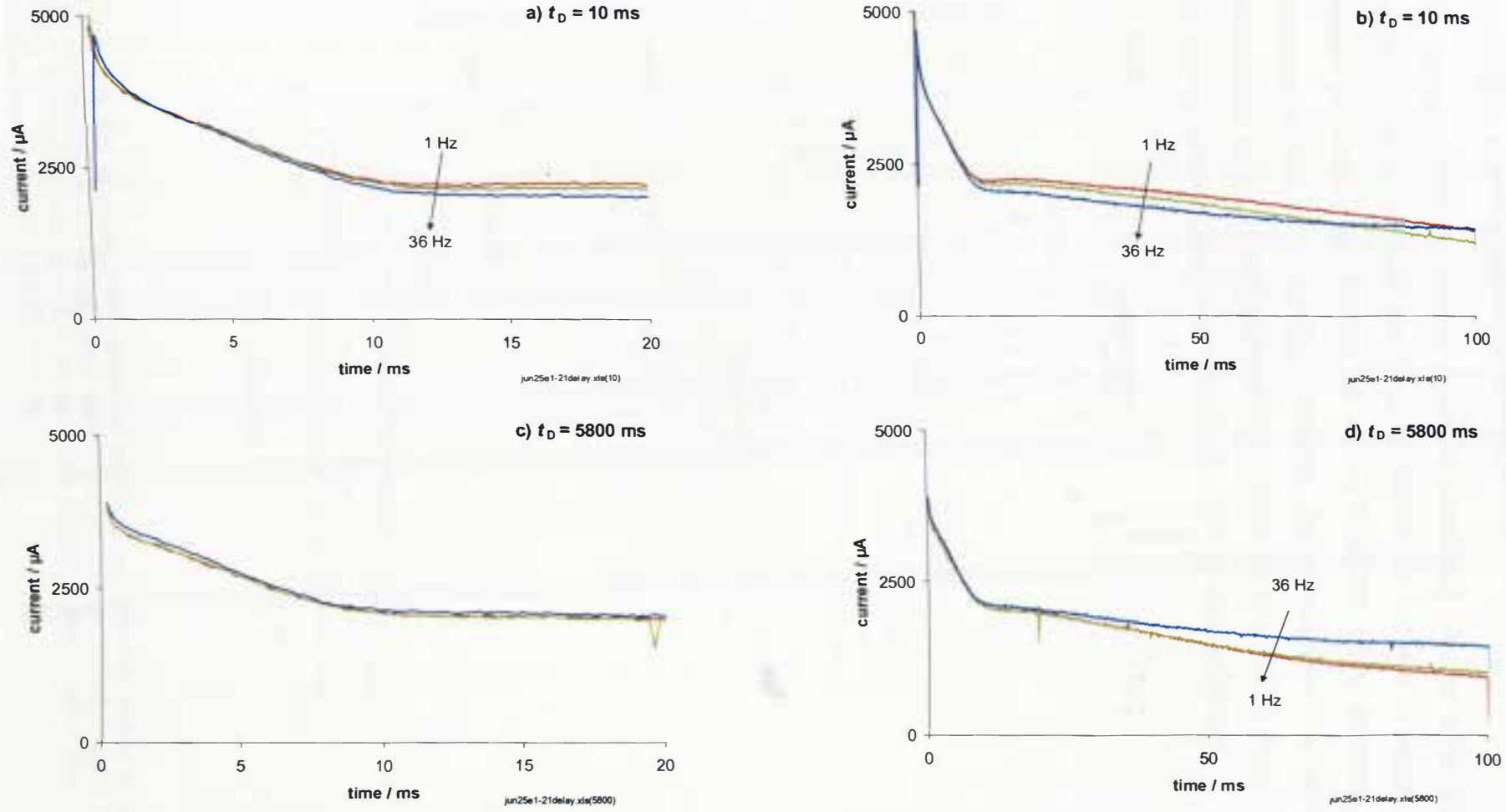


Figure 4.27 Coating pulse current versus time for section 2 (left) and section 3 (right) for 10 ms (top) 5800 ms (bottom) delays at various rotation speeds. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV= +400; t_D /ms = 10, 5800; $W_{SP} = W_{CP}$ /Hz = 1..36.

4.4.4.3 Effect of coating potential on coating current

The current curves for coating pulses of increasing coating pulse applied potentials (Figure 4.28) show that while the duration of section 1 of current curve remains unchanged, the duration of section 2 of the curve decreases with increasing applied pulse potential. However, the current values in section 2 increase with increasing applied potential and hence the total charge drawn during this section, calculated from the area under the curve remains unchanged.

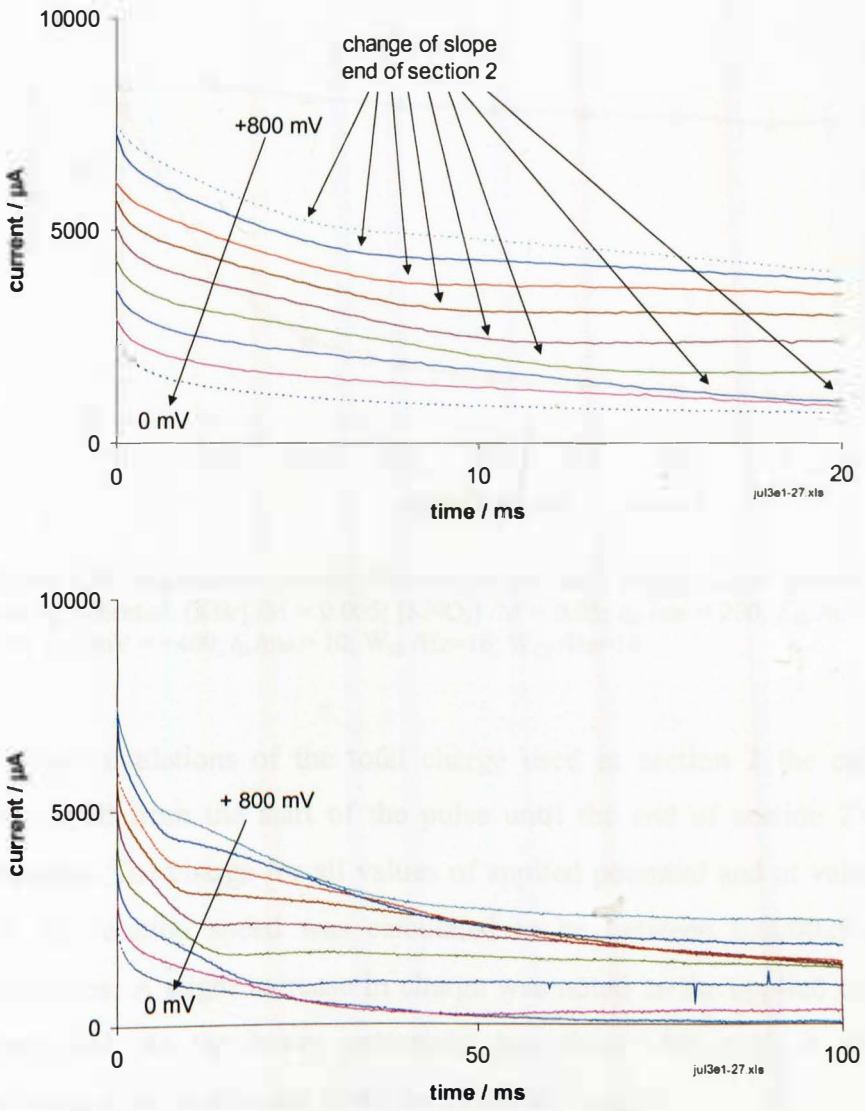


Figure 4.28 Plot of coating pulse currents for various applied potentials with a 10 ms delay between the stripping and coating pulses. Section 1 and 2 (top) and Section 2 and 3 (bottom). [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /mse= 200; E_{SP} /mV = -400; t_{CP} /mse= 100; E_{CP} /mV = +400; t_D /ms = 10; W_{SP} /Hz = 16; W_{CP} /Hz = 16.

A plot of applied coating pulse potential and the duration of section 2 of the process (Figure 4.29) shows this relationship. The total charge drawn during section 2 of the process was calculated and plotted for all applied potentials. This relationship was repeated at all values of rotation speed.

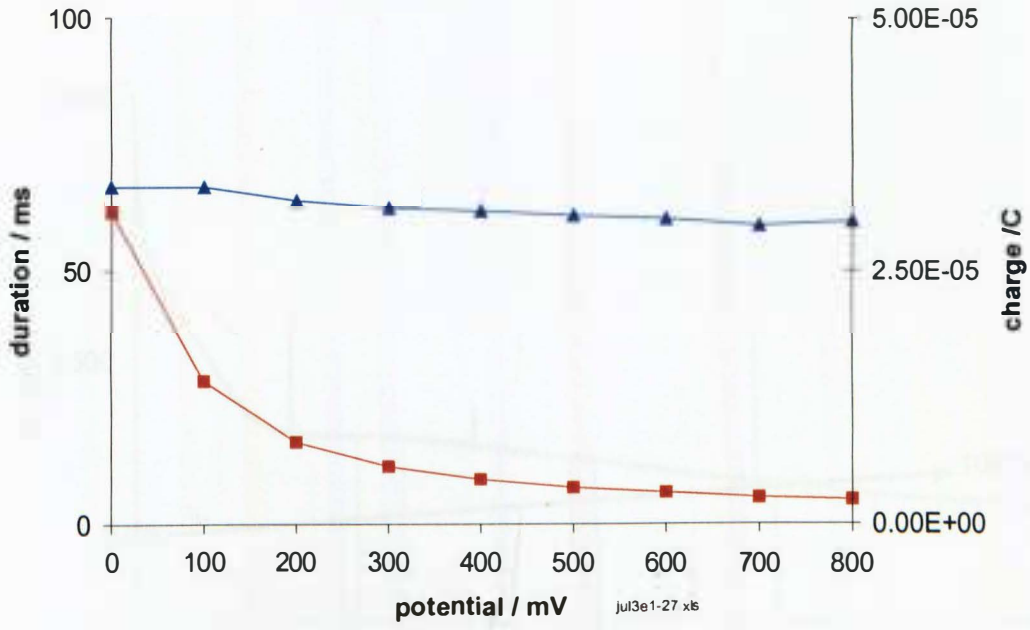


Figure 4.29 Relationship between duration (■) and total charge (▲) of section 2 against applied coating potential. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /mse= 100; E_{CP} /mV = +400; t_D /mse= 10; W_{SP} /Hz=16; W_{CP} /Hz=16.

In the calculations of the total charge used in section 2 the current has been integrated from the start of the pulse until the end of section 2 when gradient changes. The charge for all values of applied potential and at values of 1, 9, and 36 Hz rotation speed was calculated to be between 0.000029 and 0.000033 coulombs. A slight increase in charge was noted as the applied coating potential decreased. At the lower potentials, less than +300 mV, it was difficult to determine the exact point when the gradient changed.

4.4.4.4 The effect of coating pulse duration on coating current

The results of varying the coating pulse time (Figure 4.30) from 5 to 100 ms produced current curves that could be overlaid. The increase in the time and hence the increase in total silver bromide converted on the electrode did not change the coating process.

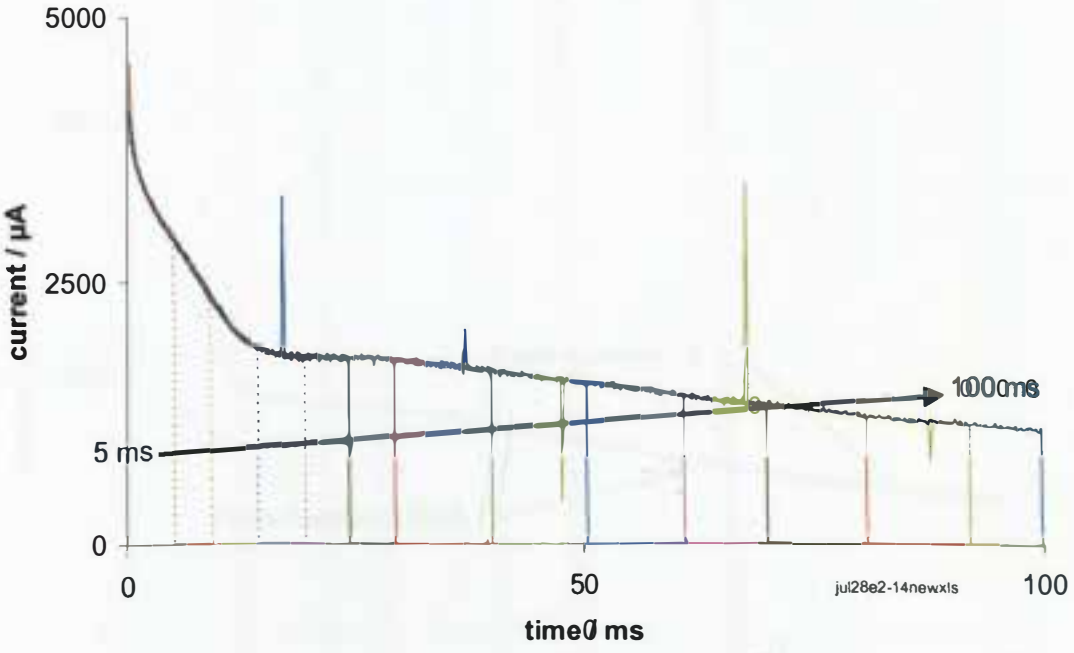


Figure 4.30 Plot of coating pulse currents for various coating pulse durations with a 300 ms delay between the stripping and coating pulses. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 5…100; E_{CP} /mV = +400; t_D /ms = 300; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

4.4.4.5 Effect of number of cycles

The clean/coat/measure technique was run for 4 hours in the standard bromide solution with the complete current and potential cycle recorded at 10 and 15000 cycles (Figure 4.31). The profile of the coating current did not change over the 15000 cycles.

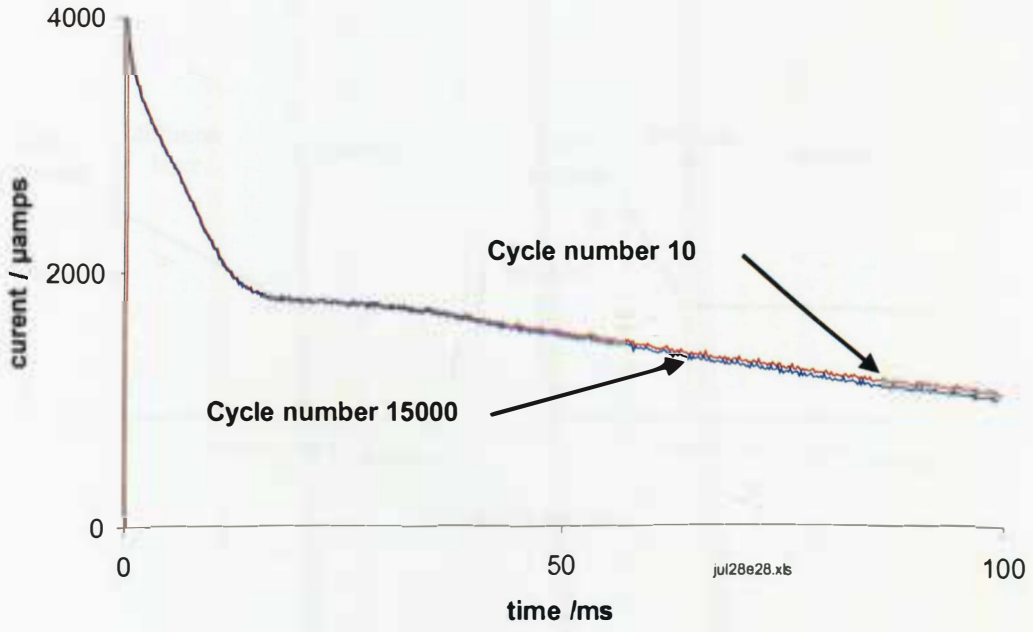


Figure 4.31 Coating pulse currents for cycle 10 and cycle 15000 of a four hour run. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /ms = 300; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

4.4.4.6 Discussion

In 4.4.2 the overall value of the coating current profiles could be seen to decrease slightly with increasing rotation speed. However in 4.4.4, when a delay was inserted between the end of the stripping pulse and the beginning of the coating pulse this relationship was reversed with the coating current increasing with increasing rotation speeds. This was confirmed for all values of stripping pulse rotation speed (Figure 4.23).

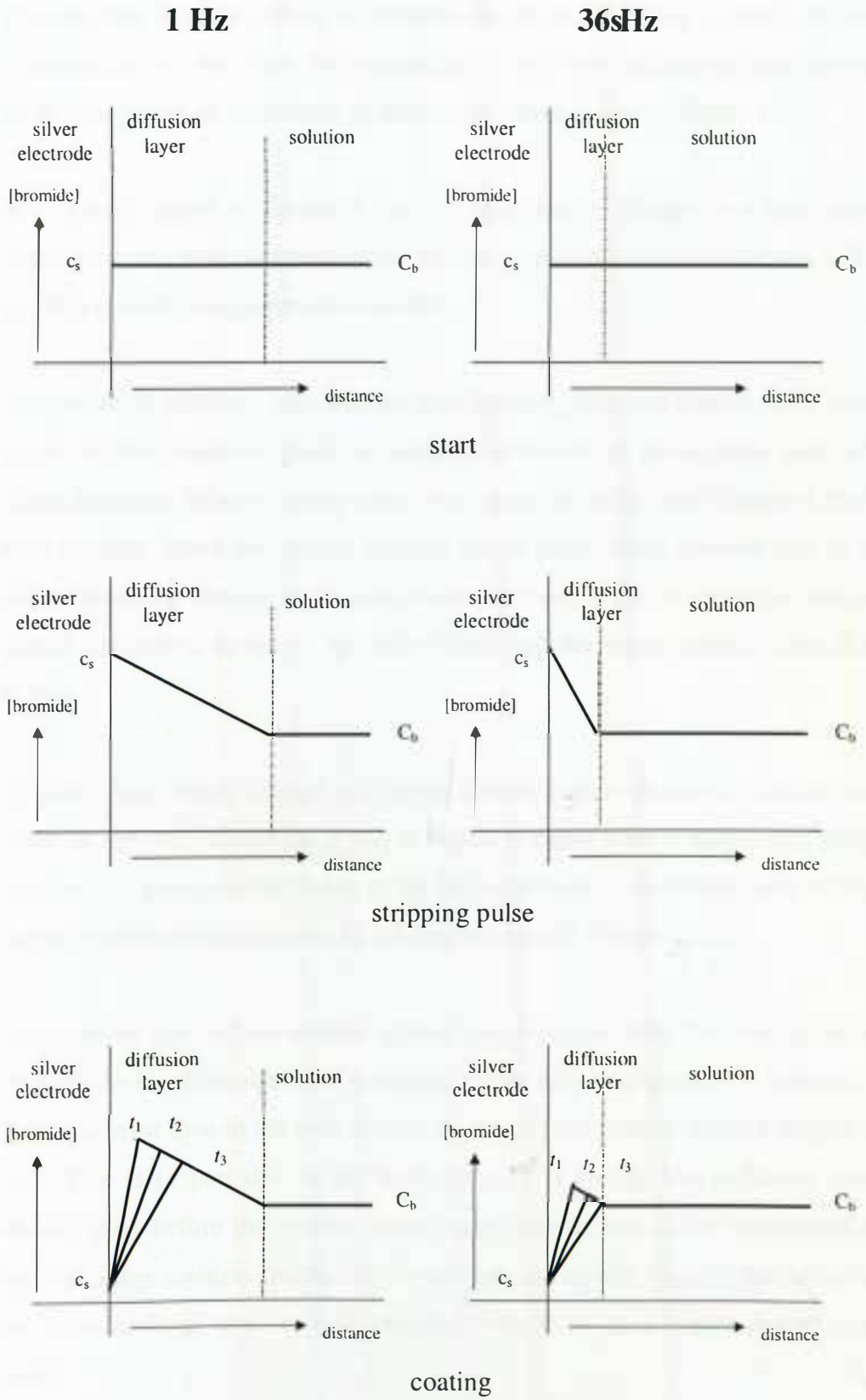


Figure 4.32 Diagram of solid silver, diffusion layer and bulk solution for 1 and 36 Hz rotation speed.

Investigating both the effect of rotation speed and duration of delay showed a relationship between these two conditions. A possible explanation was arrived at by examining all three sections of the current curve in detail (Figure 4.25).

The current profile of section 1 was not observed to change by a large amount although as has been said before this fast section of the current curve was difficult to observe with the equipment available.

The profile of section 2 was affected both by delay time and coating pulse rotation speed. At low rotation speed the current curves for all delay times were of the same shape but offset to lower values the longer the delay time (Figure 4.26a). At high rotation speed the current profiles for all delay times showed that at short delays the initial current at the start of section 2 was higher then longer delays but that at the end of section 2 all delay times had the same current value (Figure 4.26c).

At short delay times (Figure 4.27a) the current curves showed a similar current value at the start of section 2 but at higher rotation speeds the current dropped quicker to a lower current value at the end of section 2. At longer delay times the current profiles were identical for all rotation speeds Figure 4.27c).

It is thought that at low rotation speeds and with no delay the concentration of bromide in the diffusion layer produced in the stripping process is higher in the diffusion layer than in the bulk during the start of the coating process (Figure 4.32 left). This is in part due to the bromide ion not having had sufficient time to diffuse away before the coating pulse starts and part due to the thicker diffusion layer at lower rotation speeds. The lower rotation speeds impede the diffusion of the extra bromide into the bulk solution. This leads to a higher overall current value.

Similarly at higher rotation speeds and with no delay the bromide concentration in the diffusion layer from the stripping process is higher and hence the initial

current value is also higher (Figure 4.32 right). However as the extra bromide diffuses away quickly at the high rotation speed due to the diffusion layer being thinner, the current drops more quickly than at low rotation speed.

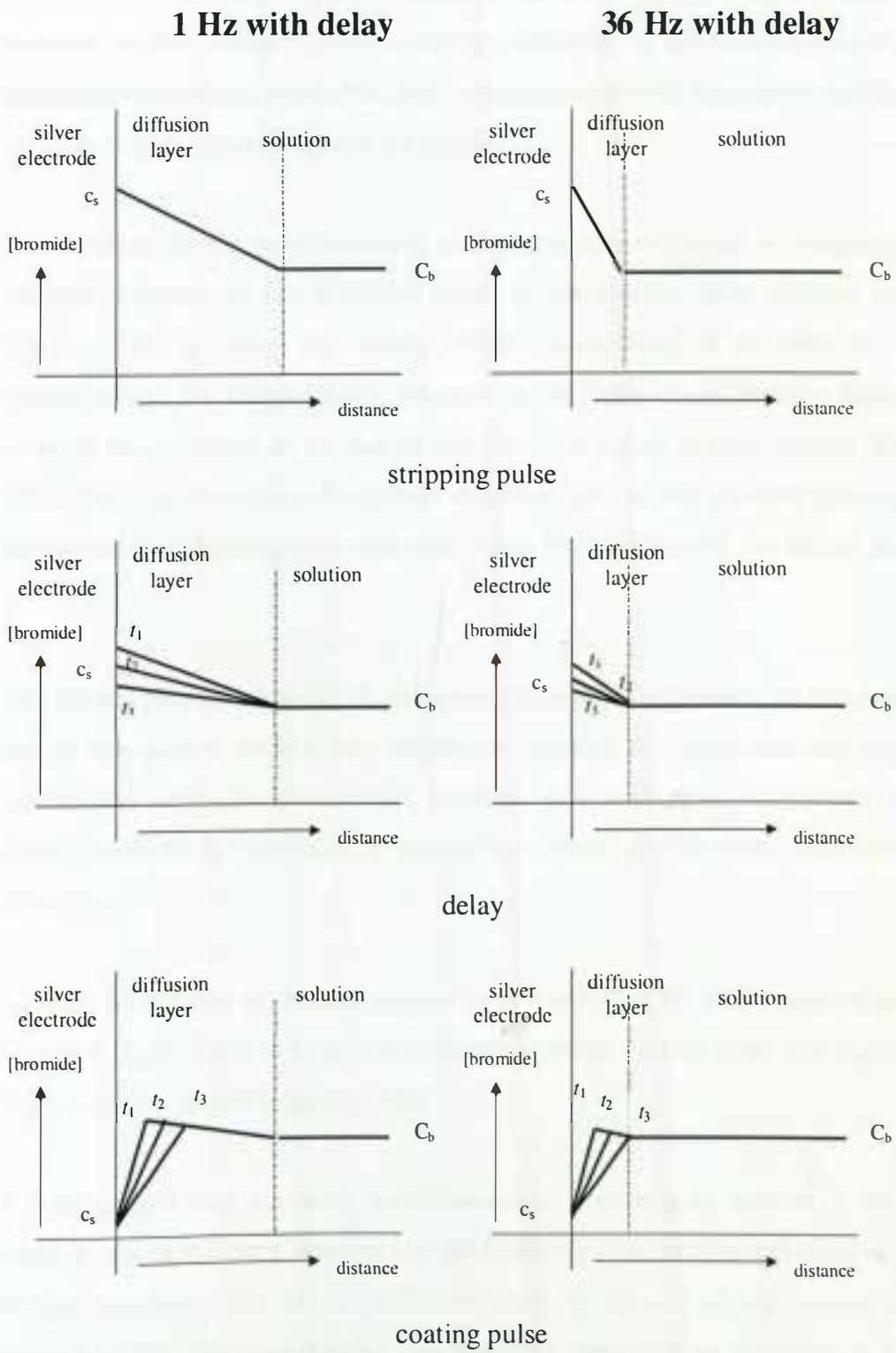


Figure 4.33 Diagram of solid silver, diffusion layer and bulk solution for 1 and 36 Hz rotation speed with delay between stripping and coating pulses.

When a delay is inserted between the stripping and coating pulse (Figure 4.33) the amount of extra bromide close to the electrode decreases due to diffusion over time. In this case for both slow and fast rotation speed, the bromide level in the diffusion layer is close to bulk concentration. In the first 5 – 10 ms, while the bromide in the diffusion layer is being converted to silver bromide and the concentration gradient across the layer is being established, the current profiles for the slow and fast rotation speeds are similar.

The duration of the delay therefore affects the current profile by reducing the available bromide in the diffusion layer. In the case of slow rotation speeds (Figure 4.26a) it causes the current profiles in section 2 to be offset to lower current values for longer delays because the diffusion layer remains higher in bromide concentration at the end of section 2. At higher rotation speeds (Figure 4,26c) the extra bromide in the thinner diffusion layer is used up more quickly and the current therefore moves to the same value for all delays by the end of section 2.

The coating profiles of section 3 also showed a marked difference. At low rotation speeds the current profile was negatively affected by delay duration (Figure 4.26b). The value of current offset could be seen to decrease with longer delay times. However at high rotation speeds the current profiles were unaffected by delay time.

At short delay times the overall current level was higher for lower rotation speeds (Figure 4.27b). While at long delay times the overall current level was higher for higher rotation speeds (Figure 4.27d).

It was thought that a similar mechanism was occurring in section 3. At low rotation speeds the extra bromide ion produced from the stripping process did not diffuse completely out of the diffusion layer by the end of the coating pulse (Figure 4.27b). The current offset was therefore dependant on the duration of the delay. The longer delay times allowed the extra bromide to diffuse away into the

bulk solution. The overall current was therefore higher for short delay times where more bromide ion was in the diffusion layer and lower for long delays where the bromide level was lower or equal to the bulk solution.

At high rotation speeds extra bromide ion was quickly diffused into the bulk solution so that by the start of section 3 the bromide ion concentration was similar to the bulk. The overall current level was therefore independent of delay time at high rotation speeds.

At short delays the overall current levels were dependant on the diffusion of the extra bromide ion away from the electrode surface. At lower rotation speeds and thicker diffusion layers the high bromide ion concentration in the diffusion layer caused higher currents. While at higher rotation speeds the thinner diffusion layer allowed the extra bromide to diffuse away quicker to allow the concentration of bromide to drop to the bulk concentration.

The profile of section 2 was also affected by the applied coating potential. At higher applied potential the duration of section 2 of the current curve was shorter, however, it can be seen (Figure 4.31) that the total charge used in section 2 of the profile is the same for all values of applied potential. It was therefore proposed that this section was related to a point when a fixed amount of charge was used or when a fixed amount of silver bromide had been converted.. The amount of charge needed to coat a monolayer of silver bromide was calculated in two ways.

Calculation 1: Based on density and volume of monolayer

Density of AgBr = 6.47 g/cm^2 (James 1977)

Atomic diameter silver = 2.52 $\times 10^{-8}$ cm

Atomic diameter bromide = 3.90 $\times 10^{-8}$ cm

Molecular weight AgBr = 187

Average thickness of monolayer assuming one atom thick

Thickness of layer = (2.52 $\times 10^{-8}$ + 3.90 $\times 10^{-8}$) / 2

$= 3.21 \times 10^{-8}$ cm

Area of 6 mm diameter silver electrode

$= 0.2826$ cm^2

Volume monolayer =thickness × area

$= 3.21 \times 10^{-8}$ cm $\times$ 0.2826 cm^2

$= 9.046 \times 10^{-9}$ cm^3

Mass of monolayer = density × volume

$= 6.47 \times 9.046 \times 10^{-9}$

$= 5.855 \times 10^{-8}$ g

Number moles AgBr in layer= mass / MW

$= 5.855 \times 10^{-8} / 187$

$= 3.131 \times 10^{-10}$

Charge = Number moles AgBr in layer × Faraday constant

Charge= $3.131 \times 10^{-10} \times 96500$

Charge = 3.021×10^{-5} C

Calculation 2: Based on unit cell and electrode area

Length of AgBr unit cell= 5.77×10^{-8} cm (James 1971)

Area of base of unit cell (2 Ag and 2 Br atoms) = 33.25×10^{-16} cm^2

Area equivalent to 1 AgBr molecule

$= 33.25 / 2 \times 10^{-16}$ cm^2

$= 16.98 \times 10^{-16}$ cm^2

Area silver electrode= 0.2826 cm^2

Number AgBr molecules in monolayer = electrode area/ AgBr unit cell area

$= 0.2826 / 16.98 \times 10^{-16}$

$= 1.69 \times 10^{+14}$

Number moles of AgBr in monolayer =number / avagardros number

$1.69 \times 10^{+14} / 6.023 \times 10^{+23}$

$= 2.82 \times 10^{-10}$

Charge = Number moles AgBr in layer × Faraday constant

$= 2.82 \times 10^{-10} \times 96500$

Charge = 2.72×10^{-5} C

The values obtained for the calculated charge required to coat a monolayer of silver bromide were in good agreement with the values of 0.000029 to 0.000033 coulombs for the total charge used in section 2 of the current profile and found empirically for all conditions. It was proposed that the initial conversion of the silver to a monolayer of silver bromide was a fast process causing the current to drop quickly as observed in section 2 of the current profiles. As the possible sites for conversion on the surface were used up, the rate of conversion and hence the current would fall quickly. After the surface had been completely coated with silver bromide, at the end of section 2, the current or rate of conversion of silver would be dependant on either the increasing impedance of the silver bromide layer as it built up or the diffusion of bromide and/or silver ions through the solid layer. A constant or slightly decreasing current value was observed in section 3 of the profiles.

The consistent profiles observed when the duration of coating pulse was varied from 5 to 100 ms (Figure 4.30) confirmed that the surface of the electrode was unaffected by the duration of the stripping and coating process and that on each cycle the newly stripped surface was the same as on the previous cycle.

The identical current profiles of the coating on the 10th and 15000th cycle of a four hour run (Figure 4.31) confirms that the stripping pulse had removed the bromide coating completely and that no residue was either left on the electrode surface or was building up on the surface.

4.4.5 Investigations of the stripping and coating current while varying the bromide concentration

4.4.5.1 Results and discussion

The stripping and coating current curves for varying potassium bromide concentrations above 0.001 M KBr (Figure 4.34) showed a similar profile to previous experiments. For the coating curves at concentrations below this no discernable section 2 was seen. At concentrations above this the duration of section 2 of the coating current curve decreased and the overall current increased as the concentration of potassium bromide increased. At high concentrations, greater than 0.01 M KBr, the current in section 3 of the curve levelled out.

The stripping current curves for potassium bromide concentrations above 0.001 M was similar to previous experiments in that the total charge for stripping was approximately equal to the coating charge.

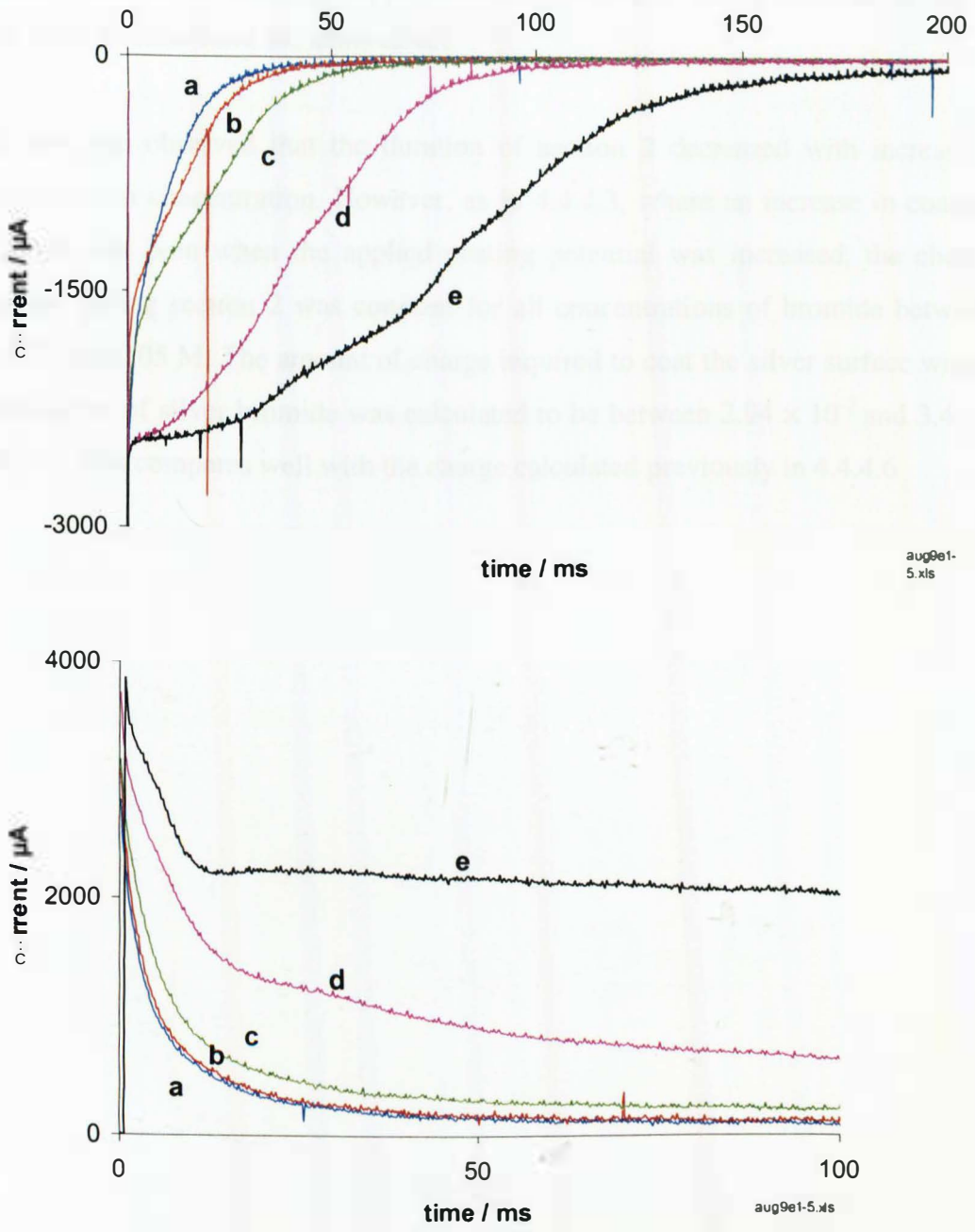


Fig 4.34. Stripping (top) and Coating (bottom) current curves for varying bromide concentrations. [KBr] /M = 0.00014(a), 0.0006(b), 0.001(c), 0.003(d), 0.013(e); [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /ms = 450; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

The increase in overall current for section 2 and 3 of the curve and the decrease in duration of section 2 for higher concentration of potassium bromide confirm the hypothesis put forward in 4.4.4.5. The hypothesis was that the higher coating currents, seen with the slower RDE rotation speeds, were caused by an increase of bromide ions, released during the stripping process and trapped in the diffusion

layer. From these results it can be observed that higher levels of bromide ion in the bulk solution have the same effect.

It was also observed that the duration of section 2 decreased with increasing bromide ion concentration. However, as in 4.4.4.3, where an increase in coating current was seen when the applied coating potential was increased, the charge passed during section 2 was constant for all concentrations of bromide between 0.001 and 0.05 M. The amount of charge required to coat the silver surface with a monolayer of silver bromide was calculated to be between 2.94×10^{-5} and 3.46×10^{-5} C. This compares well with the charge calculated previously in 4.4.4.6

4.4.6 Factors affecting the open circuit potential

For the "clean/coat/measure" technique to be successful the measured open circuit potential (VAG) or steady state potential of the coated silver electrode should be the same as a conventional silver halide electrode. The time taken to come to equilibrium and to reach this value must occur in a reasonable time after the coating pulse has finished. For the technique to be practical in a process control environment the maximum time must be 5 s. Experiments were carried out to determine this steady state potential and the effects on it of rotation speed, applied coating potential and coating pulse duration. The final measured potential was compared with that expected for a conventional silver bromide electrode. The changing open circuit potential was recorded over the first 500 ms after the coating process.

4.4.6.1 Variation of silver electrode rotation speed

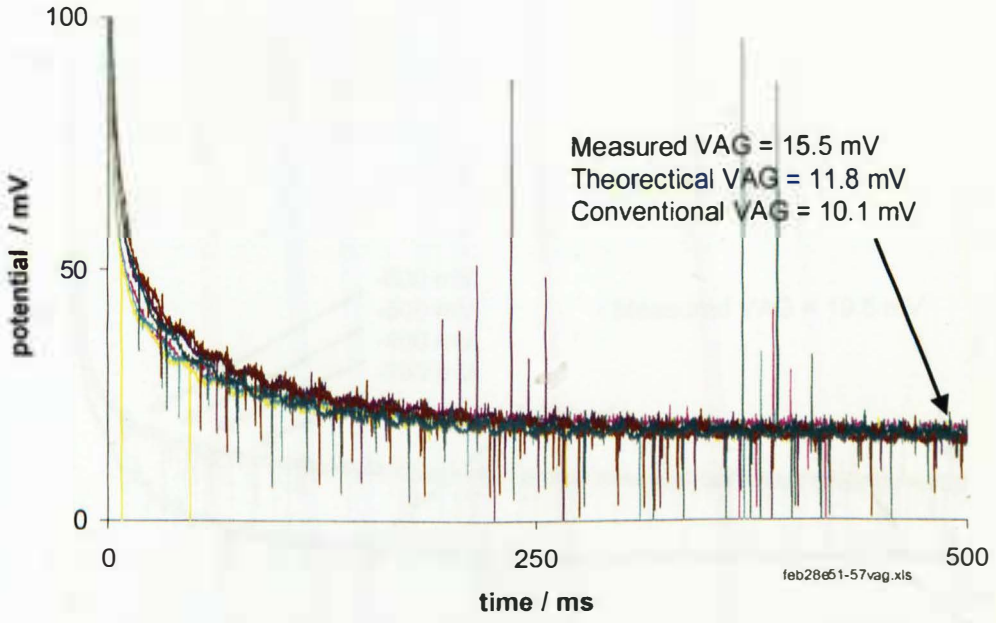


Figure 4.35 Open circuit potential for various silver electrode rotation speeds. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /msd= 0; W_{SP} = W_{CP}dHz = 1…36.

Initial experiments with the stripping and coating pulse rotation speed varied from 0 to 36 Hz and with the conditions above (Figure 4.35) showed that no affect on either the final open circuit potential or the equilibrium rate was observed.

The final open circuit potential, measured after 500 ms, was 3.7 mV more positive than the theoretical and 5.4 mV more positive than the conventional electrode.

4.4.6.2 Variation of applied stripping potential

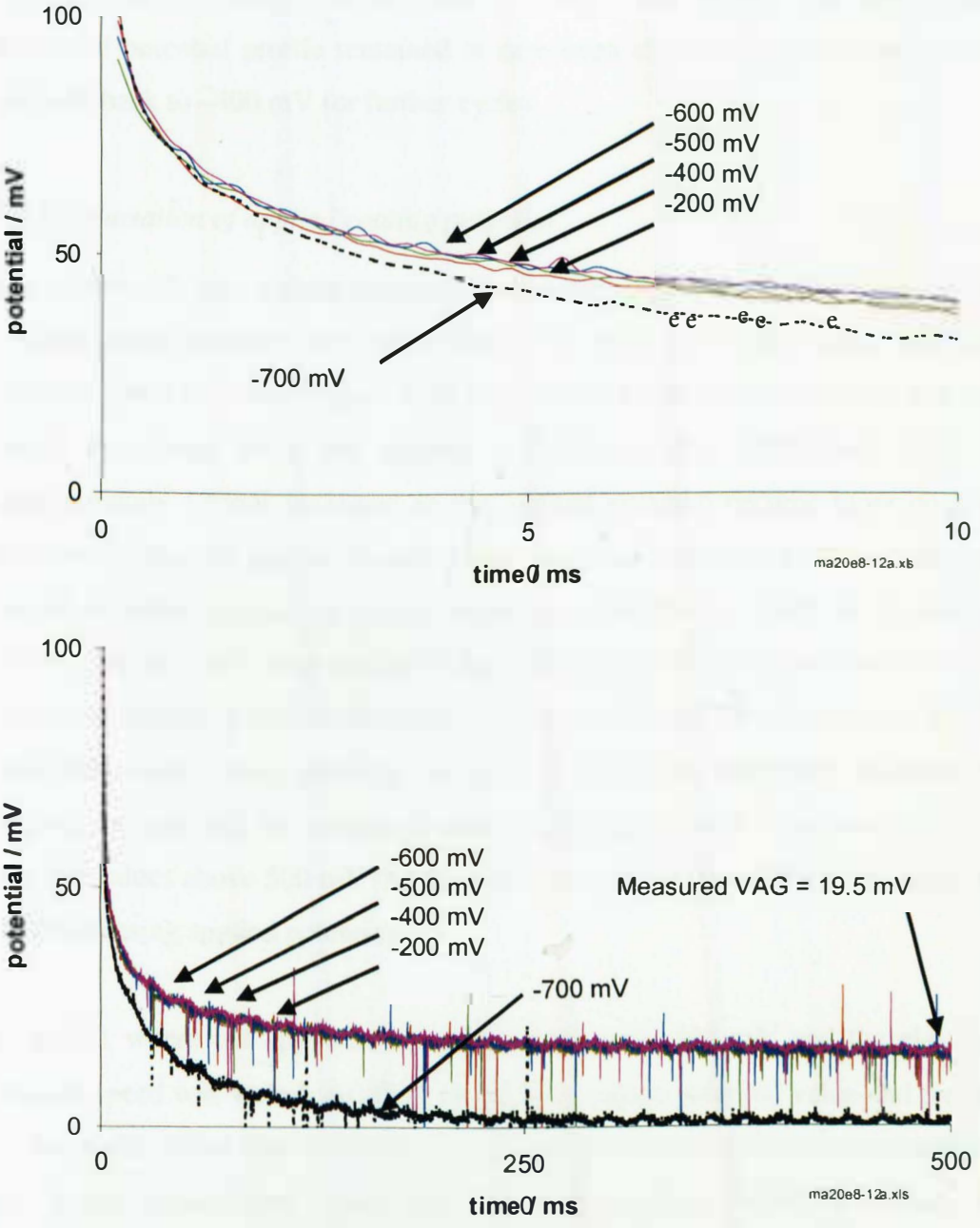


Figure 4.36 The measured potential for various stripping pulse applied potential, over the first 10 ms (top) and 500 ms (bottom) [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -200...-700; t_{CP} /ms = 20; E_{CP} /mV = +400; t_D /ms = 0; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

The profile of the open circuit potential for all value of applied stripping potential except –700 mV showed a similar trend to previous experiments with the value dropping to 19.5 mV after 500 ms. The potential curve for the –700 mV applied

stripping potential experiment dropped to zero after 500 ms. This set of experiments were carried out several times, each time the measured potential of the –700 mV applied potential showed significantly different behaviour from the other curves. An experiment was carried out where the applied stripping potential was changed to from –700 to –400 mV after 200 cycles. The open circuit measured potential profile remained at zero even after the applied potential had been set back to –400 mV for further cycles.

4.4.6.3 Variation of applied coating potential

The measured open circuit potential curves for experiments where the applied coating pulse potential was varied from 0 to +800 mV with a silver electrode rotation speed of 1 Hz (Figure 4.37 top) shows a set of curves where the time taken to change from the applied potential to the equilibrium value of approximately 13 mV increased as the applied potential became more positive. However, when the applied potential was more negative than +100 mV the open circuit potential dropped to values below zero and did not reach an equilibrium value. This behaviour was similar to that exhibited by a bare silver electrode. For values of applied potential between +100 and +500 mV the time taken for the measured open circuit potential to reach 95% of the difference between the applied voltage and the measured open circuit equilibrium value was below 50 ms. For values above 500 mV the time taken is greater than 100 ms and increases with increasing applied potential.

In 4.4.6.1 where the applied coating potential was +400 mV and the electrode rotation speed was varied, no affect in the open circuit potential value and the rate to reach this value was observed. To determine whether rotation speed affected the longer equilibrium times seen at high applied coating potentials the experiment was repeated with various rotation speeds. The time taken for the open circuit potential to reach equilibrium was reduced when the rotation speed was increased (Figure 4.37 middle and bottom).

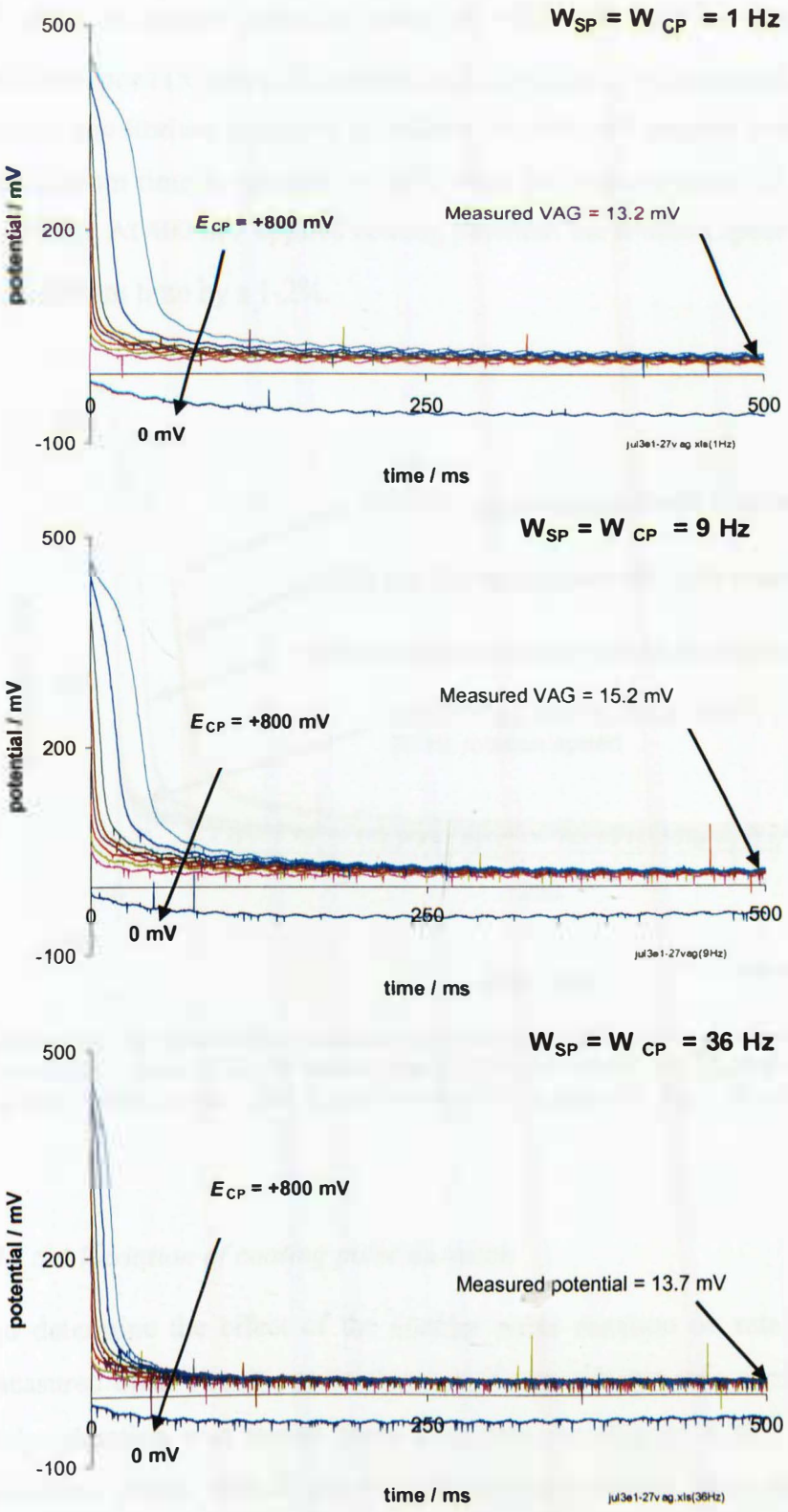


Figure 4.37 The effect of the variation of applied coating potential on measured open circuit potential at 1 (top), 9 (middle) and 36 (bottom) Hz rotation speed. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = 0….+800; t_D /mse= 10; $W_{SP} = W_{CP}$ /Hz =1,9,36.

A graph of applied potential values of +400 and +800 mV for 1, 9 and 36 Hz rotation speed (Figure 4.38) shows both the affect of rotation and applied potential on the equilibrium potential. At values of +800 mV applied coating potential the equilibrium time is reduced by 50% when the rotation speed in increased from 1 to 36 Hz. At 400 mV applied coating potential the rotation speed only changes the equilibrium time by a 1-2%.

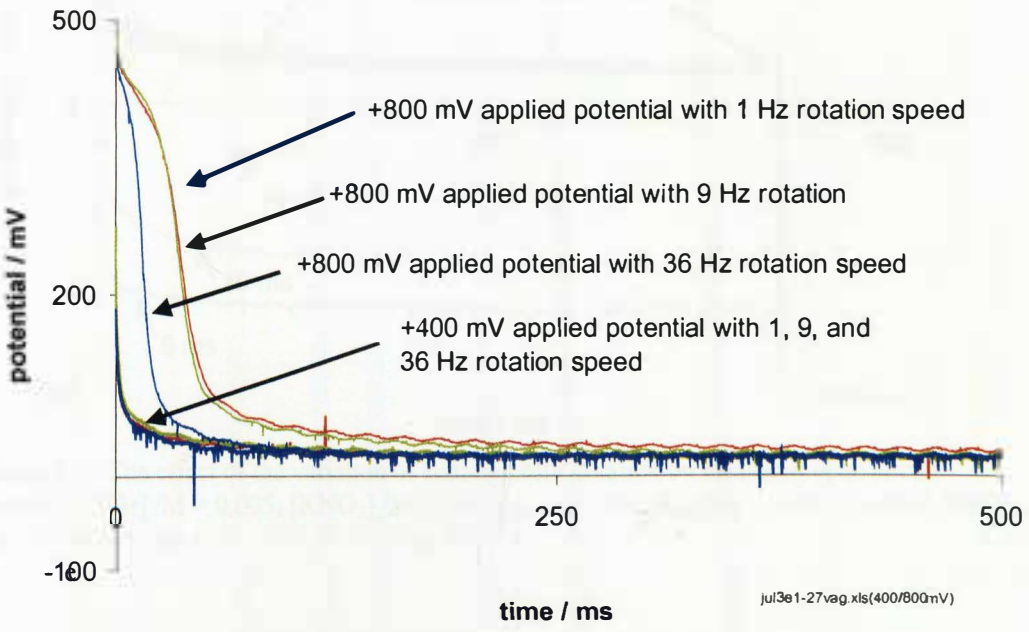


Figure 4.38 The effect of the variation of applied coating potential on measured open circuit potential at 1, 9 and 36 Hz Hz rotation speed. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400,800; t_D /ms = 10; W_{SPE} = W_{CP} /Hz = 1,9,36.

4.4.6.4 Variation of coating pulse duration

To determine the effect of the coating pulse duration on rate of change of the measured open circuit potential, a set of experiments was carried out where the pulse duration was varied from 5 to 100 ms (Figure 4.39). At coating pulse durations greater than 20 ms the open circuit potential value changed by 95% in less than 50 ms. The final measured potential value was the observed to be similar at all values of coating pulse duration greater than 20 ms.

At values below 20 ms the open circuit potential profile was offset by a large negative potential, the shorter the pulse duration the more negative the offset. The

open circuit potential fell towards a more negative potential than either the theoretical or the conventional electrode. The measured value did not reach a steady value by 400 ms but continued to fall.

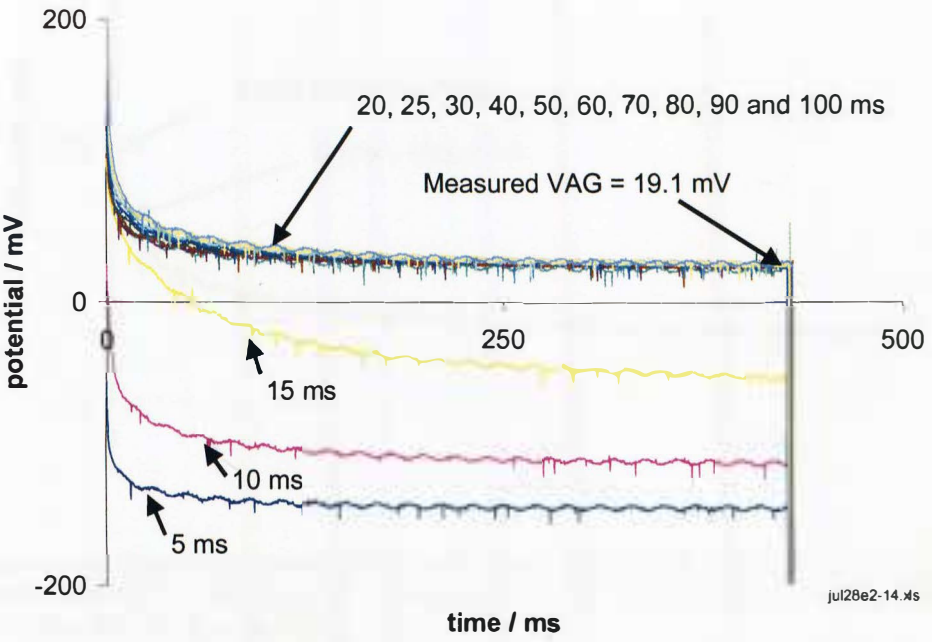


Figure 4.39 The effect of the variation of coating pulse duration on measured open circuit potential. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /ms = 5…100; $W_{SP} = W_{CP}$ØHz = 9.

4.4.6.5 Effect of number of cycles on open circuit potential

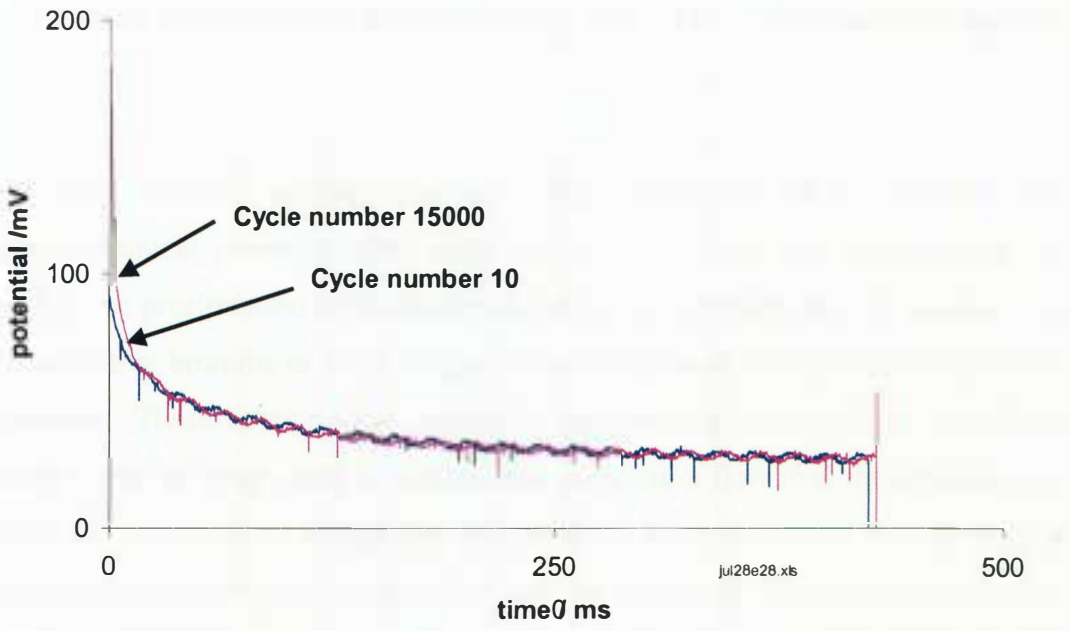


Figure 4.40 Open circuit potential for cycle 10 and cycle 15000 of a four-hour run. [KBr] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP}/mV = -400; t_{CP}/ms = 100; E_{CP} /mV = +400; t_D /ms = 300; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

The open circuit potential curves for two cycles of the technique (Figure 4.40), one at the start (cycle 15) and one at the end of a four hour run (cycle 15000) showed almost identical profiles.

4.4.6.6 Discussion - approach to the steady state open circuit potential

Initial experiments with stripping and coating applied potentials set at –400 and +400 mV and where the rotation speed of the silver electrode was varied during the stripping and coating pulse showed negligible difference in either the rate that the measured open circuit potential approached the theoretical VAG or the final potential attained (Figure 4.35). However, when the applied coating potential was increased above +500 mV the time taken for the measured open circuit potential to reach a steady value increased with increasing applied potential. This longer equilibrium time was reduced if the rotation speed of the electrode was increased.

During the coating pulse the concentration of bromide ions close to surface of the silver electrode was reduced as silver bromide was formed on the surface quicker

than could be replaced from the bulk solution. On switching to open circuit, the potential of the silver bromide electrode was therefore more positive than the equilibrium value while the surface concentration of bromide returned to the bulk level.

At more positive coating potentials than +500 mV, it is probable that electrochemical processes other than oxidation of silver were taking place. As well as the precipitation of bromide ions to form silver bromide at the surface, it is possible that bromine or other complex ions are formed at or in the surface of the electrode. These other ions or molecules can take longer to diffuse out of the surface and be swept away by the rotation convection flow than the bromide ions from the bulk take to diffuse into the diffusion layer. It is also possible that at more positive coating potentials silver ions are produced faster than bromide ions can diffuse in. The open circuit potential would therefore be more positive until the silver ions had been precipitated by bromide ions diffusing in and the surface layer returned to the bulk bromide concentration. The time taken for the measured open circuit potential to reach a steady therefore increased as the applied potential increased.

Varying the applied stripping pulse potential showed no observable difference in the open circuit potential profile and value of the measured open circuit potential if the potential was set between –200 and –600 mV. At an applied potential of –700 mV, the open circuit potential fell to approximately 20 mV more negative than either the theoretical or conventional value. At these more negative applied potentials it is possible that metal ion impurities in the system partially plated onto the electrode surface. The effect was not observed to decrease with rotation speed and the measured open circuit potential did not return to the 'expected' profile if the applied potential was changed to a more positive value during the experiment – even after several hundred cycles. The effect was therefore not caused by ions or molecules generated in the diffusion layer, which would have been swept away at higher rotation speeds, but was a permanent electrode surface effect. This effect was only removed when the silver electrode was polished.

Experiments to investigate the effect of the coating pulse duration and hence the effect of coating different amounts of silver bromide onto the electrode surface showed that no observable difference in open circuit potential profile or value when the duration was at least 20 ms. At values below this the open circuit potential was seen to drift away from the expected value to a more negative potential. In 4.4.4.5 the amount of silver bromide converted on the surface during the second section of the current curve was related to the charge drawn and it was proposed that this section of the curve related to the completion of a monolayer of silver bromide on the electrode surface. The parameters set for this experiment were the same as those used in 4.4.4.4 (Figure 4.32). From these curves it was seen that the formation of a monolayer reaches completion at around 18 ms. It was therefore thought that when the coating pulse duration was set to a value less than 18 ms, bare silver would still be exposed and in contact with the measurement solution. From earlier work (Sandifer, 1993) it has been shown that even small amounts of bare silver on the surface of the electrode can cause the open circuit potential to be unstable. The value of 18 ms for completion of a monolayer of silver bromide compares well with the open circuit potential profiles seen for these experiments with coating pulse durations set below and above that value.

The open circuit potential was unaffected by the number of cycles that had been performed on the silver surface. The current profiles for the stripping and coating currents from the 10th and 15000th cycles of a run showed no observable difference and indicated that the surface was refreshed at each cycle (Figure 4.40). The open circuit potential for these cycles also showed an identical profile confirming this conclusion.

4.4.7 The effect of bromide on the clean/coat/measure cycle.

When the potassium bromide concentration was increased from 0.0005 M to 0.013 M by adding concentrated bromide the measured open circuit potentials at 500 ms for the 0.013 M, 0.003 M and 0.001 M potassium bromide solutions were 0.7, 34.2 and 60.5 mV (Figure 4.41). These were in reasonable agreement with the values of at –0.8, 32.8 and 58.9 mV obtained for a conventional silver bromide

coated electrode left to reach equilibrium for 2 minutes. The calculated theoretical values were –6.8, 24.5 and 52.1. The offset of –6.0 mV was most likely caused by an offset in the reference potential due to the non-standard reference electrode configuration. The open circuit potential curve for 0.0005 M potassium bromide showed a drifting potential that did not reach equilibrium but that was 169.9 mV at 500 ms. The value obtained for the conventional electrode was 67.8 mV.

A further experiment where the solutions with varying bromide concentrations were measured separately and the measured potential was monitored for longer by increasing the interval between stripping-coating cycles, revealed that the measured potentials decreased by a further 1 to 2 mV over a period of 4 s (Figure 4.42). This is an important observation since it demonstrates that the potentials at 500 ms are not at steady state.

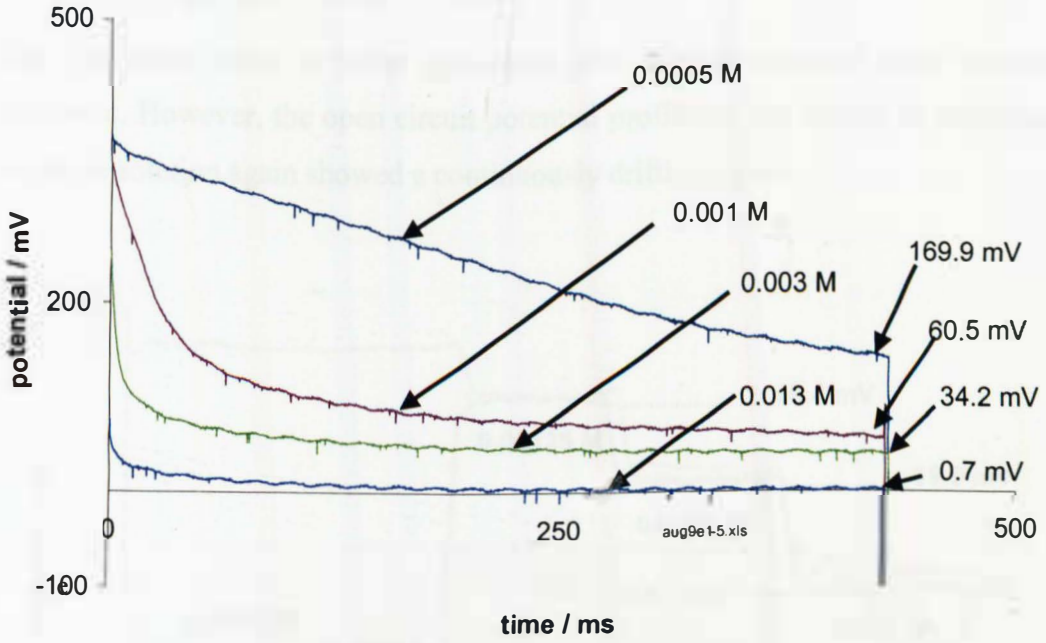


Figure 4.41 Varying Bromide concentration by addition. [KBr] /M = 0.0005…0.013; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /ms = 250; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

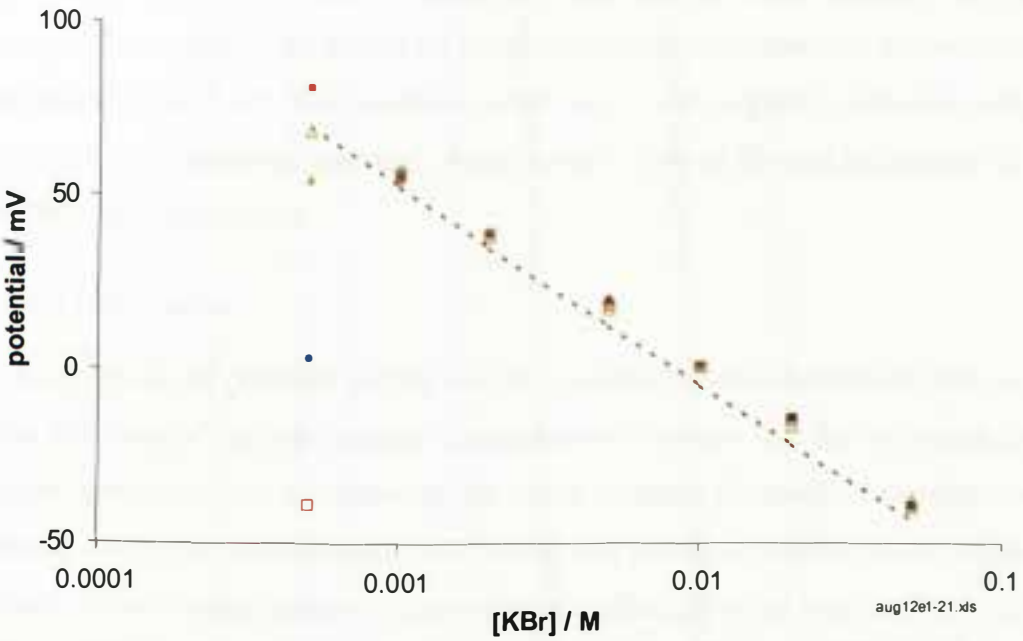


Figure 4.42 Variation of potassium bromide concentration on measured open circuit potential. CCM VAG time after start of cycle: (■) 1 s; (▲) 2 s; (●) 3 s;(□) 4 s; (\) conventional electrode. [KBr] /M = 0.0005…0.05; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /ms = 250; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

The 4 s values were in better agreement with the conventional silver bromide electrode. However, the open circuit potential profile for the 0.0005 M potassium bromide solution again showed a continuously drifting signal.

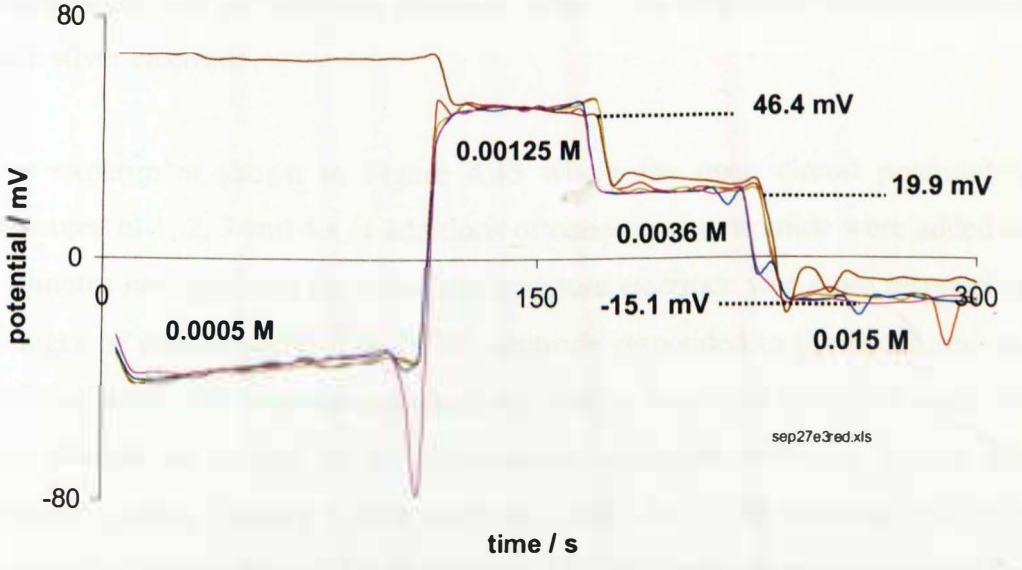


Figure 4.43 Varying Bromide concentration by addition with theoretical values marked for each concentration and the CCM VAG time after start of cycle: (—) 1 s; (—) 2 s; (—) 3 s;(—) 4 s; (—) conventional electrode. [KBr] /M = 0.0005…0.015; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /ms = 250; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

A second experiment with the bromide concentration being increased step-wise over a five-minute time period by addition of potassium bromide showed similar results (Figure 4.43). The measured value at 4 s was in good agreement with the conventional electrode potential. Again results showed deviant behaviour for the 0.0005 M concentration.

4.4.7.1 Discussion

The open circuit potential profile and the potential values observed at 500 ms for the solutions of various bromide concentrations indicate that the technique gives good agreement with the conventional silver bromide electrode at concentrations above 0.0005 M. At concentrations below, this profile is similar to that obtained when a short coating pulse or a low coating applied potential was used. It is likely that, as in those cases, a complete monolayer has not been coated onto the silver electrode.

When the monitoring of the open circuit potential was extended to 4 s, the measured value at 1, 2, 3 and 4 s was in better agreement with the conventional electrode values. The longer monitoring of the solution of 0.0005 M bromide concentration showed that after 4 s the potential value had drifted much more negative than the conventional electrode value. This behaviour was indicative of a bare silver electrode.

The experiment shown in Figure 4.45 where the open circuit potential was measured at 1, 2, 3 and 4 s as additions of concentrated bromide were added over 5 minutes indicated that the clean/coat/measure electrode was more responsive to changes of concentration. The CCM electrode responded in the cycle after each addition while the conventional electrode took at least one more full cycle. This was thought to be due to the conventional electrode having a thicker silver bromide coating causing a slow response while the CCM electrode had a thin coating that responded quickly to changes. This has been previously reported (Lin, 1989).

All three examples of experiments shown clearly indicate that the technique is capable of giving results in close agreement with convention silver bromide electrodes at concentrations above 0.0005 M. An upper limit of concentration could not be inferred from the experiments carried out for this project.

4.4.8 Results from experiments with bromide and iodide present

4.4.8.1 Effect of adding iodide to a bromide solution

Two experiments were carried out to show the effect of adding iodide to a bromide solution, the first where the bromide concentrations was at the low end of the useful range and the concentration of iodide added was lower and the second where the concentration of bromide was in the middle of the useful range and the iodide was of the same concentration. In the first experiment the measured open circuit potential at 1, 2, 3 and 4 s was observed to drop to the theoretical value of a pure iodide solution almost instantly while the conventional electrode only responded by moving more negative by a few millivolts (Figure 4.44, bottom).

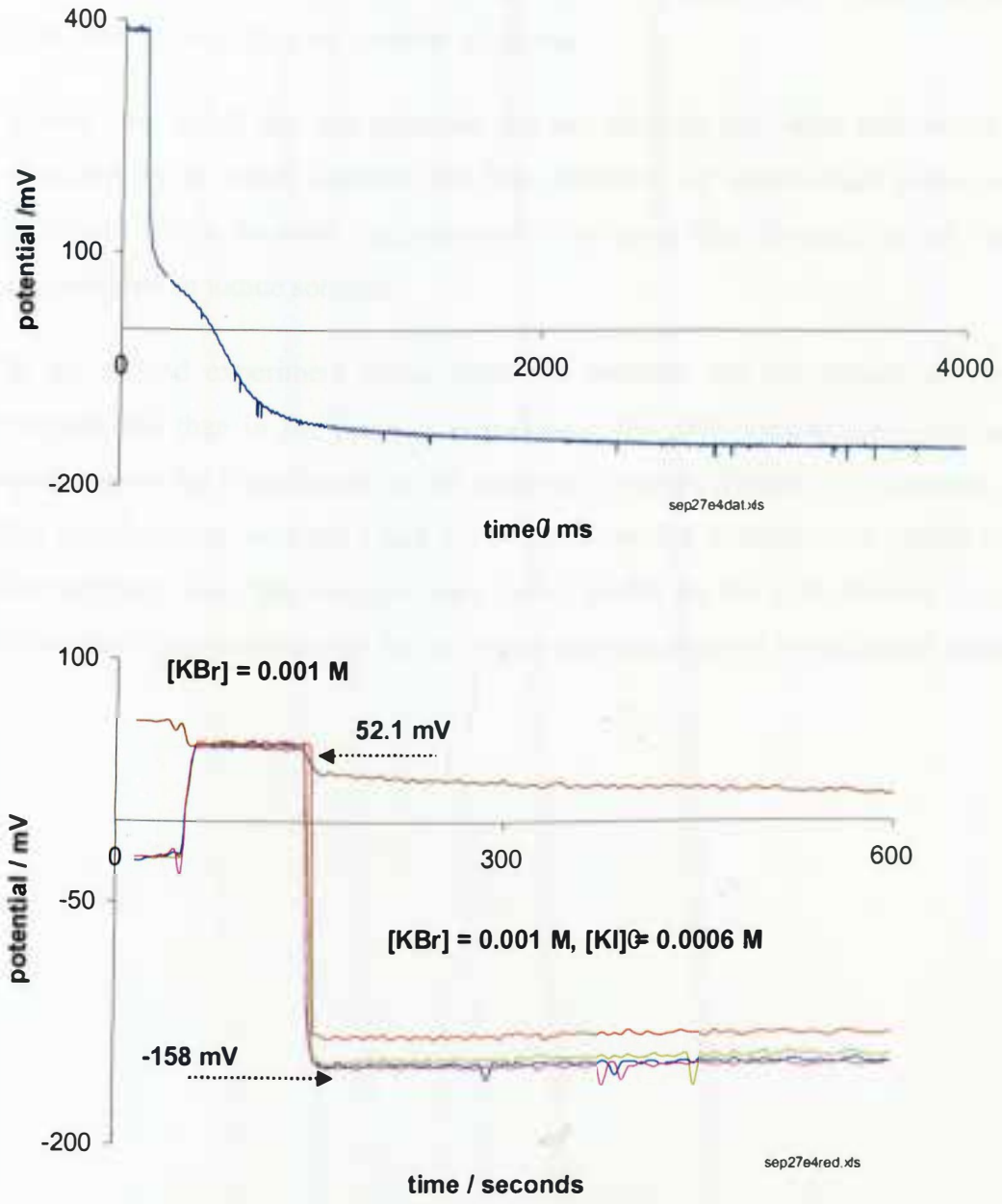


Figure 4.44 Effect of adding iodide to a bromide solution. Open circuit potential recorded over last cycle(top) and potential values recorded at 1, 2, 3 and 4 s over 10 minute experiment (bottom). CCM VAG time after start of cycle: (—) 1 s; (—) 2 s; (—) 3 s;(—) 4 s; (—) conventional electrode. [KBr] /M = 0.001, 0.001; [KI] /M = 0.0006M; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /ms = 100; E_{CP} /mV = +400; t_D /ms = 250; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

It was not possible to calculate the theoretical potential for this mixed halide solution but for this purpose the bromide was taken to have no effect on the potential when calculating the expected value. It was observed that when the iodide was added the 1 s value was now 20 to 25 mV more positive. Observing

the potential profile of the cycle (Figure 4.46, top) it was noted that the time taken for the open circuit potential to approach the equilibrium value increased significantly over the pure bromide solutions.

It was also noted that the potential did not drop to the value that would be expected for an iodide solution but first moved to an intermediate value more indicative of the bromide concentration. The curve then dropped to the value expected for an iodide solution.

In the second experiment where both the bromide and the iodide are more concentrated than in the previous experiment, the clean/coat/measure electrode again responded immediately to the addition of iodide (Figure 4.45, bottom). In this case however, both the 1 and 2 s values showed a more positive profile than the expected value. The measure open circuit profile for the cycle showed a more pronounced intermediate step for the higher concentrations of bromide and iodide.

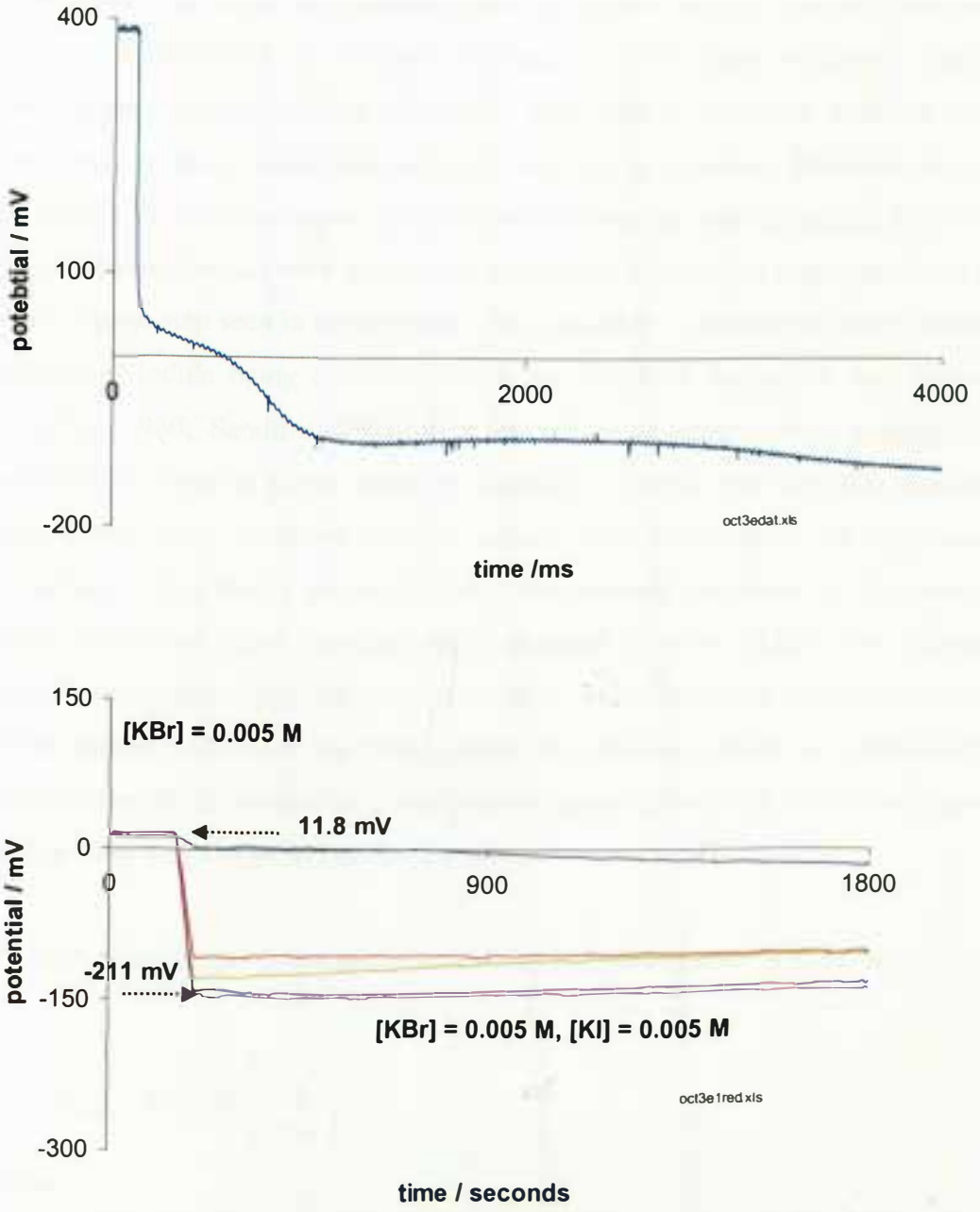


Figure 4.45 Effect of adding iodide to a bromide solution. Open circuit potential recorded over last cycle (top) and potential values recorded at 1, 2, 3 and 4 s over 10 minute experiment (bottom). CCM VAG time after start of cycle: (—) 1 s; (—) 2 s; (—) 3 s;(—) 4 s; (—) conventional electrode. [KBr] /M = 0.005; [KI] /M = 0.005; [KNO_3] /M = 0.05; t_{SP} /ms = 200; E_{SP} /mV = -400; t_{CP} /mse= 100; E_{CP} /mV = +400; t_D /ms = 250; W_{SP} /Hz = 9; W_{CP} /Hz = 9.

4.4.8.2 Discussion

The addition of iodide to a bromide solution showed that the clean/coat/measure technique responded to changes in halide much more efficiently than a conventional silver bromide electrode. The final 4 s values were in good agreement to those calculated assuming pure iodide solutions. However, the rate of change in measured open circuit potential from the end of applied pulse was much slower than had been seen for pure bromide solutions. It is proposed that the intermediate step seen in these profiles was caused by a mixture of silver bromide and silver iodide being coated on the silver electrode surface. It was reported (Rhodes, 1980; Sandifer, 1981) that thin silver bromide surface coatings are quickly converted to silver iodide by solution of iodide. For very thin coatings, just a few layers of silver bromide atoms, these conversions are very rapid, occurring in less than a second. Initially the electrode responded to the bromide ions, but as the silver bromide was converted to silver iodide, the electrode quickly responded to the iodide in the solution. This effect may have been avoided if the applied potential of the coating pulse (E_{CP}) had been made less positive after the addition of the iodide. At a less positive potential only the iodide in solution would have been converted to silver iodide.

The potential that the silver metal is oxidised and silver halide is given by;

$$E = E^{0}_{Ag/Ag^{+}} + \frac{RT}{nF} \ln \left[\frac{a_{Ag^{+}}}{a_{Ag}} \right]$$

where

a_{Ag} is taken as 1 for the solid silver and $a_{Ag^{+}}$ is defined by the solubility product of the halide present.

$$a_{Ag^{+}} = \frac{a_{X^{-}}}{K_{spAgX}}$$

For mixed halide solutions the silver ion activity at the electrode surface and the potential of the oxidation is determined by the least soluble halide. When the least soluble halide is depleted by precipitation faster than diffusion of the halide ion to the surface, the solubility product of the next least soluble halide determines the oxidation potential. Therefore the formations of the halide layers occur at different potentials. In the case of a solution of iodide and bromide using a less positive potential would ensure that only the iodide was coated.

Changing the coating potential in a real process measurement would be difficult as it is not necessarily know when this addition is to occur.

4.6 Summary

In carrying out the experiments in the previous sections a clear understanding of the parameters that were required to control the process sufficiently to be able to strip, coat and make a reproducible measurement of the open circuit potential of the silver electrode was obtained. The limits of the technique were found and possible problems for future use uncovered.

When investigating the stripping pulse it was found that applied potential must be within a window of –200 to –600 mV. At potentials lower than this the time taken to completely clean the electrode surface was too long and at applied potentials greater than this permanent damage was done to the surface of the silver electrode leading to erroneous open circuit potential measurements. The duration of the stripping pulse need only be as long as the coating pulse as at least 99% of the charge was drawn before this time. In practice an applied potential of –400 mV and stripping pulse duration of 100 ms gave good results. The stripping process was found to be unaffected by the rotation speed of the electrode.

It was necessary that the applied potential of the coating pulse was set between 100 and 500 mV, above this value other processes occurring at the electrode surface caused the open circuit potential to respond slowly when the applied

potential was switched off. Below 100 mV reliable silver bromide coating of the electrode did not occur and the open circuit potential drifted to negative values indicative of a bare silver electrode. It was found that the duration of the coating pulse was dependant on the applied potential but that the total charge passed should be greater than 3.5×10^{-5} C. Good results were achieved with applied potential set at +400 mV and the duration of the coating pulse set greater than 20 ms. Although the coating process was effected by the rotation speed, this effect was not important if the other parameters were set such that a good coating was achieved.

The open circuit potential was unaffected by the number of cycles that had occurred since the electrode had been polished. When a delay was inserted between the stripping and coating pulses the bromide concentrated during the stripping process was allowed to diffuse away. However, there was no indication that this affected the open circuit measurement and there was some evidence that a delay actually caused the response time of the open circuit potential to increase. As the speed of rotation of the silver electrode increased the response time reduced. However, the effect was not great enough to make the process dependant on rotation speed. Both the open circuit potential profile and the final value were unaffected by stripping and coating pulse duration and applied potential as long as they were in the window described above.

The technique was found to be in reasonable agreement with both theoretical calculations and a measured conventional silver bromide electrode in the concentration range 0.001 M to 0.05 M. Below 0.001 M the technique did not give reliable results. Concentrations above 0.05 M were not investigated.

The technique responded to addition of iodide, giving values in good agreement with calculations while the conventional silver bromide did not respond. However for mixed halide solution it was observed that the response time was affected and a longer time after the end of the pulse and before the measurement was made were found to be necessary.

From this investigation it was possible to determine a set of parameters that gave reliable results. These were:

Parameter	Symbol	Condition
Stripping pulse duration /ms	t_{SP}	100
Stripping pulse potential /mV	E_{SP}	$-600 < E_{SPt} < -300$
Stripping pulse rotation speed /Hz	W_{SP}	Not important
Coating pulse duration /ms	t_{CP}	100
Coating pulse potential /mV	E_{CP}	$+300 < E_{CP} <$ +500
Coating pulse rotation speed /Hz	W_{CP}	Not important
Delay between stripping and coating pulses /ms	t_D	0
Measurement time (after coating pulse)	t_m	> 500 ms [Br^-] > 3 s [Br^-] and [I^-]

Table 4.8 Optimised conditions

Chapter 5. Experiments in "clean/coat/measure" technique using cylindrical electrodes in stirred solutions with a controlled potential.

5.1 Introduction

Although the use of a rotating disc electrode gave good results for the determination of bromide in solutions containing bromide and iodide their use in production environments is not practical due to the problems associated with the rotating mechanism. This part of the project investigates the possibility of using the clean/coat/measure pulse technique with fixed electrodes in stirred solutions. Small 2 mm cylindrical silver electrodes, previously tested and reported in Chapter 3, were used to investigate the technique in a simulated emulsion manufacturing vessel containing stirred solutions. As before the cycle comprised a cleaning or stripping pulse, a coating pulse and a measurement step.

Two methods were used to produce the clean-coat pulses. The first used a programmable potential controller to apply a potential directly to the silver electrode. The current flowing through the circuit to the silver electrode was measured directly. This method differed from the potentiostat used in Chapter 4 in that the potentiostat applied a reverse potential to a large counter electrode and connected the working electrode to a virtual earth. The current flowing through the working electrode to the virtual earth was measured via an I-E converter amplifier. This method, using a programmable potential controller, will be described in this chapter.

In the second method a simple constant current circuit was used to apply a potential to the silver electrode such that the current flowing through the silver

electrode to the counter is constant. This method will be described in the next chapter, Chapter 6.

The open circuit potential or VAG process control value was taken from a fixed time after the cycle and the control signal held constant at that value until the same point in the next cycle.

Due to the large amount of data needed to be collected it was decided to base the investigation on solutions containing bromide ions. Once the system was optimised on bromide solutions, calibration curves for potassium chloride, bromide and iodide at various concentrations were obtained. Experiments were carried out using a purpose built, robust potential controller. Initially, stripping and coating pulse durations of between 100 and 400 ms were investigated in bromide ion concentrations of between 0.0001 and 0.1 M at a constant temperature of 25 °C. An example of the addition of potassium iodide to a potassium bromide solution is shown for the controlled potential system.

5.2 Equipment and instrumentation

Throughout this research project all instrumentation utilised a Compaq 486 PC fitted with Analog Devices RTI 800 series analogue to digital, digital to analogue and input/output cards. These were used to both control all necessary functions and timings and to collect all data. Software programs were written in Quick-Basic V4.0. An electronic module with pulse control and data collection circuits was designed to connect these cards to the measurement electrodes and equipment.

The simulated emulsion manufacturing system comprised a 1000 ml stainless steel beaker immersed in a water bath. A powerful overhead stirrer was used to ensure efficient mixing of solutions. Solutions were added from two Hamilton dispensers controlled by use of the serial communication line from a second PC.

Up to four electrodes plus the solution ground could be held in clamps above the vessel and immersed in the solution.

5.2.1 Analogue Devices RTI815 and RTI850 PC cards

The RTI815 and RTI850 PC cards were used to control the pulse circuit and to measure the open circuit potential of the silver electrode. These boards were set-up in slightly different modes than before to allow control of the new circuits and to collect both fast data during the cycle and the open circuit potential measurement at intervals during the cycle.

5.2.2 RTI800 software functions

The functions needed to control the RTI850 data collection card and the RTI815 input/output card described in the previous chapter were again used.

5.2.3 Programmed potential pulse controller

The pulse control interface module combined the differential circuits, previously used to measure the equilibrium potentials and described in chapter 3, and the necessary circuits to produce the cleaning and coating potential pulses. As in Chapter 4, a software program controlling the voltage output and I/O ports of the RTI815 card produced the pulses. The analogue signal was used to control the potential applied to the silver electrode while the I/O ports were used to control two reed relays, which isolated the pulse circuitry from the differential amplification circuit during open circuit measurement. Four channels of the analogue to digital RTI850 card were used to measure the potential and current of the clean/coat/measure electrode and, either a bare silver electrode and a coated silver halide electrode or two coated silver halide electrodes.

As in the case of equilibrium measurements these experiments were carried out in the simulated emulsion manufacturing vessels so that the solution addition and control equipment could be used. Simple potentiostat circuits as shown in Figure 5.1 did not give stable applied potentials. This was thought to be due to the

potential difference between the counter electrode and the earthed vessel. Due to the size of the earthed vessel large currents flowed from the counter to the vessel side. The output of the counter amplifier could never reach its required value without the amplifier becoming overloaded. The output voltage of the amplifier then dropped so that it was running at maximum output current. Larger amplifiers were tried as well as buffer amplifier stages.

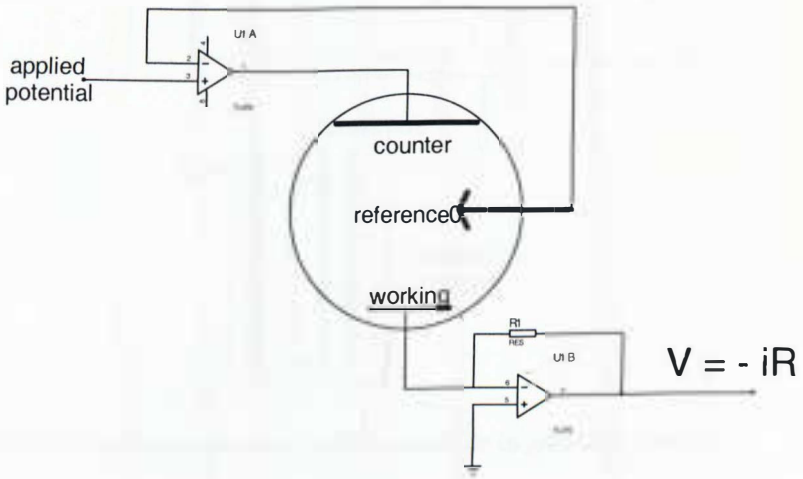


Fig 5.1 Simple potentiostat circuit

A more complex circuit where the potential was applied directly to the silver electrode rather than a counter was designed (Figure 5.2). The applied potential was referenced to the actual VAG measured by the differential circuit by using this voltage as a feedback loop to the output amplifier. The output of the amplifier was then in balance between the feedback from the VAG and the applied voltage from the PC card. The current was determined by measuring the voltage across a resistor in series with the silver electrode. The circuit also incorporated reed relays to disconnect the output pulse circuit when open circuit equilibrium measurements were being made. Although this was a more complex circuit, needing two relays, the applied potential was more stable. Considerable care was needed in laying out the circuit to avoid large ac noise in the current measurement circuit. Resistors

were mounted as close a possible to the amplifier with the length of unshielded leads kept to a minimum.

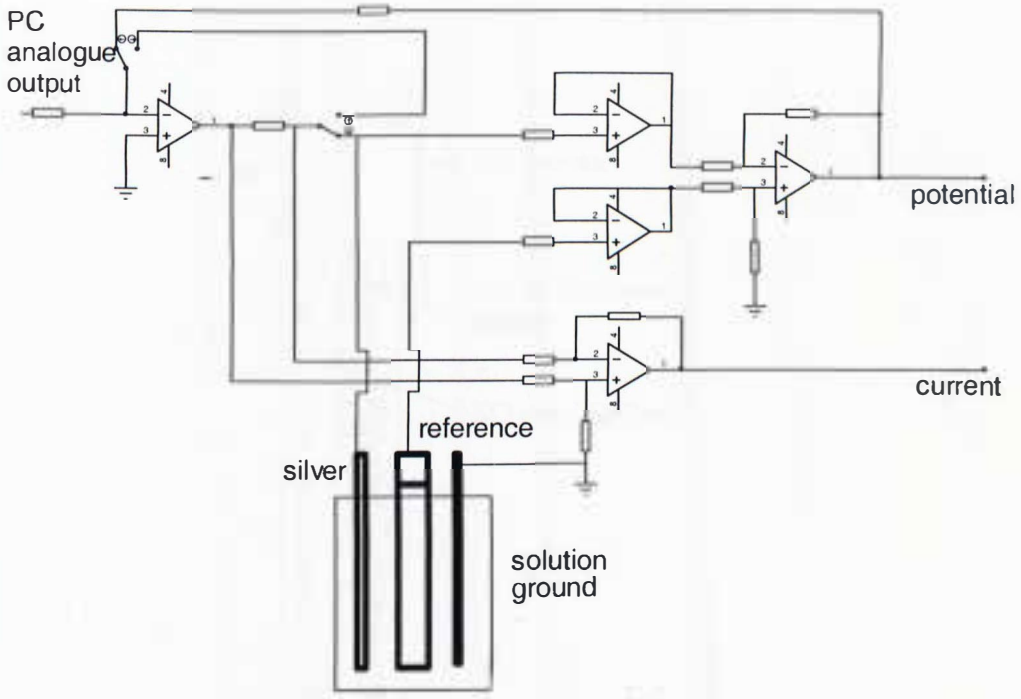


Figure 5.2 Circuit for applying potential to silver electrode in grounded vessels.

5.2.4 Electrodes

The small cylindrical silver electrodes measuring 2 mm long by 2 mm diameter and described in Chapter 3 were used for all measurements. Before each experiment the silver clean/coat/measure (CCM) electrode was cleaned and polished as described previously. The reference triple junction bridge reference system used for the equilibrium potential measurements in Chapter 3, was replaced with a double junction salt bridge with a non-commercial hydrogel reference electrode dipped into the lower bridge solution (Figure 5.3). This utilised a polymer filled reference electrode developed and patented by Kodak Ltd (Edwards, 1990) specifically for use in the measurement of photographic emulsions. In this electrode the internal fill and the upper bridge solution was replaced by hydrogels containing appropriate levels of salts. This electrode was more robust, more stable and needed less maintenance than the triple junction system. Unlike the hydrogel reference used in Chapter 4 where all three bridge solutions were replaced by hydrogels this electrode system still utilised a lower

bridge and junction. This allowed the reference electrode to be maintained at 25 °C while the lower bridge junction could be placed in a solution of higher temperature.

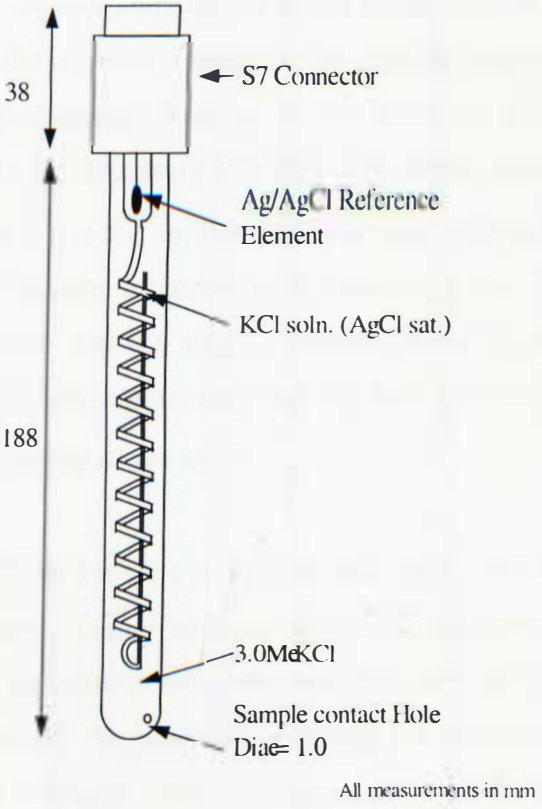


Figure 5.3 Hydrogel reference electrode

This electrode was maintained at 25 °C for the duration of the experiments, about 12 months and stored in potassium nitrate bridge solution when not in use. The reference electrode was checked against a standard silver chloride electrode in 0.1 M potassium chloride every month and was found not to drift appreciably over the duration of the experiments.

5.2.5 Software

Software to control the RTI 850 and 815 PC cards was written in Quickbasic V4.0 using the compiled library discussed in 4.2.5. On starting the program (Figure 5.5), keyboard input was entered for experiment identification purposes, pulse length, pulse voltage or current and number of cycles to be completed. In this

investigation the lengths of stripping and coating pulses were set to be identical to allow less complex non-PC based pulse equipment to be used in production. Each cycle started with the RTI800 cards being initialized and the relays switched to the open circuit position for measurement. The data collection function was started and values for the potential and current of the CCM electrode stored in memory. After a short delay, the potential necessary for cleaning was applied and the relays switched to the pulse circuit. Factors in the software converted the required applied potential into the necessary RTI 815 card output voltage. After the preset time for the cleaning pulse the applied potential was changed to the value set for the coating step for the time required for the coating pulse. The relays were then switched to open circuit and the applied potential reset to zero. The equilibrium potential of the CCM silver electrode and the two comparison electrodes were measured for the remainder of the cycle.

Data was collected from the start to end of each cycle and the applied potential and current during the cleaning and coating pulses recorded. At the end of the cycle the data stored in memory was converted into mV and μA and stored into a text file for later analysis. At preset times during the cycle open circuit potential (VAG) values were averaged from 10 consecutive points and appended to a second file. This file held VAG data for all cycles throughout the experimental run. Data was not always collected for the whole of each cycle. This allowed long times to be set between cycles with data only collected for the first part of the cycle. The cycle time was designated as t_c^e while the data collection time duration was $t_{measure}$ and the time after the start of the averaged VAG measurement as t_m^e. The stripping and coating pulse times were designated as t_{SP} and t_{CP} (Figure 5.4).

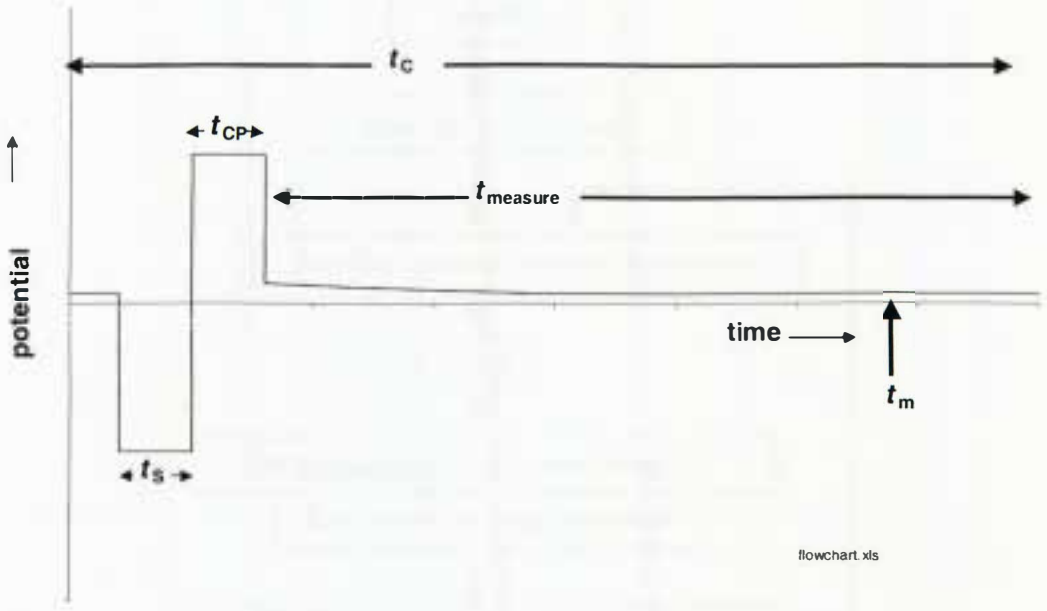


Figure 5.4 Clean/coat/measure timing cycle

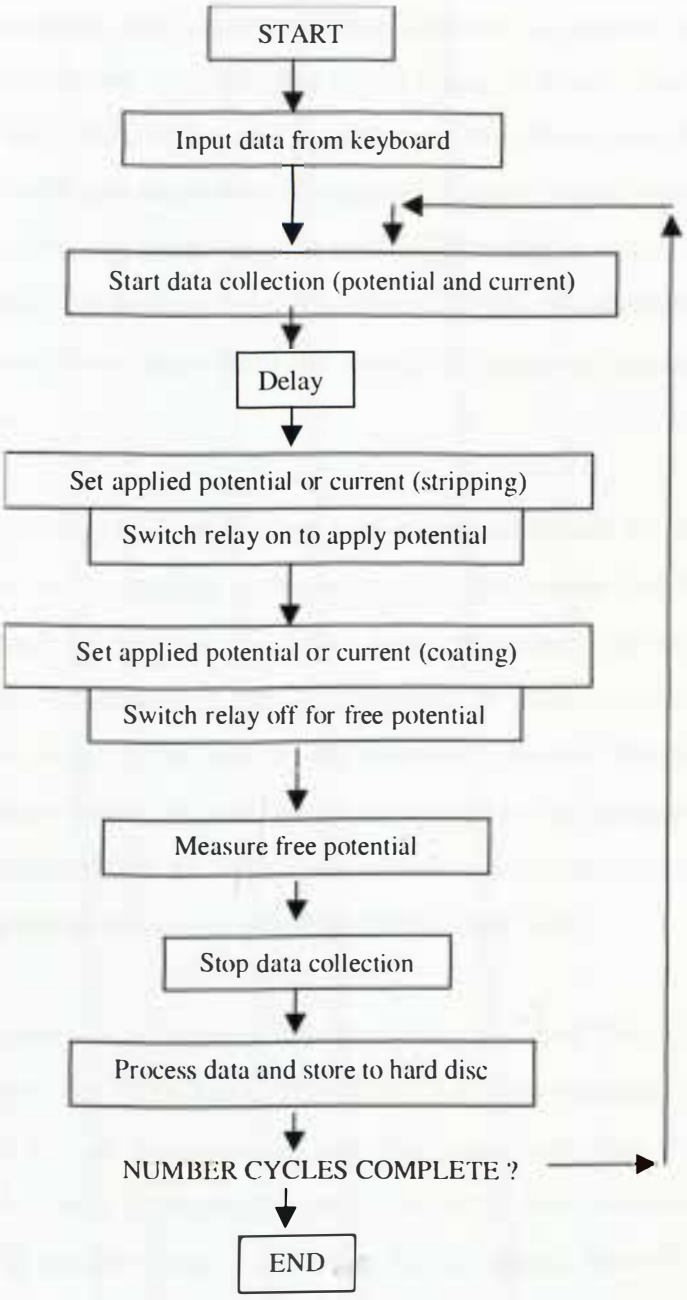


Figure 5.5 Clean/coat/measure program flow chart.

5.3 Experimental methods and details

All experiments were carried out in a 1000 ml 316 stainless steel vessel fitted into a temperature controlled water bath. For the purpose of this study the water bath was held at 25 °C for all experiments. The vessel was filled with 500 ml of the test solution and left for 30 minutes for the temperature to reach equilibrium. The

CCM silver electrode, the reference bridge junction, a platinum solution ground and a temperature probe were secured into a clamp to ensure that the position of all electrodes was identical for all experiments. The clamp was designed to hold two additional indicator electrodes if required. A glass vessel with a water jacket maintained at 25 °C and containing the salt bridge solution, was held 40 cm above the level of the test solution. At the start of each experimental run the gel reference electrode was taken from the storage solution and immersed in the salt bridge solution.

In production, photographic emulsions may be manufactured by adding the silver nitrate solution to a solution containing only potassium halide held in the production vessel. In this case no other ions are present, so the ionic strength depends only on the potassium halide. However, in most case other components are added to the vessel at the start. It was therefore assumed that the ionic strength would be at least 0.001 M and in all experiments the potassium halide test solutions contained 0.001 M potassium nitrate. Later, the ionic strength of the solution was raised to determine if it affected the final VAG.

The electrode clamp was lowered into the vessel ensuring that all the electrodes were immersed to the same level. The stirrer was then switched on to the same constant speed for all experiments and the pulse interface software started. Addition of either more concentrated potassium bromide or solutions of iodide ion were added from the dispensers by sending RS232 signals from the second PC. A small software program allowed the required volume to be entered into the PC and the addition activated by pressing the enter key when the planned time in the experiment had been reached and the solution was required.

Data collected for each experimental run was stored in two types of file; the first contained the raw data for each cycle and the second contained the VAG value averaged at 4 points in the measurement part of the cycle (D).

5.3.1 Experimental procedures

5.3.1.1 Cyclic voltammetry

As with the silver rotating disc electrode, initial experiments were carried out to investigate the applied potential required to oxidise the silver metal electrode to silver bromide and to reduce the silver bromide coating back to silver metal. To determine the correct potentials, cyclic voltametry was performed on a 0.1 M potassium bromide solution using the small cylindrical CCM electrode, a large platinum counter (Metrohm) and a silver chloride reference electrode (Corning 476029). A Princeton Applied Research PAR174 potentiostat was used with the cycle time set at 60 seconds and the potential scan range at –700 to +900 mV. Data was stored in the PC using the RTI850 PC card running a standard data-logging program supplied from Analogue Devices.

To verify that the potential pulse controller was performing as designed a cyclic voltamogram was also obtained using the controller and the same electrodes. A software control program was written to allow the applied potential to be cyclically stepped from zero through +0.9 V and –0.7 V and back to zero.

5.3.1.2 Variation of pulse duration

The software program was loaded and a series of experiments performed with the stripping and coating pulse duration, t_{SP} and t_{CP}, varied between 50 ms to 200 ms. The stripping pulse was fixed at +500 mV and the coating pulse fixed at –500 mV. The stainless steel vessel was filled with 500 ml of 0.1 M potassium bromide and allowed to reach 25 °C. The silver CCM electrode was polished and rinsed in acetone and demineralised water before each experiment. The software program was set to run for a total of 2 min with the CCM cycles timed to occur every 5 s. Data was collected from 4 channels: CCM potential, CCM current, bare silver electrode and silver bromide coated electrode for 4 seconds from the start of each cycle. This was repeated with concentrations of 0.01, 0.001, 0.0005 and 0.0001 M potassium bromide.

Parameter	Symbol	17-25kpccm.xls
Stripping pulse duration /ms	t_{SP}	50 - 200
Stripping potential /mV	E_{SP}	-500
Coating pulse duration /ms	t_{CP}	50 - 200
Coating potential /mV	E_{CP}	+500
Cycles interval /ms	t_C	5000
[bromide] /M	c_{Br}	0.0001 - 0.1

Table 5.1 Conditions used to investigate the effect of stripping and coating pulse duration

5.3.1.3 VAG value point versus time after pulse

To determine the change in VAG value with respect to time after the coating pulse two potassium bromide solutions of different concentration were tested. VAG values were calculated by averaging 10 consecutive 0.2 ms readings at 0, 0.5, 1.0, 2.0, 3.0 and 4.0 s after the start of each cycle. The VAG values at 0 s were equivalent to the last point of the cycle i.e. 5 s. An average of these VAG values over 24 cycles was then taken to determine the effect of the time after the coating pulse on the VAG. This data was recorded in a separate data file for each experiment.

Parameter	Symbol	28-29kpccm.xls
Stripping pulse duration /ms	t_{SP}	50
Stripping potential /mV	E_{SP}	-500
Coating pulse duration /ms	t_{CP}	50
Coating potential /mV	E_{CP}	+500
Delay between cycles /ms	t_C	5000
[bromide] /M	c_{Br}	0.0001, 0.1
[KNO_3] /M	c_{KNO_3}	0.001

Table 5.2 Conditions used for the investigation of the CCM VAG potential versus time after cycle start.

5.3.1.4 Variation of applied potential during coating pulse

Experiments were carried out with a fixed coating pulse length of 100 ms and with applied potentials varying from +200 mV to +600 mV. The stripping pulse was set at –500 mV for 100 ms for all experiments. The cycle duration was set at 5 s with the open circuit potential being measured for the remainder of the cycle as before.

Parameter	**Symbol**	**26kpccm10.xls**
Stripping pulse duration /ms	t_{SP}	100
Stripping potential /mV	E_{SP}	-500
Coating pulse duration /ms	t_{CP}	100
Coating potential /mV	E_{CP}	+200 - +600
Delay between cycles /ms	t_C	5000
[bromide] /M	c_{Br}	0.1

Table 5.3 Conditions used to determine the effect of coating potential on CCM VAG.

5.3.1.5 Effect of bromide concentration on CCM VAG

Potassium bromide concentrations in the range 0.0001 M to 0.1 M were investigated

Parameter	**Symbol**	**21-25kpccm.xls**
Stripping pulse duration /ms	t_{SP}	400
Stripping potential /mV	E_{SP}	-500
Coating pulse duration /ms	t_{CP}	400
Coating potential /mV	E_{CP}	+500
Delay between cycles /ms	t_C	5000
[bromide] /M	c_{Br}	0.0001 - 0.1

Table 5.4 Conditions used to determine effect of concentration on CCM VAG.

5.3.1.6 Variation of ionic strength on stripping and coating current

To determine the effect of the ionic strength on the stripping and coating currents, a solution with similar bromide concentration but two different potassium nitrate concentrations was compared using the conditions below.

Parameter	Symbol	28-29kpccm.xls
Stripping pulse duration /ms	t_{SP}	100
Stripping potential /mV	E_{SP}	-500
Coating pulse duration /ms	t_{CP}	100
Coating potential /mV	E_{CP}	+500
Delay between cycles /ms	t_C	5000
[bromide] /M	c_{Br}	0.01
[KNO_3] /M	c_{KNO_3}	0.001, 0.05

Table 5.5 Conditions used to test effect of ionic strength.

5.3.1.7 Calibration of optimised system in potassium chloride, bromide and iodide solutions

Condition	Value
t_{SP} /ms	100
E_{SP} /mV	-500
t_{CP} /ms	100
E_{CP} /mV	+500
t_C /ms	5000
VAG time after pulse /s	1,e2,e3,e4

Table 5.6 Optimised conditions for controlled potential system

The PC software was modified to average and record the VAG at fixed points after the coating pulse for each cycle. Due to the large amounts of data the current

and potential over the full cycle was not recorded. A set of optimised conditions (Table 5.6) was chosen and conditions coded into the software. The software could be run for up to 5000 cycles with the data being appended to a text file stored on the PC hard disc at the end of each cycle. The software was written to allow the data file to be imported into a spreadsheet program for analysis.

To calibrate the system six solutions at various concentrations of each halide, potassium chloride, bromide and iodide were tested. Each solution was measured for two minutes or 24 cycles with the mean of the VAG_{4s} plotted.

parameter	**symbol**	**chloride**	**bromide**	**iodide**
Stripping pulse duration /ms	t_{SP}	100	100	100
Stripping potential /mV	E_{SP}	-500	-500	-500
Coating pulse duration /ms	t_{CP}	100	100	100
Coating potential /mV	E_{CP}	+500	+500	+500
Delay between cycles /ms	t_C	5000	5000	5000
[halide] /M	c_X	0.001 – 0.5	0.001t – 0.5	0.0001 - 0.5
[KNO_3] /M	c_{KNO_3}	0.05	0.05	0.05

Table 5.7 Conditions used for calibration curves.

To determine the speed of response of the electrode system to changes in bromide concentration a series of additions of concentrated potassium bromide were added to a weak solution of potassium bromide and nitrate.

Parameter	Symbol	40kpccm.xls
Stripping pulse duration /ms	t_{SP}	100
Stripping potential /mV	E_{SP}	-500
Coating pulse duration /ms	t_{CP}	100
Coating potential /mV	E_{CP}	+500
Delay between cycles /ms	t_C	5000
[bromide] /M (by addition)	c_{Br}	0.002, 0.007, 0.025, 0.054, 0.135
[KNO_3] /M	c_{KNO_3}	0.05

Table 5.8 Condition used for the addition of concentrated potassium bromide.

5.3.1.8 Effect of addition of other halide ions

To determine whether the electrode system responded to changes in halide kind in the way shown by the rotating silver disc electrode in chapter 4, a solution of potassium iodide was added to a solution of potassium bromide and nitrate. The concentrations were chosen to simulate an emulsion manufacturing process.

Parameter	Symbol	41kpccm.xls
Stripping pulse duration /ms	t_{SP}	100
Stripping potential /mV	E_{SP}	-500
Coating pulse duration /ms	t_{CP}	100
Coating potential /mV	E_{CP}	+500
Delay between cycles /ms	t_C	5000
[bromide] /M	c_{Br}	0.1
[iodide] /M	c_I	0.02, 0.1
[KNO_3] /M	c_{KNO_3}	0.05

Table 5.9 Conditions used for the addition of a solution of potassium iodide to a potassium bromide solution.

5.4 Results and Discussion

5.4.1 Experiments with a controlled stripping and coating potential

5.4.1.1 Cyclic voltammetry

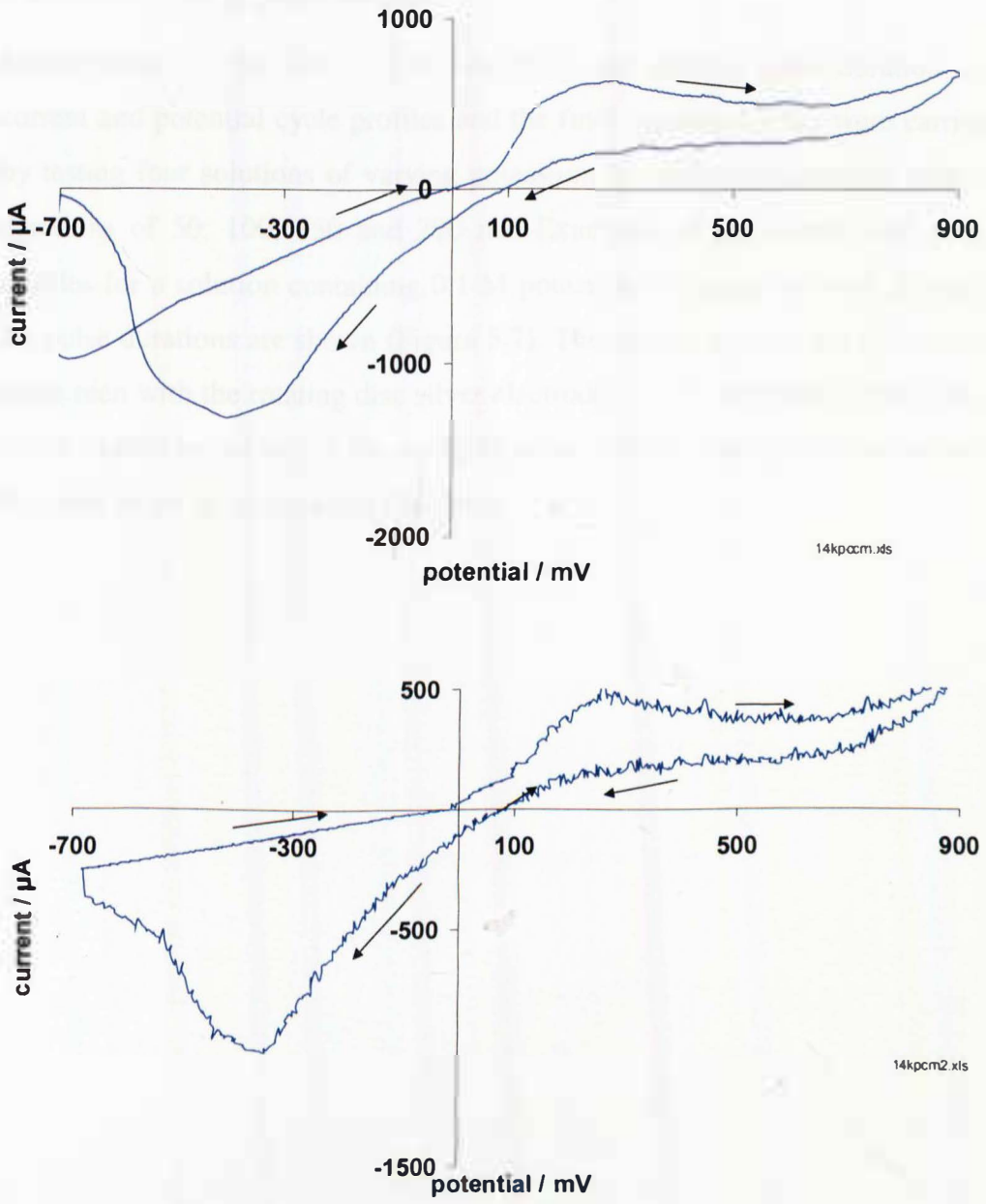


Figure 5.6 CV of potassium bromide in potassium nitrate using PAR174 potentiostat (top) and potential pulse controller module (bottom). [KBr] = 0.1 M; [KNO_3] = 0.001 M.

The cyclic voltammograms obtained using the potential pulse control was both comparable with those obtained with the rotating silver disc electrode in Chapter 4

and with the commercial PAR174 potentiostat using the same small silver electrode in stirred solution (Figure 5.6). In both cases the oxidation of silver metal to silver bromide was observed at potentials of +300 mV. The reduction wave can be observed in both of the CVs as negative peak as the silver bromide is reduced completely and the current falls back to zero.

5.4.1.2 Variation of pulse duration

Investigations of the affect of the stripping and coating pulse duration on the current and potential cycle profiles and the final measured VAG were carried out by testing four solutions of varying potassium bromide concentration with pulse durations of 50, 100, 150 and 200 ms. Examples of the current and potential profiles for a solution containing 0.1 M potassium bromide and with 50 and 200 ms pulse durations are shown (Figure 5.7). The current profiles are different from those seen with the rotating disc silver electrode: (1) the stripping current does not return to zero by the end of the stripping pulse; (2) the coating pulse does not have the same shape as observed in Chapter 4.

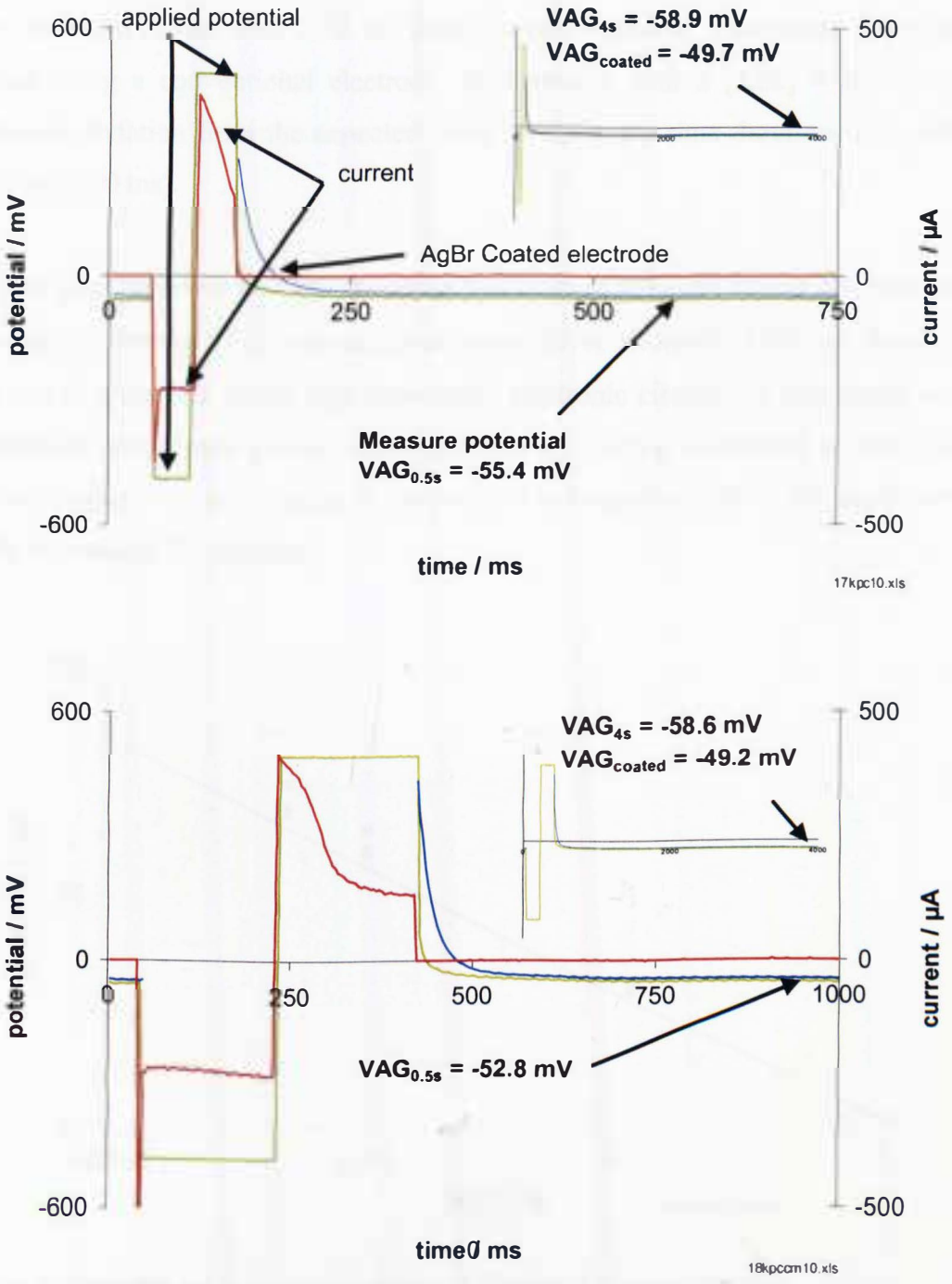


Fig 5.7 Variation of stripping and coating pulse duration 50 ms (top) 200 ms (bottom) on cycle current and free potential. (—) CCM current; (—) CCM potential; (—) conventional coated electrode potential. [KBr] /M = 0.1; [KNO_3] /M = 0.001; $t_{SP} = t_{CP}$ /ms = (top) 50, (bottom) 200; E_{SP} /mV = -500; E_{CP} /mV = +500; t_D /ms = 5000.

A plot of VAG measured at the end of the cycle for the experiments with a 50 ms and 200 ms pulse duration (Figure 5.8) shows that the VAG_{4s} was similar to that observed using the conventional coated electrode for [KBr] = 0.1 and 0.01 M at

both values of pulse duration. At [KBr] = 0.001 M and below the VAG_{4s} recorded for the experiments with a 50 ms pulse duration showed a deviation from the value using a conventional electrode. Experiments with a [KBr] = 0.0001 M showed deviation from the expected value for all pulse time durations (50, 100, 150 and 200 ms).

It was also observed that the stripping and coating pulse adversely affected the measured potential of the conventional coated silver electrode. This was found to be due to cross-talk in the high impedance electronic circuits. A new board was fabricated with better power supply stability by adding capacitors to both the power supply lines and directly to the positive and negative pins of the amplifiers. This eliminated the problem.

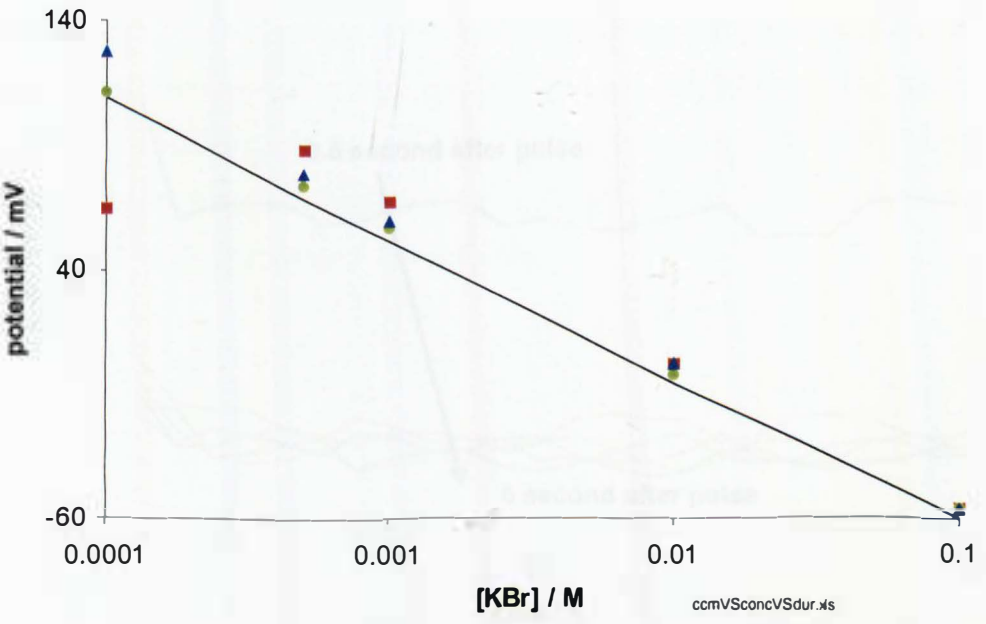


Figure 5.8 Measured and theoretical potentials as a function of [bromide] (VAG_{4s}).
(■) CCM $t_{SP} = t_{CP}$ /ms = 50 ; (●) CCM $t_{SP} = t_{CP}$ /ms = 200; (▲) coated electrode; (—) theoretical potential. [KBr] /M = 0.0001...0.1; [KNO_3] /M = 0.001; E_{SP} /mV = -500; E_{CP} /mV = +500; t_D /ms=5000.

5.4.1.3 VAG value point versus time after pulse

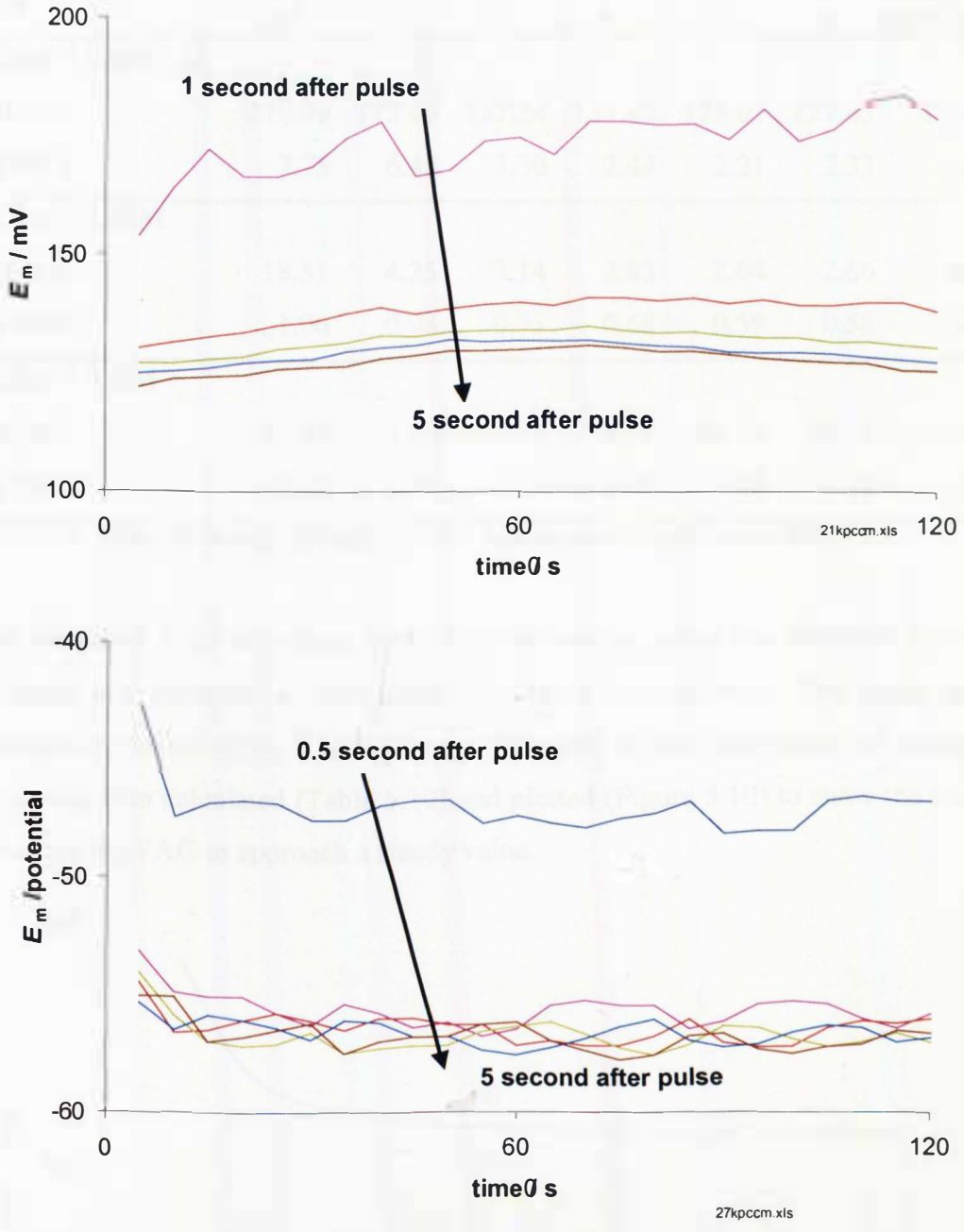


Fig 5.9 CCM VAG measured at various points after the coating pulse for [KBr] = 0.1 M (bottom) and [KBr] = 0.0001M (top) over 2 minutes (20 cycles). [KNO_3] /M = 0.001; t_{SP} = t_{CP}/ mso= 200; E_{SP} /mV = -500; E_{CP} /mV = +500; t_D /ms = 5000.

The CCM VAG was measured in two solutions of different bromide concentration at varying points after the start of the cycle. The solution were measured for two minutes or 24 cycles (Figure 5.9)

t_m /s	Potential measured after start of cycle / mV						
	0.5	1	2	3	4	5	Coated electrode
[KBr] = 0.0001 M							
MEAN	270.99	172.00	137.24	131t42	129.07	127.43	112.70
STDEV	7.75	6.48	3.30	2.44	2.21	2.33	0.17
[KBr] = 0.01M							
MEAN	18.51	4.25	3.14	2.83	2.64	2.66	0.15
STDEV	1.06	0.98	0.75	0.68	0.59	0.58	0.02
[KBr] = 0.1 M							
MEAN	-47.05	-55.60	-56.36	-56.70	-56.56	-56.71	-62.20
STDEV	2.97	1.91	1.13	2.12	1.06	1.13	0.29

Table 5.10 Mean and standard deviation of VAG measurements. Conditions as Figure 5.9.

The measured VAG at various times after the coating pulse was averaged by the software and recorded in a separate file for each experiment. The mean and standard deviation of the VAG values of all cycles at each time after the coating pulse was then calculated (Table 5.10) and plotted (Figure 5.10) to show the time taken for the VAG to approach a steady value.

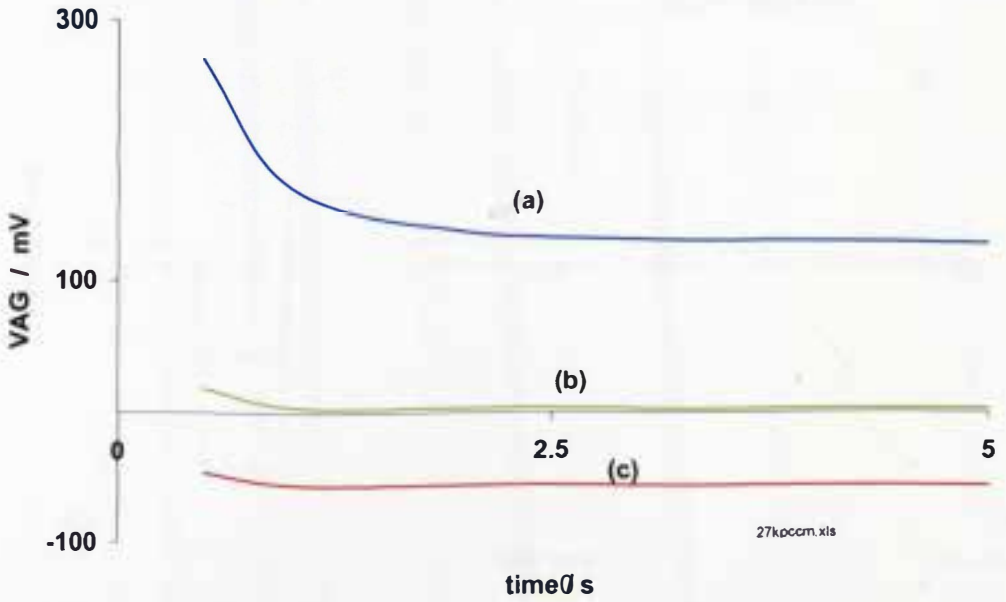


Figure 5.10 Average VAG measurements plotted versus time after cycle start for various bromide concentrations. [KBr] /M = (a) 0.0001 (—)d; (b) 0.01 M (—) ; and (c) 0.1 (—). [KNO_3] /M = 0.001; t_{SP}d= t_{CP} /msd= 50; E_{SP} /mV = -500; E_{CP} /mV = +500; t_D /ms = 5000.

The standard deviation of the VAG reduces as t_m increases. However, the standard deviation of the CCM VAG never becomes as low as that of conventional coated electrode.

5.4.1.4 Variation of applied potential during coating pulse

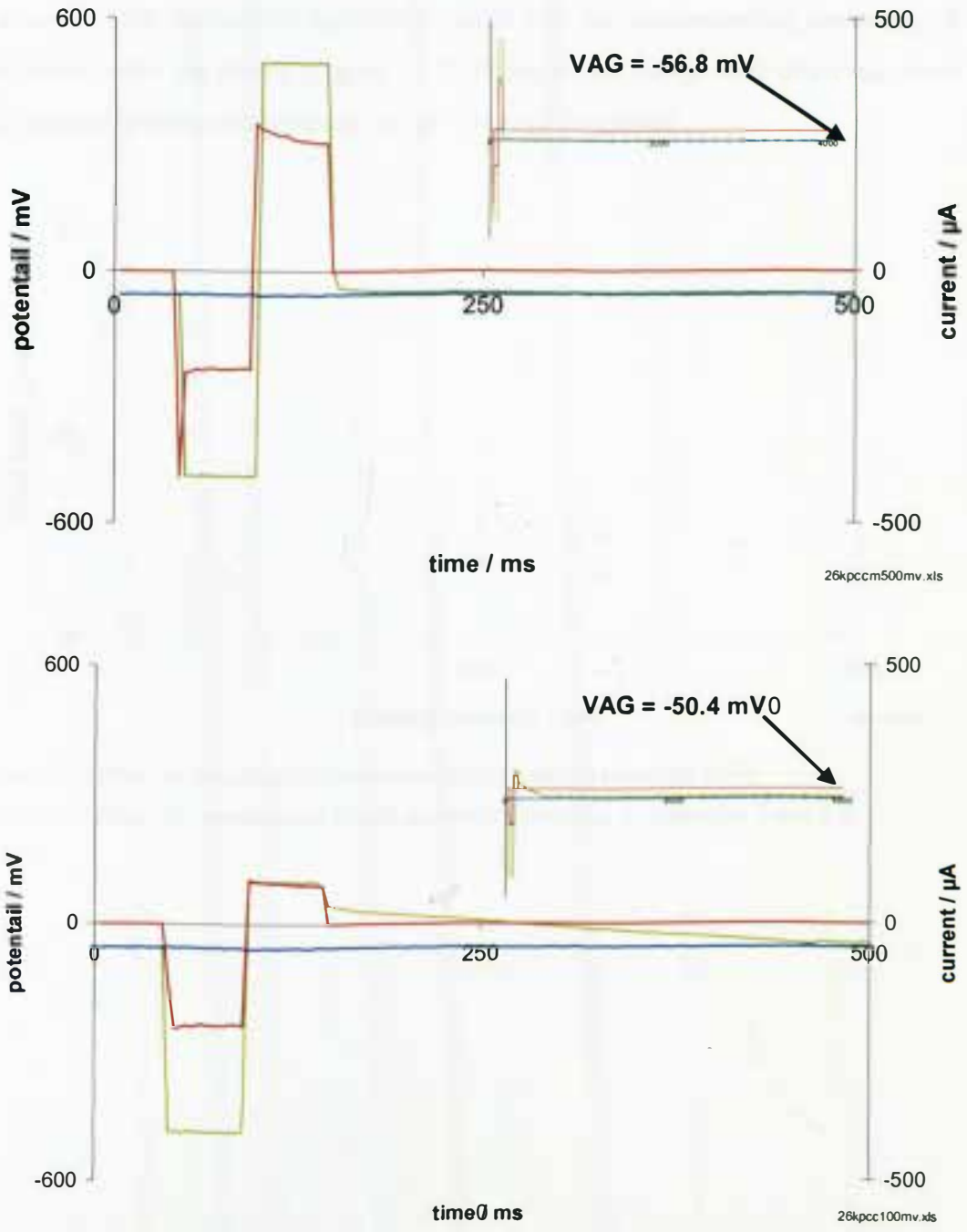


Fig 5.11 Variation of coating potential on cycle current and potential. The cycles for 500 mV (top) and 100 mV (bottom) are shown. (—) CCM current; (---) CCM potential; (—) conventional coated electrode potential [KBr] /M = 0.1; [KNO_3] /M = 0.001; $t_{SP} = t_{CP}$ /ms=50; E_{SP} /mV = -500; E_{CP} /mV = +500; t_D /ms = 5000.

To determine the effect of the coating potential on the final VAG a set of experiments was carried out where the coating potential was varied but all other conditions kept constant. Six coating potentials were investigated from +100 to +600 mV. Current and potential profiles for experiments with coating pulse potentials of +100 and +500 mV are shown in Figure 5.11. The measured VAG values 4 s after the start of the cycle together with the corresponding conventional electrode value are shown (Figure 5.12). Comparable values were observed when the applied coating potential was set at +300 mV or greater.

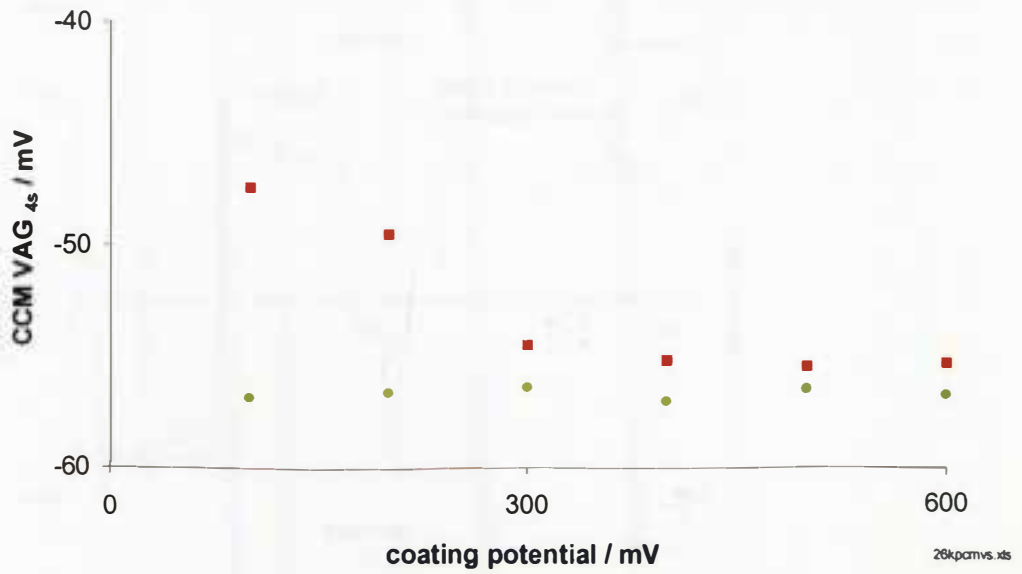


Figure 5.12 Effect of changing the applied coating potential on measured VAG.
(■) CCM VAG_{4s} ; (•) conventional coated electrode. Conditions as detailed in Table 5.3.

5.4.1.5 Effect of bromide concentration on CCM VAG

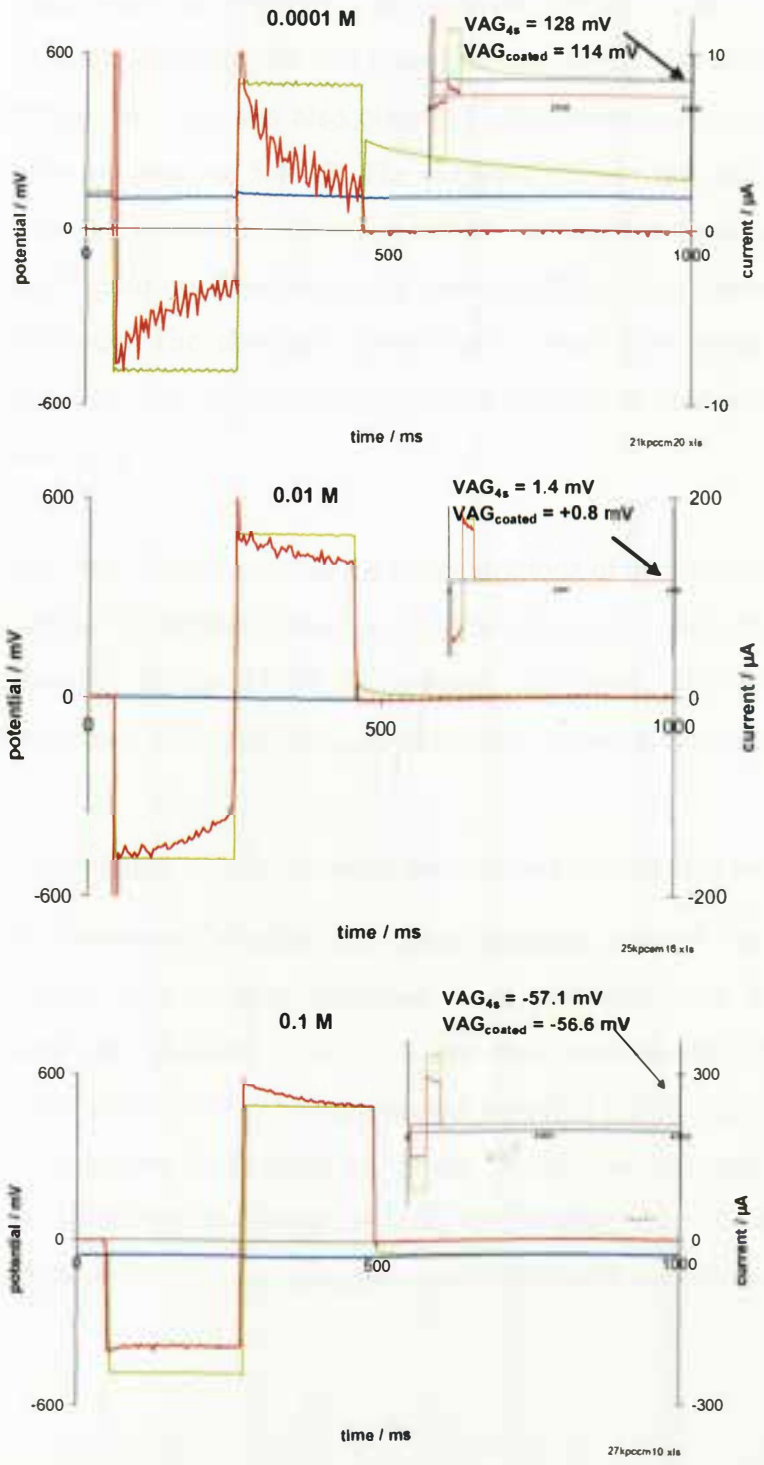


Fig 5.13 Effect of bromide concentration on measured currents and potentials.[KBr] /M; 0.1 (bottom), 0.01 (middle), 0.0001(top). (—) CCM current; (—) CCM potential; (—) coated electrode potential. [KNO_3] /M = 0.001; $t_{SP} = t_{CP}$ /ms = 200; E_{SP}/ mV = -500; E_{CP} /mV = +500; t_D /ms0= 5000.

Experiments carried out to investigate the effect of bromide concentration on the potential and current profiles (Figure 5.13) during the cycle revealed that in all cases when the bromide concentration was less than 0.1 M the current profiles were significantly different from those observed with the rotating disc electrode in Chapter 4. This was also observed when investigating the stripping and coating pulse duration in 5.4.1.2. The stripping current did not return to zero as would have been expected after the halide coating had been stripped and the coating current did not decrease in the same profile as was observed with a rotating disc electrode. The absolute current levels were also lower that would have been expected even taking into account the reduced surface area of the small cylindrical electrode.

The final VAG measured for concentrations of bromide from 0.001 to 0.1 M gave comparable results to the conventional electrode (insets in Figure 5.13). The VAG observed in the 0.0001 M bromide was more positive than the conventional coated electrode and was associated with a slow time to come to a steady reading.

5.4.1.6 Effect of ionic strength on stripping and coating pulses

To investigate whether the ionic strength effected the current and potential profiles two bromide solutions were prepared each with a concentration of potassium bromide of 0.05 M and with concentrations of potassium nitrate of 0.001 and 0.05 M. The current and potential profiles for the pulse section of the cycle (Figure 5 14) show that at the higher ionic strength the profile is similar to that observed in Chapter 4 with the rotating disc electrode. In Chapter 4 all solutions had a base electrolyte concentration of potassium nitrate at 0.05 M.

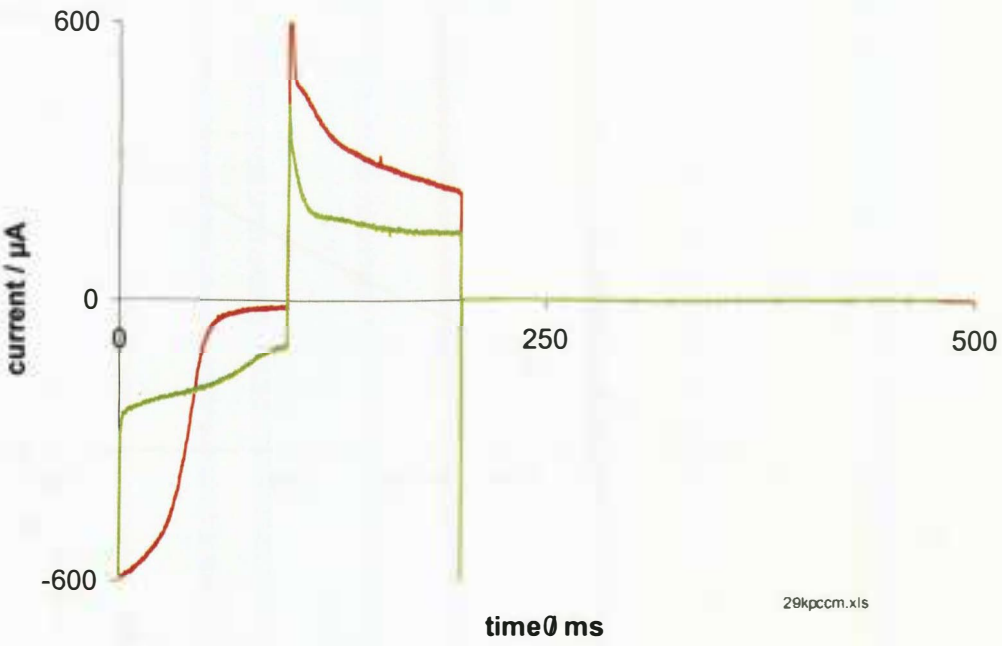


Figure 5.14 Effect of ionic strength on the measured current and potential profiles.
(—) CCM current, $[KNO_3]$/M=0.05 M; (—) CCM current,$[KNO_3]$/M=0.00de
[KBr] /M = 0.05; $t_{SP} = t_{CP}$/ms = 200; E_{SP}/mV = -500; E_{CP} /mV = +500; t_D /mse= 5000.

5.4.d.7 Calibration curves for potassium chloride, bromide and iodide using an optimized system.

All further experiments carried out on the controlled potential system used the new software, where only the VAG and conventional silver electrode potential was recorded at fixed time after the coating pulse, and the optimised conditions shown in Table 5.6.

Three sets of experiments were carried out to produce calibration curves for chloride, bromide and iodide using this new software and conditions (Figure 5.14). The results indicated that the calibration curves plotted using the VAG measured at least 2 s after the coating pulse were comparable with those of the conventional electrode over the defined concentration ranges. The measured VAG at 1 s was more positive than the conventional coated electrodes for all halides with it being between and 6 and 10 mV more positive for the iodide solutions.

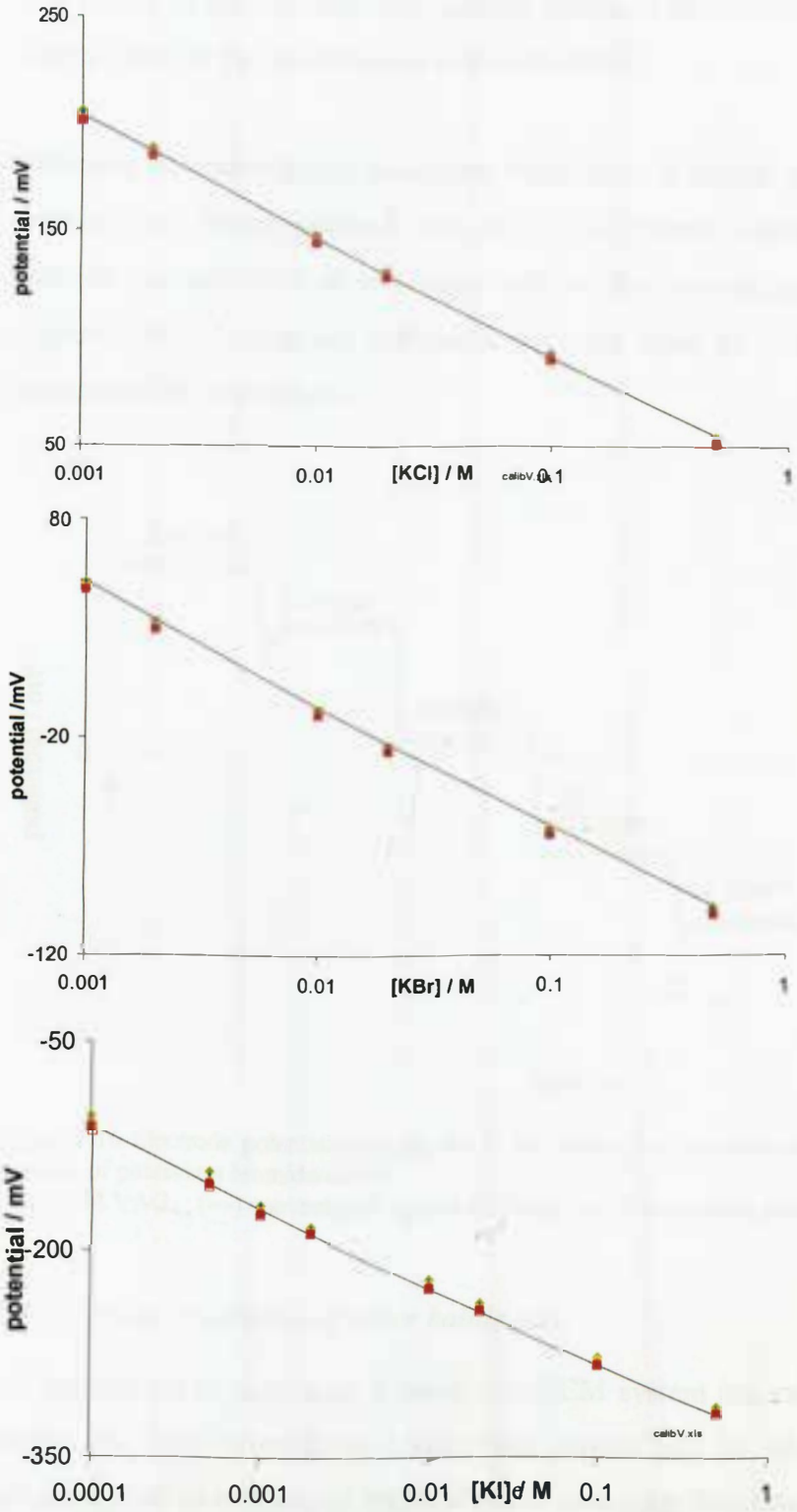


Figure 5.15 Calibration curves for chloride (top), bromide (middle) and iodide (bottom). (□) coated electrode;(♦) VAG_{1s}; (▲) VAG_{2s}; (●) VAG_{3s}; (■) VAG_{4s}; (—) theoretical potential. $[KNO_3]$ /M = 0.05; $t_{SP} = t_{CP}$ /ms=100; E_{SP} /mV = -500; E_{CP} /mV = +500; t_D /ms = 5000.

In the case of the bromide and chloride solutions the VAG measured at 1 s was within 1 mV of the conventional coated electrode.

Additions of concentrated potassium bromide to a stirred solution of potassium bromide and nitrate showed that the CCM system responded to changes of bromide concentration at the same rate as the conventional coated electrode (Figure 5.16). A constant difference between these of 1-2 mV was observed throughout the experiment.

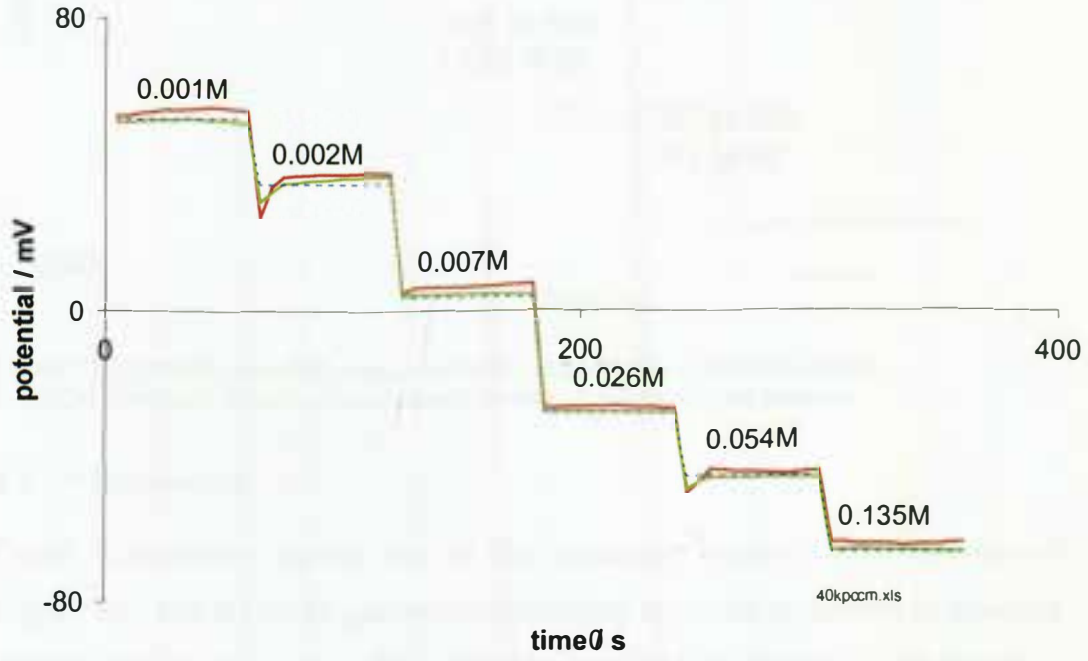


Figure 5.16 Electrode potential changes due to the addition of concentrated bromide to an initial solution of potassium bromide/nitrate.
(—) CCM VAG_{4s}; (—) conventional coated electrode; (••••) theoretical potential.

5.4.1.8 Effect of addition of other halide ions

An experiment to determine whether the CCM system responded to a change in halide ion from bromide to iodide was carried out by adding a solution of potassium iodide to a stirred solution of the potassium bromide and nitrate (Figure 5.17). The CCM VAG responded quickly to the changes of halide, with the VAG value being comparable with the theoretical calculated value. The slight delay was caused by the CCM taking 5 s to complete a full cycle.

The conventional coated electrode did not respond to changes in halide but begun to drift towards the steady state value as the experiment progressed.

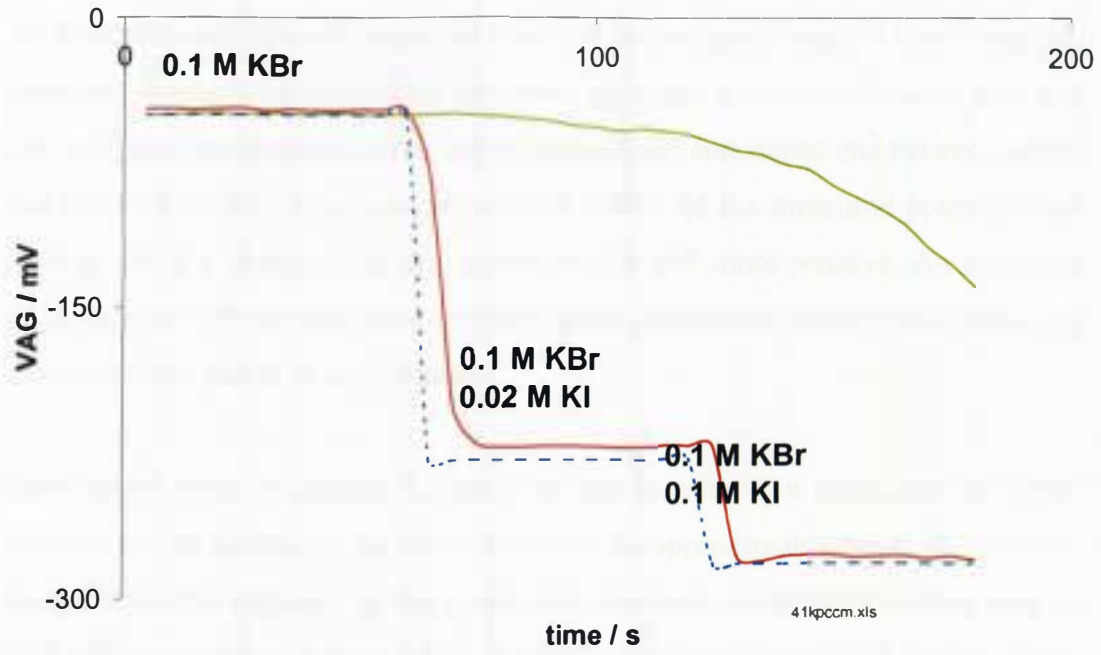


Figure 5.17 Electrode potential changes as iodide was added to a bromide solution. (—)CCM VAG_{4s}; (—) conventional coated electrode; (····) theoretical potential.

5.4.d.9 Discussions

Cyclic voltammetry carried out on the potassium bromide solutions showed (Figure 5.6) that the CCM system and cylindrical electrode performed as expected and similarly to the rotating disc electrode described in Chapter 4. The oxidation wave for silver was observed at +300 mV while the reduction waves for silver bromide appeared as a peak as the layer was completed stripped from the electrode.

In investigating the measured CCM potential and the conventional coated electrode potential, an offset was observed. This was expected from the results obtained in chapter 3 on conventional coated electrodes. Freshly prepared electrodes were seen to have a bias of 1 – 2 mV.

Investigations on the stripping and coating pulse duration showed that at 50 ms concentrations of bromide of less than 0.01 M did not give comparable results to

the conventional coated electrode (Figure 5.8). At 0.0005 to 0.001 M the measured potential was slow to reach a steady state and even after 4 s was 11 to 15 mV more positive. At concentrations of less than 0.0005 M, cycles with a 50 ms pulse duration showed measured potential values more negative than expected, behavior similar to a bare silver electrode. At pulse durations between 100 and 200 ms good comparable values were obtained for concentrations between 0.005 and 0.5 M bromide. At a concentration of 0.0001 M the measured potential was slow to reach a steady value at 4 s and was 16 mV more positive. An optimum pulse time of 100 ms was chosen to give good comparable results while reducing the time of the pulses to a minimum.

Calculations used in chapter 4, indicated that to achieve a monolayer of silver bromide on the surface of the silver electrode an approximate charge of 10×10^{-5} C cm^{-2} would be required. In this particular case with an electrode surface area of 0.94 cm^2 a charge of 0.94×10^{-5} C would be required. Table 5.17, below shows the average charge calculated from a number of cycles with 50 and 200 ms pulses at four bromide concentrations.

[bromide] /M	$t_{SP} = t_{CP} = 50$ ms	$t_{SP} = t_{CP} = 200$ ms
	Charge / 10^{-5} C	Charge / 10^{-5} C
0.0001	0.05	0.23
0.001	0.25	0.99
0.01	0.95	3.73
0.1	1.63	6.26

Table 5.16 Average measured coating charge at 50 ms and 200 ms pulse durations in four bromide concentrations. Conditions given in Table 5.6

It was found that for all pulse durations in 0.0001 M potassium bromide and for a pulse duration of 50 ms in 0.001 M the charge drawn was below that required to obtain a monolayer. In these case the CCM VAG was observed to be either more negative than the theoretical value, indicating a bare silver electrode, or did not reach the theoretical value in 4 s. This confirms the observation noted in Chapter 4 that a coating of at least a monolayer thick was needed to achieve comparable

results to a conventional coated electrode. For all measurement conditions where greater than 0.94×10^{-5} C was drawn during the coating pulse comparable VAG measurements were observed.

To limit the length of the CCM cycle to as short a time as possible, the effect of the time of the VAG measurement after the cycle start was investigated (Figure 5.9). The standard deviation of the CCM VAG potential when a sample was measured over a two minutes period improved as the time of measurement after the cycle start increased. The standard deviation (Table 5.16) was never observed to be a low as the conventional electrode. In the case of the conventional electrode the standard deviation calculated was for one electrode measured a number of times over a short period while for the CCM electrode, each cycle created a new coated electrode. The standard deviation calculated for the CCM system was for a number of different new electrodes measured once. This CCM standard deviation of 1 mV was similar to the standard deviation for a number of new electrodes measured once and reported in Chapter 3 (Table 3.3).

In high concentration of bromide, 0.01 to 0.1 M, the potential reached a comparable value within 1 s (Figure 5.10). However, at concentrations of less than 0.01 M, 3 s was required for the potential to reach a comparable value. The cycle time was set at 5 s to allow measurements to be made from 1 to 4 s after the start of the cycle. The measurement data was stored to the PC hard disc in the remaining 1 s.

Varying the applied coating potential (Figure 5.11) while keeping other conditions constant indicated that if the potential was +300 mV or more positive the potential measured was not affected (Figure 5.12). A slight constant bias was seen from the conventional coated electrode. At applied potentials of +200 mV and below the potential value was more positive at 4 s and did not reach a steady value. An optimum potential of +500 mV was chosen. For ease of operation it was also decided to set the stripping potential at –500 mV.

The current and potential profiles of the stripping and coating pulses observed during experiments using solutions of potassium bromide at varying concentrations (Figure 5.13) and with a potassium nitrate concentration of 0.001 M were not similar to those observed using a rotating disc electrode shown in Chapter 4. The stripping current did not return to zero after the silver bromide had been stripped and the coating pulse did not show the three-section shape seen in Chapter 4. The overall level of current was also less that would have been expected taking into account the reduced surface area of the cylindrical electrode. However, as described earlier the potentials measured for concentrations of bromide between 0.001 and 0.1 M were in good agreement with the conventional coated electrode. Two solutions of similar bromide concentration and with different ionic strengths were tested (Figure 5.14). The solution with the higher ionic strength showed similar profiles to those seen with a roatating disc electrode (Chapter 4) with the stripping pulse current returning to zero and the coating pulse current showing the three sections seen previously. It was thought that the lower current values might be caused by the ionic strength of the solution limiting the current at the electrode.

Optimum conditions were chosen from observations described and set as standard operating conditions in the software (Table 5.18).

Condition	**Value**
t_{SP} /ms	100
E_{SP}/mV	-500
t_{CP} /ms	100
E_{CP}/mV	+500
t_C/ms	5000
VAG time after pulse / s	1, 2, 3, 4

Table 5.12 Standard operating conditions.

During the photographic emulsion making process the ionic strength of the emulsion varies from 0.001 M at the start to 0.5 M at the end of the precipitation. The doubling of the initial volume by the addition of 1 M silver nitrate and potassium halide causes the ionic strength to increase. Although good results were achieved for the CCM method with low ionic strength, it was decided to carry out calibration experiments using a mid range ionic strength of 0.05 M potassium nitrate as a base electrolyte.

Using these standard operating conditions, calibration curves were obtained for chloride, bromide and iodide in a base electrolyte of 0.05 M potassium nitrate (Figure 5.15). The calibration curves for chloride and bromide solutions in the range 0.001 to 0.5 M were in good agreement with both the conventional coated electrode and theoretical calculated values with potentials measured at 2 s after the coating pulse. The value at 1 s after the coating pulse was less than 1 mV different from the 4 s value. The potential values for the iodide solutions 2 s after the coating pulse were in good agreement but the 1 s value was 6 – 10 mV more positive in all solutions. It was thought that as the conditions had been set up for bromide the applied coating potential was too positive for the iodide solutions. A similar observation was seen for the rotating disc electrode (4.4.6.3), when the applied potential was set too high for the bromide solutions. The time taken for the potential to reach a steady value was increased.

The response of the CCM electrode to changes in bromide concentration was found to be as good as the coated electrode (Figure 5.16). The electrode responded to bromide additions within the cycle time. The values obtained after each addition and when the solution had come to a constant concentration were also comparable with both the conventional coated electrode and the theoretical value. A slight offset was again seen with this conventional electrode.

The response of the electrode to additions of iodide was also observed to be comparable to the theoretical calculated value (Figure 5.7). The coated electrode did not respond to the iodide solution but slowly drifted towards the theoretical

value. The CCM system was therefore performing as intended and discriminating between halides.

5.5 Summary

In the previous chapter the performance of the CCM technique using a rotating disc electrode was described. This chapter describes how the technique was extended to use a small static silver electrode in stirred solutions. Two methods of the technique were investigated: the first applied a controlled potential and is described in this chapter; the second applied a constant current and will be described in the next chapter.

A new instrument were designed and fabricated to test the performance of the controlled potential method. The instrument performed as intended, giving a flexible system that could be easily modified by changing the control and data collection software.

Initial experiments were carried out to compare the controlled potential instrument with a commercial potentiostat. Good CV plots were obtained which verified that the controlled potential instrument was performing and calibrated correctly.

Experiments to determine the optimum pulse duration indicated that at concentrations between 0.1 and 0.01 M a pulse duration of 50 to 200 ms gave good CCM potentials which compared favourably with both the theoretical and conventional coated values. At concentrations between 0.01 and 0.001M pulse durations of 100 ms were required to obtain comparable values. At concentration between 0.001 and 0.0001 M The CCM electrode did not give comparable values.

The optimum coating potentials were found to be +300 mV or greater. At values more negative than this the CCM potential was slow to respond and did not give comparable values.

The ionic strength of the solution was found to affect the current profiles but not the CCM potential, recorded at the end of each cycle. Addition of higher concentrations of potassium nitrate gave similar profiles to those obtained in the rotating disc electrode investigation where the potassium nitrate was 0.05M

The optimum conditions found during the investigations were programmed into the software and calibration curves constructed for chloride, bromide and iodide. The CCM technique was found to give good comparison with both theoretical and conventional coated electrode values for concentrations of chloride in the range 0.001 to 0.5 M, bromide in the range 0.001 to 0.5 M and iodide in the range 0.0001 to 0.5 M. The speed of response of the CCM electrode was also tested and found to be as fast as the conventional coated electrode.

The response of the controlled potential CCM technique to changes of halide ion was tested in a simulated emulsion where iodide was added to a potassium bromide solution. The CCM electrode responded immediately to the change in halide whereas the coated bromide electrode drifted in a negative direction slowly throughout the run and did not reach a steady value.

Chapter 6. Experiments in "clean/coat/measure" technique using cylindrical electrodes in stirred solutions with a constant current

6.1 Introduction

This chapter describes the clean/coat/measure pulse technique using a programmed constant current to strip and coat the CCM electrodes. Small 2 mm cylindrical silver electrodes, previously used to investigate the technique with controlled potential stripping and coating were used. As before the cycle comprises a cleaning or stripping pulse, a coating pulse and a measurement step.

In this method a simple constant current circuit was used to apply a potential to the silver electrode such that the current flowing through the electrode to the vessel ground was constant. While controlling the potential, as used in the previous work, allowed the potential to be set to a value specifically for the halide ion present, in a production system this may not be known or will change during the process. Therefore a method, which sets the current to a fixed value, automatically allows the potential to rise to the potential where the silver halide is coated. The open circuit potential was measured at a fixed time after the start of the cycle.

As with the previous work on controlled potential, due to large amount of data needed to be collected it was decided to base the investigation on solutions containing bromide ions. Experiments were carried out using a purpose built, robust unit comprising a constant current circuit. Initially stripping and coating pulse durations of between 50 and 200 ms were investigated in bromide ion concentrations of between 0.0001 and 0.1 M at a constant temperature of 25°C. Examples of the addition of potassium iodide to a potassium bromide solution and

an addition of potassium iodide to a potassium chloride solution for the constant current system are given.

6.2 Equipment and instrumentation

The equipment used for the investigation of constant current stripping and coating pulses was the same experimental setup as with the controlled potential experiments accept that a new constant current pulse controller was designed and fabricated.

6.2.1 Analogue Devices RTI815 and RTI850 PC cards

The RTI815 and RTI850 PC cards were again used to control the pulse circuit and to measure the open circuit potential of the silver electrode.

6.2.2 RTI800 software functions

The functions needed to control the RTI 800 series cards and described in the previous chapter were again used.

6.2.3 Constant current pulse controller

The pulse control interface module combined the differential circuits, previously used to measure the equilibrium potentials and described in Chapter 3, and the necessary circuits to produce the cleaning and coating constant current pulses. As in the previous work, a software program controlled the constant current and measured the potential and current of the CCM electrode and a coated silver halide electrode.

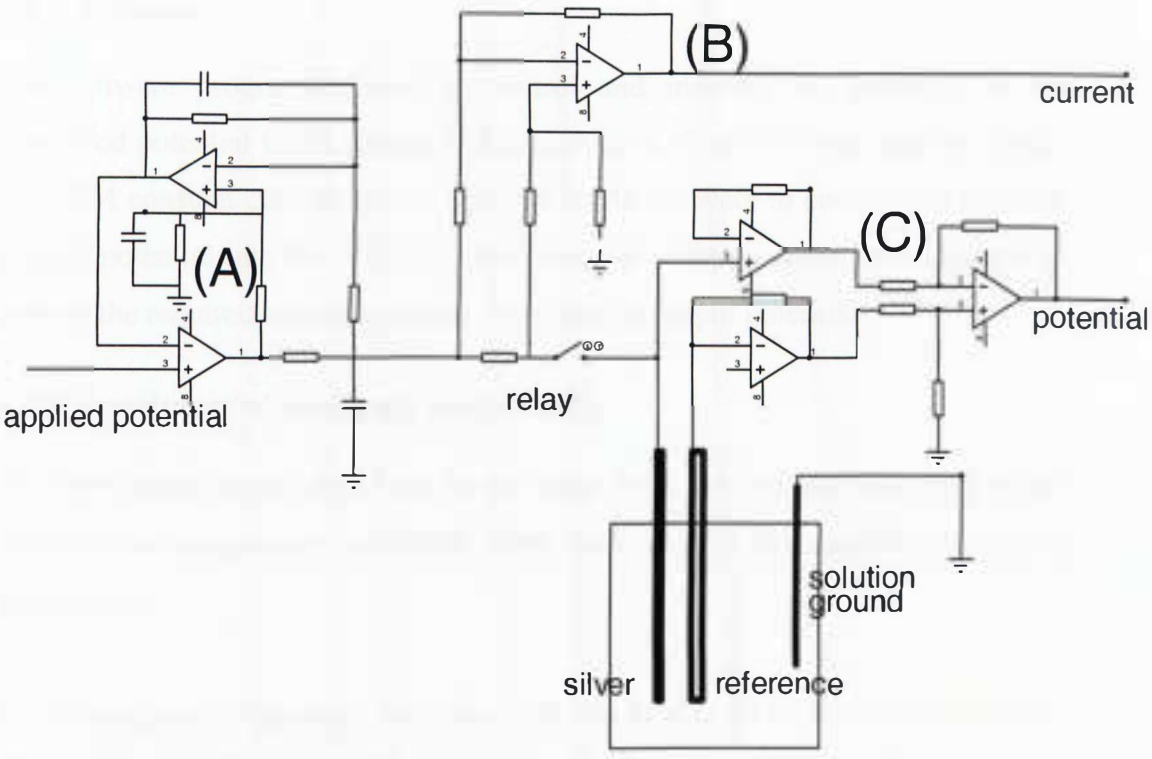


Figure 6.5 Circuit for applying a constant current to the silver electrode

The constant current pulse controller utilised a constant current feedback circuit (Figure 6.1), which generates a current through a fixed resistor to the silver electrode. The circuit maintains a constant potential across the fixed resistor and hence a constant current through the resistor by feeding back the measured potential to the generating amplifier (A). The current flowing through the silver electrode is determined by measuring the potential with a amplifier (B) across a second fixed resistor so as not to interfere with the feedback signal. The applied potential is measured by using the differential circuit described previously (C).

6.2.4 Electrodes

The small cylindrical silver electrode and the double junction salt bridge with a non-commercial hydrogel reference electrode described in Chapter 5 were used.

6.2.5 Software

The software programme used to control and measure the potential in the controlled potential CCM system and described in Chapter 5 was used to control the CCM constant current system. Factors in the software to convert the required applied potential into the RTI 815 card analogue output voltage were changed to convert the required constant current value into an output potential.

6.3 Experimental methods and details

All experiments were carried out in the same 1000 ml 316 stainless steel vessel fitted into a temperature controlled water bath used in the controlled potential experiments.

For the purpose of this study the water bath was held at 25 °C for all experiments. The vessel was filled with 500 ml of the test solution and left for 30 minutes for the temperature to reach equilibrium. The CCM silver electrode, the reference bridge junction, a platinum solution ground and a temperature probe were secured into a clamp to ensure that the position of all electrodes was identical for all experiments. The clamp was designed to hold two additional indicator electrodes if required. A glass vessel with a water jacket maintained at 25 °C and containing the salt bridge solution, was held 40 cm above the level of the test solution. At the start of each experimental run the gel reference electrode was taken from the storage solution and immersed in the salt bridge solution.

The electrode clamp was lowered into the vessel ensuring that all the electrodes were immersed to the same level. The stirrer was then switch on to the same constant speed for all experiments and the pulse interface software started. Addition of either more concentrated potassium bromide or solutions of iodide ion were added from the dispensers by sending RS232 signals from the second PC. A small software program allowed the required volume to be entered into the PC and the addition activated by pressing the enter key when the planned time in the experiment had been reached and the solution was required.

Data collected for each experimental run was stored in two type of file; the first contained the raw data for each cycle and the second contained the VAG value averaged at 4 points in the measurement part of the cycle. Raw data was not collected for the whole of the cycle because time was needed to store the data to the PC hard disc at the end before the cycle could start again.

6.3.1 Experimental procedures: constant current experiments

For all experiments the stainless steel vessel was filled with 500 ml of the test solution and the electrodes carefully placed in the same location with the solution stirred at the same constant speed. The silver electrode was polished and rinsed before each experiment.

6.3.1.1 Variation of pulse duration

Initial experiments to determine the effect of stripping and coating pulse duration were carried out on a 0.1 M potassium bromide solution with the constant current set at the level observed in the previous controlled potential experiments when the test solution concentration was 0.1 M potassium bromide. The coating current was set at +300 μA and the stripping current set to a negative value 10% higher at -330 μA, to ensure that the electrode was completely stripped. The stripping and coating pulse times were set to be equal. Pulse durations were varied from 50 to 200 ms. As in the controlled potential experiments the cycle duration was set at 5000 ms with the current and potential being recorded for 4000 ms from the start of the cycle.

Parameter	Symbol	31-35kpccm.xls
Stripping pulse duration /ms	t_{SP}	50 - 200
Stripping current /μA	I_{SP}	-330
Coating pulse duration /ms	t_{CP}	t_{SP}
Coating current /μA	I_{CP}	300
Cycles interval /ms	t_C	5000
Data collection time /ms	$t_{measure}$	4000
[bromide] /M	c_{Br}	0.1

Table 6.1 Conditions used to investigate stripping and coating pulse duration.

6.3.1.2 Variation of constant current value

The constant current setting for the coating pulse was varied from +150 to +300 μA with the stripping current setting maintained at a negative value 10% greater. The pulse durations were set at 200 ms with the test solution concentration being 0.1 M potassium bromide.

Parameter	Symbol	30kpc(a)-(d).xls
Stripping pulse duration /ms	t_{SP}	200
Stripping current /μA	I_{SP}	-170o- -330
Coating pulse duration /ms	t_{CP}	200
Coating current /μA	I_{CP}	+150 - +300
Delay between cycles /ms	t_{CY}	5000
Data collection time /ms	$t_{measure}$	4000
[bromide] /M	c_{Br}	0.1

Table 6.2 Conditions used to investigate stripping and coating constant current.

6.3.1.3 Effect of bromide concentration

To determine the useable range of the constant current CCM system, four solutions of different bromide concentration were tested. The pulse duration was set at 200 ms with the stripping and coating constant currents set at –330 and +300 μA.

Parameter	Symbol	51-55kpccm.xls
Stripping pulse duration /ms	t_{SP}	200
Stripping current /μA	I_{SP}	-330
Coating pulse duration /ms	t_{CP}	200
Coating current /μA	I_{CP}	300
Delay between cycles /ms	t_C	5000
Data collection time /ms	$t_{measure}$	4000
[bromide] /M	c_{Br}	0.0001 - 0.1

Table 6.3 Conditions used to investigate effect of bromide concentration.

6.3.1.4 Effect of addition of other halide ions

To investigate the performance of the constant current system to measure mixed halide solutions, three experiments were carried out where the changes in halide concentrations and kind simulated those conditions seen in photographic emulsion production. The first added iodide to a chloride solution, the second added iodide to a bromide solution and the third added iodide to a chloride solution followed by a silver nitrate solution to precipitate the iodide out. The CCM conditions for all three experiments were identical (Table 6.5). The amounts and timings of each addition are given below (Table 6.6). In the third experiment it was assumed that the iodide ions had been removed from solution by precipitation with the silver nitrate. In all cases the CCM potential was taken 4 s after the end of the coating pulse. The potential of an electrode coated with the initial halide kind was also measured and recorded throughout the experiment. This third experiment would determine whether the electrode could change from measuring chloride to iodide and then back to measure chloride.

Separate standard solutions of potassium chloride, potassium bromide and potassium iodide were prepared and tested to use as comparisons for the simulated emulsion samples (Table 6.4). The potassium iodide was prepared at a lower concentration to simulate better the emulsion manufacturing conditions. The CCM conditions were as Table 6.5

Solution	Concentration
KCl	0.1 M
KBr	0.1 M
KI	0.002 M

Table 6.4 Concentration of comparison standards

Parameter	**Symbol**	**51-55kpccm.xls**
Stripping pulse duration /ms	t_{SP}	200
Stripping current /μA	I_{SP}	-170
Coating pulse duration /ms	t_{CP}	200
Coating current /μA	I_{CP}	+150
Delay between cycles /ms	t_C	5000
Data collection time /ms	$t_{measure}$	4000

Table 6.5 Conditions used in emulsion simulation test

Time /s	**18HB**	**21HC**	**03CCM15G**
0 (start)	500 ml 0.1 M KCl **[KCl] = 0.1 M**	500 ml 0.1 M KBr **[KBr] = 0.1 M**	500 ml 0.1 M KCl **[KCl] = 0.1 M**
180	500 ml 0.1 M KCl 10 ml 0.1 M KI **[KCl]t≈ 0.1 M** **[KI] = 0.002 M**	500 ml 0.1 M KBr plus 5 ml 0.1 M KI **[KBr]t≈ 0.1 M** **[KI] = 0.001 M**	500 ml 0.1 M KCl plus 2 ml 0.1 M KI **[KCl]t≈ 0.1 M** **[KI] = 0.0004 M**
480			Plus 2 ml 0.1 M $AgNO_3$ **[KCl]t≈ 0.1 M**

Table 6.6 Additions and timings of simulated emulsion tests

6.4 Results and Discussion

6.4.1 Experimental results using constant current

6.4.1.1 Effect of pulse duration

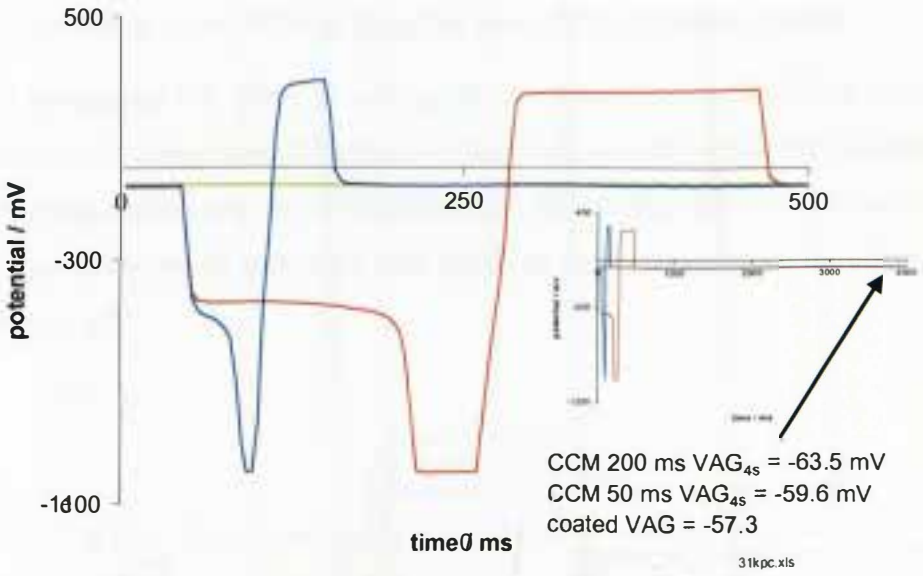


Figure 6.2 Measured potentials during and after constant current stripping and coating. (—) $t_{SP} = t_{CP} = 200$ ms; (—) $t_{SP} = t_{CP} = 50$ ms; (—) coated electrode. Conditions are given in Table 6.1

Experiments were carried out with constant current stripping and coating pulse of durations 50 to 200 ms. The potential was recorded during the stripping and coating pulse as well as during the open circuit measurement period. During the stripping pulse, the potential was maintained at approximately –450 mV by the constant current of –330 μA while the silver bromide coating was stripped off. Once this was completed the potential dropped to a negative value of less than –1000 mV. The system was limited to –1000 mV by the electronics. The current was switched to a positive value of +300 μA, where the electrode immediately began to coat with silver bromide at a potential of approximately +250 mV. This value gradually increased as more silver bromide was coated. At the end of the coating pulse the constant current was disconnected and the electrode switched to open circuit. The open circuit potential of the electrode was then measured. All values of stripping and coating pulse duration between 50 and 200 ms showed a similar behavior, stripping and coating at approximately –450 and +250 mV. The

shortest and longest duration are shown (Figure 6.2). For all pulse durations no significant difference in the measured potential at 4 s after the coating pulse, VAG_{4s}, was observed.

6.4.1.2 Effect of variation of stripping and coating constant current

To investigate the effect of varying the constant current the CCM technique was carried out using three different constant currents. As before the magnitude of the stripping current was set 10% higher than the coating current. A solution of 0.1 M potassium bromide was used with stripping and coating pulse durations of 50 ms (Figure 6.3).

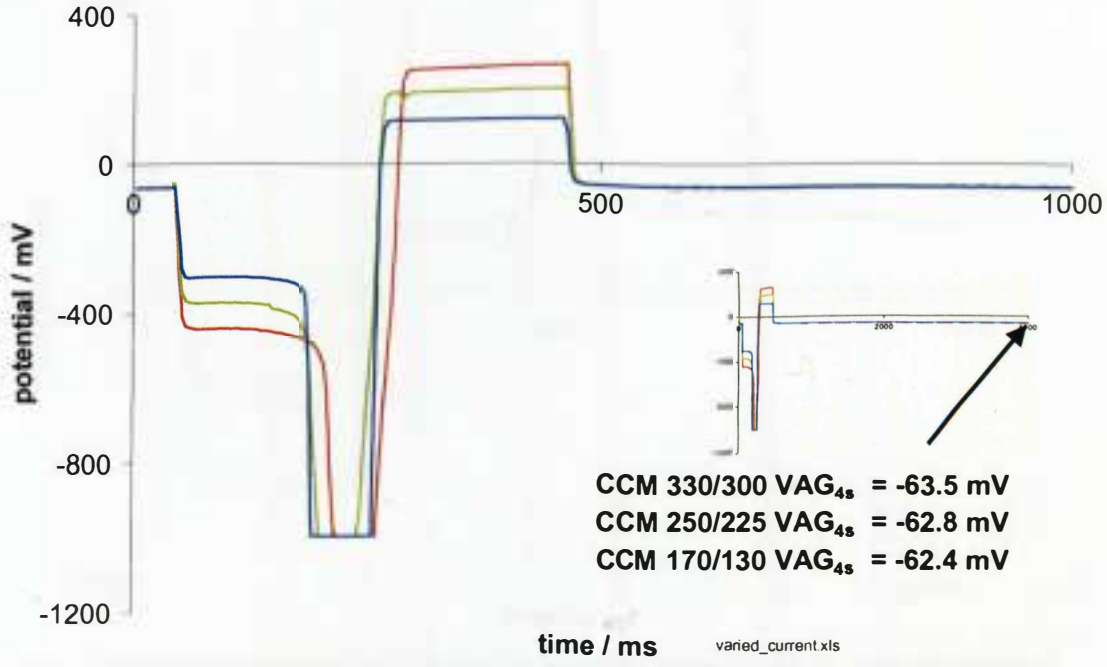


Figure 6.3 Potential profiles for stripping and coating pulses at various constant currents. (—) I_{SP}/μA = 330, I_{CP} /μA= 300 μA; (—) I_{SP} /μA= 250 μA, I_{CP} /μA= 225 μA; (—) I_{SP} /μA= 170 μA, I_{CP} /μA= 150 μA. Conditions are given in Table 6.2.

The potential of the stripping process, maintained by the constant current, became more negative as the magnitude of the stripping pulse current increased. It varied from -300 to –450 mV when the magnitude of the current increased from 170 to 330 μA. The length of the stripping process, the length of time that the electrode maintained the stripping potential, remained approximately the same at about 160 ms.

The open circuit potential, measured 4 s after the coating pulse, did not change significantly. The rate that the open circuit potentials reached that value was not significantly different for the different constant current values.

6.4.1.3 Effect of halide concentration on final potential

To determine the concentration range of the CCM constant current method, four solutions of potassium bromide, with concentrations a decade apart, were tested (Figure 6.4).

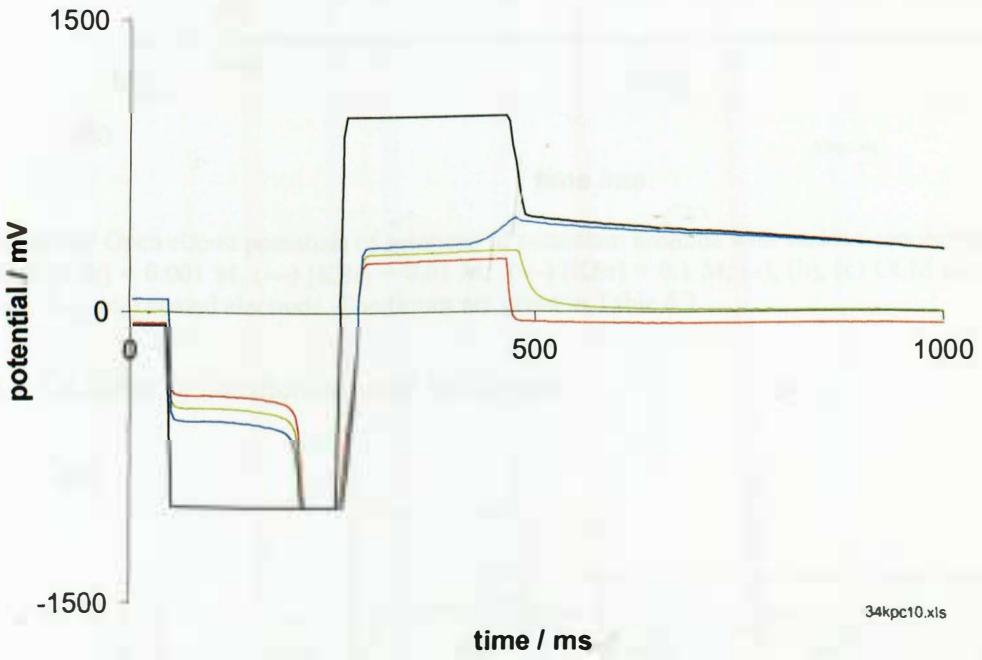


Figure 6.4 Open circuit potentials of solutions of potassium bromide with various concentrations (—) [KBr] = 0.0001 M; (—) [KBr] = 0.001 M; (—) [KBr] = 0.01 M; (—) [KBr] = 0.1 M. Conditions are given in Table 6.3

The open circuit potential was recorded from the end of the coating pulse to the end of the cycle (Figure 6.5) along with a coated silver bromide electrode. In the weakest concentration, 0.0001 M, the potential during the stripping and coating pulse exceeded –1000 and +1000 mV and the open circuit potential drifted from +1000 to –100 mV with a high level of noise on the signal. In the other three solutions the CCM electrode was in good agreement with the conventional coated

electrode at the end of the cycle. The time taken to reach a steady value increased with decreasing concentration, the 0.001 M concentration taking almost 4 s to reach the same value as the coated electrode.

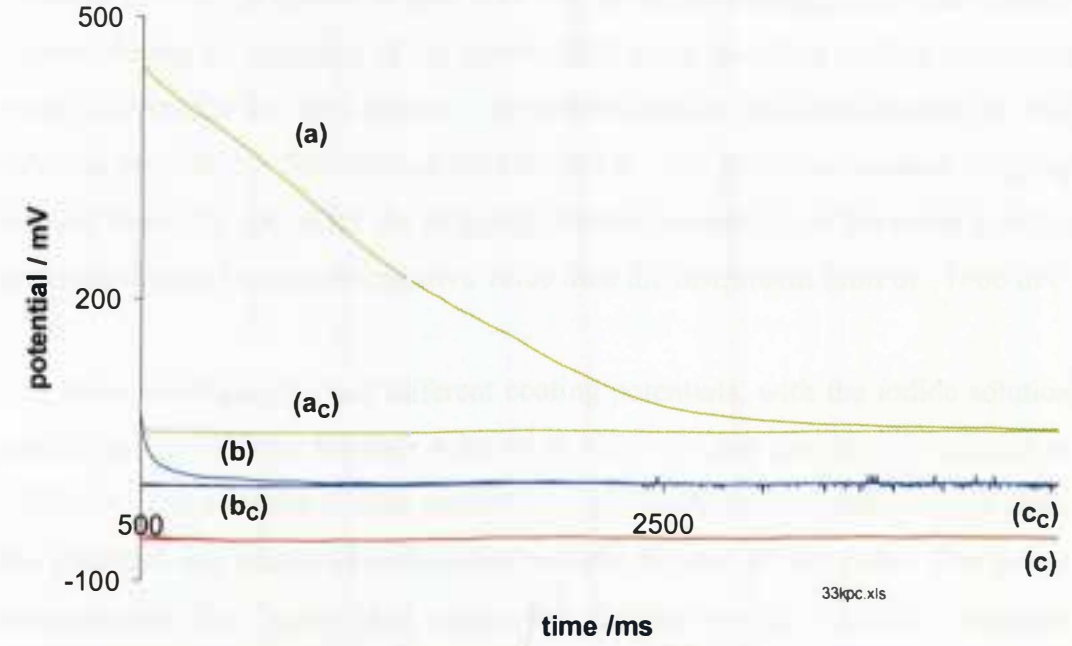


Figure 6.5 Open circuit potentials of solutions of potassium bromide with various concentrations (—) [KBr] = 0.001 M; (—) [KBr] = 0.01 M; (—) [KBr] = 0.1 M; (a), (b), (c) CCM electrodes; (a_C), (b_C), (c_C) coated electrode. Conditions are given in Table 6.3

6.4.1.4 Effect of addition of other halide ions

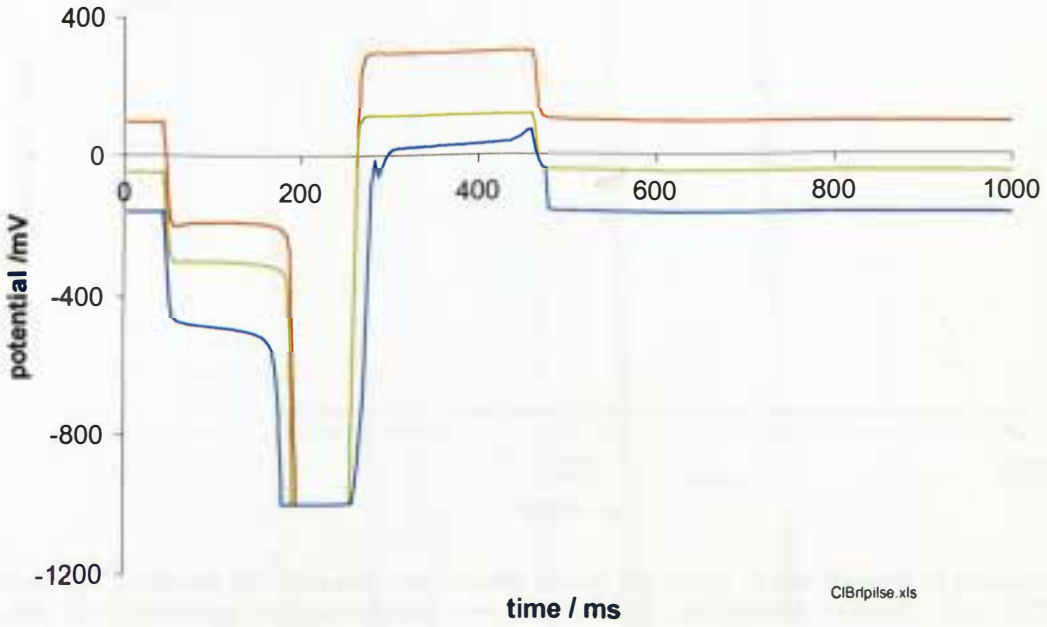


Figure 6.6 Potential profiles for standard solutions of chloride, bromide and iodide.
(—) [KI] = 0.001 M; (—) [KBr] = 0.1 M; (—) [KCl] = 0.1 M. Conditions are given in Table 6.4

The potential profiles recorded during the stripping and coating pulses of the three standard solutions of chloride, bromide and iodide using similar pulse times and constant current are shown (Figure 6.6). The potential maintained by the constant current during the stripping of the silver halide from the silver surface was found to be different for the three halides. The iodide solution was found to strip at –500 mV, the bromide at –300 mV and the chloride at –200 mV. The constant stripping current was –170 µA. After the stripping process removed then the entire coat the potential dropped to a more negative value than the instrument limit of –1000 mV.

The three solutions also had different coating potentials, with the iodide solution coating at +20 mV, the bromide solution att+120 mV and the chloride solution at +300 mV. The constant coating current was +150 µA. In the iodide coating pulse the potential was observed to increase towards the end of the pulse. The iodide concentration was lower than either the chloride or the bromide standards solutions to duplicate actual conditions in an emulsion manufacturing process.



Figure 6.7 Response of CCM and conventional coated electrodes to the addition of potassium iodide to a potassium chloride solution. (—) conventional AgCl coated electrode, (—) CCM VAG_{4s}. Conditions are given in Table 6.5 and 6.6.

In the first experiment where a chloroiodide emulsion was simulated, potassium iodide was added to a solution of potassium chloride. In this experiment the electrodes were allowed to stabilize for 3 minutes before the potassium iodide was added. After the addition of iodide the CCM electrode responded to the iodide within one cycle while the chloride coated electrode drifted towards the theoretical potential and did not reach the final value for 6 minutes (Figure 6.7). The measured open circuit potential (VAG_{4s}) and the potential from a conventional silver chloride coated electrode were recorded for a further 40 minutes. The final CCM potential of –186.5 mV was in good agreement with the theoretical value of –187.6 mV calculated for this concentration.

The potential from the cycle before iodide addition and the cycle from the end of the run, after the addition were recorded (Figure 6.8) and show that the silver chloride coating stripped at a potential of –200 mV while the silver iodide stripped at -500 mV. After the current was switched to +150 μA for the coating pulse the potential in the before addition cycle showed that the silver chloride coated at +300 mV. In the cycle after addition the coating potential was first observed to change to +20 mV for 15 ms then to rise to +300 mV.

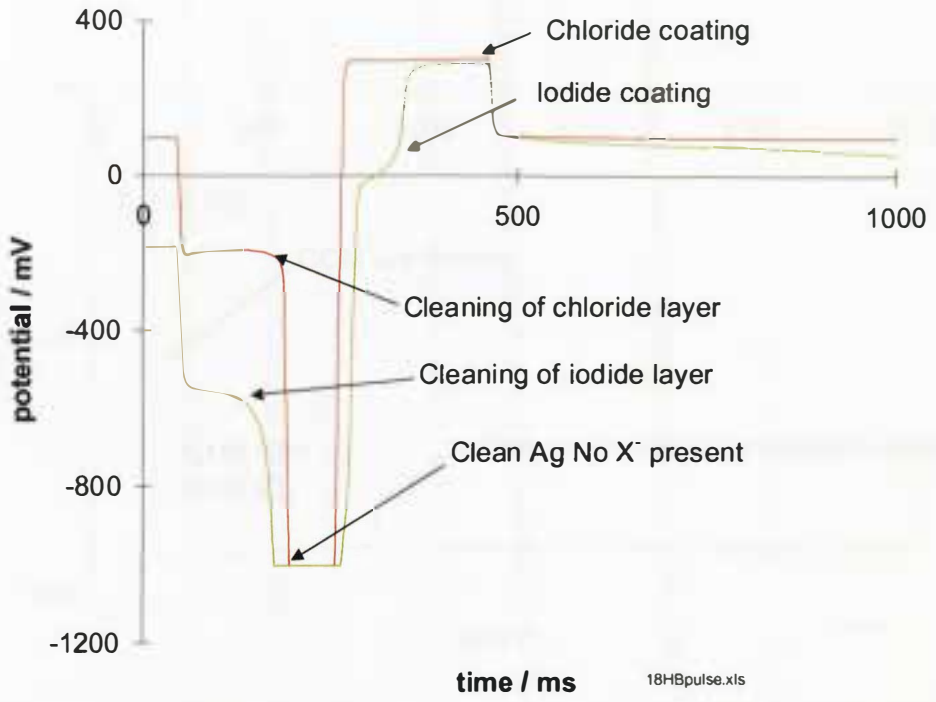


Figure 6.8 Measured potentials during the cycle immediately before (—) and after (—) the addition of potassium iodide to a solution of potassium. Conditions are given in Table 6.5 and 6.6

The second solution simulated a bromoiodide emulsion with the initial start solution containing 0.1 M potassium bromide. The electrodes were left to stabilize for 3 minutes after which time potassium iodide was added. The measured open circuit potential (VAG_{4s}) and the potential from a conventional silver bromide coated electrode were recorded for a further 40 minutes (Figure 6.9). The CCM potential was observed to respond to the change from bromide to iodide within one cycle, while the coated electrode drifted towards the theoretical value and did not reach the new value for at least 16 minutes. The CCM potential of –165.5 mV and the final coated electrode potential of -167.5 mV were in good agreement with the theoretical value of –170.5 mV calculated for this concentration.

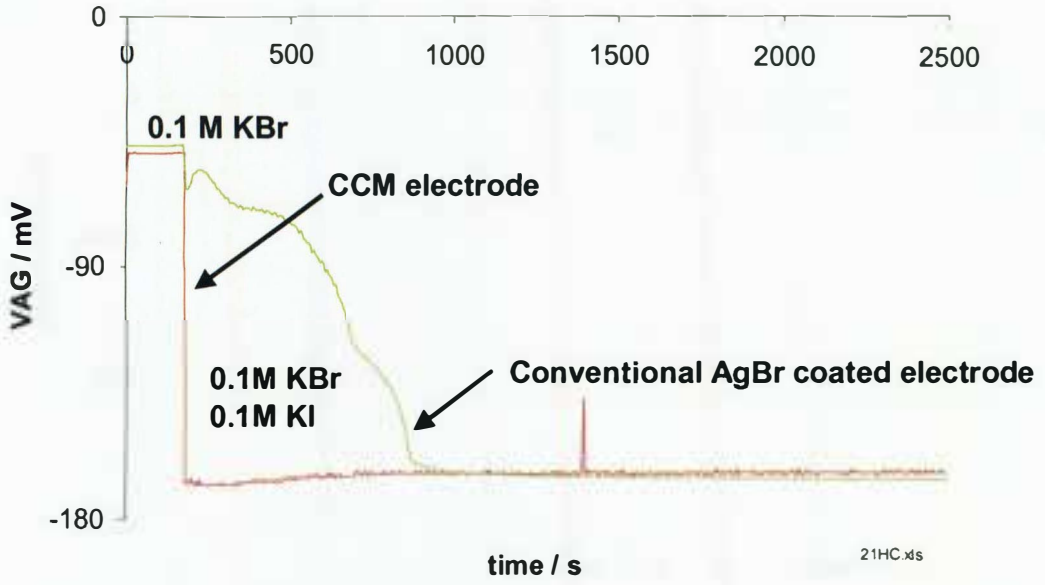


Figure 6.9 Response of CCM and conventional coated electrodes to the addition of potassium iodide to a potassium bromide solution. (—) conventional AgBr coated electrode, (—) CCM VAG_{4s}. Conditions are given in Table 6.5 and 6.6

The potential of the stripping and coating pulse was recorded for one cycle at the start, in the initial solution of bromide, and for one cycle at the end of the run in the solution with the addition of iodide (Figure 6.10). In the initial cycle the silver bromide was observed to strip of the silver metal at a potential of -300 mV and silver bromide to coat on the silver surface at a potential of +110 mV. In the cycle recorded at the end of the run and after the addition of potassium iodide the silver iodide coat was observed to strip off at –500 mV. In this cycle, when the current was switched to +150 μA for the coating pulse, the potential is first observed to change to +15 mV for 15 ms and then to rise to +100 mV.

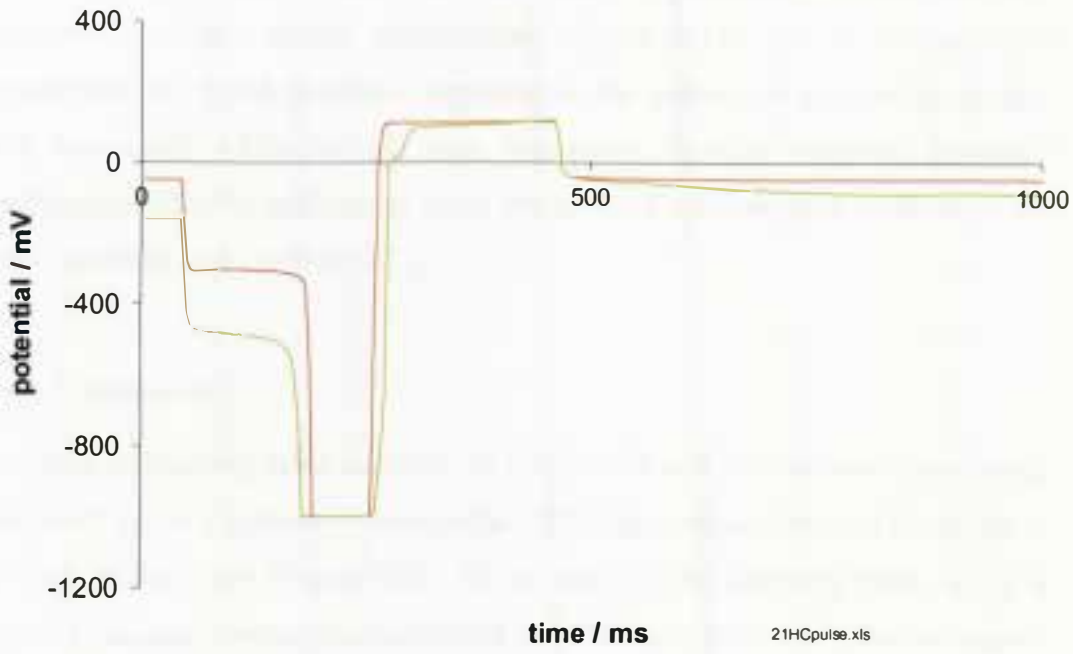


Figure 6.10 Measured potentials during the cycle immediately before (—) and after (—) the addition of potassium iodide to a solution of potassium bromide. Conditions are given in Table 6.5 and 6.6

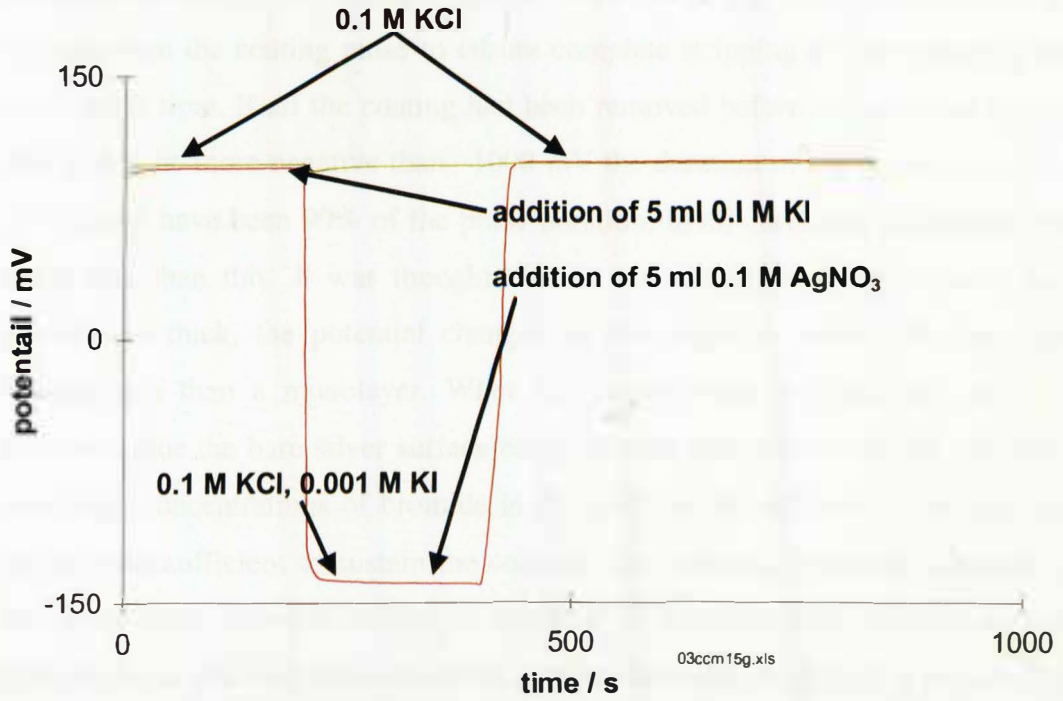


Figure 6.11 Response of CCM and conventional AgCl coated electrodes to the addition of potassium iodide to a potassium chloride solution. The iodide was subsequently removed by the addition of silver nitrate. (—) Conventional AgBr coated electrode, (—) CCM VAG_{4s}. Conditions are given in Table 6.5 and 6.6

In the third simulation, iodide was first added to potassium chloride and then removed by silver nitrate precipitation (Figure 6.11). As in the previous experiments the CCM electrode responded to the addition of the iodide solution with one cycle while in this case the silver chloride electrode remained unchanged. After the addition of silver nitrate the CCM potential returned to the initial potential in 4 cycles or 20 s.

6.4.1.5 Discussion

Stripping and coating pulse durations of between 50 and 200 ms were investigated and found not to significantly change the CCM open circuit potential measured at the end of the cycle (Figure 6.2). At the start of the stripping pulse, when a negative constant current was applied to the CCM electrode, the potential moved to a potential where it remained until the silver bromide coating had been removed. When the coat had been removed the potential rapidly changed to a negative potential limited by the instrument's capability of –1000 mV (indicating reduction of water). The constant current set for the stripping pulse was always 10 % more than the coating pulse to ensure complete stripping of the coating in the same pulse time. If all the coating had been removed before the potential rapidly changed to be more negative than –1000 mV the duration of the flat region of the plot should have been 90% of the pulse duration. In all cases this flat region was much less than this. It was thought that, as the coating was only one or two monolayers thick, the potential changed to this negative value after the layer became less than a monolayer. When the current was switched to a positive constant value the bare silver surface began to coat with silver bromide. As there were high concentrations of bromide in the solution, the diffusion layer near the surface was sufficient to sustain the current. The potential therefore remained at the silver-silver bromide oxidation potential as bromide ions diffused in and replaced those that had been converted to silver bromide. A slight rise in potential of a few millivolts was observed on the longer pulse durations (Figure 6.2). This was thought to be due to the gradual formation of the silver bromide layers inhibiting the silver oxidation process.

Variation of the stripping and coating constant current did not significantly affect the final CCM potential value (Figure 6.3). When the negative stripping current was applied, the potential of the flat region or stripping section of the plot decrease to more negative values the higher the magnitude of the negative constant current. At larger anodic currents, a more negative potential was required to maintain the higher reduction rate. The duration of the potential plateau did not significantly change with the current value as the coating current was increased proportionally. When the current was switched to a positive value the potential of the coating region increased as the constant current increased. At the larger oxidation currents a higher potential was required to maintain the higher oxidations rates. The limiting current at this concentration was not reached (Figure 6.12).

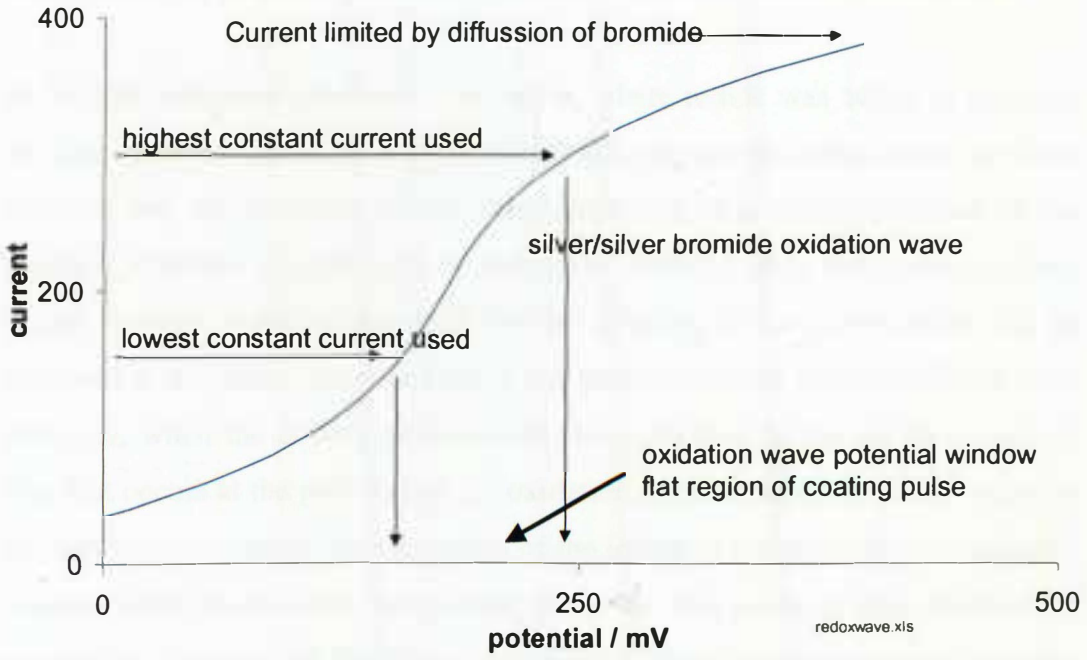


Figure 6.12 Schematic oxidation wave of silver-silver bromide

The limiting current is dependant on the concentration of bromide (see Chapter 2). At the lowest concentration of bromide investigated, 0.0001 M, the limiting current was lower than the constant current set, therefore the potential to maintain this constant current was larger than the system could support (Figure 6.4). With the instrument designed for this project the potential increased to the limit of the amplifiers and the constant current could not be maintained. At concentrations

between 0.001 and 0.1 M the limiting current was higher than the constant current used and therefore the potential was maintained within the oxidation wave window (Figure 6.12).

In the three experiments where the three halides were tested separately in standard solutions, the reduction and oxidation potentials of the three silver halides could clearly be observed (Figure 6.6). At the concentration of the test solutions the limiting current was higher than the value set by the constant current and therefore the potentials were all within the limits of the instrument. In the iodide coating pulse it was observed that the potential increased towards the end of the pulse. In this case where the iodide concentration was lower, the limiting current was close to the value set by the constant current. As iodide was depleted from the diffusion layer during the pulse the potential increased to maintain the constant current.

In the first simulated emulsion experiment, where iodide was added to chloride, the first cycle recorded before the iodide addition shows the reduction of the silver chloride and the oxidation of the silver occurring at a similar potential to the standard solutions (Figure 6.8). In the cycle recorded after the addition of the iodide, a single reduction potential for the stripping of the silver iodide can be observed at the same potential seen in the standard iodide solution (Figure 6.8). However, when the coating pulse occurs, two potential levels can be observed. The first occurs at the potential of the oxidation of silver to silver iodide. As with the standard solution the concentration of the iodide is low therefore the iodide is depleted from the diffusion layer during the pulse. The potential then rises until it reaches the potential of the silver oxidation to silver chloride where it remains until the end of the pulse due to the high concentration of bromide. The reason that a silver chloride reduction potential cannot be seen during the stripping pulse is that immediately after the end of the coating pulse the very thin silver chloride coating is chemically converted into silver iodide. This can be verified by observing the open circuit potential of the CCM electrode in the mixed chloride iodide solution (Figure 6.13). For a few hundred milliseconds the electrode responds to chloride after which time it changes to a more negative value and

responds to the iodide. It is known that silver electrodes coated with silver halide only respond to the coated halide and therefore the coating must be silver iodide to give potentials expected from a silver iodide electrode.

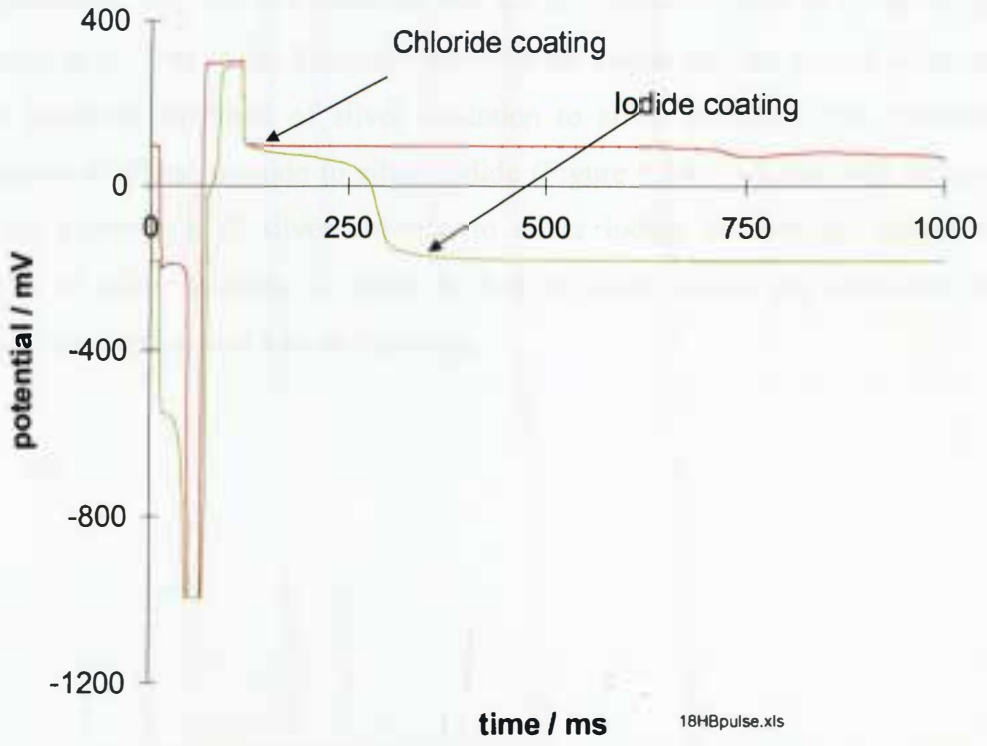


Figure 6.13 Conversion of silver chloride to silver iodide. Measured potentials during the cycle immediately before (—) and after (—) the addition of potassium iodide to a solution of potassium chloride. Conditions are given in Table 6.5 and 6.6

The CCM electrode potential recorded for the entire run (Figure 6.7) showed that the CCM technique responded to the change in halide from chloride to iodide instantly, taking only one cycle to reach the new value. The conventional coated chloride electrode, although responding to the change by beginning to drift to the new value at the time of addition, took a further six minutes before it reached and was steady at the new value. The time lag was caused by the slow process of chemical conversion of the thick coating of silver chloride to silver iodide.

In the second simulation experiment where iodide was added to a potassium bromide solution a similar profile was observed (Figure 6.10). In the pure potassium bromide solution the reduction and oxidation potentials observed from the first cycle before addition of iodide were similar to those seen in the standard bromide solution. After the addition, one reduction potential, corresponding to the

reduction of silver iodide could be seen in the stripping pulse but two oxidation potentials were observed in the coating pulse. As the iodide was at the same concentration as the previous simulation the same argument can be made for the two potentials. Viz, the first potential was the oxidation of silver to silver iodide occurring at or close to the limiting current of the iodide and the second occurred at the oxidation potential of silver oxidation to silver bromide. The chemical conversion of silver bromide to silver iodide (Figure 6.14) was less well defined than the conversion of silver chloride to silver iodide because the solubility products of silver bromide is closer to that of silver iodide and therefore the chemical conversion was a slower process.

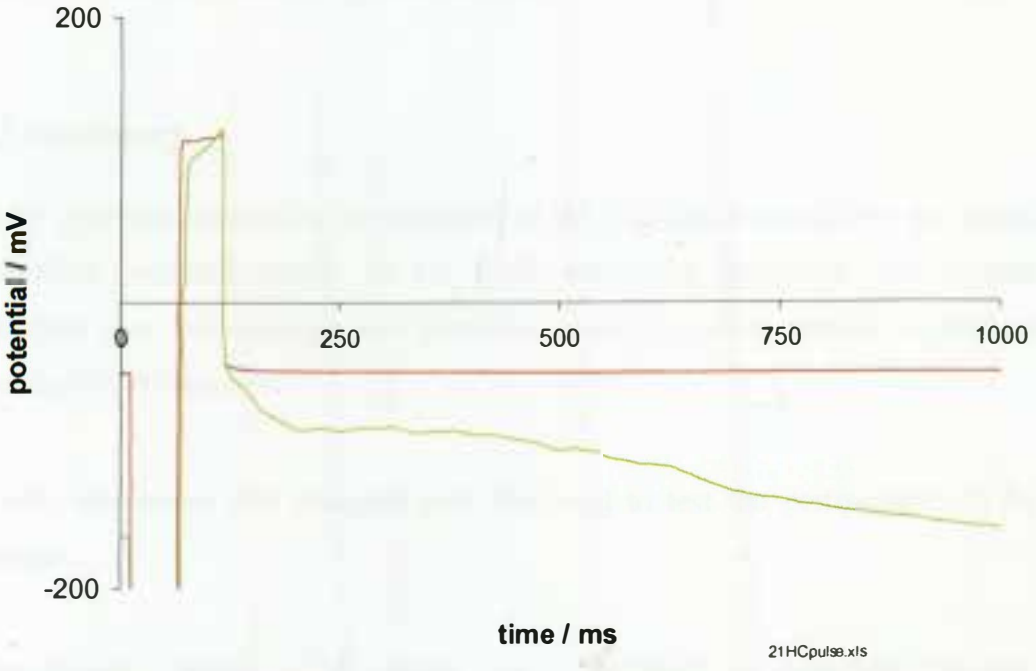


Figure 6.14 Conversion of silver bromide coating to silver iodide. Measured potentials during the cycle immediately before (—) and after (—) the addition of potassium iodide to a solution of potassium bromide. Conditions are given in Table 6.5 and 6.6

The CCM potential recorded for the entire run again, as with the previous simulation, showed that the CCM electrode responded instantly to the change from bromide to iodide while the conventional coated silver bromide electrode drifted negatively for sixteen minutes before stabilising at the same value as the CCM electrode (Figure 6.9). The silver bromide to silver iodide chemical conversion of the thick coating on the coated electrode process took longer than in

the previous case because silver bromide is less soluble in iodide than is silver chloride due to differences in solubility product.

In the third simulation experiment, iodide was again added to an initial solution containing potassium chloride, but in this case the iodide was removed by precipitation with silver nitrate after a short period to verify that the CCM electrode could return to measuring a halide with more soluble silver salt. The CCM potential recorded during the run was observed to follow the predicted potential with virtually no time lag (Figure 6.11). The slightly slower change back to a more positive potential when the iodide was precipitated was likely caused by the time taking for the iodide to completely precipitate in the large volume rather than by the response of the CCM electrode.

6.5 Summary

In the previous chapter the performance of the CCM technique using an applied controlled potential similar to the RDE work was described. This chapter describes how the technique was extended to use a constant current to strip and coat the CCM electrode.

A new instrument was designed and fabricated to test the performance of the method.

The constant current CCM system was investigated to determine optimum conditions. Stripping and coating pulse durations of between 50 and 200 ms were tested and were found to give expected CCM potentials. Constant currents for the stripping and coating pulses of between –170/+150 μA and -330/+300 μA were tested and found to be suitable for chloride, bromide and iodide. CCM potential values obtained with solutions of the three halide ions at concentrations between 0.001 and 0.1 M were in good agreement with expected values. In solutions with concentrations less than 0.001 M, using the above current levels, potentials observed during the stripping and coating pulses were above the output limits of

the instrument and the constant current could therefore not be maintained. The technique was therefore suitable for concentrations above 0.001 M.

Results from experiments which simulated emulsion manufacturing conditions indicated that the constant current technique performed well in mixed halide solutions of bromoiodide and chloroiodide. The CCM electrode responded instantly to changes in halide ions giving CCM potentials close to predicted values. The CCM electrode was not only able to measure a valid potential when the halide ion changed from chloride to iodide ion but was able to revert back to measuring chloride ion. This is not possible with the coated electrode, which will eventually change to an iodide coated electrode after chemical conversion but will not convert back to a bromide or chloride coated electrode when the iodide is removed.

The constant current technique performed well in mixed halide solutions in the concentration ranges tested.

Chapter 7. Conclusions

7.1 Introduction

The basic theory behind the proposed clean/coat/measure technique was investigated and model current and potential profiles for the coating and stripping pulses simulated (Chapter 2). Equations for the activity and steady state potential for a silver/silver halide electrode were given and values for silver chloride, silver bromide and silver iodide electrodes at various concentrations and temperatures calculated.

During the project (Chapter 3) the equilibrium potential of silver/silver halides electrodes prepared by various methods was measured and compared to the theoretical values calculated using equations defined in Chapter 2. Silver electrodes with various surface areas were coated and coatings of various thicknesses were prepared to determine the parameters that would affect the final measured potential.

A silver rotating disc electrode was used to study in detail the coating, stripping and measurement processes for a controlled potential system (Chapter 4). From this study parameters such as pulse time, coating and stripping potential and time of final measurement were investigated and an optimum method proposed.

A method using a small stationary cylindrical silver electrode was investigated for use in a process environment where a rotating disc electrode was not practical. A controlled potential pulse instrument was fabricated and tests carried out on a variety of single and mixed halide solutions (Chapter 5). A constant current pulse instrument was also fabricated and tested in similar solutions as well as in some simulated emulsion samples (Chapter 6).

7.2 Measurement of steady state potential using silver halide electrodes

Two methods were used to prepare silver electrodes for use as a comparison when investigating the new clean/coat/measure technique. The electrochemically prepared electrodes, using a constant current density, gave more precise steady state values than the electrodes coated with a chemical oxidant and a halide solution and were therefore used as the standard comparison system when investigating the new method.

Steady state potentials of silver chloride, silver bromide and silver iodide electrodes prepared by the standard method and measured in the respective single halide solutions at concentrations ranging from just above the detection limit to 1 M, showed good agreement with the theoretical values calculated in Chapter 2. Small differences between measured and calculated values were seen at concentrations near the detection limit and at the high concentrations. Extending this study to other temperatures showed similar results with similar errors being observed at the high and low concentrations.

A series of silver electrodes were fabricated with surface areas ranging from 0.8 mm^2 to 600 mm^2 ("massive" standard silver electrode) and coated electrochemically with silver bromide at the standard current density. A comparison of the measured potential with the calculated theoretical value in a wide concentration range showed no significant difference between electrodes of different surface area. The stationary electrodes used for the proposed CCM technique were designed with a surface area of 9.4 mm^2 while the rotating disc silver electrode used in the RDE experiments had a surface area of 28.2 mm^2.

Investigations were carried out to determine the thickness of the coating of the silver halide layer required to obtain a steady state potential comparable to both the standard silver/silver halide electrode and the theoretical values. Layers with varying thickness of silver halide were prepared by coating for various duration of time. Electrodes with layers calculated to be a few monolayers thick gave

comparable values, although the thinner layers were observed to dissolve into the solution within a few minutes.

These studies indicated that the electrodes with small surface areas proposed for the clean/coat/measure technique and with thin silver halide layers coated in short period of time would give measured potentials stable for the necessary measurement time and in good agreement with the standard conventionally coated "massive" silver electrodes.

7.3 Rotating disc silver electrode

Investigations to study the three processes; stripping, coating and measurement, with carefully controlled conditions of flow, were carried out using a specially fabricated silver electrode and a purpose built potential pulse controller.

The stripping pulse was observed to be independent of the flow over the electrode and only dependant on the amount of silver halide in the coated layer or the applied potential of the stripping pulse. If the controlled potential was in a window of –200 to –600 mV the silver halide layer was stripped successfully. Calculations of charge used in the stripping pulse were in good agreement with the charge used for coating. The current profile of the controlled potential stripping pulse was similar in shape to the model derived in Chapter 2. These observations fit well to the proposal that the rate of stripping is dependant on the diffusion of bromide ions through the solid silver halide layer and not the diffusion of bromide ions into the bulk solution through the aqueous diffusion layer.

The coating pulse was observed to be more complicated due to the presence of reactants from the stripping pulse left within the diffusion layer affecting the coating process. When a delay sufficient for the products of the stripping process to diffuse away was inserted between the stripping and coating pulse the coating current was observed to be dependant on the flow of solution over the electrode.

When no delay was present the coating current was inversely dependant on the flow. This was thought to be due to the reasons outlined in 4.4.4.6. However, inserting a few extra seconds into the clean/coat/measure cycle would have made the time between measurements too long in a real process situation.

The coating current profile was observed to be split into three interconnected processes. In the first few milliseconds the coating current decreased rapidly to approximately 50% of the start value. This fitted with the hypothesis outlines in 2.1.5 that predicted a sharp reduction in current due to the capacitive and faradaic currents.

This hypothesis then predicted a less rapid decrease in current as the diffusion layer was established levelling out at a diffusion limited current. However, in the experiments, an intermediate section of constant gradient was observed after the rapid decrease but before the slow decrease of current. The charge used in this section was calculated and found to be approximately equal to the charge required to coat a monolayer of the silver halide onto the silver surface. The charge used in this section was independent of the applied voltage and flow over the electrode always being approximately equal to that required for a monoloayer of silver halide.

At the end of the coating pulse the potential was switched off and the open circuit potential of the silver/silver halide electrode measured. The rate that this potential moved towards the equilibrium potential determined the time delay required before the final VAG reading could be taken. The profile and final value was initially observed to be independent of flow over the electrode. However when the applied coating potential was set too high, >+600 mV, the initial start of the profile was observed to be dependent on flow, a higher flow over the electrode increasing the rate at which it moved towards the equilibrium value. Within a set of limits this profile was independent of applied stripping and coating potential. It was observed that unless a minimum charge, approximately equal to the formation of a monolayer, was drawn, the open circuit potential drifted to an unexpected

value. This agrees with the experimental findings in Chapter 3 when electrodes were coated for very short times.

The response of the new technique to a range of bromide concentrations indicated a working range between 0.001 Maand 0.1 M. When compared to a conventional coated electrode, it was observed that in experiments where iodide was added to a bromide solution the technique performed as predicted with the CCM electrode following the theoretical VAG while the conventional electrode drifted as chemical conversion took place. The time required for the CCM VAG to reach a steady value increased in the mixed halide solution due to the coating of a mixed halide layer.

7.4 Stripping and coating under controlled potential in stirred solutions

To determine whether this technique would be suitable for a real application it was necessary to investigate the technique using static electrodes in a stainless steel emulsion manufacturing vessel. A new potential pulse controller was designed to operate in an earthed environment. As with the rotating disc electrode experiments, a set of operating conditions were found where the CCM VAG was in good agreement with the conventionally coated standard electrode.

Solutions of potassium chloride and bromide with concentrations from 0.001 M to 0.5 M and potassium iodide from 0.0001 M to 0.5 M were tested with the new technique and the conventional electrode and calibration curves plotted. The new CCM technique was in excellent agreement with both the conventional and the theoretical values. The new technique was also used to monitor a bromide solution while concentrated bromide solution was added. The CCM value responded in the same time as the conventional. When iodide was added to a bromide solution the CCM electrode responded by moving to the expected theoretical value while the conventional electrode slowly drifted in that direction.

7.5 Use of constant current stripping and coating pulses

In a production environment where there are a large number of high voltage stirrers and pumps, with inevitable grounding problems, the use of a reliable accurate potentiostat was found to be difficult. A simple solution was found by using a two electrode cell and a constant current circuit to generate the stripping and coating pulses. If the current was set at the chosen value, the potential of the working electrode was controlled by the composition of the halide solution. As with the controlled potential system, a set of operating parameters was determined at which the CCM system gave good comparison with the conventional electrode. Concentrations of bromide in the range 0.000à to 0.à M were investigated. It was found that at low bromide concentrations the current value used to ensure an adequate thickness of halide was higher than the limiting current. This resulted in the potential of the silver working electrode shifting to the maximum value of the output amplifier. Poor CCM values were observed in this low concentration because either there was insufficient coating or the higher potential affected the silver electrode potential. In solutions of mixed halide, a mixture of the silver halides were coated with the more soluble halide layer being chemically converted 1 - 2 s after the electrode had been made open circuit. The technique gave similar values to the controlled potential system. Tests were carried out on simulated emulsion solutions where bromide was added to chloride solutions and iodide was added and precipitated from bromide solutions. Results were encouraging with the CCM potentrial following the predicted values, while the conventional electrode gave values which drifted with time.

7.6 Selectivity to interfering halide ions

During the project the CCM system proved to be selective to the halide with the least soluble silver halide salt, as reported by previous workers. From the test carried out on mixed halide solutions, it was observed that although a mixed silver halide layer was initially coated it was quickly chemically converted to a layer of the least soluble silver halide. The electrode then responded to that halide and not to the mixed composition of the solution. This agrees with the work of Sandifer

(1981) on chloride electrodes, where he reports that the composition of the silver halide layer changes by chemical conversion from one halide to the other without a mixed transition phase.

7.7 Applicability to emulsion manufacturing

The technique performed well in all three halide solutions in concentration ranges similar to those expected in the emulsion manufacturing process. In the range 0.001M to 0.5 M, the observed results for single halide solutions were in good agreement with the conventional electrode system. The two systems tested, controlled potential and constant current, gave good results for mixed halide solutions, responding to changes in halide ion within a few seconds while the conventional electrode either did not respond or responded so slowly as to make it unworkable in use.

When using the RDE laboratory system and the two pulse controllers it was shown that if the applied potential or current of the stripping and coating pulses was within an optimised window, the final CCM VAG value was independent of applied potential or current. It also was observed that this open circuit potential was not sensitive to rotation speed. This technique is particularly suitable for use in manufacturing vessels where the potential or current of the working electrode may to difficult to set accurately due to ground loops and where the stirring speed may be affected by external factors such as volume of emulsion in the vessel.

Due to the cyclic nature of the technique, there was a time delay between data from successive measurements being output to a computer controlling the emulsion manufacturing process. In mixed halide solutions, a cycle of 3-4 seconds was necessary before a steady reading was available. This was caused by the coating of a mixture of silver halides and the subsequent chemical conversion to a single silver halide. Even with these problems the new technique will allow the monitoring and control of emulsions not previously manufactured under VAG control.

7.8 Instrumentation

During this project three CCM controllers were fabricated to interface to a PC with A-to-D and D-to-A cards. These units performed extremely well with large amounts of information being collected, stored and available for analysis. Small problems with interference and noise were overcome early in the project. The use of a standard PC with extra cards in a manufacturing area was considered to be too expensive to implement generally and not robust enough to install in some areas.

To overcome some of the logistic problems the author proposed three new instruments to be investigated for manufacturing areas:

- a self contained waterproof and robust CCM system with microprocessor and on-board A-to-D and D-to-A functions connected directly to the control computer without an interfacing PC;
- a similar system but with multi-channel CCM systems to allow several working electrodes to be set and read at different points in their cyclea
- an intelligent system where the value of the applied potential or constant current could be altered depending on the composition of the solution and the profile of the current and potential curves.

7.9 Completion of aims and objectives

The four objectives highlighted in Chapter 1 were completed as follows;

- the conventional silver/silver halide was evaluated and the affect of surface area and coating thickness investigated;
- the new technique was investigated using a rotating disc electrode to determine the parameters that affected the final measure potential;
- two systems were developed and field tested in emulsion manufacturing vessels with simulated emulsion samples and
- several new instruments were proposed for future trials.

7.10 Future work

Several areas of work could not be accomplished in the available time of the project or from not having sufficient access to the emulsion making vessels. The technique was not tested at various temperatures and while no problems are anticipated this should be completed before it is used to manufacture emulsions.

More investigations need to be carried out to study the measurement of mixed halide solutions with a variety of concentration and compositions. The measurement of low concentrations of one halide in high concentrations of a second or third halide should be particularly investigated as a large number of emulsion types have this composition.

Most emulsions include gelatine at between 2 % and 7 %. The effect of this should be investigated, as problems of electrode fouling at certain potentials may occur.

Emulsions also contain trace amounts of certain metals to improve sensitivity to light. These metals may plate on the working electrode and not strip off sub sequentially, allowing a non-silver surface to build up which would prevent the silver/silver halide electrode from forming.

New waterproof self-contained equipment that avoids the problems of installing a PC in a production area should be developed with the possibilities of multi-channel inputs and intelligent software worth considering.

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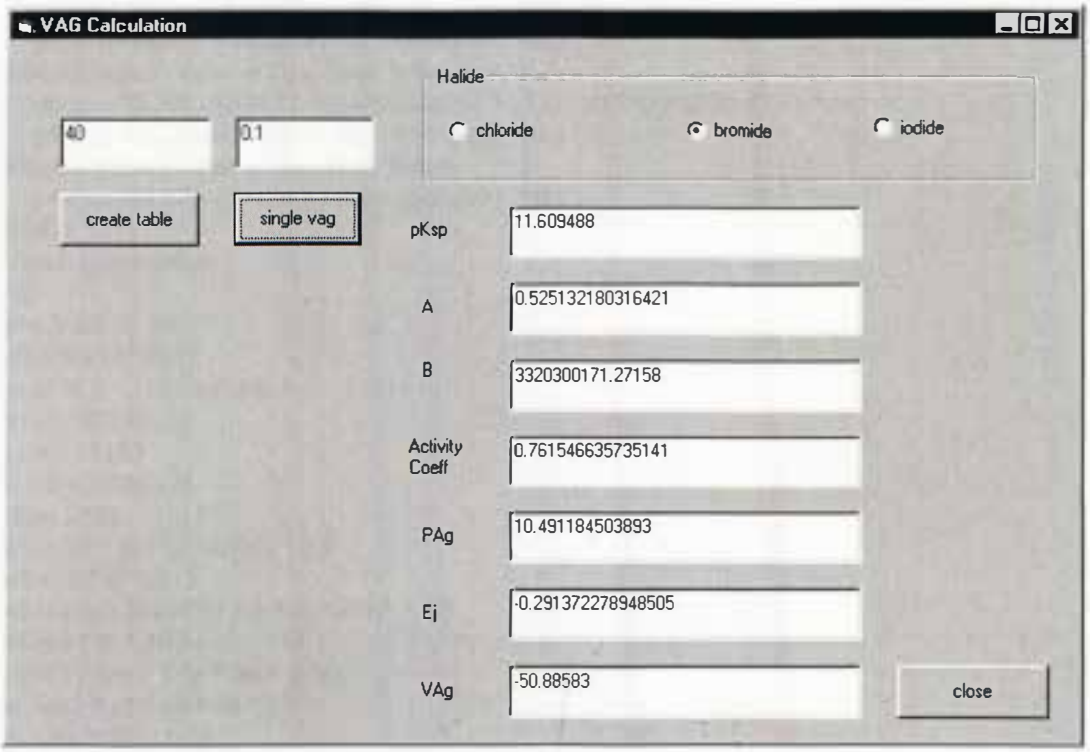
Appendix I

Visual Basic Software used to calculate theoretical potential and activity



VB6 Code

```
Option Explicit
Dim Cm As Double
Dim t As Double
Dim ystring As String
Dim A, B, ej, z, zz As Double
Dim pKsp, pag, pbr, vag As Single
Dim y, c As Double
Dim a1, a2, a3, a4, a5, ac As Double
Dim e, e0, ee, pi, k, n, d0, tk As Double
Dim b1, b2, b3, b4, bc As Double
Dim logy, si, be As Double
Private Sub calcvag()
Cm = conc.Text
t = temp.Text
tk = 273.16 + t
e = 1.6021E-19
e0 = 8.85417E-12
ee = 78.5 * (10 ^ (-0.002 * (t - 25)))
k = 1.38054E-23
pi = 3.14159
n = 6.02252E+26
d0 = 1000
'B
b1 = ((8 * pi * n) / 1000) ^ 0.5
b2 = e
b3 = 1 / ((k * tk * ee) ^ 0.5)
b4 = 1 / ((4 * pi * e0) ^ 0.5)
```

```
bc = b1 * b2 * b3 * b4
B = bc * (d00 ^ 0.5)
Text3.Text = B
'Ksp
t = temp.Text
tk = 273.16 + t
If Option1.Value = True Then 'chloride
   pKsp = -10.034 + (4663.6 / tk) + (0.013887 * tk)
ElseIf Option2.Value = True Then 'bromide
   pKsp = 13.702 - (0.0617 * t) + (0.000257 * t * t) - (0.000000558 * t * t * t)
   'pksp = -12.126 + (5868.6 / tk) + (0.015953 * tk)
ElseIf Option3.Value = True Then 'iodide
   pKsp = -12.275 + (7124.8 / tk) + (0.014951 * tk)
End If
Text10.Text = pKsp
'A
e = 1.6021E-19
e0 = 8.85417E-12
ee = 78.5 * (100 ^ (-0.002 * (t - 25)))
k = 1.38054E-23
pi = 3.14159
n = 6.02252E+26
d0 = 1000
a1 = ((2 * pi * n) / 1000) ^ 0.5
a2 = (e * e * e)
a3 = 1 / (2.302585 * ((4 * pi * e0) ^ 1.5))
a4 = 1 / (k ^ 1.5)
a5 = 1 / ((tk ^ 1.5) * (ee ^ 1.5))
ac = a1 * a2 * a3 * a4 * a5
A = ac * (d00 ^ 0.5)
Text2.Text = A
'B
b1 = ((8 * pi * n) / 1000) ^ 0.5
b2 = e
b3 = 1 / ((k * tk * ee) ^ 0.5)
b4 = 1 / ((4 * pi * e0) ^ 0.5)
bc = b1 * b2 * b3 * b4
B = bc * (d00 ^ 0.5)
Text3.Text = B
'activity coeff
If Option1.Value = True Then 'chloride
   si = 0.00000000028
ElseIf Option2.Value = True Then 'bromide
   si = 0.00000000038
ElseIf Option3.Value = True Then 'iodide
   si = 0.0000000004
End If'be = 0.0039749
logy = -(A * (Cm ^ 0.5)) / (1 + (B * si * (Cm ^ 0.5)))
logy = logy + (be * Cm)
y = 10 ^ logy
Text4.Text = y
ystring = Format(y, "0.0000")
'pAG
pbr = -Log(Cm * y) / Log(10)
pag = pKsp - pbr
Text5.Text = pag
z = (Cm0 * 73.52) + (Cm0 * 78.3)
zz = (Cm * 73.52) - (Cm * 78.3)
```

```
'Junction pot
ej = 2.5 * 8314 * (tk / 96485) * ((zz - 0) / (z - 368)) * Log(z / 368)
Text7.Text = ej
'VAG
vag = 602 - (0.1984 * pag * tk) - (0.09 * (t - 25)) - ej
Text6.Text = vag
End Sub
Private Sub cmdrun_Click()
Dim n, m As Single
Dim file As String
Dim carray(13) As Single
carray(0) = 1
carray(1) = 0.5
carray(2) = 0.1
carray(3) = 0.05
carray(4) = 0.02
carray(5) = 0.01
carray(6) = 0.005
carray(7) = 0.002
carray(8) = 0.001
carray(9) = 0.0005
carray(10) = 0.0001
carray(11) = 0.00005
carray(12) = 0.00002
carray(13) = 0.00001
file = App.Path + "\vag.txt"
Open file For Output As #1
Print #1, "pot bromide temp steps"
   For n = 20 To 60 Step 5
     For m = 0 To 13
        temp.Text = n
        conc.Text = carray(m)
        calcvag
        Print #1, n, carray(m), ystring, vag
     Next m
     Print #1, ""
  Next n
Close #1
End Sub
Private Sub cmdvag_Click()
calcvag
End Sub
Private Sub cmdend_Click()
End
End Sub
Private Sub Form_Load()
temp.Text = 40
conc.Text = 0.1
Option2.Value = True
End Sub
```

Theoretical values and activities coefficients

Chloride

ACTIVITY COEFFICIENT

Temperature / ºC

[chloride]	20	25	30	35	40	45	50	55	60
1	0.5504	0.5478	0.5451	0.5423	0.5393	0.5363	0.5331	0.5298	0.5264
0.5	0.6101	0.6077	0.6052	0.6025	0.5997	0.5968	0.5938	0.5907	0.5874
0.1	0.7527	0.7509	0.7490	0.7470	0.7448	0.7426	0.7404	0.7380	0.7355
0.05	0.8063	0.8048	0.8032	0.8016	0.7998	0.7980	0.7961	0.7941	0.7920
0.02	0.8647	0.8636	0.8624	0.8612	0.8599	0.8585	0.8571	0.8557	0.8541
0.01	0.8991	0.8982	0.8973	0.8963	0.8954	0.8943	0.8932	0.8921	0.8909
0.005	0.9257	0.9251	0.9244	0.9237	0.9229	0.9222	0.9213	0.9205	0.9196
0.002	0.9513	0.9509	0.9504	0.9499	0.9494	0.9489	0.9483	0.9478	0.9472
0.001	0.9649	0.9646	0.9643	0.9639	0.9635	0.9632	0.9628	0.9623	0.9619
0.0005	0.9748	0.9746	0.9744	0.9741	0.9739	0.9736	0.9733	0.9730	0.9727
0.0001	0.9885	0.9884	0.9883	0.9882	0.9881	0.9880	0.9878	0.9877	0.9875
0.00005	0.9919	0.9918	0.9917	0.9916	0.9915	0.9915	0.9914	0.9913	0.9912
0.00002	0.9948	0.9948	0.9947	0.9947	0.9946	0.9946	0.9945	0.9944	0.9944
0.00001	0.9963	0.9963	0.9963	0.9962	0.9962	0.9962	0.9961	0.9961	0.9960

VAG

Temperature / ºC

[chloride]	20	25	30	35	40	45	50	55	60
1	40.33	42.09	43.72	45.22	46.60	47.85	48.97	49.97	50.84
0.5	54.82	56.80	58.66	60.39	61099	63.46	64.80	66.02	67.10
0.1	89.62	92.16	94.57	96.84	98.99	101000	102.88	104.63	106.24
0.05	105.28	108.07	110.73	113.26	115.65	117.91	120.04	122.03	123.89
0.02	126.58	129.72	132.72	135.60	138.33	140.93	143.40	145.73	147.93
0.01	143.07	146.48	149.76	152.90	155.91	158.78	161.52	164.12	166.58
0.005	159.82	163.51	167.07	170.49	173.77	176.92	179.93	182.81	185.55
0.002	182.26	186.33	190.26	194.06	197.72	201.24	204.62	207.87	210.99
0.001	199.41	203.77	207.99	212.07	216.02	219.83	223.50	227.04	230.43
0.0005	216.66	221.30	225.82	230.19	234.43	238.53	242.49	246.32	250.01
0.0001	256.95	262.29	267.48	272.54	277.46	282.25	286.89	291040	295.77
0.00005	274.38	280.01	285.50	290.85	296.07	301.15	306.09	310.90	315.56
0.00002	297.45	303.47	309.36	315.10	320.71	326.18	331052	336.72	341077
0.00001	314.92	321024	327.42	333.47	339.37	345.14	350.77	356.27	361063

Bromide

ACTIVITY COEFFICIENT

	Temperature / ºC								
[bromide]	20	25	30	35	40	45	50	55	60
1	0.6013	0.5990	0.5965	0.5939	0.5913	0.5885	0.5856	0.5826	0.5795
0.5	0.6488	0.6466	0.6443	0.6419	0.6394	0.6367	0.6340	0.6312	0.6282
0.1	0.7688	0.7671	0.7654	0.7635	0.7615	0.7595	0.7574	0.7552	0.7529
0.05	0.8164	0.8149	0.8134	0.8119	0.8102	0.8085	0.8067	0.8049	0.8030
0.02	0.8697	0.8686	0.8675	0.8663	0.8651	0.8638	0.8624	0.8610	0.8596
0.01	0.9019	0.9010	0.9002	0.8992	0.8983	0.8973	0.8962	0.8951	0.8940
0.005	0.9273	0.9266	0.9260	0.9253	0.9245	0.9238	0.9230	0.9222	0.9213
0.002	0.9520	0.9515	0.9511	0.9506	0.9501	0.9496	0.9491	0.9485	0.9479
0.001	0.9653	0.9649	0.9646	0.9643	0.9639	0.9635	0.9631	0.9627	0.9623
0.0005	0.9750	0.9748	0.9746	0.9743	0.9741	0.9738	0.9735	0.9732	0.9729
0.0001	0.9886	0.9885	0.9884	0.9883	0.9881	0.9880	0.9879	0.9877	0.9876
0.00005	0.9919	0.9918	0.9917	0.9916	0.9916	0.9915	0.9914	0.9913	0.9912
0.00002	0.9948	0.9948	0.9947	0.9947	0.9946	0.9946	0.9945	0.9945	0.9944
0.00001	0.9963	0.9963	0.9963	0.9962	0.9962	0.9962	0.9961	0.9961	0.9960

VAG

	Temperature / ºC								
[bromide]	20	25	30	35	40	45	50	55	60
1	-114.36	-111.85	-109.48	-107.25	-105.16	-103.21	-101.42	-99.77	-98.26
0.5	-99.19	-96.44	-93.83	-91.35	-89.01	-86.83	-84.79	-82.90	-81.16
0.1	-63.37	-60.04	-56.84	-53.79	-50.89	-48.13	-45.53	-43.07	-40.77
0.05	-47.49	-43.90	-40.44	-37.13	-33.97	-30.96	-28.11	-25.40	-22.85
0.02	-26.02	-22.08	-18.27	-14.61	-11.10	-7.75	-4.54	-1.49	1.41
0.01	-9.46	-5.25	-1517	2.76	6.55	10.18	13.65	16.97	20.14
0.005	7.32	11582	16.18	20.39	24.45	28.36	32.15	35.71	39.15
0.002	29.79	34.67	39.40	43.99	48.42	52.71	56.83	60.80	64.62
0.001	46.94	52.11	57.13	62.01	66.73	71530	75.72	79.98	84.08
0.0005	64.19	69.65	74.97	80.13	85.15	90.01	94.72	99.27	103.66
0.0001	104.50	110.64	116.64	122.49	128.19	133.73	139.12	144.35	149.43
0.00005	121592	128.36	134.65	140.80	146.80	152.64	158.32	163.85	169.22
0.00002	144.99	151582	158.51	165.05	171.44	177.67	183.75	189.67	195.43
0.00001	162.46	169.59	176.58	183.41	190.10	196.63	203.00	209.22	215.28

Iodide

ACTIVITY COEFFICIENT

	Temperature / ºC								
[iodide]	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**
1	0.6102	0.6079	0.6055	0.603	0.6004	0.5976	0.5948	0.5919	0.5888
0.5	0.6557	0.6535	0.6512	0.6489	0.6464	0.6438	0.6415	0.6383	0.6355
0.1	0.7718	0.7701	0.7684	0.7666	0.7646	0.7626	0.7605	0.7584	0.7561
0.05	0.8182	0.8168	0.8154	0.8138	0.8122	0.8105	0.8087	0.8069	0.805
0.02	0.8706	0.8696	0.8685	0.8673	0.8661	0.8648	0.8635	0.8621	0.8606
0.01	0.9024	0.9016	0.9007	0.8998	0.8988	0.8978	0.8968	0.8957	0.8946
0.005	0.9276	0.9269	0.9263	0.9256	0.9249	0.9241	0.9233	0.9225	0.9216
0.002	0.9521	0.9517	0.9512	0.9507	0.9503	0.9497	0.9492	0.9486	0.9481
0.001	0.9653	0.965	0.9647	0.9643	0.964	0.9636	0.9632	0.9628	0.9624
0.0005	0.9751	0.9748	0.9746	0.9744	0.9741	0.9738	0.9735	0.9732	0.9729
0.0001	0.9886	0.9885	0.9884	0.9883	0.9881	0.988	0.9879	0.9877	0.9876
0.00005	0.9919	0.9918	0.9917	0.9917	0.9916	0.9915	0.9914	0.9913	0.9912
0.00002	0.9948	0.9948	0.9947	0.9947	0.9946	0.9946	0.9945	0.9945	0.9944
0.00001	0.9963	0.9963	0.9963	0.9962	0.9962	0.9962	0.9961	0.9961	0.996

VAG

	Temperature / ºC								
[iodide]	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**
1	-338.38	-335.09	-331594	-328.93	-326.07	-323.34	-320.75	-318.29	-315.98
0.5	-323.10	-319.57	-316.17	-312.92	-309.80	-306.83	-304.00	-301530	-298.75
0.1	-287.15	-282.99	-279.01	-275.18	-271549	-267.94	-264.54	-261527	-258.16
0.05	-271519	-266.81	-262.57	-258.48	-254.53	-250.73	-247.07	-243.55	-240.18
0.02	-249.69	-244.96	-240.37	-235.93	-231563	-227.48	-223.47	-219.61	-215.89
0.01	-233.13	-228.12	-223.25	-218.54	-213.97	-209.54	-205.26	-201513	-197.14
0.005	-216.33	-215504	-205.90	-200.90	-196.05	-191535	-186.79	-182.38	-178.12
0.002	-193.86	-188.19	-182.67	-177.30	-172.07	-167.00	-162.07	-157.28	-152.65
0.001	-176.70	-170.75	-164.94	-159.28	-153.76	-148.40	-143.18	-138.11	-133.18
0.0005	-159.45	-153.20	-147.10	-141.15	-135.35	-129.69	-124.18	-118.82	-113.60
0.0001	-119.15	-112.22	-105.43	-98.80	-92.31	-85.97	-79.77	-73.73	-67.83
0.00005	-101.72	-94.49	-87.41	-80.48	-73.70	-67.06	-60.57	-54.23	-48.04
0.00002	-78.65	-71.03	-63.56	-56.23	-49.06	-42.03	-35.15	-28.42	-21.83
0.00001	-61518	-53.26	-45.49	-37.87	-30.40	-23.07	-15.89	-8.86	-1598

Appendix II

Data from potential measurements at 40 °C

Chloride electrode

[KCl]	1	2	3	4	5	6	7	8	mean	std dev
1	40.1	40.9	39.5	39.8	40.2	4151	39.8	39.3	40.088	0.636
0.5	56.7	57.7	57.2	56.1	56.5	55.9	55.2	57.9	56.650	0.923
0.1	97.5	97.1	96.5	99	97.1	98.7	97.1	97.3	97.538	0.862
0.05	115.1	114.1	115.9	115.1	115.7	114.2	113.9	116.6	115.075	0.963
0.02	138.6	138.1	139.6	140	137.9	140.1	138.3	140.5	139.138	1.024
0.01	154.5	153.9	156.8	155.2	154.7	154.1	157.1	153.5	154.975	1.325
0.005	173	175.1	173.4	172.3	17157	171.3	175.2	174.2	173.275	1.479
0.002	197.7	199.2	195.7	198.2	196.8	195.3	199.3	197.9	197.513	1.483
0.001	213.1	213.9	215.6	215.1	213.7	213.9	212.9	214.7	213.613	1.095
0.0005	23151	232.6	230.8	230.1	232.8	231.7	230.5	230.1	2315213	1.059
0.0001	268.7	265.9	270.9	267.9	269.1	268.4	269.5	268.9	268.663	1.426

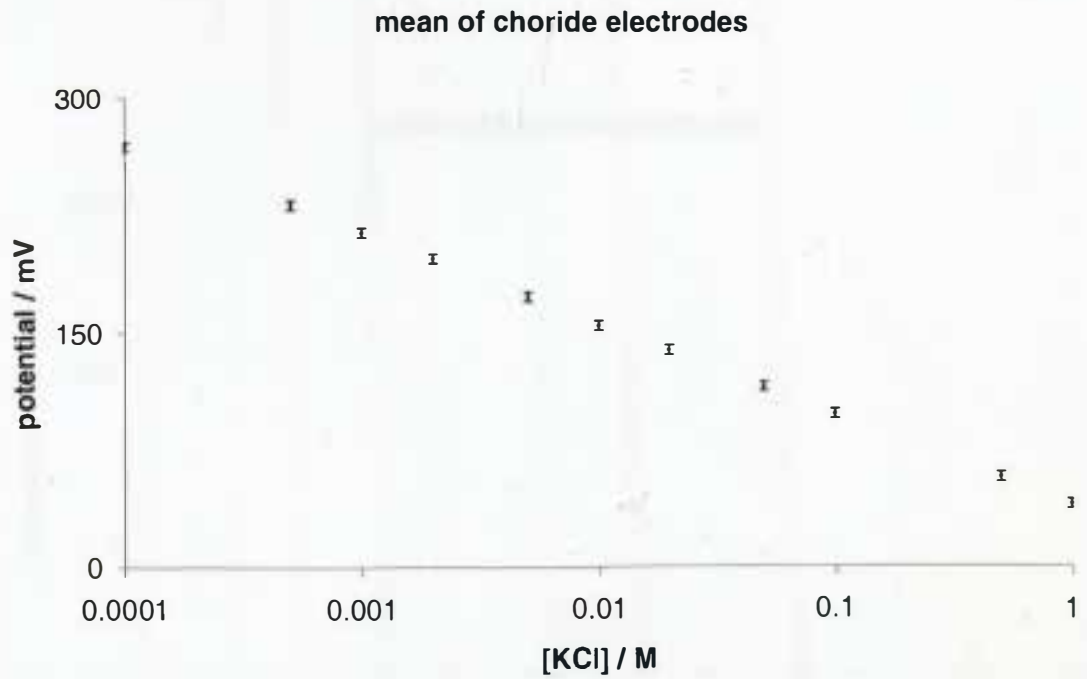


Figure A1. Full data for calibration of eight silver chloride electrodes. Error bars are drawn at 3 sigma

Data from potential measurements at 40 °C

Bromide electrode

[KBr]	1	2	3	4	5	6	7	8	mean	std dev
1	-107.9	-106.5	-108.1	-107.9	-108.3	-106.8	-107.5	-107.4	-107.550	0.680
0.5	-91	-9154	-90.5	-90.9	-91.2	-91.3	-89.3	-9152	-90.850	0.726
0.1	-52.1	-53.1	-52.4	-5156	-5152	-52	-52.5	-5159	-52.100	0.621
0.05	-35.7	-36.1	-35.9	-34.7	-35.6	-34.9	-35.7	-37.2	-35.725	0.518
0.02	-12.7	-11.9	-11.7	-12.3	-13.2	-13.7	-12.5	-12.6	-12.575	0.704
0.01	4.9	4.4	5.4	5.5	4.1	4.6	4.7	5.1	4.838	0.510
0.005	22.8	22.1	23.1	23.7	22.9	21.9	22.7	22.1	22.663	0.605
0.002	46.7	47.1	46.3	45.9	47.5	46.2	46.9	46.4	46.625	0.559
0.001	64.9	65.4	65.1	64.2	64.3	65.9	65.3	64.1	64.900	0.607
0.0005	84.7	84.5	83.8	83.4	83.6	83.9	83.7	85.9	84.188	0.479
0.0001	126.4	124.5	125.4	126.1	125.4	125.9	125.3	126.1	125.638	0.626
0.00005	145	145.9	146.8	143.6	144.6	145.1	145.9	146.3	145.400	1.039
0.00002	169.3	169.8	167.3	168.4	169.6	169.7	167.9	167.1	168.638	0.991
0.00001	187.6	189.2	187.4	186.9	185.9	189.5	188.3	187.9	187.838	15272

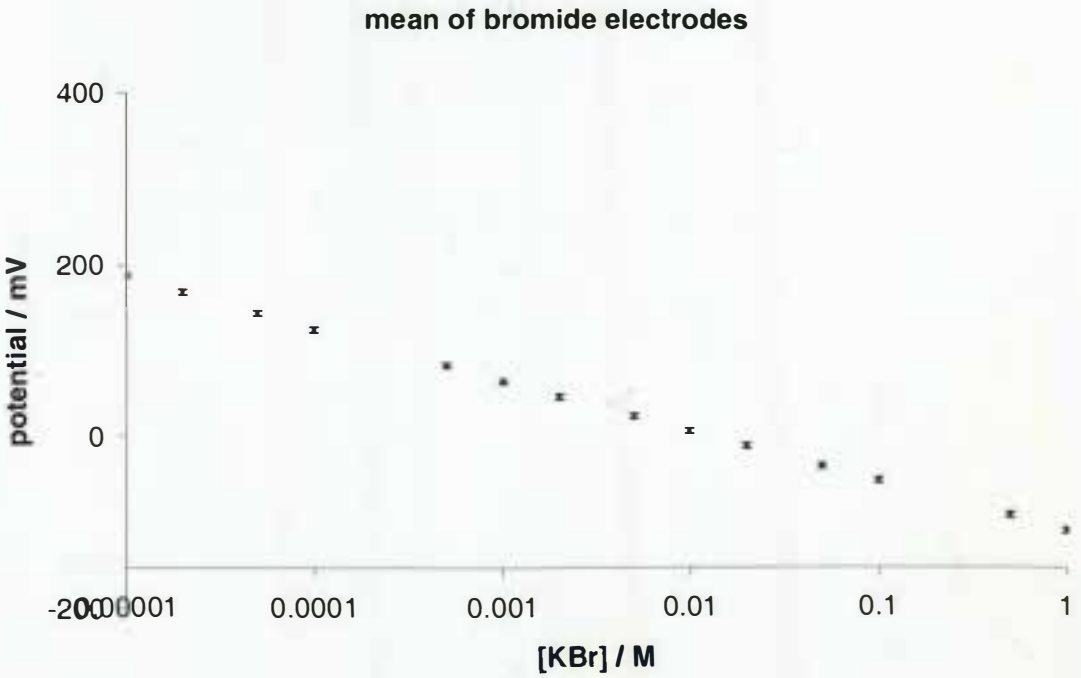


Figure A1. Full data for calibration of eight silver bromide electrodes. Error bars are drawn at 3 sigma

Data from potential measurements at 40 °C

Iodide electrode

[KI]	1	2	3	4	5	6	7	8	mean	std dev
1	-307	-306.2	-308.3	-306.0	-307.7	-306.6	-306.9	-307.5	-307.041	0.770
0.5	-300.1	-300.0	-300.7	-299.4	-300.9	-30150	-300.0	-300.4	-300.308	0.558
0.1	-270.9	-270.6	-270.0	-270.3	-27159	-269.9	-270.6	-27159	-270.762	0.771
0.05	-253.9	-252.9	-253.0	-253.3	-253.1	-253.8	-253.4	-253.9	-253.410	0.393
0.02	-230.1	-23150	-229.2	-23150	-230.6	-230.3	-230.7	-229.4	-230.280	0.688
0.01	-213.4	-213.4	-212.5	-212.6	-213.5	-213.5	-213.6	-214.1	-213.317	0.533
0.005	-195.8	-198.8	-193.6	-193.6	-199.2	-195.2	-197.1	-197.0	-196.284	2.134
0.002	-173.4	-173.0	-172.2	-172.2	-172.2	-172.2	-172.2	-172.2	-172.442	0.487
0.001	-156.2	-154.4	-155.3	-155.3	-155.3	-155.3	-155.3	-155.3	-155.307	0.491
0.0005	-137.1	-135.3	-134.9	-134.9	-134.9	-134.9	-134.9	-134.9	-135.224	0.769
0.0001	-92.9	-95.6	-94.6	-92.1	-92.5	-93.1	-92.4	-93.1	-93.285	1.195
0.00005	-74	-72.3	-72.6	-75.4	-75.1	-74.7	-73.8	-73.9	-73.968	1.117
0.00002	-52.6	-50.7	-5152	-53.2	-52.8	-52.4	-5159	-54.6	-52.429	1.205
0.00001	-35.8	-37.2	-34.8	-35.7	-36.1	-36.7	-34.6	-34.1	-35.623	1.063

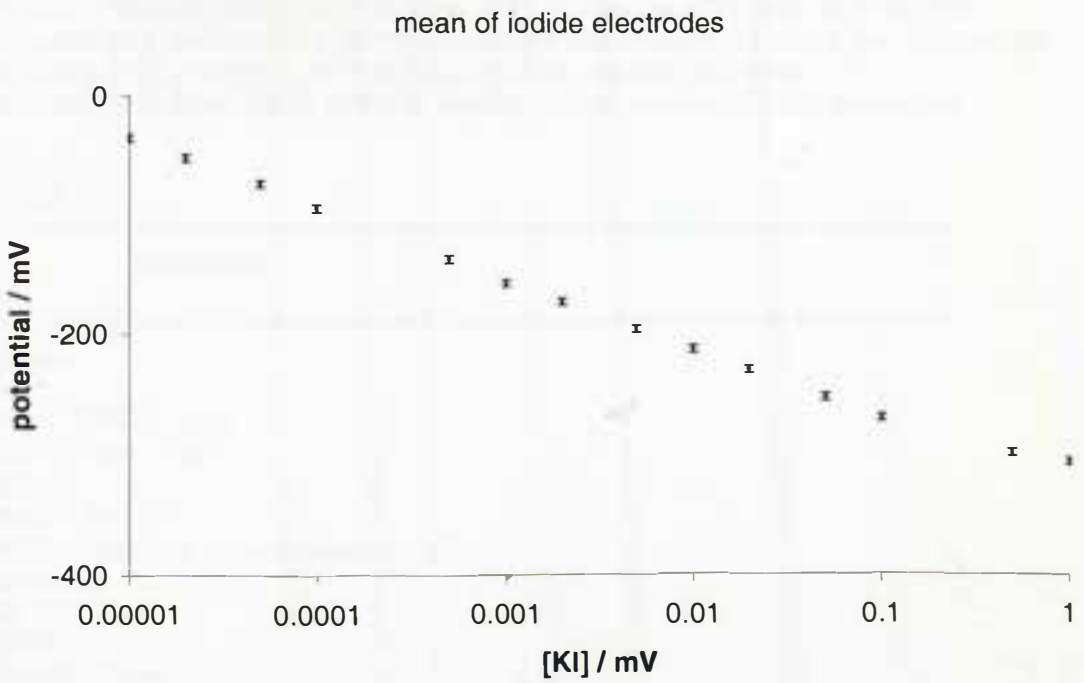


Figure A1. Full data for calibration of eight silver iodide electrodes. Error bars are drawn at 3 sigma

Appendix III

Example of CCM control and logging QuickBASIC software.

```
'*************************************************************************
'*                                                                       *
'*                    CCMKP7                                             *
'*                                                                       *
'*      CLEAN COAT PROGRAM FOR FOUR CHANNEL INSTRUMENT                   *
'*           Program for voltage pulse using the RTI850F AD card         *
'*                Storing cycle in fileXX.dat and data in file.dat       *
'*                     850BOARD=1    815 BOARD= 2                       *
'*                                S EDWARDS                              *
'*************************************************************************
DEFINT A-Z
DIM scanarray(4000)
DIM array(4000) AS SINGLE
DIM newarray(8, 1000) AS SINGLE
DIM G!(8)
DIM O!(8)
DIM CHANARRAY(8)
DECLARE SUB INITIALIZE CDECL (SEG erstat AS INTEGER)
DECLARE SUB cscan850 CDECL (BYVAL lchan, BYVAL BOARD, SEG CHANARRAY,
BYVAL range, BYVAL mult, BYVAL rcount&, SEG erstat AS INTEGER)
DECLARE SUB cscan CDECL (BYVAL lchan, SEG scanarray AS INTEGER, SEG erstat AS
INTEGER)
DECLARE SUB CHECK CDECL (BYVAL NCHAN, SEG erstat AS INTEGER)
DECLARE SUB dot815 CDECL (BYVAL lchan, BYVAL BOARD, SEG erstat AS INTEGER)
DECLARE SUB dot CDECL (BYVAL lchan, BYVAL valueout, SEG erstat AS INTEGER)
DECLARE SUB aot815 CDECL (BYVAL lchan, BYVAL BOARD, BYVAL pchan, SEG aerstat)
DECLARE SUB aot CDECL (BYVAL lchan, BYVAL valueout, SEG erstat)
DECLARE SUB delay CDECL (BYVAL minutes, BYVAL seconds, BYVAL hundredths)

SCREEN 0
COLOR 1, 7
'*************************************************************************
'*              MEASURE                                                  *
'*                                                                       *
'*************************************************************************
measure:
CLS
INPUT "RDS=?", RDS
'INPUT " SEC ", SEC
SEC= 5
PRINT " SEC= 5"
INPUT " pulse time= ?( in Millisecs) ", PU
filename:
LOCATE 20, 35
PRINT'
LOCATE 21, 30
PRINT'
LOCATE 20, 5
INPUT "Enter file start for data storage ?    ", fil$
LOCATE 21, 5
INPUT "Enter experiment title ? ", title$
title$= CHR$(34) +title$+ CHR$(34)
```

```
keyinput:
LOCATE 22, 60
PRINT0'
LOCATE 22, 5
INPUT "Press s to start program or r to redo file name and title     ", k$
IF k$ = "r" GOTO filename
IF k$ = "s" GOTO start
GOTO keyinput

start:
COLOR0, 7
CLS
GOSUB initread
GOSUB inputdat

file$0= fil$ + ".dat"
OPEN file$ FOR OUTPUT AS #1
REM ******* PRINT HEADER TO FILE *********
PRINT #1, "~",0itle$,0", file$, TIME$, DATE$
PRINT #1, "header,", "Before", "0.5sec", "1sec", "2sec", "3sec", "4sec", "coated"
CLOSE #1

REM ******** SET UP DISPLAY**********
LOCATE 2, 10
PRINT "CCMKP SOFTWARE Version 4.0"
VIEW PRINT 10 TO 20
re0= 0
TIMER ON
ON TIMER(SEC) GOSUB measure1
DO WHILE re0< RDS: LOOP
PRINT0"
PRINT " DATA COLLECTION COMPLETED"
INPUT "Press any key to return to Main Menu"; ans$
CLS
END

measure1:
COLOR 1, 7
IF re = RDS THEN RETURN
re = re + 1
PRINT " cycle ", re
GOSUB collect
RETURN

'*************************************************************************
'*                                INITREAD                               *
'*                                                                       *
'*************************************************************************
initread:
c = 4
R = 1000
NU0= R * c

CALL INITIALIZE(erstat)
IF erstat <> 0 THEN PRINT "ERROR INITIALISE="; erstat: END

CHANARRAY(0) = c
```

```
CHANARRAY(1) = 0
CHANARRAY(2) = 1
CHANARRAY(3) = 2
CHANARRAY(4) = 5
lchan = 0: BOARD = 1: range = 10: mult = 100: rcount& = NU
' 4000 readings over 4 secs
CALL cscan850(lchan, BOARD, CHANARRAY(0), range, mult, rcount&, erstat)
IF erstat <> 0 THEN PRINT "ERROR ccol="; erstat: END
lchan = 9: BOARD = 2: pchan = 0
CALL aot815(lchan, BOARD, pchan, erstat)
IF erstat <> 0 THEN PRINT "ERROR AOT="; erstat: END
lchan = 10: BOARD = 2
CALL dot815(lchan, BOARD, erstat)
IF erstat <> 0 THEN PRINT "ERROR DOT="; erstat: END
RETURN

'************************************************************************
'*                          STOREDAT                                    *
'*                                                                      *
'************************************************************************

storedat:
OPEN "calibccm.dat" FOR OUTPUT AS #1
FOR n = 0 TO 3: PRINT #1, G!(n), O!(n): NEXT
CLOSE #1
RETURN
'************************************************************************
'*                          INPUTDAT                                    *
'*                                                                      *
'************************************************************************
inputdat:
OPEN "calibccm.dat" FOR INPUT AS #1
FOR n = 0 TO 3: INPUT #1, G!(n), O!(n): NEXT
CLOSE #1
RETURN

'************************************************
'*                  COLLECT                     *
'************************************************
collect:
CO = INT((PU / 41) * 100)
lchan = 0
CALL cscan(lchan, SEG scanarray(0), erstat)
FOR count1 = 1 TO 2
FOR count = 1 TO 10000
NEXT
NEXT
'switch relay to connect current
lchan = 10: valueout = 0
CALL dot(lchan, valueout, erstat)
'output clean pulse
lchan = 9: valueout = 100
CALL aot(lchan, valueout, erstat)
FOR count1 = 1 TO CO
FOR count = 1 TO 100
NEXT
NEXT
'output coat pulse
```

```
lchan = 9: valueout = -100
CALL aot(lchan, valueout, erstat)
FOR count1 = 1 TO CO
FOR count = 1 TO 100
NEXT
NEXT
'switch off current
lchan = 9: valueout = 0
CALL aot(lchan, valueout, erstat)
'switch relay to disconnect current
lchan = 10: valueout = 1
CALL dot(lchan, valueout, erstat)
lchan = 0
DO WHILE erstat = 0
CALL CHECK(lchan, erstat)
LOOP
IF erstat <> 117 THEN PRINT "ERROR="; erstat: END


FOR CHAN = 0 TO NU - 1
cn = CHAN MOD c
RN = (CHAN \ c) + 1
array(CHAN) = ((scanarray(CHAN) / 32768) * 1000)
newarray(cn, RN)= array(CHAN)
NEXT

REM******* PRINT DATA TO FILE*********
file$= fil$ + ".dat"
OPEN file$ FOR APPEND AS #1
sum= 0
FOR RN= 1 TO 10
sum= newarray(0, RN) + sum
NEXT RN
mean0! = sum/ 10

sum = 0
FOR RN= 121 TO 130
sum= newarray(0, RN) + sum
NEXT RN
mean5!= sum / 10

sum= 0
FOR RN = 246 TO 255
sum = newarray(0, RN) + sum
NEXT RN
mean1! = sum / 10

sum= 0
FOR RN = 496 TO 505
sum = newarray(0, RN) + sum
NEXT RN
mean2! = sum/ 10

sum= 0
FOR RN = 746 TO 755
sum = newarray(0, RN) + sum
NEXT RN
mean3! = sum/ 10
```

```
sum = 0
FOR RN = 991 TO 1000
sum = newarray(0, RN) + sum
NEXT RN
mean4! = sum / 10

sum! = 0
FOR RN = 1 TO 1000
sum! = newarray(1, RN) + sum
NEXT RN
meancoated! = sum! / 1000

PRINT #1, mean0!, mean5!, mean1!, mean2!, mean3!, mean4!, meancoated!

CLOSE #1

file$ = fil$ + LTRIM$(STR$(re)) + ".dat"
OPEN file$ FOR OUTPUT AS #1

REM ******* PRINT HEADER TO FILE *********
PRINT #1, "~",title$,"", file$, TIME$, DATE$
PRINT #1, "header,", "RN", "CCM", "COATED", "BAREAG", "CURRENT","", "time";""

FOR RN = 1 TO R
PRINT #1, RN, newarray(0, RN), newarray(1, RN), newarray(2, RN), newarray(3, RN)
NEXT

CLOSE #1
RETURN
```