

## CONTENTS

	<b>Page</b>
CONTENTS	vi
LIST OF TABLES	x
LIST OF FIGURES	xii
LIST OF ABBREVIATIONS AND SYMBOLS	xiv
CHAPTER	
1. INTRODUCTION	1
1.1 Introduction	1
1.2 Basic knowledge	4
1.3 Literature review	8
1.3.1 Chemically modified electrodes	8
1.3.2 Chemically modified carbon paste electrode	9
1.3.3 Quinone compounds and their roles	14
1.4 The objectives	16
2. EXPERIMENTALS	17
2.1 Chemicals	17
2.2 Instruments and apparatus	21
2.2.1 AUTOLAB PGSTAT 100	21
2.2.2 Electrochemical cell and electrodes	21
2.2.3 Apparatus	21
2.3 Procedure	23
2.3.1 Working electrode preparation	23
2.3.2 General procedure	24
2.3.3 Blank cyclic voltammetry experiment	25
2.3.4 Cyclic voltammetry of quinone compounds	25
2.3.5 Cyclic voltammetry of silver ions in acetonitrile	26
2.3.6 Cyclic voltammetry of mercury ions in acetonitrile	26
2.3.7 Cyclic voltammetry of copper ions in acetonitrile	26

## CONTENTS (Continued)

	<b>Page</b>
2.3.8 Cyclic voltammetry of silver(I), mercury(II), and copper(II) by carbon paste electrode modified with quinone compounds	26
2.3.9 Comparison stripping voltammogram of silver(I) in differential pulse and square wave mode	27
2.3.10 Simultaneous voltammogram of Cu(II) and Ag(I) on carbon paste electrode modified with 1,8-dihydroxyanthraquinone	28
2.3.11 Comparison SWASV of Ag(I) between Ag/AgCl and Ag/AgCl double junction	28
2.3.12 Cyclic voltammetry of Ag(I) at various scan rate	29
2.4 Optimization condition for analysis	29
2.4.1 The paste composition	30
2.4.2 Electrolyte solution	30
2.4.3 pH of solution	31
2.4.4 Activation of carbon paste electrode	31
2.4.5 Preconcentration time	32
2.4.6 Instrumental parameters	32
2.4.7 Regeneration of the working electrode	33
2.5 Reproducibility	34
2.6 Calibration graph and linear range	34
2.7 Limit of detection	34
2.8 Effects of interferences	35
2.9 Determination of silver in photographic developer	35
3. RESULTS AND DISCUSSIONS	37
3.1 Cyclic voltammetry of blank solution at glassy carbon electrode	37
3.2 Electrochemical behavior of 1,4-dihydroxyanthraquinone at glassy carbon electrode	37
3.3 Electrochemical behavior of anthraquinone at glassy carbon electrode	38

## CONTENTS (Continued)

	<b>Page</b>
3.4 Electrochemical behavior of 1,2-dihydroxyanthraquinone at glassy carbon electrode	40
3.5 Electrochemical behavior of 1,5-dihydroxyanthraquinone at glassy carbon electrode	41
3.6 Electrochemical behavior of 1,8-dihydroxyanthraquinone at glassy carbon electrode	42
3.7 Electrochemical behavior of 1,4-benzoquinone at glassy carbon electrode	43
3.8 Electrochemical behavior of 4,5-dihydroxy anthraquinone-2-carboxylic acid disodium salt at glassy carbon electrode	44
3.9 Conclusion about the electrochemical behavior of quinone compounds	45
3.10 Cyclic voltammetry of silver(I), mercury(II) and copper (II) at glassy carbon electrode	46
3.11 Cyclic voltammogram of Ag(I), Cu(II) and Hg(II) at carbon paste electrode modified with quinone compounds	48
3.12 Comparison stripping voltammogram of Ag(I) in differential pulse and square wave mode	52
3.13 Stripping voltammogram of Ag(I) and Cu(II) at CPE modified with 1,8-DHAQ	53
3.14 Comparison of stripping voltammogram of Ag(I) at Ag/AgCl with Ag/AgCl double junction reference electrode	54
3.15 Cyclic voltammetry of Ag(I) at CPE modified with 1,8-DHAQ for various scan rates	55
3.16 Operational principle	57
3.17 Optimization for the conditions for silver(I) analysis	57
3.17.1 The paste composition	57
3.17.2 Electrolyte solution	61

## CONTENTS (Continued)

	<b>Page</b>
3.17.3 Effect of pH	64
3.17.4 Activation of carbon paste electrode	66
3.17.5 Preconcentration time	68
3.17.6 Instrumental parameters	72
3.17.7 Regeneration of the working electrode	78
3.17.8 Reproducibility	79
3.17.9 Calibration graph and linear range	80
3.17.10 Limit of detection	81
3.17.11 Selectivity and interferences	82
3.18 Determination of silver in photographic developer	84
4. CONCLUSION	91
REFERENCES	94
APPENDIX	109
A	110
B	111
C	112
VITAE	113

## LIST OF TABLES

Table	Page
1. The major voltammetric techniques used for trace-metal analysis and their typical concentration ranges	7
2. Sources of chemicals	17
3. The concentration of silver(I) for standard addition method	36
4. The current from stripping voltammogram of Ag(I) at various quinone compounds	49
5. The current from stripping voltammogram of Hg(II) at various quinone compounds	50
6. The current from stripping voltammogram of Cu(II) at various quinone compounds	51
7. The data of the current peaks and square root of scan rate for Ag(I)	56
8. The data of the current peaks of $1.0 \times 10^{-4}$ M Ag(I) at various paste compositions	58
9. The data of the current peaks of $0.5 \times 10^{-4}$ M Ag(I) at various paste compositions	59
10. The peak currents at various volumes of mineral oil with the constant amount of graphite powder and 1,8-DHAQ	60
11. The peak currents at various volumes of liquid paraffin with the constant amount of graphite powder and 1,8-DHAQ	60
12. The peak currents at various volumes of silicone oil with the constant amount of graphite powder and 1,8-DHAQ	60
13. Electrochemical response of silver in various electrolytes at CPE-1,8-DHAQ	62
14. The result of peak currents for Ag(I) $0.5 \times 10^{-4}$ M in 0.8 M HNO <sub>3</sub> at pH 1.00 to 9.00	64
15. The result of peak currents for Ag(I) $1.0 \times 10^{-4}$ M in 0.8 M HNO <sub>3</sub> at pH 1.00 to 9.00	65
16. Effects of activation procedures on peak current of $1.0 \times 10^{-4}$ M Ag(I)	67
17. The results of preconcentration time on peak current of $0.5 \times 10^{-4}$ M Ag(I)	69
18. The results of preconcentration time on peak current of $1.0 \times 10^{-4}$ M Ag(I)	70
19. The results of preconcentration time on peak current of $1.5 \times 10^{-4}$ M Ag(I)	71
20. The currents at various accumulation potentials of $0.5 \times 10^{-4}$ M Ag(I)	73
21. The currents at various accumulation potentials of $1.0 \times 10^{-4}$ M Ag(I)	73
22. The currents of $1.0 \times 10^{-4}$ M Ag(I) at different convection rate	75
23. The response current of $1.0 \times 10^{-4}$ M Ag(I) at different equilibrate time	76

## LIST OF TABLES (Continued)

Table	Page
24. The response current of $1.0 \times 10^{-4}$ M Ag(I) at different step potential	77
25. The response current of $1.0 \times 10^{-4}$ M Ag(I) at different pulse amplitude	77
26. The response current of $1.0 \times 10^{-4}$ M Ag(I) at different chemical regeneration	79
27. The current response of $1.0 \times 10^{-4}$ M Ag(I) at five new electrode surface	80
28. The current response in different concentration of Ag(I)	81
29. Change in SWASV peak current of $3.0 \times 10^{-5}$ M Ag(I) in presence of other ions	83
30. The results of standard addition method of Ag(I) in sample A	85
31. The results of standard addition method of Ag(I) in sample B	86
32. The results of standard addition method of Ag(I) in sample C	87
33. The results of standard addition method of Ag(I) in sample A added $1.0 \times 10^{-5}$ M Ag(I)	88
34. The results of standard addition method of Ag(I) in sample C added $2.0 \times 10^{-5}$ M Ag(I)	89
35. The silver concentrations of samples determined by standard addition method	90
36. The analytical characteristics of CPE-1,8-DHAQ	92

## LIST OF FIGURES

Figure	Page
1. The oxidation and reduction form of quinone	16
2. AUTOLAB PGSTAT 100 (Metrohm, Switzerland)	22
3. The cell with three electrode system	22
4. The complete chemically modified carbon paste electrode	24
5. Cyclic voltammogram of blank solution at glassy carbon electrode in 50 mL CH <sub>3</sub> CN containing 0.1 M TBAP	37
6. The structure of quinone compounds	39
7. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M 1,4-dihydroxyanthraquinone at GCE	40
8. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M anthraquinone at GCE	40
9. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M 1,2-dihydroxyanthraquinone at GCE	41
10. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M 1,5-dihydroxyanthraquinone at GCE	42
11. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M 1,8-dihydroxyanthraquinone at GCE	43
12. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M 1,4-benzoquinone at GCE	44
13. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M 4,5-dihydroxyanthraquinone-2-carboxylic acid at GCE	45
14. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M Ag(I) at GCE	46
15. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M Hg(II) at GCE	47
16. Cyclic voltammogram of 1.0 x 10 <sup>-3</sup> M Cu(II) at GCE	47
17. Stripping voltammogram of 1.0 x 10 <sup>-4</sup> M Ag(I) at unmodified and modified electrode with 1,8-dihydroxyanthraquinone	52
18. Differential pulse stripping voltammogram and square wave stripping voltammogram	53
19. Simultaneous stripping voltammogram of 1.0 x 10 <sup>-3</sup> M Cu(II) and Ag(I) in 0.1 M HNO <sub>3</sub> at CPE-1,8-DHAQ	54
20. Stripping voltammogram of 1.0 x 10 <sup>-4</sup> M Ag(I) in 0.2 M HNO <sub>3</sub> ; Ag/AgCl reference electrode and Ag/AgCl double junction reference electrode	55
21. The plotting between square root of scan rate with the reduction current (I <sub>pc</sub> ) and the oxidation current (I <sub>pa</sub> )	56

## LIST OF FIGURES (Continued)

Figure	Page
22. Effects of the content of 1,8-DHAQ in carbon paste mixture	59
23. Stripping voltammogram of $1.0 \times 10^{-4}$ M Ag(I) at CPE-1,8-DHAQ for 0.3 to 1.2 M of $\text{NaNO}_3$	63
24. Blank voltammogram of $\text{NaNO}_3$ 0.8 M at CPE-1,8-DHAQ with $80 \text{ mV s}^{-1}$ of scan rate	63
25. Effects of pH on stripping peak current of Ag(I) $0.5 \times 10^{-4}$ and $1.0 \times 10^{-4}$ M in $\text{HNO}_3$ 0.8 M	65
26. The response of peak current between activated (Motta and Guadalupe, 1994) and unactivated of CPE-1,8-DHAQ	68
27. Effect of preconcentration time in CPE-1,8-DHAQ on the stripping peak current of $0.5 \times 10^{-4}$ , $1.0 \times 10^{-4}$ , and $1.5 \times 10^{-4}$ M Ag(I)	72
28. Effects of accumulation potentials on stripping current of $0.5 \times 10^{-4}$ and $1.0 \times 10^{-4}$ M Ag(I) with preconcentration time of 8 min	74
29. Effect of convection rate on stripping peak of $1.0 \times 10^{-4}$ M Ag(I)	75
30. Stripping voltammogram of $1.0 \times 10^{-4}$ M Ag(I) in 0.8 M $\text{HNO}_3$ (pH 2.00) at CPE-1,8-DHAQ with 8 min preconcentration time	78
31. The Ag(I) calibration curve as current of the peak response after 8 min preconcentration time in Ag(I) solutions with varying concentration	82
32. Standard addition curve of Ag(I) in sample A	85
33. Standard addition curve of Ag(I) in sample B	86
34. Standard addition curve of Ag(I) in sample C	87
35. Standard addition curve of Ag(I) in sample A added $1.0 \times 10^{-5}$ M Ag(I)	88
36. Standard addition curve of Ag(I) in sample C added $2.0 \times 10^{-5}$ M Ag(I)	89

## LIST OF ABBREVIATIONS AND SYMBOLS

A = Ampere

Ag = Silver

Ag/AgCl = Silver/Silver chloride

AgNO<sub>3</sub> = Silver nitrate

Al = Aluminum

AQ = Anthraquinone

AQ<sup>•-</sup> = Semi anthraquinone

AQ<sup>2-</sup> = Anthraquinone dianion

As = Arsenic

As(NO<sub>3</sub>)<sub>3</sub> = Arsenic nitrate

ASV = Anodic stripping voltammetry

Bi(NO<sub>3</sub>)<sub>3</sub> = Bismuth nitrate

Ca = Calcium

Ca(NO<sub>3</sub>)<sub>2</sub> = Calcium nitrate

Cd = Cadmium

Cd(NO<sub>3</sub>)<sub>2</sub> = Cadmium(II) nitrate

CH<sub>3</sub>CN = Acetonitrile

CMEs = Chemically modified electrodes

CPE = Carbon paste electrode

CPE-1,8-DHAQ = Carbon paste electrode modified with 1,8-dihydroxyanthraquinone

CMCPE = Chemically modified carbon paste electrode

Co = Cobalt

Co(NO<sub>3</sub>)<sub>2</sub> = Cobalt(II) nitrate

Cu = Copper

Cu(NO<sub>3</sub>)<sub>2</sub> = Copper(II) nitrate

CV = Cyclic voltammogram

CVs = Cyclic voltammograms

## LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

1,8-DHAQ = 1,8-dihydroxyanthraquinone

DPASV = Differential pulse anodic stripping voltammetry

E = Potential

$E^{\circ'}$  = Formal potential

$E_{pa}$  = Oxidation peak potential

$E_{pc}$  = Reduction peak potential

Fe = Iron

$Fe(NO_3)_3$  = Ferric nitrate

g = Gram

GCE = Glassy carbon electrode

HCl = Hydrochloric acid

$HClO_4$  = Perchloric acid

Hg = Mercury

$Hg(NO_3)_2$  = Mercury(II) nitrate

$HNO_3$  = Nitric acid

$H_3PO_4$  = Phosphoric acid

Hz = Hertz

i = Current

ICP-AES = Inductively coupled plasma atomic emission spectrometry

$I_{pa}$  = Anodic peak current

$I_{pc}$  = Cathodic peak current

KCl = Potassium chloride

$KH_2PO_4$  = Potassium dihydrogen phosphate

$KNO_3$  = Potassium nitrate

KOH = Potassium hydroxide

$LiNO_3$  = Lithium nitrate

M = Molar

## LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

mA = Milliampere

Mg = Magnesium

$\text{Mg}(\text{NO}_3)_2$  = Magnesium nitrate

mg = Milligram

$\text{mg L}^{-1}$  = Milligram per litre

$\mu\text{l}$  = Microlitre

mL = Millilitre

Mn = Manganese

$\text{Mn}(\text{NO}_3)_2$  = Manganese(II) nitrate

mV = Millivolt

$\text{mV s}^{-1}$  = Millivolt per second

n = Number of electron

$\text{Na}_2\text{B}_4\text{O}_7$  = Sodium tetraborate

$\text{NaClO}_4$  = Sodium perchlorate

$\text{NaCOOCH}_3$  = Sodium acetate

$\text{Na}_2\text{CO}_3$  = Sodium carbonate

$\text{NaHCO}_3$  = Sodium hydrogen carbonate

$\text{Na}_2\text{HPO}_4$  = Disodium hydrogen orthophosphate

$\text{NaNO}_2$  = Sodium nitrite

$\text{NaNO}_3$  = Sodium nitrate

$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  = Ammonium acetate

Ni = Nickel

$\text{Ni}(\text{NO}_3)_2$  = Nickel(II) nitrate

ng = Nanogram

Pb = Lead

$\text{Pb}(\text{NO}_3)_2$  = Lead(II) nitrate

Q = Quinone

## LIST OF ABBREVIATIONS AND SYMBOLS (Continued)

$Q^{\cdot-}$  = Semi quinone

$Q^{2-}$  = Quinone dianion

rpm = Revolution per minute

s = Second

SWASV = Square wave anodic stripping voltammetry

t = time

TBAP = Tetrabutylammonium hexafluorophosphate

V = Volt

$\nu$  = Scan rate

Zn = Zinc

$Zn(NO_3)_2$  = Zinc(II) nitrate