

CONTENTS

	Page
ACKNOWLEDGEMENTS	iii
ABSTRACT (ENGLISH)	iv
ABSTRACT (THAI)	vi
LIST OF TABLES	xi
LIST OF ILLUSTRATIONS	xiii
CHAPTER 1 INTRODUCTION	1
1.1 Flow injection analysis	1
1.2 Fumaric acid	6
1.2.1 General background	6
1.2.2 Methods for fumaric acid determination	9
1.3 Ascorbic acid	11
1.3.1 General background	11
1.3.2 Methods for ascorbic acid determination	13
1.4 Thesis aim	17
CHAPTER 2 EXPERIMEN	18
2.1 Chemicals, Apparatus and Instrument	18
2.1.1 Chemicals	18
2.1.2 Apparatus and Instrument	19
2.2 Preparation of standard solution and reagent	20
2.2.1 Preparation of solutions for the determination of fumaric acid by voltammetry	20
2.2.2 Preparation of solutions for the determination of ascorbic acid by amperometric and titrimetric methods	21
2.3 System for determination of fumaric acid by batch vlotammetry and by FI voltammetry	23
2.3.1 Batch differential pulse voltammetric system	23
2.3.2 Pumping devices for FI system	24
2.3.2.1 Nitrogen gas pressure driven pumping device	24

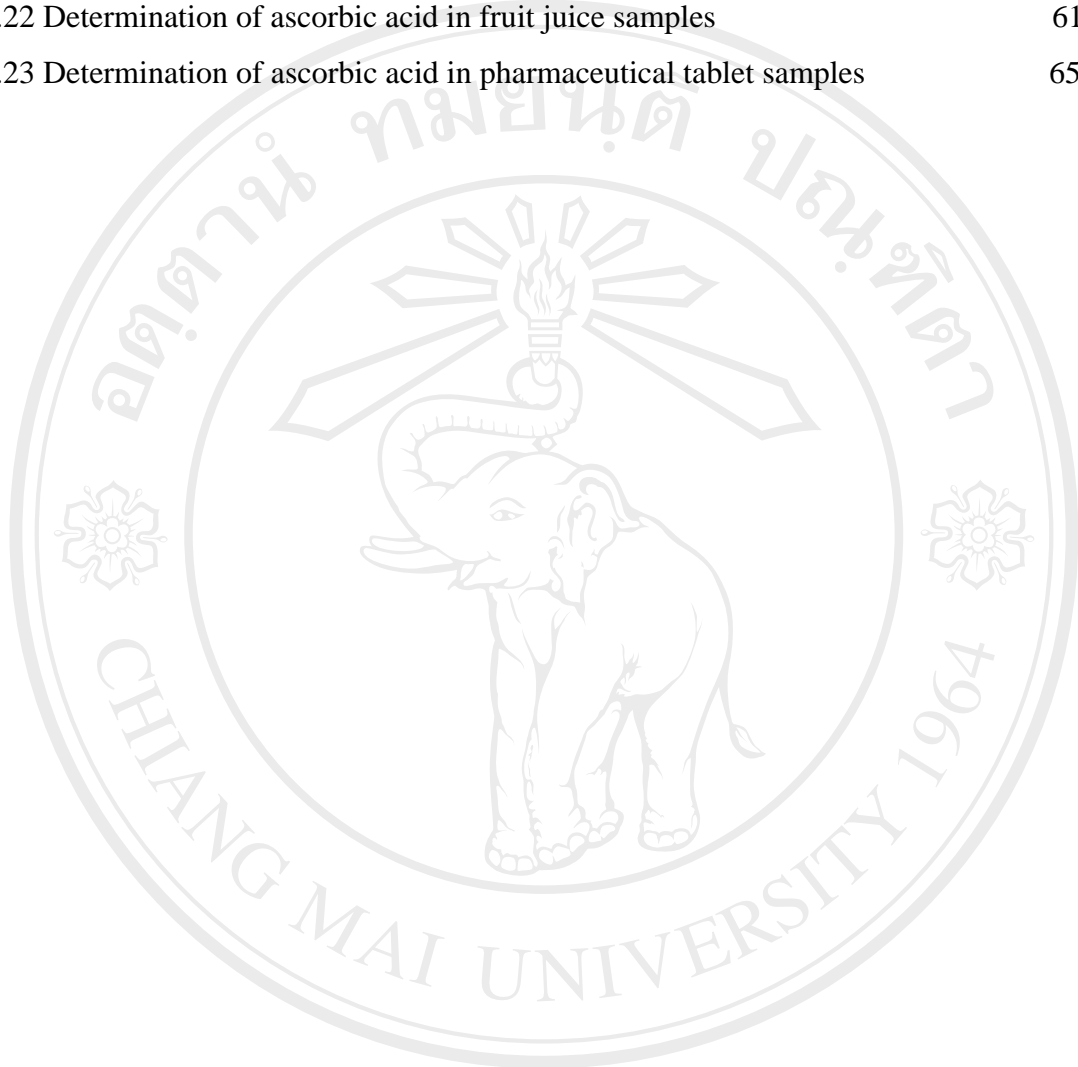
2.3.2.2 Gravity driven pumping device	25
2.3.3 FI differential pulse voltammetric system	26
2.4 Systems for determination of ascorbic acid by FI amperometry	27
2.4.1 Flow injection - amperometric system	27
2.4.2 FI amperometric system with dialysis unit for sample pretreatment	28
CHAPTER 3 RESULTS AND DISCUSSION	29
3.1 Determination of fumaric acid	29
3.1.1 Batchwise DPV system	29
3.1.1.1 Preliminary investigation on DPV system	30
3.1.1.2 Effect of tetramethylammonium bromide concentration	32
3.1.1.3 Effect of lithium chloride concentration	33
3.1.1.4 Effect of sodium chloride concentration	34
3.1.1.5 Effect of pH of electrolyte solution	34
3.1.1.6 Effect of voltammetric parameters	35
3.1.1.7 Summary of the selected conditions	38
3.1.2 Investigation on FI DPV system for determination of fumaric acid	39
3.1.2.1 Development of cost effective alternative propelling devices	39
- Nitrogen gas pressure driven pumping system	39
- Gravity driven pumping system	40
3.1.2.2 Development of a simple voltammetric flow cell	41
3.1.2.3 FI - DPV determination of fumaric acid	47
3.2 FI amperometric system for ascorbic acid determination	50
3.2.1 Optimization of the FI Amperometric Detection System	50
3.2.1.1 Type of Working Electrode	51

3.2.1.2 Effect of applied potential	52
3.2.1.3 Concentration and pH of Phosphate Buffer	53
3.2.1.4 Flow rate	56
3.2.2 FI Amperometric System with Dialysis Unit	57
3.2.2.1 Analytical characteristics of the developed method	58
3.2.2.2 Application of the developed method to fruit juice samples	61
3.2.2.3 Application to vitamin C tablet samples	63
CHAPTER 4 CONCLUSION	67
THE RELEVANCE OF THE RESEARCH WORK TO THAILAND	69
REFERENCES	70
APPENDICES	75
APPENDIX A	76
APPENDIX B	77
APPENDIX C	78
APPENDIX D	79
CURRICULUM VITAE	80

LIST OF TABLES

Table	Page
1.1 Methods for the determination of fumaric acid	10
1.2 Methods for the determination of ascorbic acid	13
1.3 Sample preparation for ascorbic acid determination	15
3.1 Condition for batchwise DPV analysis	30
3.2 Peak current obtained for 1.0 – 9.9 mg/L fumaric acid	31
3.3 Calibration graph data using various tetramethylammonium bromide concentrations	32
3.4 Calibration graph data using various lithium chloride concentrations	34
3.5 Calibration graph data using various supporting electrolyte pH values	35
3.6 Calibration graph data using various potential pulse amplitudes (U.amp)	36
3.7 Calibration graph data using various potential steps (U.step)	37
3.8 Calibration graph data using various measuring times (t.meas)	37
3.9 Calibration graph data using various step times (t.step)	37
3.10 Calibration graph data using various pulse times (t.pulse)	37
3.11 Studied range and the selected values of various voltammetric parameters	38
3.12 DPV parameters for zinc determination	43
3.13 DPV parameters for fumaric acid determination	45
3.14 Reproducibility of background current	47
3.15 Peak height signal and signal to noise ratio of fumaric acid determination by FI – DPV	48
3.16 Peak height of 100 mg/L ascorbic acid standard solution using platinum and glassy carbon electrodes as working electrode	51
3.17 Calibration graph data using different phosphate buffer concentration	54
3.18 Calibration graph data for each phosphate buffer pH	55
3.19 Calibration graph data for each phosphate buffer flow rate	57
3.20 Condition for determination of ascorbic acid by dialysis flow injection amperometry	59

Table	Page
3.21 Precision of ascorbic acid determination by dialysis FI – amperometry system	60
3.22 Determination of ascorbic acid in fruit juice samples	61
3.23 Determination of ascorbic acid in pharmaceutical tablet samples	65



ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved

LIST OF ILLUSTRATIONS

Figure	Page
1.1 Schematic diagram of a typical flow injection analysis manifold (top). The lower portion of the diagram indicates some typical instrumental options available for reagent and carrier propulsion, sample injection, sample-reagent mixing, and various detection modes	2
1.2 Molecular formula of fumaric acid	6
1.3 Tricarboxylic acid cycle	7
1.4 Buffer capacities of fumaric acid, tartaric acid, malic acid, lactic acid, citric acid and phosphoric acid buffer at different pH	8
1.5 The molecular structure of ascorbic acid	12
1.6 The reversible oxidation of ascorbic acid (I) to dehydroascorbic acid (II)	12
2.1 Metrohm 636 voltammograph. AE: auxiliary electrode, WE: working electrode, RE: reference electrode. Solution in system; 10 mL of $(\text{CH}_3)_4\text{NBr}$ (0.1M) + LiCl (0.01M) as a supporting electrolyte	23
2.2 Nitrogen gas pressure driven pumping system	24
2.3 Gravity driven pumping system	25
2.4 Manifold of FI – differential pulse voltammetric system for fumaric acid determination	26
2.5 Manifold of FI – amperometric system for ascorbic acid determination	27
2.6 Manifold of FI amperometric system with dialysis pretreatment for ascorbic acid determination	28
3.1 A calibration graph for batchwise DPV determination of fumaric acid by successive spiking standard solution of fumaric acid into an electrolyte	31
3.2 Example of voltammogram signal profiles obtained for fumaric acid determination (1, 2, 3.8, 5.7, 7.4 and 9.1 mg/L)	33
3.3 The Potential waveform for DPV	36
3.4 Different flow rates achieved from N_2 gas pressure driven system	40
3.5 Different flow rates achieved from gravity driven pumping system: constant flow rates of 0.13, 0.22 and 0.51 mL/min were obtained	41

Figure	Page
3.6 Cross section of voltammetric flow cell; (A)voltammetric vessel, (B)clamp, (C)Ag/AgCl reference electrode, (D)drop knocker, (E) HMDE, (F)Pt electrode, (G) J-shaped adapter and (H) clamp	42
3.7 Calibration graphs of Zn determination by injecting solution from minimum to maximum concentrations and maximum to minimum concentrations	44
3.8 Voltammogram of fumaric acid at (a) 0(background), (b) 20, (c) 40, (d) 60 and (e) 80 mg/L	45
3.9 Side and bottom views of a new design of a laboratory made HMDE flow cell	46
3.10 Calibration graph of fumaric acid by FI DPV	48
3.11 Relationship of background current with flow rate	49
3.12 Comparison of peak heights of 100 mg/L ascorbic acid when using platinum and glassy carbon electrodes as working electrode	52
3.13 The peak height of ascorbic acid (40 mg/L) at each applied potential	53
3.14 Effect of phosphate buffer concentration	54
3.15 Effect of phosphate buffer pH	56
3.16 Effect of phosphate buffer flow rate	57
3.17 The calibration graph of ascorbic acid using dialysis FI – amperometric method	58
3.18 Calibration graph of ascorbic acid standard by dialysis flow injection amperometric system	59
3.19 FI gram of ascorbic acid in fruit juice samples	62
3.20 Calibration graph for ascorbic acid determination in pharmaceutical tablet samples	64
3.21 FI gram of a standard calibration curve	64
3.22 FI gram of ascorbic acid in pharmaceutical tablet samples	65
3.23 Correlation graph of ascorbic acid in pharmaceutical tablet samples by proposed method and voltammetric method	66