

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	iii
ABSTRACT (ENGLISH)	iv
ABSTRACT (THAI)	vii
TABLE OF CONTENTS	x
LIST OF TABLES	xvii
LIST OF FIGURES	xxi
ABBREVIATIONS AND SYMBOLS	xxv
CHAPTER I INTRODUCTION	
1.1 Aluminium	1
1.1.1 Occurrence of aluminium	1
1.1.2 Toxicology of aluminium	1
1.1.3 Determination of aluminium	3
1.2 Quercetin	9
1.3 Flow Injection Analysis (FIA)	10
1.3.1 Introduction	10
1.3.2 Principle of FIA	11
1.3.3 Dispersion	13

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่

Copyright © by Chiang Mai University

All rights reserved

	Page
1.3.4 FIA Instrumentation	16
1.3.5 Reverse Flow Injection Analysis	19
1.4 Sequential Injection Analysis (SIA)	19
1.4.1 Programmable Flow of SIA	20
1.4.2 Sequential Injection Analyzer	21
1.4.3 SIA Dispersion Zones	25
1.4.4 Mixing and Zone Overlap of SIA	27
1.5 Research Aims	28
 CHAPTER II EXPERIMENTAL	
2.1 Instruments and Apparatus	29
2.2 Chemicals	29
2.3 Preparation of Standard Solutions and Reagents	31
2.3.1 Preparation of Standard Solutions and Reagents of rFI system	31
2.3.1.1 Aluminium stock solution 1000 mg L ⁻¹	31
2.3.1.2 Quercetin stock solution 1000 mg L ⁻¹	31
2.3.1.3 Cetyltrimethylammonium bromide stock solution 0.1 mol L ⁻¹	31
2.3.1.4 A 0.1 mol L ⁻¹ of Acetate buffer pH 5.5	32

	Page
2.3.2 Preparation of standard solutions and reagents of SIA system	32
2.3.2.1 Aluminium stock solution 1000 mg L ⁻¹	32
2.3.2.2 Quercetin stock solution 1000 mg L ⁻¹	32
2.3.2.3 Cetyltrimethylammonium bromide stock solution 0.1 mol L ⁻¹	32
2.3.2.4 A 0.1 mol L ⁻¹ of Acetate buffer pH 5.5	33
2.4 Preliminary Studies of Spectrophotometric Determination of Aluminium by Using Quercetin as Complexing Agent	33
2.4.1 Absorption spectra	33
2.4.2 Study of the composition of the Al-Quercetin-CTAB complex by Mole-ratio method	34
2.5 Procedure	34
2.5.1 Procedure for collection and treating tap water samples for aluminium (III) determination	34
2.5.2 rFIA spectrophotometric determination of aluminium using Quercetin and CTAB as complexing agent	35
2.5.2.1 Optimization of the reverse flow system	36
2.5.2.2 Linearity of calibration graph	37
2.5.2.3 Precision	38

	Page	
2.5.2.4	Detection limit	38
2.5.2.5	Accuracy of the proposed method	39
2.5.2.6	Interference studies	39
2.5.2.7	Validation method	40
2.5.3	SIA spectrophotometric determination of aluminium using Quercetin as complexing agent	40
2.5.3.1	Sequential injection method	43
2.5.3.2	Optimization of the sequential injection system	47
2.5.3.3	Linearity of calibration graph	48
2.5.3.4	Precision	49
2.5.3.5	Detection limit	49
2.5.3.6	Accuracy of the proposed method	49
2.5.3.7	Interference studies	50
2.5.3.8	Validation method	50

CHAPTER III RESULTS AND DISCUSSION

3.1 Preliminary Studies of Spectrophotometric Determination of Aluminium 51

by Using Quercetin as Complexing Agent

3.1.1 Absorption spectra 51

	Page
3.1.2 Stoichiometry of the complexes this was study by mole-ratio method	52
3.2 rFIA Spectrophotometric Determination of Aluminium Using Quercetin and Cetyltrimethyl Ammonium Bromide as A Complexing Agent	56
3.2.1 Optimization of the Reverse Flow System by Univariate Method	56
3.2.1.1 Optimum wavelength	56
3.2.1.2 Effect of pH	58
3.2.1.3 Effect of Quercetin concentration	59
3.2.1.4 Efect of % ethanol in quercetin solution	60
3.2.1.5 Effect of CTAB concentration	62
3.2.1.6 Effect of flow rate	63
3.2.1.7 Effect of reaction coil (I) length	65
3.2.1.8 Effect of reaction coil (II) length	66
3.2.1.9 Effect of reagent volume	67
3.2.1.10 Summary of the studied range and optimum conditions	69
3.2.2 Analytical Characteristics of the method	69
3.2.2.1 Linear range	69
3.2.2.2 Precision of the flow injection system	71
3.2.2.3 Calibration curve	72
3.2.2.4 Detection limit	74

	Page
3.2.2.5 Interference Studies	76
3.2.2.6 Effect of masking agents and interference	81
3.2.2.7 Determination of aluminium (III) in waters	83
3.3 SIA Spectrophotometric Determination of Aluminium Using Quercetin and Cetyltrimethyl Ammonium Bromide as A Complexing Agent	85
3.3.1 Study aspiration order	85
3.3.2 Optimization of the sequential injection system by univariate method	86
3.3.2.1 Effect of pH	86
3.3.2.2 Effect of acetate buffer concentration	88
3.3.2.3 Effect of Quercetin concentration	89
3.3.2.4 Effect of % ethanol in quercetin concentration	90
3.3.2.5 Effect of CTAB concentration	91
3.3.2.6 Effect of aspiration volumes of acetate buffer	93
3.3.2.7 Effect of aspiration volumes of Quercetin	95
3.3.2.8 Effect of aspiration volumes of CTAB	96
3.3.2.9 Effect of aspiration volumes of sample	97
3.3.2.10 Effect of flow rate	98
3.3.2.11 Effect of holding time	99

	Page
3.3.3 Analytical Characteristics of the method	101
3.3.3.1 Linear range	101
3.3.3.2 Precision of the sequential injection system	103
3.3.3.3 Calibration curve	104
3.3.3.4 Detection limit	106
3.3.3.5 Interference Studies	108
3.3.3.6 Effect of masking agents and interference	112
3.3.3.7 Determination of aluminium (III) in waters	114
CHAPTER IV CONCLUSIONS AND SUGGESTION FOR FURTHER	117
WORK	
REFERENCES	121
APPENDIX A	127
APPENDIX B	130
CURRICULUM VITAE	136
THE RELEVANCY OF THE RESEARCH WORK IN THAILAND	137

LIST OF TABLES

Table	Page
1.1 A brief review of the methods for the determination of aluminium	4
1.2 Characteristic performance of some reported spectrophometric methods for aluminium determinattion	5
1.3 A brief review of FIA and SIA for the determination of aluminium	7
2.1 The studied range for the optimization of all parameters of rFIA	37
2.2 The experimental protocol as shown in the FIAlab for windows software	44
2.3 The studied range for the optimization of all parameters of SIA	47
2.4 Preliminary experimental conditions of SIA for studying optimum pH of Al(III)-Quercetin-CTAB	48
3.1 Effect of quercetin concentrations for mole-ratio of Al-Quercetin-CTAB complex	53
3.2 Effect of CTAB concentrations for mole-ratio of Al-Quercetin-CTAB complex	54
3.3 Peak heights at various wavelength	57
3.4 Effect of pH on the sensitivity	58
3.5 Effect of concentration of quercetin on the sensitivity	60
3.6 Effect of concentration of ethanol on the sensitivity	61
3.7 Effect of concentration of CTAB on the sensitivity	62

Table	Page
3.8 Effect of flow rate on the sensitivity	64
3.9 Effect of reaction coil (I) length on the sensitivity	65
3.10 Effect of reaction coil (II) length on the sensitivity	67
3.11 Effect of reagent volume on the sensitivity	68
3.12 Univariate optimization of chemical and rFIA variables	69
3.13 Peak height at various aluminium concentrations for linearity check of the calibration graph	70
3.14 Precision verification using standard 0.2 mg L ⁻¹ aluminium	72
3.15 ΔPeak height for calibration curve	73
3.16 Calculation of detection limit of rFIA spectrophotometric determination of aluminium	75
3.17 Interference study for 0.2 mg L ⁻¹ standard aluminium by rFIA method	76
3.18 Summary of the interference effects of some ions on the responses obtained from aluminium 0.2 mg L ⁻¹	80
3.19 Effect of masking agent for mask Fe ²⁺ , Fe ³⁺ and Cu ²⁺ the response obtained from aluminium 0.2 mg L ⁻¹	81
3.20 Determination of aluminium in water samples by rFIA method	83
3.21 Comparative determination of aluminum in water sample by proposed rFIA method and ICP-MS	84

Table	Page
3.22 Sensitivity at various aspiration orders	86
3.23 Effect of pH on the sensitivity	87
3.24 Effect of concentration of acetate buffer pH 5.5 on the sensitivity	88
3.25 Effect of various concentration of quercetin on the sensitivity	90
3.26 Effect of various concentration of ethanol on the sensitivity	91
3.27 Effect of various concentration of CTAB on the sensitivity	92
3.28 Effect of various aspiration volume of 0.1 mol L ⁻¹ of acetate buffer pH 5.5 on the sensitivity	94
3.29 Effect of various aspiration volume of 350 mg L ⁻¹ of quercetin in 70 % ethanol on the sensitivity	95
3.30 Effect of various aspiration volume of 4.5×10 ⁻³ mol L ⁻¹ of CTAB on the sensitivity	96
3.31 Effect of various aspiration volume of sample on the sensitivity	97
3.32 Effect of various flow rate on the sensitivity	98
3.33 Effect of various holding time on the sensitivity	100
3.34 Optimum conditions for aluminium determination	101
3.35 Linearity of aluminium determination	102
3.36 Precision verification using various concentrations of aluminium standard	104
3.37 ΔPeak height for calibration curve	105

Table	Page
3.38 Calculation of detection limit of rFIA spectrophotometric determination of aluminium	107
3.39 Interference studies for 0.2 mg L ⁻¹ standard aluminium by SIA method	108
3.40 Summary of interference effects of some ions on the response obtained from aluminium 0.2 mg L ⁻¹ by SIA method	112
3.41 Effect of masking agent for mask Fe ²⁺ , Fe ³⁺ and Cu ²⁺ the response obtained from aluminium 0.2 mg L ⁻¹ by SIA method	113
3.42 Determination of aluminium in water sample by SIA method	115
3.43 Comparative determination of aluminium in water sample by proposed SIA method and ICP-MS	116
4.1 Comparison of the analytical characteristics between rFIA and SIA methods for aluminium determination	120

LIST OF FIGURES

Figure		Page
1.1	The chemical structure of quercetin	9
1.2	The basic components of the FIA system	12
1.3	The analog output has the form of a FIA peak	12
1.4	General types of transport in closed tubes	13
1.5	Effects of convection and diffusion on concentration profiles of analyses at the detector	14
1.6	Dispersed sample zone in flow system	15
1.7	Relationship between the rollers of a peristaltic pump and the pump tubes	17
1.8	Structure of injection zones and concentration profiles as seen by the detector	21
1.9	Schematic flow diagram of a sequential injection analyzer	22
1.10	Dispersed sample zones of SIA system	25
1.11	Forward and reversal flow of SIA system	28
2.1	Reverse flow injection systems for the determination of aluminium (III)	36
2.2	The SIA system for determination of aluminium (III)	42
2.3	SI manifold for the determination of aluminium (III) in water samples	42

Figure	Page
2.4 Senee SIA software for plot the SIA grams	43
2.5 FIALab 5.0 for windows software	44
3.1 The absorbance spectrum of Quercetin, Quercetin-CTAB, Al(III)-Quercetin and Al(III)-Quercetin-CTAB complexes	51
3.2 Mole-ratio study of Al(III)-Quercetin-CTAB system; effect of quercetin concentration.	53
3.3 Mole-ratio study of Al(III)-Quercetin-CTAB system; effect of CTAB concentration.	54
3.4 The reaction of Al(III)-Quercetin-CTAB	55
3.5 Δ Peak heights at various wavelengths	57
3.6 Relationship between pH and sensitivity of the calibration curve	59
3.7 Relationship between concentration of quercetin and sensitivity of the calibration curve	60
3.8 Relationship between concentration of ethanol in quercetin solution and sensitivity of the calibration curve	61
3.9 Relationship between concentration of CTAB and sensitivity of the calibration curve	63
3.10 Relationship between flow rate and sensitivity of the calibration curve	64

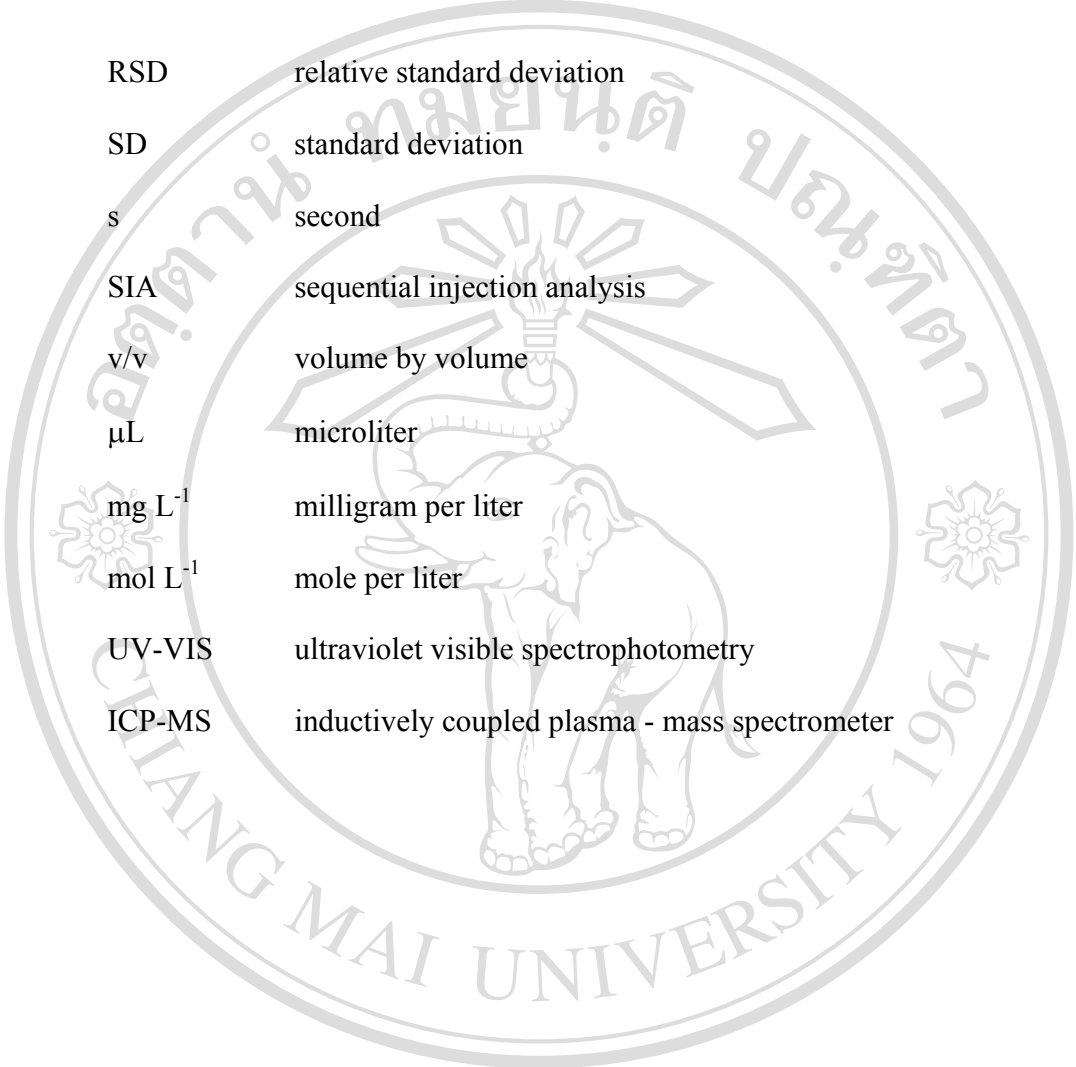
Figure	Page
3.11 Relationship between reaction coil (I) length and sensitivity of the calibration curve	66
3.12 Relationship between reaction coil (II) length and sensitivity of the calibration curve	67
3.13 Relationship between reagent volume and sensitivity of the calibration curve	68
3.14 Relationship between Δ peak height and concentration of aluminium	71
3.15 The calibration signal of rFIA spectrophotometric determination of aluminium 0.02-0.50 mg L ⁻¹	73
3.16 The calibration curve of rFIA spectrophotometric determination of aluminium	74
3.17 Relationship between various pH and sensitivity of the calibration curve	87
3.18 Relationship between various concentration of acetate buffer pH 5.5 and sensitivity of the calibration curve	89
3.19 Relationship between various concentration of quercetin solution and sensitivity of the calibration curve	90
3.20 Relationship between various concentration of ethanol in quercetin solution and sensitivity of the calibration curve	91

Figure	Page
3.21 Relationship between concentration of CTAB on the sensitivity of the calibration curve	93
3.22 Relationship between various aspiration volume of 0.1 mol L ⁻¹ of acetate buffer pH 5.5 on the sensitivity of the calibration curve	94
3.23 Relationship between various aspiration volumes of 350 mg L ⁻¹ of quercetin on the sensitivity of the calibration curve	95
3.24 Relationship between various aspiration volumes of 4.5×10 ⁻³ mol L ⁻¹ of CTAB on the sensitivity of the calibration curve	96
3.25 Relationship between various aspiration volumes of sample on the sensitivity of the calibration curve	97
3.26 Relationship between various flow rate on the sensitivity of the calibration curve	99
3.27 Relationship between various holding time on the sensitivity of the calibration curve	100
3.28 Relationship between net peak height and concentration of aluminium	103
3.29 Calibration signal of SIA spectrophotometric determination of aluminium (III) 0.02-0.60 mg L ⁻¹	105
3.30 The Calibration curve of SIA spectrophotometric determination of aluminium (III)	105

ABBREVIATIONS AND SYMBOLS

AU	absorbance unit
rFIA	reverse flow injection analysis
h	hour
i.d.	inner diameter
in.	inch
L	liter
LOD	limit of detection
LOQ	limit of quantitation
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mV	millivolt
PC	personal computer
PTFE	polytetrafluoroethylene
\bar{x}	mean
P.H.	peak height

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
 Copyright © by Chiang Mai University
 All rights reserved



RSD	relative standard deviation
SD	standard deviation
s	second
SIA	sequential injection analysis
v/v	volume by volume
μL	microliter
mg L^{-1}	milligram per liter
mol L^{-1}	mole per liter
UV-VIS	ultraviolet visible spectrophotometry
ICP-MS	inductively coupled plasma - mass spectrometer

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved