

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	iii
ABSTRACT (ENGLISH)	iv
ABSTRACT (THAI)	vii
TABLE OF CONTENTS	x
LIST OF TABLES	xvi
LIST OF ILLUSTRATIONS	xix
ABBREVIATIONS AND SYMBOLS	xxii
 CHAPTER 1: INTRODUCTION	 1
1.1 Method Development and Automation of Analytical Chemistry	1
1.2 Flow Injection Analysis (FIA)	3
1.2.1 Basic Components of FIA	3
1.3 FI On-line Preconcentration Techniques	6
1.3.1 General Characteristic of FI Methods for Separation and Preconcentration	7
1.3.2 Evaluation of FI Separation and Preconcentration Systems	8
1.3.2.1 Enrichment Factor	8
1.3.2.2 Concentration Efficiency	9

	Page
1.4 FI Separation Preconcentration and Belonging Operations	9
1.4.1 Classification of FI Separation Preconcentration Techniques	9
1.4.2 FI Adsorption Preconcentration Using a Column	10
1.4.2.1 General	10
1.4.2.2 Practical Considerations in Operation of FI Column Preconcentration	11
1.4.3 FI Adsorption Preconcentration Using a Knotted Reactor	12
1.4.3.1 General	12
1.4.3.2 Practical Considerations in Operation of FI Adsorption Using a Knotted Reactor	13
1.5 Chromium	14
1.5.1 Sources and Occurrence of Chromium	14
1.5.2 Chemistry of Chromium in Fresh Water	16
1.5.3 The Essentiality of Chromium	18
1.5.4 Human Hazard Potential	18
1.5.5 Analytical Methods for the Determination and Speciation of Cr	19
1.6 Reasons for Undertaking This Work	23
1.7 Research Aims	23
 CHAPTER 2: EXPERIMENTAL	 25
2.1 Instruments and Apparatus	25
2.2 Chemical Reagents	25

	Page
2.3 Preparation of Standard Solutions and Other Reagents	26
2.4 Procedures	31
2.4.1 A Comparison of Enrichment Factor of Knotted and Serpentine Reactors Using Flow Injection Sorption and Preconcentration for the Off-line Determination of some Trace Elements by ICP-MS	31
2.4.2 FI On-line Sorption and Preconcentration of Chromium(VI) and Total Chromium Using a Knotted Reactor with Detection by FAAS	37
2.4.2.1 Determination of Cr(VI) by FI-FAAS	37
2.4.2.2 Determination of total chromium by FI-FAAS	40
2.4.3 FI On-line Preconcentration of Low Levels of Cr(VI) with ETAAS Detection	41
CHAPTER 3: RESULTS AND DISCUSSION	48
3.1 A Comparison of Enrichment Factor of Knotted and Serpentine Reactors Using Flow Injection Sorption and Preconcentration for the Off-line Determination of some Trace Elements by Inductively Coupled Plasma Mass Spectrometry	48
3.1.1 Manifold Design and Operational Sequences	51
3.1.2 Optimization of Sample Acidity	51
3.1.3 Optimization of the Complexing Agent (APDC) Concentration	52

	Page
3.1.4 Optimization of Sample and the APDC Flow Rate	55
3.1.5 Optimization of the KR Length	55
3.1.6 Optimization of the Sample Loading Time	57
3.1.7 Rinsing the KR	58
3.1.8 Elution	59
3.1.9 Summary of the Optimum Conditions	60
3.1.10 Comparison of the Enrichment Factor of the FI Sorption and Preconcentration System on KR with that of Using SR	60
3.2 Flame Atomic Absorption Spectrometric Determination of Chromium(VI) and Total Chromium in Water Samples by FI On-line Preconcentration system Using Knotted Reactor	62
3.2.1 Manifold Design and Operational Sequences	63
3.2.2 Optimization of the Condition Used for FAAS Instrument	63
3.2.3 Optimization of the Sample Acidity, [HCl], and APDC Concentration, [APDC]	66
3.2.4 Optimization of the Sample and the APDC Flow Rate	69
3.2.5 Optimization of the KR Length	70
3.2.6 Optimization of the Sample Loading Time	72
3.2.7 Analyte Elution and Eluate Introduction	73
3.2.8 Summary of the Optimum Conditions	74
3.2.9 Oxidation of Cr(III) to Cr(VI)	75
3.2.10 Evaluation of Potential Interferences for Cr(VI)	82
3.2.11 Analytical Performance of the FI On-line Sorption	83

	Page
Preconcentration of Cr(VI) on KR	
3.2.12 The Determination of Cr(VI) and Total Chromium in Different Water Samples	89
3.3 FI On-line Preconcentration of Low Levels of Cr(VI) with Detection by ETAAS.	92
3.3.1 Manifold Design and Operational Sequences	94
3.3.2 Optimization of the Graphite Furnace Temperature Program	96
3.3.3 Optimization of the Sample Acidity, [HCl], the Concentration of Complexing Agent, [APDC], and the concentration of the Washing Solution, [WS]	99
3.3.4 Optimization of the Sample and the APDC Flow Rates	100
3.3.5 Optimization of the KR Tubing Length	102
3.3.6 Optimization of the Sample Loading Time	103
3.3.7 Optimization of the Experimental Parameters of the Elution and the Ensuring Introduction into the ETAAS	105
3.3.8 Comparative Preconcentration and Determination of Cr(VI) by On-line Sorption on KR and a Column Reactor Packed with PTFE Beads	105
3.3.9 Investigation of Interferences	114
3.3.10 Evaluation of the PTFE Beads Packed Column Preconcentration Procedure	114

	Page
CHAPTER 4: CONCLUSIONS	117
4.1 A Comparison of Enrichment Factor of Knotted and Serpentine Reactors Using Flow Injection Sorption and Preconcentration for the Off-line Determination of some Trace Elements by ICP-MS	118
4.2 Flame Atomic Absorption Spectrometric Determination of Chromium(VI) and Total chromium in Water Samples by FI On-line Preconcentration System Using Knotted Reactor	119
4.3 FI On-line Preconcentration of Low Levels of Cr(VI) with Detection by ETAAS	120
REFERENCES	123
APPENDIX A	131
APPENDIX B	135
VITA	137

LIST OF TABLES

Table	Page
1.1 FIA chromium speciation studies in water samples using atomic spectrometric method	20
2.1 List of chemical reagent	27
2.2 Operating parameters for the ICP-MS	32
2.3 Operating sequences of FI on-line preconcentration in PrepLab system	33
2.4 Flow injection operation for on-line preconcentration and elution of Cr(VI)	38
2.5 Sequences of operations for the FI on-line sorption preconcentration elution procedures for very low levels of Cr(VI)	41
2.6 Graphite furnace temperature program for the determination of Cr(VI) in the ethanolic eluate using pyrolytically coated graphite tubes with platform	47
3.1 Conditions used for determination	60
3.2 EF of the FI sorption and preconcentration system using KR and SR	61
3.3 Effect of burner height for observation on Cr(VI) determination	64
3.4 Effect of acetylene aspiration rate on Cr(VI) determination	65
3.5 Effect of acidity type on Cr(VI) determination	66
3.6 Effect of sample/APDC flow rate ratio on Cr(VI) determination	69
3.7 Effect of KR length on Cr(VI) determination	70

Table	Page
3.8 Effect of sample loading time on Cr(VI) determination	72
3.9 Optimum conditions for Cr(VI) determination	75
3.10 Effect of concentration of H ₂ SO ₄ on Cr(III) oxidation	78
3.11 Effect of concentration of K ₂ S ₂ O ₈ on Cr(III) oxidation	80
3.12 Effect of oxidation time on Cr(III) oxidation	81
3.13 Relative oxidation yield of standard mixtures of Cr(III) and Cr(VI)	82
3.14 Effect of interference study for 0.05 mg/l Cr(VI)	84
3.15 Summary of the tolerance limit of the interferent effects on the determination of 0.05 mg/l Cr(VI)	85
3.16 Relationship between peak height and concentration of Cr(VI)	85
3.17 Signal of reagent blank	87
3.18 Repeatability for Cr(VI) determination	88
3.19 Performance of the FI on-line sorption preconcentration of Cr(VI) for FAAS detection	89
3.20 Analysis of reference materials	89
3.21 Determination of Cr(VI) and total Cr in various water samples	92
3.22 Effect of pyrolysis temperature on the determination of Cr(VI)-PDC complex	97
3.23 Effect of atomization temperature on the determination of Cr(VI)-PDC complex	98
3.24 Graphite furnace temperature program for the determination of Cr(VI) in the ethanolic using pyrolytically coated graphite tubes with the platform	99

Table	Page
3.25 Effect of sample and APDC flow rate ratio on the determination of Cr(VI)-PDC complex	101
3.26 Effect of the KR length on the determination of Cr(VI)-PDC complex	102
3.27 Effect of sample loading time on the determination of Cr(VI)-PDC complex	104
3.28 Relationship of Cr(VI) concentration and integrated absorbance on the preconcentration system using KR	106
3.29 Relationship of Cr(VI) concentration and integrated absorbance on the preconcentration system using PTFE beads packed column	107
3.30 Signal of reagent blank for detection limit calculation	109
3.31 Repeatability for Cr(VI) determination	109
3.32 Performance of the FI-ETAAS on-line sorption preconcentration systems incorporating a PTFE KR or a column reactor packed with PTFE beads for the determination of Cr(VI)	110
3.33 Characteristic performance of the preconcentration system using a packed column for determination of Cr(VI)	112
3.34 Investigation of the tolerance of potentially interfering ions when using the FI system incorporating the column reactor packed with PTFE beads	115
3.35 Determination of Cr(VI) in a SRM NIST-2109, SRM NIST-1640 and a synthetic seawater sample, respectively, using the PTFE beads packed column	116

LIST OF ILLUSTRATIONS

Figure	Page
1.1 The basic components of an FIA system	4
1.2 Illustration of a knotted reactor (KR) and its secondary flow pattern	13
2.1 FI manifold and operational sequences for preconcentration	34
2.2 Configuration of reactor	36
2.3 FI manifold and operational sequences for the preconcentration, separation and determination of chromium	39
2.4 Schematic diagram of the FI-manifold for sample preconcentration and elution	42
3.1 Effect of sample acidity using a KR on the signal intensity of a 0.5 mg/l multi-elemental standard	52
3.2 The structure formula of APDC	53
3.3 Effect of APDC concentration using a KR on the signal intensities of 0.5 mg/l multi-elemental standard	55
3.4 Effect of KR length on the signal intensities of a 0.5 mg/l multi-elemental standard	56
3.5 Effect of sample loading time using a KR on the signal intensities of 0.5 mg/l multi-elemental standard	57
3.6 Effect of rinsing nitric acid concentration using a KR on the signal intensities of 0.5 mg/l multi-elemental standard	59
3.7 Effect of burner height for observation on Cr(VI) determination	64

Figure	Page
3.8 Effect of acetylene aspiration rate on Cr(VI) determination	65
3.9 Effect of acidity type on Cr(VI) determination	67
3.10 The relationship of response signal and the vertex number for Optimization	68
3.11 Effect of sample/APDC flow rate ratio on 0.10 mg/l Cr(VI) determination	69
3.12 Effect of KR tubing length on 0.10 mg/l Cr(VI) determination	71
3.13 Effect of sample loading time on 0.10 mg/l Cr(VI) determination	73
3.14 (a) tris [pyrrolidine-1-dithioato-S-S']-Cr(III) (b) bis[-pyrrolidine-1-dithioato-S-S']-[pyrrolidine-1-peroxydithioato-O,S]-Cr(III)	76
3.15 Effect of concentration of H ₂ SO ₄ on the oxidation of 0.10 mg/l Cr(III) with 0.05 M K ₂ S ₂ O ₈ at 80 °C for 30 min	78
3.16 Effect of concentration of K ₂ S ₂ O ₈ on the oxidation of 0.10 mg/l Cr(III) in 0.005 M H ₂ SO ₄ at 80 °C for 30 min	80
3.17 Effect of oxidation time on the oxidation of 0.10 mg/l Cr(III) in 0.005 M H ₂ SO ₄ with 0.001 M K ₂ S ₂ O ₈ at 80 °C	81
3.18 Relationship between peak height and concentration of Cr(VI)	86
3.19 The peak height obtained from the recorder	86
3.20 Calibration curve of Cr(VI)	87
3.21 Effect of pyrolysis temperature on the signal of Cr(VI)-PDC complex in ethanolic solution (atomization temperature was set at 2300 °C)	97
3.22 Effect of atomization temperature on the signal of Cr(VI)-PDC complex in ethanolic solution (pyrolysis temperature was set at 1100 °C)	98

Figure	Page
3.23 The relationship between the vertex numbers and response signals of Cr(VI)	100
3.24 Effect of the sample and the APDC flow rate ratio on the preconcentration of 1.0 $\mu\text{g/l}$ Cr(VI) in the KR ($L_{\text{KR}}=125$ cm) for a preconcentration period of 60 s	101
3.25 Effect of the length of the KR on the preconcentration of 1.0 $\mu\text{g/l}$ Cr(VI) for a preconcentration time of 60 s	103
3.26 Effect of sample loading time on the preconcentration of 1.0 $\mu\text{g/l}$ Cr(VI) in the KR of 125 cm	104
3.27 Calibration curve of Cr(VI) for the FI on-line preconcentration system using knotted reactor	107
3.28 Calibration curve of Cr(VI) for the FI on-line preconcentration system using PTFE beads packed column	108

ABBREVIATIONS AND SYMBOLS

$^{\circ}\text{C}$	degree celsius
<i>et al.</i>	and other people
EF	enrichment factor
ETAAS	electrothermal atomic absorption spectrometer
FAAS	flame atomic absorption spectrometer
FI	flow injection
ICP-MS	inductively coupled plasma mass spectrometer
KR	knotted reactor
mg	milligram
min	minute
ml	millilitre
mol	mole
ng	nanogram
ppb	part per billion
ppm	part per million
PTFE	polytetrafluoroethylene
%RSD	percent relative standard deviation
s	second
SD	standard deviation
SR	serpentine reactor
μg	microgram
μm	micrometre
μl	microlitre
v/v	volume by volume
w/v	weight by volume