### CONTENTS

				Page
C	ONTENTS			vii
LI	ST OF TA	BLES		Х
LI	ST OF FIG	URES		xii
Cł	HAPTER			
1	INTROD	UCTIC	DN	
	1.1	Chara	cteristic of Natural Waters	1
		1.1.1	Fresh water	1
		1.1.2	Estuarine water	2
		1.1.3	Seawater	2
	1.2	Trace	elements in Natural Waters	3
		1.2.1	River water	3
		1.2.2	Estuarine water	4
		1.2.3	Sea water	6
	1.3	Classi	fication of metals	7
	1.4	Distri	8	
	1.5	1.5 Songkhla Lake System		
	1.6	Trace	Metals Determination	12
		1.6.1	Analytical Methods	12
			1.6.1.1 ETAAS	12
			1.6.1.2 ICP-AES	13
			1.6.1.3 Voltammetry(ASV and DPASV)	14
		1.6.2	Pre-concentration Method	14
			1.6.2.1 Solvent extraction	14
			1.6.2.2 Coprecipitation	15
			1.6.2.3 Solid Phase Extraction	16
	1.7	Statist	tical Data analysis	17
	1.8	Objec	tive	18 vii

## **CONTENTS** (cont.)

2	METHO	DOLOGY	0	
	2.1	Chemicals and apparatus	19	
	2.2	Instruments	19	
		2.2.1 GFAAS (Perkin Elmer AAnalyst 800)	19	
		2.2.2 FAAS (Perkin-Elmer AAnalyst 300)	20	
		2.2.3 ICP-AES (Perkin Elmer Model Optima 4300 DV)	20	
	2.3	Optimization of GFAAS	20	
		2.3.1 Pyrolysis and atomization temperature	20	
		2.3.2 Effect of matrix modifier	21	
		2.3.2.1 The effect of using matrix modifier and without	21	
		matrix modifier		
		2.3.2.2 Type of matrix modifier	21	
	2.4	Quantification of the analysis: calibration curve and standard		
		addition curve		
	2.5	Sample collection	22	
		2.5.1 Sampling site	22	
		2.5.2 Sampling method	24	
		2.5.3 Sample preservation	24	
	2.6	Sample preparation	24	
		2.6.1 Solvent Extraction	24	
		2.6.2 Particulate digestion: Total decomposition method	25	
	2.7	Method of validation	26	
		2.7.1 Limit of detection (LOD)	26	
		2.7.2 Accuracy and precision	27	
	2.8	Statistical data analysis	28	

# 3. RESULT AND DISSCUSSION

3.1 Optimization parameters for AAnalyst 800	29
--	----

viii

Page

## **CONTENTS** (cont.)

	3.1.1	Optimi	zation of pyrolysis and atomization temperature	Page 29
	3.1.2	Effect	of matrix modifier	30
3.2	Quant	Quantification of the analysis: calibration curve and standard		
	additio	on curve		
3.3	Metho	ds of va	lidation	31
	3.3.1	Limit o	of detection (LOD)	31
	3.3.2	Accura	cy and precision	31
3.4	Trace	metals in	n surface water of Songkhla Lake System	32
	3.4.1	Trace 1	netals in dissolved phase	32
	3.4.2	Trace 1	netals in particulate phase	33
	3.1.1	Total n	netals concentration in Box and outlier plot	35
	3.1.2	Percen	t fraction of dissolved and particulate metals	38
3.5	Trace	metals-S	Salinity Profiles	47
		3.5.1	Dissolved metal-Salinity	47
		3.5.2	Particulate metal-Salinity	48
3.6	The pa	artitionir	ng of trace metals between particulate and	70
	dissol	ved pha	ses	
		3.6.1	K <sub>d</sub> -salinity Plot	71
		3.6.2	K <sub>d</sub> -PCA Plot	78
4 CONCLU	JSION			82
REFERENCI	ES			85
APPENDICE	S			93
А				94
В				100
С				101
VITAE				123

#### LIST OF TABLES

Table	]	Page
1-1	Major dissolved constituent in global rivers and in sea water	1
1-2	Dissolved (ng/L) and particulate (mg/L) trace metals concentrations in	3
	river waters	
1-3	Average concentrations (ug/L) of dissolved and particulate trace metals in	4
	some estuaries	
1-4	The species, concentration ranges, and average concentration	7
	of the elements in seawater (salinity 35 psu)	
3-1	The optimum temperature program of AAnalyst 800 for determination	29
	of Cd, Cu, Pb and Zn	
3-2	The detection limit of Cd, Cu, Pb, Zn, Al, Fe and Mn	31
3-3	The %Recovery and %RSD of Cd Cu, Pb, Zn, Al, Fe and Mn in	31
	dissolved and particulate phases	
3-4	The average concentration (in ug/L) for dissolved metal in 32	
	wet and dry seasons of Songkhla Lake System	
3-5	The average dissolved metal concentrations (in ug/L) of other	33
	natural water	
3-6	The comparison of dissolved trace metal concentrations (in ug/L)	33
	in the Outer Songkhla Lake collected in 1987 and 2004	
3-7	The average concentration of Cd, Cu, Pb and Zn in mg/kg and Al,	34
	Fe and Mn in g/kg in particulate matters of Songkhla Lake water	
	in wet and dry season	
3-8	Comparison of metal concentrations (mg/kg) in particulate	35
	matters of this study to other esstuaries	
	other estuaries	
3-9	The comparison of particulate trace metal concentrations	35
	(in mg/kg) in the Outer Songkhla Lake collected in 1987 and 2004)	
3-10	The average log $K_d$ value (L/g) in wet and dry season of	70
	Songkhla Lake System	

Х

## LIST OF TABLES (cont.)

Table	1	Page
3-11	The categories of metals in Songkhla Lake System in wet and dry	78
	season	
A- 1	Stock solution and all chemical reagents list	94
A- 2	List of apparatus	94
A- 3	The parameters used for Perkin Elmer AAnalyst 800	95
A- 4	The parameters used for Perkin Elmer AAnalyst 300	95
A- 5	The parameter used for Perkin Elmer Model Optima 4300 DV	96
A- 6	The GPS positions of sampling site and salinity at Thale Noi	96
C-1	The pyrolysis and atomization temperature study	101
C-2	The comparison of the absorbance of Cd, Cu, Pb and Zn with and	104
	without matrix modifier	
C- 3	The absorbance of 2.0 ug/L Cd standard working solution at various	105
	matrix modifier	
C- 4	The absorbance of 50 ug/L standard working solution at various	105
	types of matrix modifiers	
C- 5	The detection limit study of dissolved metal	106
C- 6	The detection limit study of particulate metal	107
C- 7	The %RSD study of dissolved metals	108
C- 8	The %RSD study of particulate metals	108
C- 9	The %Recovery study of dissolved and particulate metals	109
C- 10	The dissolved metal concentrations in wet and dry season in Thale Noi	111
C- 11	The dissolved metal concentrations in wet and dry season in Inner Lake	112
C- 12	The dissolved metal concentrations in wet and dry season in Middle Lake	113
C- 13	The dissolved metal concentrations in wet and dry season in Outer Lake	114
C- 14	The particulate metal concentrations in wet and dry season in Thale noi	115
C- 15	The particulate metal concentrations in wet and dry season in Inner Lake	116
C- 16	The particulate metal concentrations in wet and dry season in Middle Lake	e117
C- 17	The particulate metal concentrations in wet and dry season n Outer Lake	118

### LIST OF FIGURES

Figur	e	Page
1-1	Map of Songkhla Lake System	11
2-1	The station of water sampling in Songkhla Lake System	23
	(The number indicated the location of sampling sites).	
2-2	The schematic of sample preparation	26
3-1	Box and outlier plot of Cd, Cu, Pb and Zn in each area of Songkhla	37
	Lake System	
3-2	Box and outlier plot of Al, Fe and Mn of Songkhla Lake System	38
3-3	The percent fraction of dissolved and particulate Cd (ng/L) in	40
	wet and dry season	
3-4	The percent fraction of dissolved and particulate Cu (ng/L) in	41
	wet and dry season	
3-5	The percent fraction of dissolved and particulate Pb ( $\mu g/L$ ) in	42
	wet and dry season	
3-6	The percent fraction of dissolved and particulate Zn ( $\mu g/L$ ) in	43
	wet and dry season	
3-7	The percent fraction of dissolved and particulate Al ( $\mu g/L$ ) in	44
	wet and dry season	
3-8	The percent fraction of dissolved and particulate Fe ( $\mu$ g/L) in	45
	wet and dry season	
3-9	The percent fraction of dissolved and particulate Mn ( $\mu$ g/L) in	46
3- 10	wet and dry season Concentrations and distributions of dissolved and particulate Cd in Inner	: 49
5 10	Lake	
3-11	Concentrations and distributions of dissolved and particulate Cu in Inner Lake	r 50
3-12	Concentrations and distributions of dissolved and particulate Pb in Inner	51
3- 13	Lake Concentrations and distributions of dissolved and particulate Zn in Inner	. 50
5-15	Concentrations and distributions of dissolved and particulate Zn in Inner Lake	52
3-14	Concentrations and distributions of dissolved and particulate Al in Inner Lake	53

#### LIST OF FIGURES (cont.)

Figure	Pa	age
3- 15	Concentrations and distributions of dissolved and particulate Fe in Inner Lake	54
	Concentrations and distributions of dissolved and particulate Mn in Inner Lake	55
3- 17	Concentrations and distributions of dissolved and particulate Cd in Middle Lake	56
	Concentrations and distributions of dissolved and particulate Cu in Middle Lake	57
3- 19	Concentrations and distributions of dissolved and particulate Pb in Middle Lake	58
	Concentrations and distributions of dissolved and particulate Zn in Middle Lake	59
	Concentrations and distributions of dissolved and particulate Al in Middle Lake	60
3-22	Concentrations and distributions of dissolved and particulate Fe in Middle Lake	61
	Concentrations and distributions of dissolved and particulate Mn in Middle Lake	62
	Concentrations and distributions of dissolved and particulate Cd in Outer Lake	63
3-25	Concentrations and distributions of dissolved and particulate Cu in Outer Lake	64
3-26	Concentrations and distributions of dissolved and particulate Pb in Outer Lake	65
3-27	Concentrations and distributions of dissolved and particulate Zn in Outer Lake	66
3-28	Concentrations and distributions of dissolved and particulate Al in Outer Lake	67
3- 29	Concentrations and distributions of dissolved and particulate Fe in Outer Lake	68
3- 30	Concentrations and distributions of dissolved and particulate Mn in Outer Lake	69
3- 31	The $K_d$ profile of Cd, Cu, Pb, Zn, Al and Fe in wet and dry	72
	season in Inner Lake	
3-32	The $K_d$ profile of Mn in wet and dry season in Inner Lake	73
3-33	The $K_d$ profile of Cd, Cu, Pb, Zn, Al and Fe in wet and dry season	74
	in Middle Lake	
3- 34	The $K_d$ profile of Mn in wet and dry season in Middle Lake	75

#### LIST OF FIGURES (cont.)

Figure	2		Page	
3- 35	The $K_d$ profile of Cd, Cu, Pb, Zn, Al and Fe in wet and dry season		76	
	in Outer Lake			
3-36	The $K_d$ profile of Mn in wet and dry season in Outer Lake		77	
3- 37	The PCA loaing plot of $K_d$ wet and dry season		80	
C- 1	The pyrolysis and atomization curve for Cd, Cu, Pb and Zn		102	
C-2(a)	) The absorbance of 2 ug/L of Cd at optimum pyrolysis and		103	
	atomization temperature			
C- 2(b	)The absorbance of 25 ug/L of Cu at optimum pyrolysis and	103		
	atomization temperature			
C-2(c)	) The absorbance of 50 ug/L of Pb at optimum pyrolysis and		103	
	atomization temperature			
C- 2(d	)The absorbance of 2 ug/L of Zn at optimum pyrolysis and		104	
	atomization temperature			
C-3(a)	Comparison between calibration curve and standard addition		119	
	curve of Cd			
C- 3(b	)Comparison between calibration curve and standard addition		119	
	curve of Cu			
C-3(c)	Comparison between calibration curve and standard addition		120	
	curve of Pb			
C- 3(d	)Comparison between calibration curve and standard addition		120	
	curve of Zn			
C-3(e)	Comparison between calibration curve and standard addition		121	
	curve of Al			
C-3(f)	Comparison between calibration curve and standard addition		121	
	curve of Fe			
C- 3(g	C- 3(g)Comparison between calibration curve and standard addition			
	curve of Mn			