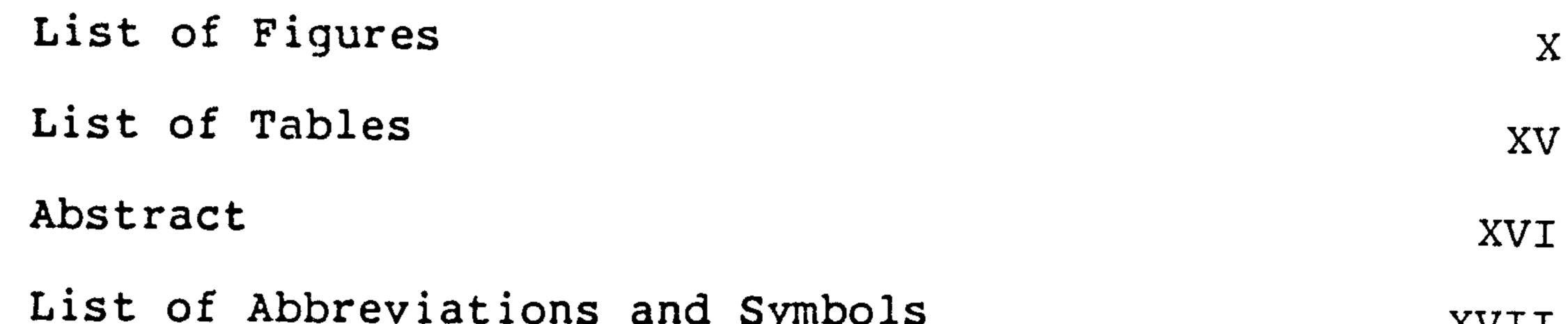
TABLE OF CONTENTS



v

	XVII
Acknowledgements	XIX
CHAPTER 1	
INTRODUCTION	1
1.1 Chemical Speciation	1
1.2 Speciation Methods	3
1.2.1 Theoretical Methods	5
1.2.2 Experimental Methods	6
1.2.2.1 Size Separation Techniques	6
1.2.2.1 (a) Ultrafiltration	7
1.2.2.1 (b) Dialysis	9
1.2.2.1 (c) Gel Permeation Chromatography	11
1.2.2.2 Ion Exchange	13
1.2.2.3 Electrochemical Methods	16
1.2.2.3 (a) Ion selective Electrode Potentiometry	16
1.2.2.3 (b) Anodic Stripping Voltammetry	18
1.2.2.4 Bioassay Methods	21
1.2.2.5 Speciation Schemes	23
1.3 Comparison of Speciation Methods	24

V

1.3 Comparison of Speciation Methods

1.4 Research Objectives

CHAPTER 2

.

FREE METAL SPECIATION TECHNIQUES

32

•

27

2.1 Introdu	ction	32
2.1.1	Ion Selective Electrode Potentiometry	32
2.1.2	Ion Exchange Column Equilibration	36
2.1.3	Metal Ion Buffers	39
2.2 Experime	ental	41

2.2.1	Chemicals	43
2.2.2	Preparation of Metal Ion Buffers	43
2.2.3	Ion Selective Electrode Measurements	44
2.2.4	Ion Exchange Column Equilibration Measurements	46
2.3 Results	and Discussion	49
2.3.1	Ion Selective Electrode Potentiometry	49
2.3.1.1	ISE Response vs. Time	49
2.3.1.2	Selection of pH Buffers	51
2.3.1.3	Calibration of ISE	53

2.3.1.4	Reproducibility of the ISE	55
2.3.2	Ion Exchange Column Equilibration Technique	55
2.3.2.1	Breakthrough Volume	55
2.3.2.2	Calibration of the IEX Method	57
2.3.2.3	Reproducibility	61
2.3.2.4	Effect of Calcium on the IEX Method	61
2.3.3	Method Comparison	63

75

75

78

78

CHAPTER 3

COMPARISON WITH ENZYME BIOASSAY

3.1 Introduction

3.2 Experimental

3.2.1 Chemicals

vi

3.2.2	Enzyme Bioassay Procedure	. 79
3.3 Results	and Discussion	. 82
3.3.1	Enzyme Inhibition Model	82
3.3.2	Characterization of the Enzyme Assay Model	84
3.3.2.1	Reaction Kinetics	84
3.3.2.2	Reproducibility of Enzyme Assay	89
3.3.2.3	Effect of pH on Enzyme Assay	91
3.3.2.4	Effect of Ligand Concentration	· 95
3.3.3	Methods Comparison	98
3.3.3.1	Enzyme Assay vs. Calculated Speciation	98
3.3.3.2	Enzyme Assay vs. ISE	· 104
3.3.3.3	Enzyme Assay vs. IEX	110
3.4 Conclusi	ons	115

•

CHAPTER 4

٠

ANALYTICAL UT	ILITY OF MEMBRANE COATED ELECTRODES	117
4.1 Introduct	tion	117
4.1.1	Nafion Ion Exchange Polymer	119
4.1.2	Cellulose Acetate Polymer	123
4.2 Experiment	ntal	126
4.2.1	Chemicals	126
4.2.2	Determination of Ion Exchange constants	127
4.2.3	Mercury Plating on Glassy Carbon Electrode	128

4.2.4 Membrane Coating Procedure

.

- 4.2.5 Metal Preconcentration Experiments with 129 the Nafion Coated Glassy Carbon Electrode
- 4.2.6 Metal Speciation Experiments with Nafion 130 Coated GCE
- 4.2.7 Metal Speciation Experiments with Cellulose 132

Acetate Coated MCGCE

- 133 4.3 Results and Discussion
 - 133 4.3.1 Ion Exchange Coefficients of Nafion Ionomer
 - Preconcentration Factors 4.3.2 137
 - Application of Nafion Coated MCGCE to Metal 4.3.3

	Ion Analysis	139
4.3.3.1	Exchange Kinetics	141
4.3.3.2	Effect of Film Thickness	144
4.3.3.3	Comparison of Nafion Coated MCGCE vs. Nafion Coated GCE	149
4.3.3.4	Effect of Ionic Strength and pH	152
4.3.3.5	Calibration and Reproducibility of the Nafion Coated MCGCE	154
4.3.3.6	Effect of Surfactants	159
4.3.3.7	Determination of Iron	161

4.3.4	Application of Nafion Coated MCGCE to Speciation Analysis	167
4.3.5	Application of Cellulose Acetate Coated Electrode to Metal Speciation	179
4.3.5.1	Metal Speciation in Citric Acid Systems	189
4.3.5.2	Speciation in Humic System	194

4.4 Conclusions

199

CHAPTER 5

.

TRACE METAL INTERATIONS WITH HUMIC MATTER UNDER CONTINUOUS FLOW CONDITIONS 203

5.1	Introduc	tion	203
5.2	Experime	ntal	208
5.2	2.1	Chemicals	208
5.2	2.2	Preparation of Humic Ac	id 209
5.2	2.3	Preparation of Peat	210

5.2.4	Peat Column Experiments	210
5.2.5	Analysis of Trace Metals	212
5.3 Results	and Discussion	215
5.3.1	Characterization of Humic Acid	215
5.3.1.1	Sodium Form of Humic Acid	215

5.3.1.2	Conversion of Humic Acid to the Proton Form	217
5.3.1.3	Functional Group Content	220
5.3.1.4	Potentiometric Titration	222
5.3.2	Trace Metal Interaction with Peat	227
5.3.2.1	Functional Group Content of Peat	227
5.3.2.2	Metal Uptake Experiments	228
5.3.2.3	Desorption Experiments	234
5.3.3	Reproducibility of Peat Column Experiments	240

5.3.4	Comparison woth Batch Experiments	240
5.3.5	Application to Synthetic Rain Water	244
5.4 Conclusi	ons	250
CHAPTER 6		
CONCLUSIONS		252

LIST OF REFERENCES

•

255

$\mathbf{i}\mathbf{x}$

.

LIST OF FIGURES



4

68

73

- 1-1 Classification Scheme for Trace Metal Species in Natural Waters (obtained from Hunt and Wilson, 1986)
- Schematic Representation of Potentiometric 2 - 145

Measurements.

- 2-2 Schematic of Ion Exchange Experiments 47
- 2-3 Potential-Time Curves for the Copper Ion 50 Selective Electrode
- 2 4ISE Calibration Curves in Absence of 52 Strong Complexing Ligands
- Copper Ion Selective Electrode Calibration 2-5 54
- 58 2-6 Equilibration of Ion Exchange Columns
- 2-7 Calibration Curve for the Ion Exchange 60 Method
- Comparison of Ion Selective Electrode and 2-8 66

Calculated Speciation for Copper Citrate System

- 2-9 Comparison of ISE and Calculated Speciation for Copper Citrate System
- Comparison of Speciation Results for 2-10 69 Copper/Picolinic Acid System
- Comparison of Speciation Results for 2-11 70 Copper/Bicine System
- Comparison of Speciation Results for 71 2-12 Copper/Sulfosalicylic Acid System
- Comparison of IEX and ISE Speciation 2-13 72 Results for Copper/Humic Acid System

- Comparison of IEX and ISE Speciation 2-14 Results for Copper/Albumin System
- 80 Schematic of FIA Measurements of 3-1 Phenolphthalein 85
- Effect of K_1 on the Inhibition Profile 3-2
- Effect of K₂ on the Inhibition Profile 86 3-3

3-4 Effect of Ligand Concentration on Inhibition 87 Profile

- 3-5 Enzyme Assay Reaction 88
- **3-6** Phenolphthalein Released from Conjugate 90 as a Function of Time
- 3-7 FIA Peak Profiles for a Typical Assay 92 Experiment

3-8 Reproducibility of Enzyme Inhibition 93 Profiles for Copper-Citrate System

.×

- 3-9 Effect of pH on the Inhibition Profiles 94 of Copper-Citrate System
- 3-10 Effect of Citric Acid Concentration on 96 Inhibition Profiles
- **3-11** Effect of Bicine Concentration 97 on Inhibition Profiles
- 3-12 Inhibition Profiles for Calculated 99 Speciation in Copper-Ligand Systems
- 3-13 Inhibition Profiles for Calculated 100 Speciation in Copper-Ligand Systems

3-14 Enzyme Inhibition Profiles for Copper-EN 103 and Copper-Citric Acid Systems

- **3-15** Copper Ion Selective Electrode 106 Calibration in NaNO₃ and EN Systems
- 3-16 Inhibition Profiles for ISE Measurements 107 in Copper-Ligand Systems
- 3-17 Inhibition Profiles for ISE Measurements 108 in Copper-Ligand Systems
- 3-18 Inhibition Profiles for ISE Measurements 109 in Copper-Ligand Systems
- 3-19 Inhibition Profiles for IEX Measurements 111 in Copper-Ligand Systems

3-20 Inhibition Profiles for IEX Measurements 112 in Copper-Ligand systems

- 3-21 Inhibition Profiles for IEX measurements 113 in Copper-Ligand Systems
- 4-1 BAS Flow Cell Used in Speciation Experiments 131

xi

4-2	Schematic for Ion Exchange Using Nafion	136
	811X Tubing and Dowex $50\overline{W}-X8$.	

- 4-3 Ion Exchange Calibrations Using Cu/NTA 138 Metal ion Buffers
- 4-4 DPP Polarogram for Cu, Pb, Cd and Zn at 140 Nafion Coated MCGCE
- 4-5 Equilibration of Nafion Coated GCE with 142

145

150

151

170

172

Cation Solutions

- 4-6 Calibration Curves of Cadmium at Nafion Coated MCGCE
- 4-7 DPP Polarogram for Copper at Nafion Coated MCGCE and Nafion Coated GCE
- 4-8 Calibration Curves for Copper at Nafion Coated MCGCE
- 4-9 Effect of Ionic Strength on Nafion 153 Equilibrations
- 4-10 Effect of Calcium on the Nafion 155 Equilibration
- 4-11 Calibration Curves for Nafion Coated 157

MCGCE

- 4-12 Calibration Curves for Nafion Coated MCGCE 158
- 4-13 Effect of Gelatin on DPASV Signal of 160 Copper
- 4-14 Fe(III) Calibration Using DPP and Nafion 164 Coated GCE
- 4-15 Effect of Camphor on Fe(III) at Nafion 165 Coated GCE
- 4-16 Effect of Copper on Fe(III) at Nafion 166 Coated GCE
- 4-17 Free Copper Speciation by Nafion Flow Cell 168 Method

4-18 Voltammograms of Copper and Copper/Citric Acid Systems at Nafion GCE

4-19 Comparison of Calculated and Experimental Speciation for Titration of Copper with Citric Acid



4-20 Comparison of Calculated and Experimental 173 Speciation for Titration of Copper with Bicine

- 4-21 Comparison of Calculated and Experimental 174 Speciation for Titration of Copper with Picolinic Acid
- 4-22 Comparison of Calculated and Experimental 175 Speciation for Titration of Copper with

Phthalic Acid

- 4-23 Comparison of Calculated and Experimental 176 Speciation for Titration of Copper with Glycine
- 4-24 Comparison of ISE and Nafion Coated GCE 180 Measurements for Titration of Copper with Humic Acid
- 4-25 Effect of Hydrolysis Time on DPASV Current 181 of Cellulose Acetate Coated MCGCE
- 4-26 Effect of Hydrolysis Time on DPASV Current ¹⁸² of Cellulose Acetate Coated MCGCE
- 4-27 DPASV Calibration for Copper, Lead, 184 Cadmium and Zinc with CA Coated MCGCE

4-28	Effect of Camphor on CA Coated MCGCE	185
4-29	Effect of Hydrolysis Time on Sensitivity of CA Coated MCGCE in Copper Ion Analysis	186
4-30	Effect of Hydrolysis Time on Sensitivity of CA Coated MCGCE in Cadmium Ion Analysis	187
4-31	Effect of Hydrolysis Time on Peak Currents of Cd/NTA System at CA Coated MCGCE	190
4-32	Effect of Hydrolysis Time on the DPASV Response of Lead at CA Coated MCGCE	192
4-33	Effect of Hydrolysis Time on the DPASV Response of Copper at CA Coated MCGCE	193

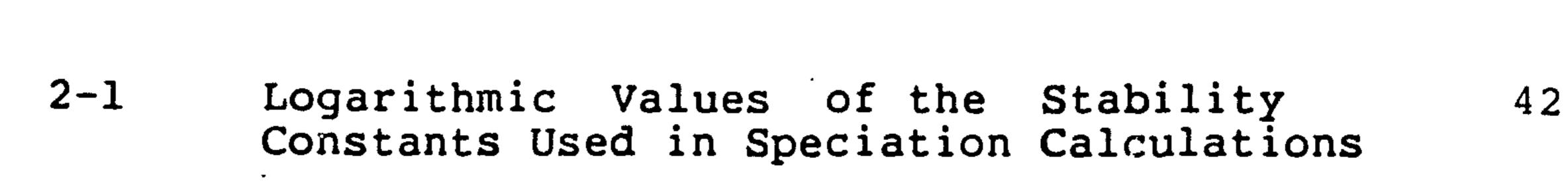
- 4-34 DPASV Voltammograms for Cu/HA System at 196 Bare and CA Coated Electrode
- 4-35 Titration Curves of Copper and Humic Acid 197 at Cellulose Acetate Coated Electrodes

198

4-36 Binding Isotherms of Copper onto Humic Acid by DPASV with Cellulose Acetate Coated MCGCE

- 4-37 Binding Isotherm of Methyl Viologen onto 200 Humic Acid by DPP Using Cellulose Acetate Coated MCGCE
- 5-1 Schematic Diagram for Column Peat Studies 211
- 5-2 Schematic Diagram for Ion Exchange/HPLC 214 Determination of Cations
- 5-3 Chromatogram of Seven Component Metal 216 Mixture
- 5-4 Schematic Diagram for Preparation of 219 "Nafion HA"
- 5-5 pH vs. Time Profile for Titration of Sodium 221 Humate with Dowex 50 in Proton Form
- 5-6 Potentiometric Titration of Sodium HA and 224 Nafion HA
- 5-7 Derivative Plots of Fig. 5-6 226
- 5-8 Copper Binding to Peat in Flow Mode 229
- 5-9 Binding of Cu, Cd and Zn to Peat in 231 Flow Mode
- 5-10 Metal Binding to Peat in Seven Metal Ion 233 Mixture
- 5-11 Acid Desorption of Metals from Peat 236
- 5-12 Elution of Lead and Copper from Peat 237 with 1 mM HNO3
- 5-13 Effect of Calcium on the Binding of 239 Metals to Peat
- 5-14 Batch Equilibration of Metal Ions with 243 Peat
- 5-15 Effect of Simulated Rain Water I on 247 Metal Content of Peat
- 5-16 Effect of Simulated Rain Water II on 248 Metal Content of Peat
 - 5-17 Effect of Simulated Rain Water III on 249 Metal Content of Peat

LIST OF TABLES



Table

~

.

Page

2-2	Reproducibility of the ISE Method	56
2-3	Reproducibility of the IEX Method	62
2-4	Effect of Calcium on the IEX Method	64
4-1	Cation Exchange Constants for Nafion 117 Polymer	134
4-2	Metal Enrichment Factors at Nafion Coated Electrode in the DPP Mode	143
4-3	Metal Ion Concentrations in Water Samples	162
4-4	Multication Speciation in Citric Acid Solution	178
— •		~ 7 ~ ~

5-1 AAS Operation Conditions for Trace Metals 213

5-2 Functional Group Contents of Different 223 Forms of Humic Acid

- 5-3 Reproducibility Data of Peat Column 241 Adsorption Experiments
- 5-4 Reproducibility Data of Peat Column 242 Desorption Experiments
- 5-5 Synthetic Rain Water Composition 246

XV