

Electrodialysis in flow injection systems

by

Cornelius Johannes Hattingh

Submitted in partial fulfilment of the requirements of the degree

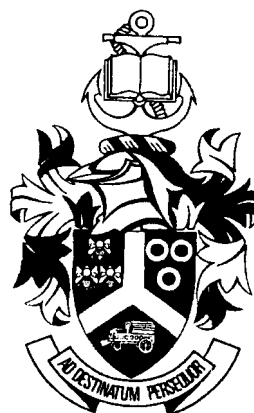
Philosophiae Doctor

in the Faculty of Science

University of Pretoria

Pretoria

October 1999



Summary

Electrodialysis in flow injection systems

by

Cornelius Johannes Hattingh

Supervisor: Professor JF van Staden

Department of Chemistry

University of Pretoria

Degree: Philosophiae Doctor

Flow injection analysis (FIA) is a continuous flow technique developed in the early 1970's. FIA is based on reproducible sample injection, accurate timing and controlled dispersion. This technique is very versatile due to the control of the variables and can easily be automated. This technique is very suitable for routine laboratory analysis. By introducing various sample modifying techniques in tandem with the FIA system, samples can easily be modified. Some modifying techniques are analyte pre-concentration, sample dilution and sample cleanup. Passive dialysis can be used very successfully for sample dilution and cleanup. Problems arise when samples with low analyte concentration have to be analysed. For this reason an electrolysers unit, equipped with a passive membrane, was developed. The history, development and theory of membranes and membrane processes are discussed. A study of the movement of ions, in solution and across a passive membrane, under the influence of an applied d.c. electrical potential is given. Passive

membranes were evaluated for use in the proposed system. The following factors influencing the efficiency of electrodialysis in the FI system were studied: The flow rate of the donor and acceptor channels; the applied d.c. electrical potential; injection loop volumes; flow direction in the electrodialyser unit. An investigation was done into on-line analyte pre-concentration and regulated dilution probabilities of the electrodialysis system. Systems that were evaluated are the following: The determination of chloride in water effluents; The determination of copper and zinc in pharmaceuticals; The direct and indirect determination of phosphate in fertilisers. A comparative study between the advantages and disadvantages of the passive dialysis and electrodialysis system is given.

Elektrodialise in vloeï inspuit sisteme

deur

Cornelius Johannes Hattingh

Voorgelê ter vervulling van 'n deel van die vereistes vir die graad

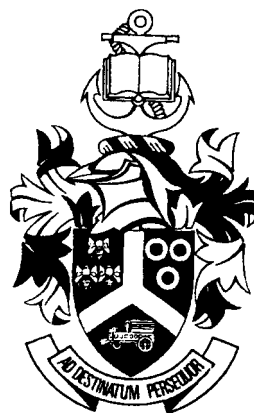
Philosophiae Doctor

in die Fakulteit Natuurwetenskappe

Universiteit van Pretoria

Pretoria

Oktober 1999



Samevatting

Elektrodialise in vloeï inspuit sisteme

deur

Cornelius Johannes Hattingh

Studieleier: Professor JF van Staden

Departement Chemie

Universiteit van Pretoria

Graad: Philosophiae Doctor

Vloeï inspuit analise (VIA) is 'n kontinue vloeïtegniek wat aan die begin van die 1970's ontwikkel is. VIA is gebaseer op herhaaldelike monsterinspuiting, akkurate tydmeting en gekontroleerde dispersie. Hierdie tegniek is baie veelsydig weens die beheer van veranderlikes. Hierdie tegniek kan ook maklik ge-outomatiseer word. Hierdie tegniek is verder baie toepaslik vir gebruik in roetine laboratoria. Deur verskeie monstermodifikasie tegnieke in die VIA sisteem in te sluit kan monsters verander word om die sisteem se toepassing te optimiseer. Somige modifikasietegnieke sluit in die analietprekonsentrasie, monster verdunning en suiwing van monsters. Passiewe dialise kan met sukses vir monster verdunning en suiwing aangewend word. Probleme ontstaan egter indien die analiet konsentrasie reeds laag is. Om hierdie rede is 'n elektrodialiseerder, wat toegerus is met 'n passiewe membraan, ontwikkel. 'n Kort inleiding rakende die ontwikkeling van die analitiese proses word gegee. Die geskiedenis, ontwikkeling en teorie van membrane en

membraanprosesse is bespreek. 'n Studie van die beweging van ione, in 'n oplossing en oor 'n passiewe membraan, onder die invloed van 'n toegepaste direkte stroom elektriese potensiaal is gedoen. Passiewe membrane vir gebruik in die voorgestelde elektrodialiseerder is ge-evalueer. Die volgende faktore wat die effektiwiteit van elektrodialise in die VI sisteem beïnvloed, is bestudeer: die vloeitempo van die skenker- en ontvangerstrome; die toegepaste direkte stroom spanning; die inspuit volumes; vloeirigting in die elektrodialiseerdeeenheid. 'n Ondersoek na analiet prekonsentrasie en beheerbare aanlynverduunnings deur die elektrodialise sisteem is uitgevoer. Die volgende sisteme is ge-evalueer: Die bepaling van chloried in afvloeiwaterv; die bepaling van koper en sink in farmaseutiese produkte; die direkte en indirekte bepaling van fosfaat in kunsmis. 'n Verglykende studie van voor- en nadele van passiewe en elektrodialise word gegee.



Hierdie werk is opgedra aan my vrou

Elsa

ACKNOWLEDGMENTS

I wish to acknowledge with thanks the significant contributions of the following people:

1. Jesus Christ, since I can do all things through Christ who strengthens me.
2. Prof J F van Staden (supervisor), for his excellent academical leadership, positive criticism and motivation during the project.
3. Mr R Dumas, for his technical assistance with the building of some parts of the instrumentation.
4. Ms Carol du Sautoy and Ms Niam Rampersadh who read parts of the manuscript and offered numerous helpful suggestions and corrections.
5. Ms Karin van der Merwe who helped with the typing of Chapter 3.
6. All my friends at Medunsa, University of Pretoria and the University of the North for their moral support.
7. My parents, Koos and Rina Hattingh, for their support (morally and financially) and motivation, not only during this project, but also during all my previous years of study.
8. To my dear wife, Elsa. Thank you very much for your support, understanding and sense of perseverance which carried me through the last part of my studies.

Electrodialysis in flow injection systems

Chapter 1.	Introduction	1
1.1	The Analytical process	1
1.2	Analytical chemistry and the need for automisation	2
1.2.1	Flow-based techniques used for analysis	3
1.2.2	Separation techniques	4
1.2.2.1	Dialysers in FIA systems acting as sample pretreatment tools	6
1.3	Objective of the project	9
1.4	References	11
Chapter 2.	Introduction into Membranes and Membrane Processes	13
2.1	Introduction	13
2.2	Definition of Membrane and a Membrane Process	13
2.3	Introduction to some Membrane Processes	17
2.3.1	Osmosis	17
2.3.2	Pressure driven membrane processes	18
2.3.2.1	Microfiltration	19
2.3.2.2	Ultrafiltration	20
2.3.2.3	Nanofiltration/Reverse Osmosis	20
2.3.3	Pervaporation	23
2.3.4	Liquid membranes	24
2.3.5	Dialysis	25
2.3.5.1	The history and development of dialysis	25
2.3.5.2	Definition and the process of dialysis	26
2.3.6	Electrodialysis	29
2.3.6.1	History and development of electrodialysis	29
2.3.6.2	The process of dialysis	30
2.4	Characterisation and Structure of Membranes	31

2.4.1	Porous membranes	33
2.4.2	Non-porous membranes	36
2.4.3	Carrier membranes	37
2.5	Membrane materials	37
2.6	References	39
Chapter 3.	Theoretical background of the movement of particles in a solution and across a membrane	40
3.1	Introduction	40
3.2	Ion transport	42
3.2.1	Ion motion: the empirical facts	42
3.2.2	The mobilities of ions	47
3.2.3	The measurement of transport numbers	56
3.2.4	Conductivities and ion-ion interaction	57
3.3	Diffusion and transport in solutions	59
3.3.1	Diffusion: the thermodynamic view	60
3.4	Diffusion	64
3.4.1	The diffusion equation	64
3.4.2	Properties of the solution	67
3.4.3	Diffusion with convection	69
3.4.4	The statistical view of diffusion	71
3.5	Transport in membranes	72
3.5.1	Introduction	72
3.5.2	Driving forces	74
3.5.3	Transport through porous membranes	76
3.5.4	Transport through nonporous membranes	78
3.5.5	Transport through membranes: A unified approach	87
3.5.5.1	Reverse osmosis	94
3.5.5.2	Dialysis	95
3.5.5.3	Gas permeation	97

3.5.5.4	Pervaporation	98
3.5.5.5	Electrodialysis	98
3.6	References	102
Chapter 4.	The evaluation of passive membranes for use in electro dialysis systems: Determination of chloride	100
4.1	Introduction	100
4.2	Experimental	102
4.2.1	Reagents and solutions	102
4.2.1.1	Standard chloride solution	102
4.2.1.2	Colour reagent	103
4.2.2	Instrumentation	103
4.2.3	Flow system	106
4.3	Results and discussion	107
4.3.1	Applied potential	108
4.3.2	Flow rates of the donor and the acceptor streams	111
4.3.3	Interferences	114
4.3.4	Calibration and comparison of the Spectrapore and the Technicon membranes	115
4.3.5	Samples	117
4.4	Conclusions	118
4.5	References	120
Chapter 5.	Determination of Copper (II) ions in multivitamin tablets after enhancement of mass transfer across the neutral membrane and the preconcentration of the dialysate ions	122
5.1	Introduction	122
5.2	Experimental	125
5.2.1	Reagents and solutions	125
5.2.2	Instrumentation	126
5.2.3	Flow system	129

5.2.4	Procedure	129
5.2.4.1	Operation of pumps and valves	129
5.3	Results and discussion	132
5.3.1	Flow rate of the donor stream	133
5.3.2	Applied potential	134
5.3.3	Injection loop volume	138
5.3.4	Flow direction of the donor and the acceptors channels	139
5.3.5	Interferences	140
5.3.6	Data and calibration of the optimised system	140
5.3.7	Samples	142
5.4	Conclusions	143
5.5	References	145
Chapter 6.	Determination of zinc in pharmaceutical products using an electrolysers incorporated into the flow injection system	148
6.1	Introduction	148
6.2	Experimental	150
6.2.1	Reagents and standards	150
6.2.2	Instrumentation	151
6.2.3	Flow system and procedure	153
6.3	Results and discussion	156
6.3.1	Applied potential across the membrane	157
6.3.2	Flow rates of the donor and acceptor streams	159
6.3.3	Injection loop volume	160
6.3.4	Addition of electrolyte	161
6.3.5	Interferences	161
6.3.6	Data and calibration of the optimised system	163
6.3.7	Samples	164
6.4	Conclusions	166
6.5	References	167

Chapter 7. The determination of phosphate	169
7.1 Introduction	169
7.2 Experimental	170
7.2.1 Indirect determination of phosphate	171
7.2.1.1 Reagents and solutions	171
7.2.1.1.1 Standard barium solution	171
7.2.1.1.2 Standard phosphate solution	171
7.2.1.2 Instrumentation	171
7.2.1.3 Flow system	172
7.2.1.4 Procedure	174
7.2.1.4.1 Operation of pump and valves	175
7.2.1.5 Results and discussion	178
7.2.1.5.1 Barium concentration	178
7.2.1.5.2 Applied potential	179
7.2.1.5.3 Flow rates of the donor and acceptor streams	181
7.2.1.5.4 Reaction coil	183
7.2.1.5.5 Injection loop volumes	185
7.2.1.6 Data and calibration of the optimised system	178
7.2.2 Direct determination of phosphate	194
7.2.2.1 Reagents and solutions	194
7.2.2.1.1 Standard phosphate solution	194
7.2.2.1.2 Colour reagent	195
7.2.2.1.3 Electrolyte solution	195
7.2.2.2 Instrumentation	195
7.2.2.3 Flow system	196
7.2.2.4 Procedure	197
7.2.2.4.1 Operation of pumps and valves	198
7.2.2.5 Results and discussion	200
7.2.2.5.1 Flow rate of the donor and acceptor channels	201



7.2.2.5.2	Applied potential	203
7.2.2.5.3	Injection loop volume	205
7.2.2.5.4	Influence of added electrolyte	205
7.2.2.5.5	Interferences	207
7.2.2.5.6	Data and calibration of the optimised system	208
7.2.2.5.7	Samples	208
7.3	Conclusions	210
7.4	References	212
Chapter 8.	Conclusions	213
Addendum A		i
Addendum B		xi
Addendum C		xii