Sequential-injection Analysis

Graham D. Marshall

Sequential-injection Analysis

by

Graham Dean Marshall

Submitted in partial fulfilment of the requirements for the degree, Doctor in Philosophy in the Faculty of Science, University of Pretoria, Pretoria.

May 1994

Sequential-injection Analysis

by

Graham Dean Marshall

Supervisor : Professor Jacobus F. van Staden
Department of Chemistry, University of Pretoria

Co-supervisor : Prof Jaromir Ruzicka
Department of Chemistry, University of Washington, USA

Degree : Doctor of Philosophy

Sequential-injection Analysis

by

Graham Dean Marshall

Supervisor: Prof Jacobus F van Staden

Department of Chemistry: University of Pretoria

Co-supervisor: Prof Jaromir Ruzicka

Department of Chemistry: University of Washington, USA

Degree: Doctor of Philosophy

Synopsis

Process Analytical Science (PAS) is a rapidly developing sub-discipline of Analytical Science. Tried and tested analytical principles are applied in modified instrumental architectures that enable the real-time monitoring of key process constituents. Process Analyzers are becoming vital and valuable components of sophisticated distributed control strategies. Their acceptance and usefulness is resulting in ever increasing demands on the process analysis researcher. Chemical sensors, first believed to be the ultimate solution for the process controller, have not enjoyed the wide spread application initially predicted. Their long term reliability has not materialized in all but a few cases. An intermediate or alternative approach is required which will incorporate the conceptual simplicity and size of sensors and the predictable and controlled environment of well established flow-based sample

manipulation procedures such as flow-injection analysis (FIA) and the various branches of chromatography.

This study describes the development of such a technique which has been called Sequential-injection Analysis (SIA). The theoretical basis on which the technique is founded is outlined together with the progression of thinking which lead to its conceptualisation. Its successful implementation depends entirely on microprocessor controlled flow programming. The development of a device control and data acquisition package was mandatory and is described. The study then focuses on establishing the operational parameters affecting the design of a SIA manifold.

Having established the manifold design principles, SIA is evaluated as an approach to sample manipulation. The wet chemical unit operation of trace enrichment is applied to SIA. Although the use of SIA for many traditional FIA applications is envisaged, the use of SIA principles with chemical sensors as the means of detection is seen as the ultimate application of this flow-based analytical technique. Some would be so bold as to claim that it is possibly the basis of successful implementation of chemical sensors. Its usefulness and advantages over FIA in such an application is demonstrated. The hardware requirements for the future optimum development of this approach to process analysis as well as some future areas of work conclude the study.

Sequential-injection Analysis

deur

Graham Dean Marshall

Promotor: Prof Jacobus F van Staden

Departement Chemie: Universiteit van Pretoria

Medepromotor: Prof Jaromir Ruzicka

Departement Chemie: Universiteit van Washington, VSA

Graad: Doktor van Filosofie

Samevatting

Die wetenskap van prosesanalise is 'n snelontwikkelende subdissipline van die Analitiese Wetenskap. Beproefde analitiese beginsels word aangewend in gewysigde instrumentasie wat die monitering van hoof prosesbestanddele in reële tyd moontlik maak. Prosesanaliseerders word steeds belangriker en waardevoller komponente in gesofistikeerde verspreide-beheer strategieë. Hulle aanvaarding en nuttigheid bring eskalerende eise mee vir die prosesanalitiesenavorser. Chemiese sensors wat eers beskou is as die eindoplossing vir prosesbeheer, geniet nie die wydverspreide toepassing wat oorspronklik voorspel is nie omdat hulle langtermyn betroubaarheid net in 'n paar gevalle bewys is. 'n Tussentydse of alternatiewe benadering, wat die konseptuele eenvoud en grootte van die sensors kombineer met die voorspelbare en beheerde milieu van goed gevestigde vloeigebaseerde monsterhanteringsprosedures, soos vloei-inspuitanalise (VIA) en chromatografie, word benodig.

Hierdie studie beskryf die ontwikkeling van so 'n tegniek wat sekwensiële-inspuitanalise (SIA) genoem word. Die teoretiese basis waarop die tegniek berus, word geskets saam met die vooruitgang in denke wat gelei het tot sy totstandkoming. Die suksesvolle implementering van die tegniek maak volkome staat op vloeibeheer deur midel van 'n mikroverwerker. Die ontwikkeling van 'n apparaatbeheer- en dataverkrygingsprogram was daarom noodsaaklik en word beskryf. Daarna fokus die studie op die bepaling van bedryfsparameters wat die ontwerp van 'n SIA vloeisisteem beïnvloed.

Nadat die ontwerpbeginsels vir die vloeisisteem vasgestel is, word SIA geëvalueer as 'n benadering tot monster-manipulasie. Spoorverryking as eenheidsbewerking word aangewend ten opsigte van SIA. Al word die gebruik van SIA beoog vir sommige tradisionele VIA aanwendings, word die gebruik van SIA beginsels met chemiese sensors as metingswyse beskou as die uiteindelike aanwending van hierdie vloei-gebaseerde analitiese tegniek. Sommige sal hulle verstout om te sê dat dit moontlik die basis vir die suksesvolle implementering van chemiese sensors is. Die nut en voordele bo VIA in so 'n aanwending word aangetoon. Die studie word afgesluit met die hardeware behoeftes vir die toekomstige optimum ontwikkeling van hierdie benadering tot prosesanalise, en 'n aantal toekomstige studievelde.

Table of Contents

List of Figures

Acknowledgments

Exodus 31:3 ..... and I have filled him with the Spirit of God, with skill, ability and knowledge in all kinds of crafts-- What do we have that has not come from almighty God?

A work such as this is never the result of a single individuals efforts. Numerous people, by their encouragement, tolerance, motivating, and cooperation contribute beyond what they imagine. This work would not have been completed without the constant encouragement and interest by my wider family, Bible study group, friends, and colleagues.

First and foremost, this work was made possible by the permission and indulgence of Mintek's management, specifically Tina Pohlandt-Watson, Ron Mallett, Mike Nicol, and Peter Jochens. Their encouragement and willingness to allow me to follow my head, as well as their readiness to listen and buy into some of my ideas, make my place of work also a place of enjoyment.

My colleagues and peers remain a constant source of inspiration. Sydwell Williams taught me all I know about electronics. Malcolm Taylor challenges me to apply the combined wisdom of the existing literature and to write in such a way as to maintain the readers interest. Dick Groot challenges me to understand the "why" behind my

observations. Deon Barnes is a fitting fellow competitor, always challenging me to keep up with him and consider the unlikely option.

Prof Koos van Staden, my supervisor, also had a vital role to play. His constant enthusiasm, and interest in the work made the effort worthwhile. His understanding and patience when other responsibilities slowed progress is also gratefully acknowledged.

How do you compute the contribution from your family and even begin to express adequately due appreciation? They have tolerated hours of absence, countless outstanding chores, frequent outbursts and selfishness as the pressure mounted, and the hours of clickity-clack from the computer keyboard. This they have endured stoically and, often unknowingly, provide that vital support when it appears that the last straw is about to break the camels back.

Sharon, Andrew, Stephen, and Nicole, I have done this as much for YOU as for me!

Here I stand on the edge of an ocean of truth. I have picked up a few grains of sand, but the whole ocean lies beyond me, unknown.

– *Isaac Newton*