UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The determination of trace elements in complex matrices by electrochemical techniques

by

Caren Billing

Submitted in partial fulfillment of the requirements for the degree

MAGISTER SCIENTIAE

In the Faculty of Science
University of Pretoria
Pretoria
October 2000

© University of Pretoria

UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

The determination of trace elements in complex matrices by electrochemical techniques

by

Caren Billing

Supervisors: Prof Jacobus F. van Staden
Department of Chemistry
University of Pretoria
Dr Dick R. Groot
Analytical Science Division
Mintek

Degree: Magister Scientiae

SYNOPSIS

Some problems in the determination of trace impurities in complex matrices by stripping voltammetry was investigated. Two separate analyses were studied, namely the determination of cobalt in a zinc electrolyte and the determination of arsenic in high purity gold. In both cases matrix exchange was employed, thus flow systems were designed which included an on-line deoxygenation system. In the former case, a flow cell containing a hanging mercury drop electrode with perpendicular mercury and solution flow was designed. Cobalt was complexed by dimethylglyoxime (DMG) and determined by adsorptive stripping voltammetry. Interference from zinc was removed by chelating it with citrate. In the latter case, a wall-jet cell was used with a gold film plated onto a glassy carbon substrate as the working electrode. Arsenic was determined by anodic stripping voltammetry. Interference from the large excess of gold present was prevented by forming the kinetically inert gold (I) complex. The pH of the solution was

adjusted to 3 to prevent electrode passivation, while avoiding decomposition of the gold (I) cyanide complex. However, copper was found to be a major interference in this analysis. This project demonstrated that electroanalytical techniques could be used for the determination of trace elements in complex matrices.

Die bepaling van spoor elemente in komplekse monsters met elektrochemiese tegnieke

deur

Caren Billing

Leiers: Prof Jacobus F. van Staden
Departement van Chemie
Universiteit van Pretoria
Dr Dick R. Groot
Analitiese Wetenskap Afdeling
Mintek

Graad: Magister Scientiae

SAMEVATTING

Enkele probleme met die bepaling van spoor onsuiwerhede in komplekse monsters is met stropingsvoltammetrie ondersoek. Twee verskillende ontledings is bestudeer; naamlik, die bepaling van kobalt in 'n sink elektroliet en die bepaling van arseen in hoë suiwerheid goud. In albei gevalle is matrysuitruiling gebruik, waarvoor vloeisisteme ontwerp is wat ook aanlyn-suurstofonttrekking ingesluit het. Eerstens is 'n vloeisel met 'n hangende kwikdruppel elektrode ontwerp waar die kwik- en oplossingvloei loodreg op mekaar is. Kobalt is met dimetielglioksiem (DMG) gekomplekseer en bepaal deur middel van adsorptiewe stropingsvoltammetrie. Die steuring van sink is oorkom deur die sinksitraatchelaat te vorm. Tweedens is 'n muurspuitsel gebruik waar die werkende elektrode 'n goudfilm glasagtige koolstof elektrode was. In die bepaling van arseen met anodiese stropingsvoltammetrie is sianied gebruik om die goud te komplekseer as die goud(I)sianiedkompleks. Steuring deur die groot oormaat goud is voorkom deur die

vorming van die kineties inerte goud(I)sianiedkompleks. Die pH van die oplossing was 3 om passivering van die elektrode te verhoed, terwyl dit terselfdertyd voorkom dat die goud(I)sianiedkompleks ontbind. Die projek het aangetoon dat koper erg steur in hierdie bepaling. Dit bewys dat elektroanalitiese tegnieke vir die bepaling van spoor elemente in komplekse monsters gebruik kan word.

ACKNOWLEDGEMENTS

I thank Mintek for providing me with the opportunity to do an MSc and for providing the resources and the support that was required.

In particular, I thank Dr Dick Groot for all his assistance and insight, and for persevering with me through all the highs and the lows.

I thank Prof. Koos van Staden for affording me the opportunity to do this MSc under his supervision and for his patience during the times when work was going slow due to other work pressures.

I thank my family and friends for all their support and encouragement.

And lastly, but certainly not least, I thank my husband Dave for all the time he spent encouraging me, advising me and listening to me. Thank you for always being there, for making the meals and helping me where you could during those nights and weekends spent in front of the computer.

CONTENTS

Synopsis I
Acknowledgements V
Contents VI
List of Abbreviations X

Chapter 1 – Introduction 1
1.1) Determination of cobalt in zinc electrolytes 4
1.2) Determination of arsenic in gold 7
1.3) References 9

Chapter 2 – Electrodes 12
2.1) Working electrodes 12
2.1.1) Mercury electrodes for the determination of cobalt 12
2.1.1.1) Theory 12
2.1.1.2) Experimental 14
2.1.2) Thin gold film electrodes for the determination of arsenic 17
2.1.2.1) Theory 17
2.1.2.2) Experimental 20
2.1.2.3) Results 26
2.2) Reference electrodes 27
2.3) Auxiliary electrodes 27
2.4) References 27

Chapter 3 – Flow Cells 30
3.1) Theory 30
3.2) Flow cell for a HMDE 30
3.2.1) Flow cell for the SMDE used for the determination of cobalt in a zinc electrolyte 33
3.3) Wall-jet cells 37
3.3.1) Wall-jet cell used for the determination of arsenic in high purity gold 41

3.4) References 43

Chapter 4 – Deoxygenation 45

4.1) Introduction 45

4.2) Semi-permeable membranes in a nitrogen atmosphere 48

4.3) Experimental 51

4.3.1) Testing deoxygenation using the flow cell for the SMDE 53

4.3.2) Testing deoxygenation in the wall-jet cell 57

4.4) Discussion 61

4.5) References 62

Chapter 5 – Flow System 64

5.1) Theory 64

5.2) Data collection 67

5.2.1) Potential waveforms 67

5.2.2) IR compensation 71

5.3) Flow system for the SMDE 73

5.3.1) Set-up 73

5.3.2) Testing the flow system 78

5.3.2.1) Flow Rate 79

5.3.2.2) Reproducibility 79

5.3.2.3) Flow cell charateristics 80

5.3.2.3a) Effect of flow rate 80

5.3.2.3b) Effect of scan rate 84

5.3.2.3c) Effect of concentration 84

5.3.3) FlowTEK procedures 86

5.4) Flow system for the wall-jet cell 88

5.4.1) Set-up 88

5.4.2) Testing the flow system 89

5.4.2.1) Flow Rate 89

5.4.2.2) Flow cell characteristics 90

5.4.2.2a) Effect of flow rate 90

5.4.2.2b) Effect of inlet-electrode separation 90

5.4.3) FlowTEK procedures 92

5.5) References 94

Chapter 6 –Determination of Cobalt in a Zinc Electrolyte 96

6.1) Supporting electrolyte 96

6.2) Adsorptive stripping voltammetry 99

6.3) Background 100

6.4) Experimental and results 102

6.4.1) Supporting and stripping electrolyte compositions 102

6.4.1.1) Sodium citrate concentration 102

6.4.1.2) pH 105

6.4.1.3) Cobalt concentration 107

6.4.1.4) DMG concentration 109

6.4.1.5) Dilution factor of the zinc electrolyte 110

6.4.2) Experimental conditions 112

6.4.2.1) Adsorption time 112

6.5) Discussion 116

6.6) References 118

Chapter 7 –Determination of Arsenic in High Purity Gold 120

7.1) The dissolution of gold 120

7.2) Arsenic 121

7.3) Background 122

7.4) Experimental and results 123

7.4.1) pH of plating solutions 123

7.4.2) Deposition potential 133

7.4.3) Reproducibility 133

7.4.4) Stripping electrolytes 134

7.4.4.1) Hydrochloric acid 134

7.4.4.2) Sulphuric and hydrochloric acid 138

7.4.5) Interferences 143

7.4.5.1) Cobalt 143

7.4.5.2) Silver 144

7.4.5.3) Copper 144

7.5) Discussion 146

7.6) References 148

Chapter 8 – Conclusion 151

Appendix – FlowTEK Set-up 154

LIST OF ABBREVIATIONS

ac	alternating current
AdSV	adsorptive stripping voltammetry
ASV	anodic stripping voltammetry
BSWV	Barker square wave voltammetry
CSV	cathodic stripping voltammetry
CV	cyclic voltammetry
DMG	dimethylglyoxime
DPSV	differential pulse stripping voltammetry
DPV	differential pulse voltammetry
GCE	glassy carbon electrode
HMDE	hanging mercury drop electrode
LSSV	linear sweep stripping voltammetry
LSV	linear sweep voltammetry
MFE	mercury film electrode
NPV	normal pulse voltammetry
OSWV	Osteryoung square wave voltammetry
PSA	potentiometric stripping analysis
SMDE	static mercury drop electrode
SWV	square wave voltammetry
TLD	thin layer detector
TMFE	thin film mercury electrode
WJC	wall-jet cell
WJE	wall-jet electrode