

ELECTROCHEMICAL CELLS FOR TRACE ELEMENT PRECONCENTRATION
IN ATOMIC SPECTROMETRY.

By

David Akuban Ogaram, B.Sc., M.Sc.

January 1985.

A Thesis Submitted for the Degree of
Doctor of Philosophy
of the University of London.

Department of Chemistry,
Imperial College of Science
and Technology,
London. SW7 2AY.

ABSTRACT

Two cells have been developed and tested for trace element preconcentration for inductively coupled plasma atomic emission spectrometry (ICP-AES). The procedure for their use in this role is to deposit the trace element from its flowing electrolyte solution onto a solid electrode by an electrochemical reduction over an adequate period to give a measurable signal. The deposit is then redissolved in a limited volume of the electrolyte solution by electrochemical oxidation and nebulised into the plasma from which its emission signal is obtained.

The two cells are the concentric cup platinum cell (CCP) and the reticulated vitreous carbon cell (RVC). Both are hydrodynamically controlled flow-through cells and have similar dependence of limiting current (i_L) on solution volume flow rate (v_f):

$$\text{for the CCP cell ; } i_L \propto v_f^{0.33}$$

$$\text{RVC cell ; } i_L \propto v_f^{0.37}$$

confirmed by experiment. The performance of each cell at trace concentrations has been established. Deposition efficiencies are 7.5 and 35.6% for the CCP and RVC cells respectively. Cadmium can be determined by this technique using the CCP cell down to $265 \times 10^{-12} \text{ mol cm}^{-3}$ for 600 seconds deposition while the RVC cell determines copper down to $3.15 \times 10^{-12} \text{ mol cm}^{-3}$ for only 300 seconds. The calibration curve is rectilinear over 5 orders of magnitude. Both cells have been tested with analysis of seawater as a real sample.

The RVC cell is most effective for preconcentration owing to its high surface to volume ratio.

ACKNOWLEDGEMENTS

I am grateful to my supervisor Professor W.J. Albery for placing the facilities of the Department at my disposal and for his guidance and interesting discussions in electrochemistry. I am indebted particularly to Dr R.D. Snook for his guidance throughout the entire project, for the useful discussions and for the unwavering concern and support at my time of financial crisis. I am also grateful to Dr G. Stephenson and Dr D.J.M. Bernal of the Department of Mathematics for their advice on the formulation of and solution by numerical methods for equation 3.29.

I am thankful to the Government of the Republic of Uganda for the financial support during this research which support was always one cycle out of phase with the College timetable.

My grateful thanks to all the technicians in the electrical, glass blowing, and mechanical workshops for ensuring that the equipment was in good working order. In particular I am thankful to Mike Pritchard for the fabrication of the two cells. I would also like to thank Miss Kay Randall for typing this thesis.

To all members of the Trace Lab thanks for being such a jolly co-operative group. Thanks particularly to Paul E. Zaft for the many critical discussions and John Dean for proof-reading this work.

My special thanks to all the Antelopes, those with us and those no longer with us, for their patience, sacrifices and encouragement before and throughout this research.

CONTENTS

	PAGE
Title page	1
Abstract	2
Acknowledgements	3
Contents	5
Preface	9
 CHAPTER 1 INTRODUCTION	 10
1.1 The Need for Preconcentration.	11
1.2 Techniques used in Trace Analysis.	13
1.3 Commonly used Preconcentration Techniques.	20
1.4 Electrochemical Preconcentration for ICP-AES.	22
1:4.1 Introductory Concept of ASV.	23
1:4.2 Introductory Concept of ICP-AES.	29
i) Emmission of Energy	29
ii) The Distribution of Atomic Populations.	31
iii) The Shape of Spectral Lines.	32
iv) Self Absorption.	34
v) Ionisation Equilibrium.	36
vi) The Plasma Source.	38
1.5 The Purpose of this Work.	39
 CHAPTER 2. THE THEORY OF ELECTROCHEMICAL PRECONCENTRATION CELLS.	 40
2.1 Introduction.	41
2.2 Fundamentals of Hydrodynamic Voltammetry.	42
2.3 Hydrodynamic Voltammetry at Solid Electrodes.	49

2:4.1	Platinum.	53
2:4.2	Glassy Carbon.	55
2:4.3	Reticulated Vitreous Carbon.	57
2.5	Cell Design Considerations	59
2:5.1	General Objectives.	59
2:5.2	Working Electrode Geometry.	59
2:5.3	Working Electrode Materials.	60
2:5.4	Working Electrode Placement.	61
2:5.5	The Cell.	62
CHAPTER 3	THE CONCENTRIC CUP CELL.	64
3.1	The Cell.	65
3.2	Theory.	67
3:2.1	The Differential Equation for Transport.	68
3:2.2	The Velocity Profile.	71
3:2.3	The Geometrical Factor, ϕ .	75
3:2.4	Mathematical Solution.	79
3.3	Experimental Section.	84
3:3.1	Instrumentation and Reagents.	84
3:3.2	The Reference Electrode.	86
3:3.3	The Working Electrode Pretreatment.	87
3:3.4	Test of the Concentric Cup Cell.	87
3:3.5	The Dependence of Limiting Current on Solution Volume Flow Rate.	88
3:3.6	Dependence of Limiting Current on the Working Electrode Position.	89
3:3.7	i) Volume Flow Rate Index Dependence on Working Electrode Position.	94

ii) Test with a Depositible Species.	94
3:3.8 Comparison of Experiment with Theory.	98
3:3.9 Anodic Stripping Experiments (ASV)	101
3:3.10 ASV with ICP-AES Experiments:	
i) Instrumentation.	103
ii) Optimisation of the ICP-AES.	112
iii) Operation of the ASV/ICP-AES System.	113
iv) ASV Preconcentration of Cadmium for ICP-AES.	114
v) Efficiency of the Concentric Cup Cell.	115
vi) Dependence of Signals on Deposition Time.	118
vii) Analysis of a Real Sample.	118
3.4 Results and Discussion.	121
 CHAPTER 4 THE RETICULATED VITREOUS CARBON CELL.	126
4.1 The Cell.	127
4.2 Theory.	129
4.3 The Working Electrode Pretreatment.	130
4.4 Instrumentation and Reagents.	132
4.5 Test of the RVC Cell.	132
4.6 Dependence of Limiting Current on Solution Volume Flow Rate.	133
4.7 The Useful Potential Range of RVC.	136
4.8 Experiments a Depositible Species.	139
4:8.1 Dependence of Limiting Current on Solution Volume Flow Rate.	142
4:8.2 ASV with Cadmium.	142
4.9 ASV Preconcentration of Copper for ICP-AES.	142
4:9.1 Dependence of Signal on Deposition Time.	146

4:9.2	Dependence of Signal on Stripping Potential Scan Rate.	148
4:9.3	Efficiency of the RVC Cell.	148
4:9.4	Precision of the ASV Preconcentration for ICP-AES.	152
4:9.5	Calibration Curve for Copper.	154
4:9.6	Analysis of a Real Sample.	155
4.10	Discussion of Results.	157
CHAPTER 5 THE ASV/ICP-AES INTERFACE.		164
5.1	The Problem.	165
5.2	The Metering Spray Valve.	168
5.3	Operation of the Metering Spray Valve.	171
5.4	Experiments with the Metering Spray Valve.	173
CHAPTER 6. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK.		180
REFERENCES		184

PREFACE

The work reported here straddles the two fields : electrochemistry and spectroscopy. In the literature of analytical applications of these fields the units used in expressing concentration are different. For electrochemistry the most common unit is mol dm^{-3} (or its order expression mol l^{-1}). In spectroscopy however the unit is the non SI $\mu\text{g cm}^{-3}$ (parts per million -ppm) or ng cm^{-3} (parts per billion -ppb). Comparison of this work with the literature therefore would require switching from one unit to the other accompanied by the required conversions. To maintain some degree of consistence and simplify conversions this work uses the unit mol cm^{-3} so that by multiplying by 1000 the SI acceptable unit commonly used in electrochemical work mol dm^{-3} is readily obtained and on multiplying by the gramme molecular weight of the species the spectroscopy unit $\mu\text{g cm}^{-3}$ results. Hence a 1 ppm copper solution is expressed in this work as $15.76 \times 10^{-9} \text{ mol cm}^{-3}$ and can easily be read as $15.76 \times 10^{-6} \text{ mol dm}^{-3}$. Although 15.76×10^{-9} should be written in scientific notation as 1.576×10^{-8} the engineering notation whereby all exponents change as multiples of three e.g. 10^{-3} , 10^{-6} , 10^{-9} , 10^{-12} has been adopted so that $15.76 \times 10^{-9} \text{ mol cm}^{-3}$ can be read as 15.76 n mol cm^{-3} . Elsewhere in the work SI units are used.

CHAPTER 1.
INTRODUCTION.

1:1 The Need for Preconcentration

Preconcentration as a means of increasing detection power has become a significant aspect of measurement of concentrations of elements that are lower than 10^{-6} M. The need to measure elements present in such low concentrations has been increasing rapidly in the past decade arising from different fields of interest in society.

In the academic field it is needed in the measurement of rate constants and equilibrium constants. In pharmaceutical synthesis it is required to establish the content of new products. In manufacturing industry both the raw material and the finished product must satisfy legal requirements designed to protect the manufacturer and the consumer. The measurement provides the desired information. For reasons of economy in some industries e.g. film processing it is required to ensure that expensive materials e.g. Silver are not lost through effluents and to determine the efficiency of recovery of such materials. In addition, statutory requirements with the watchful eyes of bodies like the Factories Inspectorate, ensure that toxic waste is not released as effluents at levels which are harmful to the environment.

By far the most intensive interest in trace measurement is in environmental and nutritional aspects of human health. Here the greatest activity is in the determination of toxic elements¹; beryllium, arsenic, cadmium, lead, mercury, whose presence in the environment whether in air, water, soil or plant and animal tissue must be monitored continuously to establish the level of

contamination and its sources. The activity is stirred up by revelation in medicine that each of these elements in excess amounts² is capable of causing a variety of health hazards to man. Cadmium for example causes babies to be born underweight to mothers over-exposed to it³. It causes prostatic cancer;^{4,5} anosmia (loss of sense of smell);^{6,7} inhibition of metalloenzymes;⁸ has a disputed effect on the cardiovascular system;^{3,9,10,11,12,13} and has acute effects symptomised by severe nausea, vomiting, diarrhoea, muscular cramp and salivation¹⁴ which can be followed by shock and death within 24 hours or by acute renal failure and cardio-pulmonary depression and death within 7-14 days.¹⁵ Application of trace element analyses are extended in the monitoring of occupational environments to protect the workers from exposure to adverse levels² of toxic elements. In the nutritional studies, the object is to determine trace elements that play a vital role in maintaining good health. Such elements are the first row transition metals; vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc.¹⁶ In clinical chemistry it is important to obtain a timely and accurate measurement of these metals as a diagnosis since their marginal deficiencies or excesses may not be indicated by symptoms of disease. Some of these metals e.g. Se, are both toxic and essential and there is a very narrow margin between the concentration at which it is considered essential^{16,17}, and one in which it is toxic^{18,19,20}. hence the analytical technique must be precise.

In all these fields the concentration of the element to be measured can be so low as to require special techniques. Cadmium

for example is present in the environment at levels shown in Table I.

Area	Concentration	Reference
50 Urban sites (UK)	0.001-0.020 $\mu\text{g}/\text{m}^3$	21
Rain (US)	0.6 $\mu\text{g}/\text{L}$	22
North Sea, Irish Sea	0.0004 ppm (range 0.00001-0.00041)	23
Soil (under pasture) Devon, Tamar Valley	1.6 ppm (range 0.7-4.5)	24

Table I : Typical Concentrations of Cadmium in the Environment.

Typical concentrations of trace elements in the environment are quite readily available in the literature: for the general environment, ^{25,3,23} for sea water, ^{26,27} in human liver ^{28,29}, kidney ^{30,31,32}, and brain ^{33,34,35,36}.

1:2 Techniques used in Trace Measurement.

Techniques most reliably used in the determination of trace elements in these fields are : X-ray Fluorescence ³⁷; Atomic Absorption Spectrometry, Neutron Activation Analysis, Anodic Stripping Voltammetry and Atomic Emission Spectrometry. The performances of these techniques have been studied and compared. Based on published work, Filby and Shah ³⁸ compared detection limits for Neutron Activation Analysis, Atomic Absorption Spectrometry and Atomic Emission Spectrometry for 21 trace metals. Based on their own work Cushing and Ranticelli ³⁹ compared the same techniques. Wheeler et al. ⁴⁰ compared Atomic Absorption

Spectrometry with X-ray Fluorescence for copper in blood. Uthe and Armstrong⁴¹ have reviewed the different techniques as used for the determination of mercury. A more recent and extensive review giving comparison of these techniques for trace elements is given by Pinta.⁴²

Although neutron activation analysis stands out as the most sensitive, has no sources of contamination, unimportant matrix effects and is capable of multielement determination, it requires access to an atomic reactor with a flux of slow (thermal) neutrons of 10^{15} to 10^{18} neutrons $m^{-2} s^{-1}$ for high sensitivity. Few laboratories can fulfil this. Moreover, decay periods of up to one month may be necessary to allow measurement of some long-lived nucleides. Also its initial capital cost is very high.⁴³ It is therefore unsuitable for routine work.

X-ray Fluorescence offers simplicity in sample presentation, is non destructive and permits multielement determination. However, its performance is greatly affected by the form and type of matrix containing the element to be measured. This gives a corresponding variation of its sensitivity. Overall, compared with other techniques, its sensitivity is low.

The techniques that are therefore outstanding and are most widely used for routine determination of trace elements are; Atomic Spectrometry (both atomic absorption and atomic emission) and Anodic Stripping Voltammetry. For both of these the concentration

of the trace element is a task that stretches the performance of the technique to the limit. The concentration is below the limit of detection or just above it such that the signal relative to background cannot be detected or reliably quantified. It is for this reason that preconcentration is a significant aspect of trace element determination.

Anodic Stripping Voltammetry, (ASV), itself a preconcentrating technique in electroanalysis, was first thought to be the most sensitive measurement technique available^{44,45,46} at the time medicine was beginning to highlight the significance of trace metals to man. It was immediately demonstrated to be sensitive for trace elements^{47,48,49,50} and was used to determine Silver in rain water and snow at 10^{-10} M level. These results showed ASV to be more sensitive than neutron activation analysis for that element.⁵¹ Further applications were for arsenic,^{52,53} and gallium⁵⁵ at nanogram levels.⁵⁴ Detection limits for lead and cadmium at 10^{-11} M level have been reported.⁵⁶ It has also been shown to have better sensitivity than both flame and nonflame atomic absorption spectrometry for ten heavy metals using a rotating disc electrode and deposition times of only two minutes.⁵⁷ It has been used for simultaneous multielement determination^{58,59,60} and at 10^{-9} M level for lead, zinc, copper and cadmium in spring water.⁶¹ It has found application in a variety of fields; in pharmacological analysis,^{62,63} and for ecological,⁶⁴ clinical,^{65,66,67} water, effluent^{47,48,51,68,69,70} and biological samples.^{71,72} Its applications have been subject to extensive reviews^{47,48,49,50,60,63,73,64} which confirm its position as a

useful technique.

However anodic stripping voltammetry does not have a wide simultaneous multielement capability and low concentration leads to a correspondingly low Faradaic current. Also in the process of generating this current in sufficient electrolyte the double layer capacitive current and electrolysis currents from impurities are also generated. This leads to low analyte signal to background ratios and consequently poor sensitivity. Various attempts have been made to extract the Faradaic current from others and have resulted in the following modes of ASV: differential pulse,^{74,75} phase selective AC,^{76,77} stair case,⁷⁸ subtractive,⁷⁹ hydrodynamically modulated⁸⁰ and ASV with collection.⁸⁶ Although these have improved sensitivity the effect is not eliminated entirely.

Simultaneous multielement determination is limited, particularly on solid electrodes by the thickness of the deposited layer. This requires that only one atomic layer of deposit is made for different elements to strip at their own potentials. If more than one monolayer is deposited, they all tend to strip off together resulting in loss of stripping peak resolution. On the other hand one atom layer on the electrode is a tiny quantity of species and therefore results in a tiny Faradaic current. Although this can be increased by using a bigger surface area electrode this too increases the capacitive current and undesirable surface reaction currents from impurities.

Furthermore at solid electrodes, more so at high potential scan rates, multiple stripping peaks are obtained where a single peak is expected.^{82,83,84,85} For high sensitivity, better precision and accuracy a sharp single peak is favoured. High potential scan rates are used where possible to obtain it. The production of multiple peaks which cover a wide potential range with a poorly defined position relative to the background complicates interpretation of currents, lowers sensitivity and makes multielement determination impossible. Simultaneous multielement determination by anodic stripping voltammetry also suffers from overlapping of stripping signals due to similar redox potentials of some metals e.g. copper and bismuth, and cadmium and thallium.

The other outstanding measurement technique for trace metals is atomic spectroscopy which includes atomic absorption and atomic emission techniques. Atomic absorption spectrometry is a capable and well studied technique.⁸⁶⁻⁸⁹ Reviews of its applications are numerous.^{89,90,42,86,91} Its advantages and disadvantages are also known. In particular its simultaneous multielement capability is limited by the need to change the light source for each element. The availability of multielement lamps and their scope is narrow. Atomic emission techniques are therefore preferable since they offer both sensitivity and simultaneous multielement capability.

There are currently six types of emission techniques depending on the nature of excitation used: flame, electric arc, spark, glow discharge, laser and plasma. The latter two being the most recent additions. Plasma excitation has continuously gained widespread use

and superiority over all other atomic emission techniques. In itself there are three types depending on the method of plasma generation : these are : DC arc, microwave and inductively coupled (radiofrequency) plasmas and it is inductively coupled plasma atomic emission spectrometry (ICP-AES) that has dominated the plasma techniques and all recent developments in trace element measurement.

The possibility of using ICP-AES for determining elements was first investigated by Greenfield⁹² and independently, by Wendt and Fassel.⁹³ Detection limits for a few elements were reported. Subsequently ICP-AES was used for determination of various elements in solution⁹⁴⁻¹⁰⁵ and for simultaneous multielement determination.^{106,107} It has been assessed against other techniques for this use¹⁰⁸⁻¹¹¹ for which it has a principle advantage. Its ability to detect low concentrations was demonstrated by determining detection limits experimentally for 69 elements and comparing with other atomic spectrometry techniques.¹¹² Its versatility has been demonstrated by its application to sample matrices ranging from steels,^{100,109,111,113-117} rocks,^{99,101,115,119-121} fresh and seawaters,^{102,109} wastes and effluents^{109,115,116,122} plant materials,^{98,123} soils,^{94,105,123} oils,^{107,124,125} organics^{115,124} chemical reagents¹²⁶ and biological materials.^{105,124,126,127} In all of these applications the ICP-AES requires mainly dissolution and dilution as the only sample treatment before analysis. Its use has been subject to reviews^{92,96,105,108,109} at all stages of its development and more recently and rigorously.^{121,129-131} These reviews describe the

principle advantages of the ICP-AES as : wide linear dynamic concentration range of up to 5 orders of magnitude above the detection limit, a precision of the order of 1% which is comparable to other techniques (and its magnitude is mainly due to instability of the sample introduction system) and negligible interference effects in comparison with other techniques. It is therefore an excellent tool for trace element determination. However, ICP-AES has its own shortcomings.

Many samples require dissolution in mineral acid solution. This results in an increase of the viscosity of the solution and a corresponding decrease in the uptake rate of the nebuliser and consequently a decrease of the emission signal. Matrix matching of the blank is required. Moreover while dilution will reduce the viscosity it decreases the emission signal due to the dilution of the species of interest. Furthermore the process of nebulisation itself generates undesirable noise due to instability in the nebuliser gas flow. It is this noise which is the major component of noise in ICP-AES.

For easily ionizable elements such as the alkali metals Li, Na, K, whose ionisation energy is of the order of 5eV and less, the energy of the plasma is enough not only to raise a large population of atoms to excited state but also to ionise them thus loading the plasma with more electrons. The effect of this is to shift the ionisation equilibrium of the substrate element to favour no ionization, hence, the ion line of this element is suppressed while

its atom line is enhanced. This effect is discussed more in section 1:3.2 ahead. The presence of alkali elements in the matrix of the substrate in amounts of the order of $10,000 \mu\text{g}/\text{cm}^{-3}$ interferes with analysis of other elements. This is the case in seawater analysis. It contains dissolved alkaline elements in quantities enough for the interference to occur. Furthermore direct simultaneous multielement determination of seawater is impracticable with pneumatic nebulisation as the sample introduction. This is first because of blocking of the nebuliser by the solid left behind by evaporation of the solvent during nebulisation : Seawater contains 3.5% dissolved solids. Secondly, background shifts and stray light effects ¹³²⁻¹³⁴ interfere with the measurement.

For the more difficult elements, the elements whose ionisation energy is close to 10eV and over, such as arsenic, antimony, cadmium, lead, tellurium, tin and selenium, the plasma energy is not enough to raise a large population of the species to a level in which their emission intensity is adequate for the desired sensitivity to be achieved. The ICP-AES gives relatively low detection limits for these trace elements when using nebulisation as sample introduction. Yet, most of these are the elements of major interest in environmental and health monitoring. Preconcentration is therefore very important for the determination of trace elements with the ICP-AES.

1:3 Commonly Used Preconcentration Methods

There are numerous sample preparation schemes designed to both

preconcentrate the trace elements and separate them from major interfering components of their own matrices prior to analysis. For atomic spectrometry most widely used are : coprecipitation,¹³⁵⁻¹³⁷ chelation and extraction (liquid liquid extraction),¹³⁸⁻¹⁴⁰ and chelating ion exchange resin.¹⁴¹⁻¹⁴⁶

Coprecipitation is a lengthy process. Often two days are required for complete precipitation. Solvent extraction is also time consuming especially because it involves an increased sample manipulation. Relatively large amounts of reagents and large container surface areas are brought into contact with the sample which contains only the trace element. This gives rise to unacceptably high blanks. Time and care in cleaning glassware and working areas is therefore necessary to prevent significant contamination.

Chelating ion exchange resin does not give very certain results either. The most commonly used resin is Chelex-100.^{145,147,148,141} Its use has been reviewed.¹⁴² It has some potentially serious disadvantages. It has an affinity for alkaline earths¹⁴⁹ and these are abundant in seawater. If, for example, zinc is the trace element to be determined, the more abundant calcium will displace it from the resin. Besides the resin also contains an immobilised anionic group which must be given a counter cation. For seawater this will be one of the abundant ions sodium, calcium, magnesium and when eluted these lead to light scatter in the plasma. Furthermore it retains silver, mercury and tin very strongly. Its use therefore requires more separations to avoid

these effects. More recently poly(dithiocarbamate) chelating resin has been used^{143,146,150} and reviewed.¹⁵¹ This resin has a better performance than Chelex-100 but the technique is still lengthy and tedious.

1:4 Electrochemical Preconcentration

Electrochemical preconcentration has been less widely used for atomic spectrometry despite that whenever it has been used good performance has been reported¹⁵²⁻¹⁵⁷ and without the problems posed by the preconcentration techniques mentioned above. It is easily adaptable to the ICP system of detection and for continuous flow measurements. In addition it is reproducible, can be controlled and is inexpensive. It is for these advantages that electrochemical preconcentration was chosen for use with the ICP-AES in this work. In particular, anodic stripping voltammetry (ASV) is combined with the ICP-AES into one system : ASV/ICP-AES to achieve lower detection limits for electroreducible trace elements.

The procedure to achieve this is in two stages. First the trace element is deposited from its flowing electrolyte solution onto a working electrode by electrochemical reduction over a long enough period to accumulate a measurable amount of analyte. Secondly the deposit is redissolved in a limited volume of the electrolyte by electrochemical oxidation. This now concentrated solution is nebulised into the plasma from which its emission signal is obtained. The first stage is preconcentration and the second is detection. ASV plays a part in both. This differs from the approach in the above references¹⁵²⁻¹⁵⁷ in which the working

electrode, usually a tungsten wire, is transferred into the atom cell and the deposit released by vaporisation using a heating current. The approach reported here is an on-line one. The principles of operation involved in each step will now be described.

1:4.1 Introductory Concept of ASV

ASV like any other electroanalytical technique is based on the phenomenon discovered by Heyrovsky¹⁵⁸ that the current flowing between the counter electrode, CE, and the working electrode, WE, in a cell at a given potential is related to the bulk concentration of the reacting species. The Faradaic current is quantitative while the potential is qualitative. If the electrochemical reaction is represented as :



when the reaction proceeds to the right the electron flow is from the WE to the solution yielding a cathodic current, i_- . This is the deposition step. When it proceeds to the left, the electron flow is from the solution to the WE yielding an anodic current, i_+ . This is the stripping or redissolution step. The highest current invariant with potential attained for any of the reactions is the limiting current, i_L . It corresponds to the situation when all the species reaching the electrode surface is transformed. For cathodic deposition this corresponds to all Ox species reacting at the surface being transformed into Red. The potential E of the reaction is related to the activities of the reactant and product by the Nernst equation :

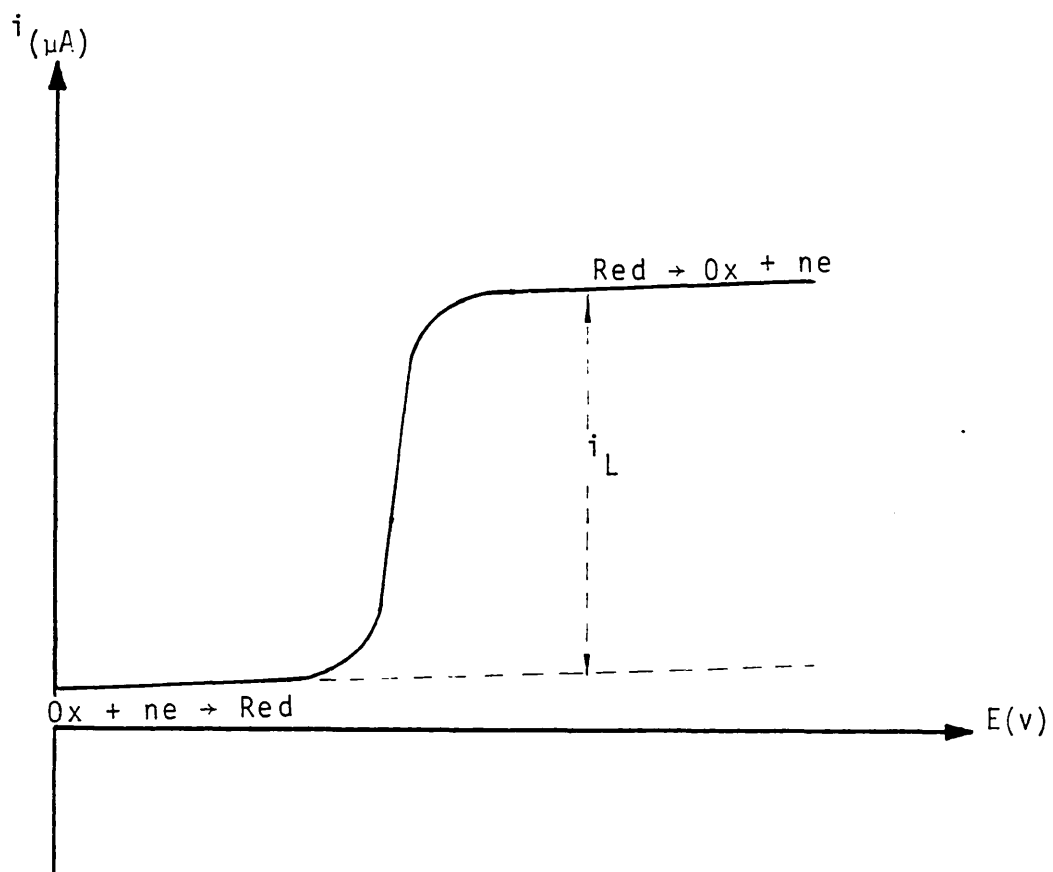


Figure 1.1 : Schematic Current-Potential Curve.

$$E = E^0 + \frac{RT}{nF} \ln \frac{A_{ox}}{A_{Red}} \quad (\text{Volt}) \quad 1.2$$

where E^0 is the standard potential (Volt). R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (K), n is the number of electrons transferred in the reaction, F is the Faraday constant (96487 C mol^{-1}) and A_{ox} and A_{Red} are the activities of the oxidised and reduced species respectively. Equation 1.2 can be rewritten as :

$$E = E^0 + \frac{RT}{nF} \ln \frac{\gamma_{ox} C_{Box}}{\gamma_{Red} C_{BRed}} \quad 1.3$$

where γ_{ox} and γ_{Red} are the activity coefficients of the oxidised and reduced species respectively and C_{Box} and C_{BRed} are their bulk concentrations (mol dm^{-3}). By Heyrovsky's relation

$$i_t = k_1 C_B \quad 1.4$$

where i_t is the current at time t and k_1 is the proportionality constant it is possible to replace C_{Box} and C_{BRed} in equation 1.3 with their current equivalents. The result is :

$$E = E^0 + \frac{RT}{nF} \ln \frac{\gamma_{ox}}{\gamma_{Red}} \cdot \left\{ \frac{D_{Red}}{D_{ox}} \right\}^{1/2} + \frac{RT}{nF} \ln \frac{i_L - i_t}{i_t} \quad 1.5$$

where D_{ox} and D_{Red} are the diffusion coefficients of the reduced and oxidised species respectively. Equation 1.5 is a description of the current - potential curve or voltammogram for a redox system. Figure 1.1 is a schematic diagram of this equation. A more rigorous treatment of the current dependence on solution flowrate is given in chapters 3 and 4 for each cell.

In either side of the current - potential curve a different reaction is proceeding under the effect of a potential difference.

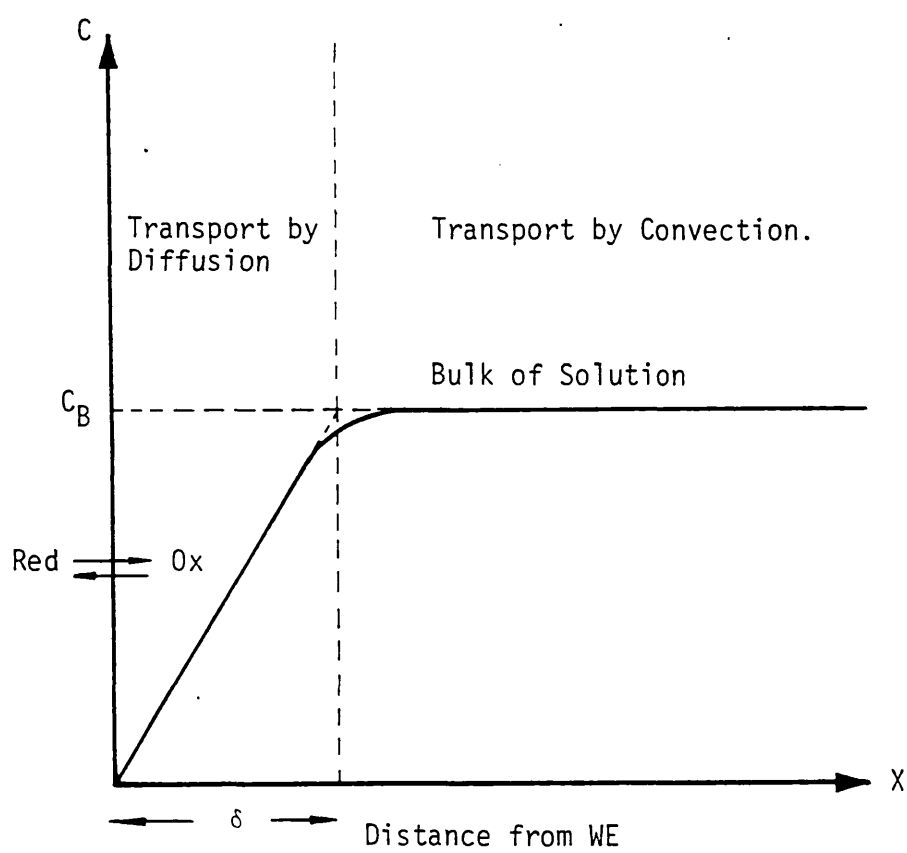


Figure 1.2 : Schematic concentration profile at WE.

During an anodic stripping voltammetry experiment, for the deposition step, the reaction potential chosen is well away from the inflection of the curve where only i_L is the current flowing and is held there at constant conditions for the desired length of time. For the desired reaction to occur however, it must be preceded by several physical processes : the transport of the species to the vicinity of the WE surface; its diffusion from the bulk through the region of changing concentration, δ , the diffusion layer; its adsorption on to the WE surface; and the electron transfer that transforms the species into a solid. Figure 1.2 is a representation of this process. On redissolution these processes occur in reverse. The two processes convection and diffusion determine the size of the current generated hence the quantities of the species involved for a given WE.

The quantity, q , of the species deposited is proportional to the current, i_L , and the time, τ , for which it has flowed. From Faradays laws it can be shown that

$$q = \frac{i_L \tau M}{nF} \quad 1.6$$

where M is the relative atomic weight of the species. The total quantity, Q , of the species in the solution that has flowed in time τ is

$$Q = C_B M V \quad 1.7$$

where V is the volume that has flowed. It is possible to obtain the overall efficiency of the deposition for the duration of the reaction :

$$\text{Efficiency (Conversion)} = \frac{q}{Q} \cdot 100 \quad \% \quad 1.8$$

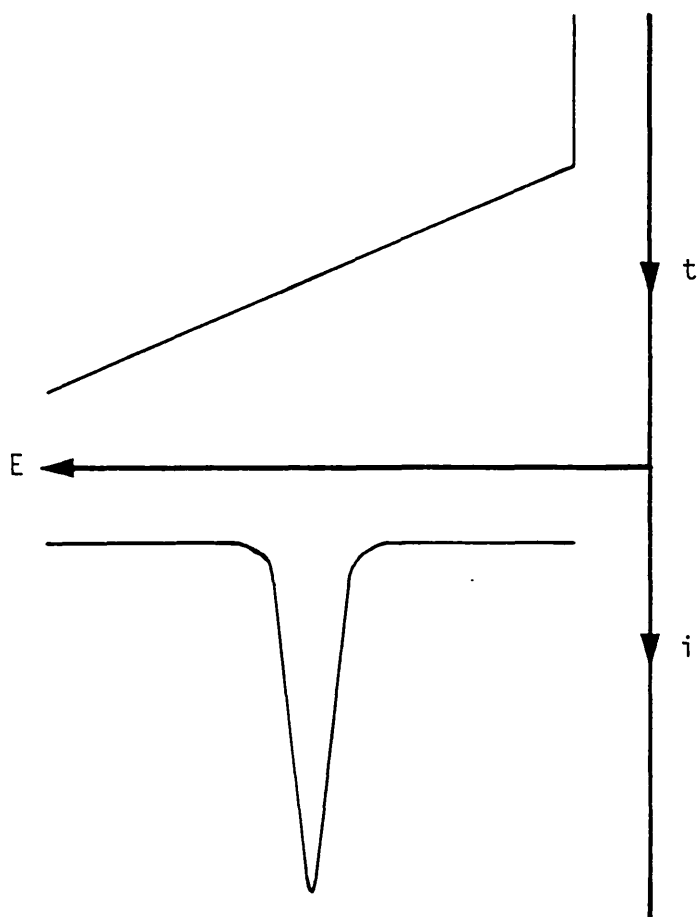


Figure 1.3 : Schematic Anodic Stripping Experiment.

Different potential programmes can be used to strip off the deposit. These can be pulsed, differentially pulsed or linear sweep. In this work only linear sweep is used. A schematic diagram of a linear sweep anodic stripping experiment is shown in Figure 1.3.

1:4.2 Introductory Concept of ICP-AES

When energy from a source is supplied to atoms of a given species, the electrons in the atoms are promoted to higher energy levels which are characteristic of the nature of the species. The energy levels may be broadened, shifted or split by interactions with external fields such as magnetic, electric or microfields when these are present. When the electrons fall back to lower energy levels they emit radiation the intensity of which depends on the population of atoms in each of the high energy states, the transition probabilities and absorption and re-emission by neighbouring atoms. The measurement of emission line shapes, shifts, widths and intensities can therefore yield information about the particle densities, temperatures, pressures or environment of the atom. For quantitative analysis, information about the particle densities are of particular interest. It is the intention in this section to describe the relation between the emission intensity and the concentration or population of the emitting species and how it is affected by physical factors obtaining in the source.

(i) Emission of Energy

For any atom an extensive number of possible energy states

exists. A supply of energy from an external source will raise its electrons to a higher energy state, k of energy, E_k . For optical spectra only transitions of valence shell electrons are of concern. A transition to a lower state i of energy E_i results in spontaneous emission of a photon of energy :

$$h\nu_o = E_k - E_i \quad 1.9$$

where h is Planck's constant (6.626×10^{-34} Js) and ν_o is the frequency (Hz) of the radiation in vacuum. When the lower of the two states is the ground state ($i = 0, E_o = 0$) the emitted spectral line is called a resonance line.

From Einstein's theory of radiation, the intensity of the emission, I_{ki} , is directly dependent on its transition probability, A_{ki} , namely the probability per second that an atom in a state k will spontaneously radiate its energy and return to a lower state i . It is expressed as :

$$I_{ki} = A_{ki} h \nu_{ki} n_k \quad 1.10$$

where n_k is the population of atoms (m^{-3}) in state k_i . If ΔV is a small volume of the plasma in which the emitting atoms are, then $n_k \Delta V$ is the number of excited atoms in it and the power, P , radiated by them is :

$$P = A_{ki} h \nu_o n_k \Delta V \quad (W) \quad 1.11$$

not all this power is measured. The monochromator views the plasma through a slit of definite width and length hence of area ΔA that subtends a small solid angle at the plasma at a distance, L (m), from the receiving slit surface along the line of view. L is given by $\Delta V / \Delta A$. Since radiation is emitted into the total space of the

solid angle 4π steradians then the power per unit area i.e. the brightness, B , is

$$B = \frac{A_{ki} h \nu_o n_k L}{4\pi} \quad (\text{Wm}^{-2} \text{Sr}^{-1}) \quad 1.12$$

and is the desired relation between brightness of the spectral line and the population or concentration of the emitting species.

(ii) The Distribution of Atomic Populations

For a system in equilibrium at temperature T , if there are n_k particles with energy E_k and n_i with energy E_i , the ratio of the particles occupying the two energy states is given by the Boltzmann formula :

$$\frac{n_k}{n_i} = \frac{g_k}{g_i} \exp -(E_k - E_i)/kT \quad 1.13$$

where k is the Boltzmann constant ($1.380 \times 10^{-23} \text{ JK}^{-1}$), and g_k, g_i are statistical weights of the k^{th} and i^{th} state respectively and are calculatable from angular momentum number J_n using the relation

$$g_n = 2J_n + 1 \quad 1.14$$

It is convenient to express the population in any one state as a fraction of the total number, N , of particles of the species present in all states where

$$\begin{aligned} N &= n_0 + \dots + n_i + \dots + n_k + \dots \\ &= \frac{n_0}{g_0} (g_0 + \dots + g_i \exp -E_i/kT + \dots + g_k \exp -E_k/kT + \dots) \\ &= \frac{n_0}{g_0} \sum_{j=0}^{\infty} g_j \exp -E_j/kT \end{aligned} \quad 1.15$$

The quantity $\sum_{j=0}^{j=\infty} g_j \exp - E_j/kT$ is given the symbol $Z(T)$ and

and is called the partition function. Hence

$$N = \frac{n_o}{g_o} Z(T)$$

or

$$n_o = \frac{N}{Z(T)} g_o \quad 1.16$$

Similarly for any given state, k , the population n_k is :

$$n_k = \frac{N}{Z(T)} g_k \exp - E_k/kT \quad 1.17$$

and substituting for n_k in equation 1.12.

$$B = \frac{A_{ki} h \nu_o L}{4\pi} \cdot \frac{N}{Z(T)} \cdot g_k \exp - E_k/kT \quad (\text{Wm}^{-2}\text{Sr}^{-1}) \quad 1.18$$

(iii) The Shape of Spectral Lines

The emitted spectral line is not a discrete frequency but consists of a range of frequencies spread around the resonant frequency ν_o giving the line a finite width. This broadening is due to a combination of several physical processes which interfere with the emission and are summarised below. Detailed considerations can be found in spectroscopic literature such as references 159-163.

Natural broadening results from an atom spending a finite time in an excited state. From the uncertainty principle there is uncertainty in the energy E_k and therefore the frequency has a finite width. This is of the order 10^{-5} nm and is negligible.

Doppler broadening is caused by the thermal motion of emitting particles along the line of observation. It is symmetrical about

the mean frequency of the line. The Doppler half-width, $\Delta\nu_D$, can be obtained from the formula¹⁶⁴

$$\Delta\nu_D = \frac{v_o}{c} \left\{ \frac{8RT \ln 2}{M} \right\}^{1/2} = 7.162 \times 10^{-7} v_o \left\{ \frac{T}{M} \right\}^{1/2} \quad 1.19$$

where M is the atomic weight of the particle and the other symbols as defined before.

Lorentz or Pressure broadening is caused by collisions of emitting particles with any other particles in the source such as argon atoms or ions in the case of the ICP. Depending on the concentration and temperature of the foreign particles the effect apart from broadening is also to shift the line, cause asymmetry and a significant reduction of its height. Detailed considerations of mathematical descriptions of the resulting line profile can be found in spectroscopic literature such as references.^{160,165-166} The broadening half-width, $\Delta\nu_L$, can however be estimated from the formula¹⁶⁷:

$$\Delta\nu_L = \frac{2\sigma_L^2}{\pi} \left\{ 2\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right\}^{1/2} \quad 1.20$$

and the shift $\Delta\nu_s$ by¹⁶⁷

$$\Delta\nu_s = 0.36\Delta\nu_L \quad 1.21$$

where σ is the collision cross-section and P is the foreign particle pressure or concentration in the source. M_1, M_2 are the atomic weights of the two colliding particles.

Stark broadening is caused by presence of strong, non-uniform electric fields or moving electrons or ions. These split the energy levels of the emitting particles. Due to motion in the source the emitted lines are diffused. Particles of low mass numbers are broadened more than those with high mass. In particular, for hydrogen like particles the stark effect is linear and proportional to electron density. It has therefore become useful for measurement of electron densities in the plasma.

The Zeeman broadening is caused by splitting of the energy levels by presence of a magnetic field. Since this is deliberate the Zeeman effect is not an interference.

(iv) Self Absorption

The absorption of emitted radiation on its passage out of the source by particles of the same species in the same source is called self absorption. It rises from the same process in which atoms in a lower state absorb energy and rise to a higher state (section 1:1.1) and has two consequences : it broadens the spectral line; and it decreases the desired brightness of the emission. In extreme cases the absorption at the central frequency can cause a minimum to appear in the spectral profile. This is called self-reversal.

If the atoms at the depth L of the source give emission of brightness B_0 and the absorption coefficient at the frequency ν is k_ν , then the transmitted brightness by Beer-Lambert's law is :

$$B(\nu) = B_0 \exp (- k_\nu L) \quad 1.22$$

The brightness of emission along the visual line is not uniform owing to temperature variation along the line outward. The total transmitted brightness, B^1 , in all L is therefore an integrated output.

$$B^1 = \int_0^L B(l) dl \quad 1.23$$

consequently the absorbed power is :

$$B^1(\nu) = B_0 [1 - \exp(-k_\nu L)] \quad 1.24$$

or

$$A_\nu = \frac{B^1(\nu)}{B_0} = 1 - \exp(-k_\nu L) \quad 1.25$$

where A_ν is the absorbtivity, the ratio absorbed power to incident power, and is equal to the emissivity, B_B , of an ideal blackbody at a given temperature and frequency (Kirchoff's law of radiation).

Hence

$$B(\nu) = A_\nu \cdot B_B(\nu) \quad 1.26$$

$B_B(\nu)$ is obtainable from Plank's law and is $\frac{2h\nu^3}{c^2} \exp(-E_k/kT)$.

A_ν varies with ν and has to be integrated over the spectral profile. The integral value, A_T , defined as

$$A_T = \int_0^\infty \left\{ 1 - \exp(-k_\nu L) \right\} d\nu \quad (s^{-1}) \quad 1.27$$

is called the total adsorption factor. For low concentrations i.e. k_ν is small, and for small values of L ,^{168,169}

$$A_T \approx \frac{\lambda^2 g_k N A_{ki}}{8\pi g_i} \quad (m^{-1} s^{-1}) \quad 1.28$$

and for large concentrations, k_ν large, and L large with a Voight

profile¹⁷⁰ :

$$A_T = \left\{ \frac{2\lambda_o^2 g_k N L a_{ki} \Delta v_D}{8\pi g_i (\ln 2)^{1/2}} \right\}^{1/2} \quad 1.29$$

where Δv_D is the Doppler half width

$$a = (\ln 2)^{1/2} \cdot \frac{\Delta v_L}{\Delta v_D}$$

Δv_L is the Lorentz half-width

Equations 1.28 and 1.29 can be used in turn in 1.26 resulting in :

$$B = \frac{1}{4\pi} \cdot h\nu_o \frac{Ng_k}{g_i} A_{ki} L \exp(-E_k/kT) \quad (\text{Wm}^{-2}\text{s}^{-1}) \quad 1.30$$

and

$$B = \frac{h\nu_o^2}{C} \left\{ \frac{g_k N L a_{ki} \Delta v_D}{\pi g_i (\ln 2)^{1/2}} \right\}^{1/2} \exp(-E_k/kT) \quad 1.31$$

Equation 1.30 is applicable to low concentrations while 1.31 is applicable to high concentrations where self absorption is a serious effect degrading the brightness - concentration relation to a square root relation.

(v) Ionisation Equilibrium

The plasma is a high temperature excitation source. A significant population of atoms in it is therefore ionised. For a species M, the ionisation equilibrium is :



with equilibrium constant, $S_M(T)$, at temperature T being

$$S_M(T) = \frac{N_{M^+} \cdot N_e}{N_M} \quad 1.33$$

where N is the population of species per cubic metre and $S_M(T)$ is also called the Saha ionisation constant and is a function of

temperature with which it is related according to the well known Saha Equation :

$$S_M = \frac{(2\pi m)^{3/2} \cdot (kT)^{5/2}}{h^3} \cdot \frac{Z_{M^+}(T)}{Z_M(T)} \exp(-E_m/kT) \quad 1.34$$

where m is the mass of an electron (0.910×10^{-30} kg), E_M is the ionisation energy (eV) of M and $Z_{M^+}(T)$, $Z_M(T)$ are the partition functions of the atom and ion respectively. Other symbols are defined before. The degree of ionisation, α , in terms of the equilibrium constant is :

$$\alpha = \frac{S_M(T)}{N_e + S_M(T)} \quad 1.35$$

where N_e is the electron number density. The fraction not ionised is $1 - \alpha$. Equation 1.18 can therefore be written as :

$$B = \frac{NLh\nu_o}{4\pi} \cdot \frac{(1-\alpha)}{Z(T)} \cdot g_k A_{ki} \exp(-E_k/kT) \quad 1.36$$

Since the exponential term increases with temperature and $1-\alpha$ decreases with it, the result is that each spectral line has a temperature of maximum intensity where the two effects cancel out.

The equilibrium in equation 1.32 can be shifted one way or the other, for example to the left by easily ionisable elements. This causes a suppression of the ion line and enhancement of the atom line (section 1:1.3). The actual magnitude of this shift has however been found negligible.¹⁷¹⁻¹⁷³ Both the excitation temperature and electron number density were little affected. The main explanation¹⁷⁴ is that the electron number density in the plasma arises from the ionization of the inert sustaining gas, argon, and this is far in excess of that from the ionization of

substrate or interferent. The argon ionization is favoured since a large population of its atoms is in excited states, some metastable, from which energy to ionize them is lowered to approximately 4eV. The exact mechanism by which this is achieved is however yet uncertain.¹⁷⁵⁻¹⁷⁹

(vi) The Plasma Source

It must be pointed out that the plasma is a complex state of matter. The simplified approach based on Local Thermal Equilibrium (LTE) has to be used with restraint. A plasma is a hot and radiant volume of gas in which a significant fraction of atoms is ionized and the atoms, ions and electrons are existing together. In particular the electrons are further than the Debye radius from the ions and Debye radius is smaller than the dimensions of the plasma. The Debye radius is the farthest distance from the nucleus of an atom over which the nucleus has any hold of an electron. It is given by the relation :

$$e_D = \left\{ \frac{\epsilon_0 kT}{e^2 \left(N_e + \sum \frac{1}{2} z^2 N^z \right)} \right\}^{1/2} \quad 1.37$$

where ϵ_0 is the permittivity of free space, e is the electron charge (1.602×10^{-19} C), and z is an ionization stage. The other symbols are as defined before. Although it contains charged species the plasma is neutral. It is also not in equilibrium.¹⁸⁰ If it were it would be characterised by a single temperature of the equilibrium. Various efforts have been made to measure temperatures such as : excitation temperature of the different states;

ionization temperature ; and rotational temperature of species in plasmas. All these have been found different. In addition the mechanisms of excitation processes occurring in it are still uncertain.

The Purpose of this Work

The forerunner of on-line electrochemical preconcentration technique for ICP-AES used a wall-jet cell to obtain a 3-fold preconcentration factor from a 10 minutes deposition time for copper.¹⁸¹ A 3-fold preconcentration factor is undesirably low and a 10 minutes deposition time is undesirably long. It was therefore clear that a significant improvement of preconcentration and detection limits can be achieved only by the use of cells with high deposition efficiency and low internal volume.

The purpose of this work was therefore to develop high efficiency electrochemical cells for on-line trace element preconcentration for use with the ICP-AES. The main pursuit was the design of flow-through cells which are compatible with the ICP-AES yet have all the capabilities of normal electrochemical cells. Two different approaches of the problem are followed : the tubular geometry which leads to the concentric cup cell; and flow through porous media which leads to the Reticulated Vitreous Carbon Cell. These cells are described, tested and evaluated for the purpose they are designed for.

CHAPTER 2.
THE THEORY OF ELECTROCHEMICAL
PRECONCENTRATION CELLS.

2.1 Introduction

As mentioned in chapter 1, the magnitude of the current at the WE is determined by

- i) the kinetics of the electrode process
- ii) the formation of final products
- iii) the transport of species to and from the WE.

The kinetics of the electrode process are usually fast for the electron transfer as occurs in deposition and stripping of a metal and depend upon the applied potential. In this work the use of the applied potential is mainly to "turn" the reaction on or off. The rate of the reaction therefore is controlled by the mass transport of the species - diffusion and convection. This can be increased by increasing transport. Little can be done to increase the diffusion component of transport since it depends on the nature of the species and that of the solution. Convection however can be well defined and accurately controlled. The technique of obtaining current-potential relationship due to redox reactions in which convection is the major contributor and is controlled is hydrodynamic voltammetry.

It can be achieved in two ways. Either the WE is rotated in a standing solution and the measured current is proportional to the angular velocity of the rotation or the solution is forced to flow over a stationary WE and the current is proportional to the velocity of the flowing solution.

The main advantage of hydrodynamic voltammetry over voltammetry in "quiet" solutions is that of high mass transfer

leading to higher sensitivity and efficiency. This has been demonstrated by the performance of electrode configurations such as the rotating disc electrode,¹⁸² tubular electrode¹⁸³ and wall-jet electrode.¹⁸⁴ Other advantages include simplicity, predictability of performance, experimental elegance and flow through capabilities for on-line measurements. Furthermore, as operating conditions can be set and held constant, hydrodynamic voltammetry becomes time independent and can therefore be used for steady state measurements. It is for these advantages that hydrodynamic voltammetry was most suitable as a base for the electrochemical preconcentration cells of this work.

Fundamentals of Hydrodynamic Voltammetry

Hydrodynamics is the study of motion of an incompressible fluid under an applied force and its interaction with its boundaries. The factors that affect the motion of a fluid in its containing boundaries are : its fluid viscosity (μ); density (ρ); mean velocity (v_m); characteristic length of the geometry of the boundaries (L); the state of the surfaces of the boundaries (smooth or rough); hydrostatic pressure gradient (P) and whether the flow is laminar or turbulent.

For the motion of a fluid of constant density and viscosity the effect of these factors is expressed by the well known Navier-Stokes equation which in vectorial notation is :

$$\rho \left(\frac{\partial \mathbf{V}}{\partial t} + \mathbf{V} \cdot \nabla \mathbf{V} \right) = -\nabla p + \mu \nabla^2 \mathbf{V} + \rho \mathbf{g} \quad 2.1$$

where $\mathbf{g}$ is the acceleration of gravity and the bold face symbols

are vectors. The flow of the fluid is along the surface of the boundary and must fulfil the principle of conservation of mass. Hence the equation of continuity :

$$\nabla \cdot \mathbf{V} = 0 \quad 2.2$$

It is often convenient to express these physical factors of motion of a fluid in a group form of dimensionless numbers which give a measure of the relative magnitude of their effects. One such number is expressed as :

$$\frac{\rho v L}{\mu} = \frac{v}{\nu} L = Re \quad 2.3$$

where

$$\nu = \frac{\mu}{\rho} \quad (\text{cm}^2 \text{s}^{-1})$$

and is known as kinematic viscosity. Re is the well known Reynolds number. It is a measure of viscous forces relative to inertial forces within the flow. It therefore is an indicator of the velocity distribution within the flow. At high Re values inertial forces dominate while at low values the viscous stress is dominant. Indeed the influence of viscosity is confined to a thin region close to the surface and the remainder of the flow is progressively less affected. The fluid immediately adjacent to the surface is therefore stationary relative to flow at the bulk. The thin region in which fluid velocity is changing from that of its free stream to zero at the surface is known as the hydrodynamic or Prandtl boundary layer, δ_H , after its discoverer.

When mass transfer occurs by diffusion from the flowing fluid such as induced by application of potential to the surface, the diffusion is normal to fluid flow. Another boundary layer is

established. The region in which the concentration is changing from C_B at bulk to C_e at the electrode surface is known as the diffusion layer, δ_D . This layer is very important in voltammetry since its structure has a significant effect on the rate of electrode reaction¹⁸⁵. The two boundary layers are illustrated in figure 2.1. Another dimensionless number is often used to indicate the relative growth of the hydrodynamic boundary layer compared with the diffusion layer :

$$\frac{V}{D} = Sc \quad 2.4$$

where D ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient of the diffusing species and Sc is the Schmidt number. It has the value of the order of 10^3 for the diffusion of electrolytes in aqueous solution at room temperature. In heat transfer the same number is referred to as the Prandtl number, Pr . It represents the ratio of momentum diffusion to concentration diffusion.

The flux of the dissolved species, i , of interest to the surface may be expressed as¹⁸⁶:

$$J_i = -nU_i F C_{Bi} \nabla \phi - D_i \nabla C_{Bi} + C_{Bi} V \quad 2.5$$

where J_i is the flux of i ($\text{mol cm}^2 \text{s}^{-1}$)

U_i is the mobility of i in solution ($\text{cm}^2 \text{mol}^{-1} \text{J}^{-1} \text{s}^{-1}$)

C_{Bi} is the bulk concentration of i (mol cm^{-3})

ϕ is the electrostatic potential (V)

D_i is the diffusion coefficient of i ($\text{cm}^2 \text{s}^{-1}$)

V is the fluid velocity (cm s^{-1})

The rest of the symbols are as defined before. The first term on the right hand side of the equation represents the motion of the charged species under the influence of an electric field of the

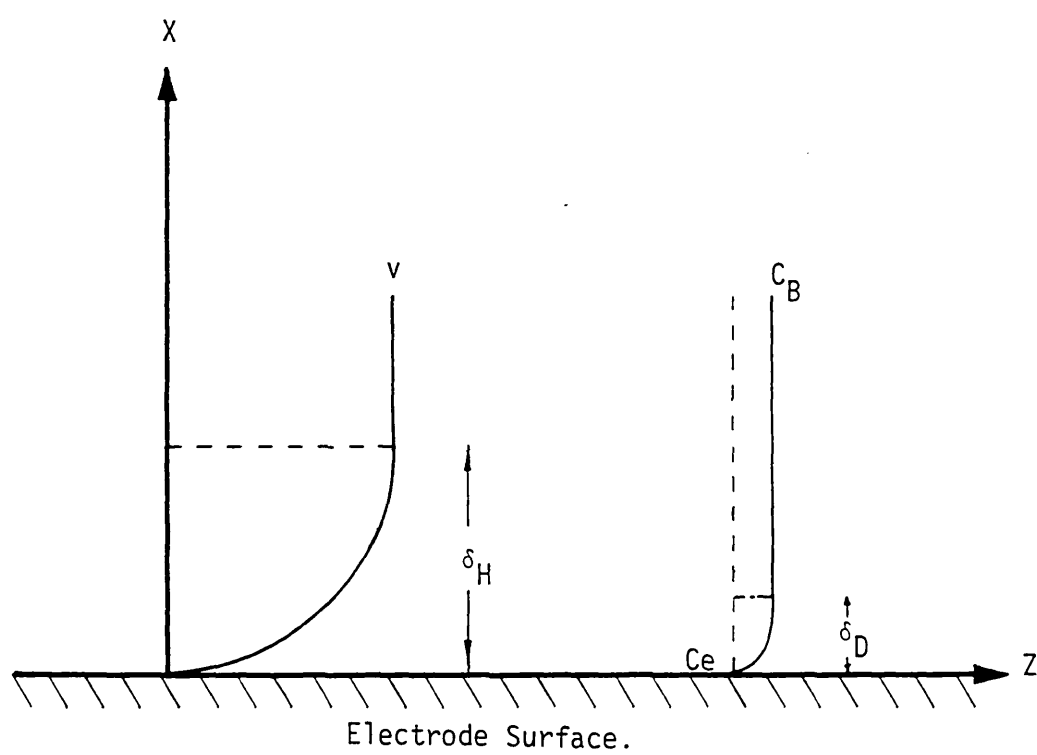


Figure 2.1 : The hydrodynamic and diffusion layers.

electrode often referred to as migration. Its contribution to mass transfer can be arranged non operative by inclusion of inert electrolyte in relatively large quantities. This is done in all this work. The second term represents mass transfer due to diffusion of the species under the influence of concentration gradient. The third term represents mass transfer by convection under the influence of motion of the fluid.

A further dimensionless number can be introduced at this juncture. This is the Sherwood number, Sh , also called the Nusselt number in heat transfer. It is defined by the relation :

$$Sh = \frac{jL}{D_i(C_{Bi} - C_{ei})}$$

It is a measure of the relative magnitude of total flux of the species i to the surface due to both convection and diffusion against the flux resulting from diffusion only. It is therefore relevant in voltammetry.

Mass transfer in flowing systems must fulfil the principle of conservation of mass. Hence the equation of material balance :

$$\frac{\partial C_B}{\partial t} = -\nabla \cdot J_i \quad 2.6$$

providing no reactions occur in the bulk of the fluid.

The flux of charged species constitutes a current, i , hence

$$i = F[n]j_i \quad (C s^{-1}) \quad 2.7$$

For an electrode surface of area A (cm^2) therefore the limiting current is

$$i_L = nFAJ_i \quad 2.8$$

Using the value of J_i in equation 2.5 in 2.6 gives

$$\frac{\partial C_{Bi}}{\partial t} = n_i F \nabla \cdot (U_i C_{Bi} \nabla \phi) + \nabla \cdot (D \nabla C_{Bi}) - v \cdot \nabla C_{Bi} \quad 2.9$$

On eliminating the migration term

$$\frac{\partial C_{Bi}}{\partial t} = \nabla \cdot (D_i \nabla C_{Bi}) - v \cdot \nabla C_{Bi} \quad 2.10$$

This is the convective diffusion equation that is the basis of hydrodynamic voltammetry. Its solution together with equation 2.7 within the conservation principles yields the desired current-flow rate dependence for a particular geometry of the electrode. However the mathematical problems caused by many flow systems are not always easy to handle. Complete solutions can only be found for simple geometries, even then some assumptions are used to simplify the equation.

The earliest and authoratative application of hydrodynamics to electrochemical phenomena was by Levich^{187,188} who solved the equation for the rotating disc electrode and tested it with experiment. He also formulated the equation for the tubular electrode, the plate electrode and determined the relation between δ_D , δ_H and velocity of the fluid for the rotating disc. Consequently several geometries have been studied and solutions to their mass transfer equations have been confirmed with experiment. Table 2 is a summary of such studies on various electrode geometries commonly in use in voltammetry.

More recently the use of porous materials for electrodes has been gaining ground. Consequently solutions to mass transfer

Electrode Geometry	Limiting Current Equation	Dependence on flow	Reference
Plate	$i_L = 0.68nFD^{2/3}v^{-1/6}v^{1/2}bLC_B$	$i_L \propto v^{1/2}$	188, 189, 190
Conical	$i_L = 0.77nFD^{2/3}v^{-1/6}v^{1/2}L^{-1/2}C_B$	$i_L \propto v^{1/2}$	191, 192
Rotating Disc	$i_L = 0.62nFAD^{2/3}v^{-1/6}\omega^{1/2}C_B$	$i_L \propto \omega^{1/2}$	187, 188, 196-201
Tubular	$i_L = 2.01nF\pi R^{2/3}D^{2/3}L^{2/3}v^{1/3}C_B$	$i_L \propto v^{1/3}$	183, 193 194, 195
Wall jet	$i_L = 1.60nFD^{2/3}K_v^{-5/12}a^{-1/2}R^{3/4}v^{3/4}C_B$	$i_L \propto v^{3/4}$	184
Rotating Sphere	$i_L = 0.474nFD^{2/3}v^{-1/6}\omega^{1/2}C_B$	$i_L \propto \omega^{1/2}$	202, 203, 204 205
Carbon Fibre	$i_L = 2.72nFD^{2/3}v^{-1/6}L_n A_n B v^{1/2}C_B$	$i_L \propto v^{1/2}$	206

Table 2 : Current - flowrate relations for common Electrolyte geometries.

where b is the width of cone normal to flow,

L is characteristic length : slant height for a cone, length for plate or tube or fibre,

ω is angular velocity

A is area of electrode

A_n is number of carbon fibres in electrode,

B is the breadth of the fibre

R is radius of the tube

K is a mass transfer coefficient of the wall jet

a is the diameter of the jet nozzle.

equations in such materials have been reported^{207,210} and their use reviewed.^{211,212} A discussion of these is given in chapter 4 where such an electrode is discussed. Hydrodynamic voltammetry has also been done on other extended surface electrodes such as carbon cloth,^{213,214} gold cloth²¹⁵ and platinum mesh.²⁰⁷ Although these designs have high mass transfer they are susceptible to turbulence.

In this work two approaches are followed. The first is based on the tubular geometry and the other on porous electrodes. Both are flow through cells. This is desirable because of some advantages that flowing sample voltammetry offers. It leaves the experimenter some freedom to set rapid and reproducible convection to the WE surface. Since the sample is flowing there is no concentration depletion of the species of interest. Flowing systems have a self cleaning property. This is always desirable in analysis. Furthermore, collection and handling of multiple sample fractions is avoided. There is also an attractive possibility of automation. Mass transfer considerations for these cells is considered in the next two chapters.

Hydrodynamic Voltammetry at Solid Electrodes

Solid electrodes have been used in voltammetry much earlier than mercury electrodes : thirty years before Heyrovsky²¹⁶ used mercury electrodes (1922) solid electrodes made out of gold, platinum, and silver were studied.²¹⁷ Practical problems such as electrode history encountered in such studies were reported.²¹⁸ The existence of limiting currents was demonstrated and described with equations.²¹⁹ But the development of the dropping mercury

electrode, DME, which did not have memory effect quickly overshadowed voltammetry at solid electrodes. This continued until inadequacies of the DME became apparent where upon attention split between development of better mercury electrode techniques and on the other hand development of solid electrode techniques with similar or better performance to that of the DME.

In polarography, (voltammetry at mercury electrodes, invariably the DME), work hinges on the principle that the species of interest forms an amalgam with mercury when deposition procedures are carried out. For species more noble than mercury this is not possible. The anodic range of mercury is relatively low owing to its oxidation at 0.4V (vs SCE). This is even lower in alkaline solution or halide solution or in any solution containing ions that react with mercurous or mercuric ions.²²⁰ To determine such species therefore solid electrodes must be used. Besides in ASV and for preconcentration purposes such as of concern in this work the mercury drop has a finite volume into which the trace element has to diffuse to or diffuse out of on stripping. A finite time is therefore required for the species to reach the surface where the reaction occurs. This is undesirable. Moreover being a liquid mercury electrodes cannot mechanically withstand high solution flow velocity, rotation or vibration required to achieve high mass transfer and low detection limits. Furthermore it is difficult to design and incorporate a liquid type electrode into a on-line continuous monitoring system, although it has been tried²²¹. In addition, because mercury is volatile, highly toxic and

expensive, it is less attractive for routine uses. This is not to denigrate the importance of the DME. Indeed, the DME has maintained a high profile owing to its main advantage of a continuously renewable surface which is relatively free of adsorption of species and therefore is highly reproducible in performance. This and its recent developments have been reviewed by Bond.²²²

Solid Electrode Materials

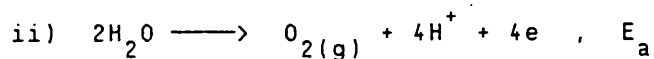
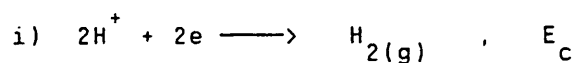
A host of solid electrode materials is available for use in voltammetry.^{220,223,224} They fall into three broad classes : (a) the elemental metals; (b) conducting carbon based materials; (c) and semiconductor materials. For class (a), while many of the metals have been used,²¹² more commonly used are the noble metals such as platinum, gold, rhodium, and silver. Class (b) includes; glassy carbon, graphite, pyrolytic graphite vitreous carbon, carbon paste, carbon fibre,²⁰⁶ boron carbide and most recently reticulated vitreous carbon.²²⁵ Class (c) materials are high resistance solids and are not widely used. They will not be discussed further. Earlier studies and uses of class (a) and (b) materials than 1969 have been reviewed by Meites²²⁰ and more extensively by Adams.²²³ A comparative study of their potential ranges has been done by Alder et al.²²⁴ Hampton and Larkin²²⁶ have done a comparative study of the capacitive currents of different materials with mercury. It suffices here to give just a summary of this and a review of the more recent work.

The main problems encountered in voltammetry at solid

electrodes are adsorption and charging current. Solid electrodes are surface active owing to coulombic and specific forces present on them. They therefore adsorb from solution species that may be the electroactive species of interest; a product of the electrochemical reaction; or a neutral species from solution. The magnitude of this activity varies with the nature of solid electrode material used, the surface concentration of the adsorbate and the potential of the WE.^{227,228} It leads to a decrease of the useful surface area of the WE, a generation of undesirable background currents when these species themselves undergo electrochemical reactions hence leads to poor sensitivity and reproducibility of performance. The extreme effect can be complete passivation of the WE or catalysation of the reaction of interest.^{227,228} To achieve reliable results therefore care in renewing electrode surface and in extending adsorbable species must be exercised. This is inconvenient, tedious and can change the character and geometry of the WE surface.

Another limitation, when sensitivity is the priority, is that the diffusion layer capacitive currents on solids electrodes is high compared to mercury hence poor sensitivity results.

A further problem is that of the useful potential range required in aqueous solutions. This is defined in terms of two background reactions that can generate reaction currents depending on operating conditions : i) the reduction of hydrogen ions at cathodic potentials, E_c , that liberates hydrogen gas; and ii) the oxidation of water at anodic potentials, E_a , that liberates oxygen.



The potentials E_{c} and E_{a} can be obtained from the Nernst equation and are²²⁴:

$$E_{\text{c}} = -0.059 \text{ pH} \quad 2.11$$

$$E_{\text{a}} = 1.23 - 0.059 \text{ pH} \quad 2.12$$

where pH is the pH of the aqueous solution. A plot of these equations for a given material gives the useful potential range for the material as the region bounded between the two lines. For some materials the experimental range differs from the theoretical one when the material exhibits activation over potential.

Useful potential ranges have been established for widely used materials and the review by Adams²²⁴ gives adequate details except for the more recent materials many of which are covered by Hampton and Larkin.²²⁶ The elemental metals generally have a lower cathodic range than mercury but a much higher anodic range and in all a useful range of the order of 1V. The carbon based materials have a wider range in both anodic and cathodic directions with a useful range of the order of 2V.

The materials that have been most widely used in fabrication of electrodes for hydrodynamic voltammetry are : for class (a) materials, Platinum; and for class (b), glassy carbon.

Platinum

Much of the published work on the studies, applications and nature of this material has been reviewed extensively by Adams²²⁴

and will only be mentioned here.

Platinum has a useful potential range of 1.1V (vs SCE) in hydrochloric acid (0.1M) for anodic processes and -0.91V in sodium hydroxide (0.1M) for cathodic processes. The anodic value is higher than predicted by equation 2.12 owing to an overpotential for hydrogen and hence has a small cathodic range where its use beyond -0.3V in acid solution is not reliable. The DME can be used at potentials more negative than -2.0V depending on electrolyte. At potentials close to hydrogen evolution it adsorbs hydrogen at two distinct potentials corresponding to strongly bound and weakly bound atoms. When the electrode potential is changed to between 0 and 0.5V the adsorbed hydrogen undergoes oxidation giving rise to residual current. Apart from the hydrogen oxidation, bright platinum surface itself undergoes oxidation at this potential range to an oxide if an anodic potential scan is done. If a cathodic scan is then done the oxide layer undergoes dissolution at 0.0V giving rise to residual current. A bright platinum surface also adsorbs halide ions, hydrogen and oxygen molecules.

The more recent studies of platinum have been to establish the nature of the species formed, the mechanism of its formation and the interactions between different species. Thacker and Hoare^{229,230} demonstrated the presence of adsorbed oxygen on platinum and other noble metals and further demonstrated the passivation of bright platinum²³⁰ due to this adsorption. Novak and Conway²³¹ demonstrated that halide ion adsorption competes with oxide formation on platinum and that chloride ions block the

formation of surface oxide.²³² Chialvo et al.²³³ established that repeated anodic formation and cathodic dissolution of the surface oxide changes the morphology of the platinum surface. Sakamoto and Takamura²³⁴ have shown that some metallic ad-atoms e.g. lead on noble metals carry out electrocatalysis of anodic reactions of some organic compounds such as amines. This indicates potential applications in electrocatalysis similar to application of the important catalytic behaviour of the oxide layer²³⁵ that has found use in anodic detection of alcohols, carbohydrates and other organic compounds.²³⁶

Despite its surface activity and low potential useful range, platinum has continued to be used for fabrication of electrodes mainly for electrode kinetic and mass transfer studies. It has been used in different geometries such as the rotating disc,²³⁷⁻²³⁸ rotating ring disc,²³⁹⁻²⁴³ conical,¹⁹¹ spherical,²⁰⁵ tubular²⁴⁴⁻²⁴⁵ and wire²⁴⁶ electrodes. It can be turned to any geometry.

Glassy Carbon

This is a mechanically hard and gas impermeable form of electrically conducting carbon.²⁴⁷ It is formed when polymers are pyrolysed directly into a form of carbon which retains the original morphology without passing through a plastic phase. From x-ray studies it is deduced²⁴⁸ that glassy carbon has a network structure consisting of tangled aromatic ribbon molecules which are cross-linked by highly strained C-C covalent bonds with a wide spectrum of bond energies. As an electrode material for voltammetry²⁴⁹ it has a useful potential range of 1.2V to 1.6V in basic media and is

usable in both aqueous and non aqueous media. Like other solid electrode materials glassy carbon has a high double layer capacitive current. In sulphuric acid (1M) at 1V min^{-1} potential scan rate this is $210\mu\text{F cm}^{-2}$ ²⁵⁰. There is presence of active specific sites on its surface ²⁵⁰ which in aqueous media have a high activity in chemisorption of oxygen ²⁵⁰ and reducing it in solution ²⁵¹⁻²⁵³ depending on the pH and potential. These sites have been shown ²⁵⁴ to be a variety of oxide containing functional groups such as quinone, lactone, cyclic anhydride, carbonium groups, chromate and phenol which are formed when the material is exposed to oxidising conditions such as exposure to atomic oxygen, chromic acid and other oxidising agents. These functional groups are present in other forms of carbon electrode materials as well.

Glassy carbon is the most likely material chosen for electrodes that are used in analysis since the noble metals have a finite stability in mercury and this is often deposited as a film on solid electrodes to improve their reproducibility and cathodic potential range. It has overshadowed its group members : carbon paste being soft is inconvenient to use; wax impregnated graphite has a short life in acid media; and pyrolytic graphite is porous and cannot be polished to renew the surface.

Glassy carbon has been used in geometries such as rotating ring disc ²⁵³⁻²⁵⁷ which has found application in analysis of sea water ²⁵⁸; and it is most widely used in the wall jet ²⁵⁹ geometry.

Reticulated Vitreous Carbon (RVC)

This is the most recent addition to the carbon based solid electrode materials. It is made by controlled degradation, in an inert atmosphere, of cross-linked polymers of the phenol-aldehyde types, and was developed by Chemotronics International, Ann-Arbor (Michigan) in 1976. It is presently manufactured by Fluorocarbon Co. (California). By their description, RVC is an open pore (honey comb) structure which is 90-97% void depending on its porosity grade and with high surface to volume ratio, see Plate 1. The highest grade has $65 \text{ cm}^2 \text{ cm}^{-3}$ ratio.

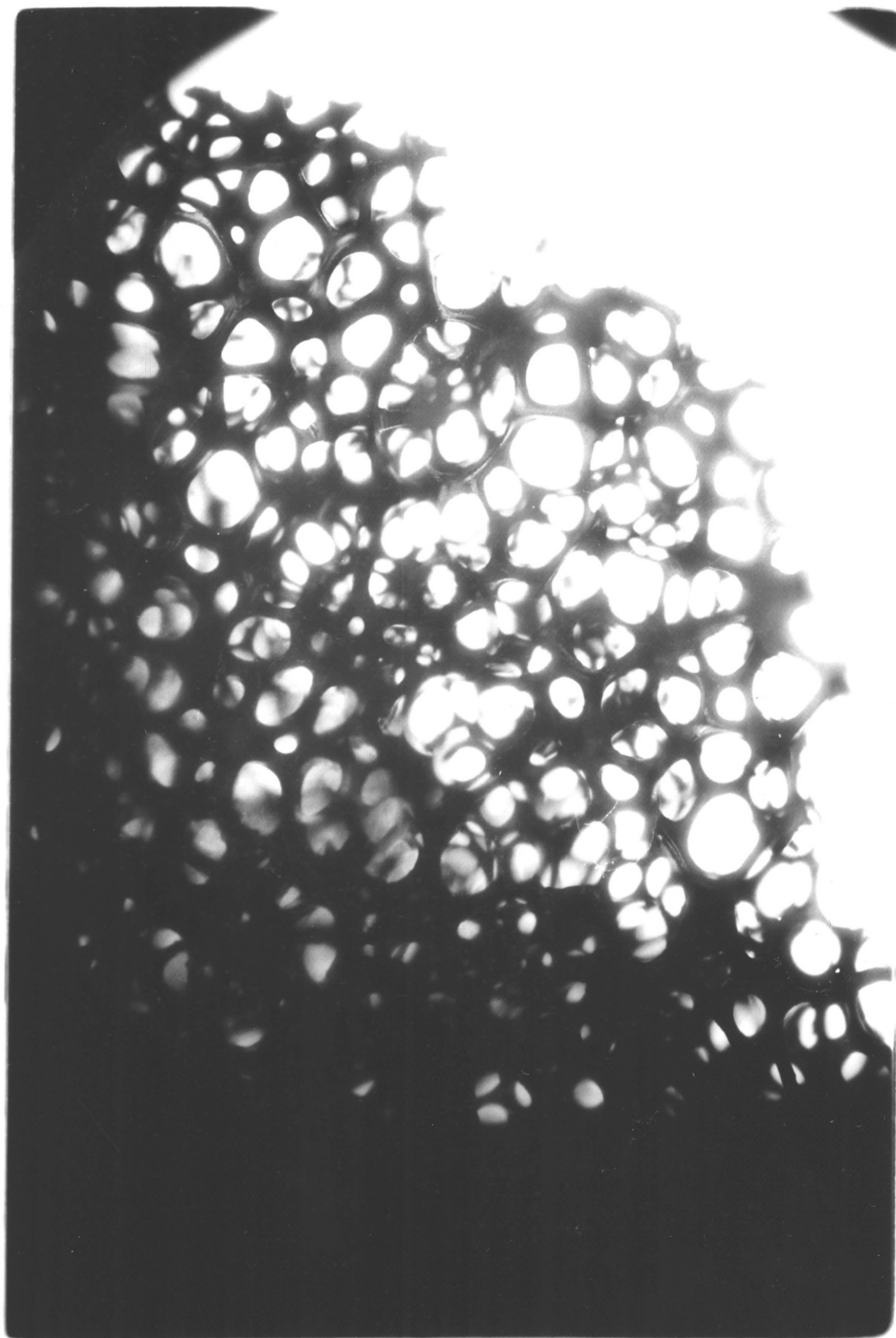
Early experience of its use in voltammetry²⁶⁰⁻²⁶² indicated that it has low resistance to fluid flow, is chemically inert, has a wide useful potential range and has, relative to other solid electrodes, reproducible performance. For a list of data on its physical properties reference²⁵⁷ is most complete.

Thorough information on electrode history, pretreatment and activity of its surface is not yet available. However it has been observed that RVC increases its sensitivity as much as 150% of its original value as it ages²⁶³ and that its background current rises with its age and levels off at an undesirably high value leading to electrode failure within two weeks of use.²⁶⁴

It has been used with success for on-line flow through analysis,^{256,265-270} and for flow injection in liquid chromatography.²⁷¹⁻²⁷³ It has been used as a tubular,²⁷⁴⁻²⁷⁵ rotating disc²⁶⁰ and wall jet electrode²⁶⁷.

Plate I : The Microporous Nature of RVC.

45 mm Represent 100 μm .



Because of its large surface area it was chosen for one of the cells fabricated in this work for preconcentration.

Cell Design Considerations

General Objective

In electrochemical preconcentration for ICP-AES, the main objective in cell design is to produce cells capable of preconcentration within the desired operating conditions compatible with both the ICP-AES and ASV. The main controlling requirement is imposed by the ICP-AES namely that not more than 3 g min^{-1} of water be introduced into the plasma at any given moment since this extinguishes the plasma. This condition requires that solution flow rates through the cell at the time of stripping into the ICP-AES are kept below $167 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ depending on the operating radio frequency forward power of the ICP-AES and the efficiency of the nebulisation of the sample. Furthermore it is the deposit on the WE that is of interest when it is redissolved. The concentration should be maximised as much as possible hence stripping into a small volume of solution is important.

WE Geometry

The aim here is to select a geometry that permits flow-through capability and yet have the highest possible current flow rate ($i_L \propto v^x$) relation in order to achieve high mass transfer rates. As in table 2, the index x of the flowrate is either $1/3$, $1/2$ or $3/4$. The higher it is the higher the mass transfer. However, the solution flow must remain laminar within the acceptable flowrate of the system. It is easy to generate turbulence in some geometries such

as the wall jet hence one has to resort to a lower index.

For a preconcentration cell the efficiency of electrolysis (equation 1.8) and the time taken to do it are important especially when the amount of sample available is small. The aim therefore is to achieve complete electrolysis of the flowing substrate from a single passage of the substrate solution. A step towards this is to minimise the volume, V , of the solution in the cell and maximise the area, A , of the WE such that the ratio V/A is small. However, the larger A is the more non-uniform the current distribution in the WE is likely to be. This is undesirable since the predictability of performance is decreased. Besides a large A leads to a large diffusion layer charging current and higher residual currents.

WE Material

As there are numerous available electrode materials the main considerations of choice are the useful potential range, reproducibility of performance, magnitude of residual currents, extent of useful life and how easy it is to work it into desirable shapes.

The choice for the useful potential range is done by deciding first which species the electrode is required to electroreduce and oxidise and in which media, then choose the material that covers the potentials at which these reactions occur within safe limit from oxygen and hydrogen evolution (equations 2.11 and 2.12). Many trace elements of interest in this work are electroreduced at

potentials of up to -1.2V (vs SCE). A material of wide cathodic range is therefore desirable. If the reactions of hydrocarbons were of interest then a material of wide anodic range would be the choice.

Since the surface phenomenae at the WE require that the surface be cleaned or renewed to achieve reproducibility the material chosen should be capable of effective pretreatment. If pretreatment is polishing then it is not a good idea to shape that material into a tube in which the active surface is the inner surface. Hence glassy carbon is rarely used in form of tubular electrodes. Materials that cannot stand up to chemical pretreatment by reducing or oxidising agents are not desirable either.

The compatability of the WE material with base electrolytes is important since a reaction between them can alter the physical character of the WE such as geometry, and surface activity leading to high residual currents or short useful life.

It is also important that the material chosen is easy to shape into the desirable geometries and maintain that geometry for all its useful life.

Electrode Placement

In this work only three electrode system is of concern in order to ensure that the problem of solution resistance which leads to a potential drop in the cell is minimised, and to provide

greater flexibility in the location of electrodes and ensure that virtually no current passes through the RE but only between the WE and the CE.

The main objectives are that the WE and the RE are placed as close as possible so that the potential drop (iR drop) between them is negligible; the RE must be placed out of the WE-CE current path so that the current flows through the most direct route. Because of the available flexibility of potentiostat control, the RE can be located such that any leaks of its electrolyte through the ceramic disc at its tip is well away from the WE and does not interfere with the purity of the substrate solution. The CE can also be located such that products from any reactions on it such as the production of oxygen gas do not interfere with the processes at the WE. One such interference is that the oxygen gas bubbles can sit at the WE-CE current path and stop current flow. The WE can also be placed in the path of solution flow so that a non uniform distribution of solution is avoided. This is important since careless WE placement can lead to non uniform reaction on the surface and consequently non uniform current and potential distribution. Furthermore, by symmetrical placement of the RE, CE and WE symmetrical potential control can be achieved and this avoids presence of potential gradients on the WE due to varying path lengths.

The Cell

The effect of a big cell volume is to increase the peak width due to signal spread and decreasing peak height due to dilution. What

is required is a sharp peak of big height. This can be achieved by reducing cell volume to the volume represented by the desired peak shape at the normal operating conditions. In addition a big cell volume requires availability of a big sample volume. This is not desirable in this work where the ability to analyse small samples is an advantage.

Other considerations on the cell are that it be demountable in order to facilitate cleaning, pretreatment and replacement of short lived parts; it is transparent so that the onset of the undesirable processes can be observed, for example, formation of gas bubbles; its internal surface be smooth to avoid easy generation of turbulence and trapping of impurities at the edges and that it should be adjustable so that the volume of the cell or position of the WE can be chosen to suit some particular experimental conditions. It is an advantage if the adjustment is calibrated. It is also important that the cell body be inert to all the chemicals it is likely to be exposed to in the place of use. Plexiglass has been most widely used for cell bodies and teflon "O" rings at the joints to prevent leaks.

CHAPTER 3.
THE CONCENTRIC CUP PLATINUM CELL.

3.1 The Cell

Figure 3.1a is a schematic diagram of this cell. The main aims of its design were : to increase the ability to electrolyse more substrate within convenient analysis time; to minimise dilution of the deposited amount when stripped in the cell; and to achieve electrolysis of flowing substrate from a single passage of the substrate solution past the working electrode surface.

The first aim was achieved by increasing the surface area to 0.31 cm^3 . The second aim by decreasing the effective cell volume into which the substrate is stripped and prevent it from mixing with the bulk solution. To do this the WE was placed into a concentric cup whose dimensions allowed an annulus of flowing solution less than 1mm thin between it and the WE probe. This had the advantage of increasing the velocity of the solution over the WE surface. The cup was positioned with its upper rim 1mm above the level of, and between the centres of, the CE and RE tips on one line and 2mm distant from either of them. The third was achieved by the tubular geometry of the cup and the WE probe. Figure 3.1C shows the overall solution-flow through the cell. The presence of the cup round the WE also means that reaction products at the CE do not directly interfere with the processes at the WE. Furthermore, any leakages of solutions from the WE compartment through the ceramic bridge do not mix with the substrate solution at the vicinity of the WE but are swept into waste flow.

The cell is constructed from plexiglass, is completely demountable and is leakproofed at joints with teflon rings. The RE

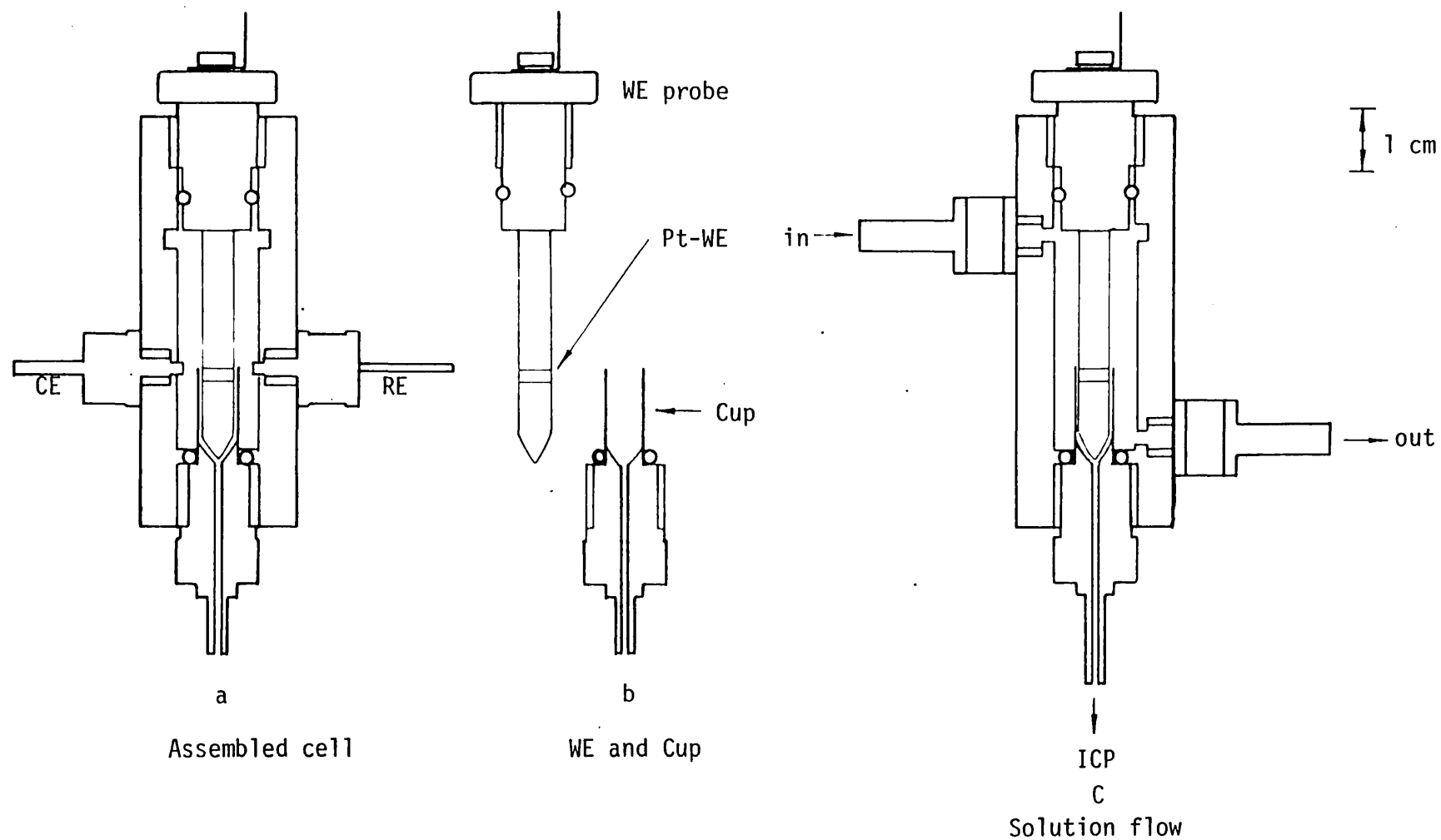


Figure 3.1 : The Concentric Cup Cell (Schematic)

is a silver-silver chloride (Ag/AgCl). The WE is a platinum cylinder of 5mm diameter and 2mm long pressed into an adjustable probe carrying an external current lead (Figure 3.1b).

3.2 Theory

Because of the peculiar design of this cell in which the WE is in a concentric cup with separation between them being 0.1mm, the geometry of the WE is considered to be fundamentally different from that of a tubular electrode. The flow past the WE parallel to it is more closely described as flow through a concentric annular passage between two circular cylinders, figure 3.2, rather than flow through a tube. The problem of mass transfer to the WE is then treated as that of mass transfer in annular passages with the limiting case on one hand being the problem of parallel plates and on the other that of a circular tube without an inner cylinder.

Electrodes involving an annulus have been used before in electrochemistry.²⁷⁶⁻²⁸⁰ However, there have been large discrepancies in results. Lin et al.²⁷⁶ using circular cylinders of radius ratio 0.5 fitted their results into an equation in which they assumed that the behaviour of mass transfer in an annulus is similar to that of a tube of equivalent diameter. But Friend and Metzner²⁷⁷ showed that mass transfer in an annulus cannot be represented by the same equations of flow in tubes by merely replacing the tube diameter with equivalent diameter of the annulus. Bazan and Arvia²⁷⁸ using a similar type electrode obtained by correlation an equation in which the limiting current-flowrate

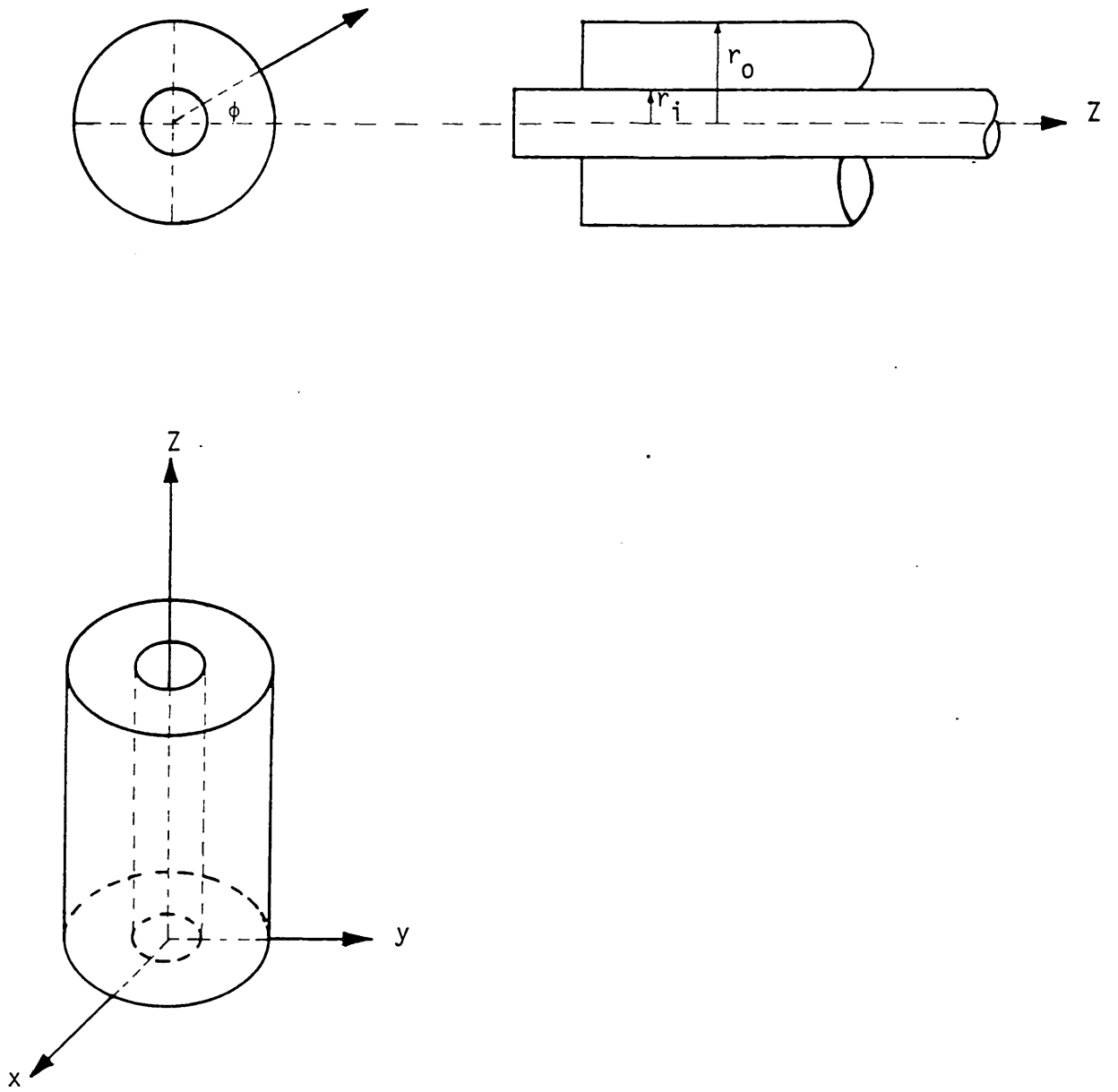


Figure 3.2 : The Co-ordinate System.

$$J = -D \frac{\partial c}{\partial x}$$

where x is the distance depending on the coordinates used. The resulting convective diffusion equation in cylindrical coordinates is :

$$\frac{\partial c}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left(rD \frac{\partial c}{\partial r} \right) + \frac{\partial}{\partial \phi} \left(\frac{D}{r} \frac{\partial c}{\partial \phi} \right) + \frac{\partial}{\partial z} \left(rD \frac{\partial c}{\partial z} \right) \right\} - \left\{ v_r \frac{\partial c}{\partial r} + \frac{v_\phi}{r} \frac{\partial c}{\partial \phi} + v_z \frac{\partial c}{\partial z} \right\} \quad 3.1$$

This equation is similar to that of a tube. Since there is circular symmetry about the z axis the variable c is independent of the angular coordinate ϕ . Hence

$$\frac{\partial}{\partial \phi} \left(\frac{D}{r} \frac{\partial c}{\partial \phi} \right) = 0$$

$$\frac{v_\phi}{r} \frac{\partial c}{\partial \phi} = 0$$

Far from the entry region of the annulus, for a fully developed flow, the diffusional flux has no z coordinate dependence. Hence

$$\frac{\partial}{\partial z} \left(rD \frac{\partial c}{\partial z} \right) = 0$$

It can also be assumed that radial convection is insignificant relative to axial convection. Hence

$$v_r \frac{\partial c}{\partial r} = 0$$

Equation 3.1 therefore reduces into :

$$\frac{\partial c}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left(rD \frac{\partial c}{\partial r} \right) \right\} - v_z \frac{\partial c}{\partial z} \quad 3.2$$

For steady state flow

$$\frac{\partial c}{\partial t} = 0$$

Hence equation 3.1 is further reduced into :

$$\frac{1}{r} \left\{ \frac{\partial}{\partial r} \left(rD \frac{\partial c}{\partial r} \right) \right\} = v_z \frac{\partial c}{\partial z}$$

or

$$\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} = \frac{v_z}{D} \frac{\partial c}{\partial z} \quad 3.3$$

3:2.2 The Velocity Profile

Using similar considerations as above but this time considering momentum in the differential control volume similar to that in figure 3.3, or from the Navier-Stokes equation 2.1, the z component of the solution momentum is :

$$\rho \left\{ \frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\phi}{r} \frac{\partial v_z}{\partial \phi} + v_z \frac{\partial v_z}{\partial z} \right\} = -g \frac{\partial p}{\partial z} + \mu \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \phi^2} + \frac{\partial^2 v_z}{\partial z^2} \right\} \quad 3.4$$

where ρ is the density of the solution, p is the static pressure, μ is the kinematic viscosity and g is the gravitational constant as in the previous case, v_ϕ and v_r can be set to zero and assuming no ϕ dependence,

$$\frac{\partial v_z}{\partial z} = 0, \quad \frac{\partial^2 v_z}{\partial z^2} = 0$$

Hence equation 3.4 simplifies into

$$\frac{\mu}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) = g \frac{\partial p}{\partial z} \quad 3.5$$

On integrating equation 3.5 twice with respect to r the result is :

$$v_z = \frac{g}{4\mu} \frac{dp}{dz} r^2 + C_1 \ln r + C_2 \quad 3.6$$

where C_1 and C_2 are constants of the integrations. At the walls the solution is stationary hence the boundary conditions

$$r = r_0, \quad v_z = 0$$

$$r = r_1, \quad v_z = 0$$

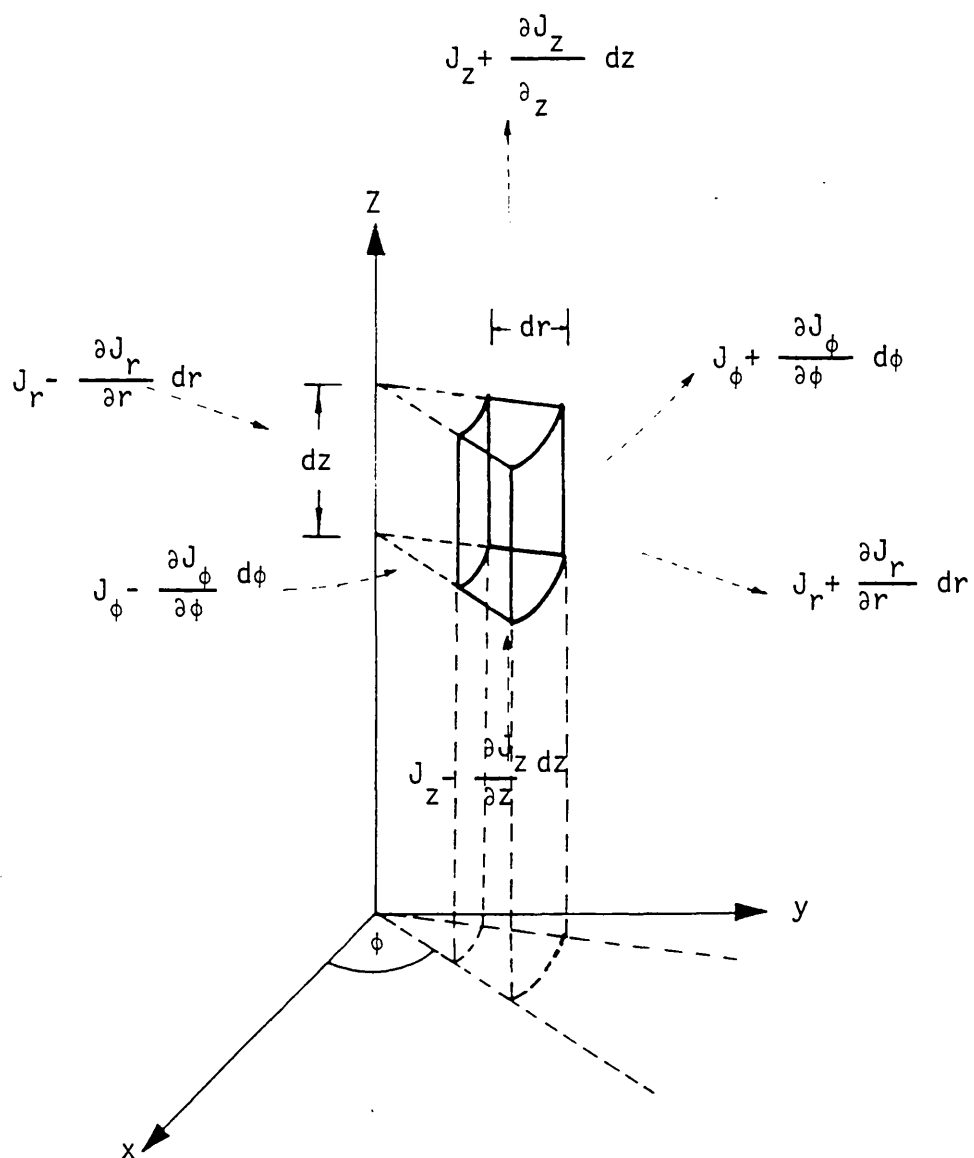


Figure 3.3 : The Differential Control Volume Element for the Concentric Cup Cell.

Using these in turn in 3.6 and solving simultaneously the resulting equations are :

$$C_1 = \frac{\frac{g}{4\mu} \frac{dp}{dz} (r_o^2 - r_i^2)}{\ln r_i / r_o} \quad 3.7$$

and

$$C_2 = \frac{g}{4\mu} \frac{dp}{dz} \left\{ r_o^2 - \frac{(r_o^2 - r_i^2)}{\ln r_i / r_o} \ln r_o \right\} \quad 3.8$$

Hence equation 3.6 becomes :

$$v_z = \frac{g}{4\mu} \frac{dp}{dz} \left\{ \left(\frac{r^2}{r_o^2} - 1 \right) - \frac{(r_i^2 / r_o^2 - 1)}{\ln r_i / r_o} \ln r / r_o \right\} \quad 3.9$$

If

$$r_i / r_o = \kappa$$

and

$$B = \frac{1 - \kappa^2}{\ln 1/\kappa}$$

Then 3.9 can be written in brief form as :

$$v_z = \frac{g}{4\mu} \left(-\frac{dp}{dz} \right) \left\{ 1 - \frac{r^2}{r_o^2} + B \ln r / r_o \right\} \quad 3.10$$

or

$$v_z = \frac{g}{4\mu} \left(-\frac{dp}{dz} \right) (1 - \bar{r}^2 + B \ln \bar{r}) \text{ where } \bar{r} = \frac{r}{r_o}$$

It is convenient to express the velocity in terms of the mean velocity, v_m , rather than the pressure gradient. If m_f is the total mass flow rate through the annulus, then

$$m_f = \int_A v_z \rho \, dA \quad 3.11$$

Where A is the flow cross-section area of the annulus perpendicular to flow axis and dA is its differential increment. But

$$m_f = A v_m \rho \quad 3.12$$

hence substituting in equation 3.11

$$v_m = \frac{1}{A\rho} \int v_z \rho dA \quad 3.13$$

For axisymmetric flow in a circular cylindrical annulus

$$dA = 2\pi r dr$$

$$\text{therefore } A = 2\pi \int_{r_i}^{r_o} r dr = \pi(r_o^2 - r_i^2) \quad 3.14$$

and substituting for A in equation 3.13 results in

$$v_m = \frac{2}{r_o^2 - r_i^2} \int_{r_i}^{r_o} v_z r dr \quad 3.15$$

On substituting for v_z from 3.10 and evaluating the integral

$$v_m = \frac{g}{8\mu} \left(-\frac{dp}{dz} \right) (1 + \kappa^2 - B) \quad 3.16$$

Dividing equation 3.10 by equation 3.16 and making v_z the subject,

$$v_z = \frac{2v_m \left(1 - \frac{r^2}{r_o^2} + B \ln r/r_o \right)}{(1 + \kappa^2 - B)} \quad 3.17$$

or

$$v_z = \frac{2v_m}{M} \left(1 - \frac{r^2}{r_o^2} + B \ln r/r_o \right)$$

where

$$M = 1 + \kappa^2 - B = \frac{1 - \kappa^4}{1 - \kappa^2} - \frac{1 - \kappa^2}{\ln 1/\kappa} \quad 3.18$$

Equation 3.17 gives the velocity to be used when solving the differential equation 3.3

If maximum velocity, $v_{z(\max)}$, occurs at a point between the

two cylinders denoted by $r = \lambda r_0$ then the value of $v_{z(\max)}$ can be found by substituting λr_0 for r in equation 3.17 upon which

$$v_{z(\max)} = \frac{2v_m}{M} (1 - \lambda^2 + B \ln \lambda) \quad 3.19$$

Figure 3.4 shows the velocity distribution across an annular passage.

By multiplying equation 3.16 by the annular crosssectional area, $\pi(r_0^2 - r_i^2)$, the volume flowrate, v_f , of the solution is obtained :

$$v_f = \frac{\pi g}{8\mu} \left(-\frac{dp}{dz}\right) r_0^2 (1 - \kappa^2) (1 + \kappa^2 - B) \quad 3.20$$

Equations 3.20, 3.19, 3.17 and 3.16 are all different from the corresponding equations for flow in tubes.

3:2.3 The Geometrical Factor, ϕ .

The constants B and M which affect the flow characteristics and are functions of the fixed dimensions r_i and r_0 can be isolated in order to find out their effects at the two walls. This can be done from the change of velocity at the walls. If

this is expressed as the velocity derivative, $\frac{dv_z}{dr}$, then by differentiating equation 3.17 i.e.

$$v_z = \frac{2v_m}{M} \left(1 - \frac{r^2}{r_0^2} + B \ln r/r_0 \right)$$

$$\frac{dv_z}{dr} = \frac{2v_m}{M} \left(\frac{-2r}{r_0^2} + \frac{B}{r} \right) \quad 3.21$$

and at the inner wall, $r = r_i$, where $r_i = r_0 \kappa$ by definition,

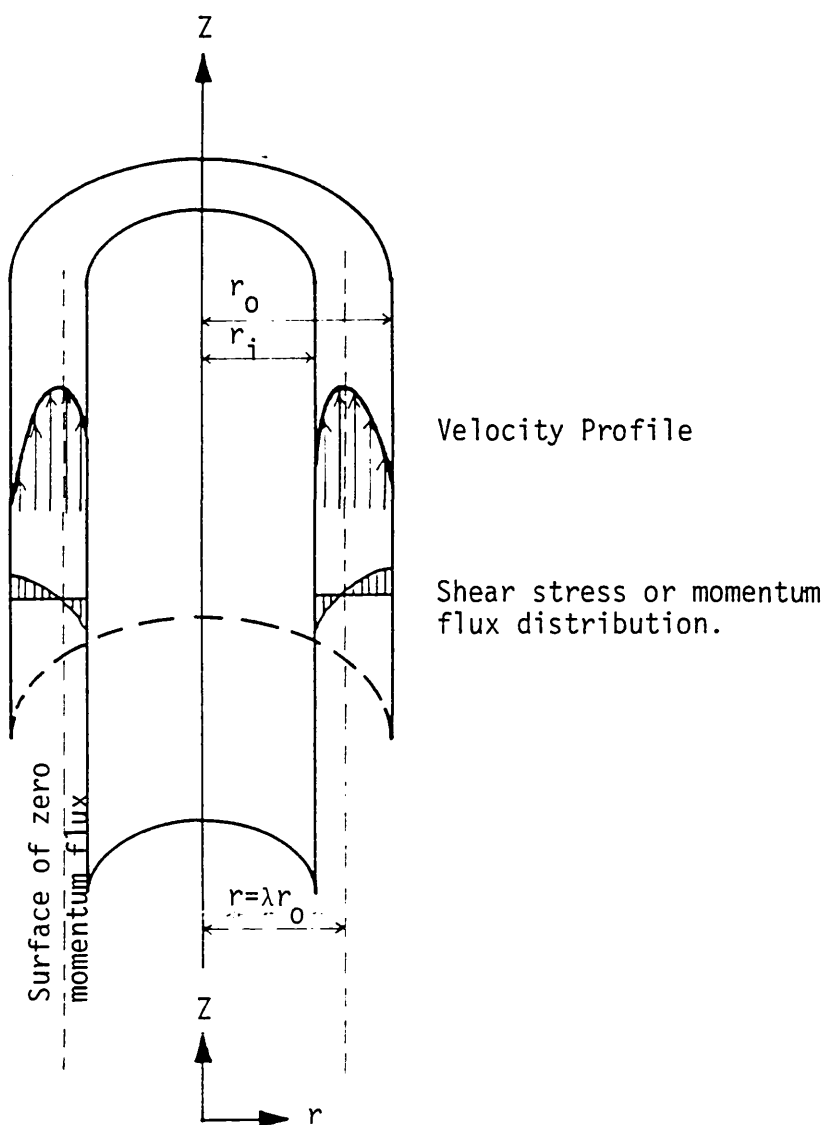


Figure 3.4 : Prevailing annular velocity profile for laminar flow.

$$\left(\frac{dv_z}{dr}\right)_{r=r_i} = \frac{2v_m}{r_o \kappa M} (-2\kappa^2 + B) \quad 3.22$$

From the equivalent diameter, de , (in heat transfer referred to as the hydraulic diameter, D_h , defined as

$$de = 2(r_o - r_i) = 2(1 - \kappa r_o) \quad 3.23$$

$$r_o = \frac{de}{2(1 - \kappa)} \quad 3.24$$

Hence substituting for r_o , B and M in equation 3.22 and simplifying,

$$\left(\frac{dv_z}{dr}\right)_{r=r_i} = \frac{8v_m}{de} \cdot \frac{\kappa-1}{2\kappa} \cdot \left\{ \frac{1-\kappa^2 - 2\kappa^2 \ln 1/\kappa}{1-\kappa^2 - (1+\kappa^2) \ln 1/\kappa} \right\} \quad 3.25$$

Let

$$\phi_i = \frac{\kappa-1}{2\kappa} \cdot \left\{ \frac{1-\kappa^2 - 2\kappa^2 \ln 1/\kappa}{1-\kappa^2 - (1+\kappa^2) \ln 1/\kappa} \right\} \quad 3.26$$

then ϕ_i is a function of the geometry of the annulus only and

$$\left(\frac{dv_z}{dr}\right)_{r=r_i} = \frac{8v_m \phi_i}{de} \quad 3.27$$

Similarly

$$\phi_o = \frac{1-\kappa}{2} \cdot \left\{ \frac{1-\kappa^2 - 2 \ln 1/\kappa}{1-\kappa^2 - (1+\kappa^2) \ln 1/\kappa} \right\} \quad 3.28$$

A plot of $\phi^{1/3}$ against κ for an annular passage, figure 3.5, shows the effect of geometry on the flow character at both the inner and outer wall. The value $\kappa = 0$ corresponds to flow through a tube without an inner cylinder and $\kappa = 1$ corresponds to flow between two parallel plates. Furthermore $\phi \rightarrow 1$ for a tube and $\phi \rightarrow 1.50$ for parallel plates. Between these ends $\phi_i > 1.50$. It can therefore be seen from figure 3.5 that utilising the inner cylinder obtains the maximum effect from geometry.

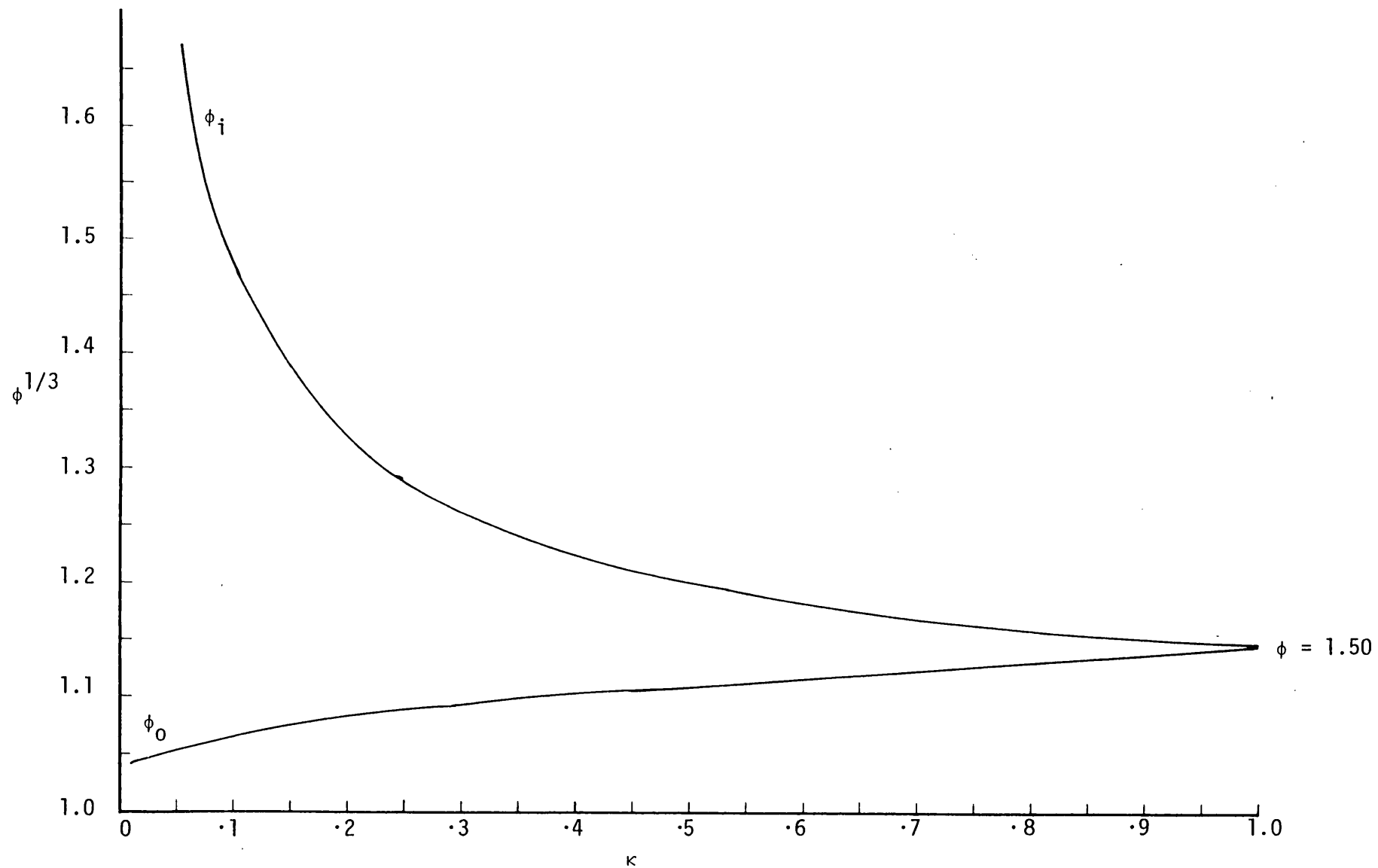


Figure 3.5 : Variation of the Geometric factor, ϕ , with radius ratio, κ .

3:2.4 Mathematical Solution

Equation 3.3 is the same for mass transport in a tube, annulus, and parallel plates except for the velocity, v_z , expressions. Its solution for the tube and parallel plates has been reviewed and described in detail by Brown²⁸⁹ who outlined a computer program to evaluate it. A more recent review with tabulation of solutions is given by Skelland.²⁹⁰ However the solution of the annulus between its limiting cases hasn't received corresponding treatment especially in electrochemistry.

For the annulus equation 3.3 can easily be expressed in dimensionless variables θ , $\bar{r}$, $\bar{z}$ and becomes :

$$\frac{\partial^2 \theta}{\partial \bar{r}^2} + \frac{1}{\bar{r}} \frac{\partial \theta}{\partial \bar{r}} = \frac{v_z(\bar{r})}{D} \frac{\partial \theta}{\partial \bar{z}} \quad 3.29$$

where θ is a dimensionless concentration variable

$$\text{given by } \theta = \frac{C_i - C}{C_i - C_B} \quad 3.30$$

in which C_i is the concentration at the wall ($r = r_i$), C is the concentration at any point r between the walls. C_B is the concentration at the bulk ($r = r_\infty$); $\bar{r}$ is a dimensionless radial distance given by

$$\bar{r} = \frac{r}{r_o} \text{ and lies between the walls } (\kappa < \bar{r} < 1);$$

$\bar{z}$ is a dimensionless axial distance given by

$$\bar{z} = \frac{zD}{de^2 v_m} = \frac{z/de}{Re.Sc} \quad 3.31$$

and Re , Sc are Reynolds and Schmidt numbers defined before (equations 2.3 and 2.4) respectively. $v_z(\bar{r})$ is the velocity profile as a function of $\bar{r}$ given by

$$v_z(\bar{r}) = \frac{2v}{M} \left(1 - \bar{r}^2 + B \ln \bar{r} \right) \text{ i.e. equation 3.10.}$$

The rest of the symbols are as defined before. Equation 3.29 is to be solved with the following assumptions :

- i) there is a fully developed profile with a constant concentration at the bulk that is invariant with length.
- ii) there is a uniform radial flux which is constant and there is zero concentration at the wall ($r = r_i$)
- iii) the solute concentration is low and its flux to the wall does not affect axial velocity.
- iv) the walls $r = r_i$ and $r = r_o$ are impermeable and there are no end effects,
- v) the solution is incompressible.

The boundary condition:

- i) initial condition;

Before commencement of diffusion which follows application of a potential, the substrate concentration throughout the solution is C_B , hence

$$\theta = 1 \text{ for all } \bar{z} \quad 3.32$$

- ii) Infinite distance condition;

The effect of applied potential is limited within the diffusion layer. Outside of this i.e. at $r = \infty$ the initial conditions prevail. Hence

$$C = C_B \text{ at } r \rightarrow \infty \text{ for all } \bar{z}$$

$$\text{and } \theta = 1 \quad \bar{r} = 1 \text{ for all } \bar{z} \quad 3.33$$

- iii) Surface condition, inner wall active;

At the inner wall, $r = r_i$, the diffusing species is destroyed. Hence

$$C = 0, \quad r = r_i \text{ for all } \bar{z}$$

$$\text{and } \theta = 0, \quad \bar{r} = \kappa \text{ for all } \bar{z} \quad 3.35$$

It is required to find the flux of substrate to the wall when
a) the inner wall is active and b) the outer wall is active.

By the method of separation of variables in which a solution of the type

$$\theta(\bar{r}, \bar{z}) = R(\bar{r}) \cdot Z(\bar{z}) \quad 3.36$$

is sought, where R is some function of $\bar{r}$ only and Z is a function of $\bar{z}$, it can be shown²⁹¹ that

$$Z = C \exp -\lambda_e^2 \bar{z} \quad 3.37$$

and

$$\frac{d^2 R}{d\bar{r}^2} + \frac{1}{\bar{r}} \frac{dR}{d\bar{r}} = -\lambda_e^2 v_2(\bar{r}) R \quad 3.38$$

where λ_e is a separation constant and C is an arbitrary constant. Equation 3.38 is a second order ordinary differential equation with a boundary problem of the Sturm-Liouville type for R . The Sturm-Liouville problem is extensively studied^{292,293,294} in mathematics. The function is continuous in the region $\kappa < \bar{r} < 1$ between the walls.

Substituting for $v_z(\bar{r})$ in equation 3.38,

$$\frac{d^2 R_n}{d\bar{r}^2} + \frac{1}{\bar{r}} \frac{dR_n}{d\bar{r}} + \lambda_{e_n}^2 \cdot \frac{2v_m}{M} (1 - \bar{r}^2 + B \ln \bar{r}) R_n = 0 \quad 3.39$$

where $\lambda_{e1}, \lambda_{e2}, \dots, \lambda_{en}$ are an infinite set of eigenvalues in increasing order for which R satisfies the boundary conditions

$\bar{r} = \kappa$, $\bar{r} = 1$ and $R_1, R_2, \dots, R_n$ are the corresponding values of R . It is first necessary to solve equation 3.39 in order to solve equation 3.29. This is done by numerical integration and the required eigenvalues are obtained by iterative method of Berry and de Prima.²⁹⁵

Using the values of Z obtained from equation 3.37 and R obtained from equation 3.36 the required solution is :

$$\theta(\bar{r}, \bar{z}) = \sum_{n=0}^{\infty} C_n \cdot R_n(\bar{r}) \cdot \exp(-\lambda_{en}^2 \cdot \bar{z}) \quad 3.40$$

where $C_1, C_2, \dots, C_n$ are coefficients of the series corresponding to the values of R .

By requiring equation 3.40 to satisfy the boundary condition 3.32 i.e. $\theta(\bar{r}, 0) = 1$ then it becomes :

$$1 = \sum_{n=0}^{\infty} C_n R_n(\bar{r}) \quad 3.41$$

Upon multiplying both sides of equation 3.41 by $\bar{r} R_n v_z(\bar{r})$, and integrating numerically between the region where the annulus exists, the coefficients of the series can be obtained :

$$C_n = \frac{\int_{\kappa}^1 \bar{r} R_n v_z(\bar{r}) d\bar{r}}{\int_{\kappa}^1 \bar{r} R_n^2 v_z(\bar{r}) d\bar{r}} \quad 3.42$$

The required flux of material to the wall at any value of $\bar{z}$ can be obtained from the slope of the concentration profile at the wall expressed by equation 3.40. The solution is

$$\phi_i = 2.2396 (1-\kappa) \left[\frac{B/\kappa - 2\kappa}{18(1-\kappa)^2 M} \right]^{1/3} (\bar{z})^{-1/3} \quad 3.43$$

$$\phi_o = -2.2396 (1-\kappa) \left[\frac{B-2}{18(1-\kappa)^2 M} \right]^{1/3} (\bar{z})^{-1/3} \quad 3.44$$

where ϕ is the dimensionless flux to the wall :

$$\phi_i = -2(1-\kappa) \left\{ \frac{\partial \theta}{\partial \bar{r}} \right\}_{\bar{r} = \kappa}$$

$$\phi_o = 2(1-\kappa) \left\{ \frac{\partial \theta}{\partial \bar{r}} \right\}_{\bar{r} = 1}$$

The negative sign is used to indicate that the flux to the inner wall is opposite to that of the outer wall. Rewriting in terms of the geometric factor, ϕ , equations 3.43 and 3.44 become respectively

$$\phi_i = 1.0767 \phi_i^{1/3} (\bar{z})^{-1/3} \quad 3.45$$

and

$$\phi_o = 1.0767 \phi_o^{1/3} (\bar{z})^{-1/3} \quad 3.46$$

yielding the general equation

$$\phi = 1.0767 \phi^{1/3} (\bar{z})^{-1/3} \quad 3.47$$

$$\text{since } Sh = \frac{Jde}{(C_e - C_B)D} \quad \text{and} \quad \bar{z} = \frac{z/de}{Re \cdot Sc}$$

where de , the equivalent diameter, is the characteristic length, equation 3.47 becomes :

$$Sh = 1.0767 \left[\frac{\phi \cdot Re \cdot Sc \cdot de}{z} \right]^{1/3} = \frac{J \cdot de}{C_B D} \quad 3.48$$

On substituting for Re , Se , de and rearranging,

$$J = 0.8546 DC_B \left[\frac{\phi \cdot v_m}{(1-\kappa) r_o z D} \right]^{1/3} \quad 3.49$$

since $i_L = nFJ$ (equation 2.7), equation 3.49 becomes :

$$i_L = 0.8546 n FDC_B \left[\frac{\phi v_m}{(1-\kappa) r_o z D} \right]^{1/3} \quad 3.50$$

where z is the axial length of the WE denoted by L or X for other geometries in literature (Table 2)

It is convenient to express v_m in terms of the solution volume flowrate, v_f , since it is easier to measure the latter experimentally. This can be achieved by dividing equation 3.16 by equation 3.20 upon which

$$v_m = \frac{v_f}{\pi r_o^2 (1-\kappa^2)} \quad 3.51$$

and equation 3.50 then becomes

$$i_L = 0.5835 n FDC_B \left[\frac{\phi v_f}{r_o^3 (1-\kappa^2) (1-\kappa) z D} \right]^{1/3} \quad 3.52$$

This, or 3.50, is the equation against which the behaviour of the concentric cup cell is tested.

3.3 Experimental Section

3.3.1 Instrumentation and Reagents

The solution flow control was achieved using a peristaltic pump of variable flowrate type Pharmacia P-3. The solution flowed through silicon rubber tubing of internal diameter 2.1mm from sample container to the cell. Calibration of this flow system for solution volume flow rate was done by setting the pump to a desired scale and weighing the solution collected over a known length of

time from which v_f was calculated. This was done using KCl (0.1M). A plot of weight of solution against setting on the scale was made.

For potential control of the cell the Princeton Applied Research Corporation potentiostat type PAR 174 was used and signals recorded on the Bryans x-t recorder type 27000 for anodic stripping experiments or the Bryans x-y recorder type 29000 A4 for cyclic voltammetry. The potentiostat-chart recorder arrangement was calibrated by measuring the resistance of each current range setting of the PAR 174 with a Fluke model 8010A high accuracy (0.03%) multimeter when the PAR was set to dummy cell and a circuit of known resistance and potential. The current corresponding to the chart-recorder trace obtained from each current range setting was calculated from the known potential and resistance using Ohm's law. Table 3.1 shows full scale deflection currents for the Bryan's 27000 x-t chart recorder for the shown current range settings on the potentiostat.

Potentiostat	Chart Recorder	Scale	Current
Current range	Trace full scale	Resistance	
(mA)	(mV)	(M Ω)	($\text{A} \times 10^{-7}$)
10	60	0.21	2.70
5	115	0.41	2.67
2	300	1.07	2.67
1	600	2.12	2.69
0.5	1200	4.24	2.74
0.2	2550	10.43	2.74

Table 3.1 : Potentiostat - Chart recorder Calibration.

All reagents used were BDH "AnalaR" grade except for the base electrolyte KCl which was BDH "aristar" grade. They were used without further purification. All solutions were made using milli Q water^{296,297} of resistance 18M Ohms and stored in plastic bottles cleaned over a period of 4 weeks. The cleaning¹ involved filling the bottles with 1:1 mixture of water and HCl (36%), allowing to stand for one week at room temperature, emptying, and rinsing with water. They were then filled with a 1:1 mixture of water and nitric acid and allowed to stand for a further week before emptying and rinsing with milli Q water. After filling with milli Q water and allowing to stand for a further two weeks the bottles were emptied, rinsed with fresh milli Q water and were ready for use.

3:3.2 The Reference Electrode

The procedure of preparation of this electrode is mainly from Janz and Taniguchi.²⁹⁹

The silver wire of diameter 1mm was polished with a 0.3 μ slurry of alumina and washed under a stream of milli Q water. The silver chloride layer was deposited on it electrolytically from dilute HCl (0.1M) using 2 μ A cm⁻² current density for 30 hrs in darkness. The other electrode was a platinum wire of similar dimensions. The silver wire with the silver chloride deposit was then washed with water again and stood in KCl (1.0M) overnight in darkness. It was washed once more with water, rinsed with the electrolyte and fixed in position in the cell containing the electrolyte KCl (1.0M) in the reference cell compartment. The electrode is then referred to as Ag/AgCl (1.0M) and has the

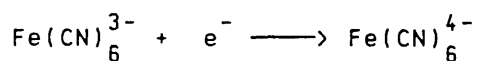
potential -0.222V measured against the standard hydrogen Electrode. The reference cell was replaced each day with fresh electrolyte before starting experiments.

3:3.3 The WE Pretreatment

As discussed in section 2.3, to minimise surface effects and achieve reproducibility, the platinum electrode was subjected to polishing with a slurry of 1µm alumina on cotton wool. The same procedure was repeated using 0.3 µm alumina and continued until the electrode was bright and shiny. It was rinsed with milli Q water and stood in a 1:1 mixture of chromic and sulphuric (98%) acids. After 3 minutes it was washed under a stream of milli Q water and fixed into place in the cell filled with KCl (0.1M) already purged with argon gas. It was then cyclised 5 times at scan rate 20 mV s⁻¹ between 0.05V and -1.1V (vs Ag/AgCl (1.0M)) prior to sample introduction. This procedure was carried out before each experiment.

3:3.4 Test of the Concentric Cup Cell

This was done using the reversible electron transfer reaction



in the base electrolyte KCl (0.5M) A 1.0M stock solution of the base electrolyte was made by dissolving 74.55g of KCl (aristar) in milli Q water and made up to mark in a 1L standard flask. 5L of this stock solution was made this way and stored for all experiments. The reactants for the above reaction were a 1:1 mixture of K₄Fe(CN)₆ and K₃Fe(CN)₆ of concentration 0.0004M in either species. A 0.1M stock solution of this mixture was made by dissolving 4.224g of K₄Fe(CN)₆·3H₂O and 3.293g of K₃Fe(CN)₆ in

water in a 100cm^3 flask and stored in darkness. 1cm^3 of this was diluted with 125cm^3 of KCl (1M) and made up to mark with milli Q water in a 250cm^3 standard flask. The resulting solution was 0.0004M in $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.5M in KCl. This was purged with argon for 20 minutes and pumped through electrochemical cell.

The operating conditions were :

Initial potential : 0.4V

Potential scan range : 1.5V

Potential scan rate : 5mVs^{-1}

Current range : 2mA

Solution volume flow rate : $0.05\text{cm}^3\text{s}^{-1}$

WE position : 0.2cm inside cup

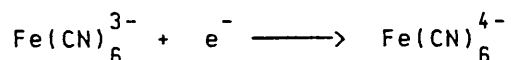
Cyclic voltammograms were obtained from which the potentials of the anodic and cathodic peaks were read, converted to SHE and their average found.

The mean of these average potential was 0.380V with standard deviation 0.002 . This was compared with the reference value by Kolthoff³⁰⁰ under similar conditions viz 0.3754V . The two values are of reasonable agreement.

3:3.5 Dependence of Limiting Current on Solution Volume Flow Rate

Since the current, i_L , is proportional to the volume flow rate, v_f , raised to the power x , a plot of $\log i_L$ against $\log v_f$ gives x as the gradient.

The relation for the concentric cup cell was investigated using the reaction :



The reagent was $\text{K}_3\text{Fe(CN)}_6$ (0.0005M) in KCl (0.1M). A 0.1M stock solution of this was made by dissolving 32.926g of $\text{K}_3\text{Fe(CN)}_6$ in milli Q water in a 1000 cm^3 standard flask and made to mark. When required 5 cm^3 of this solution and 100 cm^3 of KCl (1.0M) were diluted with milli Q water in a 1000 cm^3 flask. The resulting solution was 0.0005M in Fe(CN)_6^{3-} and 0.1M in KCl . This was purged with argon for 20 minutes and pumped through the cell at set flow rates between 17 and 170 $\mu\text{l s}^{-1}$ (1 and 10 mL per minute). Operating conditions were as above (section 3:3.4). Voltammograms were recorded from each flow rate and limiting currents measured from them. Figure 3.6 shows a typical $\log i_L / \log v_f$ plot for this cell. The mean gradient for 5 runs is 0.33 with standard deviation 0.02. The linear regression coefficients are better than 0.99.

3:3.6 Dependence of Limiting Current on WE position

The WE position is defined as the position of the central line across the WE, normal to the axial coordinate, and is measured in cm from the entrance to the cup (figure 3.7). The above experiment (section 3:3.5) was repeated for each position of the WE inside the concentric cup. Figure 3.8 shows the $\log i_L / \log v_f$ plots for the WE positions set. Individual points are omitted from the regression lines in order to avoid uncertainty due to scatter. Using two fixed flow rates and varying WE position the corresponding variation of i_L is shown in figure 3.9.

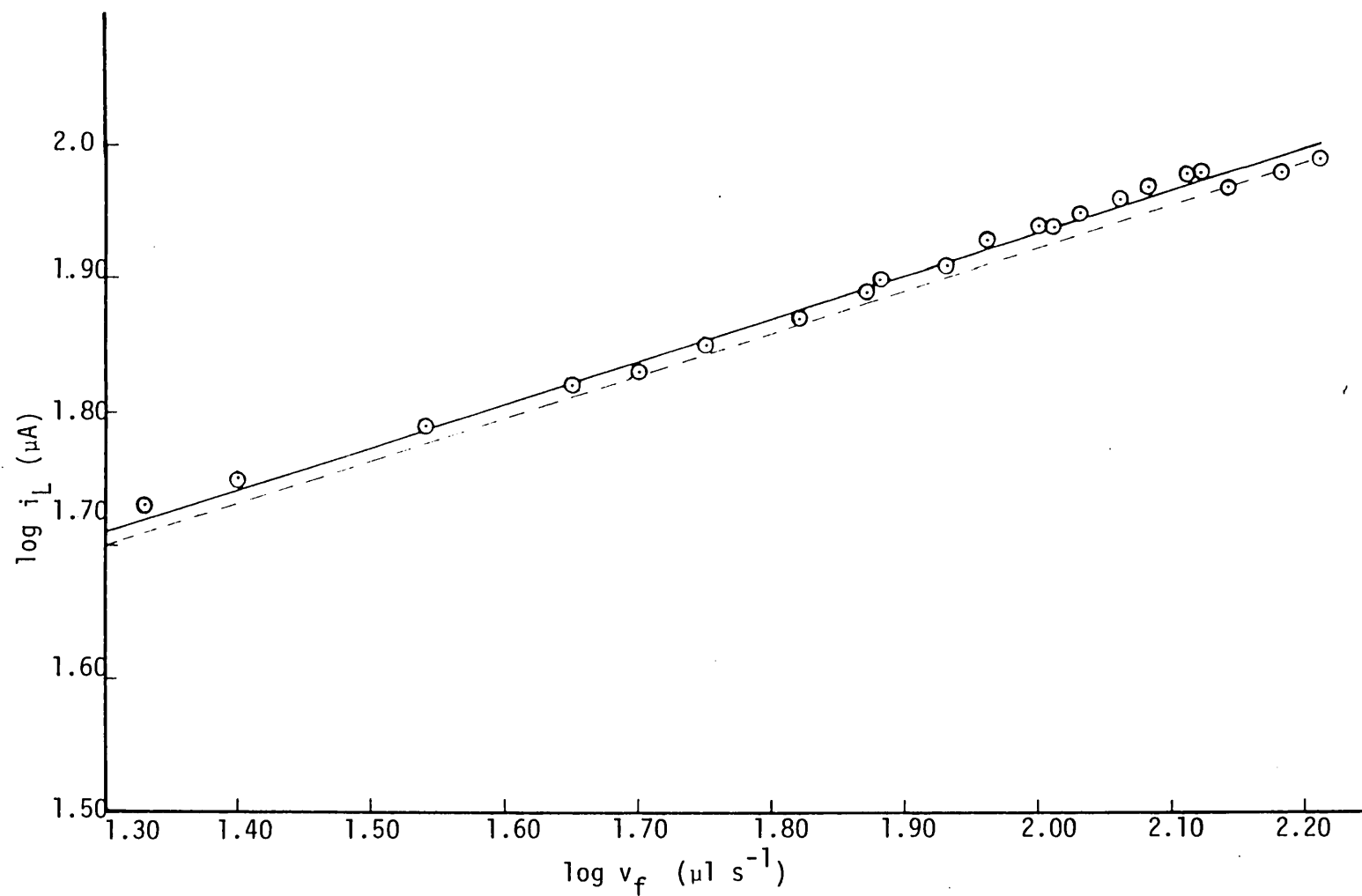


Figure 3.6 : Dependence of limiting current, I_L , on solution volume flow rate, v_f , for $K_3Fe(CN)_6$ (0.5mM) in KCl (0.5M) at WE position 0.2 cm. The dashed line is the theoretical curve.

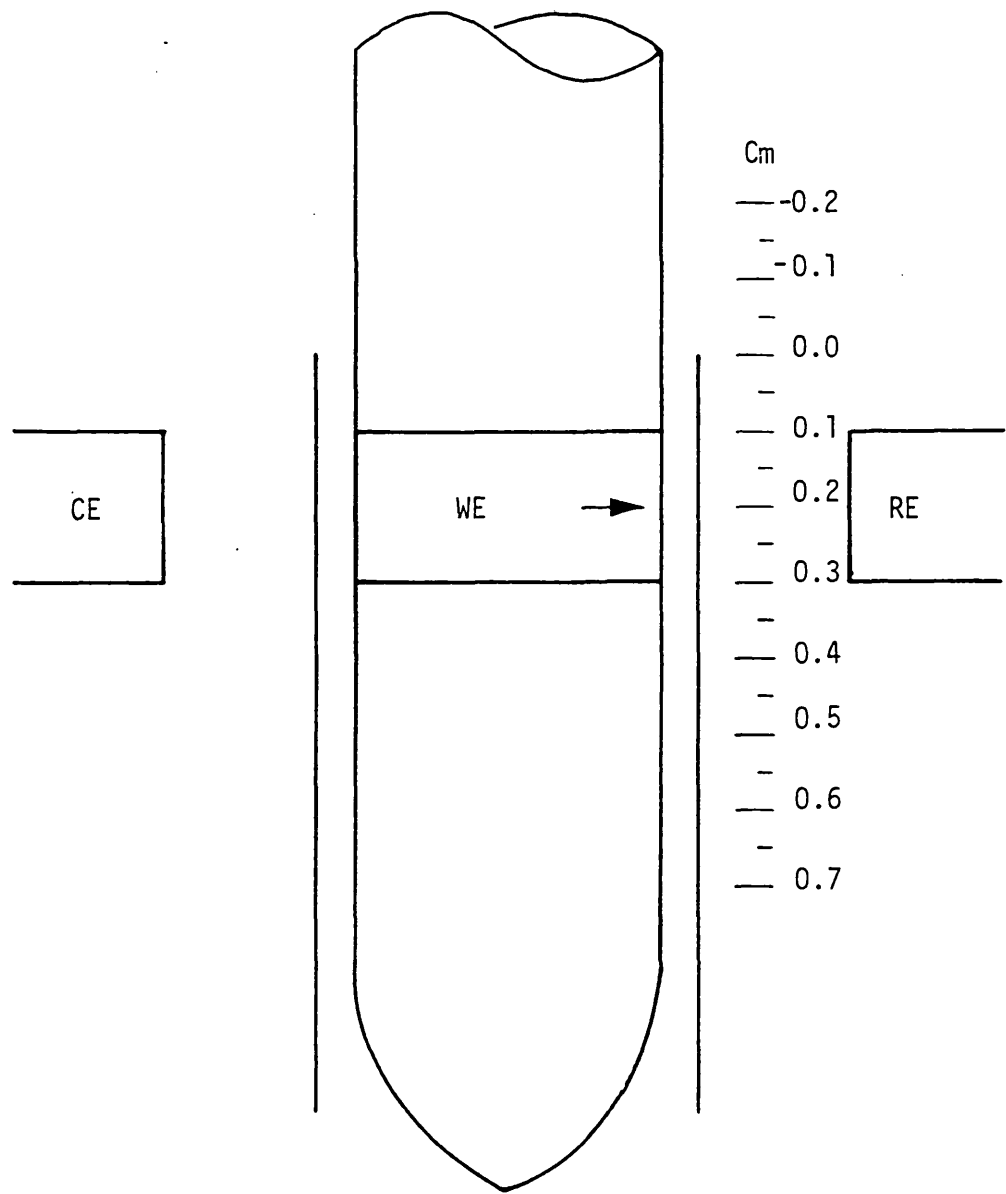


Figure 3.7 : Definition of WE position. Negative positions are outside the cup.

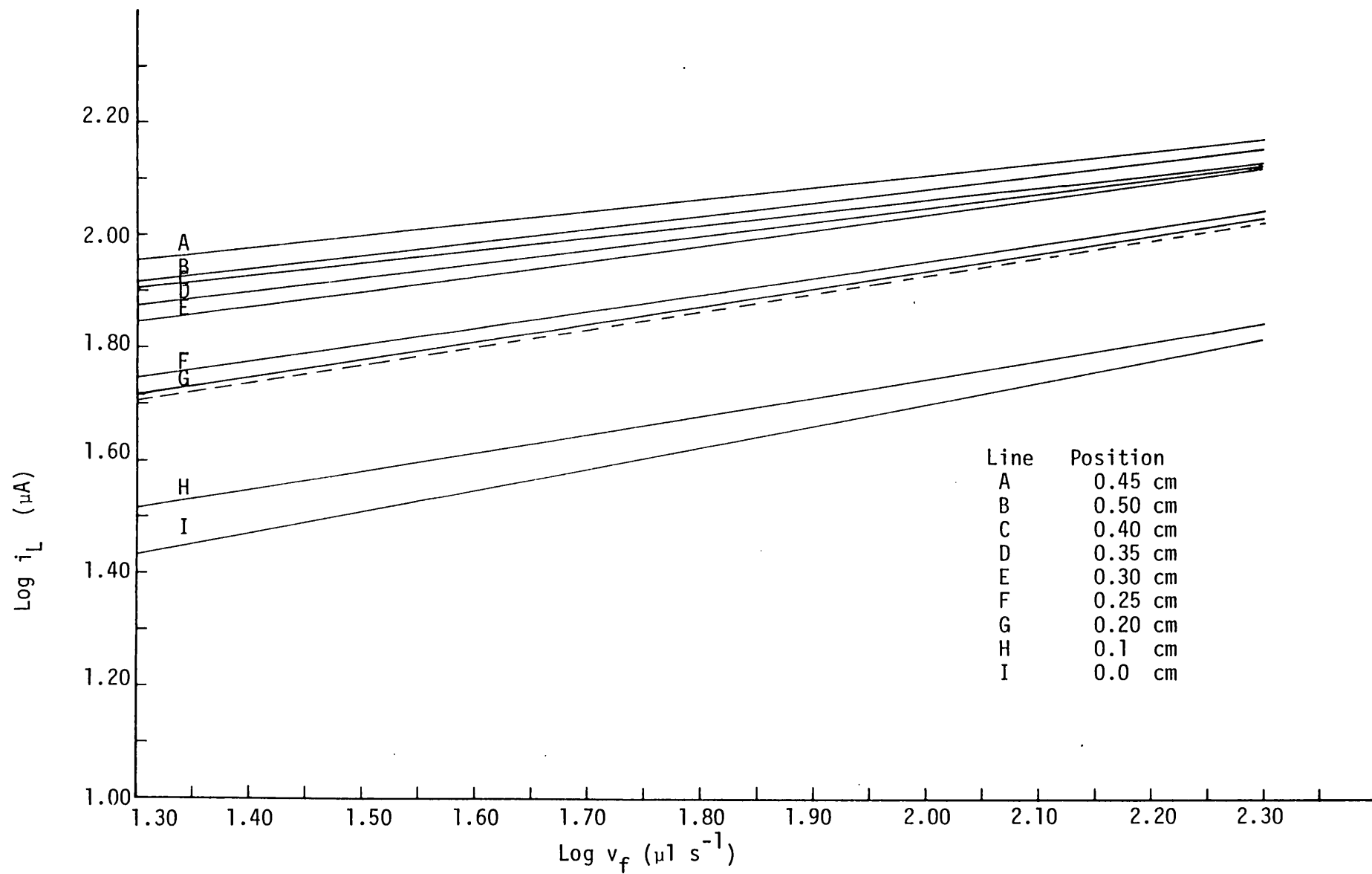


Figure 3.8 : Dependence of i_L on v_f at different WE positions for $K_6Fe(CN)_6$ (0.5 mM) in KCl (0.1 M).
The dashed line is the theoretical curve at WE position 0.2cm.

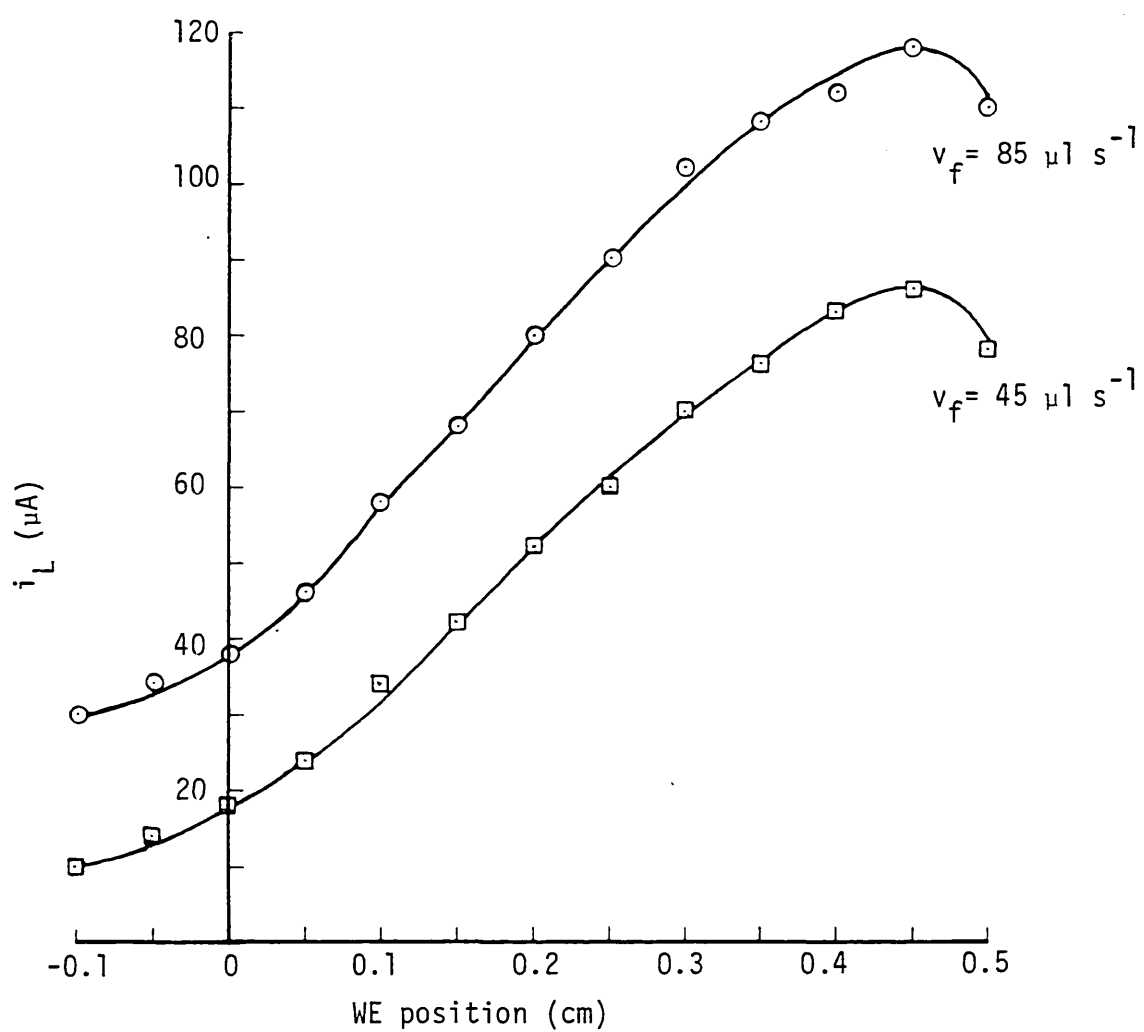


Figure 3,9 : Dependence of i_L on WE position at constant v_f for $\text{Fe}(\text{CN})_6^{3-}$ (0.5 mM) in KCl (0.1M)

3:3.7 (i) Volume Flow Rate Index Dependence on WE Position

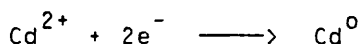
The gradients of the current vs flow rate lines (figures 3.8) were obtained and are tabulated in Table 3.10. These were plotted against WE positions see figure 3.8. This shows that the v_f index decreases gently as the WE is pushed further into the cup.

WE Position (cm)	Gradient	Correlation coefficient
0.50	0.21	0.96
0.45	0.28	0.97
0.40	0.25	0.98
0.35	0.28	0.99
0.30	0.28	0.98
0.25	0.35	0.99
0.20	0.33	0.99
0.10	0.41	1.00
0.00	0.37	0.99

Table 3.2 : Volume flowrate power at different WE positions.

3:3.8 (ii) Test with a Depositible Species

This was done using a reversible reaction



a $1000 \text{ } \mu\text{g}/\text{cm}^3$ stock solution of cadmium was made by dissolving 0.2032g of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ in milli Q water and made to mark in a 100 cm^3 standard flask. 3 cm^3 of this and 10 cm^3 of KCl (1.0M) were diluted to mark in a 100 cm^3 flask. The resulting solution was $267 \times 10^{-9} \text{ mol cm}^{-3}$ ($30 \text{ } \mu\text{g}/\text{cm}^3$) in cadmium and 0.1M in KCl. This was purged with argon and pumped through the cell as before. The solution flow rate was varied. $E_{1/2}$ was obtained from voltammograms. It was -0.855 V (vs Ag/AgCl (1M)). A typical cyclic voltammogram for cadmium is shown in figure 3.11. The stripping

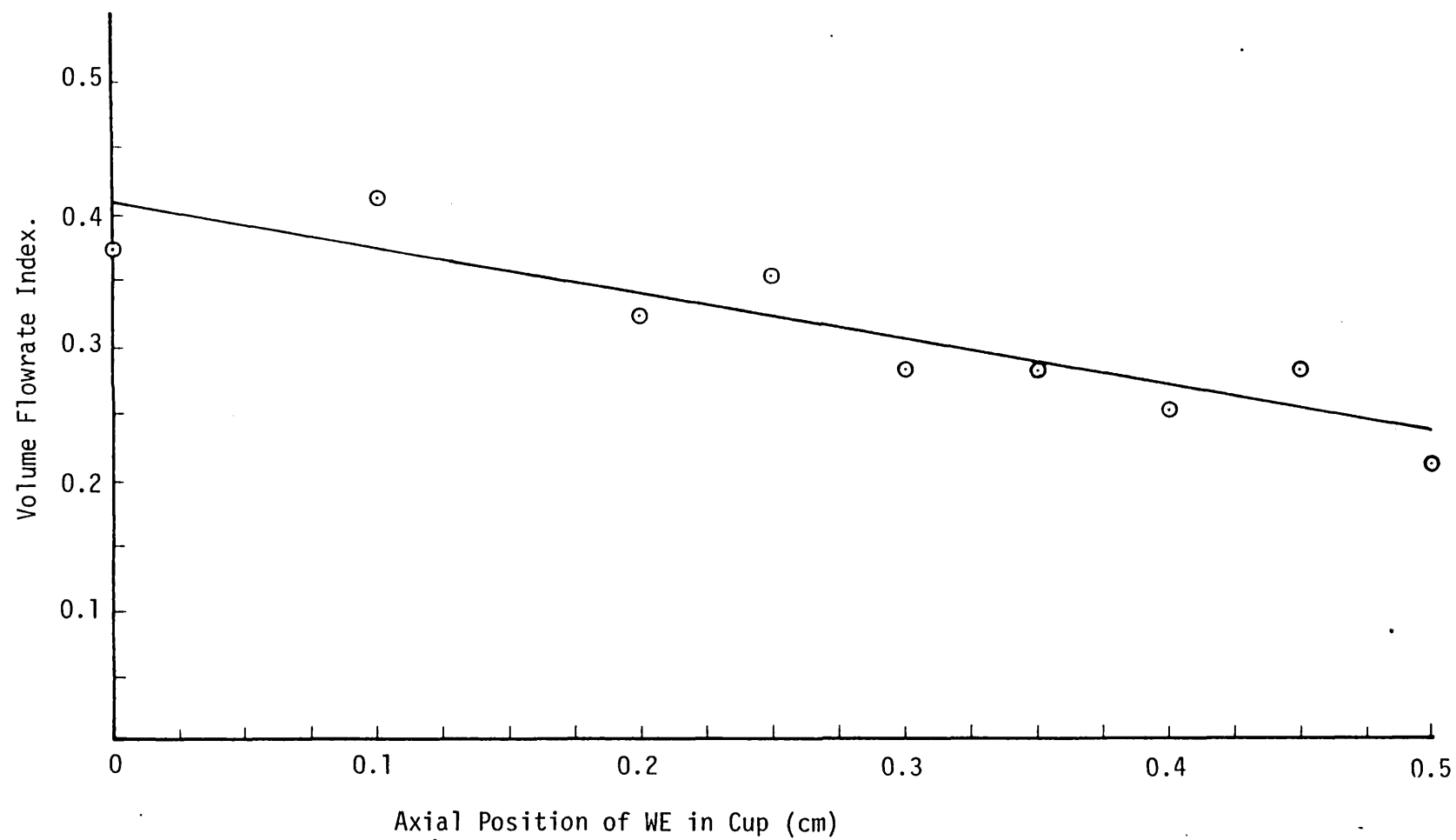


Figure 3.10 : Dependence of index of v_f on WE axial position.

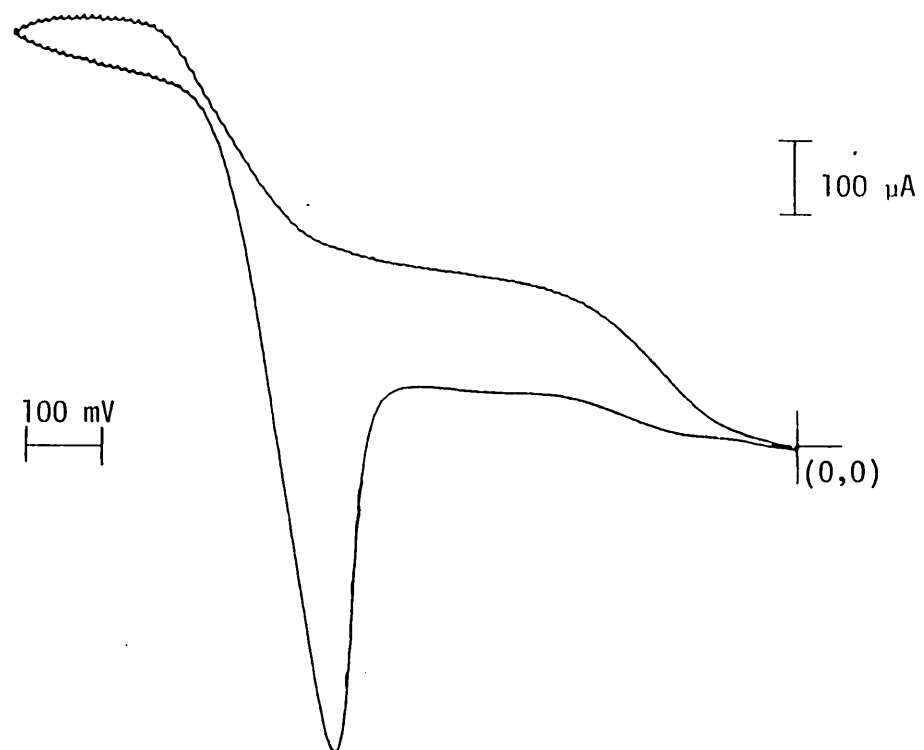


Figure 3.11 : Typical cyclic voltammogram for Cd ($89.0 \text{ n mol cm}^{-3}$) in KCl (0.1M) at $v_f = 57 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ measured against Ag/AgCl (1.0M).

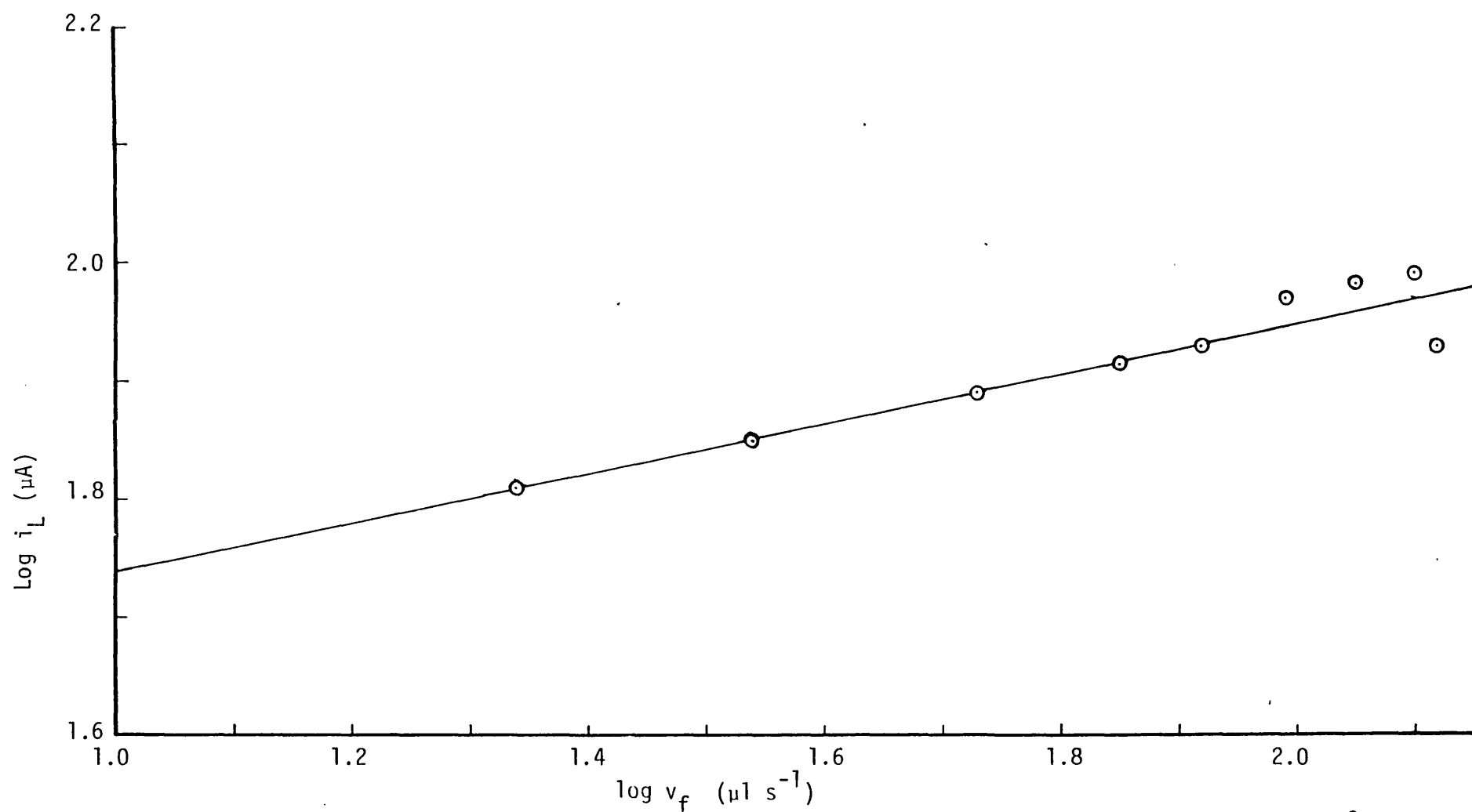


Figure 3.12 : Typical dependence of I_L on v_f for a depositable species; Cd ($267 \text{ n mol cm}^{-3}$) in KCl (0.1M).

peak was at -0.646V . Several voltammograms were run for each flow rate and i_L obtained from them. Figure 3.12 shows a typical $\log i_L / \log v_f$ plot at the WE position 0.5 cm . A definite scatter of points is present beyond $v_f = 83\text{ }\mu\text{l s}^{-1}$ ($5\text{ cm}^3\text{ min}^{-1}$). The gradient is the same as that for the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ reaction. The similarity was the same when the WE position was varied but the scatter persisted (see figure 3.13). At a lower concentration ($2\mu\text{g/cm}^3$) the scatter was slightly shifted to higher flow rate.

3:3.8 Comparison of Experiment with Theory

The dependence of the limiting current on solution volume flow rate experiment (section 3:3.5) was repeated using the electro-reduction of ferricyanide to ferrocyanide. The position of the WE in the cup was 0.2 cm since this is the position where the dependence was to the power $1/3$ as obtained by experiment. The result for the concentration $0.0005\text{M Fe}(\text{CN})_6^{3-}$ in KCl (0.1M) is plotted in figure 3.6 continuous line. Using equation 3.52 and the diffusion coefficient $0.76 \times 10^5\text{ cm}^2\text{s}^{-1}$ for $\text{Fe}(\text{CN})_6^{3-}$ in KCl (0.1M) from Stackelberg et al.³⁰¹ and the WE parameters : area = 0.31 ; $z = 0.2\text{ cm}$, the values of the corresponding limiting currents were calculated and plotted, dashed line. The experiment was then repeated for the depositable species cadmium ($17.8\text{ n mol cm}^{-3}$) in KCl (0.1M). This is shown in figure 3.14. The theoretical curve for $\text{Fe}(\text{CN})_6^{3-}$ has also been inserted in fig 3.8 to show its position in the overall performance of the cell.

3:3.9 Anodic Stripping Experiments (ASV)

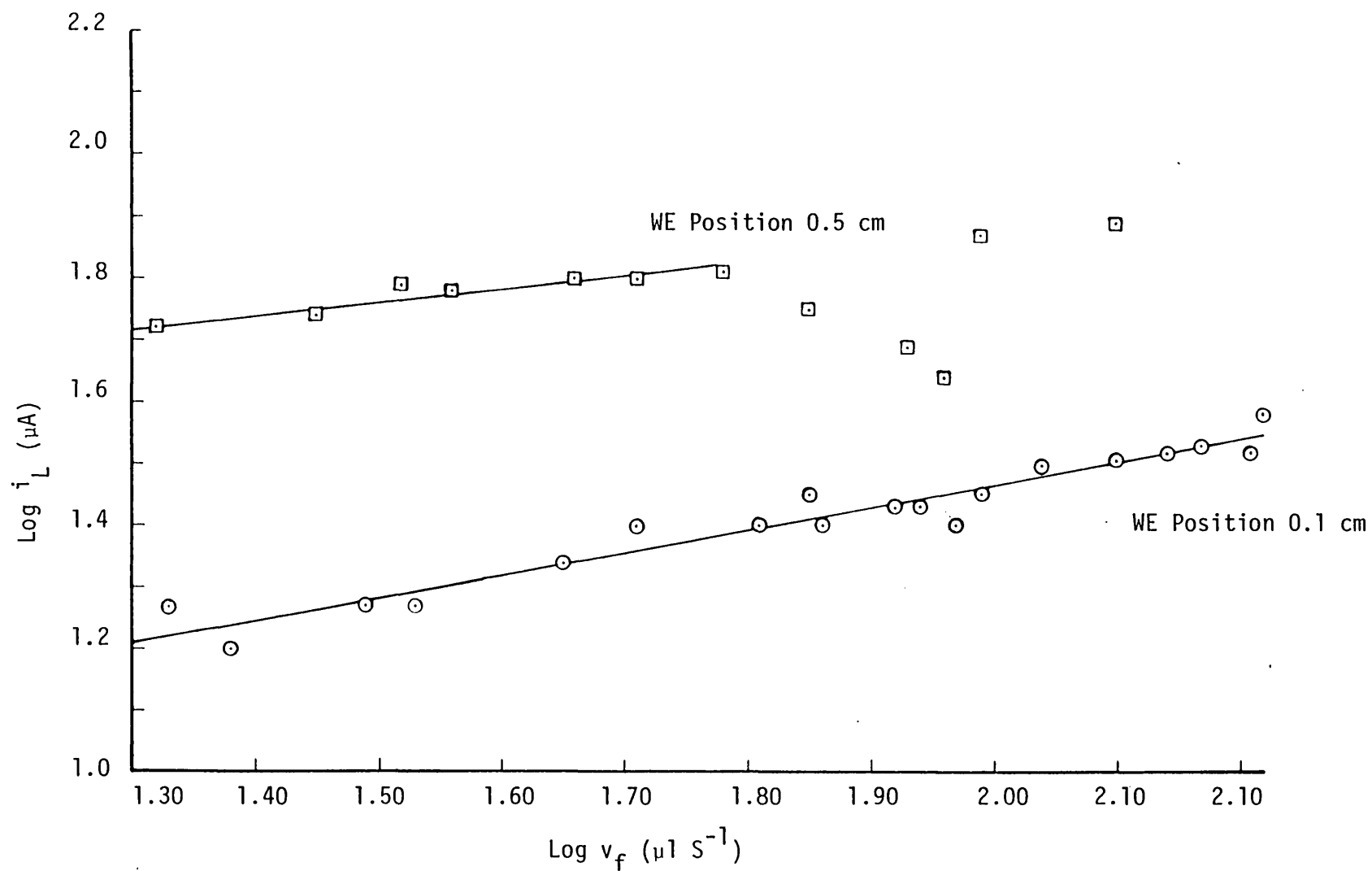


Figure 3.13 : Dependence of i_L on v_f for Cd ($267 \text{ n mol cm}^{-3}$) in KCl (0.1M) at two different WE axial positions.

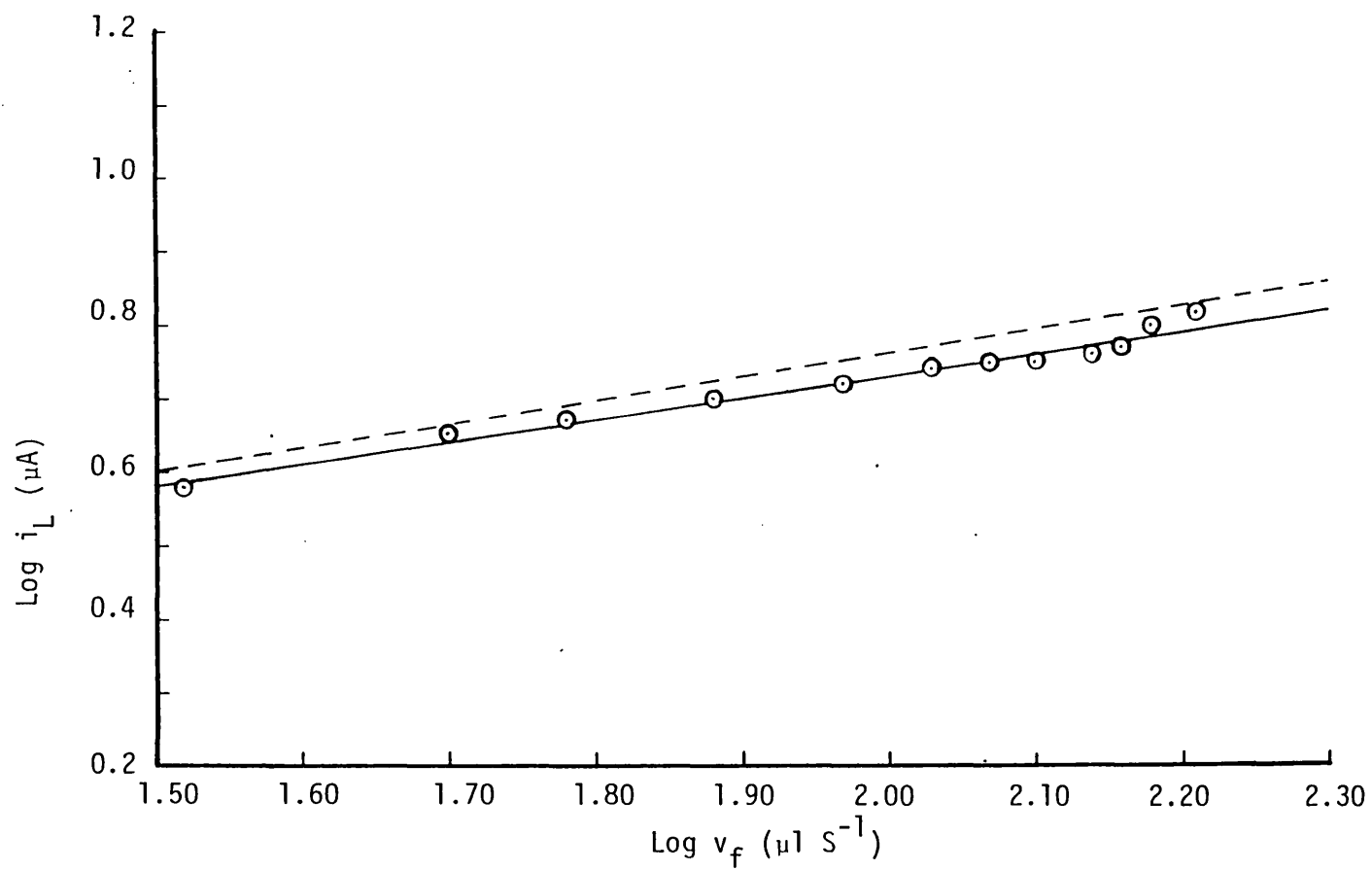


Figure 3.14 : Comparison with theory; Dependence of i_L on v_f for Cd ($17.8 \text{ n mol cm}^{-3}$) in KCl (0.1M) at WE axial position 0.2 cm.

An experiment was done to find the relation between the stripping current, i_s , and the deposition time, τ . This was done by pumping a $17.8 \text{ n mol cm}^{-3}$ solution of Cd^{2+} in KCl (0.1M) at $50 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ through the cell at the WE position 0.2 cm. Deposition potential was set at -1.050V (vs Ag/AgCl (1M)). All solutions were buffered with phosphate buffer (mixture of 0.01M Na_2HPO_4 and 0.01M $\text{Na H}_2\text{PO}_4$), pH 6.9. Stripping was done with anodic scan rate of 500 mV s^{-1} with a set range of 0.75 v. τ was varied between 60 and 1200 seconds. A plot of i_s against τ was linear passing through the origin with a gradient 1.32 and linear correlation coefficient 0.99.

A calibration curve for cadmium was then determined by repeating the above experiment at τ fixed as 600 seconds and concentration of cadmium varied between 89×10^{-12} and $17.8 \times 10^{-9} \text{ mol cm}^{-3}$. The curve is linear passing through the origin with a gradient of 42.72 and a linear correlation coefficient 0.99, figure 3.15.

Similar runs of the experiment were made to find the experimental detection limit of the concentric cup cell on its own. This was done using the WE position 0.45 cm, which is the position of highest current (figure 3.9), and the solution volume flow rate $50 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ as before. The stripping peak current equal to 3σ (σ is the standard deviation of the measurements) corresponded to a concentration of $8.90 \times 10^{-9} \text{ M}$ of cadmium for a 600 seconds deposition time.

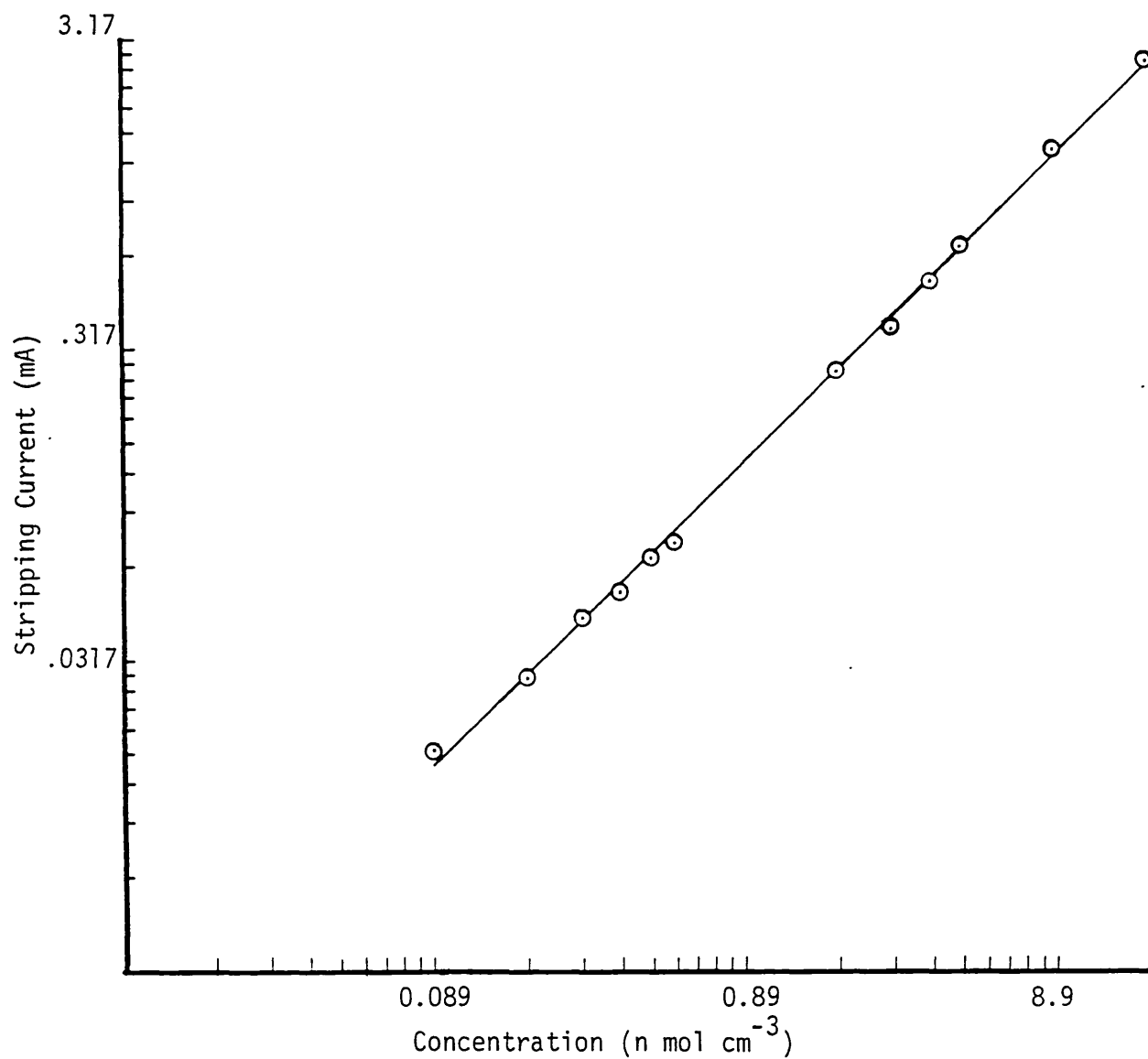


Figure 3.15 : Calibration curve for Cd^{2+} in KCl (0.1M) using ASV on its own at $v_f = 48.3 \times 10^{-3} \text{ cm}^3 \text{ S}^{-1}$ and $\tau = 600 \text{ S}$.

The deposition experiments have also been done with copper in KCl (0.5M) at pH 3.5. Multiple peaks were obtained at the scan rate used, figure 3.16. A typical variation of stripping peak currents with deposition time is shown in figure 3.17 for the two highest peaks. The top curve is for the highest peak and the lower curve for the other peak.

3:3.10 ASV with ICP-AES Experiments

Instrumentation

The electrochemical system has been described above (section 3:3.1). It is inserted into the spectroscopic system to form the hybrid system hence forth called the ASV/ICP-AES. The whole arrangement of this system is shown as a block diagram in figure 3.18. A description of the ICP-AES part of it follows :

- i) The Generator, Matching network, induction coil.

The high frequency (HF) source used is the International Plasma Corporation Generator model 120-127. This is a fixed frequency crystal controlled generator with variable capacity of power output up to 2kW at 27.12 MHz. Its power was fed through a coaxial cable RG8/u of length 45 cm to a matching network and a water cooled induction coil of 1.5 turns made of copper tubing 6mm O.d. The diameter of the coil was 26 mm. The matching network consisted of two capacitors : a 3/4 turn air capacitor (lower); and a 30-turn vacuum capacitor (upper). These served to match the impedance of the plasma to that of the induction (or load) coil and output circuit of the HF generator. The generator was equipped with a meter for monitoring : the DC power input to it after

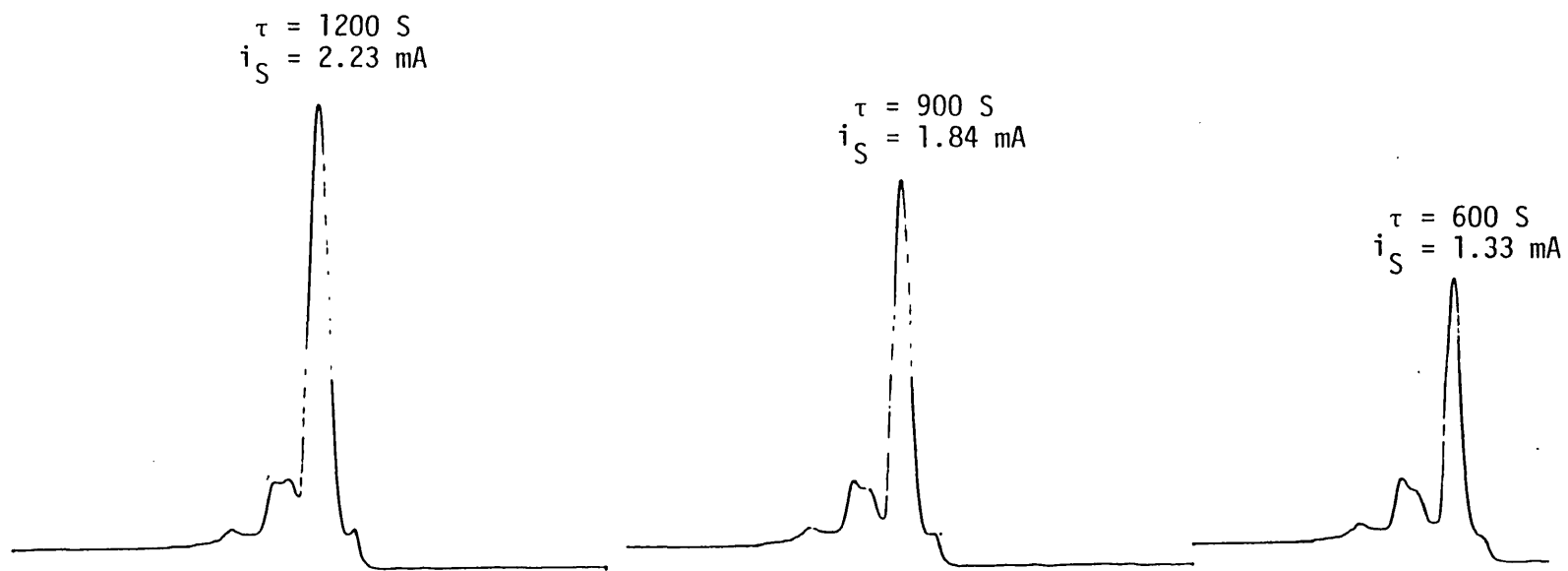


Figure 3.16 : Typical multiple peaks for Cu^{2+} ($15.76 \times 10^{-9} \text{ mol cm}^{-3}$) in KCl (0.1M) at $v_f = 57 \times 10^{-3} \text{ cm}^3 \text{ S}^{-1}$.

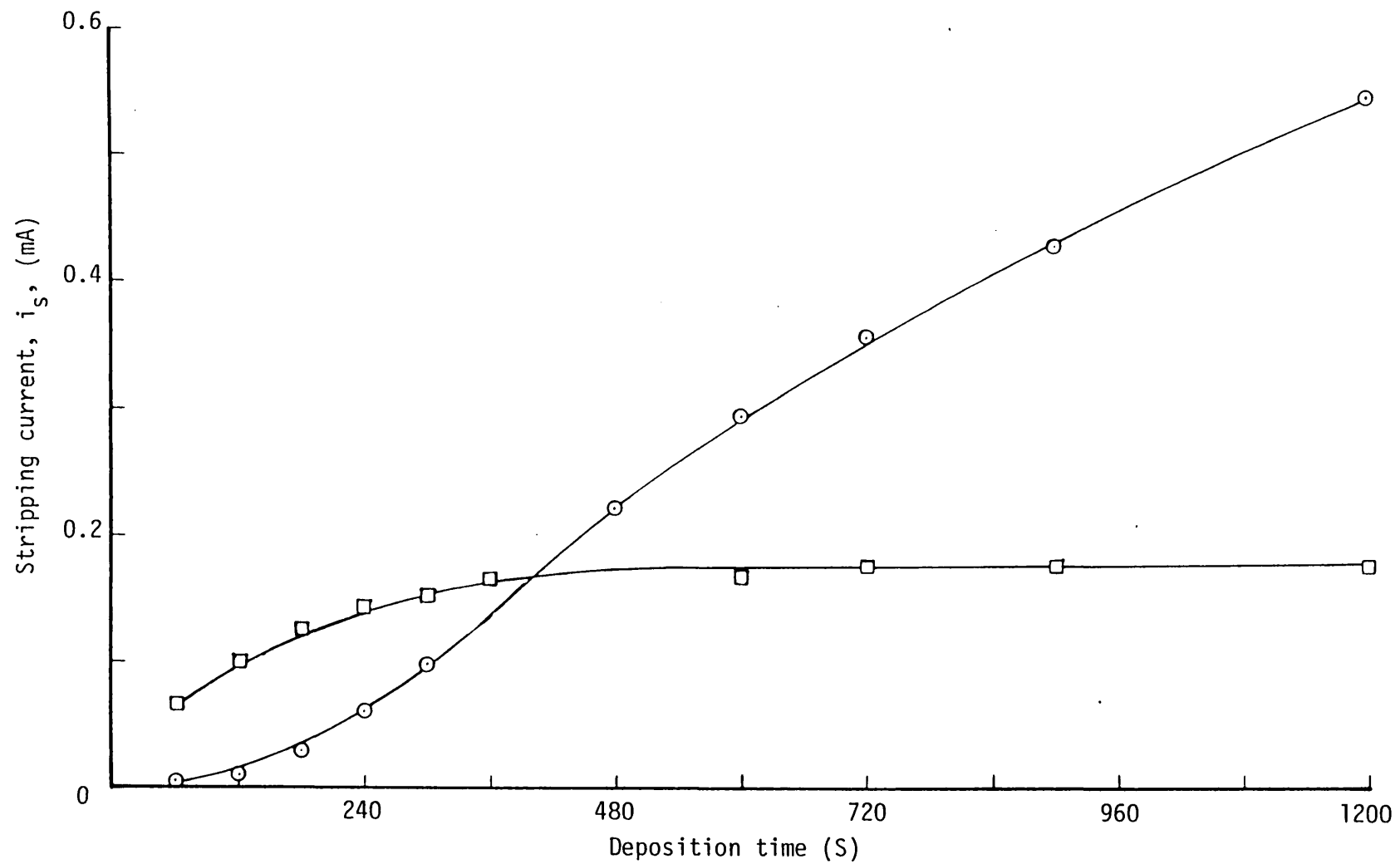


Figure 3.17 : Dependence of two stripping peaks of Cu^{2+} ($15.8 \times 10^{-9} \text{ mol cm}^{-3}$) in KCl (0.5M) on deposition time, τ .

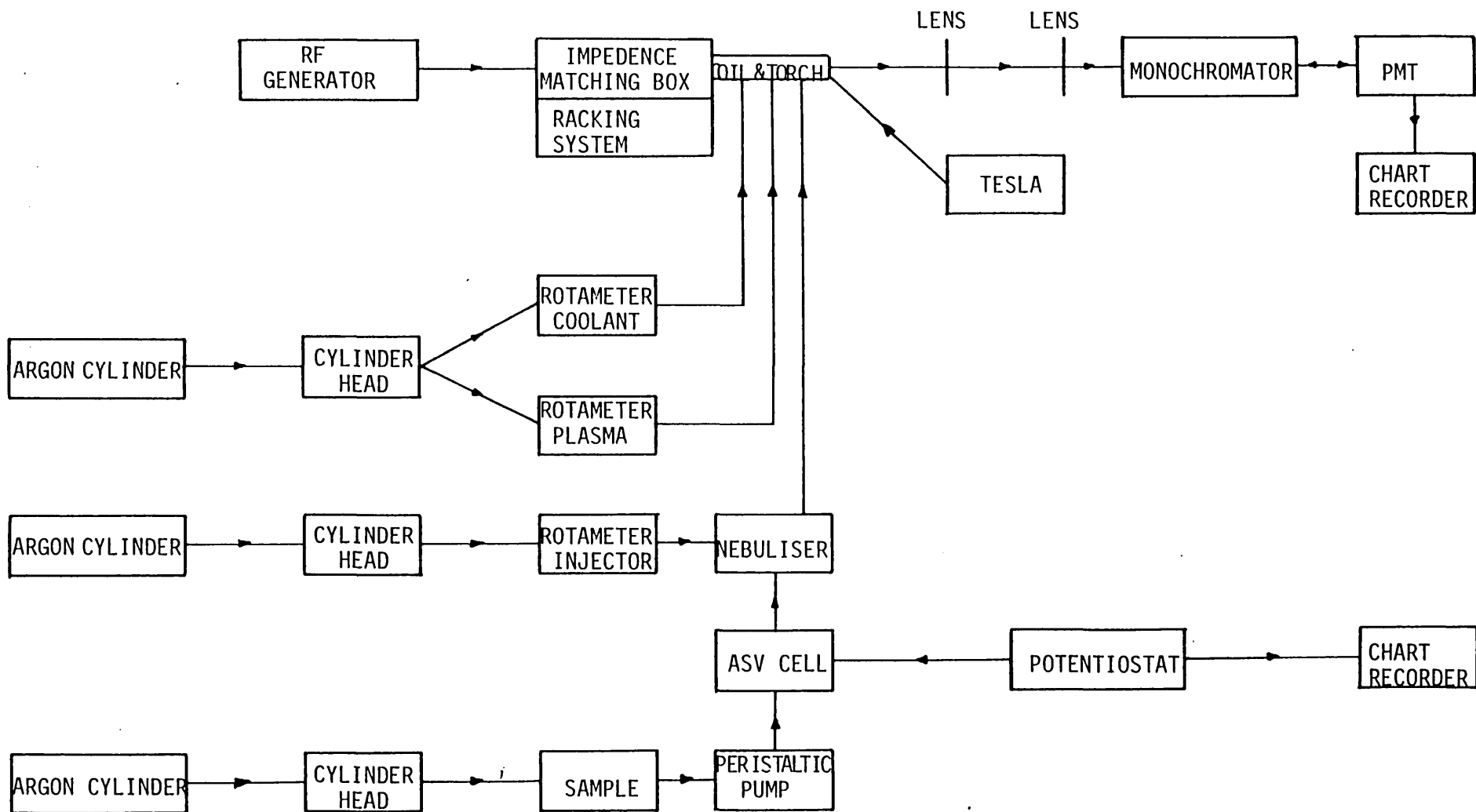


Figure 3.18 : Block diagram of the ASV/ICP-AES system.

rectification of the 3-phase mains supply; the forward HF power supplied by the generator to the matching network; and the reflected power returning from the matching box to the generator. It is also fitted with a fan to cool the final power amplifier valve.

The torch and induction coil are enclosed in a demountable aluminium box to screen off HF radiation from interfering with nearby electronics and for safety of people working in its vicinity. The box has an opening at the top to facilitate exhaust of plasma gases and fumes through a hood and duct mounted from the roof. It also has two apertures : one on the operators side and which is covered with cobalt-blue glass (smalted) for the operator to view the plasma; and the other aperture is for the optical detection system consisting of a monochromator and photomultiplier.

The assembly of the matching box and the plasma torch is mounted on a racking mechanism constructed for fine adjustments in the x, y, z axes so that the plasma and tail-flame can be viewed by the optical system at required points.

ii) The Plasma Torch

This was a demountable torch made from three concentric quartz tubes. The conventional size (see figure 3.19) quartz tubes were used. These were mounted on a brass base. The base was of loose fit so that during mounting of the tubes, the space between the glass and brass could be filled with araldite or silicon rubber and allowed to set to form a tight fit holding the tubes in place. The

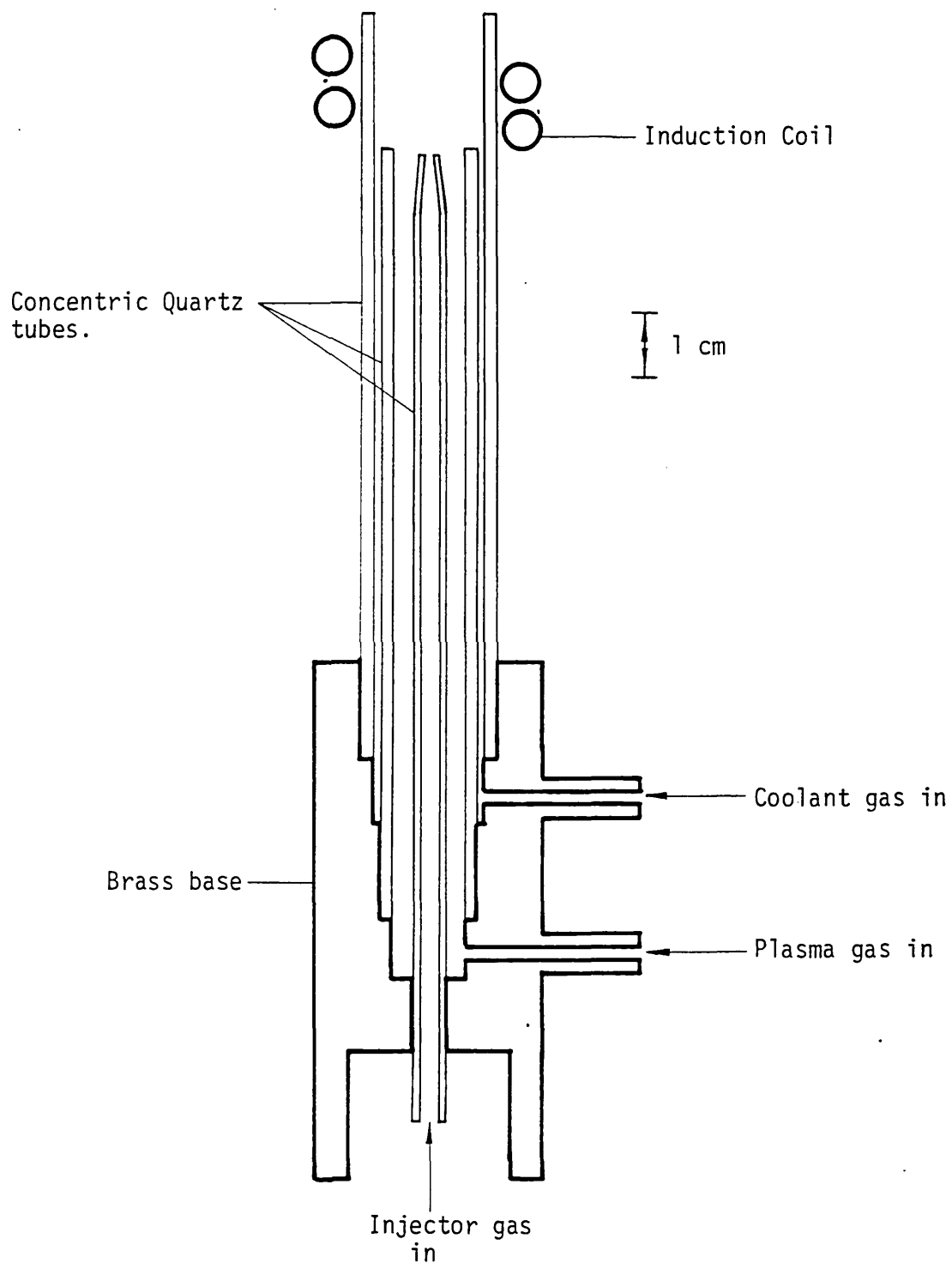


Figure 3.19 : The demountable plasma torch.
Conventional size drawn to actual size.

torch is shown in figure 3:19.

iii) The Optical Signal Detection System.

This consisted of a monochromator, a photo-multiplier tube (PMT), a photomultiplier power supply and a chart recorder. A 1:1 image of the plasma was focussed on to the monochromator entrance slit using two convex quartz lenses in line. Each lens was of 4 cm diameter and 7.5 cm focal length. One lens was placed 30 cm from the plasma and the other 30 cm from the entrance slit. The entrance slit was 80 cm distant from the plasma.

The monochromator was a scanning type, Rank Hilger Monospek 1000, with an optical path 1m and f/8 aperture using diffraction grating 1200 lines per mm blazed at 330 nm. The photomultiplier tube used for UV-visible range was EMI 6256B fitted to the exit slit at the end window of the monochromator to cover the wavelength range 190-670 nm.

The photomultiplier power supply was the Brandenburg model 475R. This has a continuously variable output up to 2kW connected to a fast response model of Servoscribe Chart recorders, type RE 541.20, via a 22k Ω resistance.

iv) The Sample Introduction System.

This consisted of a concentric nebuliser and a dual tube spray chamber. Both are made of glass. The nebuliser was from Meinhard Associates, model T-230-A2. It is shown schematically in figure 3.20. The dual tube spray chamber is similarly shown in figure 3.21. The purpose of the nebuliser is to break the sample solution into fine aerosol particles size less than 5 μ m in diameter. This

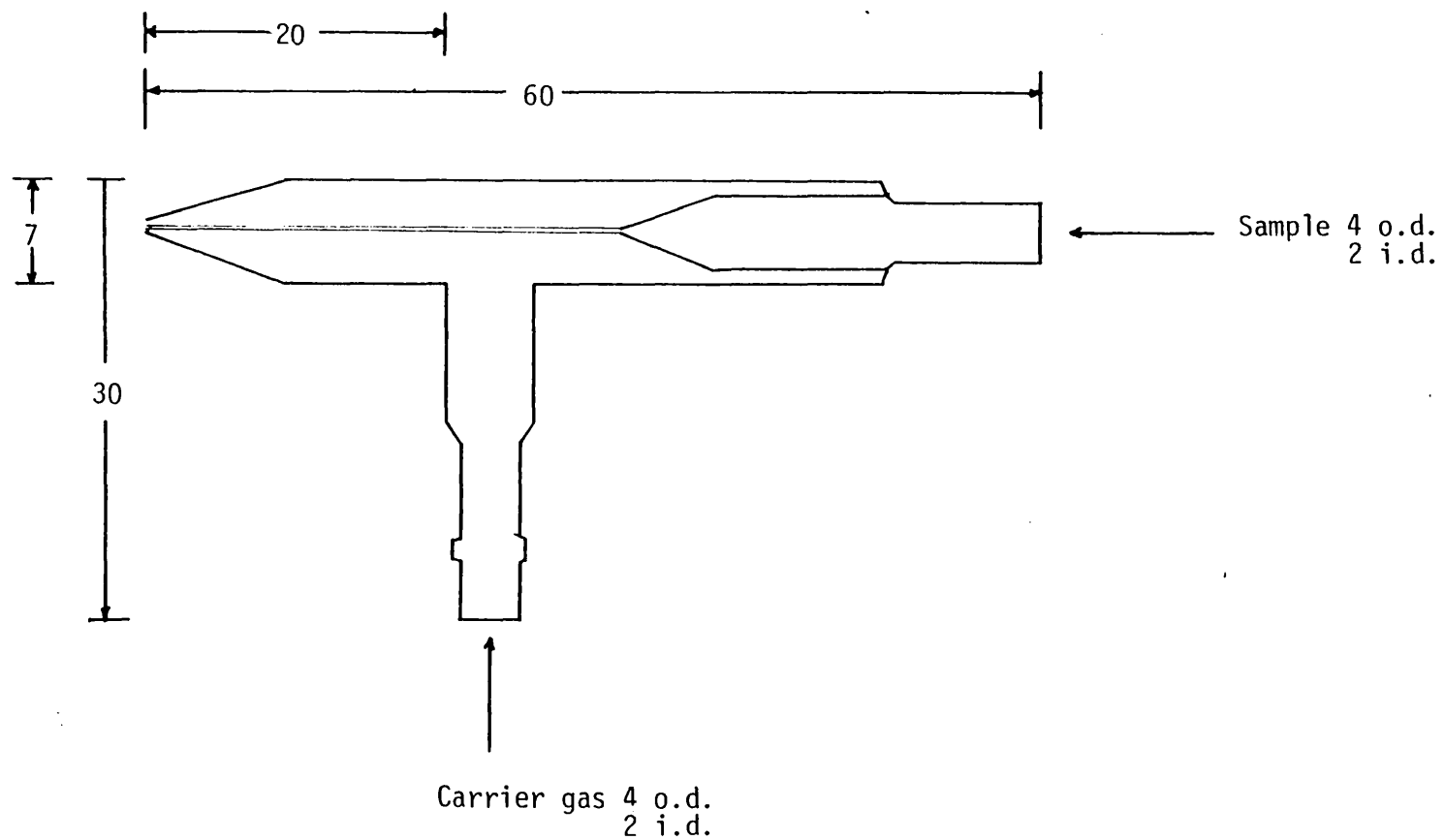


Figure 3.20 : The Meinhard Nebuliser (Schematic). Twice the actual size. Dimentions in mm.

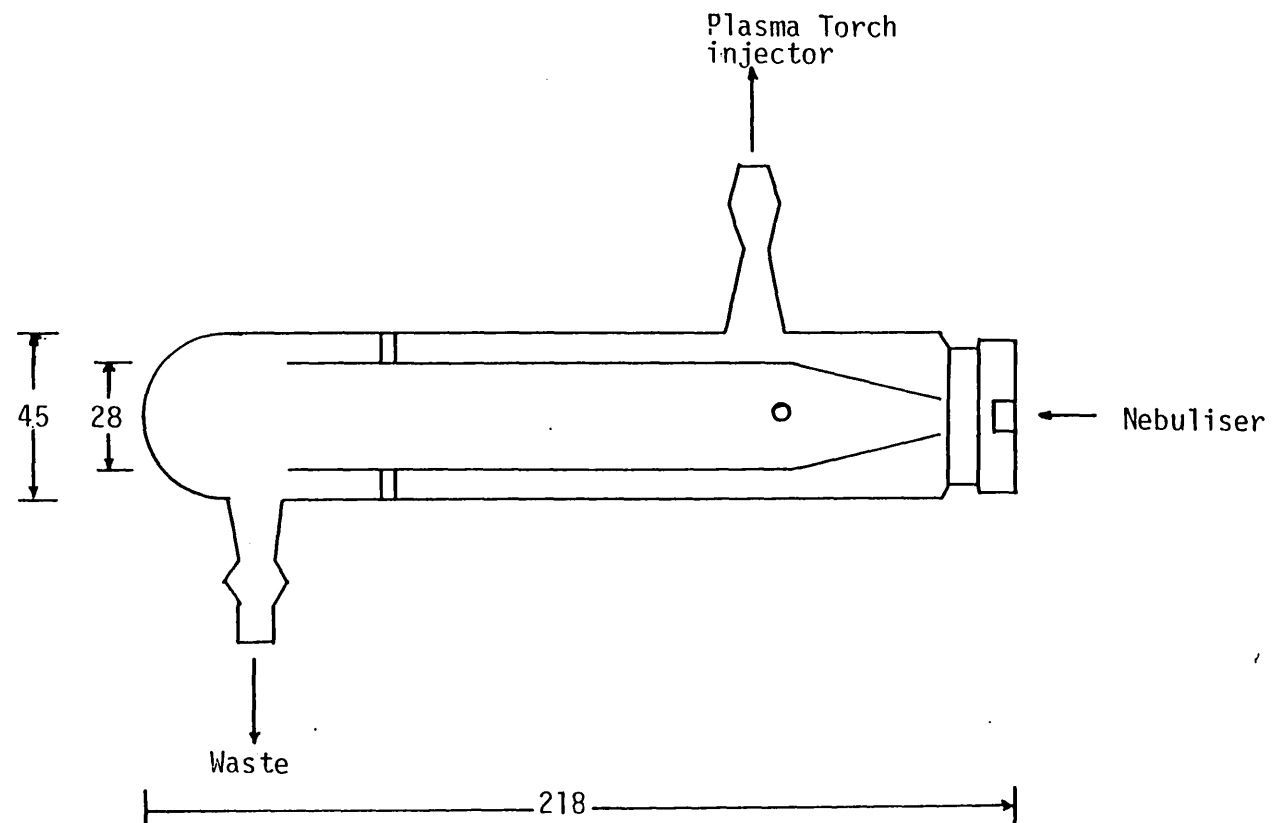


Figure 3.21 : Dual Tube Spray Chamber (Schematic)
Dimentions in mm.

is achieved by the carrier gas creating a region of low pressure at the tip of the nebuliser into which the sample is sucked and nebulised. Consequently the dual tube spray chamber is used to separate out undesirable particles by surface impaction, smooth out pressure changes and direct the desired aerosol to the plasma while the undesirable one goes to waste.

Optimisation of the ICP-AES

The magnitude and quality of signals from this system depend on the variables : forward RF power; viewing height; coolant, injection and plasma gas flow rates; size of the monochromator viewing slit; and photomultiplier power supply. For maximum performance on a given element optimisation has to be done with respect to each of these variables. Signal to noise ratio, S/N , is obtained experimentally and plotted as a function of the variable and the position of maximum value on the plot is the optimal point for the variable. The other diagnostic parameter is signal to background, S/B , ratio which is obtained by a similar procedure. When analysis for several elements is of concern it is time-consuming to carry out reoptimisation each time the element is changed. Consequently "compromise operating conditions" are used. These are operating conditions for which the group of analysed elements are acceptably close to their optimal points.

In this work compromise conditions were used.

Operating the ASV/ICP-AES System

The ICP is lit the normal way and left to "warm" up for twenty minutes. During this time the ASV system is undergoing pretreatment as described in section 3:3.3. The ICP-AES operating conditions are then set for the detection of the species of interest by dialing up the required wavelength, opening the entrance slit, adjusting gas flow rates, forward RF power, viewing height, photomultiplier power supply and sensitivity scale and speed on the chart recorder to the desired values. It is next necessary to check if the performance of the ICP-AES on the day is the same as on previous experiment days. This is done by nebulising a standard solution of the species kept for the purpose the S/N obtained compared with that of the previous days at the same operating conditions. If the S/N values do not agree further adjustments of the system are made to retain comparability.

There are two ways of obtaining signals from the ICP-AES : either the wavelength of the species is scanned while nebulising the solution continuously or the wavelength is fixed on line and the solution is nebulised for only the time required to obtain a signal. For the ASV/ICP-AES work the latter was used since when stripping is done the required peak appears for a definite time only. The first method would therefore require synchronising the peak appearance with the monochromator wavelength scan and this is impractical on a manual system. It was however necessary to check if drifting off the line set occurred when using the latter method.

With both systems set to the desired operating conditions and

the substrate solution flowing through the cell into the nebuliser, the deposition potential and clock were switched on simultaneously. Towards the end of deposition the chart recorder was set to run. At the end of deposition time the stripping scan was switched on and the resulting stripping peak recorded. It was only necessary to maintain the cell connected to the nebuliser when deposition time was less than 3 minutes. For longer deposition times the performance of the detection system could be checked while deposition was in progress and the cell would be connected to the nebuliser towards the end of this process.

ASV Preconcentration of Cadmium for ICP-AES

The following operating conditions were used :

Cadmium	Wavelength	228.80nm
ICP-AES :	Forward RF power	1000W
	Photomultiplier power supply	1000V
	Observation height	20 mm
	Coolant argon gas flow	13 l min ⁻¹
	Injector argon gas flow	0.8 l min ⁻¹
	Plasma argon gas flow	0.5 l min ⁻¹
	Viewing slit width	35 μ m
Potentiostat :	Deposition potential	-1.050 V (vs Ag/AgCl)
	Stripping potential scan rate	500 mVs ⁻¹
	Potential scan range	0.75 V
	Current range	2 mA

Deposition time (τ) 600 seconds.

Solution volume flow rate (v_f) $50 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ ($3 \text{ cm}^3 \text{ min}^{-1}$).

Different concentrations of cadmium in KCl (0.1M) were pumped through the cell at the above conditions. Stripping peaks monitored with ICP-AES for each solution were obtained using the procedure above. Typical peaks are shown in figure 3.22 with traces and scans of the original solution using ICP-AES on its own. The variation of stripping peaks with concentration is shown in figure 3.23 for the hybrid system. The linear correlation coefficient is 0.99.

Similar experiments were done to determine the experimental detection limit for cadmium at the above conditions. The stripping peak equal to 3σ corresponded to a concentration $270 \times 10^{-9} \text{ mol dm}^{-3}$ (0.03 ppm) for the hybrid system and $8.0 \times 10^{-7} \text{ mol dm}^{-3}$ (0.09 ppm) for the ICP-AES on its own.

The ratio : hybrid system signal/ICP-AES signal, here referred to as preconcentration factor, was consistent at 3.1 with standard deviation 0.3 for experiments done on different days.

Efficiency of the Concentric Cup Cell

The efficiency defined as amount taken out by the cell divided by amount flowing through the cell (Section 1 : 4.1) was determined using the ICP-AES. The solution of Cd $17.8 \text{ n mol cm}^{-3}$ ($2 \mu\text{g/cm}^3$) was pumped through the cell at the above experimental conditions. A signal invariant with time was obtained with solution flowing through the cell into the ICP without deposition. When the

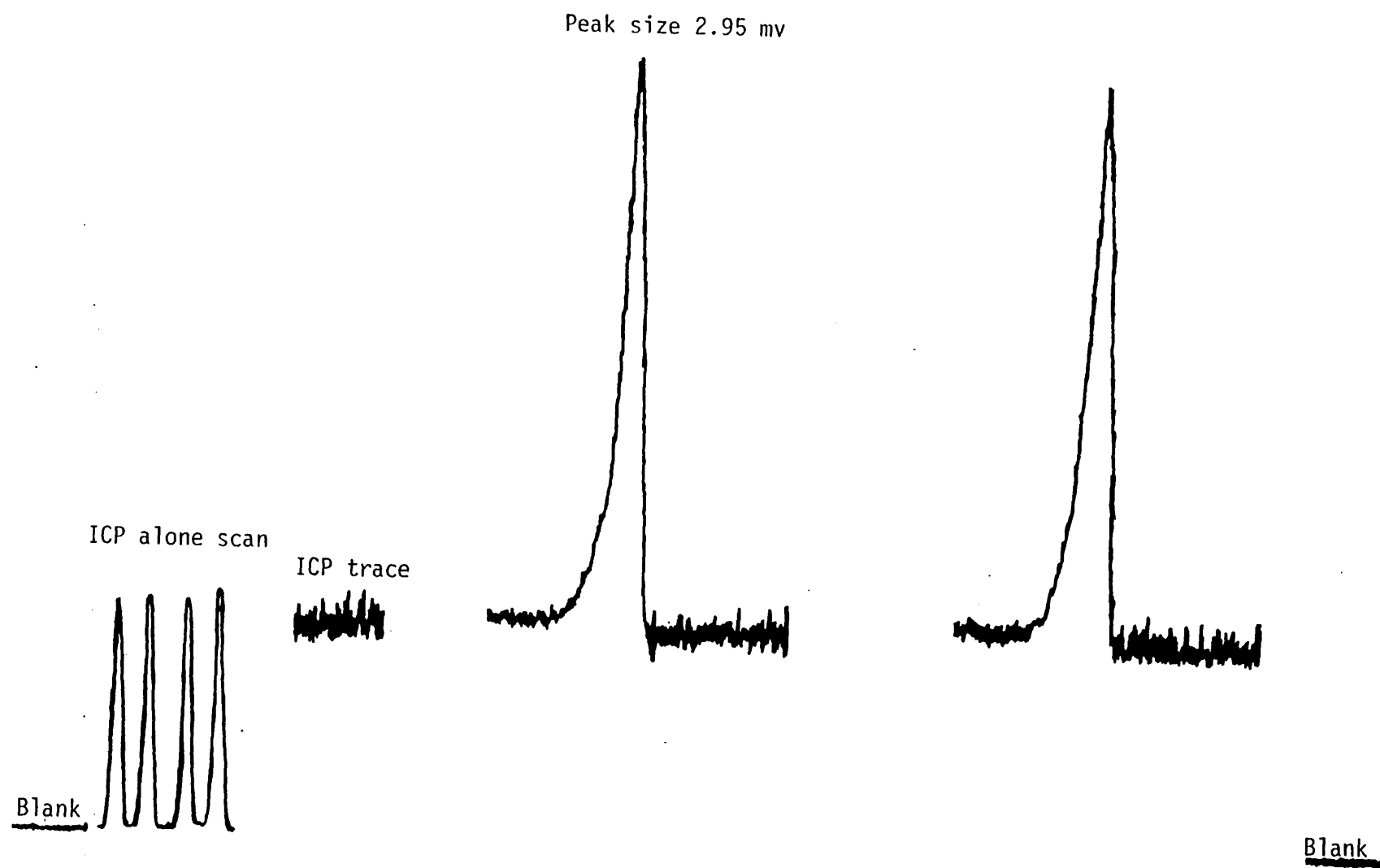


Figure 3.22 : Typical ASV/ICP-AES signals for Cd^{2+} ($17.8 \times 10^{-9} \text{ mol cm}^{-3}$) in KCl (0.1M), $\tau = 600 \text{ S}$.

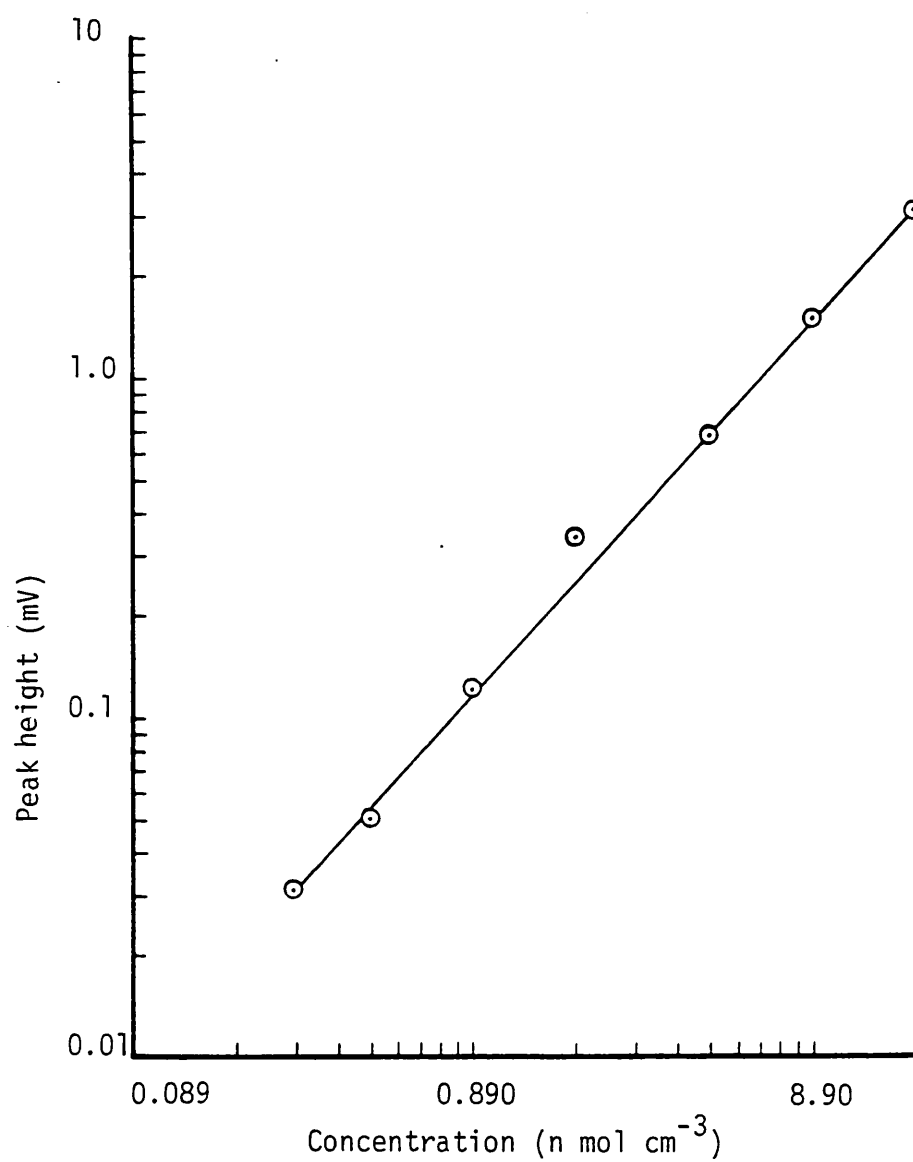


Figure 3.23 : Calibration curve for Cd^{2+} using ASV/ICP-AES

deposition potential was switched on the signal decreased and was once more invariant with time. The efficiency was then calculated as :

$$\frac{\text{Change of signal}}{\text{Signal at no deposition}} \times 100$$

The efficiency obtained by this method was 7.5% and did not change significantly with concentration.

Dependence of Peak height on Deposition Time

Experiments in section 3:3.9 were repeated except that this time the stripping signals were detected with ICP-AES. For cadmium the relation was, as expected, linear similar to that in section 3:3.9. For copper there was no observable curvature, such as observed in figure 3:17 for ASV on its own. figure 3.24.

Analysis of a Real Sample

The ICP-AES system was used for analysis of harbour water (Brighton) for cadmium. Since the sample concentration was expected to be low and matrix effects possible, the method of standard additions was used. No further supporting electrolyte was required since seawater contains enough electrolyte. The sample was filtered with a whatman 542 filter paper and standard additions made when required. All samples were purged with argon as before and operating conditions for cadmium as above were used. Because of the light scatter resulting from sodium in sea-water, after deposition, the cell was flushed with a purged KCl (0.1M) blank before stripping into the ICP. The graph for the standard additions is shown in figure 3.25 together with an ASV standard addition curve recorded simultaneously. The correlation coefficients are better than 0.99.

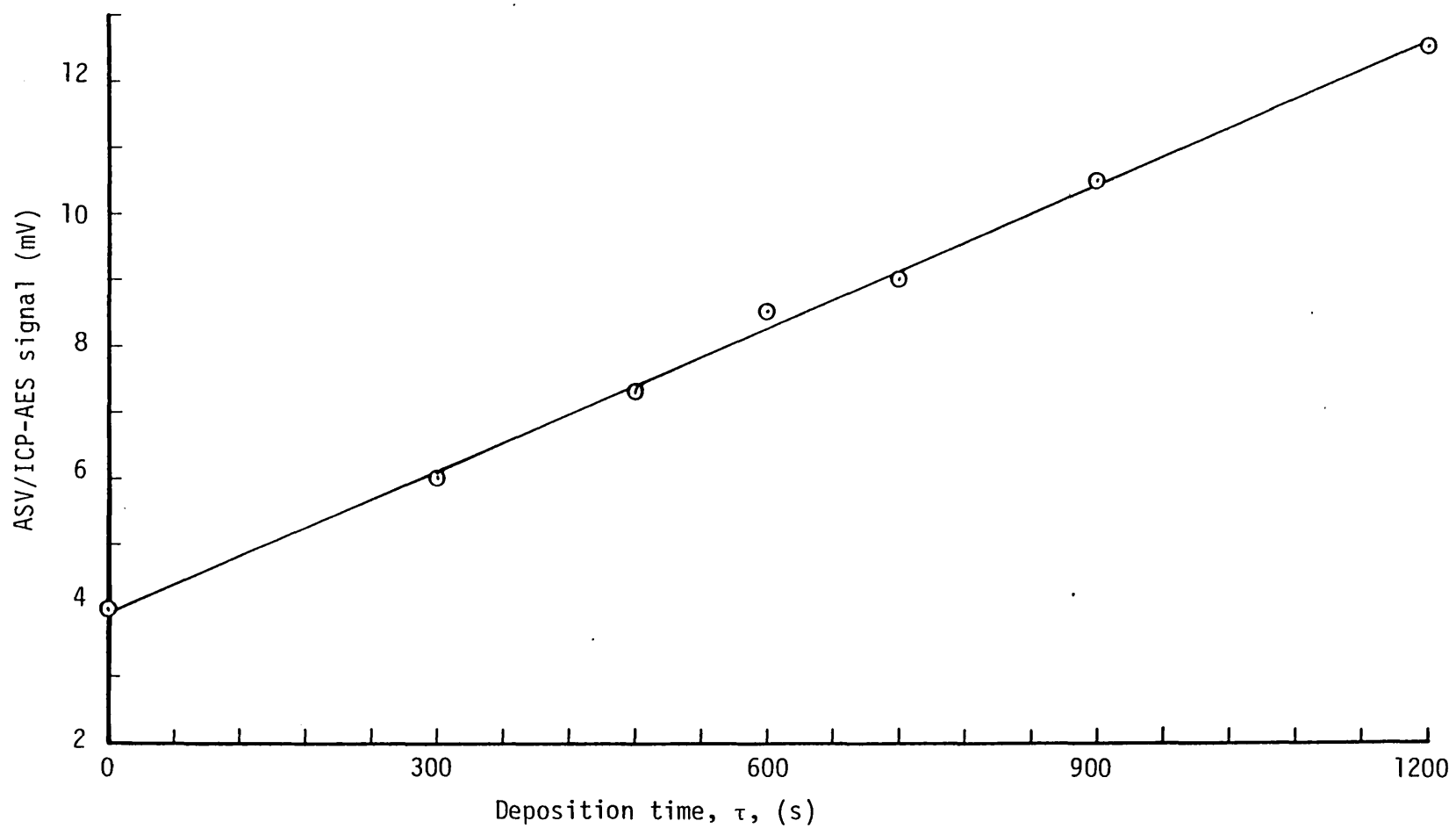


Figure 3.24 : Dependence of stripping peak size on deposition time for Cu ($15.8 \text{ n mol cm}^{-3}$) in KCl (0.1M)

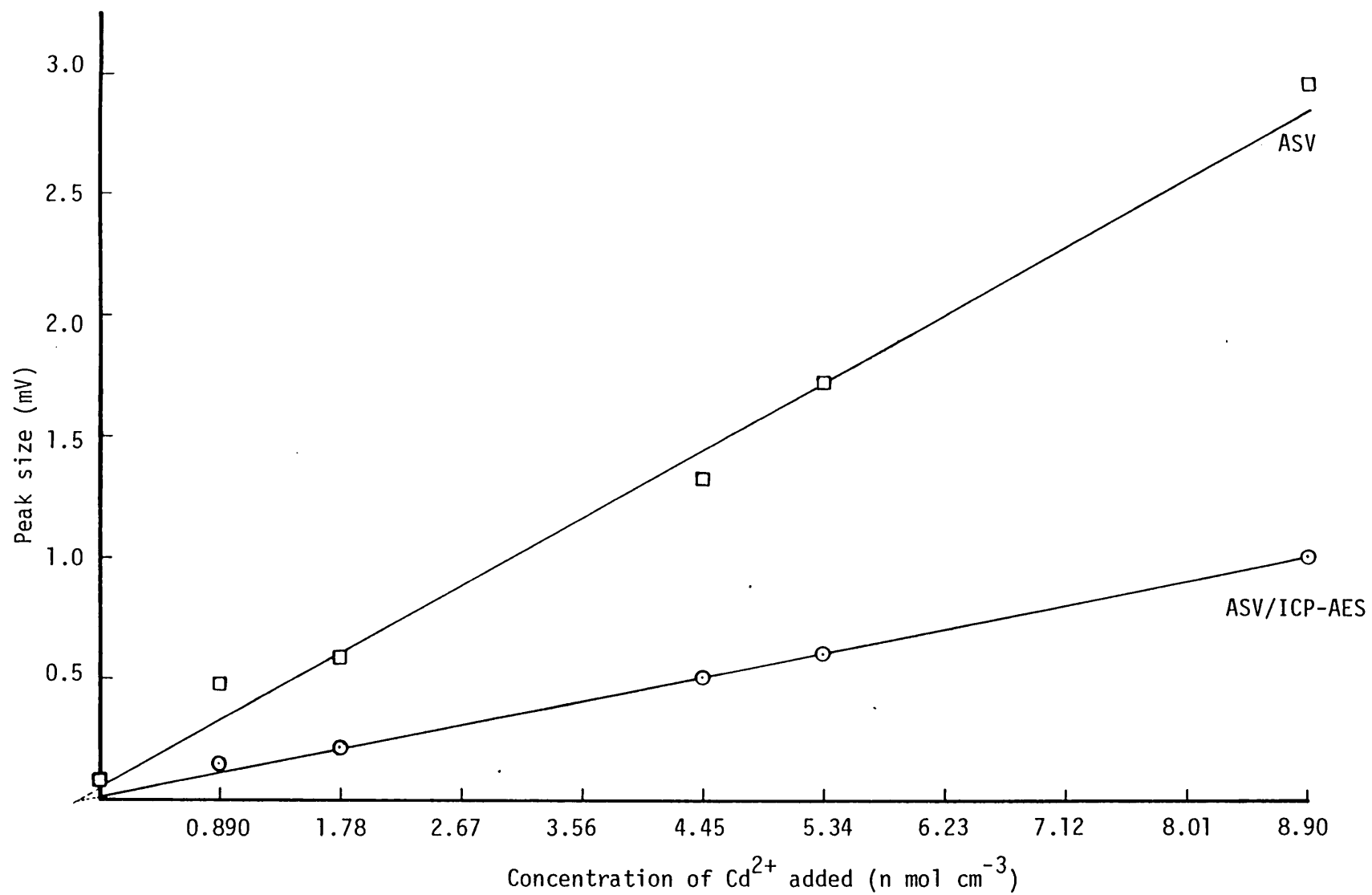


Figure 3.25 : Standard addition analysis of seawater for Cd^{2+} using ASV/ICP-AES and ASV on its own.

The required cadmium concentrations are 17×10^{-9} and 18.7×10^{-9} mol dm⁻³ for ASV/ICP-AES and ASV respectively. The agreement between the two is reasonable.

3.4 Results and Discussion

From figure 3.6 the exponent 0.33 obtained experimentally for the i_L , v_f dependence is in complete agreement with the theoretical equation 3.52. Further to this, figure 3.6 shows that the agreement holds also for the magnitude of the currents and holds for all the solution flowrates 8×10^{-3} - 170×10^{-3} cm³ s⁻¹ (0.5 - 10 cm³/min) investigated. It is also fulfilled by depositable species but in this case it breaks down at solution flowrates higher than 100 cm³ s⁻¹ (figure 3.12). The breakdown point is observed to shift to higher flowrates as the concentration of the substrate is decreased. It is also observed to disappear as the WE is moved out of the cup (fig 3.13).

It can therefore be suggested that this scatter is due to turbulence, which manifests itself only in the cup and that interferes with deposition especially at high flowrates. However laminar flow has been shown³⁰² both experimentally and theoretically to be maintained in a concentric annular passage for $Re < 2000$ where

$$Re = \frac{v_m \text{ de}}{\nu} = \frac{v_m \cdot 2r_o(1-K)\rho}{\mu}$$

On using typical experimental values for aqueous solutions : $\mu = 0.01$ poise; $\rho = 1 \text{ g cm}^{-3}$; and for the cell $r_o = 0.26$ cm, $K = 0.96$,

$v_m = 170 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$, it can be seen that $Re \ll 2000$ and no turbulence is expected within the experimental conditions.

Considering a hexagonal close packed unit for the Cd^0 deposited on the WE surface and atomic radius of cadmium as $154 \times 10^{-12} \text{ m}$ it can be shown that one monolayer coverage is equivalent to $390 \text{ } \mu\text{C cm}^{-2}$ or $123 \text{ } \mu\text{C}$ for this WE. For solution flowrate $6.3 \text{ cm}^3 \text{ min}^{-1}$ with $C_B = 1.78 \times 10^{-8} \text{ mol cm}^{-3}$ the limiting current is $6 \mu\text{C s}^{-1}$ hence it would take only 20s to complete a monolayer coverage. If it takes 3 minutes to obtain a voltammogram from which to measure i_L , 10 monolayers shall have been formed then dendritic growth^{303,304} begins to interfere with mass transport. The effect of dendrites in an annulus of thickness $100 \mu\text{m}$ can be significant. However since the cell is designed for trace analysis concentrations that lead to dendritic growth are uncommon.

Another factor that can lead to scattering as observed may arise from imperfection leading to some eccentricity in the construction of the cell. This would lead to non-uniform deposition on the WE surface. The alternating points in figure 3.10 are attributed to this effect.

The theoretical line divides figure 3.8 into two sections with only a central section WE position $0.2 - 0.3 \text{ cm}$ complying with theory. The slightly higher exponent than expected observed at positions below 0.2 cm indicate turbulence.²⁷⁹ The lower currents indicate an undeveloped concentration profile. These observations are expected because the WE at these positions is at the entrance

region of the annular passage where both the velocity and concentration profiles are developing. Here equation 3.52 does not apply because of assumption (i) section 3:2.4. The hydrodynamic entrance length for an annular passage and for flow between parallel plates has been studied.²⁸³ It can be approximated by the relation

$$Z_e = \frac{Re \cdot d_e}{20} \quad 3.53$$

where Z_e is the entrance length. If $Re = 200$ and $d_e = 0.02$ then $Z_e < 2$ mm.

For WE positions further than $0.2 \longrightarrow 0.3$ cm the exponent of v_f is lower than expected and the currents are higher. This is attributed to the changing geometry of the cup since near these positions the cup curves towards the exit. Back pressure from the exit was not expected since the cross-section area of the exit orifice was twice the cross-section area of the annular passage hence laminar flow was maintained.

As mentioned in section 3.2 the concentric annular geometry lies between the tube ($\kappa \longrightarrow 0$) and parallel plates ($\kappa \longrightarrow 1$). For this particular cell the annulus is very thin ($\kappa = 0.96$). It is therefore expected to be close to the case of flow between parallel plates. The problem of flow between parallel plates has been investigated by Tobias and Hickman.³⁰⁵ The limiting current is given by the equation (in symbols consistent with the above) :

$$i_L = 0.9783 n F D C_B \left[\frac{v_m}{h D Z} \right]^{1/3} \quad 3.54$$

where $h = r_0(1-\kappa)$ is the distance between parallel plates. Using typical values as in section 3:3.8 it can be seen that the concentric annulus equation (3.52) gives currents only 0.2% higher than the above equation for parallel plates. It is therefore correct within experimental error to use the equation for parallel plates for the concentric cup cell. This can also be seen in figure 3.5 where $\phi \longrightarrow 1.50$ for parallel plates. By using $\phi = 1.50$ and h in place of d_e in equation 3.48 equation 3.54 immediately follows. The use of the tubular electrode equation

$$i_L = 5.306 \times 10^5 n D^{2/3} Z^{2/3} v_f^{1/3} C_B$$

however yields currents far lower than equations 3.52 and 3.54. It can therefore be seen that the use of a concentric annulus yields higher mass transfer than both the parallel plates and the tubular geometries. The magnitude of the mass transfer improves as the radius, κ , decreases. But since a small radius leads to a thick annulus and so would be undesirable for preconcentration purposes.

The efficiency of the cell, the preconcentration factor and the detection limit obtained with the ICP-AES are all low despite the considerations to maximise the electrochemical performance. While the efficiency 7.5% is quite high relative to usual electrochemical cells, for significant improvement of detection ability for the ICP-AES, much higher efficiency is required. This is because of the dilution and efficiency of the sample introduction system of the ICP-AES. A full discussion of this is

presented in Chapter 5. It suffices to say here that two approaches were followed in order to improve further, to the concentric cup cell, the preconcentration performance. First the use of large surface area materials such as possible only from porous materials to dramatically increase electrolysis (chapter 4) and secondly the use of a sample introduction system to the ICP that avoids dilution and losses such as those present in the normal system (chapter 5).

CHAPTER 4.
THE RETICULATED VITREOUS CARBON CELL.

4.1 The Cell

As mentioned above the ICP-AES requires a large amount of sample to obtain a signal compared to the amount deposited electrochemically on to the WE. Both the Wall Jet cell and the concentric cup cell could not be used to deposit sufficient substrate to produce the desired concentration factor. It was therefore necessary to use a very large surface area material, RVC, in a confined space in order to increase the amount of deposit and so achieve a large preconcentration factor. The relation of electrolysis current to the surface area hence to amount deposited can be seen in equation 2.8.

The RVC cell is shown schematically in figure 4.1. The electrode material, RVC, has been described in section (2.4). To ensure that hydrodynamic flow was maintained through it a disc 0.3 cm thick and of a diameter 0.4 cm was used. Large diameter discs were not used since they are more susceptible to nonuniformity in potential distribution. To ensure no mixing and dilution with solution in the rest of the cell the disc was fitted into a cup similar to the concentric cup cell. Because RVC is a brittle material particular care was exercised in fitting it in to place in the cup. In order to achieve a good electrical contact and uniform potential distribution all round the RVC a concentric graphite cylinder was fitted inside the cup to contain the RVC firmly. An earlier version of the cell used glassy carbon instead of the graphite on account of similarity with RVC but this proved unsatisfactory since fragile edges of RVC could break off causing loss of electrical contact. The external electrical contact was

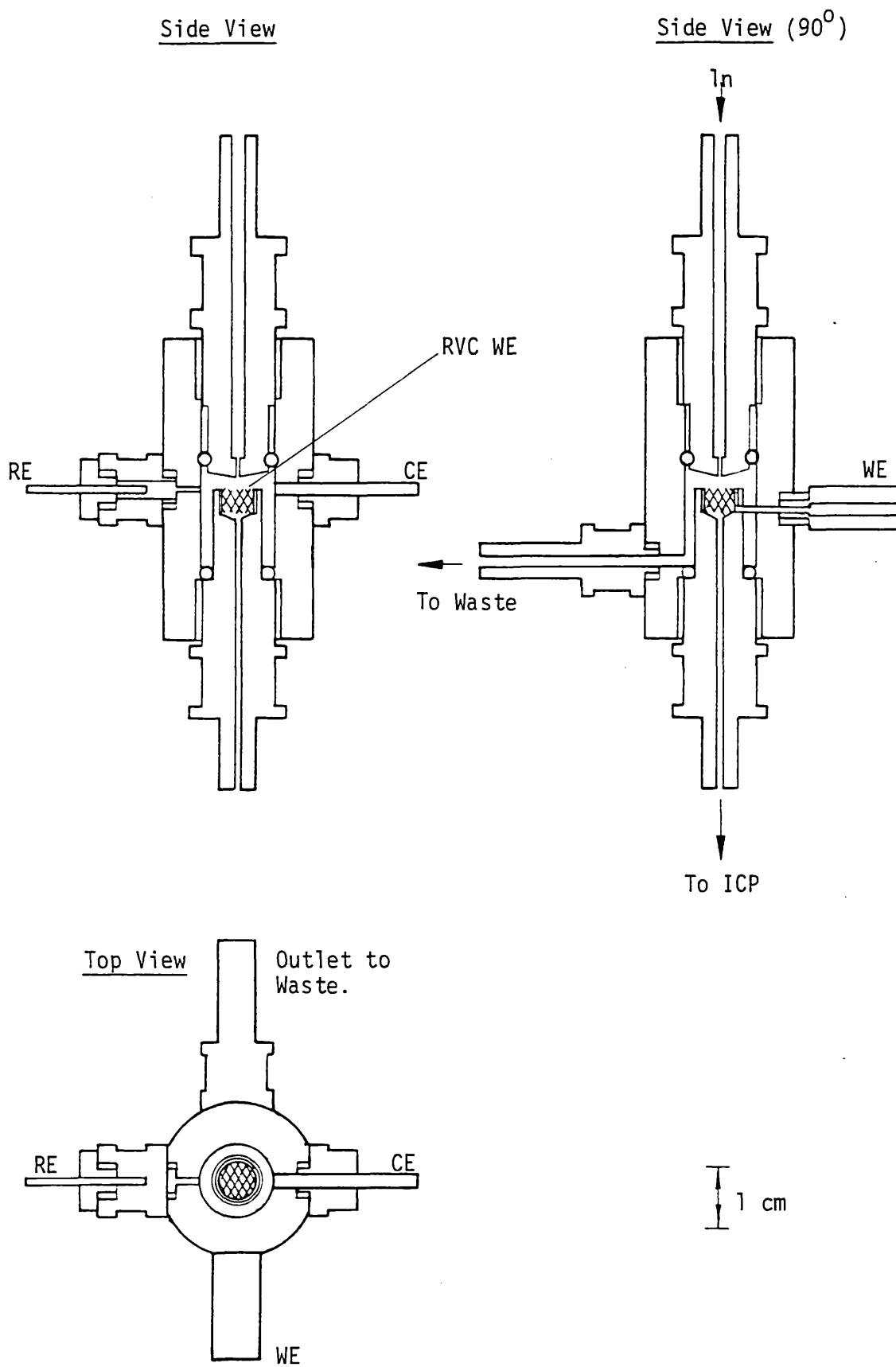


Figure 4.1 : Schematic Diagram of the RVC cell.
Actual size.

made through a small hole drilled into the plastic cup and filled with graphite pencil. This could be advanced forward gently by turning a brass screw fitted to the side of the cell if electrical contact needed to be reestablished. The solution was introduced into the cell from the top through a jet the height of which above RVC was adjustable. The CE and RE were similar to those in the concentric cup cell in nature and position. The rest of the cell construction was also similar.

4.2 Theory

The mass transfer problem through porous materials has been developed and tested for electrochemical uses by Sioda²⁰⁷ and more recently by Newman and Tiedemann.²¹¹ For the case of RVC Blaedel and Wang²⁶¹ have presented and verified experimentally the equation:

$$i_L = nFC_B v_f \{1 - \exp(-jsa^{1-\alpha} v_f Z)\} \quad 4.1$$

where n, F, C_B, v_f , and Z are as defined before;

j is a proportionality constant

s is the specific surface of the porous electrode

a is the cross-sectional area of the electrode

α is the exponent of the flow regime.

The degree of conversion, R , is defined as :

$$R = \frac{i_L}{nFC_B v_f} = 1 - \exp(-jsa^{1-\alpha} v_f^{1-\alpha} Z) \quad 4.2$$

The specific surface of the porous electrode, s , can be calculated from the equation :

$$s = (1 - \epsilon)r \quad 4.3$$

where ϵ is the porosity of the material (97% void)

r is the surface to volume ratio, (65:1)
and the specific volume flow rate i.e. flow rate per unit cross-section, q , can be calculated from the relation

$$q = v_f/a \quad 4.4$$

where upon equation 4.1 can be written as :

$$i_L = jnFC_B q^\alpha \quad 4.5$$

The RVC cell is therefore tested against equation 4.1 by making a $\log i_L$ vs $\log v_f$ plot from which α is evaluated as the gradient and the constant $jnFC_B$ as the intercept.

4.3 WE Pretreatment

The need for electrode pretreatment has been discussed in chapter 2. For RVC pretreatment procedures available are limited. Polishing cannot be done since the material is porous. Chemical cleaning cannot be done to a large extent because the necessary strong oxidising agents used such as chromic acid attacks plexiglass and turns it into an opaque white solid. Furthermore strong organic solvents such as acetone that could be used also dissolve plexiglass and cause extensive cracks of the cell body. In addition the RVC disc is fixed in place because of the necessity to maintain good electrical contact and so cannot be taken out for cleaning.

The alternative left is electrochemical pretreatment. For other forms of carbon and other solid materials the standard electrochemical pretreatment procedures have been established mainly by trial and error. However for glassy carbon a detailed

investigation into its electrochemical pretreatment has been carried out by Engstrom³⁰⁶ recently. For RVC, being a new material, there is no established pretreatment procedure at all. It was therefore necessary to investigate the effect of preanodisation; voltage dependence of a pretreated electrode; and time dependence of anodisation. Because of the similarity between RVC and glassy carbon the investigation was based on that of Engstrom. The experimental details can be found in the reference above. Only the results will be given here.

The optimum procedure for RVC is very similar to that employed when using glassy carbon; hold the potential of the WE at 1.5V (vs Ag/AgCl (1M)) for 5 minutes; change it to -1.1V and hold it for a further 3 minutes, then cyclise it 5 times between those potentials in a flowing purged solution. The limiting potentials 1.5V and -1.1V however depend on the nature of the base electrolyte. When a chloride containing electrolyte such as HCl or KCl is used potentials close to 1.5V and above liberate $\text{Cl}_2(\text{g})$ which attacks RVC and so it is safer to limit preanodisation to 1.2V. For acidic media the potential -1.1V cannot be achieved since large amounts of $\text{H}_2(\text{g})$ is liberated and besides overloading the potentiostat with electrolysis current the hydrogen gas gets trapped in the RVC pores thereby breaking electrical contact and the bubbles are quite difficult to remove.

It was found necessary before any experiment to rinse the cell with the base electrolyte and to dislodge any gas bubbles trapped in the RVC by reversing the solution flow i.e. pump the solution

into the cell through the exit and drive out the bubbles through the inlet at the top. This was more effective than using the normal flow and more convenient than using a vacuum pump.

4.4 Instrumentation and Reagents

The instrumentation used in this investigation is the same as that described in chapter 3. The only difference is the substitution of the RVC cell for the concentric cup cell. For some of the work the reagents are also the same as in chapter 3. Where differences occur the reagents and their preparations are given in full.

4.5 Test of the RVC Cell

The RVC Cell was evaluated initially using the conversion of ferricyanide to ferrocyanide reaction as in section 3:3.4. The test solution was made from stock solutions by diluting: 1 cm³ of K₃Fe(CN)₆ (0.1M), K₄Fe(CN)₆ (0.1M) mixture; 125 cm³ of KCl (0.1M), 25 cm³ of Na H₂PO₄ (0.1M); and 25 cm³ of Na₂HPO₄ (0.1M) with milli Q water to the mark in a 250 cm³ volumetric flask. This solution was 0.0004M in Fe(CN)₆³⁻, 0.5M in KCl and 0.01M in phosphate buffer. This was purged with argon as before. The operating conditions were:

Initial potential	+ 0.6V
Potential scan rate	5mVs ⁻¹
Potential scan range	0.1V
Reference electrode	Ag/AgCl (0.1M)
Solution volume flow rate	57 x 10 ⁻³ cm ³ s ⁻¹

Cyclic voltammograms were run from which the cathodic and anodic reaction potentials were obtained. The sum of these divided by 2 was found for each run of the experiment and converted to the Standard Hydrogen Electrode (SHE) by addition of the Ag/AgCl reaction potential (viz 0.222V). The mean of the $\text{Fe}(\text{CN})_6^{4-}$ reaction found was 0.220V with standard deviation of 0.008V. RVC being a recent material there is no reference standard measurement for this reaction at these conditions in the literature with which this experimental value can be compared. However using the measured value in the Nernst equation the standard potential E^0 of the reaction was calculated to be 0.241V compared to the value 0.350V in tables of standard electrode potentials. It has not been possible to corroborate and explain this anomaly yet.

Cyclic voltammograms were similarly obtained in order to identify reaction potentials of cadmium $17.8 \times 10^{-9} \text{ mol cm}^{-3}$ in KCl (0.1M) buffered at pH 7.0 as above and for copper $31.5 \times 10^{-9} \text{ mol cm}^{-3}$ in KCl (0.1M) at pH 4 buffered with potassium hydrogen phthalate (0.025M). Typical voltammograms for copper are shown in figures 4.2 and 4.3 respectively. Figure 4.3 is for copper in sulphuric acid (0.2M).

4.6 Dependence of Limiting Current on Solution Volume Flow Rate

The electroreduction of the ferricyanide ion was used once more. A 0.0004M solution of $\text{Fe}(\text{CN})_6^{3-}$ in KCl (0.5M) buffered with sodium phosphate (0.01M) was made from stock solutions as described above and purged with argon. The purging with argon was continued throughout the duration of the experiment. The solution volume

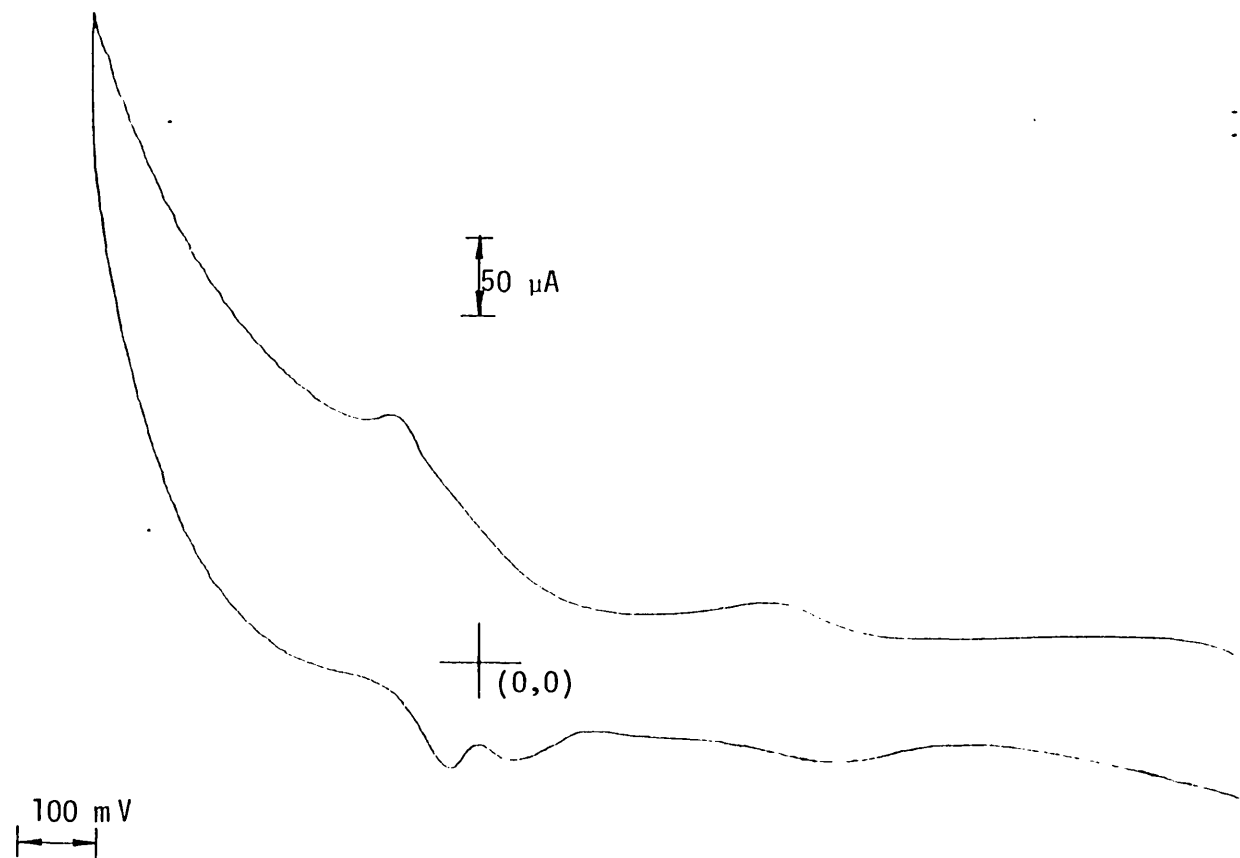


Figure 4.2 : Typical Cyclic Voltammogram for Cu ($15.8 \text{ n mol cm}^{-3}$) at $v_f = 57.0 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ measured against Ag/AgCl (1.0M)

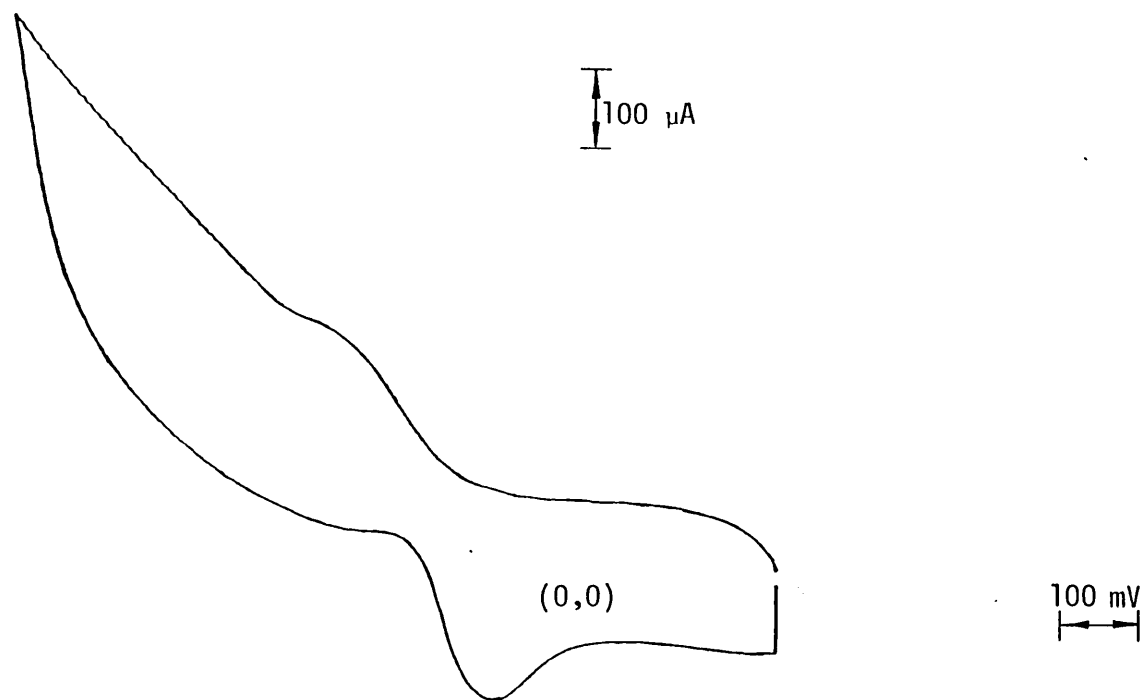


Figure 4.3 : Typical cyclic voltammogram for Cu ($3.15 \text{ n mol cm}^{-3}$) in H_2SO_4 (0.2M) at $v_f = 57.0 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ measured against Ag/AgCl (1.0M).

flowrate was varied between $8.3 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ ($0.5 \text{ cm}^3 \text{ min}^{-1}$) and $167 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ ($10 \text{ cm}^3 \text{ min}^{-1}$). For each flowrate a voltammogram was obtained by scanning the WE potential from 0.6V to -0.6V at 5 mV s^{-1} vs Ag/AgCl (1.0M). The limiting current was worked out from the voltammogram. A typical plot of $\log i_L$ against $\log v_f$ is shown in figure 4.4. This experiment was repeated over different days with different solutions. Table 4.1 shows values of the exponents of v_f obtained from these plots.

Solution	Exponent of v_f
Cd ($1.78 \times 10^{-8} \text{ mol cm}^3$ in KCl (0.1M)	0.35
$\text{K}_3\text{Fe}(\text{CN})_6$ (0.0008M) in KCl (0.5M)	0.38
$\text{K}_3\text{Fe}(\text{CN})_6$ (0.0004M) in KCl (0.5M)	0.38
$\text{K}_3\text{Fe}(\text{CN})_6$ (0.0004M) in KCl (0.5M)	0.36
$\text{K}_3\text{Fe}(\text{CN})_6$ (0.0004M) in KCl (0.5M)	0.37
$\text{K}_3\text{Fe}(\text{CN})_6$ (0.0004M) in KCl (0.5M)	0.36

Table 4.1 : Volume flowrate exponent from $\log i_L$ vs $\log v_f$.

The mean value of the flowrate index is 0.37 and has a standard deviation of 0.01 corresponding to a relative standard deviation, RSD, 2.7%. All the linear regression coefficients were better than 0.99.

4.7 The Useful Potential Range of RVC

The background electrochemical processes in aqueous solutions that yield currents which limit the useful potential range of electrode materials have been discussed in chapter 2. For established materials such as platinum, glassy carbon etc. the

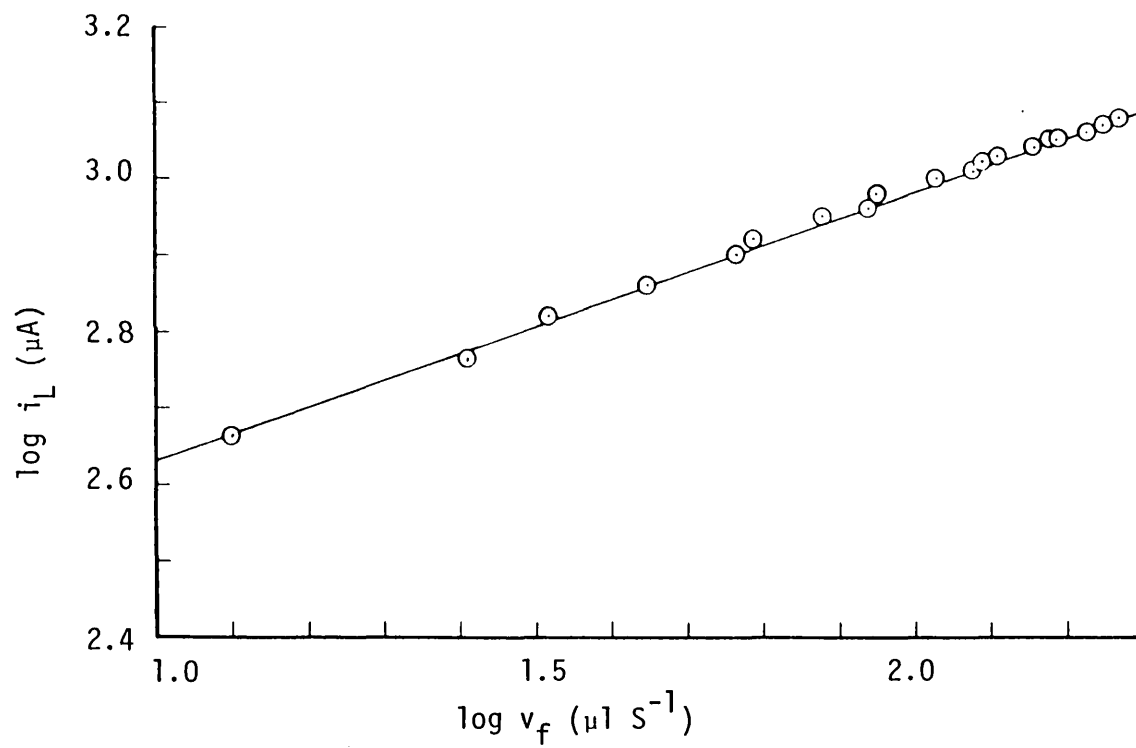


Figure 4.4 : Dependence of i_L on v_f for $Fe(CN)_6^{3-}$ (0.5mM) in KCl (0.5M) at pH 7.

limiting potentials are readily available in the literature. For RVC these had to be established.

The reagents used are summarised in table 4.2 below :

pH	Reagents in 100 cm ³ of solution
1	67 cm ³ HCl (0.2M) 25 cm ³ HCl (0.2M)
2	6.5 cm ³ HCl (0.2M) 25 cm ³ KCl (0.2M)
4	100 cm ³ KCl (0.1M) HOOC-C ₆ H ₄ -COOK (0.025M) Buffer
6.86	100 cm ³ KCl (0.1M) Na ₂ HPO ₄ (0.025M)/NaH ₂ PO ₄ (0.025M) Buffer
9	100 cm ³ KCl (0.1M) Na ₂ B ₄ O ₇ ·10H ₂ O (0.1M)
12	26.9 cm ³ NaOH (0.1M) 50 cm ³ Na ₂ HPO ₄ (0.05M)
13	66 cm ³ NaOH (0.2M) 25 cm ³ KCl (0.2M)

Table 4.2 : Solutions for potential range determination for RVC.

The stock solutions of buffers above were made as follows : potassium hydrogen phthalate (0.1M) by dissolving 5.1055g $\text{COOH-C}_6\text{H}_4\text{COOK}$ in milli Q water in 250 cm^3 flask and made to mark; Borax 0.1M by dissolving 9.5345g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ as above; and sodium phosphate 0.1M by dissolving 7.8005g of $\text{Na H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and 17.908g $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ similarly in 500 cm^3 flask.

An approximately 1M HCl stock solution was made by diluting 20 cm^3 of 36% acid (1.18 specific gravity) in a 250 cm^3 flask with milli Q water. 10 cm^3 of this was diluted in 100 cm^3 flask and standardised by titration against primary standard, NaHCO_3 (0.1M), using bromothymol blue (0.04% w/v) indicator. This acid was in turn used to standardise NaOH solution.

All solutions were made by dilution from stock when required, purged with argon, and pumped through the pretreated electrode at the volume flowrate $57 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$. The potential was scanned between 1.3V and -1.2V at 5mVs^{-1} while the current-potential trace was obtained. The potentials at which the background reaction gave currents in excess of 2% of the expected electrolyte current were noted for each pH value investigated. A plot of potential against pH is shown in figure 4.5 for the jet position 2mm above the WE with the working electrode fully flooded.

4.8 Experiments with a depositable species

Both cadmium and copper have been equally used in the investigation of this cell. However more will be reported on copper

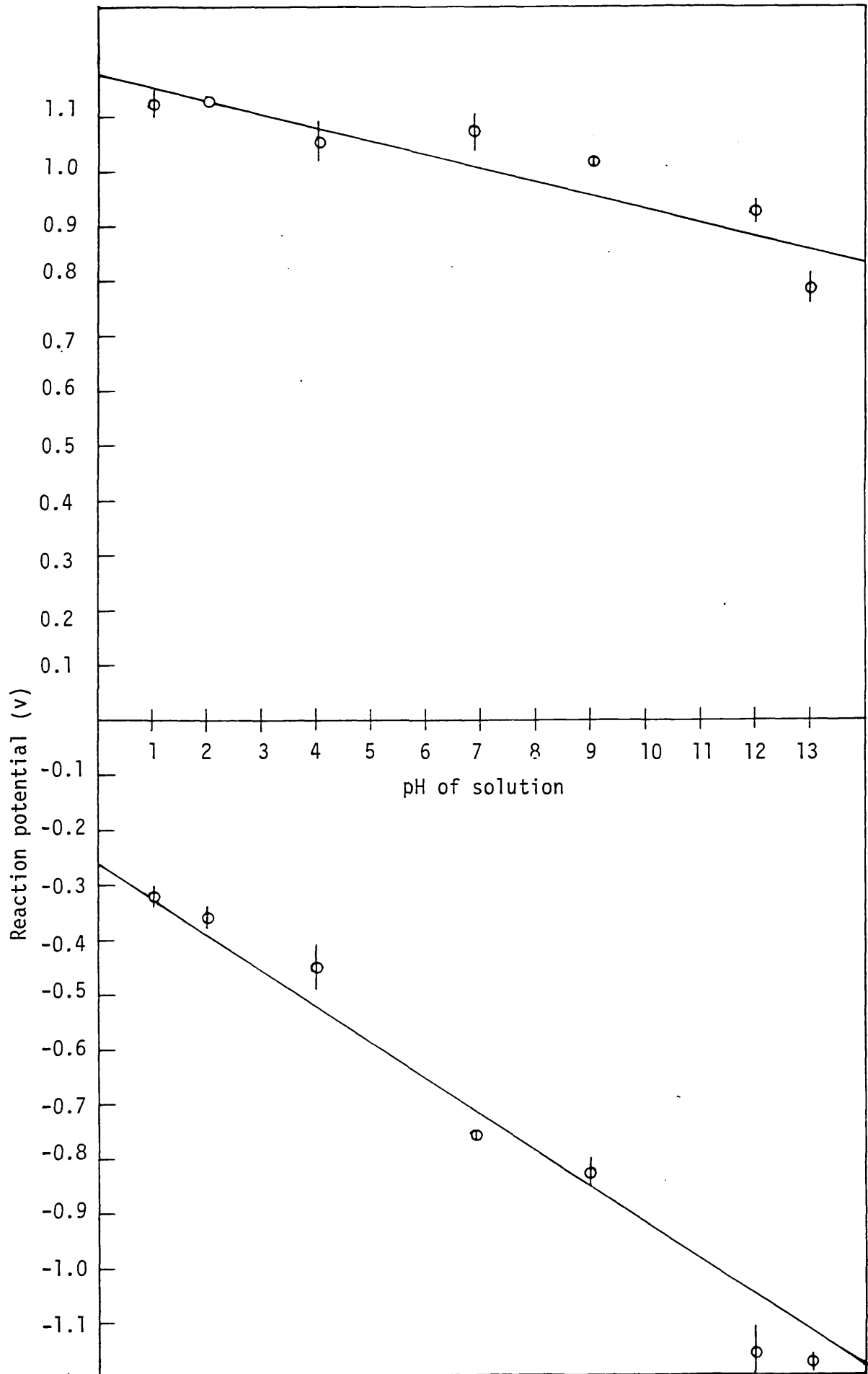
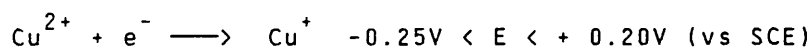
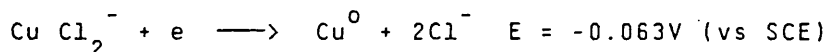
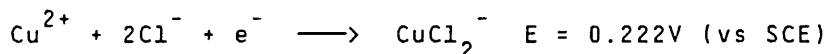


Figure 4.5 : Variation of useful potential range of RVC with pH of aqueous solution.

since its coverage with the concentric cup cell was not adequate owing to the fact that its optimum deposition occurs in solutions of low pH yet at these pH values the cathodic and range of platinum is close to the copper deposition potential. Copper itself was investigated using two different base electrolytes : KCl (0.1M); and H_2SO_4 (0.2M). The typical cyclic voltammograms have already been shown (figures 4.2 and 4.3). Copper in KCl (0.1M) shows two anodic peaks while in H_2SO_4 (0.2M) only one large peak is obtained. This is expected since the reduction and oxidation of Cu^{2+} in chloride medium occurs in two distinct steps^{307,308}:



the reverse of which are also true. This is so because the first reaction which is the rate controlling reaction step is stabilised^{309,310} through the reactions :



In the sulphate medium there is no such stabilisation. The Cu^+ formed from the reduction of Cu^{2+} is further reduced³¹¹ to Cu^0 before significant quantities diffuse off the WE. Only one peak is therefore obtained. For experiments with ICP-AES there was no significant difference between the two base electrolytes as far as signal size and the number of peaks is concerned. However better precision (RSD 3%) was obtained from the KCl electrolyte than from H_2SO_4 (RSD 5%). This is attributed to the better pH control carried out in the KCl solution. For this reason the KCl electrolyte was used for most of the experiments.

Dependence of Limiting Current on Solution Volume Flowrate

For both cadmium and copper the dependence is linear yielding a gradient that is in complete agreement with that for the non depositable species $\text{Fe}(\text{CN})_6^{3-}$ (table 4.1). Similar to the observation with concentric cup cell for a depositable species there is a significant scatter of points : figure 4.6.

ASV with Cadmium

It was necessary to find the relation between the stripping peak and concentration prior to the use of this cell for analytical purposes. This was done by varying the concentration of cadmium with the other operating conditions fixed at: deposition time 300s; solution volume flowrate $58 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$; deposition potential -1.0V; and stripping potential scan rate 200 mV s^{-1} . The base electrolyte was KCl (0.1M) as before. Figure 4.7 shows the desired relation plotted on a log-log paper. It is linear within the range of concentrations investigated, with a gradient of 0.63.

4.9 ASV Preconcentration of Copper for ICP-AES

The instrumentation and procedures of this investigation are the same as those described in section 3:3.10. Because the copper stripping signal observed with ICP-AES showed a significant variation with pH of the base electrolyte it was necessary to establish the optimum pH. The following solutions of known pH, each containing Cu^{2+} ($1.58 \times 10^{-9} \text{ mol cm}^{-3}$) as a chloride were used (table 4.3).

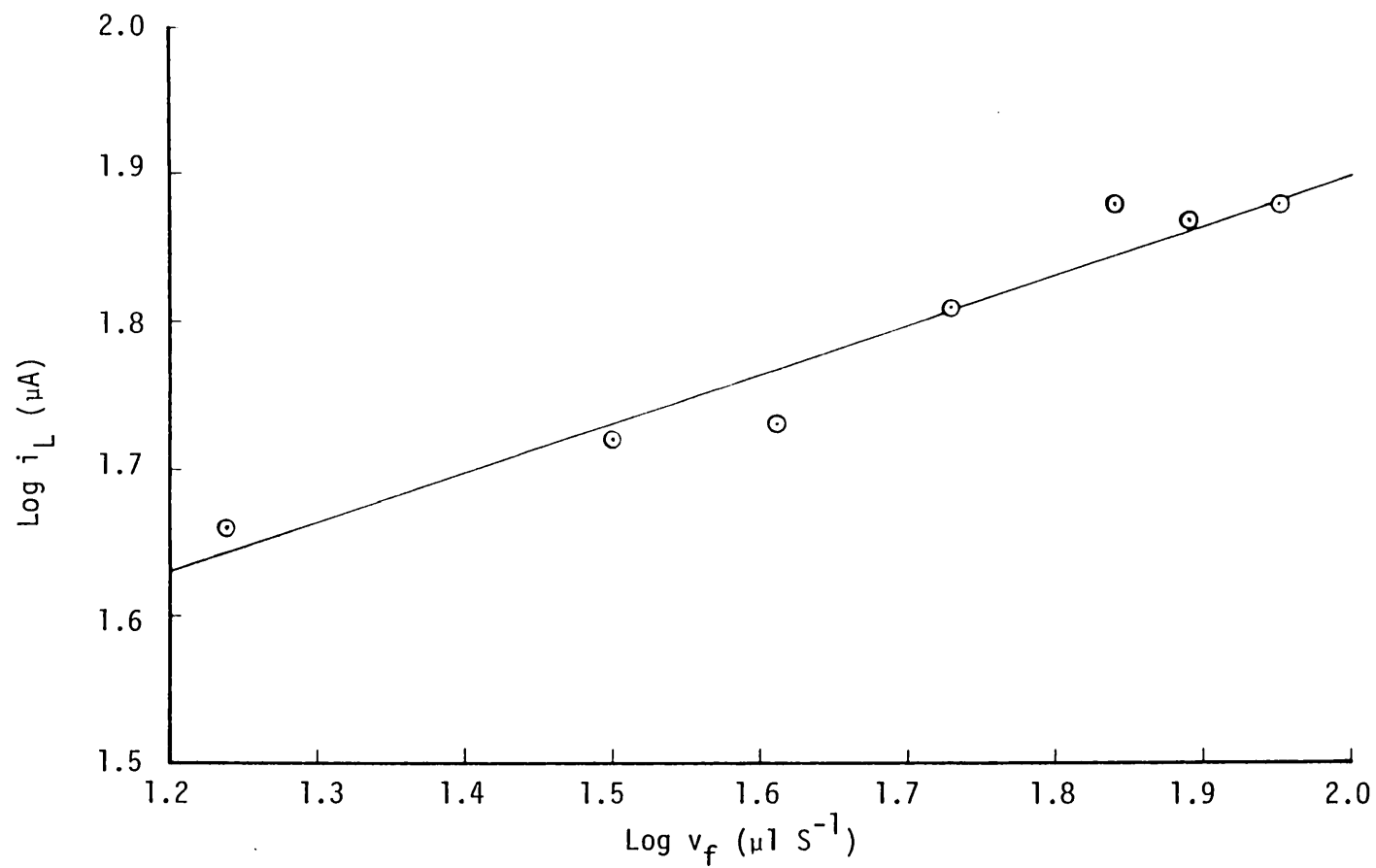


Figure 4.6 : Dependence of i_L on v_f for a depositable species Cd ($17.79 \text{ n mol cm}^{-3}$) in KCl (0.1M).

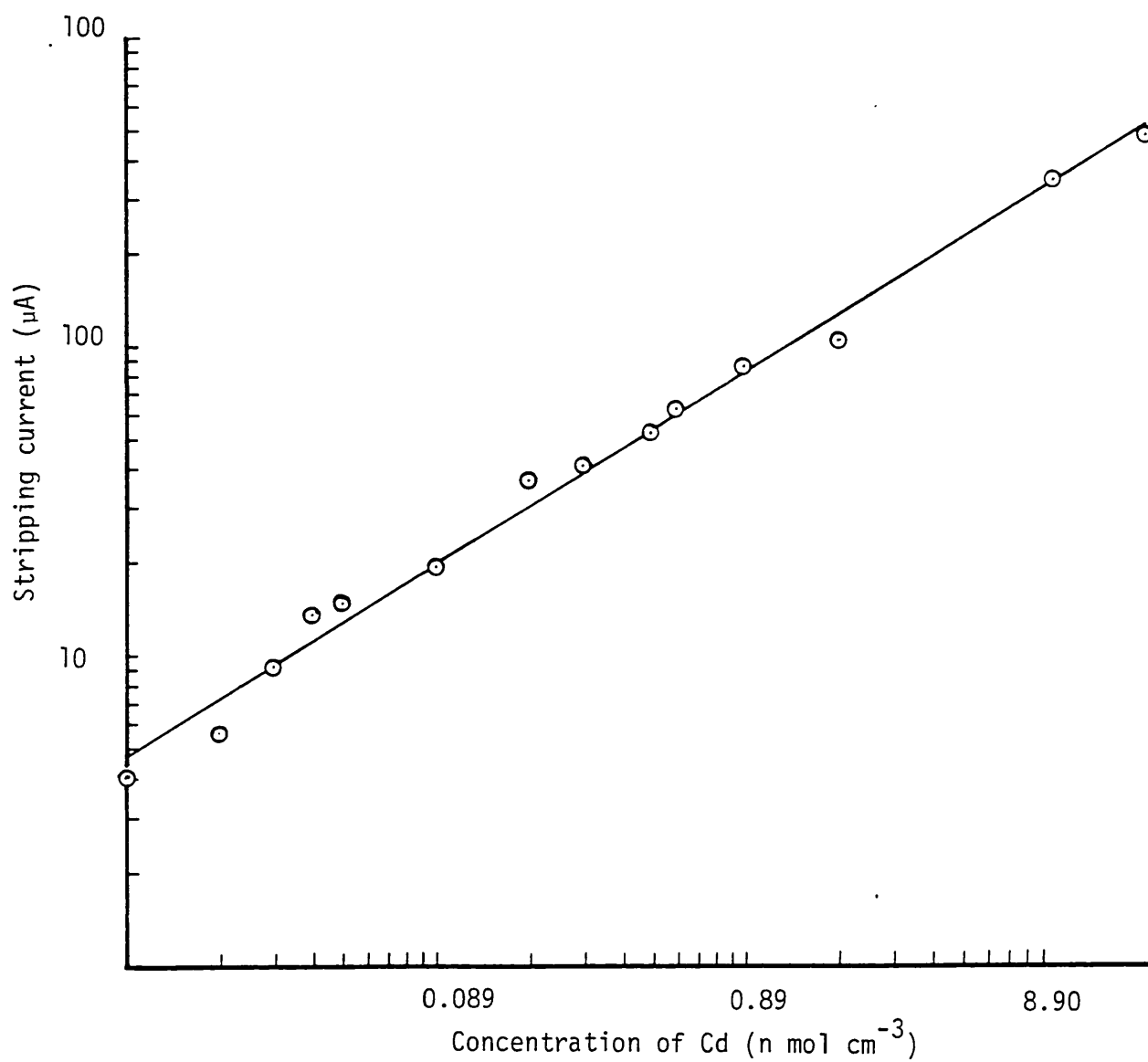


Figure 4.7 : Dependence of stripping current on concentration for Cd in KCl (0.1M) at pH 7.5.

pH	Solution
1	67 cm ³ HCl (0.2M) 25 cm ³ KCl (0.2M)
2	6.5 cm ³ HCl (0.2M) 25 cm ³ KCl (0.2M)
2.5	50 cm ³ HOOC.C ₆ H ₄ .COOK (0.1M) Buffer 38.8 cm ³ HCl (0.1M)
4	100 cm ³ KCl (0.1M) HOOC.C ₆ H ₄ .COOK (0.025M) Buffer
6.86	100 cm ³ KCl (0.1M) Na ₂ HPO ₄ (0.025M) Buffer
9	100 cm ³ KCl (0.1M) Na ₂ B ₄ O ₇ · 10H ₂ O (0.1M) Buffer
12	26.9 cm ³ NaOH (0.1M) 50 cm ³ Na ₂ HPO ₄ (0.05M) Buffer

Table 4.3 : Solutions for pH dependence of copper signals.

The final volume of solution in each case was 100 cm³.

The experimental operating conditions were :

Copper wavelength : 324.75 nm

ICP-AES : Forward RF power	1000 W
Photomultiplier power supply	1000 V
Observation height	20 mm
Coolant argon gas flow	13 l min ⁻¹
Injector argon gas flow	0.8 l min ⁻¹
Plasma argon gas flow	0.5 l min ⁻¹
Viewing slit width	35 μ m
Potentiostat : Deposition potential	-0.4V (vs Ag/AgCl)
Stripping potential scan rate	200 mV s ⁻¹
Potential scan range	0.75V
Current range	5 mA

Solution volume flowrate $57 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$

Deposition time 300 s.

Stripping signals were obtained for each solution and the blank stripping peak was subtracted. The result is plotted in figure 4.8. The optimum pH was found to be between 2.5 and 3. The rest of experiments with copper were done using KCl (0.1M) adjusted with HCl (1.0M) drops to this pH and buffered as above. The pH adjustment was checked with a pH meter. At these conditions the preconcentration factor defined and determined as in chapter 3 was 12.8.

Dependence of Signal on Deposition Time

For a given concentration of copper, at the above listed

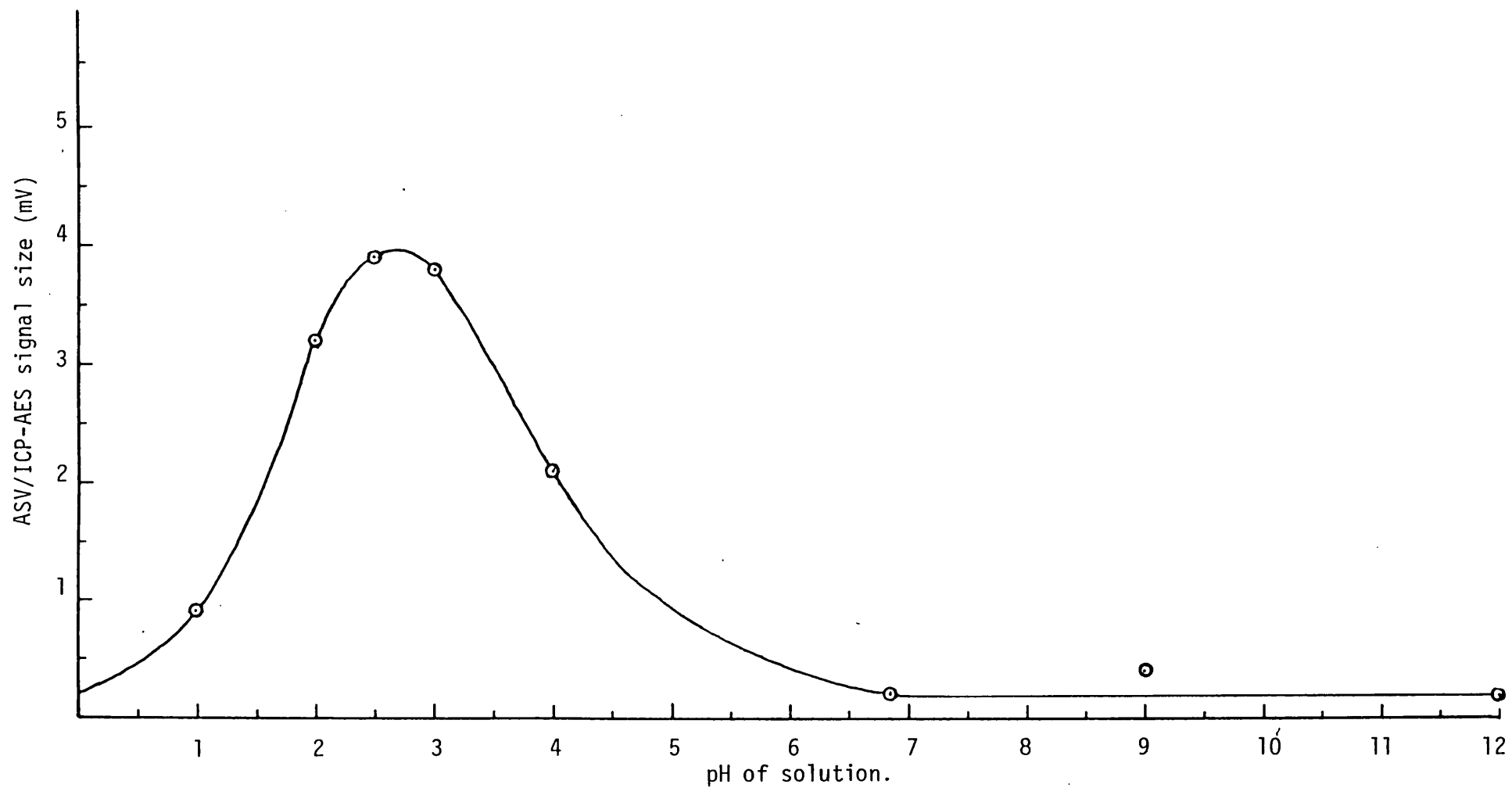


Figure 4.8 : Dependence of ASV/ICP-AES peak size on pH of solution for Cu ($1.58 \text{ n mol cm}^{-3}$)

operating conditions, the deposition time was varied between 60 and 1200 seconds. The concentration of the solution was then increased and the experiment repeated. A log-log plot of the signal against deposition time is shown in figure 4.9. It clearly establishes the upper limit of concentration for which the cell can be used.

Dependence of Signal on Stripping Potential Scan Rate

The experiment above was repeated for a copper concentration $1.58 \times 10^{-9} \text{ mol cm}^{-3}$ with the only variable being stripping potential scan rate. It was necessary to establish this dependence because the ICP-AES signal dependence on the concentration decreases, due to dilution, as the duration of release from the WE surface increases. The dependence is shown in figure 4.10. Beyond scan rates 200 mV s^{-1} there is no advantage. Below 100 mV s^{-1} there is a serious reduction of signal. All further work was therefore done at the scan rate 200 mV s^{-1} which lies on the plateau of the graph.

Efficiency of the RVC Cell

This was determined using the method described for the concentric cup cell section 3:3.10 and solution of copper as in the sub-section above with all operating conditions the same. For a fully submerged WE with the solution jet 2 mm above, the efficiency was 35.6%. The effect of the jet position above the WE was investigated and is shown in figure 4.11. There is a significant decrease as the jet is moved away from the WE.

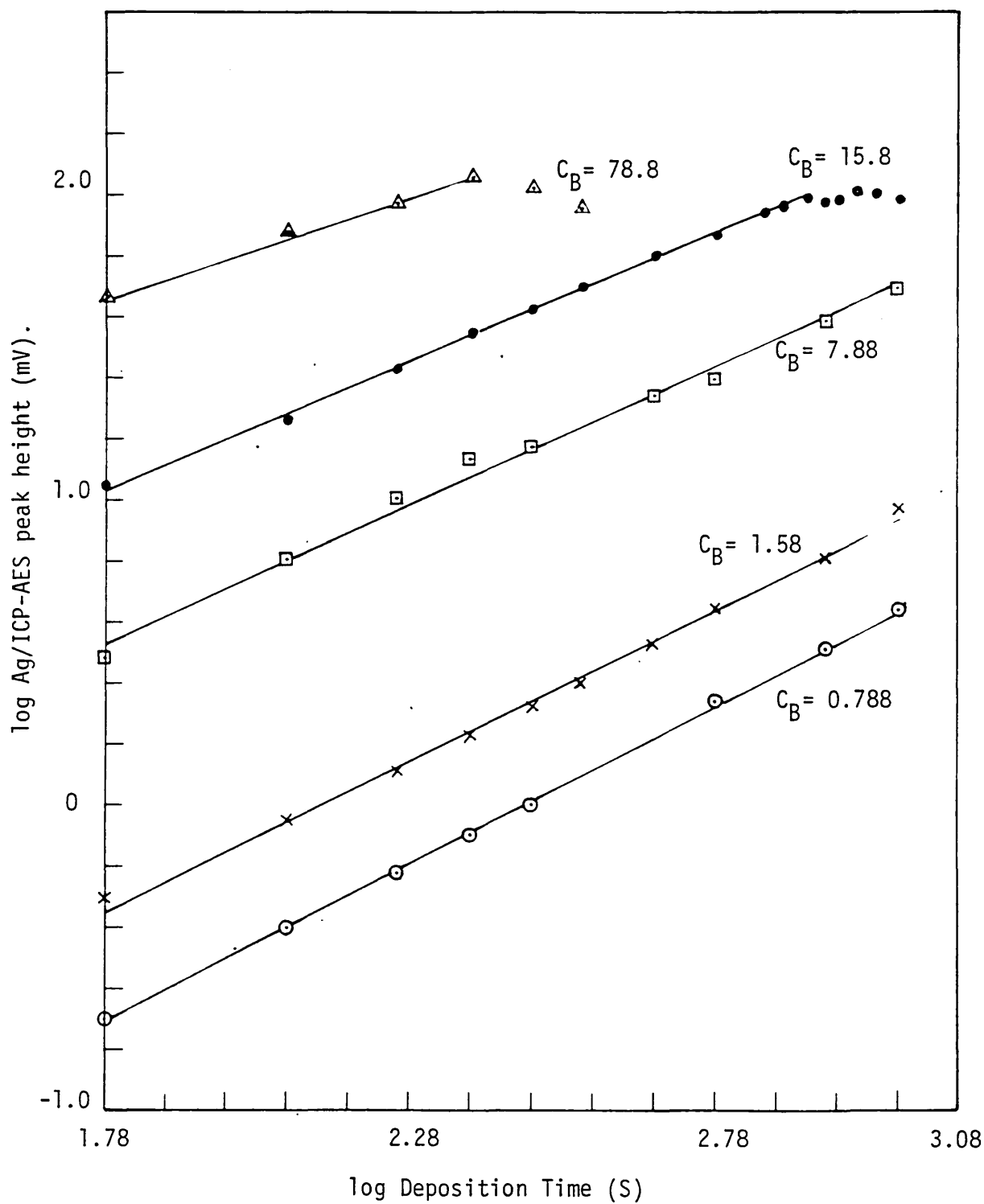


Figure 4.9 : Dependence of ASV/ICP-AES peak size on deposition time for Cu in KCl (0.1M) for the concentrations shown on curves units : n mol cm^{-3}

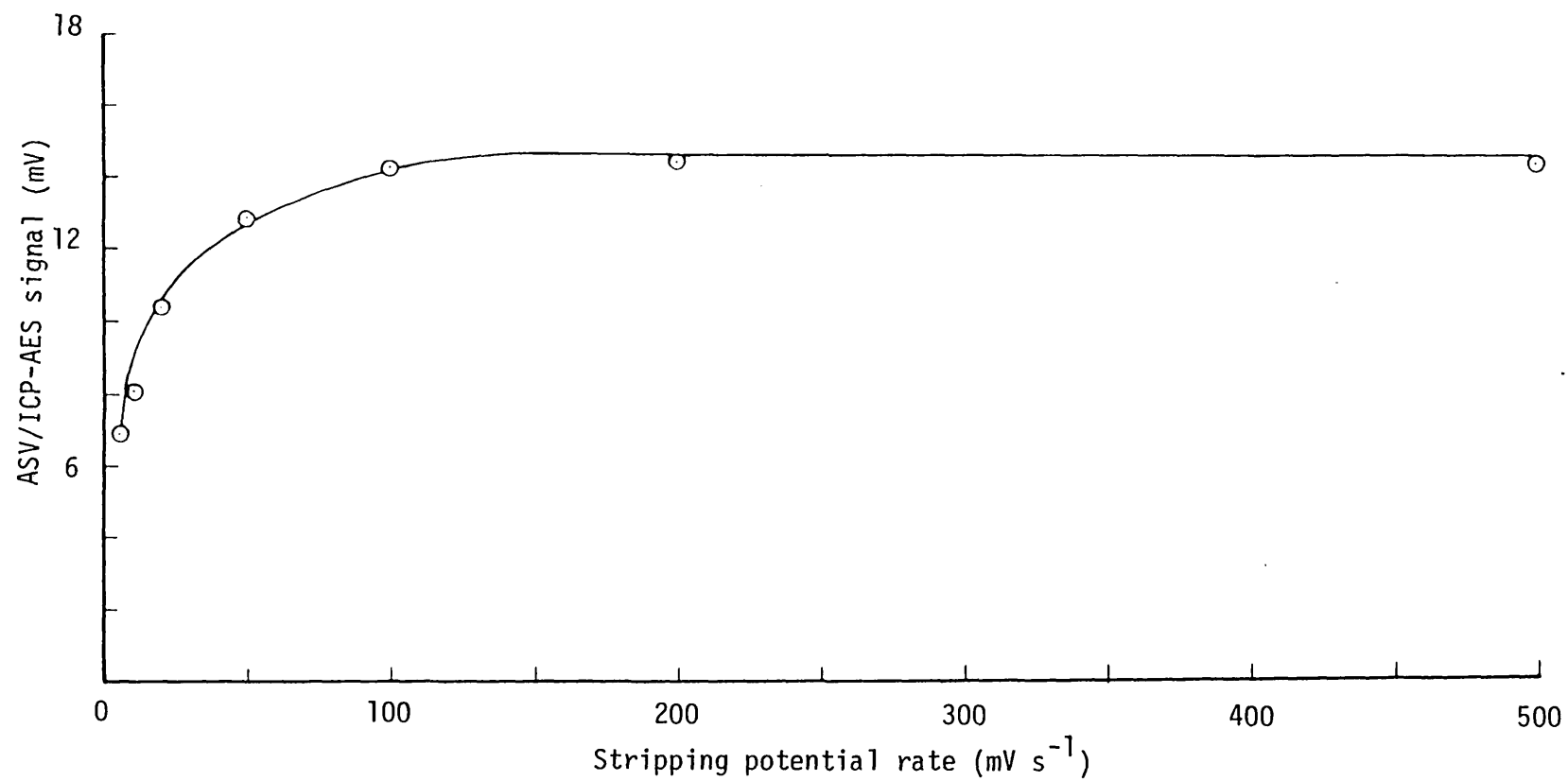


Figure 4.10 : Dependence of stripping peak size on potential scan rate for Cu ($1.58 \text{ n mol cm}^{-3}$) in KCl (0.1M).

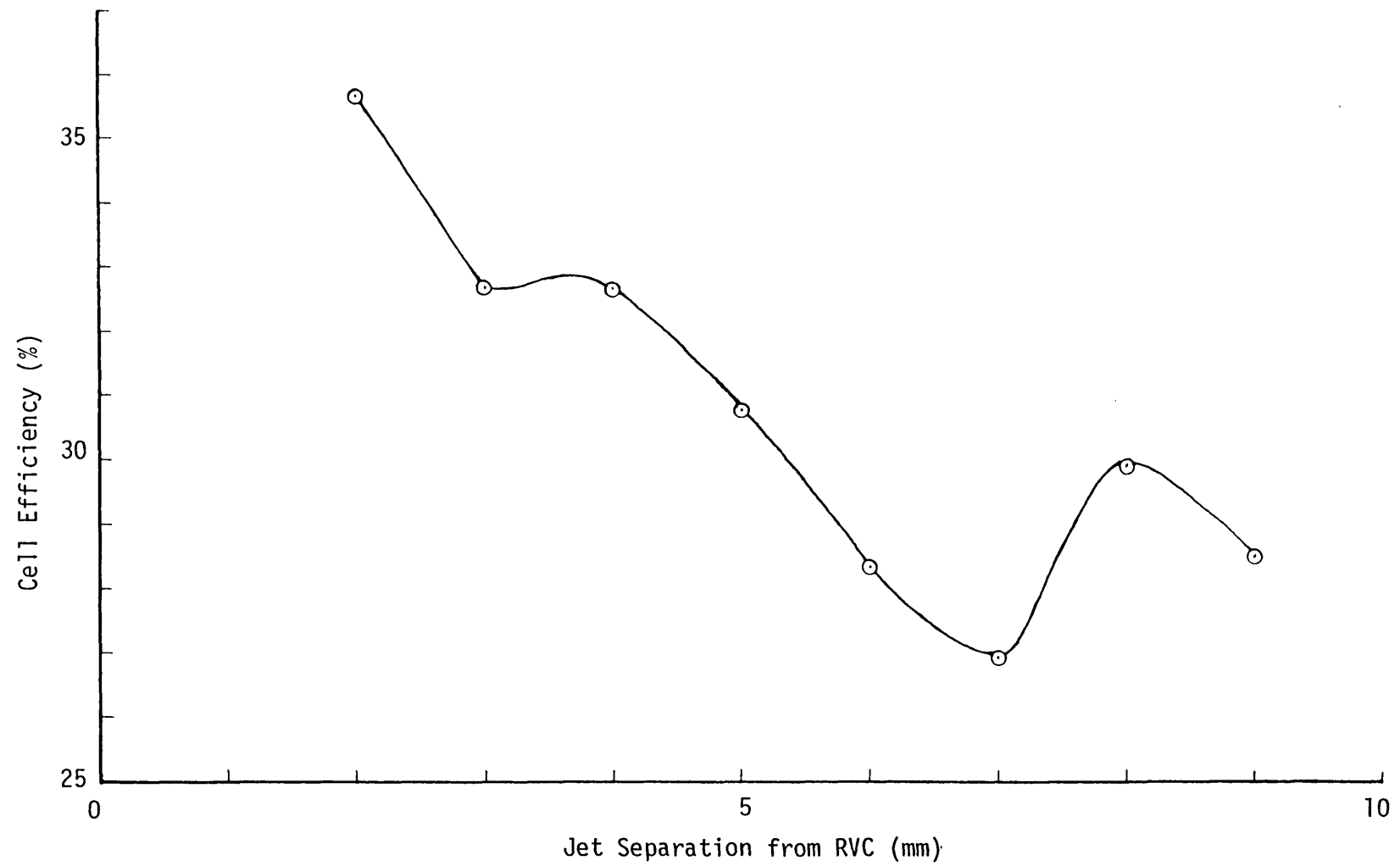


Figure 4.11 : Dependence of Efficiency with Distance of Jet from the RVC.

However the efficiency was observed to double when the solution flow rate was halved and was 100% when the solution passed through the cell drop by drop. This observation has also been confirmed by Blaedel and Wang²⁶⁴ who explained it by saying that the efficiency is proportional to the residence time of the substrate in the porous electrode. The difficulty with drop by drop sample flow is that of maintaining the RVC submerged so that it is all electroactive. Any gas bubbles that may get into the cell through the solution flow tubes quickly occupy the RVC and the experiment has to be restarted after removing the gas bubbles. A safe solution flowrate is the one used for the experiments in this section.

Precision of the ASV Preconcentration for ICP-AES

An analytical system is only useful if it can repeat its performance over a given period of time and the results of the measurements agree with each other. It was therefore necessary to establish for this system how well the measurements agree. This was done using Cu^{2+} ($1.58 \times 10^{-9} \text{ mol cm}^{-3}$) in KCl (0.1M) at pH 3.5 as in the above experiments and same operating conditions. Stripping peaks from the same solution on the same day are shown in figure 4.12 for copper. For measurements on 21 different days the relative standard deviation, RSD, defined as

$$\text{RSD} = \frac{100\sigma}{\bar{x}}$$

where σ is the standard deviation and $\bar{x}$ is the mean of the measurements, was 5.1% and for 6 measurements made on different solutions on the same day was 1.7% for that level of concentration.

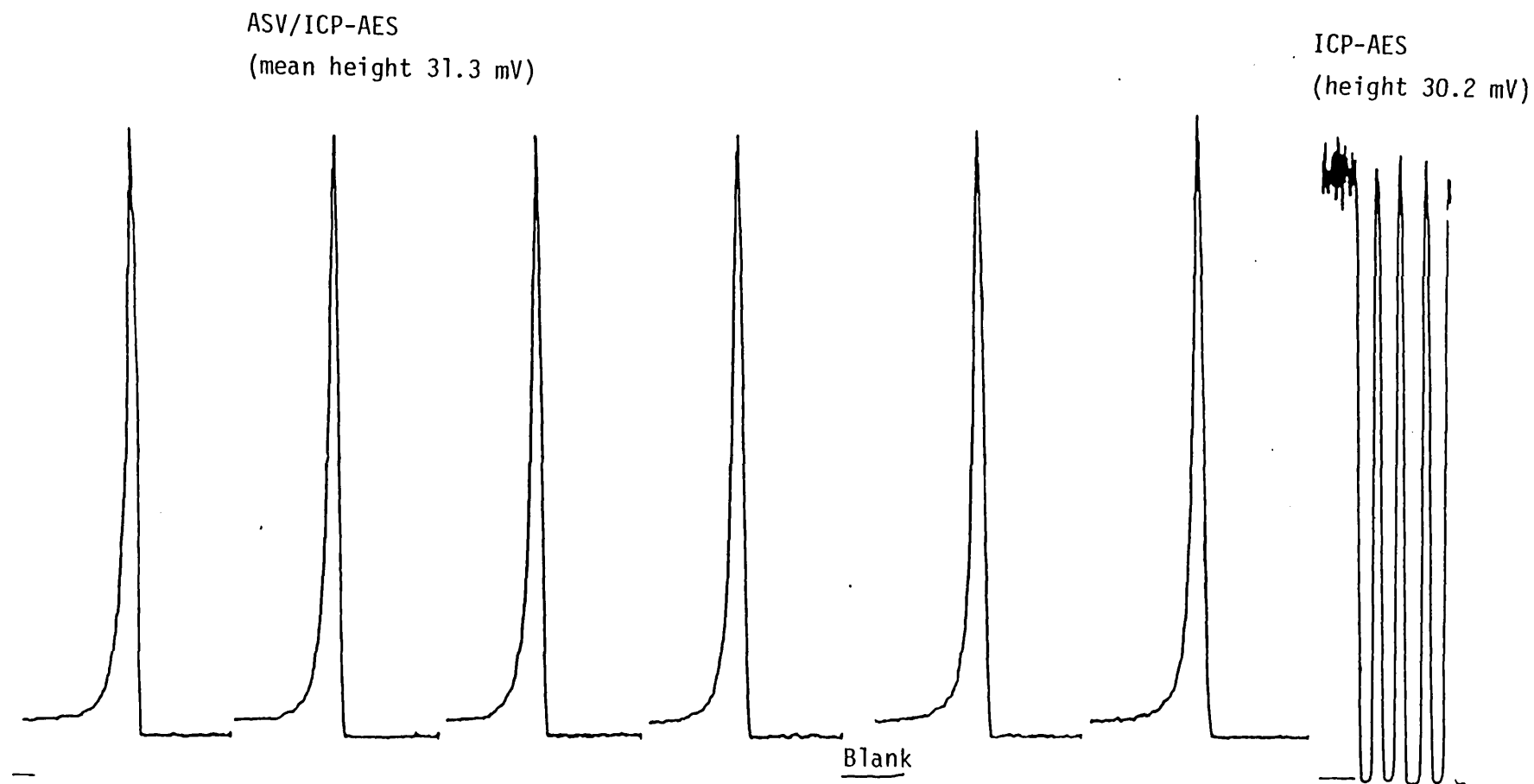


Figure 4.12 : Typical ASV/ICP-AES peaks using the RVC cell for Cu ($15.8 \text{ n mol cm}^{-3}$) in KCl (0.1M) showing reproducibility and magnitude compared to ICP alone signal for Cu ($158 \text{ n mol cm}^{-3}$)

Calibration Curve for Copper

Different concentrations of copper in the base electrolyte were made from stock solutions as described before. The purging of solutions and pretreatment of the cell were also done as described before. Experimental operating conditions were set as in the preceding sub-sections. Stripping peaks were obtained for each solution.

For solutions with copper concentration less than ($0.05 \mu\text{g cm}^{-3}$) $787.9 \times 10^{-12} \text{ mol cm}^{-3}$ rigorous purification of the base electrolyte was required. Several attempts were made to remove copper traces from it by use of ion selective resin Amberlite IRC 178. This failed because no reproducibility was achieved and the level of the blank was not reduced significantly below $31.52 \times 10^{-12} \text{ mol cm}^{-3}$. The technique that proved effective was to electrochemically "scrub" the base electrolyte using the RVC cell. To achieve this the electrolyte was pumped through the cleaned and pretreated cell at a very slow flowrate ($8 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$) with the cell operating conditions set as above for deposition of copper. At these conditions the residence time of the solution inside the RVC was long and deposition efficiency greater than 80% was possible. The cell activity was monitored by recording the current trace so that if this decreased the electrode had to be cleaned and pretreated before continuing. A significant lowering of the blank ICP-AES stripping signal was achieved this way. The use of RVC electrodes for removal of undesirable electroactive species from solutions was shown from this experience to be important. However

different cell design particularly the use of thicker RVC discs would be required for high removal efficiency and shorter electrolysis time. A similar use has recently been reported by Wang and Dewald.²⁶⁹

The final calibration curve following this cleaning process is shown in figure 4.13. It is linear over four orders of magnitude and extends down to $3.15 \times 10^{-12} \text{ mol cm}^{-3}$ for deposition time of 300 seconds. Below this concentration even the scrubbing of the base electrolyte was not effective in reducing the blank.

Analysis of a Real Sample

The ultimate test for any analytical system is with a real sample. For this cell the test was done on the analysis for copper in tap water since this could not be done by the ICP-AES in this laboratory on its own. 100 cm^3 of tap water was pipetted into a 250 cm^3 flask, 25 cm^3 of KCl (1.0M) was added, and made up to mark with milli Q water and purged with argon as before. It was pumped through the cell after the preliminary procedures as described before. The operating conditions have also been given above. Using the mean of the signals obtained from stripping the concentration in the 250 cm^3 flask was read off from the calibration line for copper (figure 4.13). The concentration in the original 100 cm^3 was then worked out and was $252 \times 10^{-12} \text{ mol cm}^{-3}$ ($0.016 \mu\text{g cm}^{-3}$). This value is higher than 132 nM obtained by Schieffer and Blaedel²⁷⁰ using ASV with collection. However the two authors checked their ASV result against that of AAS for the same sample and obtained a

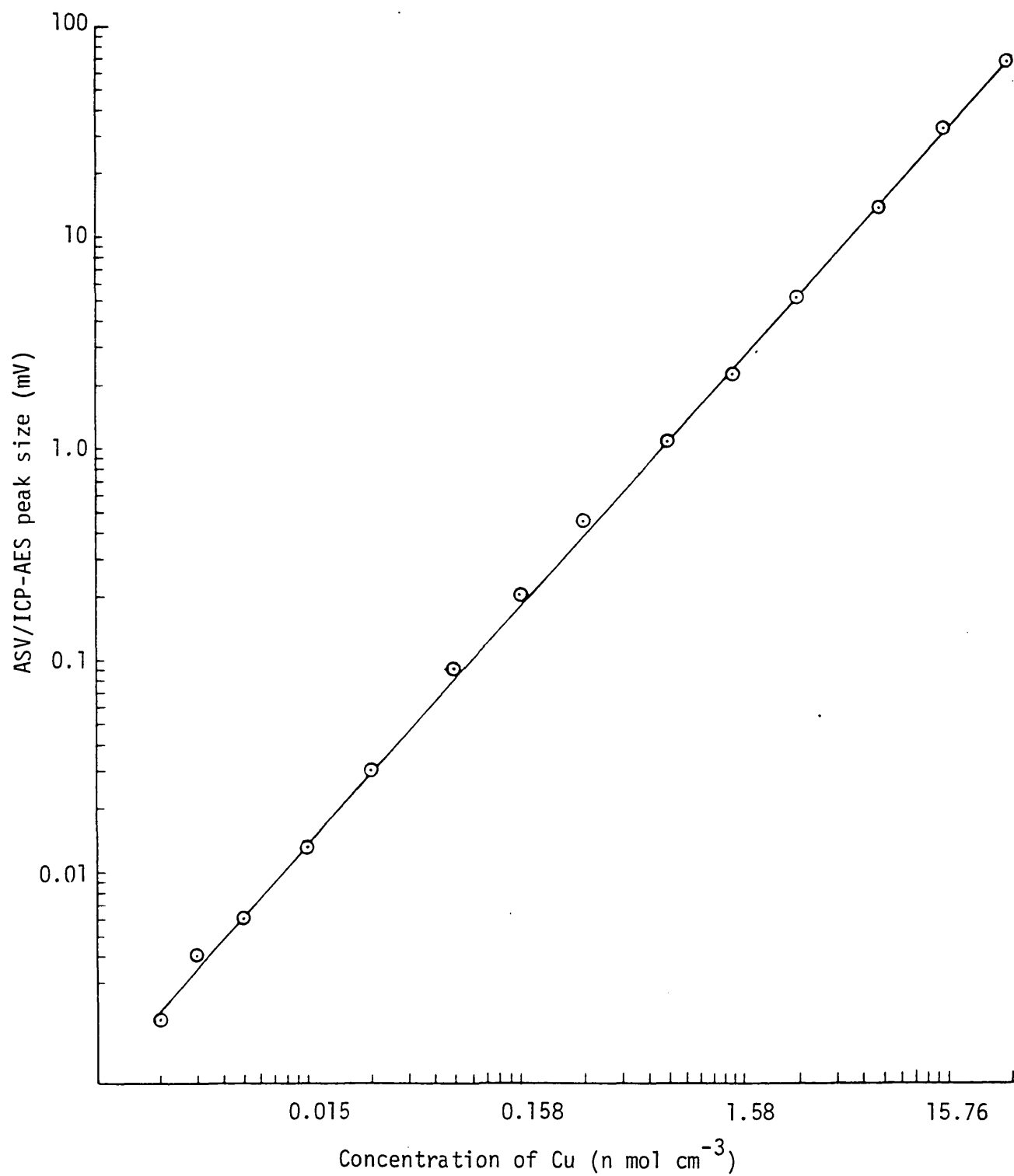


Figure 4.13 : Calibration curve for Cu in KCl (0.1M) using the RVC cell.

concentration 240 nM which is in reasonable agreement with the result $252 \times 10^{-12} \text{ mol cm}^{-3}$ of this work. It is probable that their ASV result was low because they used a solution pH 5 and this according to section 4.7 would underestimate the copper content.

It was also required to test the cell with a more difficult sample in which the analysis for copper is of particular interest. This was seawater. It was collected in cleaned plastic bottles from Brighton Harbour. The water was filtered with a Whatman filter paper Type 541 to remove particulate matter, purged with argon and pumped through the cell with experimental conditions set for copper as already described above. After 300 s deposition the cell was flushed with blank KCl (0.1M) until the sodium D line from the sodium chloride content of seawater disappeared from the plasma. This was done as above to avoid the spectral interference from the said line as discussed in section 1.2. Stripping was then done into the blank and the size of the peaks measured. The corresponding concentration was read off from the calibration graph. The mean concentration was $1.26 \times 10^{-9} \text{ mol cm}^{-3}$ ($0.08 \mu\text{g cm}^{-3}$) with RSD 3.7%. This seems to be a high copper content but since this was harbour water the value is not unexpected. The high human activity such as obtaining at the harbour is expected to raise the copper content above its natural level. In particular the sample was taken from near a power station in which copper cooling water vessels are used.

4.10 Discussion of Results

The useful potential range of RVC (figure 4.5) is slightly

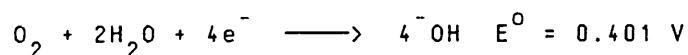
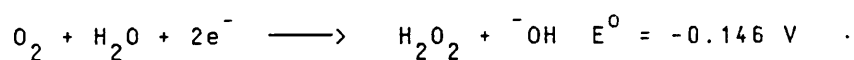
narrower than that of glassy carbon as obtained by Zittel and Miller²⁴⁹. It is wider in basic solution than in acid and can be obtained for any pH from the equation

$$E = 1.43 + 0.04 \text{ pH}$$

where E is the range measured in volts against Ag/AgCl. This equation results from plotting the difference between cathodic and anodic potentials of figure 4.5 against pH. The background currents are high compared to glassy carbon and continuously rise with its age. In this work the background was observed to rise from 18.9 μA to 83.8 μA in 60 days of use. This causes the S/B ratio for an electrochemical measurement to diminish. This rise of background has also been observed by Blaedel and Wang²⁶⁴ who attributed it to formation of surface active oxides. However this phenomenon does not affect the ASV/ICP-AES signal. One RVC disc was used in this cell for 10 months without any significant change in the ASV/ICP-AES signal. This indicates that the processes responsible for the rise in the background do not inhibit deposition or stripping and are acceptable if the measurement of current is not the analytical measurement. The useful life of RVC can therefore be extended beyond two weeks. More importantly the reproducibility from day to day is maintained.

The overall reproducibility of the system reported above is of the order of that obtainable from the ICP-AES on its own and is satisfactory. The surface activity on RVC is the least reproducible process. If the preliminary procedure of WE pretreatment is carried out carefully the stated reproducibility follows. However

sufficient purging of the solution is also required since a 10-12% decrease of signal occurs and there is a significant irreproducibility of peak size when a non-purged solution is analysed. This is attributed to changes in pH of solution to which copper is sensitive to (see ahead). Air saturated aqueous solutions contain dissolved oxygen. Oxygen dissolves in cold water at the rate 4.89 cm^3 per 100 cm^3 of water. At the electrode potentials at which copper experiments are carried out dissolved oxygen can undergo several electrochemical reactions³¹² :



The generation of the ^-OH ion resulting from these reaction changes the pH of solution. This in turn reduces the copper signal as described in section 4.7. For ASV measurements on their own better reproducibility is obtained as expected by coating the RVC with a mercury film using a mixture of Hg_2Cl_2 (0.5mM) and KCl (0.1M) at -0.75V (vs Ag/AgCl (1M)). This method, first used on RVC by Blaedel and Wang²⁶⁴, has been used with this cell for analysis of cadmium from a graphite rod residue following its use for sample introduction to the ICP-AES.

The efficiency of conversion in RVC increases as the residence time of the solution in it increases. It can therefore be increased by using slow solution flow or by using a thicker disc of RVC where the thickness is measured along the direction of solution flow. However a slow flow leads to a low convective mass transfer to the WE and a greater thickness leads to non-uniform potential

distribution and greater distortion of laminar hydrodynamic flow. In addition slow flowrates that yield high efficiency are of the order $8.0 \times 10^{-3} \text{ s}^{-1}$ ($1/2 \text{ cm}^3 \text{ min}^{-1}$) and are incompatible with the nebuliser uptake rate. This is because the carrier gas of the nebuliser must have enough force to create the desired aerosol particles as dictated by the geometry of its orifice and in addition to overcome the magnetohydrodynamic force of the plasma, and so the nebuliser has an uptake rate of the order of $50 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ which is much greater than the above for the cell. The flowrate through the cell ($57.0 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$) used for the experiments was therefore a compromise between the requirement of the ICP-AES and that of ASV. The corresponding conversion efficiency is higher than obtained from conventional electrochemical cells and was satisfactory. Its increase as the solution jet is moved closer to the WE is attributed to the fact that closer to the WE the solution jet has enough force to enable it to spread, on impact with the RVC, along the surface normal to the direction of flow and so the substrate is exposed to all the reactive surface of the electrode. The undulations in the curve are attributed to inaccuracy in the screw thread that is used for positioning the jet above the RVC. At the points of undulation the jet is off the central axis of the RVC causing spreading to be available only to one side of the surface.

For copper in KCl (0.1M) base electrolyte the Stripping Signal is greatly affected by the pH of solution (figure 4.8) and copper experiments must be done in the pH range 2-3.5. This is attributed

to the fact that in basic solution the Cu^{2+} ion is removed as an insoluble oxide $\text{Cu}(\text{OH})_2$ hence is not available for deposition. This process also occurs³⁰⁹ in very acidic solutions ($\text{pH} < 2$) owing to the electrolysis of water which liberates OH^- ions at the diffusion layer then the pH within the layer can be as high as 9 and copper is once more removed as an insoluble oxide. For acceptable reproducibility it was therefore important to do experiments under correct and constant conditions for copper.

From the dependence on deposition time (figure 4.9) it can be seen that the stripping signals are limited by size to 100mV. Using the flowrate ($57 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$) the efficiency (35.6%) and the corresponding deposition time (200 s) for the solution concentration $78.79 \times 10^{-9} \text{ mol cm}^3$ the copper deposit corresponding to this limit is 20.6 μg . This need not cause concern because it is well above what can be deposited from trace concentrations for which the cell is designed. The quantity, Q , of electricity demanded by 20.6 μg of Cu^0 on stripping can be calculated from Faradays laws of electrolysis expressed as :

$$Q = \frac{m}{M} nF$$

where m is the mass of the species, M is its relative atomic mass and the other symbols as defined before. It is $62.65 \times 10^{-3} \text{ C}$. Since

$$Q = it$$

where i is the current and t is the time taken to strip, at stripping scan rate of 200 mV s^{-1} t is of the order of 1 second. The current demand of this process is therefore in excess of 60 mA and the limit in figure 4.9 is caused by the potentiostat which displays an overload message at 10 mA current.

The dependence of the stripping signal on scan rate arises because of dilution. When the WE deposit is stripped slowly at a fixed solution flowrate the volume of solution, low in the substrate content, that has flowed in the duration of stripping is high. The substrate is therefore diluted. When the scan rate is increased the duration of stripping decreases. A small volume flows and the substrate is concentrated hence the increase in the size of the signal. No further advantage is obtained beyond scanrate 200 mV s^{-1} owing to finite time required by the process of dissolution on its own. The higher scan rates were not therefore used in order to avoid the high charging currents they generate. The relationship is similar to that obtained with the concentric cup cell.

Within the range investigated the calibration curve for copper is linear extending to two orders of magnitude lower than the ICP-AES alone can achieve in the named conditions. The linearity down to such low concentrations has also been observed by Dewald and Tougas in their recent paper²⁷² in which they investigated the hydroquinone reaction of concentration between 10^{-8} and 10^{-5} M . Lower limits can be achieved with longer deposition times than 300 seconds and the limit is set by the purity of reagents used and the level of cleanliness of the environment within which the analysis is done.

It can be concluded therefore that the RVC cell achieves better detection levels with the ICP-AES and achieves shorter deposition times yet retains the quality of results associated with

ICP-AES. It is a much cheaper cell to fabricate than the concentric cup cell. It can be used for electrochemical measurements on its own but then its useful life is limited by rise in background to only a few weeks. This however is not a problem since RVC is a cheap and disposable material.

CHAPTER 5.
THE ASV/ICP-AES INTERFACE

5.1 The Problem

The role of a sample introduction system in ICP-AES has been mentioned in section 3:3.10 where a description of the system used in this work is also given. The experimental operating conditions of the system are set by the requirements of the plasma and optimised by the procedures already mentioned. The plasma requires the sample in a form of aerosol of particle size $5\text{ }\mu\text{m}$ in diameter or smaller so that it can be desolvated and atomised and excited or ionised without a significant change in the plasma thermodynamic characteristics. It also requires the sample to have a residence time in the plasma long enough for the said processes to occur and attain completion or equilibrium. The required residence time is in the range 1-2 ms for a plasma operating at 1.2kw RF forward power. Already mentioned is a requirement to overcome the magnetohydrodynamic force so that the sample can travel through the plasma where the required processes occur. The resulting optimum experimental operating conditions for the sample introduction therefore are that the injector gas flow rate is typically $17\text{ cm}^3\text{ s}^{-1}$ and the pressure is $2 \times 10^5\text{ Nm}^{-2}$. The sample is then aspirated through the nebuliser at the rate $30 \times 10^{-3}\text{ g s}^{-1}$.

Two main problems arise after aspiration : dilution; and the efficiency of aerosol transport to the plasma. The use of ASV in ICP-AES is essentially a flow injection³¹³ type measurement. The sample band after stripping should therefore travel in the carrier stream without further mixing, spreading or dilution along the way. This is not possible where the stream has to pass through a dual-

tube spray chamber where mixing and separation of aerosol particles occurs and contact with large surface is increased. Considering the RVC cell and for Cu^{2+} ($15.76 \times 10^{-9} \text{ mol cm}^{-3}$) in H_2SO_4 (0.2M) at the experimental conditions for deposition (chapter 4) the typical limiting current is 61.8 μA . For a 300s deposition time and using equation 1.6 this corresponds to 6.1 μg of Cu^0 . On stripping this redissolves in a solution of the volume of the electrode viz $134 \times 10^{-3} \text{ cm}^3$ resulting into a concentration of $714 \times 10^{-9} \text{ mol cm}^{-3}$. This solution is then aspirated and nebulised into the spray chamber which has a volume 296 cm^3 . A dilution of the order 300 fold is therefore imposed.

The other problem - efficiency - defined as :

$$\frac{\text{amount of sample reaching the plasma}}{\text{amount of sample aspirated}} \times 100$$

was determined for this system by collecting the aerosol with anhydrous calcium chloride packed in a U tube and put in place of the plasma torch when the experimental conditions were set as in Chapter 3. The increase in weight was noted. It corresponds to 1.92% efficiency.

The situation in which great care is taken to obtain a substrate deposit then it is diluted 300 fold and 98.08% of it goes into a waste drain is unsatisfactory. The first attempt to minimise these two problems resulted in the use of a cyclone spray chamber in place of the dual-tube chamber. The operation of the cyclone chamber is that the aerosol is introduced tangentially into the chamber then it is forced to flow spirally downwards for the

heavier particles and upwards for the small and desired particles. The chamber was of volume 220 cm^3 and transport efficiency 3%. This was not a significant improvement.

The problem that remains is of interfacing the ASV cell with the plasma. In the light of the above situation the departure from the use of the conventional nebuliser/spray chamber configuration for the ICP-AES as described was imperative. What was required was a device with the following desirable characteristics :

- i) is a metering dispenser for volumes of the order 100-200 μl ,
- ii) dispenses the solution in form of aerosol of droplet size less than 5 μm .
- iii) Operates by keeping a continuous flow of argon gas while the metered solution is injected into the stream from a separate inlet which can be closed independently.
- iv) Operates from a compressed argon line at cylinder pressure $2 \times 10^5 \text{ N m}^{-2}$,
- v) fits directly to the cell and close to the plasma,
- vi) chemically compatible with aqueous solutions used in electrochemistry,
- vii) Easy to grip, simple actuation for sample injection, leak proof, and occupies little space.

Such a device precludes the use of extensive tubing and yet is capable of producing the required size of aerosol from the operating conditions of both the ASV and ICP-AES systems without need of a large size spray chamber. The device was designed and made. It was called a "metering spray valve" since it admits a measured volume of solution, nebulises it and has a one way flow

action.

The relationship derived by Nukiyama and Tanasawa³¹⁴ for the generation of aerosols by flow gas through orifices :

$$d_s = \frac{585}{V} \left(\frac{\sigma}{\rho} \right)^{0.5} + 597 \left\{ \frac{\eta}{(\sigma \rho)^{0.5}} \right\}^{0.45} \left\{ \frac{10^3 Q_i}{Q_g} \right\}^{1.5} \quad 5.1$$

where d is the aerosol mean diameter (μm)

V is the velocity difference between the gas and solution flows (m s^{-1})

σ is the surface tension of solution (dyn cm^{-1})

ρ solution density (g cm^{-3})

η is the solution viscosity (p)

Q_i volume flow rate of liquid ($\text{cm}^3 \text{ s}^{-1}$)

Q_g is volume flow rate of gas ($\text{cm}^3 \text{ s}^{-1}$)

has been used to predict aerosol particle size issuing from the metering spray valve.

5.2 The Metering Spray Valve

Figure 5.1 is a schematic diagram of this valve. The body is made of Kelaf a material superior to teflon in mechanical strength, chemical inertness and temperature response. The tip consists of two orifices : the outer one is 0.3 mm in diameter and is for outflow of argon gas; the inner one is 0.2mm in diameter and is for the solution outflow. Figure 5.2 shows the location of the inner orifice which is lower than the outer one so that the aerosol issuing from it is enclosed in a jacket of argon whose flow is

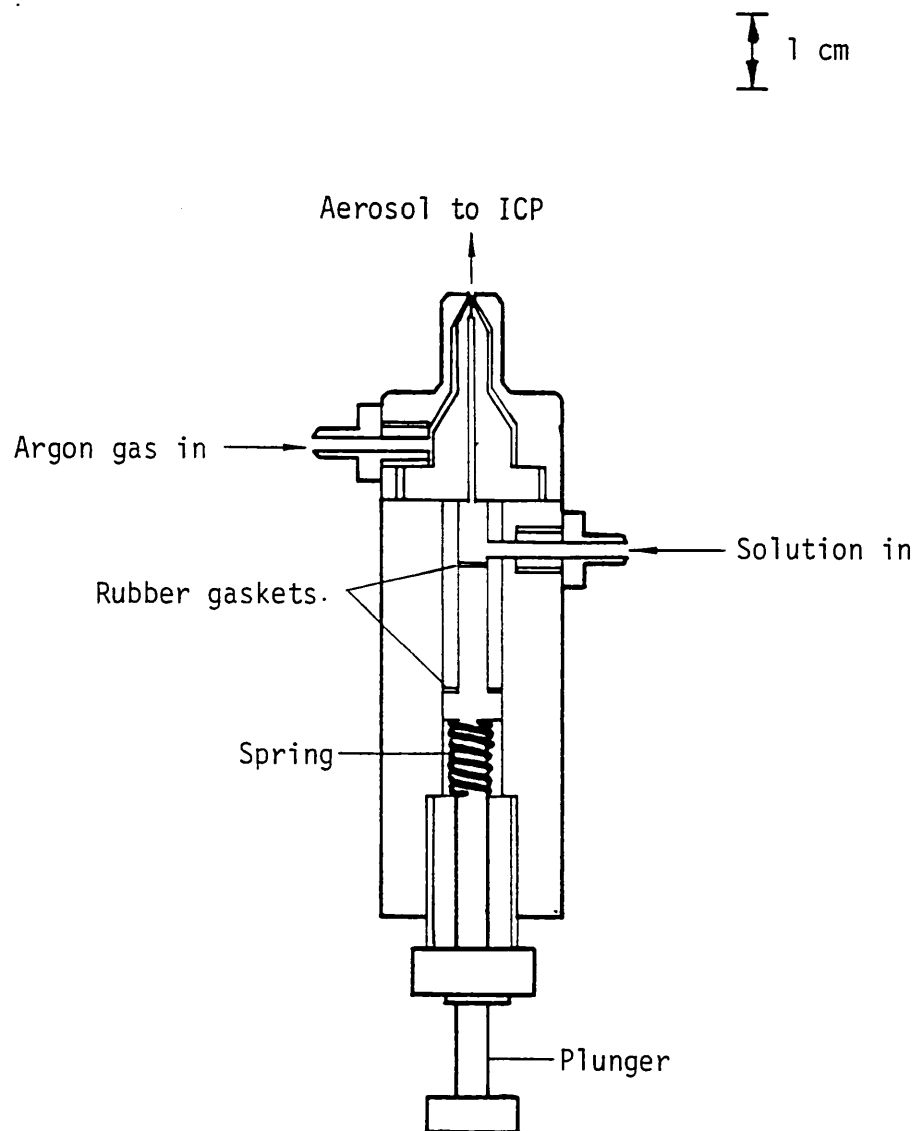


Figure 5.1 : Schematic diagram of the metering spray valve.
Actual size.

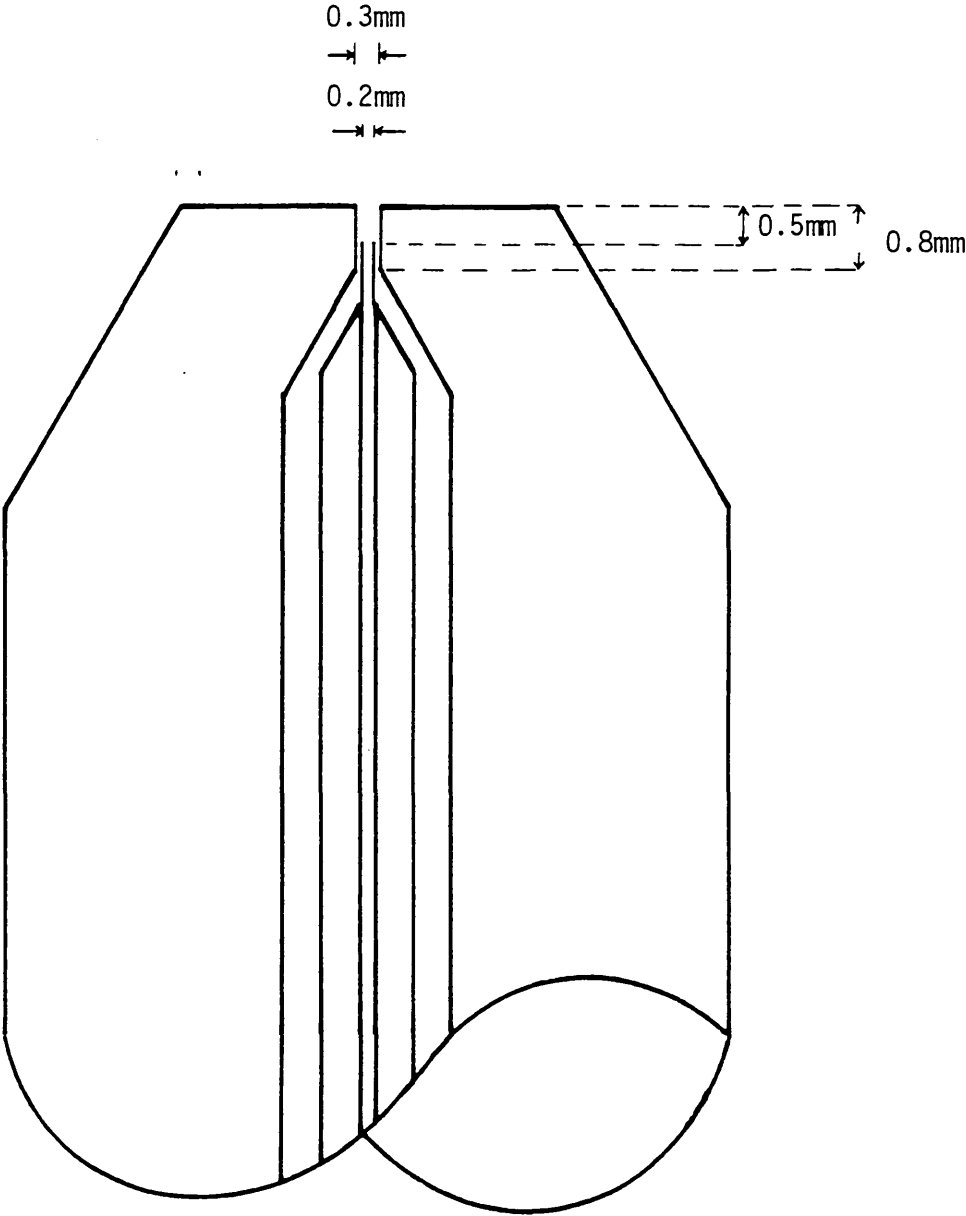


Figure 5.2 : Location of exit orifice of metering spray valve.

laminar and has parallel edges at the exit. The particles that are too heavy to move with the stream fall out of the protective jacket and are collected by impaction down the stream at the surfaces of the Y-shaped chamber from which they flow to waste. The light particles continue with the gas stream to the plasma. At the injector gas flow rate $17 \text{ cm}^3 \text{ s}^{-1}$ and pressure $2 \times 10^5 \text{ N m}^{-2}$ the velocity of argon at the exit is 235 m s^{-1} and the solution uptake rate was measured to be $50 \times 10^{-3} \text{ s}^{-1}$. The plunger that expels the solution is made of a steel rod with a teflon head and rubber gasket. Its forward action comes from a spring behind it strong enough to overcome $4 \times 10^5 \text{ N m}^{-2}$ pressure. It is mounted on a standard screw thread 26 turns per inch so that the volume of solution can be set by advancing it forward or backwards.

The accompanying glass spray chamber is shown in figure 5.3. The Y shape was chosen so that one end was the inlet, the other two outlets for the desired aerosol (upper) and waste (lower). The angles of the Y were chosen so that gravity would assist the run off of the condensed particles down and the momentum of the gas stream would not drive the condensed liquid up the incline to the plasma. Both inclines were 30° established by trial and error.

The cell and the spray valve were connected with an adapter and the spray valve was similarly connected with the Y chamber.

5.3 Operation of the Metering Spray Valve

When electrochemical deposition is in progress the solution

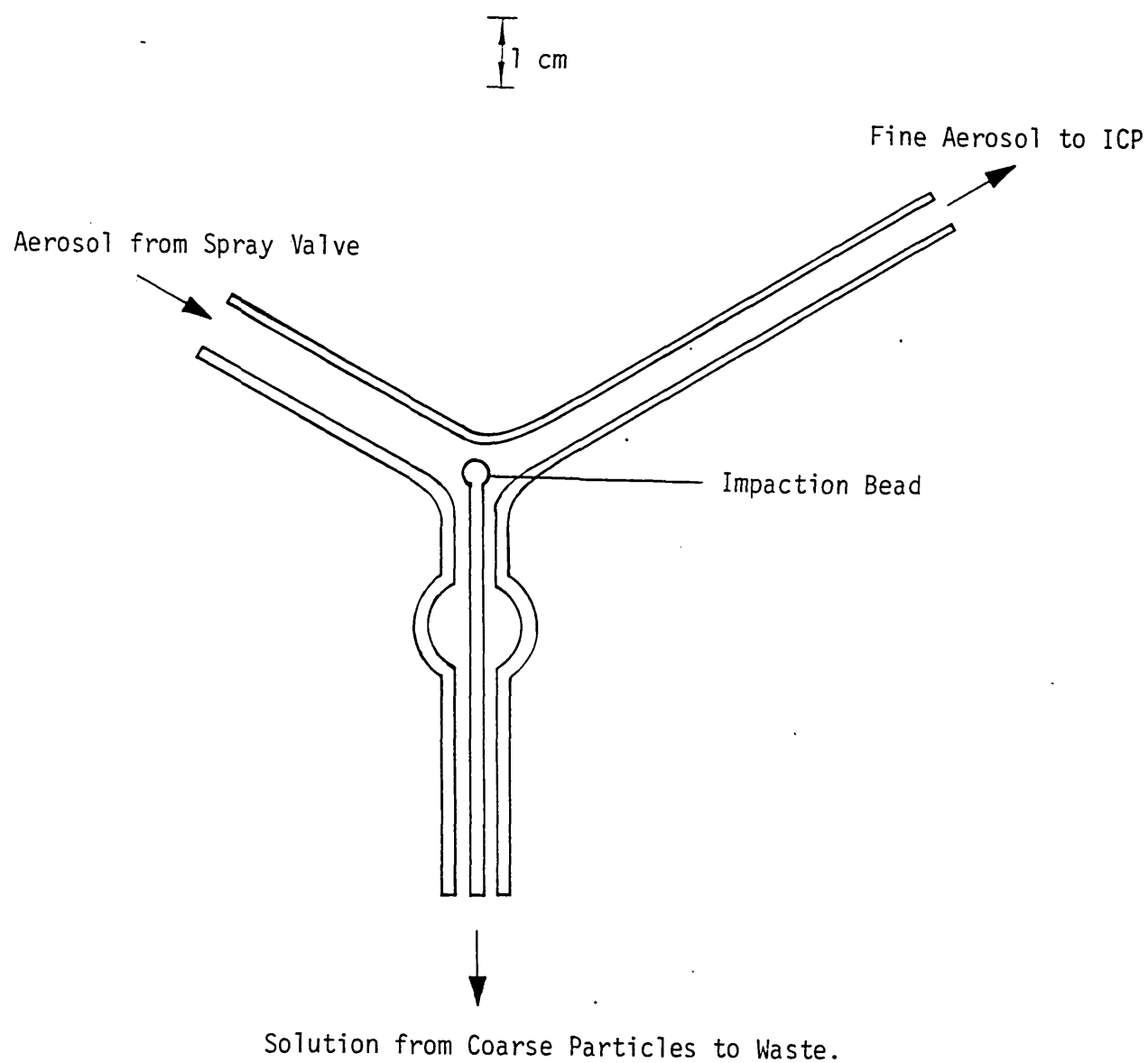


Figure 5.3 : The Y shaped Spray Chamber. Actual size.

flows through the cell into the spray valve as in the operating experimental conditions described previously (section 4.9) and is nebulised. The volume of the spray valve is set to correspond with the electrode volume of the cell and the plunger is locked at the "argon" position. In this position the spray valve is operating as an ordinary nebuliser which facilitates checking of the viewing wavelength of the species without affecting the electrochemical process. At the end of the desired deposition time the plunger of the spray valve is released. The solution flow through both the cell and the spray valve stops and the volume of the latter is emptied. Stripping is then done in the standing solution. The plunger is pulled back to original position, the flow of solution resumes, and the spray valve volume fills up with the required now concentrated solution. If the solution flow rate through the cell is $50 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ for the RVC cell this takes less than 2s. The plunger is released again. The concentrated solution is expelled, nebulised and the signal obtained. The plunger is then pulled back for another deposition process to proceed. This is the initial stage. Throughout these events the argon flow through the outer orifice is maintained at the operating experimental conditions.

5.4 Experiments with the Metering Spray Valve

It was of foremost interest to find out if this device would work at all as a departure from conventional nebuliser/spray chamber system and the quality of signals it would give. A solution of Cu^{2+} ($15.8 \times 10^{-9} \text{ mol cm}^{-3}$) in KCl (0.1M) was used under the experimental conditions already described. When used as a

continuous solution flow nebuliser the typical analytical signals obtained are shown in figure 5.4 for the spray valve. The spray valve signal is 5.7 mV compared with the Meinhard's 2.7 mV. The spray valve signals however have a higher irreproducibility (RSD 2.7%) compared with the Meinhard (RSD 1.9%). When the solution is metered and injected by the plunger spring action the signal increases to 11.5 mV and is shown in figure 5.5 together with a signal obtained from the same procedure on a blank solution. This indicates that the increase in signals is not due to a pressure change such as obtained when a graphite rod thermal atomisation is used³¹⁵. The same procedure was repeated for the RVC cell deposit of copper over 300s and stripped into a standing solution. The signal obtained was 90 mV. The improvement in magnitude was considered significant since the ICP-AES on its own using the Meinhard nebuliser gave signal of 2.7 mV and ASV/ICP-AES using the RVC cell and the Meinhard for the same conditions gave 31.9 mV.

It has already been shown in section 5.1 above that under the conditions of this experiment the quantity of copper deposited is 6.1 μg resulting in a concentration of $45.3 \mu\text{g cm}^{-3}$ ($714.4 \times 10^{-9} \text{ mol cm}^{-3}$). If the band of this concentrate does not spread in the stream, is not diluted, and is not lost along the way then the ICP-AES would record a signal 122.4 mV as obtained from a calibration curve for copper using ICP-AES on its own. The 90 mV actually recorded indicates that 73.5% of the deposit did get to the plasma by this method. It has therefore been a fair success.

This is attributed to a combination of the production of a fine aerosol from a 0.2 mm orifice and the selection by metering of

Peaks obtained by scanning Cu line $\lambda = 324.7 \text{ nm}$

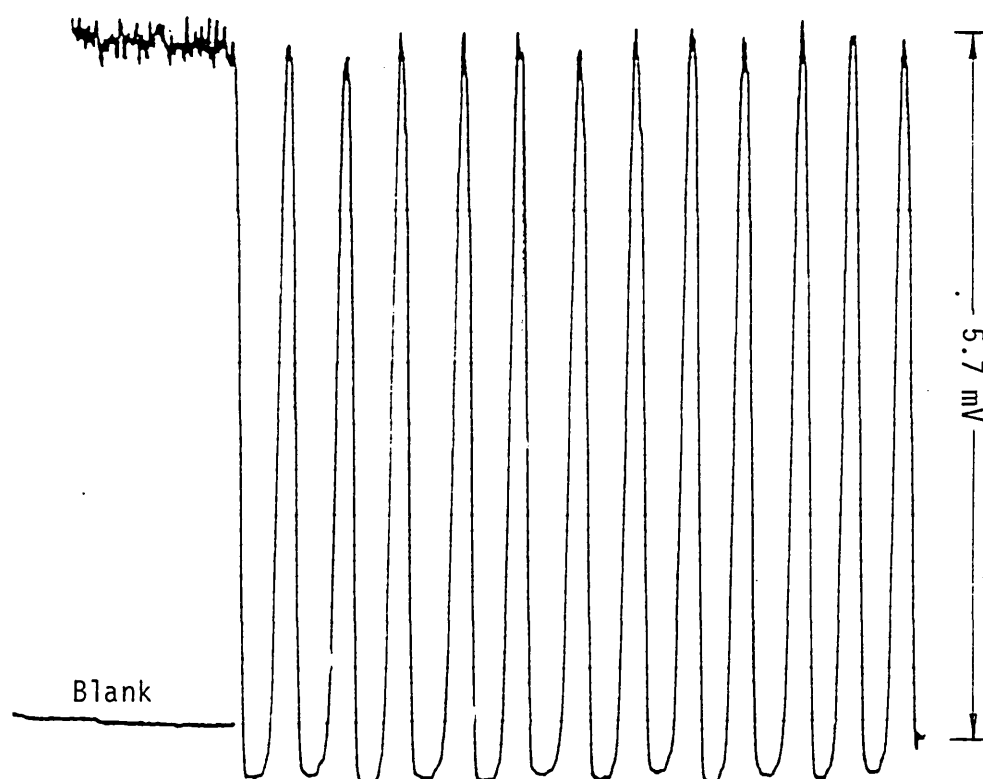


Figure 5.4 : Typical peaks obtained with the metering spray valve operating as a nebuliser. The solution is Cu ($15.8 \text{ n mol cm}^{-3}$) in KCl (0.1M).

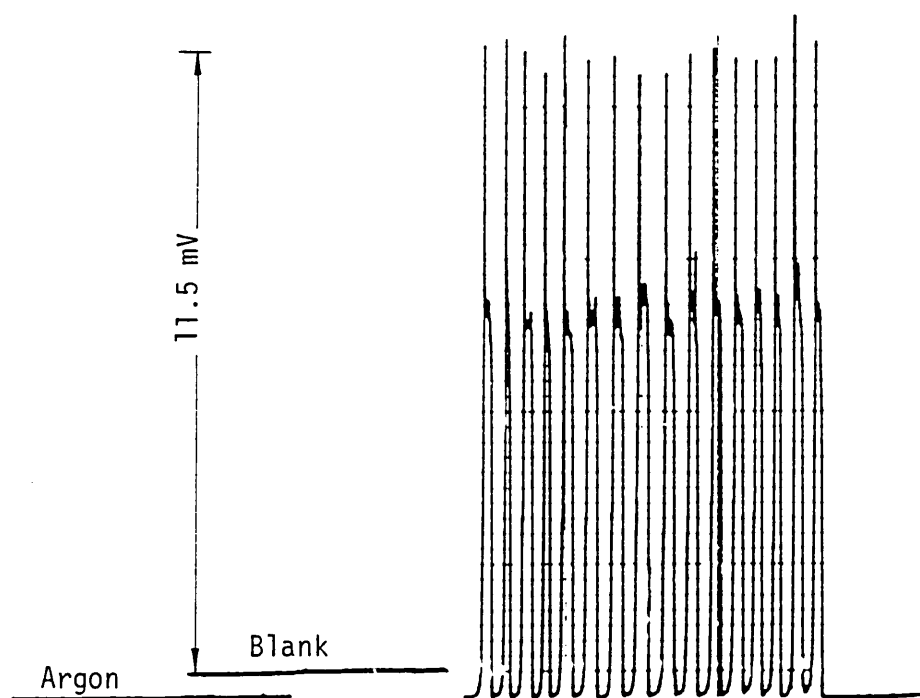


Figure 5.5 : Typical signal obtained from the spray valve when sample is spring injected into plasma. The solution is Cu ($15.8 \text{ n mol cm}^{-3}$) in KCl (0.1M).

the concentrated solution only from the cell and nebulising it into argon free of solvent in front, behind, and jacketed at the sides which ensures that no dilution from any solvent aerosol particles occurs.

However a 100% metering out of the concentrate from the cell was not practical. The distribution of the substrate in the volume of solution in the cell as it flows out was obtained by setting the volume of the spray valve to 20 μL and the solution injected repeatedly into argon until the signal decreased to the original. The distribution is shown in figure 5.6. Tailing due to dilution by advancing fresh solution is observed at the hind end. The volume of the spray valve therefore requires to be set to leave out the tail end of the band. It was consequently set at 100 μL . A further loss of concentrate is from the removal of undesirable size particles at the Y tube chamber. The value 73.5% is therefore not unexpected.

The size of the sample orifice in the spray valve would suggest that clogging may be a problem when high dissolved solids (> 3%) are used since this is a widely observed phenomenon with nebulisers³¹⁶ for use with ICP-AES. To check this a Cu^{2+} ($15.8 \times 10^{-9} \text{ mol cm}^{-3}$) in KCl (1.0M), which is 7.5% in dissolved solid, was nebulised continuously at the above experimental conditions for 4 hours. The emission signal was checked every hour. No significant decrease in signal was observed hence clogging of the nebuliser was not observed. This is attributed to the high pressure, of the order

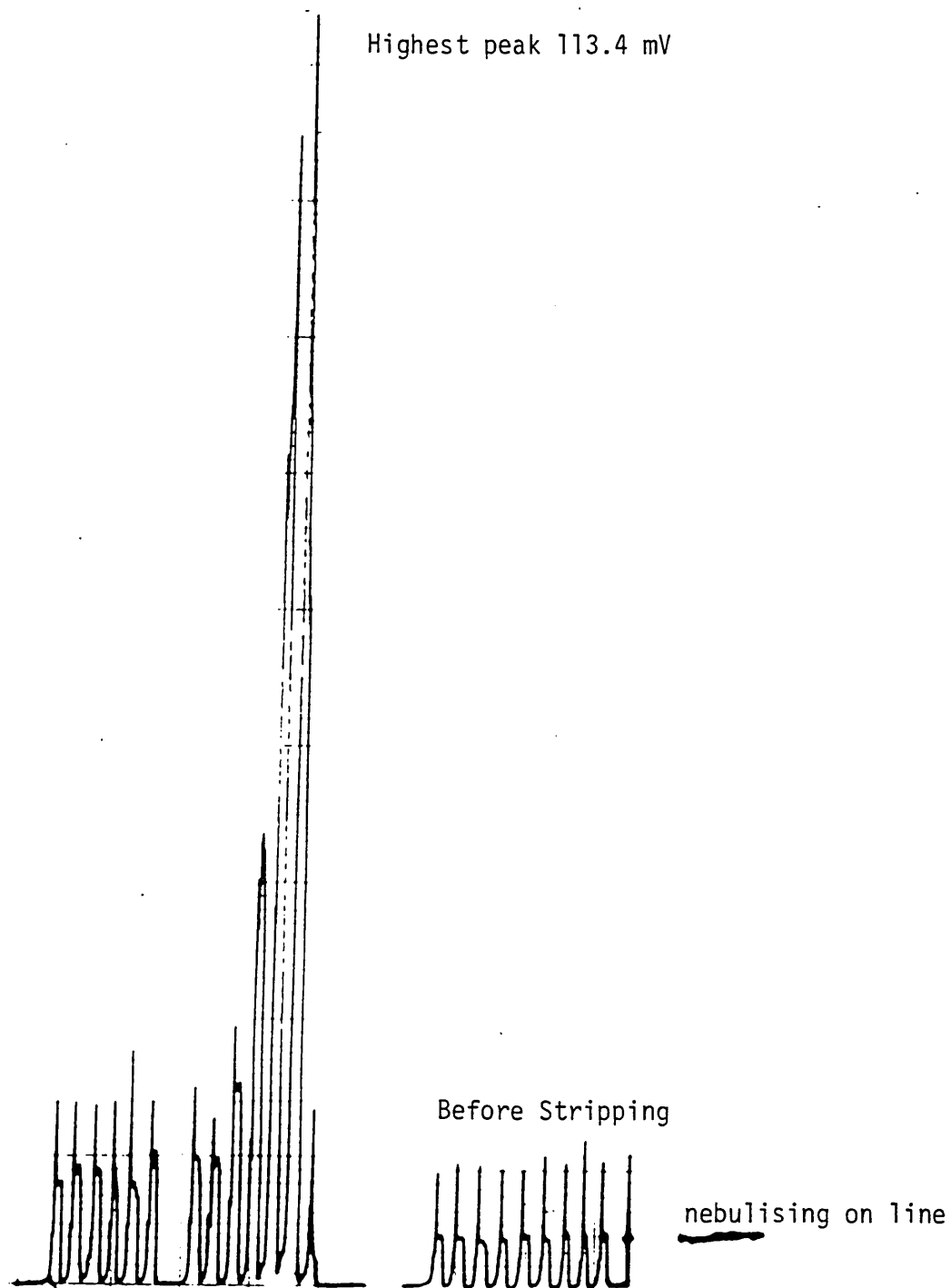


Figure 5.6 : Distribution of substrate in 20 μl injections
 from 180 S deposit of Cu ($15.8 \text{ n mol cm}^{-3}$),
 $v_f = 57 \times 10^{-3} \text{ cm}^3 \text{ S}^{-1}$

$4 \times 10^5 \text{ N m}^{-2}$, obtaining in the interface system which results from the argon gas and the pump pressure and ensures mechanical removal of particles that might lodge in the orifice.

However it has not been possible yet to complete experimental work on evaluation of this device. In particular it was not possible to establish the size distribution of aerosol particles it generates and to establish the minimum size and shape of Y tube chamber to use it with, in the duration of this work.

CHAPTER 6.

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK.

It is possible in practice to use hydrodynamically controlled electrochemical cells for on-line preconcentration with ICP-AES. The required cells are simple in design, easy and cheap to fabricate and have long useful life. Their performance is theoretically predictable.

The cells that have been most successful in performance are those that by design have a high mass transfer capability and yet are compatible with operating conditions required by ICP-AES. These are the concentric cup and the Reticulated Vitreous Carbon cells. High solution flowrates ($< 50 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$) online cannot be used to achieve high mass transfer except when the flow is diverted away from the plasma after the cell. Large surface area electrodes are desired instead. In particular the use of porous electrode materials achieves the desired level of mass transfer at low flow rates. It is however essential to enclose the WE in as small a volume as possible to ensure that the high concentration of the substrate formed on stripping is not diluted within the cell. The use of a cup in both named cells satisfactorily achieves this effect.

Besides the WE pretreatment, purging of solutions for oxygen and control of pH that are necessary for reproducible analytical signals in electrochemistry it is particularly required in preconcentration for ICP-AES to use a fast stripping potential scan rate in order to avoid dilution of the substrate by the flowing solution.

The deposition times required to achieve acceptable magnification of analytical signals are short and are of the order 300s. The calibration curves of the ASV/ICP-AES system are linear and the detection limits are several orders of magnitude lower than for ICP-AES on its own : for the concentric cup they are lower by one order; and for the RVC cell by two orders. These are also better than detection limits for either of the cells on its own using ASV under the same conditions. The detection limits can be lowered further by increasing deposition time. The final limit is set by the blanks and the environment in which the analysis is done. The quality of measurements are the same order as those obtained by ICP-AES on its own. The preconcentration capability of the RVC cell has been most satisfactory owing to its large surface area. It however has an upper plating limit corresponding to 20 μg of copper for which the analytical signal does not increase. This is thought to be the limit set by the potentiostat current demand rather than the cell. It is far above what can be obtained from the trace level concentrations for which the cell is designed.

The cells can be used independently for ASV measurements. However large capacitive currents arising from large surface area restrict their usage by linear sweep voltammetry from achieving the low detection levels as the combined system. The RVC cell in particular cannot be used for ASV on its own after a period of three weeks in use because of the large background currents it develops. Its performance with the ICP-AES is not affected by this phenomenon.

The main problem in using electrochemical cells with ICP-AES is the cell-plasma interface. Unacceptable losses of the substrate and dilution occur at the interface. A simple modification can however be made to minimise these. Such modification must improve the quality of nebulisation, eliminate dead volume, and have high uptake efficiency. The use of a demountable variable volume metering spray valve has improved the interface to a desirable level of 73.5% uptake to the plasma.

Evaluation of the spray valve has not been completed and further work is required to establish its aerosol characteristics. Improvement on its design are also required in order to automate its operation and eliminate operators error, improve its leakproofness, enable it to divert high solution flow rates from the cell away from the ICP during deposition, and to make it generate a finer aerosol so that losses within the interface are eliminated as much as possible.

It is also required to establish the value of electrochemical preconcentration for ICP-AES with respect to multielement analysis and for speciation since these studies have not been done yet.

REFERENCES.

1. Houtman, J.P.W. and Van Den Hamer, C.J.A.
Physiological and Biochemical Aspects of Heavy Elements in
our Environment : Proceedings of the Symposium, Utrecht,
The Netherlands 9th May 1974.
Publ. Delft University Press 1975.
2. Threshold Limit Values for Chemical Substances and Physical
Agents in the Workroom Environment (1980).
Publ. ACGIH P.O. Box 1937 Cincinnati OH 45201.
3. Friberg, L., Piscator, M., Nordberg, C.F. and Kjellstrom, T
Cadmium in the Environment.
2nd Ed. 1974.
Publ. CRC Press Inc. Cleveland, Ohio.
4. Kipling, M.D. and Waterhouse, J.A.H.
Lancet 1 : 730-731 (1967).
5. Leman, R.A., Lee, T.S. and Wagoner, J.K.
New York Acad. Sci. Meeting on Carcinogenesis (1975).
6. Adams, R.G. and Grabtree, N.
Brit. J. Ind. Med. 18 : 216-221 (1966).
7. Potts, C.L.
Ann. Occ. Hyg. 8 : 55-61 (1965).
8. Valee, B.L. and Ulmer, D.D.
Ann. Rev. Biochem. 41 : 91-128 (1972).
9. Glauser, S.C., Bello, C.T. and Glauser, E.M.
Lancet 1 : 717-718 (1976).
10. Hine, C.H., Wright, J. and Goodman, D.
Toxicol. Appl. Pharm. 25 : 439-499 (1973).
11. Morgan, J.M.
Arch. Env. Health. 24 : 364-368 (1972).
12. Schroeder, H.A.
J. Chronic Dis. 18 : 647-656 (1965).
13. Thind, G.S.
J. Air Poll. Contr. Ass. 22 : 267-270 (1972).
14. Arena, J.M.
Poisoning : Chemistry-Symptoms-Treatment. III
Publ. Thomas Springfield 1963.
15. Wisniewska-Knypl, J.M., Jablonska, J. and Myslak, Z.
Arch. Toxikol. 28(1) : 46-55 (1971).

16. Underwood, E.J.
Trace Elements in Human and Animal Nutrition.
4th Ed. 1977.
Publ. Academic Press, N.Y.
17. Burk, R.F.
Trace Elements in Human Health Vol 2 : 105-133.
Publ. Academic Press, N.Y. (1976).
18. Rosenfield, I. and Beath, O.A.
Selenium.
Publ. Academic Press, N.Y. 1964.
19. Ganther, H.E. and Corcoran, C.
Biochemistry, 8 : 2557-2563 (1969).
20. Nguyen, V.D., Valenta, P. and Nurnberg, H.W.
Sci. Total Environ. 12 : 151 (1979).
21. McInnes, G.
Warren Spring Laboratory LR 277 (AP) 1978.
22. Schlesinger, W.H., Reiners, W.A. and Knopman, D.
Env. Poll. 6 : 39-47 (1974).
23. Bouquiaux, J.
Problems of Contamination of Man and His Environment by
Mercury and Cadmium.
Luxemberg, EUR 5075 : 23-46 (1973).
24. Davies, B.E.
Oikos, 22 : 366-372 (1971).
25. A Report on an Inter-Departmental Working Group on Heavy
Metals. Lead in the Environment and its Significance to
Man.
HMSO Pollution Paper No.2. 1974.
26. Park, P.K.
in : Water and Aqueous Solutions.
Ed. Horne, R.A.
Publ. Wiley - Interscience 1972.
27. Spencer, D.W., Robertson, D.E., Turrekiam, K.K. and
Folson, T.R.
J. Geophy. Res. 75 : 7688 (1970).
28. Evenson, M.A. and Anderson, C.T.
Clin. Chem. 21(4) 537-543 (1975).
29. Johnson, C.A.
Anal. Chim. Acta. 81 : 69-74 (1976).
30. Curry, A.S. and Knott, A.R.
Clin. Chim. Acta. 30 : 115-118 (1970).

31. Livingston, H.D.
Clin. Chem. 18(1) : 67-72 (1972).
32. Piscator, M. and lind, B.
Arch. Env. Health, 24 : 426 (1972).
33. Backer, E.T.
Clin. Chim. Acta. 24 : 233-238 (1969).
34. Hanig, R.C. and Aprison, M.H.
Anal. Biochem. 21 : 169-177 (1967).
35. Harrington, W.W., Netsky, M.G. and Brown, M.D.
Clin, Chim, Acta. 21 : 55-60 (1968).
36. Seyers-Verbeke, J., Defrise-Gussenhoven, E., Ebinger, G.,
Loewenthal, A. and Massart, D.L.
Clin. Chim. Acta. 57 : 309-314 (1974).
37. Analytical Aspects of Mercury and other Heavy Metals in the
Environment.
Ed. Frei, R.W.
Publ. Gordon and Breach Science Publishers 1975.
38. Filby, R.H. and Shah, K.R.
in : Activation Analysis and Application to Environmental
Research.
Analytical Aspects of Mercury and other Heavy Metals in the
Environment.
Ed. Frei, R.W. and Hutzinger, O.
Publ. Gordon and Breach Science Publishers : 153-196 (1976)
39. Cushing, C.E. and Ranticelli, L.A.
Northwest Sci. 46 : 115-121 (1972).
40. Wheeler, R.M., Liebert, R.B., Zabel, T., Chaturvedi, R.P.,
Valkovic, V., Phillips, G.C., Ong, P.S., Cheng, E.L. and
Hrgovcic, M.
Med. Phys. 1 : 68-71 (1974).
41. Uthe, J.F. and Armstrong, F.A.J.
The Microdetermination of Mercury and Organomercury
Compounds in Environmental Materials.
in : Analytical Aspects of Mercury and Other Heavy Metals
in the Environment.
Ed. Frei, R.W. and Hutzinger, O.
Publ. Gordon and Breach Science Publishers : 1-53 (1975).
42. Pinta, M.
Modern Methods for Trace Element Analysis.
Publ. Ann Arbor Science (Mich.) 1978.
43. Winefordner, J.D.
Comparison of Spectroscopic Methods.
in : Trace Analysis Spectroscopic Methods for Elements.

- Ed. Winefordner, J.D.
Publ. Wiley - Interscience 1976.
44. De Mars, R.D. and Shain, I.
Anal. Chem. 29 : 1825-1827 (1957).
45. Jacobs, E.S.
Anal. Chem. 35 : 2112-2115 (1963).
46. Perone, S.P. and Birk, J.R.
Anal. Chem. 37 : 9-12 (1965).
47. Kemula, W. and Kublik, Z.
in : Advances in Analytical Chemistry and Instrumentation.
Ed. Reilley, C.N.
Publ. Interscience, N.Y. 1963.
48. Shain, I.
in : Treatise on Analytical Chemistry. Part 1, vol 4.
Ed. Kolthoff, I.M. and Elving, P.J.
Publ. Wiley Interscience, N.Y. : 2533-2568 (1967).
49. Barendrecht, E.
in : Electroanalytical Chemistry : A series of advances,
vol 2.
Ed. Bard, A.J.
Publ. Marcel Dekker : 53-109 (1967).
50. Brainina, K.Z.
Stripping Voltammetry in Chemical Analysis.
Publ. John Wiley 1974.
51. Eisner, U. and Mark, H.B.
J. Electroanal. Chem. 24 : 345-355 (1970).
52. Trushima, L.F. and Kaplin, A.A.
Zh. Anal. Khim. 25 : 1616-1619 (1970).
53. Kaplin, A.A., Veits, N.A. and Stromberg, A.G.
Zh. Anal. Khim. 28 : 2192-2196 (1973).
54. Davis, P.H., Dulude, G.R., Griffin, R.M., Matson, W.R. and
Zink, E.W.
Anal. Chem. 50(1) : 137-143 (1978).
55. Moorhead, E.D. and Davis, P.H.
Anal. Chem. 47(4) : 622-630 (1975).
56. Batley, G.E. and Florence, T.M.
J. Electroanal. Chem. 55 : 23-43 (1974).
57. Copeland, T.R. and Skogerboe, R.K.
Anal. Chem. 46(14) : 1257A-1267A (1974).
58. Danielson, L.G., Jagner, D., Josefson, M. and Westerlund, S.

- Anal. Chim. Acta. 127(1) : 147-156 (1981).
59. Tindall, G.W., Bruckenstein, S.
J. Electroanal. Chem. 22(3) : 367-373 (1969).
60. Ishii Takeshi and Aikoh Hiroami.
Okayama Rika Daigaku Kiyo, A 17 : 41-44 (1981) abst.
61. Ben-Basat, A.H.I., Blinderman, J.M., Salomon, A. and Wakshali, E.
Anal. Chem. 43(3) : 534-537 (1975).
62. Wang, J., and Dewald, H.D.
Anal. Lett. 16(B12) : 925-931 (1983).
63. Smyth, W.E., Dadgar, D., and Smyth, M.R.
Tr. Ac. Trends Anal. Chem. (Pers. Ed.) 1(9) : 215-218 (1982).
64. Nurenberg, H.W.
Pure Appl. Chem. 54(4) : 853-878 (1982).
65. Jagner, D., Danielson, L.G., and Aren, K.
Anal. Chim. Acta. 106 : 15-21 (1979).
66. Jagner, D., Josefson, M. and Westerlund, S.
Anal. Chim. Acta. 128 : 155-161 (1981).
67. Jagner, D., Aren, K.
Anal. Chim. Acta. 117 : 165-169 (1980).
68. Piotrowicz, S.R., Springer-Young, R., Puig, J.A., and Spencer, M.J.
Anal. Chem. 54(8) : 1367-1371 (1982).
69. Wang, J. and Dewald, H.D.
J. Electrochem. Soc. 130(9) : 1814-1818 (1983).
70. Kovavskii, N.Y., Kovckovdova, L.T., Pryazhevskaya, I.S., Belenskii, V.S., Shapovalov, E.N., Popkova, S.M.
J. Anal. Chem. of the USSR 36(11 Pt 2) : 1639-1645 (1981).
71. Adejou, S.B. and Bond, A.M.
Anal. Chem. 55(13) : 2076-2082 (1983).
72. Maienthal, E.J. and Koch, W.F.
NBS Spec. Publ. (US) 656 : 77-80 (1983) Abstr.
73. Vydra, F., Stulik, K. and Julakova, E.
Electrochemica Stripping Analysis.
Publ. Halstead Press, N.Y. 1977.
74. Flato, J.B.
Anal. Chem. 44(11) : 75A (1972).

75. Copeland, T.R., Christie, J.H., Osteryoung, R.A. and Skogerboe, R.K.
Anal. Chem. 45 : 2171-2174 (1973).
76. Underkofler, W.L., Shain, I.
Anal. Chem. 37 : 218-222 (1965).
77. Velghe, N. and Claeys, A.
J. Electroanal. Chem. 35 : 229-235 (1972).
78. Eisner, U., Turner, J.A. and Osteryoung, R.A.
Anal. Chem. 48 : 1608-1610 (1976).
79. Steeman, E., Temmerman, E. and Vermbinnen, R.
Anal. Chim. Acta. 96 : 177-181 (1978).
80. Miller, B. and Bruckenstein, S.
Anal. Chem. 46(13) : 2026-2033 (1974).
81. Laser, D. and Ariel, M.
J. Electroanal. Chem. 49(1) : 123-132 (1974).
82. Vassos, B.H. and Mark, H.B.
J. Electroanal. Chem. 13 : 1-9 (1967).
83. Tindall, G.W. and Bruckenstein, S.
Anal. Chem. 40(7) : 1051-1054 (1968).
84. Tindall, G.W. and Bruckenstein, S.
Electrochim. Acta. 16(2) : 245-253 (1971).
85. Vicente, S. and Bruckenstein, S.
Anal. Chem. 45(12) : 2036-2043 (1973).
86. L'vov, B.V.
Atomic Absorption Spectrochemical Analysis.
Publ. Adam Hilger, London. (1970).
87. Christian, G.D. and Feldman, F.J.
Atomic Absorption Spectroscopy : Application in
Agriculture, Biology and Medicine.
Publ. Wiley - Interscience, N.Y. (1970).
88. Price, W.J.
Analytical Atomic Absorption Spectrometry.
Publ. Heyden, London. (1972).
89. Kirkbright, G.F. and Sargent, M.
Atomic Absorption and Fluorescence Spectroscopy.
Publ. Academic Press, London. 1974.
90. Willis, J.B.
Analysis of Biological Materials by Atomic Spectroscopic
Technique. A review of progress in the last decade.
in : Proceedings of 3rd International AAS and AFS Congress.

Paris. (1971).

91. Willis, J.B.
Endeavour 32 : 106-111 (1973).
92. Greenfield, S.I., Jones, I.L.L. and Bery, C.T.
Analyst 89 : 713-720 (1964).
93. Wendt, R.H. and Fassel, V.A.
Anal. Chem. 37 : 920-922 (1965).
94. Kirkbright, G.F., Ward, A.F. and West, T.S.
Anal. Chim. Acta. 62 : 241-251 (1972).
95. Nakashima, R., Sasaki, S. and Shibata, S.
Anal. Chim. Acta. 70 : 265-274 (1973).
96. Kirkbright, G.F., Ward, A.F. and West, T.S.
Anal. Chim. Acta. 64 : 353-362 (1973).
97. Scott, R.H., Fassel, V.A., Kniseley, R.N. and Nixon, D.E.
Anal. Chem. 46(1) : 75-80 (1974).
98. Scott, R.H. and Strasheim, A.
Anal. Chim. Acta 76 : 71-78 (1975).
99. Scott, R.H. and Kokot, M.L.
Anal. Chim. Acta 75 : 257-270 (1975).
100. Butler, C.C., Kniseley, R.N. and Fassel, V.A.
Anal. Chem. 47 : 825-829 (1975).
101. Scott, R.H., Strasheim, A. and Kokot, M.L.
Anal. Chim. Acta 82 : 67-77 (1976).
102. Winge, R.K., Fassel, V.A., Kniseley, R.N., De Kalb, E. and Haas, W.J.
Spectrochim. Acta. 32B : 327-345 (1977).
103. Gunn, A.M., Kirkbright, G.F. and Opheim, L.N.
Anal. Chem. 49 : 1492-1494 (1977).
104. Alder, J.F., Gunn, A.M. and Kirkbright, G.F.
Anal. Chim. Acta. 92 : 43-48 (1977).
105. Dahlquist, R.L. and Knoll, W.J.
Appl. Spectrosc. 32 : 1-29 (1978).
106. Boumans, P.W.J.M. and De Boer, F.J.
Spectrochim. Acta. 27B : 391-414 (1972).
107. Fassel, V.A., Peterson, C.A., Abercrombie, F.N. and Kniseley, R.N.
Anal. Chem. 48 : 516-519 (1976).

108. Boumans, P.W.J.M., De Boer, F.J., Dahmen, F.J., Hoelzel, H. and Meier, A.
Spectrochim. Acta. 30B : 449-469 (1975).
109. Boumans, P.W.J.M. and De Boer, F.J.
Proc. Analyt. Div. Chem. Soc. 12 : 140-152 (1975).
110. Boumans, P.W.J.M. and De Boer, F.J.
Spectrochim. Acta. 30B : 309-334 (1975).
111. Greenfield, S.
Proc. Analyt. Div. Chem. Soc. 13 : 279-284 (1976).
112. Fassel, V.A. and Kniseley, R.N.
Anal. Chem. 46 : 1110A-1164A (1974).
113. Hoare, H.C. and Mostyn, R.A.
Anal. Chem. 39 : 1153-1155 (1967).
114. Fassel, V.A. and Dickinson, G.W.
Anal. Chem. 40 : 247-249 (1968).
115. Greenfield, S., Jones L.I., McGeachin, H.M. and Smith, P.B.
Anal. Chim. Acta 74 : 225-245 (1975).
116. Ohls, K., Koch, K.H. and Grote, H.
Z. Anal. Chem. 284 : 177-187 (1977).
117. Ohls, K., Koch, K.H. and Grote, H.
Z. Anal. Chem. 287 : 10-14 (1977).
118. Boumans, P.W.J.M., Bastings, L.C., De Boer, F.J. and Van Kollenburg, L.W.J.
Z. Anal. Chem. 291 : 10-19 (1978).
119. Burman, J.O., Ponter, C. and Bostrom, K.
Anal. Chem. 50 : 679-680 (1978).
120. Wemyss, R.B. and Scot, R.H.
Anal. Chem. 50 : 1694-1697 (1978).
121. Burman, J.O. and Bostrom, K.
Anal. Chem. 51 : 516-520 (1979).
122. Capar, S.G., Tanner, J.T., Friedman, M.H. and Boyer, K.
Environ. Sci. Tech. 12 : 785-790 (1978).
123. Jones, J.B.
Comm. Soil Sci. Plant Anal. 8 : 349- (1977).
124. Greenfield, S. and Smith, P.B.
Anal. Chim. Acta. 59 : 341-348 (1972).
125. Saba, C.S. and Eisentraut, K.J.
Anal. Chem. 49 : 454-457 (1977).

126. Newman, E.J. and Farrow, R.N.
Proc. Analyt. Div. Chem. Soc. 15 : 311-315 (1978).
127. Kniseley, R.N., Fassel, V.A. and Butler, C.C.
Clin. Chem. 19(8) : 807-812 (1973).
128. Irons, R.D., Schenk, E.A. and Giauque, R.D.
Clin. Chem. 22(12) : 2018-2024 (1976).
129. Barnes, R.M.
C.R.C. Rev. Anal. Chem. 7 : 203-296 (1978).
130. Greenfield, S.
Analyst 105 : 1032-1044 (1980).
131. Robin, J.P.
Prog. Analyt. Atom. Spectrosc. 5 : 79-110 (1982).
132. Larson, G.F., Fassel, V.A., Winge, R.K. and Kniseley, R.N.
Appl. Spectrosc. 30 : 384-391 (1976).
133. Fassel, V.A., Katzenberger, J.M. and Winge, R.K.
Appl. Spectrosc. 33 : 1-5 (1979).
134. Larson, G.F. and Fassel, V.A.
Appl. Spectrosc. 33 : 592-599 (1979).
135. Burrell, D.C.
Anal. Chim. Acta. 38 : 447-455 (1967).
136. Tzeng, J.H. and Zeitlin, H.
Anal. Chim. Acta 101 : 71-77 (1978).
137. Hiraide, M., Ito, T., Kawaguchi, H. and Mizuike, A.
Anal. Chem. 52(6) : 804-807 (1980).
138. Krembling, K.K. and Peterson, H.
Anal. Chim. Acta 70 : 35-39 (1974).
139. Miyazaki, A., Kimura, A., Bansho, K. and Umezaki, Y.
Anal. Chim. Acta 144 : 213-221 (1981).
140. Bengtsson, M. and Johnson, G.
Anal. Chim. Acta 158 : 147-156 (1984).
141. Riley, J.P. and Taylor, D.
Anal. Chim. Acta 40 : 479-485 (1968).
142. Riley, J.P. and Skirrow, G.
in : Chemical Oceanography. Vol III ch 19. 2nd Edn. Page 278-289.
Publ. Academic Press, N.Y. 1975.
143. Miyazaki, A. and Barnes, R.M.
Anal. Chem. 53(2) : 299-304 (1981).

144. Sturgeon, R.E., Berman, S.S., Desaubriers, J.A.H.,
Mykytiuk, A.P., McLaren, J.W. and Russel, D.S.
Anal. Chem. 52(11) : 1585-1588 (1980).
145. Berman, S.S., McLaren, J.W. and Willie, S.N.
Anal. Chem. 52(3) : 488-492 (1980).
146. Miyazaki, A. and Barnes, R.M.
Anal. Chem. 53(2) : 364-366 (1981).
147. Kingston, H.M., Barnes, I.L., Brady, T.J. and Rains, T.C.
Anal. Chem. 50(14) : 2064-2070 (1978).
148. Davey, E.W. and Soper, A.E.
in : Industrial Methods in Oceanography.
Ed. Gibbs, T.R.P.
Jr. Ed., Adv. Chem. Ser. 147 (1975).
149. Leyden, D.E. and Underwood, A.L.
J. Phys. Chem. 68(8) : 2093-2097 (1964).
150. Barnes, R.M. and Genna, J.S.
Anal. Chem. 51(7) : 1065-1069 (1979).
151. Barnes, R.M.
Biol. Trace Elem. Res. 6(1) : 93-103 (1984).
152. Fairless, C. and Bard, A.J.
Anal. Chem. 45(13) : 2289-2291 (1973).
153. Lund, W. and Larsen, B.V.
Anal. Chim. Acta 70(2) : 299-310 (1974).
154. Lund, W. and Larsen, B.V.
Anal. Chim. Acta 72(1) : 57-62 (1974).
155. Lund, W., Larsen, B.V. and Gundersen, N.
Anal. Chim. Acta 81(2) : 319-324 (1976).
156. Newton, M.P. and Davis, D.G.
Anal. Chem. 47(12) : 2003-2009 (1975).
157. Wolff, E.W., Landy, M. and Peel, D.A.
Anal. Chem. 53(11) : 1566-1569 (1981).
158. Heyrovsky, J.
J.R.S. Trans. Faraday Soc. 19 : 785-788 (1924).
159. Griem, H.R.
Plasma Spectroscopy
Publ. McGraw-Hill, N.Y. 1964.
160. Griem, H.R.
Spectral Line Broadening by Plasmas.
Publ. Academic Press, N.Y. 1974.

161. Kuhn, H.G.
Atomic Spectra.
Publ. Academic Press, N.Y. 1962.
162. Mitchell, A.C.G. and Zamansky, M.W.
Resonance Radiation and Excited Atoms.
Publ. Cambridge University Press, London 1961.
163. Sobel'man, I.I.
Introduction to the Theory of Atomic Spectra.
Publ. Permagon Press, Elmsford, N.Y. : 1972 Pages 377-465.
164. Mitchner, M. and Kruger, C.H.
Partially Ionised Gases.
Publ. John Willey, N.Y. 1973.
165. Traving, G.
in : Plasma Diagnostics Ch. 2.
Publ. Lochte-Holtgreven, W.
Edtn. North Holland 1968.
166. Breene, R.G.
in : The Shift and Shape of Spectral Lines.
Publ. Permagon Press. 1961.
167. Parsons, M.L., McCarthy, W.J. and Winefordner, J.
Appl. Spectrosc. 20 : 223-230 (1966).
168. Peters, T.
Naturwissenschaften, 41 : 571-572 (1954).
169. Weiss, R.
Z. Phys. 138 : 170-182 (1954).
170. Lovett, R.J. and Parsons, M.L.
Spectrochim. Acta 32B : 421-436 (1977).
171. Mermet, J.M. and Robin, J.
Anal. Chim. Acta 75(2) : 271-279 (1975).
172. Kalnicky, D.J., Fassel, V.A. and Kniseley, R.N.
Appl. Spectrosc. 31 : 137-149 (1977).
173. Kalnicky, D.J., Fassel, V.A. and Robin, J.
Spectrochim. Acta 33B : 35-78 (1978).
174. Boumans, P.W.J.M. and De Boer, F.J.
Spectrochim. Acta 32B : 365-395 (1977).
175. Batal, A. and Mermet, J.M.
Can. J. Spectrosc. 27(2) : 37-45 (1982).
176. Boumans, P.W.J.M.
Spectrochim. Acta 37B(1) : 75-82 (1982).

177. Blades, M.W.
Spectrochim. Acta 37B(10) : 869-879 (1982).
178. Robin, J.P.
Prog. Anal. Atom. Spectrosc. 5 : 70-110 (1982).
179. De Galan, L.
Spectrochim. Acta 39B(4) : 537-550 (1984).
180. Mermet, J.M.
Spectrochim. Acta 30B : 383-396 (1975).
181. Long, S.E. and Snook R.D.
Analyst. 108 : 1331-1338 (1983).
182. Albery, W.J. and Hitchman, M.L.
Ring-Disc Electrodes.
Publ. Clarendon Press, Oxford. 1971.
183. Blaedel, W.J. and Klatt, L.N.
Anal. Chem. 38(7) : 879-883 (1966).
184. Yamada, J. and Matsuda, H.
J. Electroanal. Chem. 44(2) : 189-198 (1973).
185. Parsons, R.
Adv. Electrochem. Electrochem. Eng. 1 : 1-64 (1961).
186. Newman, J.
Adv. Electrochem. Electrochem. Eng. 5 : 89-135 (1967).
187. Levich, V.G.
Acta Physicochim. URSS 17 : 257-307 (1942).
188. Levich, V.G.
Physicochemical Hydrodynamics.
Publ. Prentice - Hall 1962.
189. Levich, V.G.
Discussions Faraday Soc. 1 : 37-43 (1947).
190. Trumpler, G. and Zeller, H.
Helv. Chim. Acta. 34 : 952-958 (1951).
191. Jordan, J., Jarvic, R.A. and Ranz, W.E.
J. Am. Chem. Soc. 80(15) : 3846-3852 (1958).
192. Kirowa - Eisner, E. and Gileadi, E.
J. Electrochem. Soc. 123(1) : 22-24 (1976).
193. Klatt, L.N. and Blaedel, W.J.
Anal. Chem. 39(10) : 1065-1072 (1967).
194. Alkire, R. and Mirarefi, A.A.
J. Electrochem. Soc. 120(11) : 1507-1515 (1973).

195. Coles, B.A. and Compton, R.G.
J. Electroanal. Chem. 127(1) : 37-105 (1981).
196. Gregory, D.P. and Riddiford, A.C.
J. Chem. Soc. 731 : 3756-3764 (1956).
197. Albery, W.J.
Trans. Faraday Soc. 62 : 1915-1919 (1966).
198. Albery, W.J. and Bruckenstein, S.
Trans. Faraday Soc. 62 : 1920-1931 (1966).
199. Albery, W.J., Bruckenstein, S. and Napp, D.T.
Trans. Faraday Soc. 62 : 1932-1937 (1966).
200. Albery, W.J., Bruckenstein, S. and Johnson, D.C.
Trans. Faraday Soc. 62 : 1938-1945 (1966).
201. Albery, W.J., Bruckenstein, S.
Trans. Faraday Soc. 62 : 1946-1954 (1966).
202. Chin, D.T.
J. Electrochem Soc. 118(9) : 1434-1438 (1971).
203. Chin, D.T.
J. Electrochem Soc. 118(11) : 1764-1769 (1971).
204. Newman, J.
J. Electrochem. Soc. 119(1) : 69-71 (1972).
205. Chin, D.T.
J. Electrochem. Soc. 120(5) : 631-635 (1973).
206. Dasgupta, S.
Ph.D. Thesis, London University 1975.
207. Sioda, R.E.
Electrochim. Acta 15(5) : 783-793 (1970).
208. Lago, M.E., Bohm, U. and Placho, F.
Int. J. Heat Mass Transfer 14(6) : 813-823 (1971).
209. Kumar, I.
Int. J. Heat Mass Transfer. 14(11) : 1759-1770 (1971).
210. Sioda, R.E.
J. Electroanal. Chem. 34 : 411-418 (1972).
211. Newman, J.S. and Tiedemann, W.
Adv. Electrochem. Eng. 11 : 353-438. (1978).
212. Hampton, N.A. and McNeil, A.J.S.
RSC Specialist Reports : Electrochem. 8 : 1-53 (1983).
213. Hand, R., Carpenter, A.K., O'Brien, C.J. and Nelson, R.F.

- J. Electrochem. Soc. 119(1) : 74- (1972).
214. Yanive, D. and Ariel, M.
J. Electroanal. Chem. 79(1) : 159-167 (1977).
215. Blaedel, W.J. and Boyer, S.L.
Anal. Chem. 45(2) : 258-262 (1973).
216. Heyrovsky, J.
Phil. Mag. 45 : 303-315 (1923).
217. Le Blanc, M.
Z. Phys. Chem. 12(3) : 333-358 (1893).
218. Russ, R.
Z. Phys. Chem. 44(6) : 641-732 (1902).
219. Salomon, E.
Z. Phys. Chem. 25(2) : 365-371 (1898).
220. Meites, L.
Polarographic Techniques.
2nd Ed., Publ. Interscience, N.Y. 1965 Ch. 8 : 411-464.
221. Blaedel, W.J. and Strohl, J.H.
Anal. Chem. 36(2) : 446-446 (1964).
222. Bond, A.M.
Modern Polarographic Methods in Analytical Chemistry.
Publ. Marcel Dekker Inc. N.Y. 1980.
223. Adams, R.N.
Electrochemistry at Solid Electrodes.
Ch. 2 : 19-42.
Publ. Marcel Dekker Inc., N.Y. 1969.
224. Alder, J.F., Fleet, B. and Kane, P.O.
J. Electroanal. Chem. 30(3) : 427-431. (1971).
225. Wang, J.
Electrochim. Acta 26(12) : 1721-1726 (1981).
226. Hampton, N.A. and Larkin, D.
Electrochim. Acta 15(4) : 581-587 (1970).
227. Pospisil, L. and de Levie, R.
J. Electroanal. Chem. 25(2) : 245-254 (1970).
228. de Levie, R.
J. Electrochem. Soc. 118(8) : 185c-192c (1971).
229. Thacker, R. and Hoare, J.P.
J. Electroanal. Chem. 30(1) : 1-14 (1971).
230. Hoare, J.P., Thacker, R. and Wiese, C.R.

- J. Electroanal. Chem. 30(1) : 15-23 (1971).
231. Novak, D.M. and Conway, B.E.
Faraday, Trans. I 77(10) : 2341-2359 (1981).
232. Conway, B.E. and Mozota, J.
Faraday Trans I 78(1) : 1717-1732 (1982).
233. Chialvo, A.C., Triaca, W.E. and Arvia, A.J.
J. Electroanal. Chem. 146 : 93-108 (1983).
234. Sakamoto, M. and Takamura, K.
Bioelectrochem. Bioenerg. 9 : 871-882 (1982).
235. Conway, B.E. and Novak, D.M.
J. Electroanal. Chem. 99(2) : 133-156 (1979).
236. Hughes, S. and Johnson, D.C.
Anal. Chim. Acta 149 : 1-10 (1983).
237. Miller, B., Bellavance, M.I. and Bruckenstein, S.
J. Electrochem. Soc. 118(7) : 1082-1089 (1971).
238. Bruckenstein, S., Bellavance, M.I. and Miller, B.
J. Electrochem. Soc. 120(10) : 1351-1356 (1973).
239. Tindall, G.W. and Bruckenstein, S.
Anal. Chem. 40(7) : 1051-1054 (1968).
240. Smyrl, W.H. and Newman, J.
J. Electrochem. Soc. 119(2) : 212-219 (1972).
241. Cadle, S.H. and Bruckenstein, S.
Anal. Chem. 44(13) : 2225-2226 (1972).
242. Geiger, T. and Anson, F.C.
Anal. Chem. 52(14) : 2448-2450 (1980).
243. Menezes, S., Miller, B. and Schnelmeyer, L.F.
J. Electrochem. Soc. 128(10) : 2167-2169 (1981).
244. Blaedel, W.J. and Boyer, S.L.
Anal. Chem. 43(12) : 1538-1540 (1971).
245. Blaedel, W.J. and Schieffer, G.W.
Anal. Chem. 46(11) : 1564-1567 (1974).
246. Kolthoff, I.M. and Jordan, J.
J. Am. Chem. Soc. 76(13) : 3843-3845 (1954).
247. Yamada, S. and Sato, H.
Nature 193 : 261-262 (1962).
248. Jenkins, G.M. and Kuwana, K.
Nature 231 : 175-176 (1971).

249. Zittel, H.E. and Miller, F.T.
Anal. Chem. 37(2) : 200-203 (1965).
250. Panzer, R.E. and Elving, P.J.
J. Electrochem. Soc. 119(7) : 864-874 (1972).
251. Taylor, R.J. and Humffray, A.A.
J. Electroanal. Chem. 64(1) : 347-354 (1973).
252. Taylor, R.J. and Humffray, A.A.
J. Electroanal. Chem. 64(1) : 63-84 (1975).
253. Taylor, R.J. and Humffray, A.A.
J. Electroanal. Chem. 64(1) : 95-105 (1975).
254. Lowde, D.R., Williams, J.O., Attwood, P.A., Bird R.J.,
McNicol, B.D. and Short, R.T.
Faraday Trans. 1 75(10) : 2312-2324 (1979).
255. Florence, T.M.
J. Electroanal. Chem. 27(2) : 273-281 (1970).
256. Kopanica, M. and Vydra, F.
J. Electroanal. Chem. 31(1) : 175-181 (1971).
257. Bately, G.E. and Florence, T.M.
J. Electroanal. Chem. 55 : 23-43 (1974).
258. Sipos, L., Kozar, S., Kontusic, I. and Branica, M.
J. Electroanal. Chem. 87(1) : 347-352 (1978).
259. Wang, J. and Ariel, M.
J. Electroanal. Chem. 83(1) : 217-224 (1972).
260. Norvell, V.E. and Mamantov, G.
Anal. Chem. 49(9) : 1470-1471 (1977).
261. Blaedel, W.J. and Wang, J.
Anal. Chem. 51(7) : 799-803 (1979).
262. Wang, J.
Electrochim. Acta 26(12) : 1721-1726 (1981).
263. Blaedel, W.J. and Wang, J.
Anal. Chem. 52(1) : 76-80 (1980).
264. Blaedel, W.J. and Wang, J.
Anal. Chem. 51(11) : 1724-1780 (1979).
265. Strohl, A.N. and Curran, D.T.
Anal. Chem. 51(3) : 353-357 (1979).
266. Strohl, A.N. and Curran, D.T.
Anal. Chem. 51(7) : 1050-1053 (1979).

267. Wang, J. and Dewald, H.D.
Talanta 29(6) : 453-456 (1982).
268. Wang, J. and Dewald, H.D.
Anal. Chem. 55(6) : 933-936 (1983).
269. Wang, J. and Dewald, H.D.
J. Electrochem. Soc. 130(9) : 1814-1818 (1983).
270. Schieffer, G.W. and Blaedel, W.J.
Anal. Chem. 50(1) : 99-102 (1978).
271. Wieck, H.J., Heider, G.H. and Yacynych, A.M.
Anal. Chim. Acta 158(1) : 137-141 (1984).
272. Curran, D.T. and Tougas, J.P.
Anal. Chem. 56(4) : 672-678 (1984).
273. Strohl A.N. and Curran, D.T.
Anal. Chem. 51(7) : 1045-1049 (1979).
274. Wang, J. and Freiha, B.A.
Anal. Chim. Acta 151(1) : 109-116 (1983).
275. Blaedel, W.J. and Yim, Z.
Anal. Chem. 52(3) : 564-566 (1980).
276. Lin, C.S., Denton, E.B., Gaskill, H.S. and Putnam, G.L.
Ind. Eng. Chem. 43(9) : 2136-2143 (1951).
277. Friend, W.L. and Metzener, A.B.
A. I. Ch. E. Jl. 4(4) : 393-402 (1958).
278. Bazan, J.C. and Arvia, A.J.
Electrochim. Acta 9(5) : 667-684 (1964).
279. Ross, T.K. and Wragg, A.A.
Electrochim. Acta 10(11) : 1093-1106 (1965).
280. Wragg, A.A. and Ross, T.K.
Electrochim. Acta 12(10) : 1421-1428 (1967).
281. Newman, J.
Ind. Eng. Chem. 60(4) : 12-27 (1968).
282. Bird, R.B., Stewart, W.E. and Lightfoot, E.N.
Transport Phenomenon.
Publ. John Willey Inc. N.Y. 1960 Ch. 2 : 34-70.
283. Hatton, A.P. and Quarmby, A.
Int. J. Heat Mass Transfer 5(10) : 973-980 (1962).
284. Reynolds, W.C., Lundberg, R.E. and McCuen, P.A.
Int. J. Heat Mass Transfer 6(6) : 483-493 (1963).

285. Reynolds, W.C., Lundberg, R.E. and McCuen, P.A.
Int. J. Heat Mass Transfer 6(6) : 495-535 (1963).
286. Heaton, H.S., Reynolds, W.C. and Kays, W.M.
Int. J. Heat Mass Transfer 6(6) : 763-781 (1964).
287. Sutherland, W.A. and Kays, W.M.
Int. J. Heat Mass Transfer 7(11) : 1187-1194 (1964).
288. Worsoe-Schmidt, P.M.
Int. J. Heat Mass Transfer 10(4) : 541-551 (1967).
289. Brown, G.M.
A. I. Ch. E. Jl. 6(2) : 179-183 (1960).
290. Skelland, A.H.P.
Diffusional Mass Transfer.
Publ. John Willey, N.Y., 1974, Ch. 5 : 109-220.
291. Stephenson, G.
Mathematics for Scientists. 2nd Ed.
Publ. Longmans, London, 1973, Ch 24 : 461-486.
292. Titchmarsh, E.C.
Eigenfunction Expansions Associated with Second Order
Differential Equations.
Publ. Oxford (Clarendon Press). 1946.
293. De Prima, R.C. and Boyce, W.E.
Elementary Differential Equations and Boundary Value
Problems.
Publ. John Willey, N.Y. 1977 : P.532-544.
294. Milne, W.E.
Numerical Solution of Differential Equations.
Publ. John Willey, N.Y. 1953.
295. Berry, V.J. and De Prima, C.R.
J. Appl. Phy. 23(2) :195-198 (1952).
296. Millipore (UK) Ltd, Harrow, Midx. England.
297. Knott, A.R.
Atomic Absorption Newsletter 14 : 126-132 (1975).
298. Moody, J.R. and Lindstrom, R.M.
Anal. Chem 49(14) : 2264-2267 (1977).
299. Janz, G.J. and Taniguchi, H.
Chem. Rev. 53 : 397-437 (1953).
300. Kolthoff, I.M.
J. Phys. Chem. 39(7) : 945-954 (1935).
301. Von Stakelberg, M. Pilgram, M. and Toome, V.

- Z. Electrochem. 57 : 342-350 (1953).
302. Prengle, R.S. and Rothfus, R.R.
Ind. Eng. Chem: 43(3) : 379-386 (1955).
303. Bockris, J.D. and Reddy, A.K.W.
Modern Electrochemistry Vol 2. Ch. 10 : 1173-1230.
Publ. Plenum/Rosetta 1970.
304. Wranglen, G.
Electrochim. Acta 2(1-3) : 130-146 (1960).
305. Tobias, C.W. and Hickman, R.G.
Z. Phys. Chem. 229(3/4) : 145-166 (1965).
306. Engstrom, R.C.
Anal. Chem. 54(13) : 2310-2314 (1982).
307. Napp, D.J., Johnson, D.C. and Bruckenstein, S.
Anal. Chem. 39(4) : 481-485 (1967).
308. Bruckenstein, S. and Prager, S.
Anal. Chem. 39(10) : 1161-1163 (1967).
309. Peters, D.G. and Cruser, S.A.
Electroanal. Chem. 9(1) : 27-40 (1965).
310. Latimer, W.M.
Oxidation Potentials. 2nd Ed.
Publ. Prentice Hall, N.Y. 1952 P. 184.
311. Nekrasov, L.N. and Berezina, N.P.
Dokl. Acad. Nauk. SSSR. 142 : 855 (1962).
312. Cotton, F.A. and Wilkinson, G.
Advanced Inorganic Chemistry.
Publ. Interscience Publishers. N.Y. 2nd Ed. 1966 P. 366.
313. Greenfield, S.
Spectrochim. Acta 38B(1/2) : 93-105 (1983).
314. Nukiyama, S. and Tanasawa, Y.
Experiments on the Atomisation of Liquids in Air Stream.
Translator : Hope, E.
Defence Research Board. Department of National Defence;
Ottawa, Ontario, Canada. 1950.
315. Gunn, A.M., Millard, D.L. and Kirkbright, G.F.
Analyst 103 : 1066-1073 (1978).
316. Browner, R.F. and Boorn, A.W.
Anal. Chem. 56(6) : 875A-888A (1984)