

THE AUTOMATION OF ELECTROANALYTICAL TECHNIQUES

A Thesis Submitted
for the
Degree of Doctor of Philosophy
by
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London

September, 1983

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ABSTRACT

The work described in this thesis involves the automation of electroanalytical techniques using microprocessor control with the aim of developing a fully automated system for the analysis of arsenic, phenols and cresols in water.

This work was done in conjunction with the Laboratory of the Government Chemist which has the task of monitoring water supplies around the country. At present this task is done by spectrochemical techniques: a typical detection limit is 32 nM for phenol.

The electroanalytical technique used in this work was the wall-jet ring-disc double electrode system which was a development from the rotating ring-disc double electrode. In both systems a titrant is generated at the disc electrode. In this work bromide is oxidized to bromine, which then travels downstream to the ring electrode. In the absence of a substrate a certain fraction of the bromine is detected at the ring electrode. In the presence of a substrate which will react with bromine no ring current is detected until sufficient bromine is being produced at the disc to reach the ring before reacting with the substrate. The disc current required is a function of the concentration of substrate and hence can be used to determine its concentration. Ring-disc titration plots can be analyzed in two different ways. The recording of titration curves and their subsequent analysis was automated using a microcomputer. For arsenic a lower limit of detection of 2 μ M was achieved and 5 μ M for phenol.

The rise time experiment was then automated using the microprocessor. This experiment allows us to determine the time taken for the ring current to stabilize after the disc current has been changed.

The recording of titration curves is relatively slow (typically one minute) and a faster method was desired. The autotitration experiment was previously developed and involved analogue measurements. A digital counterpart was developed allowing continuous analysis with concentration determinations occurring every two seconds, the time delay being required to allow the ring current to stabilize.

The possibility of distinguishing between various phenols and cresols was discussed. This would be possible due to a variation in the reaction rates with the bromine which gives rise to deviations from the ideal titration curve which assumes an infinitely fast reaction between the bromine and the substrate.

The experimental results were compared with theoretical predictions of the wall-jet theory which has recently been worked out in this laboratory.

I would like the Ring on Disc

ACKNOWLEDGEMENTS

I would like to thank:

Professor W. J. Albery and Dr B. P. Levitt for their advice, help and encouragement during the course of this work;

Dr N. J. Goddard for instructing me in the ways of microprocessing;

The members of Professor Albery's research group for many useful discussions;

The Laboratory of the Government Chemist for financial support;

The Science and Engineering Research Council for supporting me during the course of this work.

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Chapter One

Introduction

A Preamble

This work has been directed towards developing an automated on-line technique for the detection and quantitative determination of arsenic, phenols and cresols in water, notably industrial effluent into rivers. In such organizations as the Laboratory of the Government Chemist (LGC), with whose collaboration this work was done, this analysis is carried out at present using colorimetric techniques which are accurate but suffer from the disadvantage of being expensive and difficult to use in an on-line continuous mode. In the case of phenols and cresols this analysis is performed with a reaction with 4-amino-antipyrine in an oxidation reaction in the presence of $K_3Fe(CN)_6$ where the coupling is para to the phenol group (32); this latter characteristic results in the drawback of this technique not being so sensitive to substrates such as p-cresol. Using such techniques the lower limit reached with, for example, phenol has been 98 nM ($9\mu g\ l^{-1}$), and with pre-concentration using chloroform extraction the lower limit has been 32 nM.

What was desired was a simple chemical system, preferably with no moving parts, which could be readily connected to a microcomputer for automation. Such a system could be an electrochemical one and it is with such a system that this work is concerned.

B Electroanalytical Techniques

Electrochemistry concerns itself with the phenomena associated with the passing of currents of electricity through solutions and with

the activity at the interface between the solution and the electrodes. More specifically it is an investigation of the fate and the effects of the ions present in the solution; one of the factors involved is the number of ions present and as a consequence we have a means of determining this number and hence a method concentration measurement - this is the area of electroanalytical chemistry.

The study of electrochemistry has been undertaken for many years and much has been learnt about the nature of ions and their chemical and physical properties. Electrochemistry is an involved subject and there are a number of parameters that can be used for making analytical determinations. These include conductometric techniques where the conductance of an electrolyte solution is measured and from which information can be extracted. More specific techniques are concerned with the behaviour of the solution at the electrode-solution interface itself where the potential difference across the interface and the current flowing are the relevant phenomena. These phenomena can be readily measured with accuracy and precision and it is such measurements that comprise the study of this thesis. Charge and its accumulation is a third parameter which can be studied and measured, but, as with conductometry, it has not been studied here and so it will not be discussed.

(a) The Oxidation and Reduction of Electroactive Species

An important area is concerned with the oxidation or reduction of electrochemical species at the electrode where electron transfer occurs; one method available is coulometry in which a current is measured over a period of time and a time-current integral is obtained which is a measure of the total charge passed. Voltammetry is the

measurement of instantaneous current and potential values.

Coulometry is a titration technique in which an electrochemical reaction is allowed to go to completion where the consumption of the species under analysis can be determined in two ways. A constant current can be passed and the end-point detected by a chemical indicator or a physical one such as a shift in electrode potential. Alternatively the working electrode can be controlled, thereby isolating the relevant electrode reaction and observing a drop to zero current when the end-point has been reached. It is assumed that the electron transfer reaction has 100% current efficiency and the number of electrons involved in the reaction per molecule is known. Any reducible or oxidizable species can be detected with a typical sensitivity of 10^{-6} Molar. One drawback is that the reaction must be allowed to go to completion and this would not make a particularly suitable technique for on-line analysis where analyses should be as short as possible. Further complications would arise with phenols and cresols since there may be more than one electrochemical site. In addition reaction products may undergo further chemical reaction, eg polymerization, which may interfere with the electrode causing electrochemical inhibition.

In the second approach, voltammetry, the relationship between current and potential is observed and in Figure 1.1, which shows what is typically observed, two distinct areas can be observed, the limiting current value and the current increasing to this final value. This suggests that two processes are at work and they are the rate of electrode reaction and the rate of diffusion of the electroactive species to the electrode from the bulk of the solution. The former is dependant on the potential of the electrode (the greater the potential

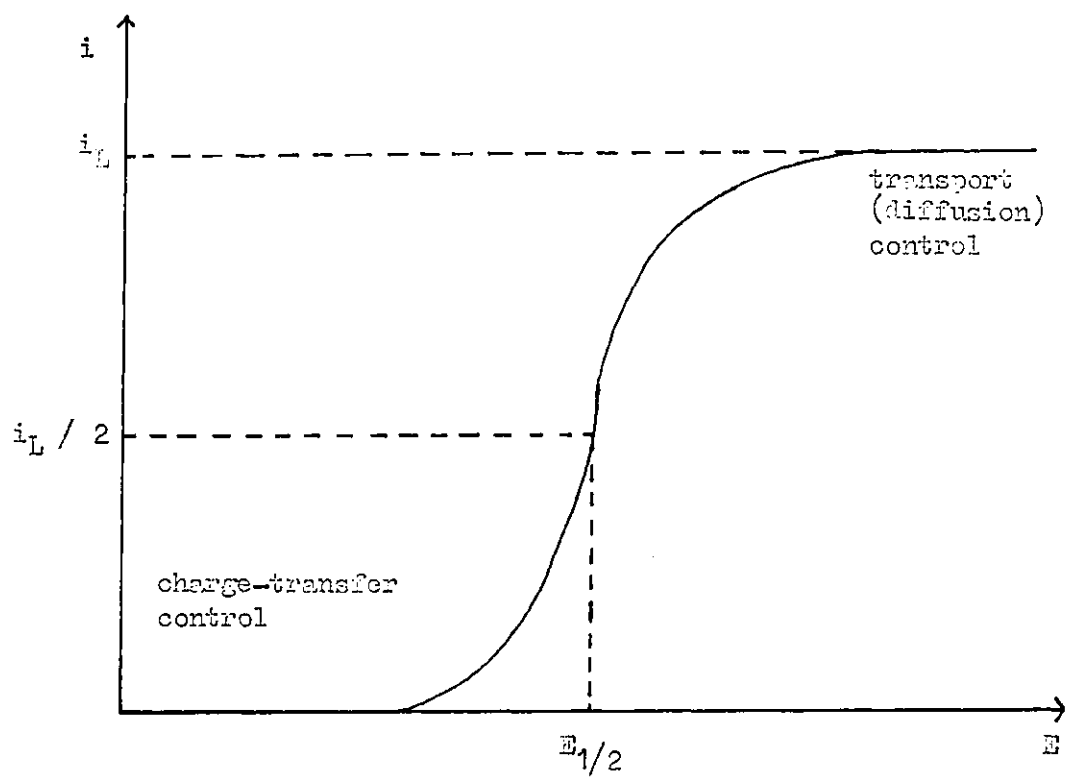


Figure 1.1 A schematic voltammogram

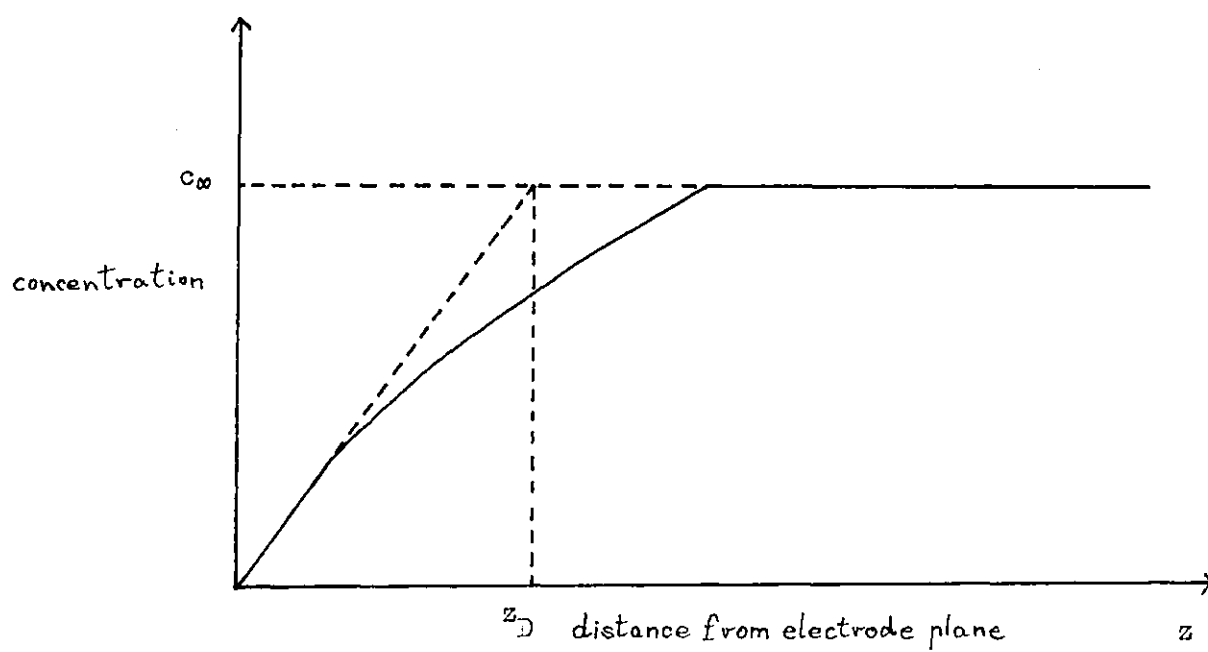


Figure 1.2 A schematic concentration profile near the electrode surface, for the case of a limiting current

the greater the rate) and so determines the current measured. Thus as the potential is increased so the current increases once a threshold has been reached. Since we are dealing with a stationary electrode in a stationary solution the electroactive species near to the electrode will be consumed first and thus a concentration gradient will be set up so allowing the species from the bulk of the solution to diffuse to the electrode; in addition there is migration due to the applied electric field but this can be made negligible by the addition of a supporting electrolyte. These two processes comprise the transport process and if its rate is lower than that of the electrode reaction rate (as determined by the potential) the overall rate of reaction and hence the current will be transport controlled - this current is known as the limiting current and is dependant on the bulk concentration, C_0 . This dependency gives rise to possibilities of analytical application. Thus a diffusion layer has been established which, as time progresses, as more electroactive is consumed, becomes larger. In Figure 1.2 a schematic concentration profile close to the electrode is shown and it can be seen that the concentration at the electrode, C , is zero since all the species reacts as soon as it arrives at the electrode surface. The half-wave potential, $E_{1/2}$, is a characteristic of the electrode reaction (1) and can sometimes be used for identification.

Fick's First Law describes the dependence of the diffusion-limit current on the thickness of the diffusion layer,

$$i = n F A j = n F A D \left(\frac{\partial C}{\partial z} \right)_{z=0} = n F A D \left(\frac{C_{\infty} - C_0}{z_D} \right)$$

$$\Rightarrow i_L = n F A D \left(\frac{C_{\infty}}{z_D} \right) \quad (1.1)$$

since $C_0 = 0$ at the electrode surface, where Z_D is the thickness of the diffusion layer, n is the number of electrons transferred per molecule of electroactive species, F is the Faraday constant, A is the area of the electrode, D is the diffusion constant of the electroactive species and C_0 is the bulk concentration of that species. As we have seen Z_D is time dependent and this dependence can be determined from Fick's Second Law for semi-infinite linear diffusion (a stationary electrode in a stationary solution), which is the transport equation for a planar electrode,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (1.2)$$

where z is the distance from the electrode plane and where the boundary conditions are,

$$z = 0, t = 0 \Rightarrow C = C_0$$

$$z = 0, t > 0 \Rightarrow C = 0$$

$$z \rightarrow \infty, t \geq 0 \Rightarrow C = C_0$$

Laplace transforms (Appendix 1) allow equation 1.2 to be solved giving the concentration $c(z,t)$ and hence a concentration gradient. The limiting current is given by,

$$i_L(t) = n F A \frac{D^{1/2} C_0}{\pi^{1/2} t^{1/2}} \quad (1.3)$$

We can see that the current decreases with $t^{1/2}$ as expected due to the increase in the diffusion layer, Z_D . In addition density gradients are produced which gives rise to natural convection and so deviations

from this equation. But for short periods of time good agreement is found between theory and experiment and this relationship between $i_L(t)$ and C_0 allows various electroanalytical techniques to be applied, eg pulse voltammetry (2,3), differential pulse voltammetry (4) and differential double pulse voltammetry (5).

The difficulty encountered here is that not only do we need to control the potential but we also need to accurately monitor the time - it would be preferable to achieve a time independent system. This can be achieved in two different ways. The first method adopted was the continual renewal of the electrode surface and thus by such means we are effectively recreating the conditions when $t = 0$. This is what occurs in the dropping mercury electrode (DME) in which drops periodically grow, with a periodically growing current being measured beginning with a fresh solution. Equation 1.3 can now be modified to allow for the changes which are brought about by these time - dependent periods and the increase in electrode size; we obtain,

$$i_L(t) \propto D^{1/2} t^{1/6} C_{\infty} \quad (1.4)$$

This equation still applies to a plane electrode and therefore the diffusion layer must be much less than the radius of the drop. This technique is known as polarography.

The second method, which results in a genuine time -independent system, involves limiting the thickness of the diffusion layer by using a forced convection system where an imposed and controlled transport of the electroactive species to the electrode is set up and so fixing the extent of the diffusion layer. This can be effected in two different ways; either by rotating or vibrating the electrode such that the solution is impelled towards the electrode, or alternatively

the solution is made to flow past the electrode. In this work the latter method was used for limiting the diffusion layer. Using such techniques voltammograms can be obtained; however with phenols and cresols there are no simple oxidation or reduction products which means that voltammetry is not very suited to this task.

(b) Potentiometry

Potentiometry is another possible technique for analytical purposes; it is a form of voltammetry in which the current is held at a constant value, usually zero, while the potential of the electrode is measured. A well defined reaction at local equilibrium is necessary and the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \left(\frac{c_O}{c_R} \right) \quad (1.5)$$

gives the concentration dependence of the electrode potential, where c_O is the concentration of the oxidized form of the species and c_R is the reduced form. Since there is zero current there will be no concentration gradients and c_O and c_R will be the same as the bulk concentration. The problems with this technique include a logarithmic response which results in poor sensitivity, gradual poisoning and interfering ions although the latter problem is being overcome with the use of ion-selective electrodes.

(c) Reactions with species which are electroactive

The problems encountered with direct potentiograms or voltammograms of the aromatics under investigation can be overcome by using a species which will both chemically react with the aromatic and will also be electroactive in a simple and well-defined manner. We are

then able to perform what is essentially a back titration. One such example is the use of electrogenerated bromine where the bromine generated in situ reacts with the substrate under analysis and the amount of unreacted bromine is then determined. This has been established for some time having been used by Szebelledy and Somogyi (6) in their coulometric titrations and later by Krivis, Supp and Gazda (7) and Christian, Knoblock and Purdy (8) in coulometric titration of ammonia using hypobromite.

Such titrations take some time to perform, sometimes several minutes, since they necessitate an end-point to be determined, i.e. there must be complete reaction between the substrate and the titrant. This problem can be overcome by the double electrode flow systems where the titrant is generated at one electrode, transported to another electrode, in the diffusion layer such that only small amounts are actually titrated, where it is then detected. It is with such a system that this work is involved.

C Forced Convection Electrode Systems

We have seen that two problems have arisen; firstly that electrolysis under semi-infinite diffusion gives rise to time-dependent diffusion layers and currents, and secondly that titrations need to go to completion in order to obtain an end-point. As a consequence lengthy periods of time were required for analysis which makes it unsuitable for on-line analysis. The first problem was dealt with by defining a diffusion layer thickness by applying a forced convection; the second problem can be overcome by a back titration which effectively occurs in the diffusion layer and by using a second electrode to determine the remaining titrant. In this section we will

look more closely at the forced convection electrode systems available.

The equations used previously are not now valid since we now have two major factors determining the transport of electroactive species to the electrode; firstly, as before, the concentration gradient across the diffusion layer which previously was taken as being linear in the Nernst description and secondly the transport of the electroactive species to the electrode by forced convection which will also determine the diffusion layer thickness. We must therefore allow for the hydrodynamic parameters such as the flow patterns and the flow rates and equation 1.2 must be modified to accomodate these effects; the diffusion layer is now described by the following convection-diffusion mass transport equation:

$$\frac{\partial c}{\partial t} = D \nabla^2 c - \underline{v} \cdot \nabla c \quad (1.6)$$

The functional dependence of the fluid velocity vector, $\underline{v}$, upon the co-ordinates of the system must first be known before equation 1.6 can be solved for a particular system. Before this, however, the solution to the fluid flow equations must be obtained with the appropriate boundary conditions, they being the Navier-Stokes equation, which describe the effects of forces on the fluid, and the equation of continuity which deals with the conservation of matter. The solution of these hydrodynamic equations is complex and will not be looked at in this work; in chapter two the solutions for the convection-diffusion equation used here will be presented.

The various forced convection systems that have been developed

will now be looked at and later on compared. As mentioned previously two different approaches can be taken, either the electrode is set in motion, ususally rotated or vibrated, or alternatively the solution is made to flow past the electrode. The first of these approaches was originally pursued and the rotating disc electrode (RDE) was one of the first successful systems to be developed and much of the work done in this laboratory was done with this system. The first technique to be developed in this laboratory pursuing the second approach was the tubular electrode (TE) in which an electrode was placed in the base of a tube through which the solution would flow and so past the electrode. A later flow system was one in which the solution is fired through a fine nozzle at a circular disc which constituted the electrode, (cf the RDE).

(a) The Rotating Disc Electrode

A disc of the electrode material, often platinum though other substances are used, eg glassy carbon, is surrounded by a coplanar, circular mantle of a non-conducting material (usually Teflon or Araldite). This is then supported in solution by a stainless steel shaft which is rotated. The steel shaft also provides the electrical contact with the disc electrode. Von Karman (9) obtained an approximate solution for this system (one of the few cases where an explicit solution of the stationary (time-independent) form of the Navier-Stokes equation is possible); this was then improved by Cochran (10). The solution immediately adjacent to the electrode is stationary relative to the electrode but as one moves away from it (as z increases) the solution is less well held and it is flung out centrifugally; the solution is then replaced from below - thus the

overall effect is of the rotating electrode sucking solution towards itself from the bulk of the solution; the flow of the solution can be seen in Figure 1.3. We can envisage the layer adjacent to the electrode as constituting a hydrodynamic boundary layer and it can be approximately given by:

$$\delta_o \approx 3 \left(\frac{\nu}{\omega} \right)^{1/2} \quad (1.7)$$

where ν = kinetic viscosity (viscosity/density)

ω = rotation speed.

It can be seen that the viscosity has an effect; the thickness of this layer is typically 0.1 - 1 mm.

The task is now to find the diffusion layer thickness in order that we might find the dependence of the limiting current on the bulk concentration as previously. In order to do this we must find the velocity of the fluid perpendicular to the disc. This was done by Levich (11) who used the first term in Cochran's solution:

$$u_z = -(\nu\omega)^{1/2} (0.510z_1^2 - 0.333z_1^3 + 0.103z_1^4 \dots) \quad (1.8)$$

where z_1 is a dimensionless quantity given by:

$$z_1 = z(\omega/\nu)^{1/2}; \quad (1.9)$$

the negative sign indicating the flow of solution towards the electrode. The convection-diffusion mass transport equation can now be solved and the thickness of the diffusion layer is given by:

$$\delta = z_D = 1.6 D^{1/3} \omega^{-1/2} \nu^{1/6}; \quad (1.10)$$

typical values for z_D are 5 - 50 μm . One notes that the transport

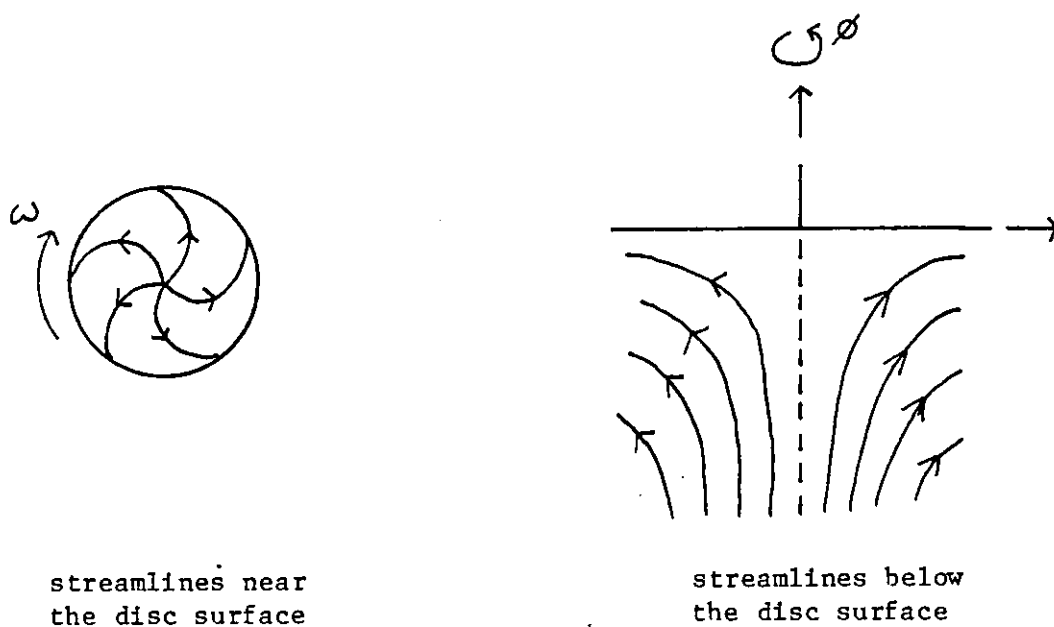
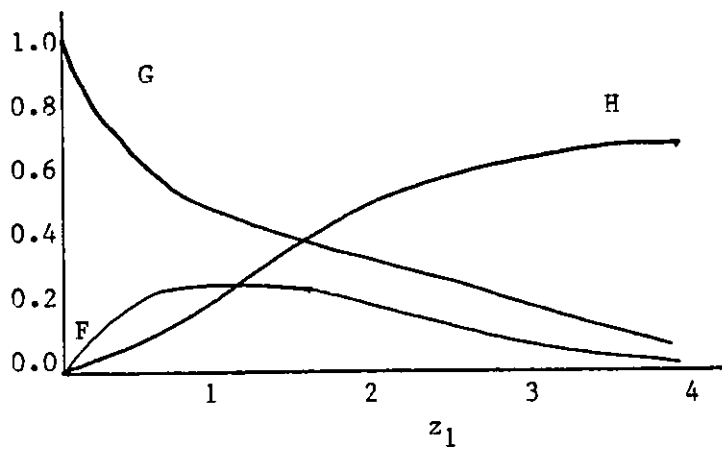


Figure 1.3 Streamlines for the rotating disc electrode



$$v_r = r\omega F(z_1)$$

$$v = r\omega G(z_1)$$

$$v_z = -(\nu\omega)^{1/2}H(z_1)$$

Figure 1.4 Flow functions at the rotating disc electrode

boundary layer is independent of r , that is to say the disc surface is uniformly accessible. Rearrangement of the equation gives us:

$$z_D = 1.6 \left(\frac{D}{\nu} \right)^{1/3} \left(\frac{\nu}{\omega} \right)^{1/2} \quad (1.11)$$

where $(D/\nu)^{1/3}$, the (Schmidt number) $^{1/3}$ (10 for aqueous solutions), relates the hydrodynamic (viscosity) boundary layer to the diffusion layer. We can see from Figure 1.4 that there is some convection in the diffusion layer, when $z < 0.1z_1$. In addition z_D is dependent on ω , the rotation speed, and that by varying this speed we can vary the flux to the disc, the limiting current for the RDE system is:

$$i_L = 0.62 n F \pi r^2 D^{2/3} \omega^{1/2} \nu^{-1/6} C_\infty \quad (1.12)$$

We observe a simple linear relationship between this current and the bulk concentration of the electroactive species which thus affords us an electroanalytical technique; alternatively diffusion co-efficients can be obtained if the concentration is known. Extensive use of the RDE system has been made for kinetic and analytical work and Riddiford has written a review of this (12); detailed solutions for the hydrodynamic equations and for the convection-diffusion equation can be found in Levich's book (13).

(b) The Tubular Electrode

Later developments have introduced the second type of forced flow electrode where the electrode is stationary and the solution is made to flow past it. The first of this type was the tubular electrode (TE) in which the electrode is embedded in a channel through which the

solution passes; however, unlike the RDE, the electrode is not uniformly accessible. The limiting current is given by:

$$i_L = 5.31 \cdot 10^5 n D^{2/3} X^{2/3} V_f^{1/3} a_o \quad (1.13)$$

where $V_f^{1/3}$ = volume flow rate of the solution,

X = length of the electrode.

As will be seen the TE has a smaller dependency on the flow rate than the wall-jet electrode and this means less sensitivity although the advantage is irregularities in the flow rate such as pulsing become less of a problem. Two other disadvantages are the difficulties in cleaning and maintaining the electrode and the greater complexity of the theory.

(c) The Wall-Jet Electrode

In this system the solution is forced to flow perpendicularly into a wall where it then splays outwards radially over the wall. This concept is not new and has been described by Glaubert in 1956 (14); the fluid flow is depicted in Figure 1.5 and the diffusion layer is indicated. Using Glaubert's results Yamada and Matsuda (15) were able to arrive at the expression for the limiting current i_L :

$$i_L = 1.60 n F D^{2/3} \nu^{-5/12} V_f^{3/4} a^{-1/2} r^{3/4} C_o \quad (1.14)$$

where a = nozzle diameter

V_f = flow rate

r = radius of the electrode

We can see here as well that there is a $r^{3/4}$ dependency which

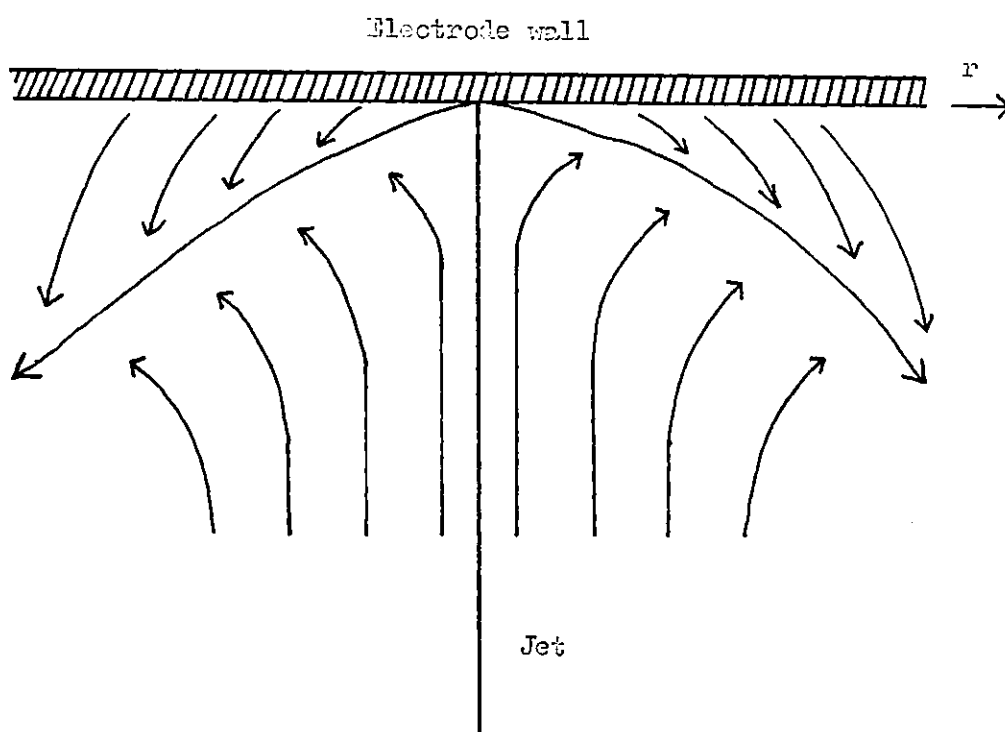


Figure 1.5 The fluid flow in the wall-jet electrode

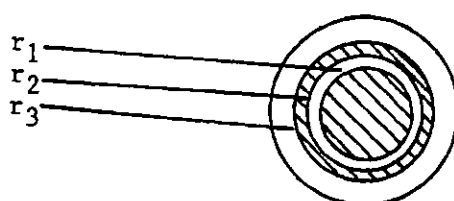


Figure 1.6 The ring-disc electrode geometry

shows that the electrode surface is not uniformly accessible to the solution; that is to say the diffusion layer varies with r . Both the nozzle diameter and the kinematic viscosity affect the limiting current since they will affect the flow of solution to the electrode. The wall-jet electrode (WJE) has a higher flow rate dependence ($v_f^{3/4}$) than the TE ($v_f^{1/3}$) which give it a greater sensitivity (this being one reason for the preferential use of the former), though the penalty is that there is also a greater sensitivity to fluctuations in the flow rate as will be discussed later. Since both the TE and the WJE are flow through systems they are both suitable for on-line analysis though the WJE has the advantage of being more easily cleaned and maintained.

There have been studies on the WJE under turbulent flow by Pungor and others (16 - 18); and studies by Chin and Tsang (19) have investigated the stagnation region where the jet hits the electrode surface. This system has been used as an electrochemical detector for high pressure liquid chromatography for many organic compounds (20, 21) and in anodic stripping voltammetry (22).

(d) The Double Electrode System

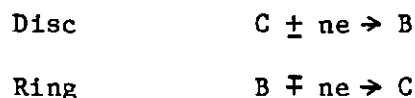
In these systems the fluid flow is exactly the same, the difference is that a second electrode has been inserted so that the products of the first electrode reaction may be detected. In the rotating electrode system and in the wall-jet system the second electrode is in the form of a ring electrode which is concentric with the ring electrode and is separated from it by an insulating annulus of a non-conducting material (see Figure 1.6).

The rotating ring-disc electrode (RRDE) and the wall-jet ring-

disc electrode (WJRDE) are similar in many ways and what follows is applicable to both. In this work the latter has been used and in chapter two the system will be described in greater detail.

As mentioned earlier we should like to be able to produce electrochemically a species which will react with the substance under analysis, whose electrochemical reactions are too complex for easy electrochemical determination, so allowing an indirect analysis. This task has been achieved by the double electrode system.

At the disc the chemical species required is electrochemically produced, the disc being known as the generator; this species then travels downstream to the ring electrode, which is known as the detector, where it is converted back to the original substance.



The bulk concentration of B is zero since it is being produced at the disc; at the ring its concentration is zero since it is being detected as a limiting current. The intermediate B travels away from the disc, some going across to the ring where it is detected with the rest escaping into the solution (see Figure 1.6). The fraction of B which reaches the ring is known as the collection efficiency, N_o , and is simply:

$$N_o = \frac{-i_R}{i_D} \quad (1.15)$$

the negative sign arising since the two reactions are the reverse of each other.

The first stage is to obtain a theoretical expression for N_0 in order to determine the bulk concentration and to find the parameters for optimum design for a double electrode cell. This is achieved by solving the convection-diffusion equation in the three zones of the disc, insulating annulus and ring with the aid of Laplace transformations. In this situation the transport of B is brought about by diffusion normal to the electrode and by radial convection, and where radial diffusion is negligible. N_0 was first calculated approximately by Ivanov and Levich (23). Alberly and Bruckenstein later found the exact solution which was (24,25):

$$N_0 = 1 - F\left(\frac{\alpha}{\beta}\right) + \beta^{2/3} [1 - F(\alpha)] - (1 + \alpha + \beta)^{2/3} [1 - F\left\{\left(\frac{\alpha}{\beta}\right)(1 + \alpha + \beta)\right\}] \quad (1.16)$$

where the function F is given by:

$$F(x) = \frac{3^{1/2}}{4\pi} \ln \frac{(1 + x^{1/3})^3}{(1 + x)} + \frac{3}{2\pi} \arctan \frac{(2x^{1/3} - 1)}{3^{1/2}} + \frac{1}{4} \quad (1.17)$$

and where α and β are functions of the geometry of the electrode:

$$\begin{aligned} \alpha &= (r_2/r_1)^3 - 1 \\ \beta &= (r_3/r_1)^3 - (r_2/r_1)^3 \end{aligned} \quad (1.18)$$

where r_1 , r_2 and r_3 are the radii as given in Figure 1.6. The constant $\beta^{2/3}$ is the proportionality constant between the two limiting currents for the disc and ring:

$$i_{R,L} = \beta^{2/3} i_{D,L} \quad (1.19)$$

It is important to observe that N_0 is predicted to be solely a function of the electrode geometry and is not dependent on the rotation speed or the flow rate; good agreement has been obtained between theory and experiment for the RRDE (25,26). Part of the aim of this thesis was continue the work of verifying the theory by experiment as begun by Brett (27). Typical values of N_0 are between 0.10 and 0.25 and a program has been written to calculate values for N_0 and $\beta^{2/3}$ which will be presented later. The next step is to find an expression for the concentration of the species under analysis.

If a reagent A is present which will react with the intermediary B the ring current will not be as great as it would have been if A were absent; thus we must determine by how much the ring current is reduced in the presence of A. In the diffusion layer titration technique (28) there exists the sample under analysis (A), the species (B) which is produced electrochemically from C; when there is no disc current the concentration of B is zero, while those of A and C are uniform throughout the solution. As the appropriate disc current (ie in the anodic or cathodic direction) is increased the intermediate B is formed at the disc but is removed immediately by reaction with A and so b (the concentration of B) is uniformly zero (assuming a steady state and a fast reaction - more will be said about this later). But now the concentration of A, a, will not be the same in the diffusion layer as in the bulk of the solution (see Figure 1.7). As the disc current is increased the concentration of A at the disc surface, a_0 , will decrease until such a time that $a_0 = 0$; at this point the disc current is given the symbol M. The transport of A to the electrode is diffusion limited and M is given by:

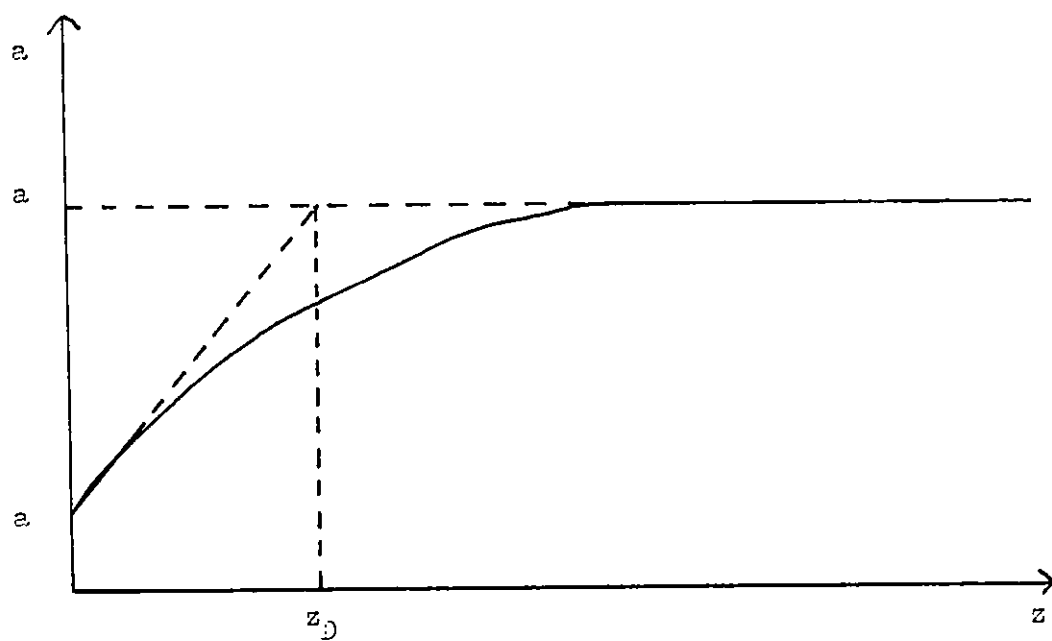


Figure 1.7 The variation in concentration of A with z

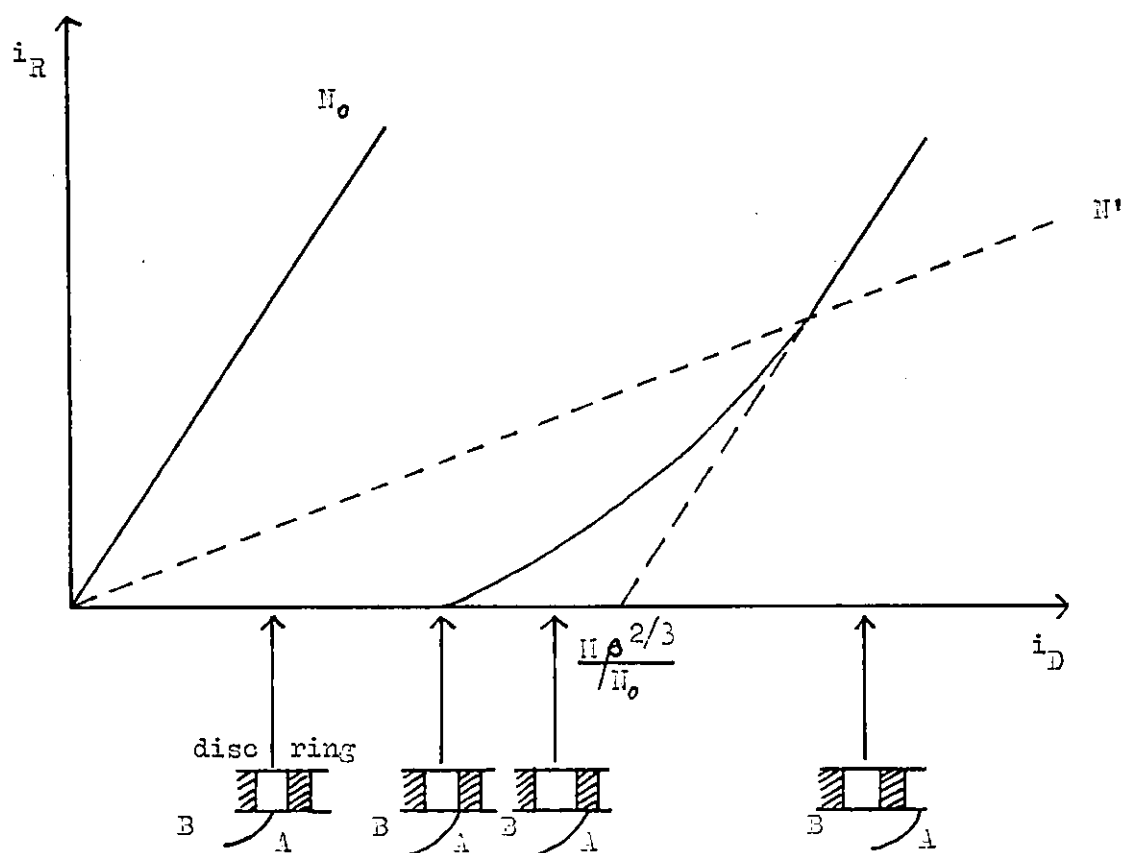


Figure 1.8 The ring-disk electrode titration curve

$$M = 0.62 n_B F A D^{2/3} \omega^{1/2} \nu^{-1/6} a_{\infty} \quad (1.20)$$

where the flux of B (controlled by the disc current) is equal to the magnitude of the flux of A (controlled by the hydrodynamic action of the cell) such that the behaviour of A can be seen as being analagous to an electroactive substance undergoing charge transfer at the disc electrode. As the disc current is further increased the flux of B will become greater than A one can envisage two regions, one in which A predominates and the other in which B predominates, these being seperated by a boundary where $a = b = 0$. However this is the situation for a limited number of cases, namely those reactions which are sufficiently fast such that we can assume a negligible reaction time which ensures a well defined boundary between the two layers. The effects of this condition not being met will be discussed later. As yet no B will be detected at the ring electrode as seen in Figure 1.8; however as the disc current increases the boundary will move outwards until it will reach the inside of the ring electrode at which point a ring current will be observed and which will increase ($i_D/M = 1.5 - 2.0$). With increasing disc current the boundary will move across the ring and the ring current will curve on upwards until the whole electrode lies in the B dominated region at which point the ring current increases linearly ($i_D = 2.5 - 3.0$). The ring current in this region is given by:

$$i_R = N_O i_D - M\beta^{2/3} \quad (1.21)$$

where the second term on the right hand side represents a limiting current at the ring electrode and can be seen as the modified form of

equation 1.17. The net result is a displacement of the collection efficiency to the right. i_R can be seen as the flux of B to the ring in the presence of A, $N_O i_D$ can be seen as the flux of B to the ring in the absence of A and $M^{2/3}$ can be seen as the limiting flux of A to the ring. We now wish to find the relationship between this displacement and the concentration of the substrate, a . If we extrapolate the linear region back to $i_R = 0$ we obtain:

$$i_D = M \beta^{2/3} / N_O$$

$$= \text{constant} \cdot B D^{2/3} \omega^{1/2} a_{\infty} \quad (1.22)$$

in the case of the rotating system and

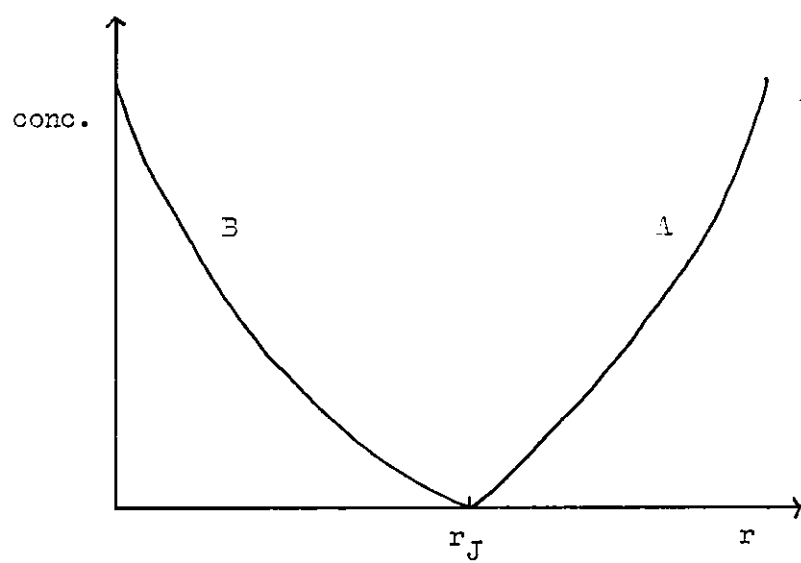
$$i_D = \frac{1.6 \beta^{2/3} k n F \nu^{-5/12} D^{2/3} a^{-1/2} r^{3/4} v_f^{3/4} a_{\infty}}{N_O} \quad (1.23)$$

in the case of the wall-jet system. We can readily see that there is a direct relationship between the concentration and the displacement and consequently we have a powerful analytical technique in the diffusion layer titration technique. We also observe a dependence on $\omega^{1/2}$ in the former case and $v_f^{3/4}$ in the latter case and this allows us to vary the displacement and hence the operating conditions. Good agreement has been obtained between theory and experiment for the RRDE using electrochemically produced bromine and As(III) down to the 10^{-7} Molar level (28).

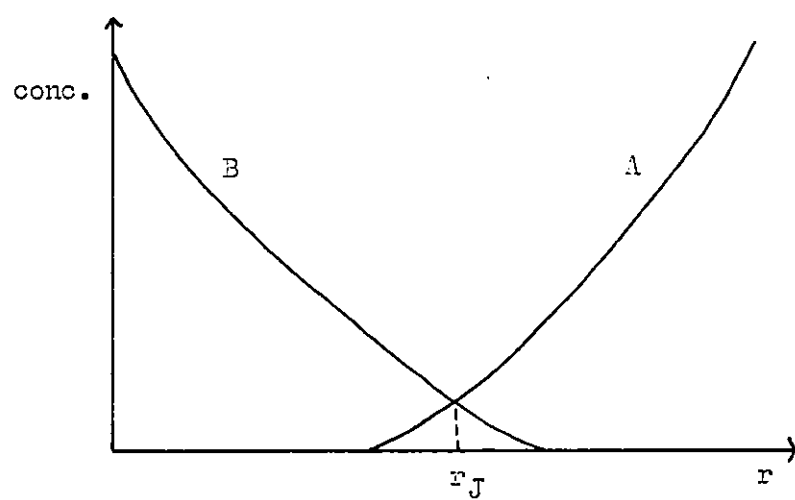
From this we are able to continue further the analysis by looking at the curved region of the plot which comes just before the linear region and this is very useful since it is sometimes not possible to

reach the linear portion of the curve, eg the concentration may be so high that complications set in before the linear portion of the curve is reached, notably the electrochemical decomposition of water. The shape of this non-linear region is determined by the passage of the reaction boundary across the ring electrode and it can be described in terms of B_J , a dimensionless parameter which describes its position, and its associated values of i_D/M (a normalized disc current), and N' ($= i'_R/i'_D$). These values can be calculated and a program, which will be presented later, has been written for obtaining such values. By comparing the theoretical predictions with those obtained by experiment we would be able to test the wall-jet theory.

However the shape of this non-linear region is also determined by the shape of the reaction boundary; we have assumed ideal conditions, that is to say the reaction between A and B is fast, effectively infinitely fast. Often this is not the case and there is an inter-penetration of A into B and B into A, the extent of this penetration depending on the rate constant k_2 ; the reaction boundary is r_J , the point at which $a = b$, see Figure 1.9. Consequently some B reaches the ring before it would have otherwise and a ring current is observed, ie the ring current threshold has been lowered and the non-linear region is less steep than it would have been otherwise. As will be seen later various measures can be taken to overcome this problem. However it does have potential use since the shape of the curve obtained will depend on the extent of the inter-penetration which in turn will be a function of the kinetics of the particular reaction under study. Since each substrate will have its own particular rate constant we have theoretical means of identification.



An infinitely fast reaction



A slower reaction

Figure 1.9 Schematic concentration profiles at the ring-disc for diffusion layer titrations

The tubular double electrode (TDE) was the forerunner of the WJRDE and was the first flow through cell used in this laboratory; diffusion layer titration curves have been obtained (29) with this system where two electrodes are placed in the wall of a channel, the upstream electrode being the generator and the downstream one being the detector. The relevant equation describing the titration curve being:

$$i_{\text{det}} = N_o i_{\text{gen}} - M \lambda^{2/3} \quad (1.24)$$

where M will have a different form and $\lambda^{2/3}$ is analogous to $\beta^{2/3}$ in the other two electrode systems. But because of the cleaning and maintaince problems and the lower flow rate sensitivity the system was not used.

D The Autotitration Technique

For analysis purposes it was considered desirable to produce an automated on-line continuous analysis system for the constant monitoring of pollutants in water, arsenic, phenols and cresols in this project. For this purpose the rotating ring-disc system is not suitable because it is only readily capable of batch analysis. This then leaves the TDE and the WJRDE and for reasons previously given the latter was chosen for this work.

The methods of analysis described in the previous section are only suitable for batch analyses, although they could be used in an on-line mode. In these methods an increasing disc current must be produced and a ring current is measured and the results are then plotted on an X-Y plotter. This process is fairly time consuming, each

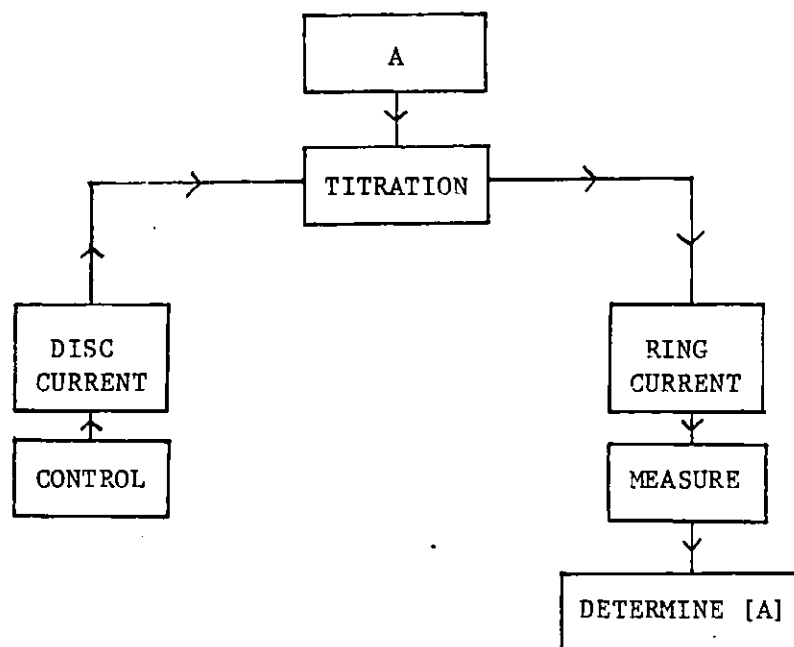


Figure 1.10 The methodology of manually recording a titration curve

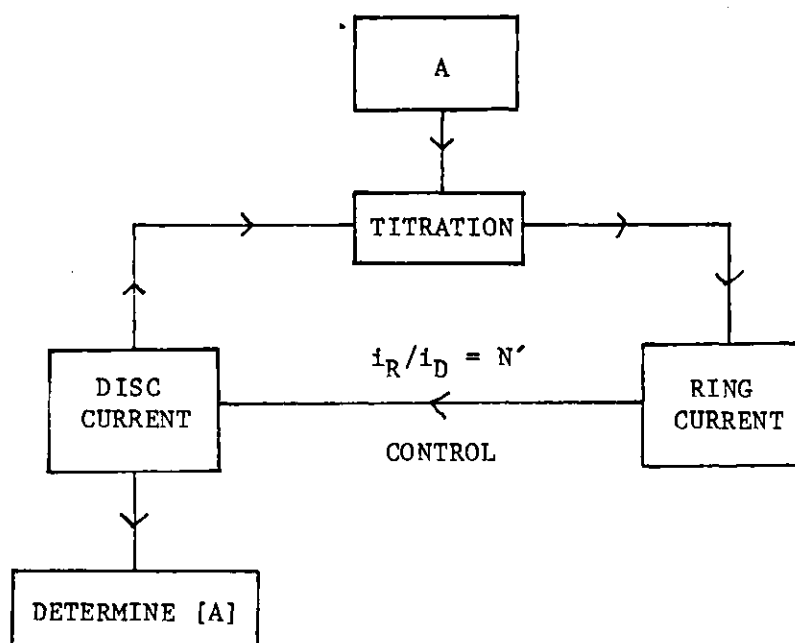
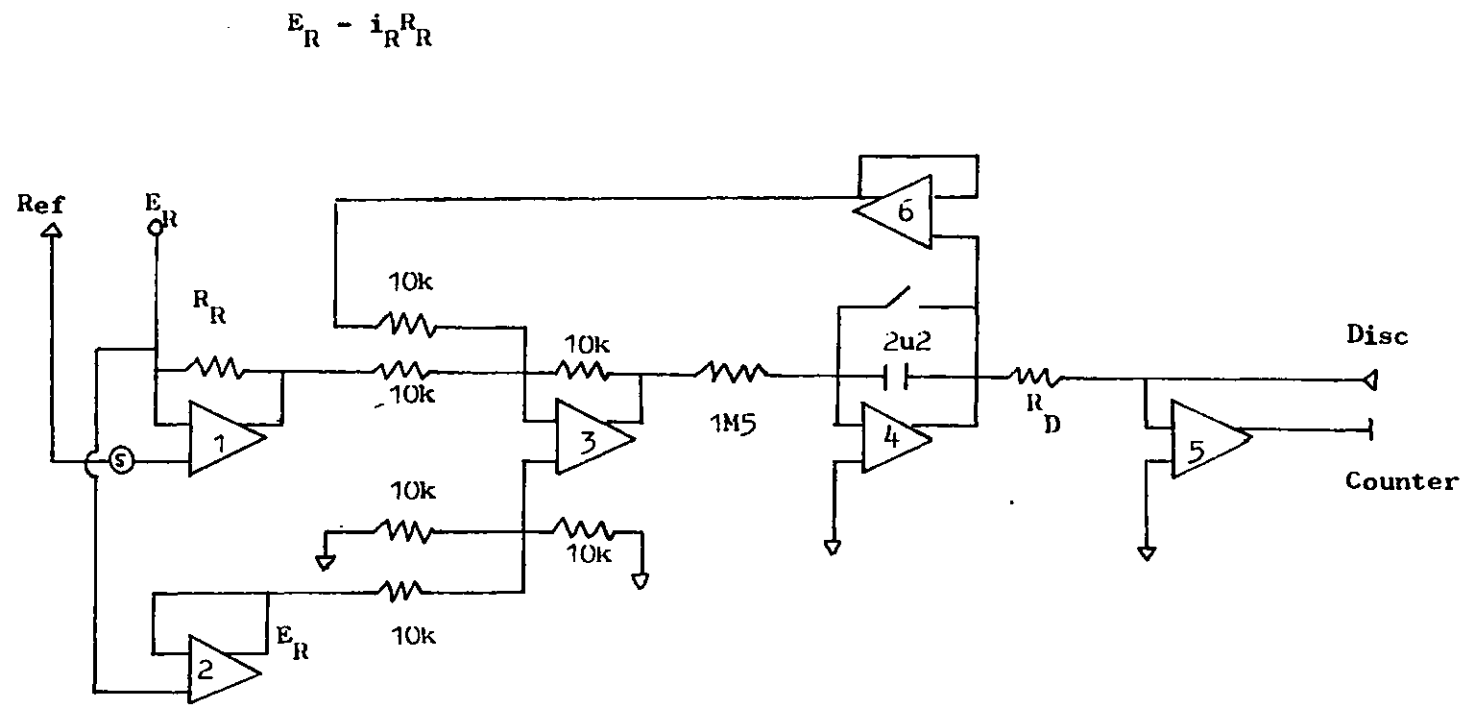


Figure 1.11 The methodology of the autotitration



$i_R R - i_D R$ 0 increase i_D
 0 decrease i_D
 = 0 hold i_D

Figure 1.12 The autotitration circuit for analogue control

titration curve typically taking 60 seconds to record. The bulk concentration of the substrate must then be determined by a manual analysis of the ring - disc current plot which in its turn is time consuming. Part of this project is to automate this process. Figure 1.10 summarises this methodology.

But for a simple continuous analysis a better technique was required and for this reason the autotitration technique has been developed (29). In this technique a line of gradient N' , which is less than N_0 , is chosen and is the ratio i_R'/i_D' . The disc current is continuously adjusted such that the ring to disc current ratio remains constant at N' . The bulk concentration, a_0 , is then proportional to the disc current and can be calculated since the value of N' is known. The value of N' can be varied depending on the system under analysis but the ideal value is such that the gradient of analysis intersects the titration curve as it enters the linear region since it is at this point that we attain the greatest sensitivity. This methodology can be seen in Figure 1.11.

There are two possible approaches for performing these autotitrations - either using analogue or digital signals. Wood has (29) developed the former and the electronic circuitry can be seen in Figure 1.12. The ring and disc currents are measured as a potential drop across the resistors R_R and R_D and the disc current is altered such that N' is always maintained. Concentrations were then calculated from the disc currents obtained. This project was concerned with the automation of this technique using a microcomputer and assessing its possibilities of analyzing samples of arsenic, phenols and cresols.

Chapter Two

The Wall-Jet Ring-Disc Electrode Theory

A Preamble

In chapter one we outlined and assessed the various double electrode systems that have been used in this laboratory and a brief description of the theory of the wall-jet titrations was given. In this chapter we shall present the theory for the wall-jet ring-disc electrode as worked out in this laboratory by Alberty and Brett (27). This will be done in four stages; (a) the work of Glauert (14), concerning the calculation of a full velocity profile for a radial laminar jet flowing over a plane wall, will be extended; (b) the derivation of the limiting current expressions for the ring and disc electrodes; (c) the derivation of the steady-state collection efficiency parameter; (d) the derivation of the titration curve parameters. The latter two are obtained using a method that had also been applied to the double tube electrode.

B (a) The Wall-Jet Velocity Profile

The wall-jet system is schematically shown in Figure 2.1 where the coordinates used in the theoretical treatment are indicated. Glauert began with the equations which described the radial laminar jet flowing over a plane wall, the Navier-Stokes equation for incompressible flow:

$$u \frac{\partial u}{\partial r} + v \frac{\partial u}{\partial z} = \frac{\partial^2 u}{\partial z^2} \quad 2.1$$

and the equation of continuity:

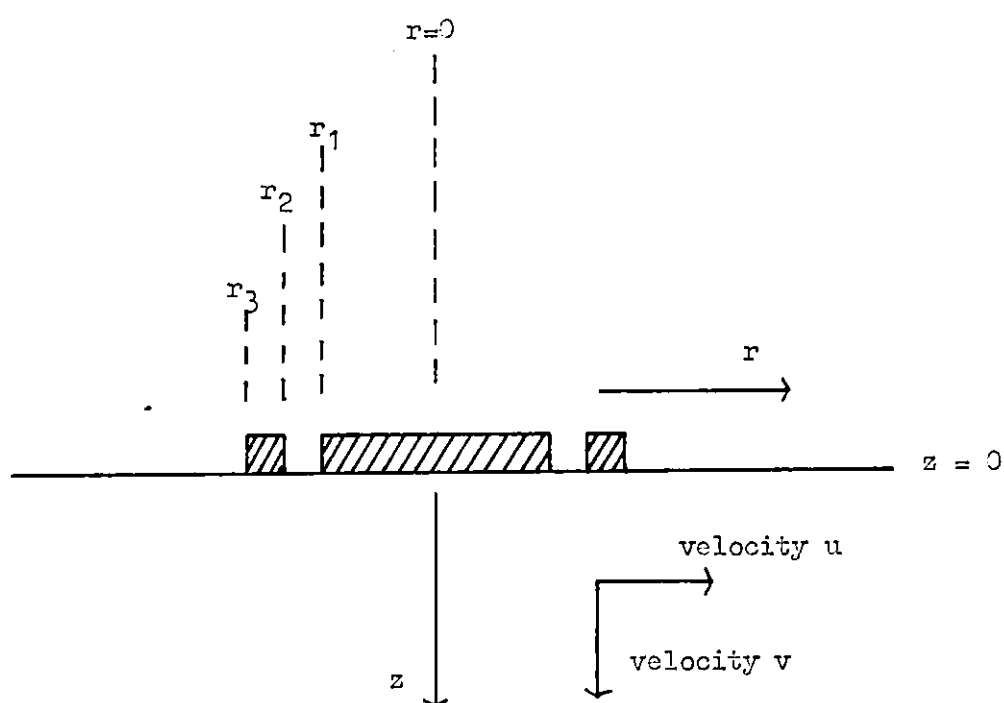


Figure 2.1 The wall-jet ring-disc electrode

$$\frac{\partial(ru)}{\partial r} + \frac{\partial(rv)}{\partial z} = 0 \quad (2.2)$$

which has the Stokes stream function, ψ , satisfying

$$ru = \frac{\partial \psi}{\partial z}, \quad rv = -\frac{\partial \psi}{\partial r} \quad (2.3)$$

With the appropriate boundary conditions he obtained the following expression for the stream function:

$$\psi = \left(\frac{40 M \nu r^3}{3} \right)^{1/4} f(\eta) \quad (2.4)$$

M is the flux of the exterior momentum flux given approximately by:

$$\begin{aligned} M &= 0.5 \text{ (typical velocity) (volume flow/radian)}^2 \\ &= 0.5 k' \left(\frac{4V_f}{\pi a^2} \right) \left(\frac{V_f}{2\pi} \right)^2 = \frac{k^4 V_f^3}{2\pi^3 a^2} \end{aligned} \quad (2.5)$$

where V_f = the volume flow rate of solution

a = the diameter of the jet of fluid (nozzle diameter)

$k' = k^4$, a proportionality constant.

$f(\eta)$ is a measure of the mass flux where η is the normalized distance z :

$$f(\eta) = \left(\frac{135 M}{32 \nu^3 r^5} \right)^{1/4} z \quad (2.6)$$

From this the radial velocity component, u , can be derived as being:

$$u = \left(\frac{15M}{2Ur^3} \right)^{1/2} f'(\eta) \quad (2.7)$$

where η , $f(\eta)$, and $f'(\eta)$ are related by a dimensionless variable, g , where $0 < g < 1$:

$$\begin{aligned} \eta &= \ln \frac{(1+g+g^2)^{1/2}}{(1+g)} + 3^{1/2} \arctan \frac{3^{1/2}g}{(2+g)} \\ f(\eta) &= g^2 \\ f'(\eta) &= 2/3g(1-g^3) \end{aligned} \quad (2.8)$$

The next stage is to find the velocity component in the z direction, v . Differentiating equation 2.4 we obtain

$$\frac{\partial \psi}{\partial r} = \frac{3}{4} \frac{\psi}{r} + \frac{f'(\eta)}{f(\eta)} \frac{\partial \eta}{\partial r} \quad (2.9)$$

and from equation 2.6 we obtain

$$\frac{\partial \eta}{\partial r} = -\frac{5}{4} \frac{\eta}{r} \quad (2.10)$$

We can now substitute equations 2.9 and 2.10 into equation 2.3 and obtain:

$$\begin{aligned} v &= -\frac{\psi}{r^2} 3-5\eta \frac{f'(\eta)}{f(\eta)} \\ &= \frac{3}{4} \left(\frac{40M}{3r^5} \right)^{1/4} \left[\frac{5}{3} f'(\eta) - f(\eta) \right] \end{aligned} \quad (2.11)$$

$$= \frac{3}{4} \left(\frac{40M}{3r^5} \right)^{1/4} h(\eta) \quad (2.12)$$

These functions, mass flux $f(\eta)$, radial velocity $f'(\eta)$ and axial velocity $h(\eta)$, are shown in Figure 2.2. We can see that the maxima for $f'(\eta)$ and $h(\eta)$ are close, $\eta = 2.03$ and 2.31 respectively, and that $h(\eta)$ passes through zero at 3.96 whereupon it becomes negative. The Prandtl boundary layer (where shear forces cease to operate) has been taken at $\eta = 6$.

Following on from this two limiting cases may be taken:

(1) Low values of η ; using equation 2.8 we may write for small

$$\begin{aligned}\eta &\approx 3g \\ f(\eta) &\approx g^2 \quad (= \eta^2/9) \\ f'(\eta) &\approx 2g/3 \quad (= 2\eta/9)\end{aligned}\tag{2.13}$$

leading to

$$\begin{aligned}u_{\eta \rightarrow \infty} &= \frac{2}{9} \left(\frac{15 M}{2 \nu r^3} \right)^{1/2} \\ &= \frac{2}{9} A \frac{z}{r^{11/4}}\end{aligned}\tag{2.14}$$

$$\text{where } A = \left[\frac{(5M)^3 \cdot 3^5}{128 \nu^5} \right]^{1/4}\tag{2.15}$$

Similarly

$$\begin{aligned}v_{\eta \rightarrow \infty} &= \frac{7}{36} \left(\frac{40 M \nu}{3 r^5} \right)^{1/4} \eta^2 \\ &= \frac{7}{36} A \frac{z^2}{r^{15/4}}\end{aligned}\tag{2.16}$$

and from equation 2.14 we obtain:

$$v_{\eta \rightarrow 0} = \frac{7}{8} \frac{z}{r} u_{\eta \rightarrow 0}\tag{2.17}$$

where we see that $v_{\eta \rightarrow 0}$ has a higher dependence on z and a lower dependence on r than $u_{\eta \rightarrow 0}$, which is what we would expect.

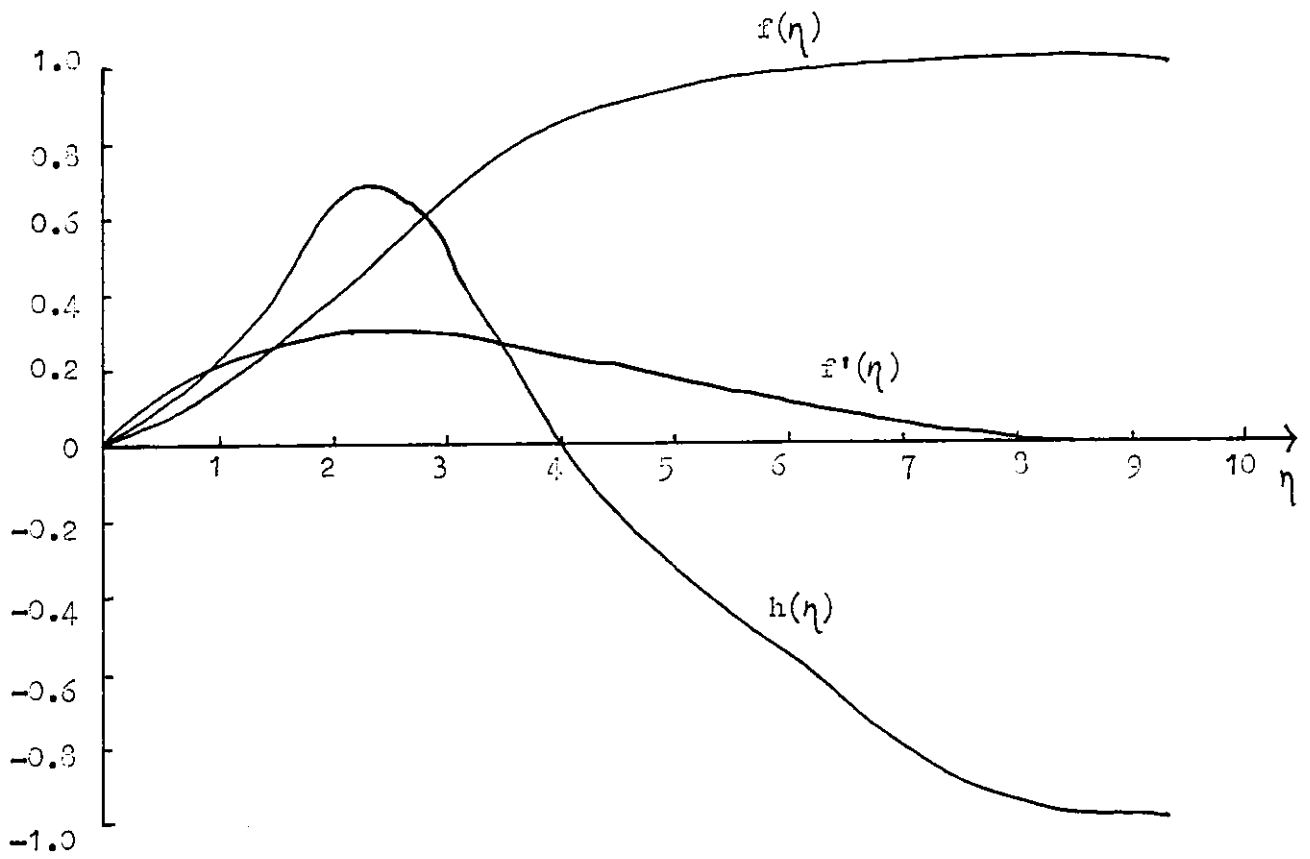


Figure 2.2 The flow functions for the wall-jet electrode

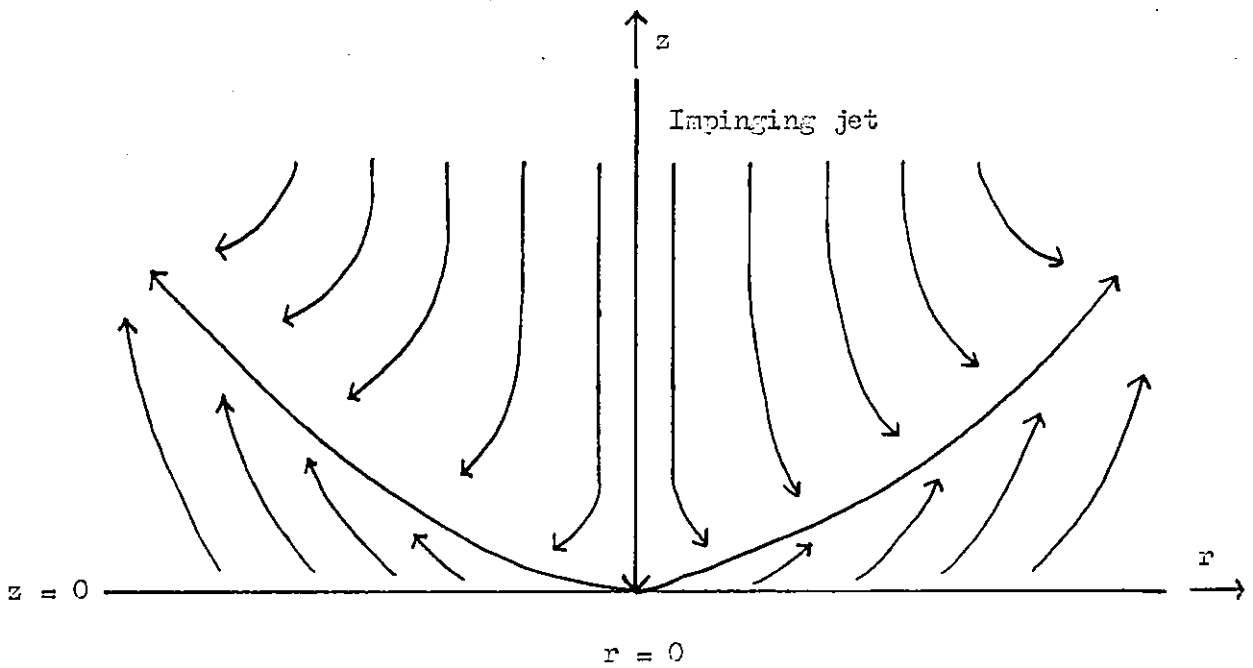


Figure 2.3 Schematic streamlines for the wall-jet electrode

(2) High values of η ; again using equation 2.8 we may write:

$$\begin{aligned}\eta &\rightarrow \infty \\ f(\eta) &\rightarrow 1 \\ f'(\eta) &\rightarrow 0\end{aligned}\tag{2.18}$$

leading to

$$u_{\eta \rightarrow \infty} = 0\tag{2.19}$$

$$v_{\eta \rightarrow \infty} = -\frac{3}{4}\left(\frac{40 M \nu}{3r^5}\right)^{1/4}\tag{2.20}$$

Consequently at large η we see that solution is moving towards the electrode in a direction perpendicular to the electrode.

Using these results schematic streamlines for the wall-jet electrode may be constructed and these can be seen in Figure 2.3. In an enclosed cell the solution at large values of z can come from both the jet and from solution being recirculated from the environs of the electrode. A further significant conclusion is that since v is directed away from the wall at small values of z we can conclude that the electrodes should always receive fresh solution from the impinging jet.

(b) The Limiting Currents at the Wall-Jet Disc and Ring Electrodes

In order to determine the limiting currents the convective-diffusion equation for the system,

$$u \frac{\partial c}{\partial r} + v \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial z^2}\tag{2.21}$$

must be solved, where the radial diffusion term, being negligible, has been omitted and where c is the concentration of electroactive species.

Using the normalized variables

$$\begin{aligned}\rho &= r/r_3 \\ c &= \left(\frac{[5M]^3}{216\nu^5} \right)^{1/4} \cdot \frac{1}{r_3^{15/4}}\end{aligned}\quad (2.22)$$

the equations 2.14 and 2.16 for the velocity components at small become

$$u = \frac{C r_3 z}{11/4} \quad (2.23)$$

$$v = \frac{7 C z^2}{8 \rho^{15/4}} \quad (2.24)$$

Since it is at small values of η that the concentration changes occur the second limiting case for u and v can be taken.

These two expressions can now be substituted into equation 2.21, thus obtaining :

$$\frac{z}{\rho^{11/4}} \frac{\partial c}{\partial \rho} + \frac{7}{8} \frac{z^2}{\rho^{15/4}} \frac{\partial c}{\partial z} = \frac{D}{C} \frac{\partial^2 c}{\partial z^2} \quad (2.25)$$

Defining the following normalized variables

$$\begin{aligned}\chi &= \left(\frac{9}{8} \right)^{1/3} \left(\frac{C}{D} \right)^{1/3} \rho^{-7/8} z \\ \xi_n &= \rho^{9/8} - \left(\frac{r_{n-1}}{r_3} \right)^{9/8} \\ \gamma_n &= \frac{c_\infty - c_n}{c_\infty}\end{aligned}\quad (2.26)$$

where $n = 1, 2$ or 3 corresponding to disc, gap or ring respectively, we can recast equation 2.25 as

$$\chi \frac{\partial \gamma_n}{\partial \xi_n} = \frac{\partial^2 \gamma_n}{\partial \chi^2} \quad (2.27)$$

as shown in Appendix 2.

This equation can now be solved using Laplace transformations; for the limiting current at the ring or disc electrode we respectively take:

$$\begin{aligned}\gamma &= \gamma_1 \text{ or } \gamma_3 \\ \xi &= \xi_1 \text{ or } \xi_3,\end{aligned}\tag{2.28}$$

and where the boundary conditions are:

$$\begin{aligned}\gamma \rightarrow 0 \quad \chi \rightarrow 0 & \quad \text{bulk concentration} \\ \gamma = 0 \quad \xi = 0 \\ \gamma = 1 \quad \chi = 1 & \quad \text{limiting current}\end{aligned}\tag{2.29}$$

The Laplace transform of equation 2.27 with respect to ξ is:

$$s\chi\bar{\gamma} = \partial^2 \bar{\gamma} / \partial \chi^2\tag{2.30}$$

and this can be solved in terms of Airey functions (30):

$$\bar{\gamma} = \text{const. Ai}(s^{1/3}\chi)\tag{2.31}$$

and using boundary condition 2.29 we obtain:

$$\bar{\gamma} = \frac{\text{Ai}'(s^{1/3}\chi)}{s \text{Ai}(0)}\tag{2.32}$$

whereupon

$$\left(\frac{\partial \bar{\gamma}}{\partial \chi}\right)_0 = \frac{\text{Ai}'(0)}{s^{2/3} \text{Ai}(0)}\tag{2.33}$$

This equation gives us the current distribution on the disc or ring electrode which we can now invert and translate back into real variables:

$$\left(\frac{\partial c}{\partial z}\right)_0 = \frac{\text{Ai}'(0)}{\text{Ai}(0) (2/3)} \left(\frac{9}{8}\right)^{1/3} \left(\frac{C}{D}\right)^{1/3} \rho^{-7/8} c_\infty \left[\left(\frac{r}{r_3}\right)^{9/8} - \left(\frac{r_{n-1}}{r_3}\right)^{9/8} \right]^{-1/3}\tag{2.34}$$

$$\left(\frac{\partial c}{\partial z}\right)_o = B \cdot r^{-7/8} (r^{9/8} - r_{n-1}^{9/8})^{-1/3} \quad (2.35)$$

$$\text{where } B = 0.190kD^{-1/3} - 5/12 v_f^{3/4} a^{-1/2} c \quad (2.36)$$

Thus the diffusion layer is given by:

$$\begin{aligned} \delta_D &= 5.26k^{-1} D^{1/3} a^{1/2} - 5/12 v_f^{3/4} r^{7/8} (r^{9/8} - r_{n-1}^{9/8})^{1/3} \\ &= 6.31Sc^{-1/3} Re^{-3/4} k^2 a^{-1/4} r^{7/8} (r^{9/8} - r_{n-1}^{9/8})^{1/3} \end{aligned} \quad (2.37)$$

$$\text{where } Sc = \nu / D \quad \text{and} \quad Re = 4k^4 v_f / \pi a \nu.$$

We note that δ_D is dependent on r , informing us that the wall-jet disc and ring electrodes are not uniformly accessible surfaces. This is also true of the tubular electrode, but it is in contrast to the rotating ring-disc electrode where the electrodes are uniformly accessible.

The limiting current is given by:

$$\begin{aligned} i_L &= nFD \int_{r_{n-1}}^{r_n} 2\pi r \left(\frac{\partial c}{\partial z}\right)_o dr \\ &= 2 nFD \cdot B \int_{r_{n-1}}^{r_n} r^{1/8} (r^{9/8} - r_{n-1}^{9/8})^{-1/3} dr \\ &= 2 nFD \cdot B (4/3) (r_n^{9/8} - r_{n-1}^{9/8})^{2/3} \end{aligned} \quad (2.38) \quad (2.39)$$

Substituting for B now gives:

(1) For the disc electrode ($n=1$)

$$i_{D,L} = 1.60knFD^{2/3} - 5/12 v_f^{3/4} a^{-1/2} c r_1^{3/4} \quad (2.40)$$

(2) For the ring electrode ($n=3$)

$$i_{R,L} = 1.60knFD^{2/3} - 5/12 v_f^{3/4} a^{-1/2} c (r_3^{9/8} - r_2^{9/8})^{2/3} \quad (2.41)$$

Thus the relationship between the two limiting currents is given by:

$$i_{R,L} = \beta^{2/3} i_{D,L} \quad (2.42)$$

$$\text{where } \beta = \left(\frac{r_3}{r_1}\right)^{9/8} - \left(\frac{r_2}{r_1}\right)^{9/8}$$

which is analagous to the equivalent equation for the RRDE, equation 1.17.

(c) Steady State Collection Efficiency

As we saw in the previous chapter the steady state collection efficiency is given by:

$$N_o = - \frac{n_D \cdot i_R}{n_R \cdot i_D}$$

Assuming a limited flux of species to the disc electrode, the conditions used in this work, we can now derive a theoretical expression for N_o .

In order to do this we need to solve the equation:

$$\chi \frac{\partial \gamma_n}{\partial \xi_n} = \frac{\partial^2 \gamma_n}{\partial \chi^2} \quad (2.27)$$

for the three zones, the disc, gap and ring, where, as seen in Figure 2.4, each γ_n is associated with a ξ_n , and where:

$$\gamma = \gamma_1 + \gamma_2 + \gamma_3$$

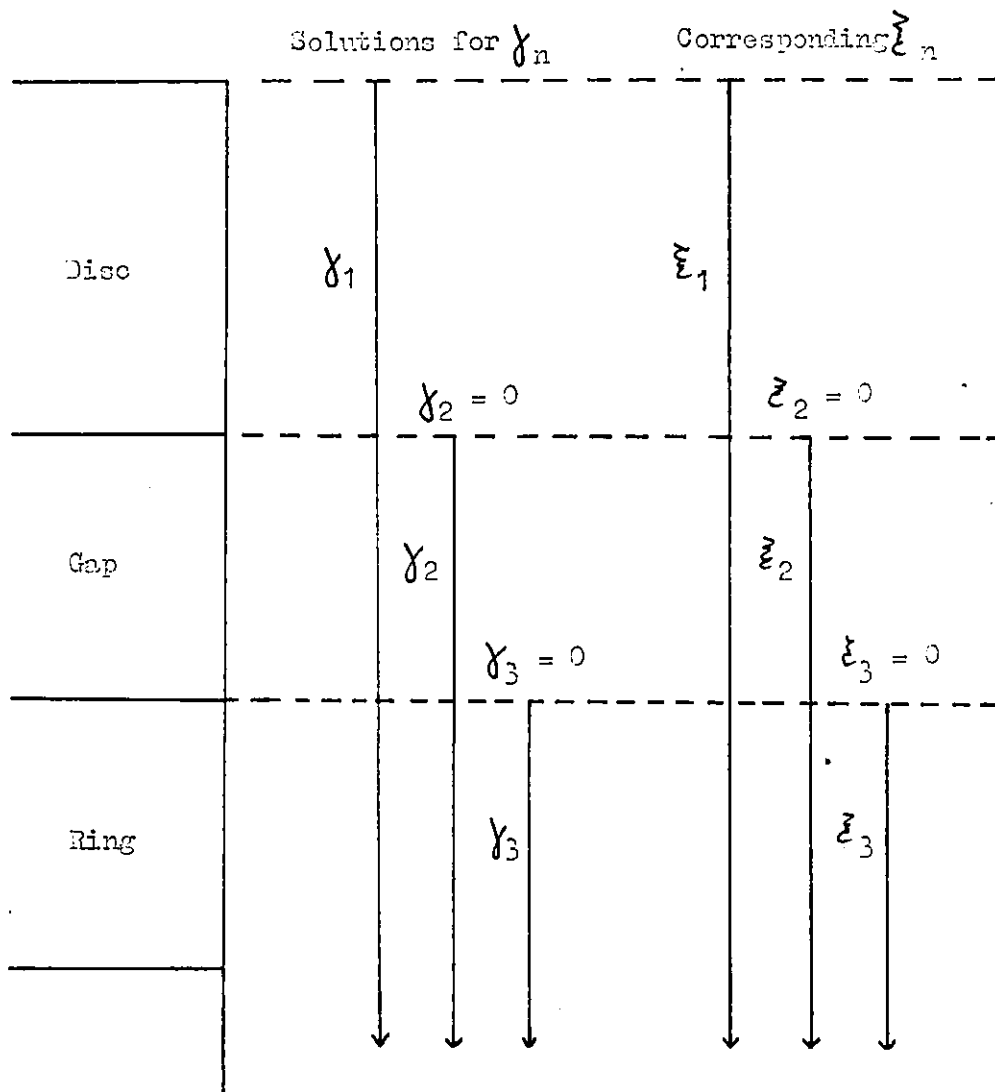


Figure 2.4 The disc, gap and ring zones for the wall-jet electrode

The boundary condition for γ_n is

$$\gamma_n = \gamma - \sum_0^{n-1} \gamma_n$$

and boundary conditions applying to all zones are:

$$\begin{aligned} \gamma_n &\rightarrow 0 & \chi &\rightarrow \infty \\ \gamma_n &= 0 & \xi_n &= 0 \end{aligned} \quad (2.43)$$

In addition there are specific boundary conditions for each zone, which, for limiting flux (equivalent to a uniform surface concentration) at the disc, are:

$$\text{Disc: } \gamma_{1,0} = 1 \quad (2.44)$$

$$\text{Gap: } \left(\frac{\partial \gamma_2}{\partial \chi} = - \frac{\partial \gamma_1}{\partial \chi} \right)_{\chi=0} \quad (2.45)$$

$$\text{Ring: } \gamma_{3,0} = -(\gamma_{1,0} + \gamma_{2,0}) = -(1 + \gamma_{2,0}) \quad (2.46)$$

We can define normalized dimensions for the three zones as

$$n = \left(\frac{r_n}{r_3} \right)^{9/8} - \left(\frac{r_{n-1}}{r_3} \right)^{9/8} \quad (2.47)$$

$$\text{such that } \theta_1 + \theta_2 + \theta_3 = 1 \quad (2.48)$$

The steady state collection efficiency may be expressed in these normalized variables as

$$N_0 = \frac{\int_0^{\theta_3} (\partial \gamma_3 / \partial \chi)_0 d\xi_3}{\int_0^{\theta_1} (\partial \gamma_1 / \partial \chi)_0 d\xi_1} \quad (2.49)$$

thus requiring us to solve two integrals.

(1) Disc zone.

The solution here, as in equations 2.32 and 2.33, is

$$\bar{\gamma}_{1,0} = \frac{Ai'(s_1^{1/3} \chi)}{s_1 Ai(0)} \quad (2.50)$$

and

$$\left(\frac{\partial \bar{\gamma}_1}{\partial \chi} \right)_0 = \frac{Ai'(0)}{s_1^{2/3} Ai(0)} \quad (2.51)$$

where s_1 is the transform variable corresponding to ξ_1 , since the boundary conditions are the same. On inverting we obtain

$$\left(\frac{\partial \gamma_1}{\partial \chi} \right)_0 = \frac{Ai'(0) \xi_1^{-1/3}}{Ai(0) \Gamma(2/3)} = \frac{Ai'(0) (\theta_1 + \theta_2)^{-1/3}}{Ai(0) \Gamma(2/3)} \quad (2.52)$$

Integration gives the denominator in equation 2.49.

$$\int_0^{\theta_1} (\partial \gamma_1 / \partial \chi)_0 d\xi_1 = \frac{Ai'(0) \theta_1^{2/3}}{Ai(0) \Gamma(5/3)} \quad (2.53)$$

(2) Gap zone

Equation 2.27 is solved with boundary condition 2.46, giving us:

$$\bar{\gamma}_2 = -\frac{\mathcal{L}_2(\theta_1 + \xi_2)^{-1/3} Ai(s_2^{1/3} \chi)}{Ai(0) \Gamma(2/3) s_2^{1/3}} \quad (2.54)$$

and at the electrode wall where $\chi = 0$:

$$\gamma_{2,0} = \frac{-\mathcal{L}_2(\theta_1 + \theta_2)^{-1/3}}{\Gamma_{(2/3)s_2^{1/3}}} \quad (2.55)$$

$\gamma_{2,0}$ is required as part of the boundary condition in the ring zone and consequently this expression must be inverted, using the convolution theorem (see Appendix 1) and so yielding:

$$\gamma_{2,0} = \frac{-I \mathcal{L}_2}{\theta_1 + \mathcal{L}_2} \quad (1/3, 2/3) \quad (2.56)$$

(3) Ring zone

For the ring zone we combine equation 2.56 and boundary condition 2.46 to obtain:

$$\begin{aligned} \gamma_{3,0} &= I \frac{\mathcal{L}_2}{\theta_1 + \mathcal{L}_2} \quad (1/3, 2/3) - 1 \\ &= -I \frac{\theta_1}{\theta_1 + \mathcal{L}_2} \quad (2/3, 1/3) \\ &= -I \frac{\theta_1}{\theta_1 + \theta_2 + \mathcal{L}_3} \quad (2/3, 1/3) \end{aligned} \quad (2.57)$$

The evaluation of the integral

$$\int_0^{\theta_3} (\partial \gamma_3 / \partial \chi)_0 d\mathcal{L}_3$$

is most easily performed in Laplace space.

$$\bar{\gamma}_3 = \frac{-I \theta_1}{\theta_1 + \theta_2 + \mathcal{L}_3} \quad (2/3, 1/3) \quad \frac{A1(s_3^{1/3} \chi)}{A1(0)} \quad (2.58)$$

$$\left(\frac{\partial \bar{y}_3}{\partial x}\right)_0 = -s_3^{1/3} \frac{\Gamma(2/3, 1/3)}{\theta_1 + \theta_2 + \xi_3} \frac{Ai'(0)}{Ai(0)} \quad (2.59)$$

Integration is achieved by the division of the Laplace variable:

$$\int_0^{\theta_3} \left(\frac{\partial \bar{y}_3}{\partial x}\right)_0 d\xi_3 = \int_0^{\theta_3} \frac{1}{s_3^{1/3}} \frac{\Gamma(2/3, 1/3)}{\theta_1 + \theta_2 + \xi_3} \frac{Ai'(0)}{Ai(0)} d\xi_3 \quad (2.60)$$

$$= - \frac{Ai'(0)}{Ai(0) \Gamma(2/3)} \int_0^{\theta_3} \xi_3^{-1/3} \frac{\Gamma(2/3, 1/3)}{1 - \xi_3} d\xi_3 \quad (2.61)$$

No can now be expressed in terms of equation 2.53 and 2.61 giving

$$N_o = \frac{2\theta_1^{-2/3}}{3} \int_0^{\theta_3} \xi_3^{-1/3} \frac{\Gamma(2/3, 1/3)}{1 - \xi_3} d\xi_3 \quad (2.62)$$

This integral, which is evaluated in Appendix 3, gives

$$N_o = G\left(\frac{\theta_3}{\theta_2}\right) + \left(\frac{\theta_3}{\theta_1}\right)^{2/3} G\left(\frac{\theta_1}{\theta_2}\right) - \theta_1^{-2/3} G\left(\frac{\theta_1 \theta_3}{\theta_2}\right) \quad (2.63)$$

We can now define α and β as being:

$$\begin{aligned} \alpha &= \left(\frac{r_2}{r_1}\right)^{9/8} - 1 \\ \beta &= \left(\frac{r_3}{r_1}\right)^{9/8} - \left(\frac{r_2}{r_1}\right)^{9/8} \end{aligned} \quad (2.64)$$

whereupon we can write equation 2.62 as:

$$N_o = G(\beta/\alpha) + \beta^{2/3} G(1/\alpha) - (1+\alpha+\beta)^{2/3} G(\beta/(\alpha(1+\alpha+\beta))) \quad (2.65)$$

$$= 1 - F(\alpha/\beta) + \beta^{2/3}(1-F(\alpha)) - (1+\alpha+\beta)^{2/3}[1-F\{(\alpha/\beta)(1+\alpha+\beta)\}] \quad (2.66)$$

It is interesting to note that this has the same form as for the RRDE and the TBE collection efficiencies, and that like these the theoretical value for N_0 is dependent only on the electrode geometry. For the RRDE the exponents in α and β are 3 as opposed to 9/8 in the WJRDE and consequently values of N_0 are lower for the latter than the former. In this respect, therefore, the RRDE has the advantage since more of the bromine produced will be involved in the concentration determination. A program, which is given in Appendix A6-1, has been written and values of N_0 and $\beta^{2/3}$ have been calculated for the cell used in this work; these values are given in Table 2.1.

(d) Diffusion Layer Titration Curves

In dealing with the diffusion layer titration curves we must consider the concentration profiles of both the electrogenerated titrant B and the other titrant A, their transport equations being:

$$u \frac{\partial b}{\partial r} + v \frac{\partial b}{\partial z} = D_B \frac{\partial^2 b}{\partial z^2} - k_2 ba \quad (2.67)$$

$$u \frac{\partial a}{\partial r} + v \frac{\partial a}{\partial z} = D_A \frac{\partial^2 a}{\partial z^2} - k_2 ba \quad (2.68)$$

These can be seen to be the same as equation 2.21 with the addition of one term which describes the fast irreversible reaction between A and B. If we assume that $D_A = D_B$ and putting

$$\gamma = \frac{b - a + a_{\infty}}{b_0 + a_{\infty}} \quad (2.69)$$

where b_0 is [B] at the electrode surface, we can subtract the two equations to give :

$$u \cdot \frac{\partial \chi}{\partial r} + v \cdot \frac{\partial \chi}{\partial z} = D \frac{\partial^2 \chi}{\partial z^2} \quad (2.70)$$

We can reduce this equation in a similar manner as we reduced equation 2.21 to equation 2.27:

$$\frac{\partial \chi_n}{\partial \xi_n} = \frac{\partial^2 \chi_n}{\partial \chi^2} \quad (2.27)$$

As with the calculation of N_0 , the boundary conditions for all zones are:

$$\begin{aligned} \chi_n &\rightarrow 0 & \chi &\rightarrow \infty \\ \chi_n &= 0 & \xi_n &= 0 \end{aligned} \quad (2.43)$$

The specific boundary conditions for the disc and gap are the same but they are different for the ring because we must allow for the passage of reaction boundary across the ring.

$$\text{Disc:} \quad \chi_{1,0} = 1 \quad (2.44)$$

$$\text{Gap:} \quad \left(\frac{\partial \chi_2}{\partial \chi} = - \frac{\partial \chi_1}{\partial \chi} \right) = 0 \quad (2.45)$$

Ring: Describe by $\xi = \xi_J$ where ξ_J represents the reaction boundary

$$\chi_{3,0} = -(\chi_{1,0} + \chi_{2,0}) + \chi_{4,0} \quad (2.71)$$

where $\chi_{4,0}$ describes the titration effect.

(1) B dominated region $\xi < \xi_J$

$$\chi_4 = \frac{a_\infty}{b_0 + a_\infty} \quad (2.72)$$

(2) A dominated region $\xi > \xi_J$

$$\frac{\partial \gamma}{\partial x} = 0 \quad (2.73)$$

For the analysis of the titration curve we require expressions for the normalized disc current i_d/M (where M is the limiting flux of A to the disc) and for N' (analogous to N_0) such that

$$N' = \frac{-i_R}{i_D} = \frac{\int_0^{\theta_J} (\partial \gamma_3 / \partial x)_0 d\xi_3}{\int_0^{\theta_1} (\partial \gamma_1 / \partial x)_0 d\xi_1} \quad (2.74)$$

The demoninator was previously evaluated in equation 2.53.

We can consider the movement of the reaction boundary; as it just begins to move from the disc i_D , $b_0 = 0$ and so from equation 2.72:

$$\gamma_{4,0} = \frac{a_\infty}{b_0 + a} = \frac{M}{i_D} \quad (2.75)$$

Equation 2.71:

$$\gamma_3 = -(\gamma_{1,0} + \gamma_{2,0}) + \gamma_{4,0} \quad (2.71)$$

can now be written as:

$$\gamma_3 = -(1 + \gamma_{2,0}) + \frac{M}{i_D} \quad (2.76)$$

This equation is analogous to equation 2.58, from which we can write:

$$\bar{\gamma}_3 = \left[-\frac{\bar{i} \theta_1}{\theta_1 + \theta_2 + \xi_3} (2/3, 1/3) + \frac{\gamma_4}{s_3} \right] \frac{Ai(s_3^{1/3})}{Ai(0)} \quad (2.77)$$

$$\left(\frac{\partial \gamma_3}{\partial x}\right)_0 = \left[-s^{1/3} \bar{I} \frac{\theta_1}{\theta_1 + \theta_2 + \xi_3} (2/3, 1/3) + \gamma_{4,0} \frac{A1'(0)}{s_3^{2/3} A1(0)} \right] \quad (2.78)$$

Since at the reaction boundary $(\partial \gamma_3 / \partial x)_0 = 0$ we can write:

$$\int_3^{-1} s^{1/3} \bar{I} \frac{\theta_1}{\theta_1 + \theta_2 + \xi_3} (2/3, 1/3) = \int_3^{-1} \gamma_{4,0} \frac{s_3^{2/3}}{s_3^{2/3}} \quad (2.79)$$

which is the equation that fixes ξ_J , the position of the reaction boundary.

We can examine two cases for the reaction boundary. Firstly when $\xi_J > \xi_3$, that is the reaction boundary has moved past the outer edge of the ring, ie we have entered the linear section of the titration curve; we can write from equation 2.78:

$$\begin{aligned} \int_0^{\theta_3} \left(\frac{\partial \gamma_3}{\partial x}\right)_0 d\xi_3 &= N_0 \text{ terms} + \int_3^{-1} \gamma_{4,0} \frac{A1'(0)}{s_3^{2/3} A1(0)} \\ &= N_0 \text{ terms} + \xi_3^{2/3} \frac{\gamma_{4,0}}{\Gamma(5/3)} \frac{A1'(0)}{A1(0)} \end{aligned} \quad (2.80)$$

To find N' we divide by equation 2.53 which gives

$$N' = N_0 - \left(\frac{\theta_3}{\theta_1}\right)^{2/3} \gamma_{4,0} \quad (2.81)$$

and since $\gamma_{4,0} = M/i_D$

$$i_R = N_0 i_D - \beta^{2/3} M \quad (2.82)$$

where β is defined by equation 2.64. The form of this equation is the same as for the RRDE and TDE.

In the second case if $\xi_J < \xi_3$ we can write from equation 2.78:

$$\int_0^{\theta_J} \left(\frac{\partial \chi_3}{\partial \chi} \right)_0 d\xi_J = \mathcal{L}^{-1} - \frac{A1'(0)}{A1(0)} \left[\frac{1}{s_3^{2/3}} \frac{\bar{I} \theta_1 (2/3, 1/3)}{\theta_1 + \theta_2 + \xi_3} - \frac{\gamma_{4,0}}{s_3^{5/3}} \right] \quad (2.83)$$

Using the convolution theorem we can invert the first term on the right hand side of this equation:

$$\mathcal{L}^{-1} \frac{1}{s_3^{2/3}} \frac{\bar{I} \theta_1 (2/3, 1/3)}{\theta_1 + \theta_2 + \xi_3} = \frac{1}{\Gamma(2/3)} \int_0^{\theta_J} t^{-1/3} \frac{\bar{I} \theta_1 (2/3, 1/3)}{\theta_1 + \theta_2 + \theta_J - t} dt \quad (2.84)$$

This integral is of the same form as equation 2.61 and N' can be evaluated in a similar manner as for N_0 as shown in Appendix 6; thus we obtain:

$$N' = G \left(\frac{\theta_J}{\theta_2} \right) + \left(\frac{\theta_J}{\theta_1} \right)^{2/3} G \left(\frac{\theta_1}{\theta_2} \right) - \left(\frac{\theta_1 + \theta_2 + \theta_J}{\theta_1} \right) G \left(\frac{\theta_1 + \theta_J}{\theta_2 (\theta_1 + \theta_2 + \theta_J)} \right) + \gamma_{4,0} \left(\frac{\theta_J}{\theta_1} \right)^{2/3} \quad (2.85)$$

We can now evaluate $\gamma_{4,0}$ ($= M/i_D$) using equation 2.79

$$\frac{M \theta_J^{-1/3}}{i_D (2/3)} = \mathcal{L}^{-1} s^{-2/3} \bar{I} \frac{\theta_1 (2/3, 1/3)}{\theta_1 + \theta_2 + \xi_3} \quad (2.86)$$

$$= \frac{\partial}{\partial \theta_J} \theta_1^{-1} s^{-2/3} \bar{I} \frac{\theta_1}{\theta_1 + \theta_2 + \theta_3} \quad (2/3, 1/3) \quad (2.87)$$

and using equations 2.53 and 2.83 we arrive at:

$$\frac{M}{i_D} \frac{\theta_J^{-1/3}}{\Gamma(2/3)} = - \frac{\partial}{\partial \theta_J} \frac{\theta_1^{2/3}}{\Gamma(5/3)} \left[N' - \frac{M}{i_D} \left(\frac{\theta_J}{\theta_1} \right)^{2/3} \right] \quad (2.88)$$

Substituting equation 2.85 for N' we obtain:

$$\begin{aligned} \frac{M}{i_D} \frac{\theta_J^{-1/3}}{\Gamma(2/3)} = & - \frac{3\theta_1^{2/3}}{2} \frac{\partial}{\partial \theta_J} \left[G\left(\frac{\theta_J}{\theta_2}\right) + \left(\frac{\theta_J}{\theta_1}\right)^{2/3} G\left(\frac{\theta_1}{\theta_2}\right) \right. \\ & \left. - \frac{(\theta_1 + \theta_2 + \theta_J)^{2/3}}{\theta_1^{2/3}} G\left(\frac{\theta_1 \theta_J}{\theta_2(\theta_1 + \theta_2 + \theta_J)}\right) \right] \end{aligned} \quad (2.89)$$

We can now differentiate as shown in Appendix 4:

$$\frac{M}{i_D} = - G\left(\frac{\theta_1}{\theta_2}\right) + \left(\frac{\theta_J}{\theta_1 + \theta_2 + \theta_J}\right)^{1/3} G\left(\frac{\theta_1 \theta_J}{\theta_2(\theta_1 + \theta_2 + \theta_J)}\right) \quad (2.90)$$

and substituting this into equation 2.85 we arrive at:

$$N' = G\left(\frac{\theta_J}{\theta_2}\right) - \left(\frac{\theta_1 + \theta_2}{\theta_1^{2/3}(\theta_1 + \theta_2 + \theta_J)^{1/3}}\right) G\left(\frac{\theta_1 + \theta_J}{\theta_2(\theta_1 + \theta_2 + \theta_J)}\right) \quad (2.91)$$

Alternatively we can express these two equations using the terms α and β_J (equations 2.64) where:

$$\beta_J = (r_J/r_1)^{9/8} - (r_2/r_1)^{9/8} \quad (2.92)$$

where $r_2 < r_J < r_3$, giving:

$$\frac{M}{i_D} = G\left(\frac{1}{\alpha}\right) - \frac{\beta_J^{1/3}}{(1+\alpha+\beta_J)^{1/3}} \quad G\left(\frac{\beta_J}{\alpha \cdot (1+\alpha+\beta_J)}\right) \quad (2.93)$$

$$N' = G\left(\frac{\beta_J}{\alpha}\right) - \frac{1+\alpha}{(1+\alpha+\beta_J)^{1/3}} \quad G\left(\frac{\beta_J}{(1+\alpha+\beta_J)}\right) \quad (2.94)$$

Again these have the same form for the RRDE and TDE.

The ring current will begin to rise from zero when:

$$M/i_D = G(1/\alpha) = 1 - F(\alpha) \quad (2.94)$$

and when $r_J = r_3$ the linear section of the titration curve will have been reached as governed by:

$$i_R = N_O i_D - \beta^{2/3} M \quad (2.82)$$

The program NOCAL1 calculates the desired number of values for r_J , β_J and their respective values of N' and M/i_D ; then for specified values of substrate concentration and flow rate it will calculate values for the theoretical disc and ring currents for the various analysis gradients. A set of such calculations for the electrode used in this work, with a substrate concentration of 58.5 uM and a flow rate of 0.1 ml s⁻¹, is given in Table 2.1.

In this chapter we have presented an outline of the theory of the wall-jet ring-disc electrode and have given an indication of how the various parameters used in this work were derived. In the results chapter we will see how closely theory agrees with experiment; in the following two chapters we will present the experimental set-up, firstly the electrochemical part (chapter 3) and secondly the control part (chapter 4).

The electrode radii: $r_1 = 3499 \text{ um}$
 $r_2 = 3738 \text{ um}$
 $r_3 = 3999 \text{ um}$

Calculated values: $\beta^{2/3} = 0.1933$
 $N_o = 0.1155$

r_J	β_J	N'	M/i_D
3738	0	0	-
3775.3	0.01210	$7.462 \cdot 10^{-4}$	0.4313
3812.6	0.02421	$2.203 \cdot 10^{-3}$	0.3743
3849.9	0.03633	$4.055 \cdot 10^{-3}$	0.3349
3887.1	0.04847	$6.167 \cdot 10^{-3}$	0.3039
3924.4	0.06062	$8.452 \cdot 10^{-3}$	0.2781
3961.7	0.07279	0.01087	0.2551
3999	0.08498	0.01338	0.2363

Taking a concentration of 58.5 uM ,
flow rate of 0.1 ml s^{-1} :

$i_D \text{ (uA)}$	$i_R \text{ (uA)}$
58.27	0.0435
67.15	0.1479
75.06	0.3043
82.70	0.5097
90.37	0.7638
98.23	1.0676
106.38	1.4232

Table 2.1 Theoretical calculations for the wall-jet electrode

Chapter Three

The Electrochemical Apparatus

A Preamble

In this chapter the experimental part of the apparatus will be discussed; firstly the wall-jet ring-disc electrode itself and the pumping system used in this work. In the second section the supporting electronics will be described.

B The Wall-Jet Electrode Assembly

(a) The Cell

A schematic diagram of the wall-jet ring-disc double electrode is given in Figure 3.1. The two concentric electrodes used in this work were made of platinum and the gap separating them was made of Araldite as was the mantle which surrounded them. This was firmly embedded into a Perspex cylinder which in turn screwed into the wall-jet cell which was also made of Perspex. The pitch of the screw was machine cut and therefore the distance between the nozzle and the electrodes can be finely adjusted. The electrodes were polished with 6 μ m and 3 μ m diamond lapping compound, 1 μ m alumina slurry and finally, and prior to each experiment, 0.3 μ m alumina slurry. Before experiments the electrodes were electrochemically cleaned (35) in the following manner: using a solution of 0.5M H₂SO₄ the electrode was first polarized at +1.55V (vs SCE) for 10s (to oxidize any impurities), then at 0.95V for 30s (to remove oxygen formed at the higher potential) and finally at -0.20V for 30s (to reduce surface oxides formed at the previous potentials); this cycle was then repeated. This cycle had always to be done manually but with the interface system it could be

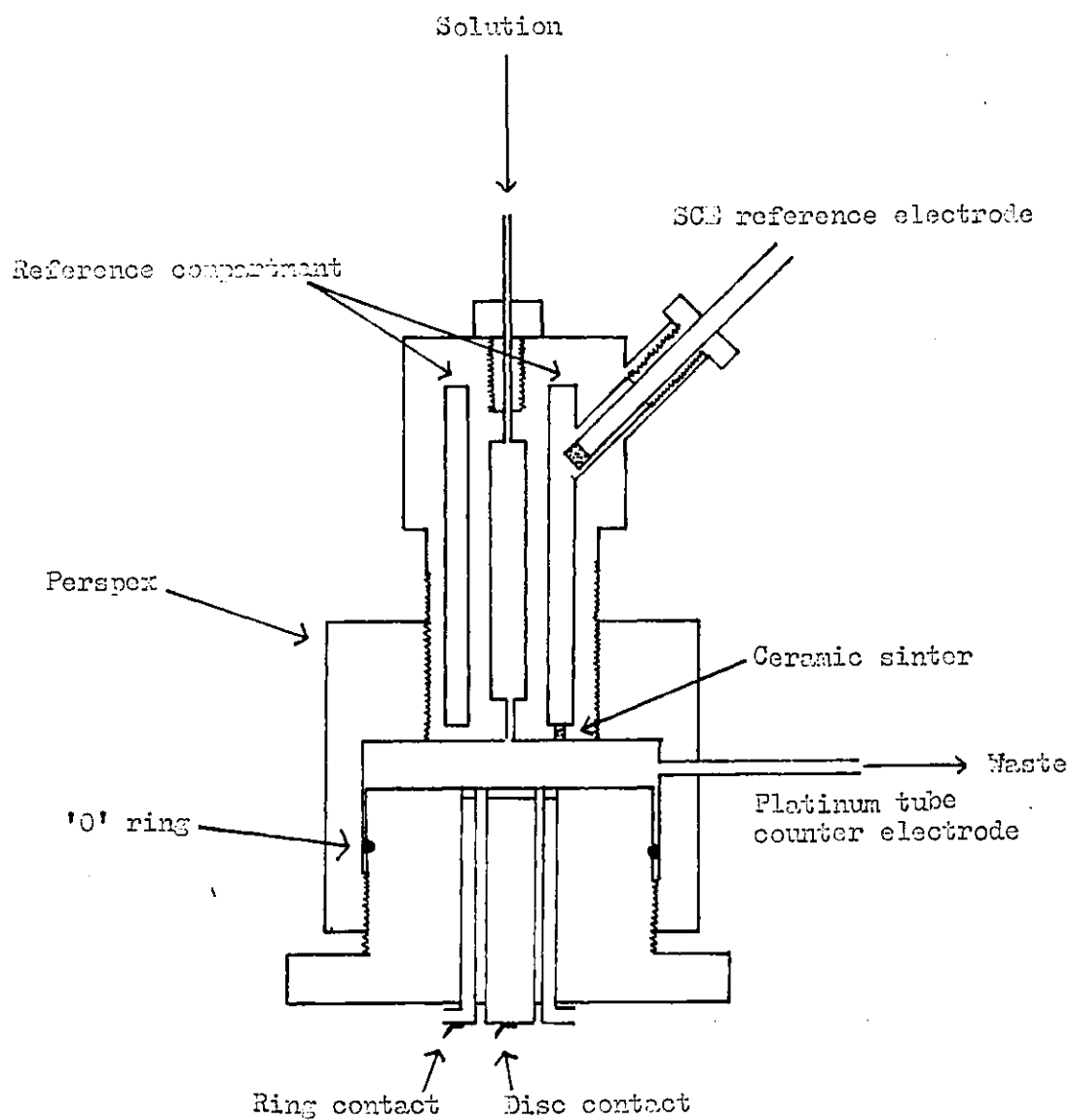


Figure 3.1 Diagram of the wall-jet ring-disc cell

done automatically and a program (described in chapter five) was written to do this. Consequently this cycle could be performed as many times as seemed necessary very easily, though five was often the number chosen.

(b) The Pumping System

The pumping system was a part which provided particular problems; as we have seen previously there is a $v_f^{3/4}$ dependency in the expressions derived in Chapter 2 and consequently we must know the flow rate as accurately as possible. Unfortunately the flow rates that we required ($0.03 - 0.2 \text{ ml s}^{-1}$) were below that which could be obtained on a commercial machine where a flow rate can be pre-set. As a result flow rates had to be measured during each experiment and this was done with a measuring cylinder and a stop clock. This system is not ideal and future work would require the development of an automated flow system where the flow rate would be controlled by the computer. One possibility could be a balance with a BCD output which could be connected to the computer.

In this work a peristaltic pump was used (Pharmacia Fine Chemicals, P3, 3 channel pump capable of producing flow rates of $1.6 \times 10^{-4} - 0.3 \text{ ml s}^{-1}$) and it was adapted so that the rotation speed of the rolls could be controlled by the computer which provided a voltage to it. In principle we could simply calibrate the pump such that a certain voltage would correspond to a certain flow rate; but unfortunately in practice this did not work since from day to day the flow rate for a given voltage would vary depending on the state of the tubing passing through the pump to the cell.

Another problem which arises is that of pulsing produced by the rolls in the pump. This characteristic cannot be completely removed

but it can be minimized by the insertion into the system between the pump and cell of a coil of tubing (about 4 m) and a glass bulb (about the size of a golf ball) which respectively act as a resistor and capacitor. The price paid is a large dead space which results in a large response time. This is no good in an on-line analysis system if the concentration is continuously fluctuating but if large quantities of a particular solution are used this is then is not so much of a problem. In this work the system was used in the "push" mode (see Figure 3.2); it can also be used in the "pull" mode where the response time is shorter but since the pressure in the tubing is less air bubbles are liable to enter the tubing and cell where they destroy the hydrodynamics; therefore the system must be very well sealed.

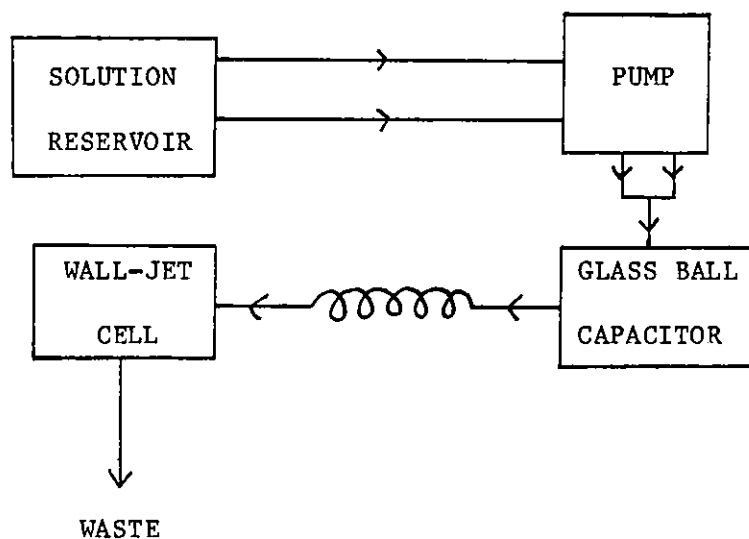
C The Supporting Electronics

In this work the control and measurements of currents and voltages, which are provided from the computer, are effected by operational and differential amplifiers.

Previously in this laboratory the control circuitry had always comprised a large Faradaic cage which housed a number of modules, variously and severally connected with banana plugs and sockets, and this included a galvanostat, potentiostat, potential sources for providing required voltages, voltage followers, subtractors and inverters. When a particular experiment was to be performed the required modules were connected - this system was known as as Oxford box.

Operational amplifiers, used for achieving the functions of these modules, consist of two inputs, one a non-inverting input (v_+) and the other an inverting input (v_-), and one output v_o (see Figure 3.3).

(1) The "Push" Mode



(2) The "Pull" Mode

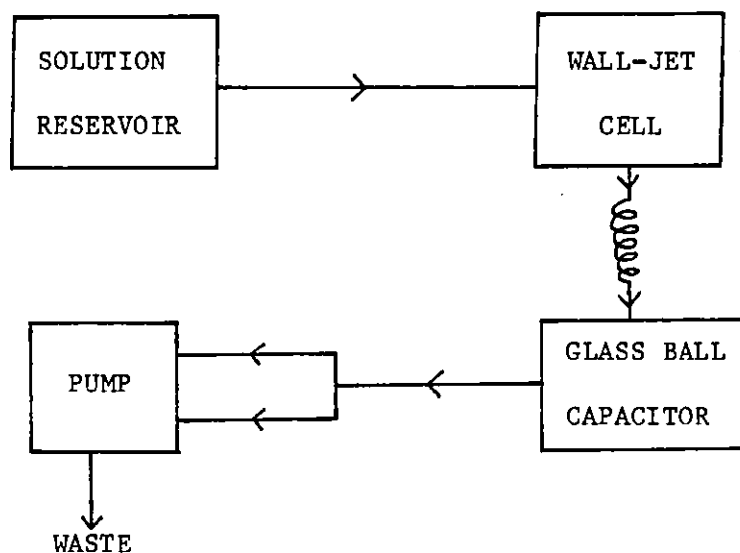


Figure 3.2 The methodologies of the "push" and "pull" pumping modes

The output voltage is proportional to the difference between the two input voltages:

$$v_o = A_o (v_+ - v_-) \quad (3.1)$$

but with an open loop amplifier only a narrow range of input voltages can be used since the gain is very high ($A_o = 120\text{dB}$) and consequently in practice a negative feedback is incorporated. The closed loop gain ($A_{o,f}$) is determined by the ratio of the feedback impedance (Z_f) to the input impedance (Z_i) if $Z_f/Z_i \ll A_o$. Equation 3.1 is still applicable but the closed loop control of v_o means that $v_+ \sim v_-$ (eg if $v_o = 1\text{V}$ then $v_+ - v_- = 1\text{ uV}$). The result is that we can assume that the two inputs are at the same potential; when the non-inverting input is at ground potential the inverting input is referred to as a virtual ground.

The second consideration is the input bias current, i_b , which is the mean of the currents flowing into the operational amplifiers inputs, $i_b = (i_{b1} + i_{b2})/2$. Ideally all these current values should be zero ($i_{b1} = i_{b2} = i_b = 0$). When this is assumed the response of the feedback circuits may be determined by applying Ohm's and Kirchoff's laws; Ohm's law and the first assumption ($v_+ = v_-$) allow us to determine the current flowing through the input impedance, Z_i . Kirchoff's law and the second assumption allow us to assume that all the current must flow through the feedback impedance and so with the aid of Ohm's law we can calculate the output voltage. Since the input bias of the operational amplifiers used in this work (LM 11 from National Semiconductor (33)) is 25 pA operational amplifier currents of over 10 nA will ensure that they behave as predicted. The amplifier also has a high input impedance ($10^{11}\Omega$) and so feedback and input

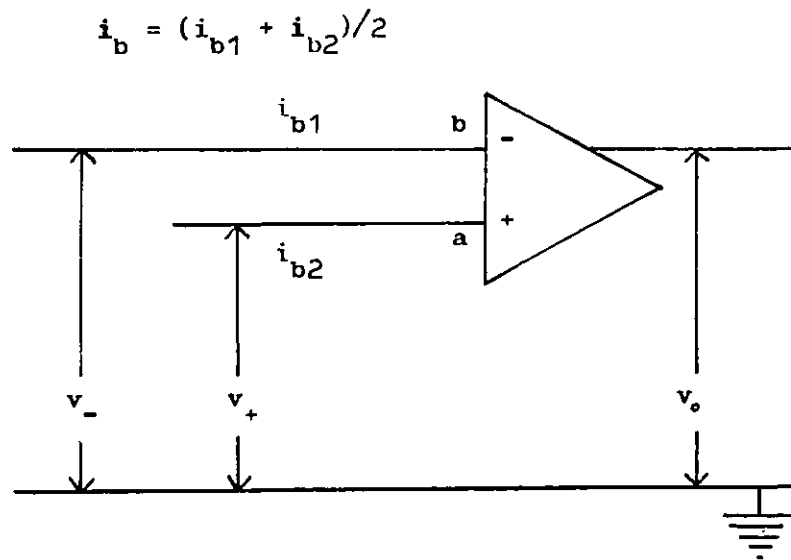


Figure 3.3 The operational amplifier

<u>Amplifier</u>	<u>LM11</u>	<u>BB 3627</u>	<u>Ideal</u>
Output voltage	$\pm 15V$	$\pm 15v$	large
Open-loop gain, A_o	120dB	-	infinite
Input impedance	$10^{11} \Omega$	$50 k \Omega$	infinite
Input offset voltage	100 μV	100 μV	zero
Temp. co-efficient	1 $\mu V/^{\circ}C$	15 $\mu V/^{\circ}C$	zero
Input bias current, i_b	25 pA	-	zero
Input offset current, i_b	0.5 pA	-	zero
Common-mode rejection	-	94 dB	infinite

Table 3.1 The operational (LM 11) and differential
(BB 3627) amplifier characteristics

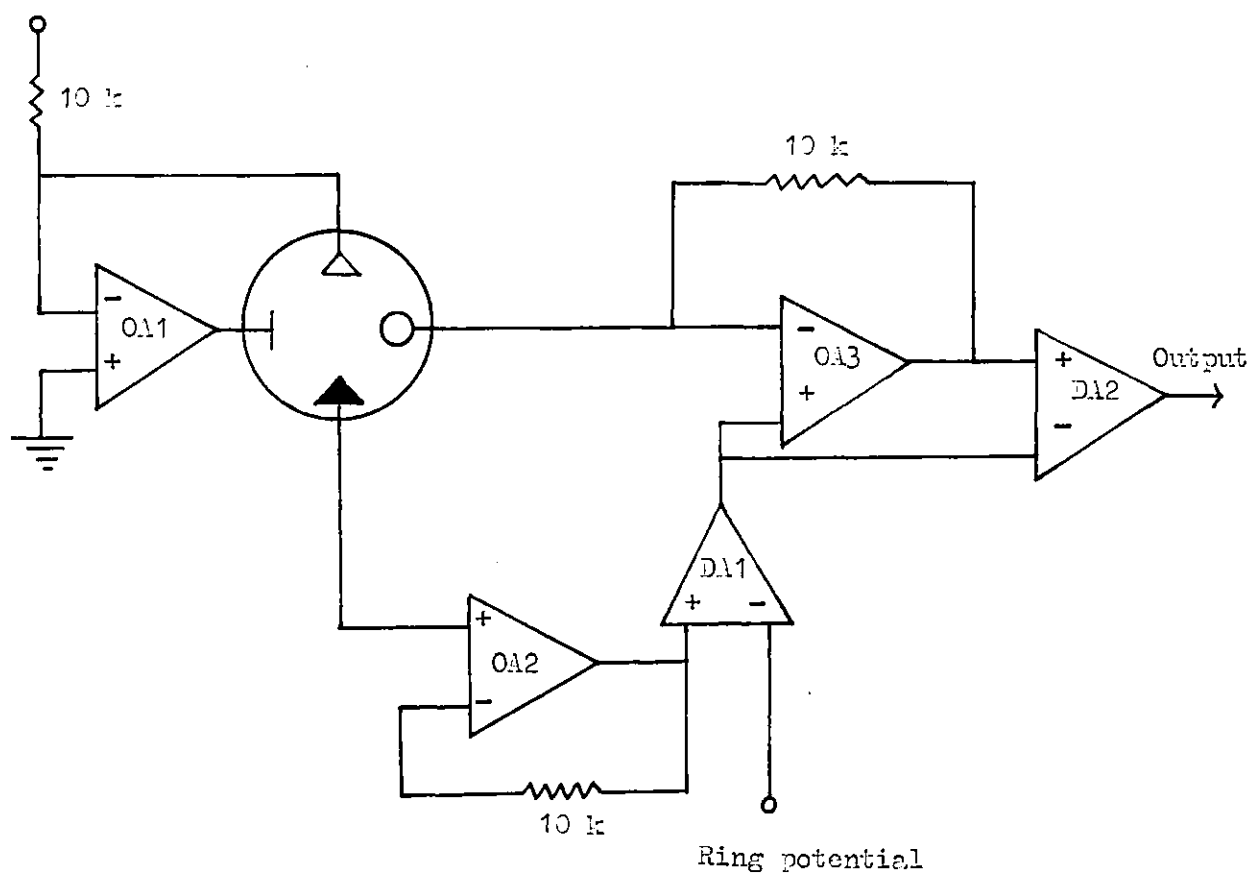
impedances of up to $10^8 \Omega$ can be used while still retaining ideal operating conditions.

A differential amplifier is one which has two inputs and one output and where the output is a function of the difference between the two inputs. Ideally the output is zero when the two inputs are identical; the common-mode rejection ratio measures the ability of the amplifier to produce a zero output under such conditions and for the ones (Burr-Brown 3627 (34)) used in this work it has a value of 94 dB typically at 25°C.

Both the operational and differential amplifiers were powered by a $\pm 15\text{V}$ dual supply, where the ground point is the mid-point of this range, thus restricting the output range to $\pm 15\text{V}$ but for this work that was sufficient. Similarly the maximum current output of 2mA was also sufficient. The various characteristics of the two amplifiers can be seen in Table 3.1.

Initially an Oxford box was to have been used in this project and the computer, instead of voltage sources and ramps, would provide the required signals and measure the ring and disc currents. However after some experimentation it was decided that it would be better if a dedicated titration unit was built. This was done and one was built after a design by Goddard. The circuit is shown in Figure 3.4 and it comprises three operational amplifiers and two differential ones. Operational amplifier 1 is used in galvanostating the disc electrode controlling the flow of current between two electrodes, the working (disc) and counter electrodes. The remaining amplifiers constitute the potentiostat and allow the ring electrode to be maintained at a constant potential and the ring current to be measured across the resistor R_R . The amplifiers have been laser-trimmed and since they are

Disc potential



OA Operational amplifier

DA Differential amplifier

△ Disc electrode

| Counter electrode

○ Ring electrode

◄ Reference electrode

Figure 3.4 The titration unit circuit diagram

so stable they need not be trimmed and so trimming circuits are not required. Thus overall there has been a considerable simplification in the circuitry needed which means that there is less opportunity for noise to be generated within the system. It is envisaged that dedicated units will be built and used when required in conjunction with the computer, eg polarography and anodic stripping voltammetry.

In order to perform a diffusion layer titration we require the disc current to be ramped and this can be achieved by ramping a voltage across the resistor R_D . Previously this was achieved by using an integrator circuit but now with the computer it can be achieved with great control over the ramp rate. The ring voltage will also be provided by the computer and the output voltage will be measured, and, knowing the value of the resistor, a ring current can be determined. The computer now holds all the necessary information and with it is able to perform all the required analyses and can present the data in the most appropriate manner.

D Experimental Conditions

Cleanliness of the glassware is of vital importance and this was achieved by washing in "Decon 90" solution and then rinsing in water which had been de-ionized in an ion-exchange column and doubly distilled, referred to as DDW. This water was also used for preparing solutions.

The chemicals used, phenol, p-cresol, arsenic trioxide, potassium bromide and sulphuric acid were of AnalaR grade. The potassium bromide contains 0.001% nitrogen compounds and so very accurate work these must be removed. This can be best done in a double electrode system by electrochemically producing bromine until the impurities have been removed;

excess bromine can be removed by heating for about six hours; however this method is not so readily controllable.



Chapter Four

The Interface Control

A Preamble

In science one area being explored is the automation of experimental techniques. Initially this only involved the collection of data and the subsequent analysis by computers; however it has now become possible for computers to collect the data for themselves and to be able to control the experiments so making the whole process automatic. The problem faced is to interface the experiment with the computer, a microcomputer in this work. Mainframe computers are far too expensive for dedication to one experiment, and in any case real-time control is impossible on a time sharing system where much of the time is spent simply in deciding which program should be run next. It was not until the minicomputer and then the microcomputer with their relative cheapness could experiment dedicated computing systems be developed. The system used was the one designed by Goddard and is a development of the work he did in Oxford (31) on automating cyclic voltammetry in studies of organic electrochromics.

B System Methodology

One way to approach the interfacing is to dedicate one particular microcomputer to one particular experiment, to determine the functions it needs to perform and then to physically connect the computer to the apparatus; that is to say to perform the interface purely in hardware. Although this is cheaper in that less hardware is required it is more expensive in time since a detailed knowledge and understanding of the particular computer is needed. This approach, in addition, is

inflexible since the hardware will have been constructed for one particular task and changes cannot be readily made. In the memory system information required must be stored and retrieved at pre-determined addresses and these must be connected with the experimental apparatus in hardware. Changes are therefore difficult.

In order to obviate these problems systems have been developed to allow greater flexibility and ease of application and in this work such a system developed by Goddard has been used. This is a general interface which has been designed so that it can be used in conjunction with different experiments where the control of the experiment is effected through software and not through hardware. In consequence knowledge of the hardware is not required.

In designing a system one must know what tasks need to be performed and what apparatus needs to be controlled. Such apparatus might include stepping motors, pumps, lights and solenoid valves - for these voltages are required. In the work of this thesis we need to provide a current (for the disc electrode) and to measure a current (from the ring electrode). Normally this is done by providing and measuring voltages over known resistors.

Secondly we must be able to provide timing, notably for purposes of sequencing but also for other needs such as integration, eg current to charge, and measuring time intervals between events.

In developing a system for the microcomputer control of an experiment there are two approaches that can be followed concerning the input/output (I/O) organization. The first approach involves the adding of various function boards into the computer alongside the computer boards themselves, the CPU board, the VDU board etc as shown in Figure 4.1. This approach has the advantage of cheapness since no

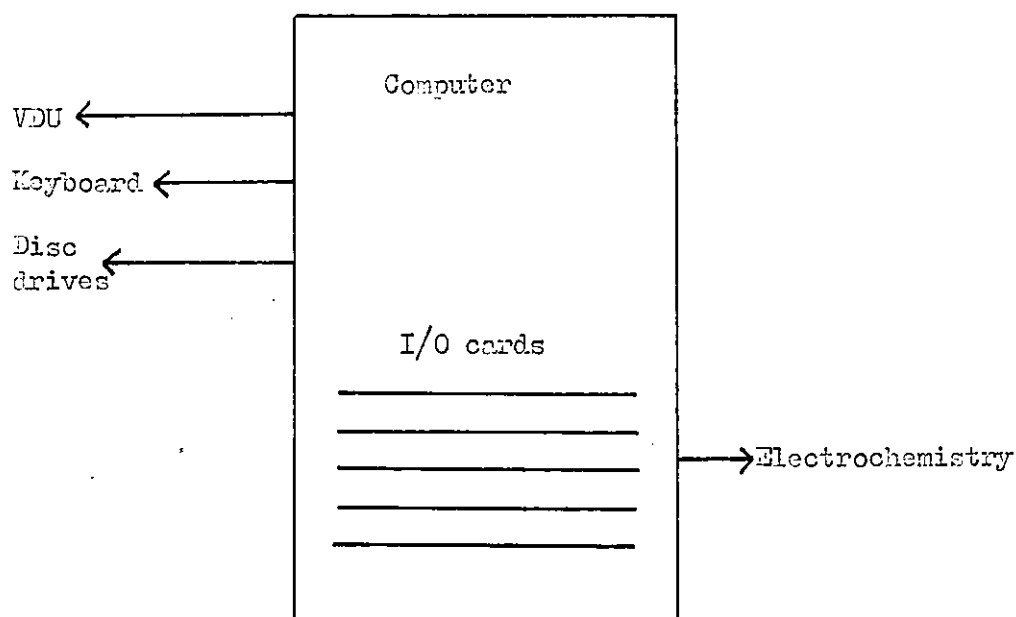


Figure 4.1 The I/O organization with the function boards inside the computer along side the computer's own boards

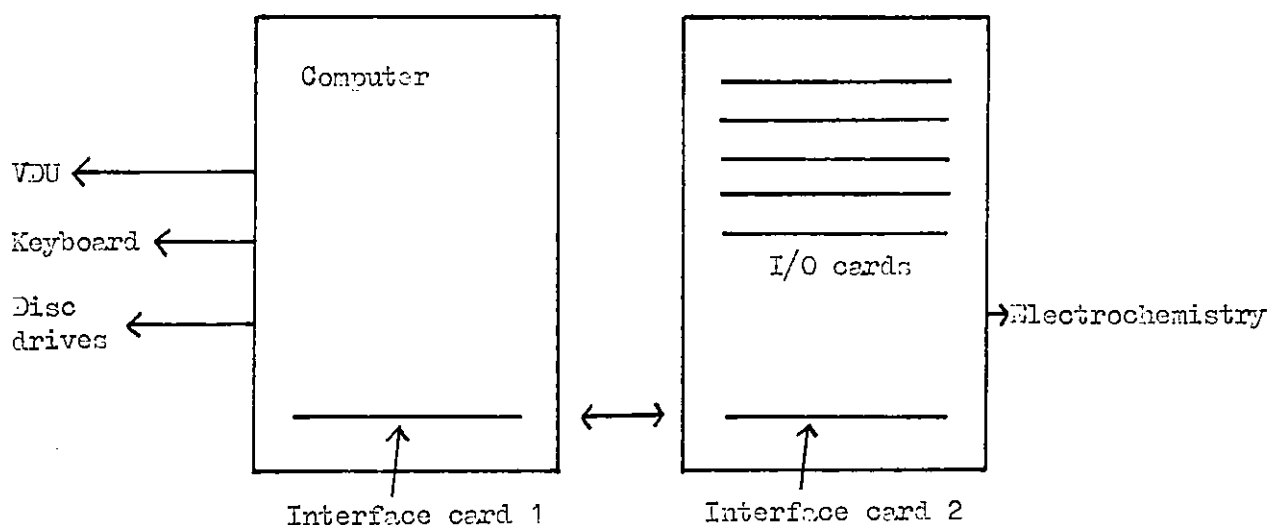


Figure 4.2 The I/O organization with the function boards inside their own rack

extra housing is required; however its disadvantages are the limited number of slots available after the computer's needs have been met, and secondly there may be the need for additional power supplies and the possibility of overheating.

The second approach is to have a second box to house the function boards, see Figure 4.2, from which the experiment can be controlled. The interface rack is connected to the computer via a specific interface card which is connected to an interface card house in the computer along side its own boards and inserted into the computer bus system. This approach has the disadvantage of greater cost and it needs its own power supply but these are greatly offset by a greatly increased capacity for more boards. Furthermore there will be no digital noise affecting the analogue components. Along the back of the rack runs a parallel set of wires carrying the computer data, address and control buses and to which the various boards can be connected. This gives rise to another great advantage of this approach since the bus in the rack need not be the same as that in the computer - which is the case in our system where the computer has a 100-S bus whereas the rack has a 50 line bus. A single interface card in the computer performs the required conversions. This means that the interface rack can be readily connected to another computer which has a different bus system and all that physically needs to be changed is the conversion card. This leads to greater flexibility. However it might be that the program needs modification.

Following on from this we must be able to send data to and from specific boards and this necessitates being able to address each board. This is done by having a number of address locations assigned for each board in memory. This can be done in two ways:

(1) The memory can be assigned from the board by wire links or switches which has the advantage of cheapness since no extra logic is required. Its disadvantage is ensuring that each board is given a different set of addresses otherwise confusion on the data bus could ensue if two different boards were being read.

(2) A second method is to have the memory assigned by the computer or interface rack so as to preclude the possibility of overlapping memory space; this is achieved in hardware using logic circuits and so has the disadvantage of higher cost since the logic for all the boards must be implemented even if only a few are being used.

It would increase the facility of the use of the system if the computer itself were able to determine the type of board in each position so that the operator need not have to tell the computer - if a large number of boards were being used this would be very tedious. This means that the operator can access each board by type and not by address. In order to do this one of each board address location is used to hold a type parameter - it is readily seen that this location must be the same for all the boards. At the machine code level the accessing is still done by the addressing of the board.

C The Interface Rack

Three types of interface racks have been built and developed for this system but only the first was used in this project and so only it will be described in detail (36).

(1) The Standard Rack

The standard rack can house up to seventeen function boards,

where the left hand slot is reserved for the controller board and it will only accept a 4E (0.8") wide front panel, the remaining slots allowing 5E (1.0") front panel boards. The rack itself comprises a standard 19" 6U high, 84E wide rack with two DIN 41612 32-way indirect edge connectors, which is mounted in a steel instrument case. The function boards are double-eurocard size (233.4 by 160 mm) printed circuit boards (see Figure 4.3). The cards are held in place by a 5E wide aluminium front panel from which also are carried any external connectors; screws can be added for greater security.

In the rear of the case are housed the power supply and fan. Two different power supplies are available, a linear power supply (+5V at 8A and +15V at 2A) when minimum noise is required, or a switch-mode supply (+5V at 20A and +15V at 2.4A) when maximum power is needed. But these supplies are protected from overloading. A mains connector, switch and 2A fuse for the power supply are at the back, where there are also the four bus connectors (see Figure 4.4).

(2) The Power Rack

This rack is similar to the standard one except that it is smaller (19" 3U sub-rack) and it will house four 20E wide modules, each containing a standard eurocard of 100 by 160mm. Again the power supply is housed at the rear along with the mains connector, switch, and the four parallel bus connectors (see Figure 4.5). This power supply is used for the internal logic. If the modules themselves are providing power supplies for switching dc levels they must have their own power supplies (eg 24V or 240V), for example, controlling stepper motors or solenoid valves.

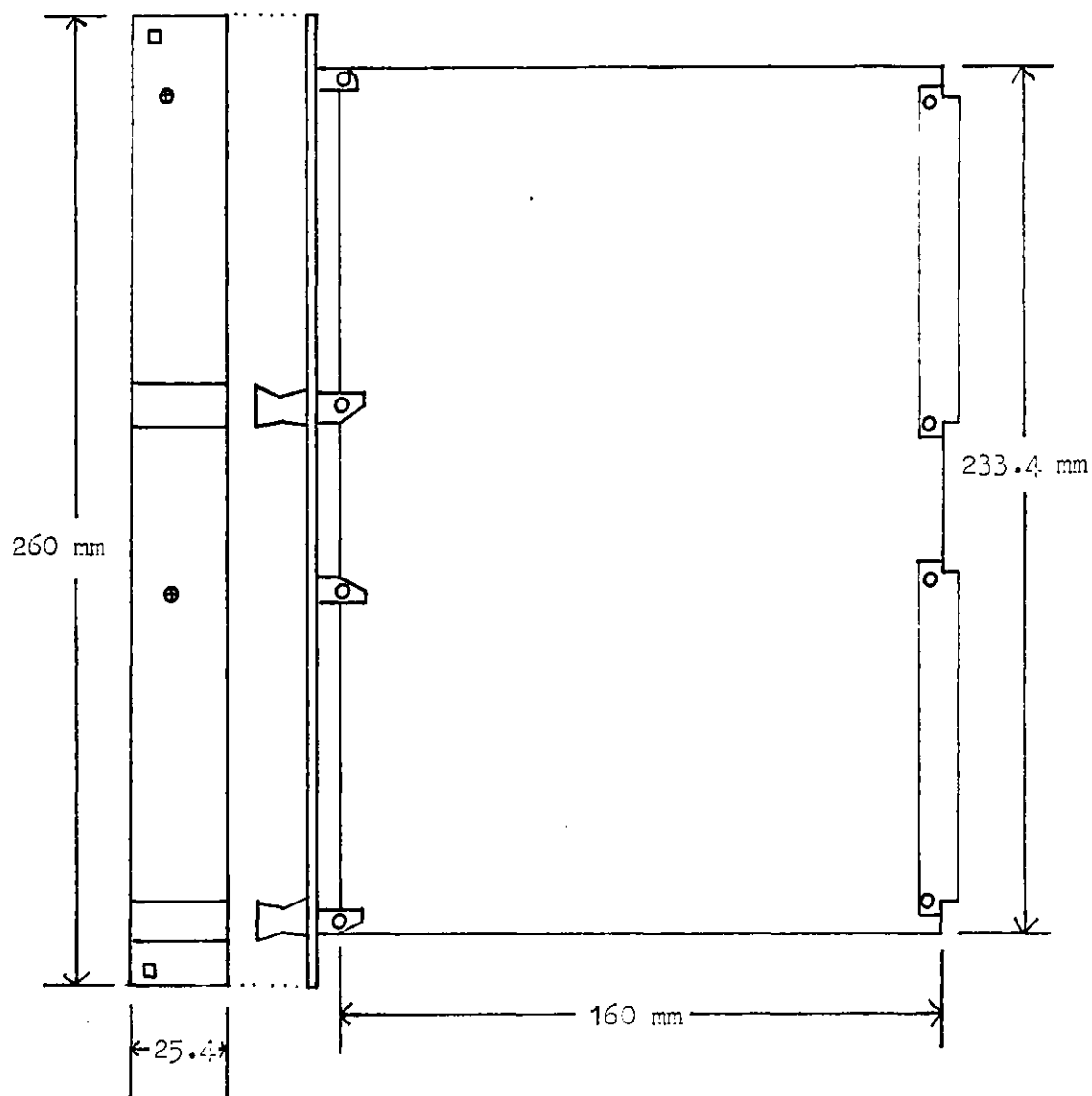


Figure 4.3 The standard interface board

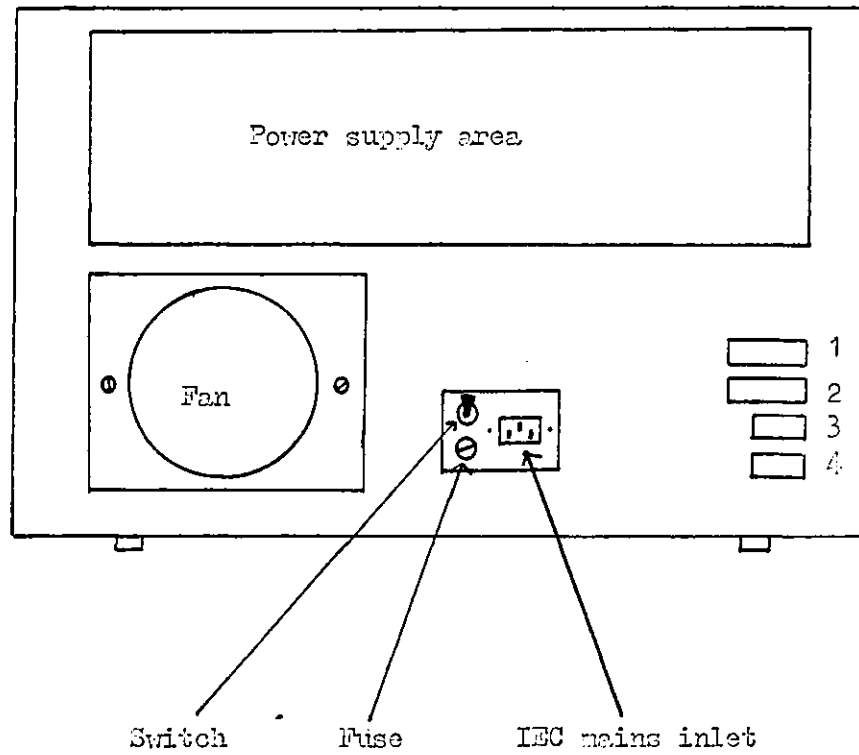


Figure 4.4 The standard rack rear panel

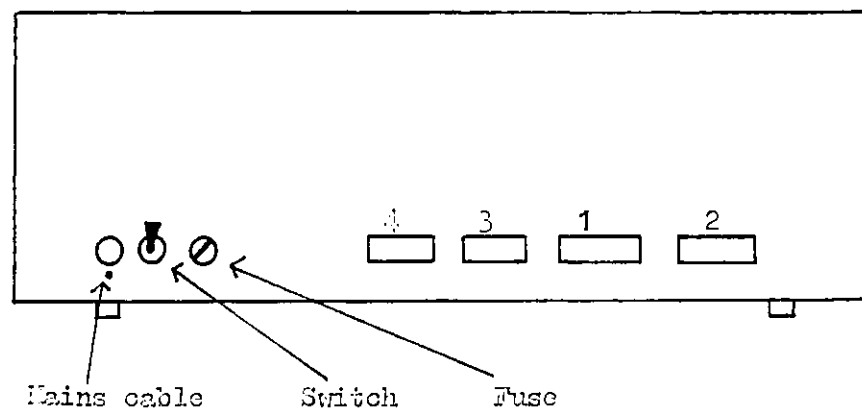


Figure 4.5 The power rack rear panel

(3) 6-Slot Backplane

This allows a system to be constructed cheaply and it comprises a simple printed circuit board whereby six function boards, a power supply and one controller card may be assembled. This system can only be used as a stand alone system with the Z80 controller card or with a host computer under a serial controller providing a RS-232 link since the parallel bus buffer card (IOR-1) cannot be accommodated.

D The Interface System

In the system there are 1024 contiguous address locations, number 0 to 1023, which are assigned to it. In the system used in this work the rack area of the memory is located at F600 to F9FF (hexadecimal) since this is the only area of memory large enough (with 40 wide character screen). Each board has eight consecutive address locations assigned to it, numbered 0 to 7, starting at address 0, 8, 16, ... 1016. Thus each system is able to accommodate up to 128 boards (1024 divided by eight). Since each standard rack can house 16 boards we can thus have a total of eight racks. How these are connected will be discussed later. Of these eight address locations (ports) the first five are accessible to the user allowing control of the external function of the board and are accessed from the application program as will be seen later. The remaining three address locations have been reserved for control functions which are common to all the boards; the first controls the interrupt status of the board, the second stores the interrupt vector and the last is the identification function which contains an eight bit-number which allows the microprocessor to identify the board. This is summarised below:

Port 0	Board dependent function
--------	--------------------------

Port 1	Board dependent function
Port 2	Board dependent function
Port 3	Board dependent function
Port 4	Board dependent function
Port 5	Interrupt control (read/write)
Port 6	Interrupt vector (read/write)
Port 7	Identification (read only)

Only boards capable of generating interrupts use ports five and six, otherwise these boards are read only and contain 00 or FF.

(1) The Interrupt Control Port

This board controls the generation of interrupts by the board and to the eight bits are assigned the following functions:

Bit 0	Interrupt enable	IE	
Bit 1	Extra control bit	CB	
Bit 2	Trigger source 0	TRO	Read/write
Bit 3	Trigger source 1	TR1	
Bit 4	X		
Bit 5	X		
Bit 6	X		Read only
Bit 7	Interrupt generated	IG	

(a) Bit 0 : IE

Bit 0 is used to enable the hardware interrupt system. When a logic one is written in the location the interrupt is enabled, allowing the external interrupt (INT) to go low when an internal interrupt occurs. This then tells the CPU that the board requires servicing.

(b) Bit 1 : CB

This bit is spare for any general purpose that might be required.

(c) Bits 2 and 3 : TR 0,1

These two bits allow a trigger source for the function board to be selected and since we have two bits four possible sources are available.

(d) Bits 4, 5, 6.

These bits are indeterminate and X indicates a 0 or 1 depending on the board.

(e) Bit 7 : IG

When the board generates an interrupt this bit goes low and it is reset when a valid INTAK (interrupt acknowledge) is returned if the board is in the highest priority interrupt generator. Alternatively it can be reset by a write operation to port 7, thus permitting software polled interrupts.

(2) The Identification Port

This read only port provides the identification number of that type of board - since an eight bit byte is stored 256 types of board are possible. In practice only 255 are possible because one type number (FF hex) is reserved for distinguishing an empty slot. Table 4.1 lists the boards currently available.

E Using the System

We have seen that each board has eight address locations assigned to it, with three common to each board. One of these is the type number for identification and it must be in the same position for each function board otherwise the computer has to know which board is

Type Number	Board function	Comment
0	Diagnostic/monitor	
1	Two 12-bit DACs	
2	32-bit parallel I/O	
3	Not assigned	
4	12 ADC	
5	Not assigned	
6	Not assigned	
7	Not assigned	Simple input/output
8	Not assigned	functions
9	X/Y graphics plotter	
10	Not assigned	
11	Not assigned	
12	32-bit/8 decade timer	
13	8 channel multiplexer	
14	3-terminal potentiostat	
15 - 62	Not assigned	
63	Prototyping card	
64	4 24V 0.5A DC switches	Power rack modules
65	4 240V AC switches	
66 - 128	Not assigned	
129	8 - 64K External RAM/ROM/EPROM	Memory and I/O functions needed to convert rack to stand-alone computer
130-191	Not assigned	
192-254	User assigned	Available for users to develop their own boards
255	No board	Indicates absence of board

Table 4.1 List of Board Type Numbers

being accessed before it can identify it. Having the same internal location for the type is convenient since it means the address decoding circuitry can be the same for all boards. It naturally follows from this to place all the common control functions into identical locations on the boards. However for locations 0 to 4, the locations for the external control functions, this is not possible since they are different for each board and they must be controlled by the application program. The common control functions are controlled by a set of ready-written machine-code programs using locations 5, 6 and 7.

The system has been designed with two goals in view, firstly the maximization of the ease of use and secondly the maximization of its flexibility. This means that we want to do all the addressing in software and to be able to use any combination of function boards. We have seen that the system can accommodate up to 128 boards and so we should like to be able to use 128 of the same board or 128 different boards. This is readily achieved by the system outlined since the boards, once inserted in the rack, can be identified by the computer, where the computer reads back 255, 11111111 in unsigned binary, from a vacant slot. If all the boards are different there is no problem since the user simply addresses the function required at any given moment. However a problem arises when there is more than one of any given type of board since the computer must be able to distinguish between them; for example we might wish to measure two voltages using two 12-bit ADC boards. Using the slot position is one possibility but then we lose the advantage of computer identification; further, we must use the same slot position each time and this would be tedious. Alternatively we could use the parameter of "number of that type"; for example counting the number of boards from the left, the lowest address

Slot	Type	Number	Board
0	255	1	No board
1	255	2	No board
2	4	1	12-bit ADC
3	1	1	Two 12-bit DAC
4	4	2	12-bit ADC
5	2	1	32-bit parallel I/O
6	255	3	No board
7	4	3	12-bit ADC
8	1	2	Two 12-bit DAC
9	255	4	No board
10	4	4	12-bit ADC
11	2	2	32-bit parallel I/O
12	9	1	X/Y graphics controller
13	4	5	12-bit ADC
14	2	3	32-bit parallel I/O
15	255	5	No board

Table 4.2 The Number/Type Addressing Scheme

location. Following on from this the actual slot position is unimportant but only the relative position of the board to others of the same type - boards of differing type are ignored. This particular kind of type/number addressing scheme is illustrated in Table 4.2 where one rack is considered. In this example we only have one X/Y graphics controller board (9,1) and in our system we can place it in any slot we choose and the program will always run. However we have five 12-bit ADCs in this rack, (4,1), (4,2), (4,3), (4,4) and (4,5). To the computer all these boards are indistinguishable but not for the user for whom they may serve different purposes, eg measuring the potential in different parts of the rat's brain. However provided we keep the ADCs in the same relative position the program will always run correctly; but if, for example, we swop (4,2) with (4,4) this will no longer be the case and in order for the program to run correctly we must respecify the boards relative positions which is easily done.

F The Complete System

The system can be controlled in two different ways:

- (1) by a host computer
- (2) by the rack's own processor.

(1) In this mode the interface racks are controlled from a host computer (a Research Machine Z80 in this work) and this can be done in three ways:

- (a) via the standard 50-way parallel bus
- (b) via the IEEE-488 parallel instrument control bus
- (c) via the RS-232 standard serial communication link.

This mode is more expensive since a dedicated host computer is

required but has the greater use as a development system where the program is constantly being changed.

(2) In this mode the interface rack is controlled by its own microprocessor which is achieved either by:

(a) a CPU board in the rack, or

(b) a CPU board outside the rack.

In the former case the microprocessor can only control that particular rack whereas in the second case it can, once supplied with its own case and power supply, control all eight racks. A program can be stored in PROM or EPROM. This is very advantageous for routine work, such as in analysis, since a host computer, and expensive part of the system, is no longer required.

Thus the development of an analytical system might involve the development of the software and any extra hardware using the mode incorporating a host computer. Once the program has been developed and modified to satisfaction it can be burnt into a PROM or EPROM and the host computer be made available for use elsewhere.

As we have seen up to eight racks can be used, but not all eight need to be used and often only one is sufficient. A 50-way bus is taken in parallel to all the racks irrespective of the number present and this supplies all the control functions needed for the operation. If only one rack is present this is sufficient and such a system is illustrated in Figure 4.6. However if more than one rack is used a problem arises since we must make certain that none of the racks overlap in the 1024 byte address space of the computer. In order to overcome this another set of bus signals is provided which establishes a unit priority daisy-chain; this is achieved by using 15-way "D"

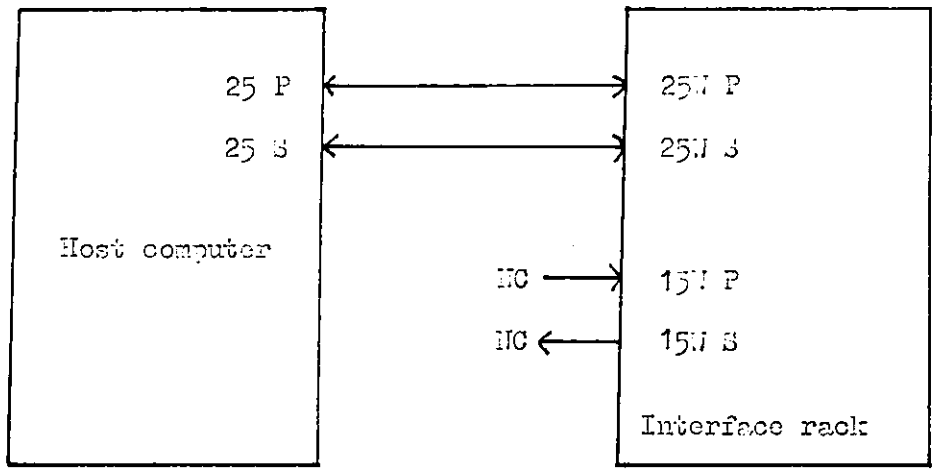


Figure 4.6 The single rack system

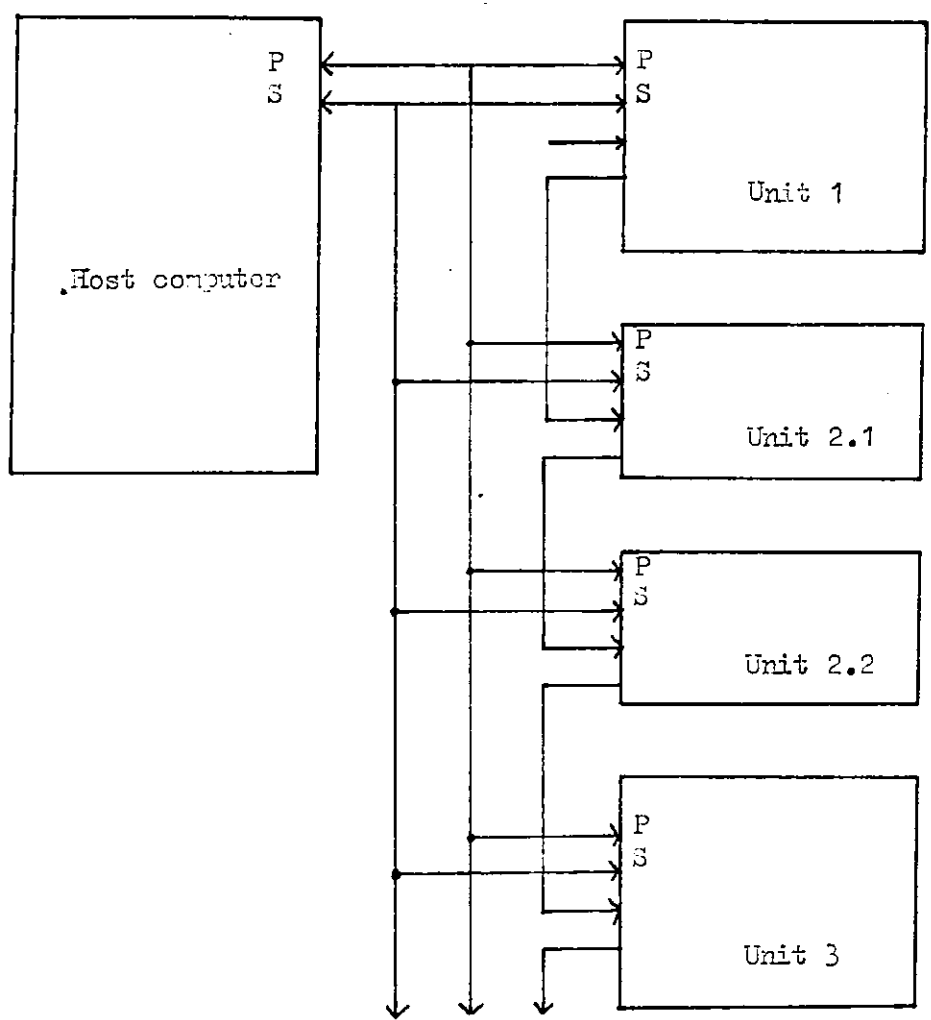


Figure 4.7 The multiple rack system

connectors on the rear of both the standard interface and power racks. This is illustrated in Figure 4.7.

G The Function Boards

A number of function boards have been developed for this system and we will now discuss the ones used in this work (41), the digital-to-analogue convertor (DAC), the analogue-to-digital convertor (ADC) and the X/Y graphics controller.

(a) Digital-to-Analogue Conversion

In this work we required two analogue signals, one for potentiostating the ring and the other for ramping the disc current. This requires one DAC board since each has two ports. As a computer only provides integral values, and we need a signal of continuous values, a conversion process is necessary. The principle of this process is as follows: for each bit of a binary number a voltage is generated, the voltage being proportional to the position of the bit in the binary number. Then, in the same way that a binary is made up from a combination of bits, a voltage output is made up from a combination, or sum, of voltages, each corresponding to one bit position. In Figure 4.8 we see a schematic diagram of a DAC. It consists of four proportional summing resistors with their respective switches. Also included is one operational amplifier, a proportional feedback resistor, R , and a 10V stable reference. This constitutes a four bit DAC. The resistors have values of R , $2R$, $4R$, $8R$ resulting in gains of -1 , -0.5 , -0.25 , -0.125 . When all the switches are open 0V will reach the operational amplifier and consequently 0V will be the final output. If we were to close the first switch corresponding to bit 0 we then pass $-10V$ through the $8R$ switch and would obtain an

10.000 V stable reference

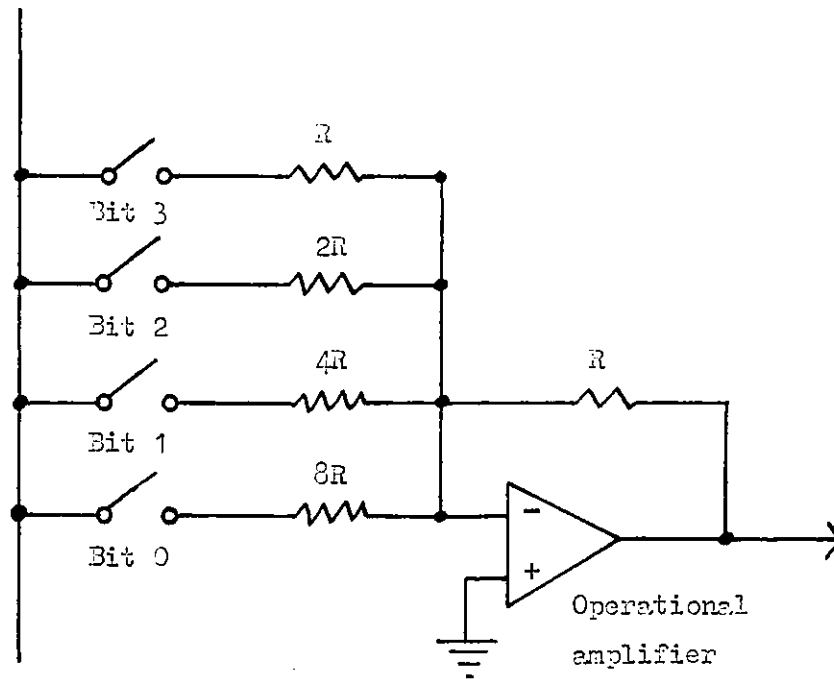


Figure 4.8 A schematic diagram of a simple 4-bit DAC

output voltage of 1.25V since there is a gain of -0.125 . In a similar way closing the second switch (bit 1) will provide 2.5V; closing all the switches would provide a total output of 18.75V ($1.25 + 2.5 + 5.0 + 10.0$ V). Thus we are able to vary the range of the DAC by varying the reference and increase the resolution by increasing the size of the resistor network. In practice currents are summed rather than voltages since they are easier to switch on and off accurately. A current-to-voltage convertor is therefore also required which means an operational amplifier *is needed*.

There are three characteristics of a DAC which describes its quality; non-linearity, differential non-linearity and settling time.

(1) The non-linearity is a measure of the accuracy of the conversion and is measured by the deviation from a theoretical transfer function. Typically it is ± 1 LSB (Least Significant Bit). See Figure 4.9.

(2) The differential non-linearity measures the standard deviation of the step size and typically it is ± 0.5 LSB (Figure 4.9).

(3) The settling time indicates the speed with which the DAC will operate and is defined as the time taken from the change in input code to the output voltage or current becoming stable to within a certain percentage of the final value. The slew rate is also a parameter used and it is the rate of change of the output with respect to time (see Figure 4.10). Naturally there is a payoff between the speed of the DAC and its cost.

The DAC used in this work was the Hybrid 336C-12 and its characteristics are given in Table 4.3. At the centre is a laser trimmed, low drift, thin film nichrome 12-bit resistor network . Two

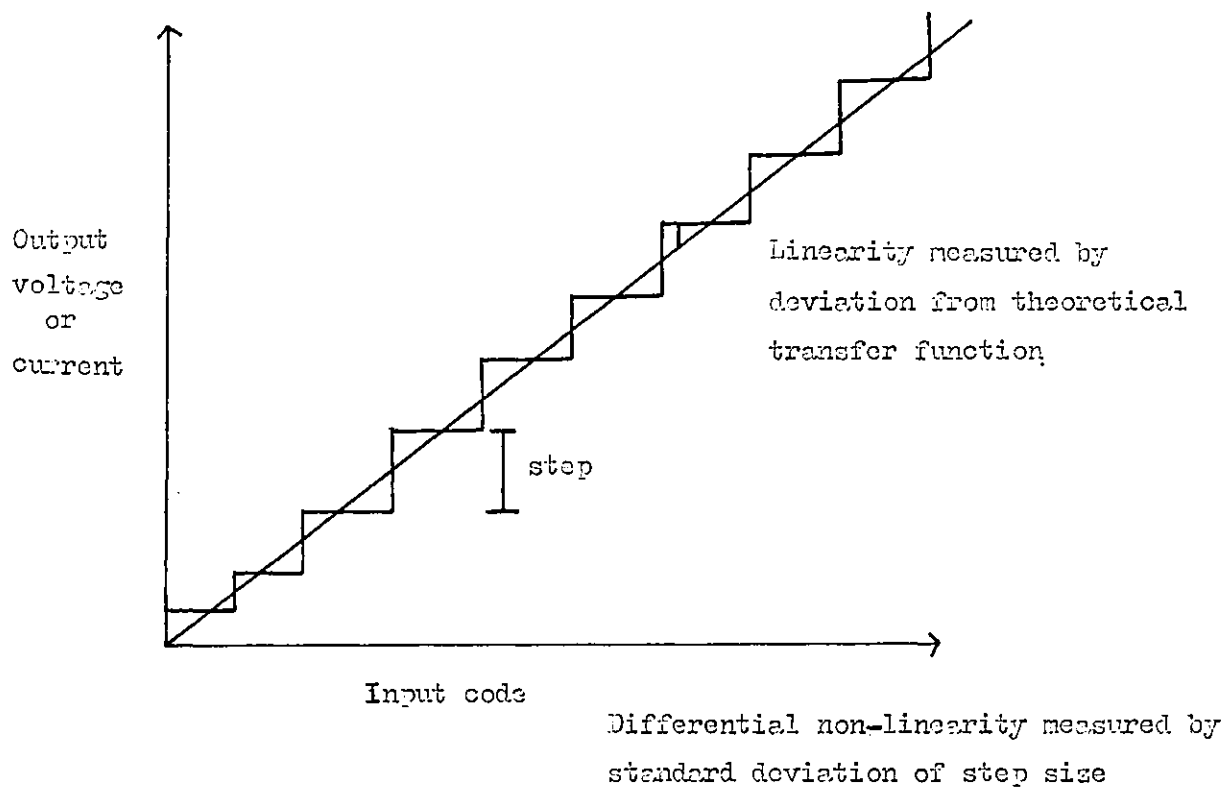
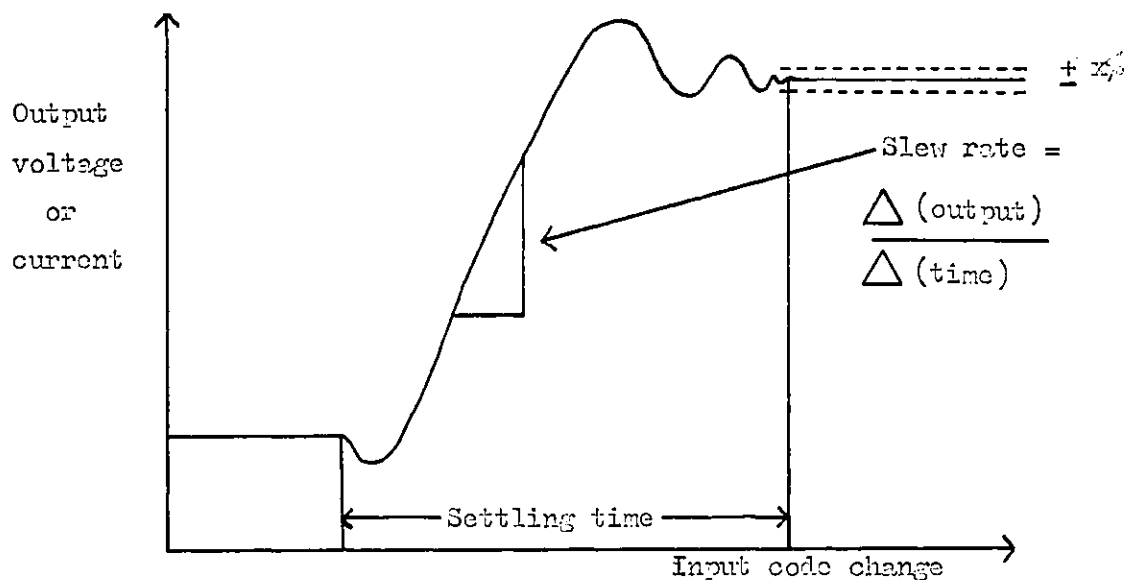


Figure 4.9 Non-linearity and differential non-linearity



Settling time = time from input code change to output stable to $\pm X_p$.

Figure 4.10 The settling time

Type :	Latched, fixed reference, voltage output	
Resolution :	12 bits	
Output ranges :	0 to +10V, $\pm 10V$	
Static performance :	Non-linearity $\pm$ LSB; differential non-linearity ± 0.5 LSB	
Dynamic performance :	Max. settling time, 10V change in 5 μs 20V change in 10 μs Slew rate 10V/ μs	
Temperature range :	-55°C to +125°C	Operating
	-65°C to +150°C	Storage

Table 4.3 The Hybrid 336C-12 DAC

Type :	Successive approximation	
Resolution :	12 bits	
Analogue inputs :	Bipolar ranges : $\pm 2.5V$, $\pm 5V$, $\pm 10V$ Unipolar ranges: 0 to +5V, 0 to +10V	
Conversion time :	17 μs typically, 20 μs maximum, 58.8 kHz	
Accuracy quantization:	at 25°C ± 0.5 LSB	
Temperature range :	-55°C to +125°C	Operating
	-65°C to +150°C	Storage

Table 4.4 The Hybrid 581C-12 ADC

output ranges are available, 0 - +10V and ± 10 V, the latter being used in this work. The non-linearity and differential non-linearity are respectively ± 1 LSB and ± 0.5 LSB. For the former range the maximum settling time is 5 μ s, and for the latter 10 μ s. The slew rate is 10V/ μ s. These are sufficient for the requirements of this work. The operating temperature range is -55°C to 125°C so it can be used in a system designed for field work.

This DAC has a 12-bit resolution and this gives rise to problem in its implementation. In order to produce a stable output the input parallel digital word must be stable. The Z80 microprocessor, like most at present, is an 8-bit processor and therefore with any DAC with up to 8-bit resolution there is no problem. However in our case we have a 12-bit DAC, requiring two 8-bit latches where 8 bits are used from the one and 4 from the other. When we change the contents of the first latch the convertor will immediately begin operating. However a few microseconds later the contents of the second latch will change and this will cause a glitch on the output signal. In order to overcome this problem a second latch is added to the low-order latch path to cause a delay in converting the lower 8 bits. The low byte is sent first, followed by the high byte where its MSB (Most Significant Bit) is 1. This bit is used to strobe the temporary holding low latch so that now the two sets of signals will arrive at the convertor simultaneously. This arrangement is shown in Figure 4.11.

(b) Analogue-to-Digital Conversion

Just as we must be able to provide analogue signals, so we must be able to measure analogue signals, in this work we must be able to measure the ring current, or more specifically a voltage across a

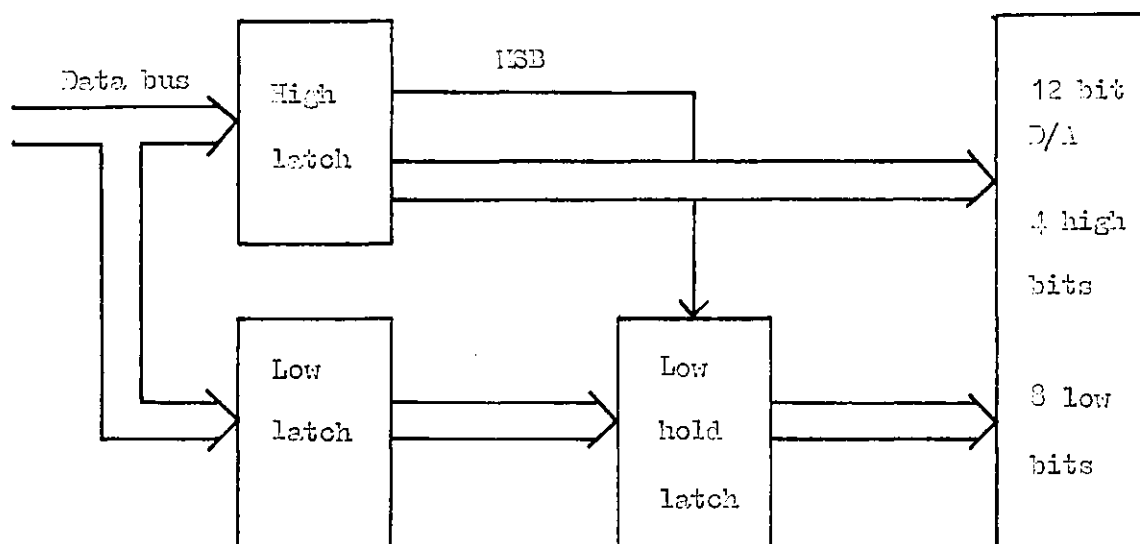


Figure 4.11 The 12-bit latching system

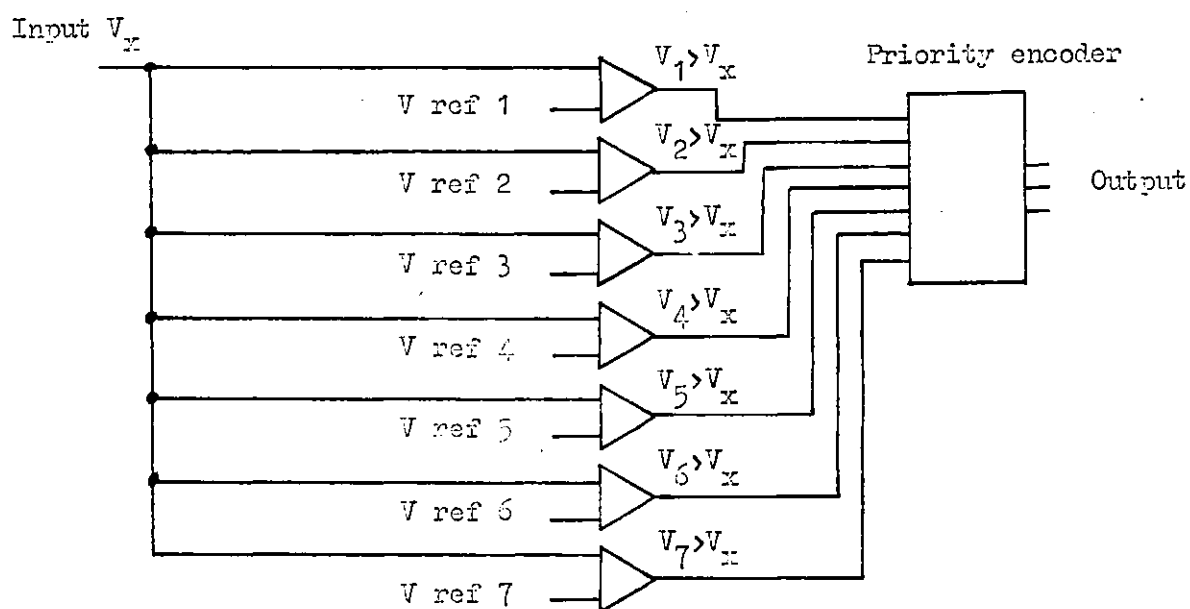


Figure 4.12 A/D conversion by direct comparison

resistor. To digitize the signal we require an analogue-to-digital convertor. There are three methods of effecting this process: integration, direct comparison and successive approximation.

(1) Integration

In essence this involves charging a capacitor up using the unknown voltage and after a certain time it is then discharged to zero with respect to a known reference voltage of opposite sign. The ratio of the two times taken will then be in the ratio as the two charges. Of the three methods this is the most accurate but it is also the slowest.

(2) Direct Comparison.

This is a very fast method of conversion but it is also the least accurate, usually with less than five bits of resolution. If n is the number of bits required then $2^n - 1$ comparators are required. If we have a 3-bit direct comparison convertor we are able to have up to eight levels of output using seven comparators. Using these as references we are able to determine whether the input voltage is less or greater than particular values and the result can be encoded as the output (see Figure 4.12). Because of the complexity of the circuit this is the most expensive method but conversion times of less than 100ns are possible.

(3) Successive Approximation

In this method a single comparator and a DAC are used where the input signal is compared with a guess, see Figure 4.13. Successive bits in our guess number are tested beginning with the MSB and if its value is greater than our input value we leave the bit on ("1"), but if it is less than the input value we switch it off ("0"). In such a

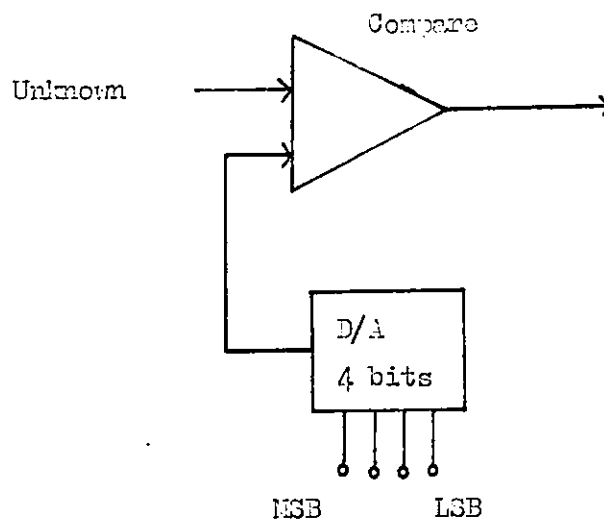
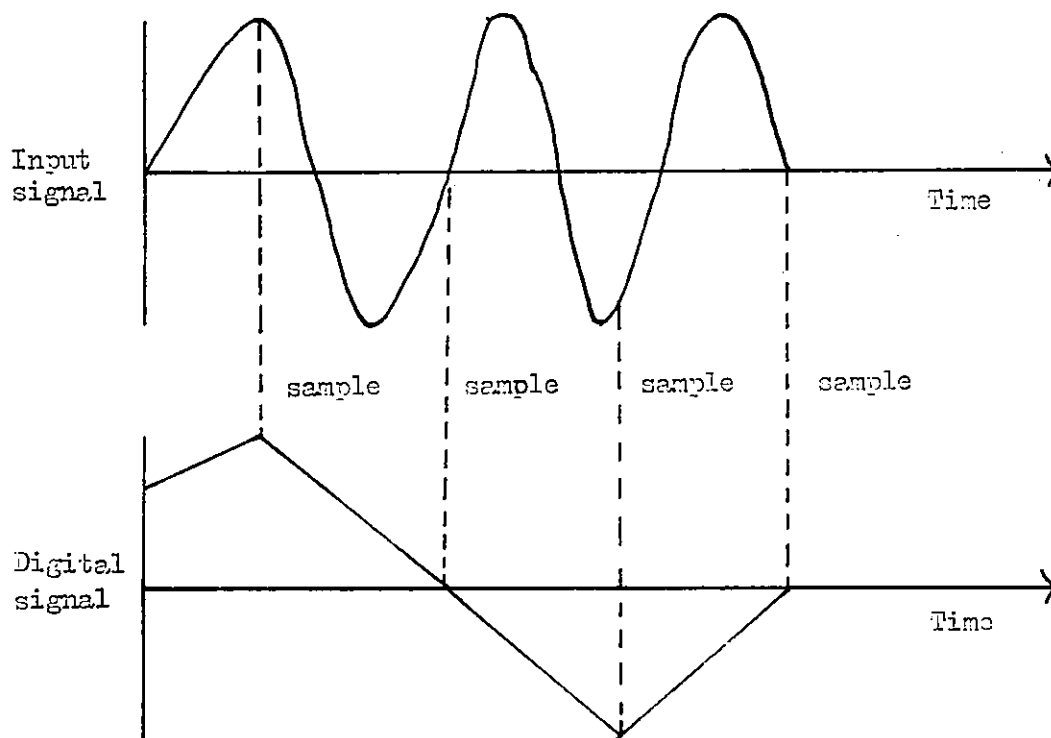


Figure 4.13 A/D conversion by successive approximation



Input signal = f Hz, sampling frequency = $4/3$ Hz $\Rightarrow$ digital signal frequency = $f/3$ Hz.

Figure 4.14 Sampling

manner our guess will approach the input value. This method lies between the other two in terms of speed and accuracy and is the one that has been incorporated in the boards used in this work. The successive approximation can be performed in two ways, either in hardware or in a mixture of hardware and software. In the former way, the one used here, a successive approximation registrar, SAR, performs the bit-shift and test-function in hardware. Alternatively a software algorithm can perform these operations.

A/D conversion has similar problems of linearity as D/A conversion; in addition there are two further problems.

Firstly the input signal must remain constant while the conversion is being performed otherwise an incorrect value will be obtained. This is solved by the insertion of a sample/hold circuit before the convertor itself though unfortunately it will introduce further errors and non-linearities.

Secondly there is the problem of sampling. If our sampling frequency is too low we will not obtain a truly representative digital signal as we can see in Figure 4.14. In order to ensure that this does not occur our sampling frequency must be at least twice that of the input frequency, and preferably more.

The ADC used in this work is the Hybrid 581C-12 and its characteristics are shown in Table 4.4. It also has 12-bit resolution, a number of unipolar and bipolar ranges and both parallel and serial outputs. It has a maximum conversion time of $20\mu\text{s}$ and a frequency of 58.8 kHz. Again its operating temperatures allow it to operate in the field. In this work the input range chosen was $\pm 10\text{V}$ and consequently the resolution possible is $20/2^{12} = 3.925 \text{ mV/bit}$.

(c) X/Y The Graphics Board

In order to provide hardware copies of visual representations developed on the VDU (Visual Display Unit) a board was developed in conjunction with an X/Y plotter, in this work the Bryans 400A. This board is a modified DAC board with one port providing analogue signals for the X coordinate and the other port for the Y coordinate. Since it is a 12-bit convertor the resolution is 1 in 2^{12} , and thus values of -2047 to 2048 are possible for each axis.

(d) Graphics Character Board

In the graphics character board are stored the sub-routines for the alphanumerics and various symbols in ROM which allow the user to print words and numbers on the Bryan plotter. These sub-routines are a series of coordinates.

Other boards available are the PI/O board and a multiplexer but as they were not used they will not be described.

H The Software

Having described the hardware we will now describe the software used in this work. BASIC was the language used in a version supplied by Research Machines. However the interpreter, which was supplied on disc, had to be modified since extra sub-routines were needed for the commands required by the interface rack. These were written and incorporated into the interpreter by Goddard. We will now present these extra commands for control of the interface.

As we have seen the system has been developed such that we can readily access a particular function board and in order to do this we must specify the type of board and its position relative to others of

its type. Thus we need two parameters. In addition each board has eight internal addresses and so we need a third parameter to specify one of these. This can be summarised as follows:

- (1) First parameter, t = type (0-254, 255 is no board),
- (2) Second parameter, n = number (1-128),
- (3) Third parameter, p = internal address (0-7).

Thus, in BASIC, a generalized routine would be:

Call "Routine" t, n, p.....

We must now divide the routines into two classes, general purpose routines and special purpose routines.

(a) General Purpose Routines

General purpose routines are used with any type of board, although some will not operate with all the boards. There are some further letters denoting certain parameters and they are b, bit number (0-15); d, 8/16 bit data; X, variable for returned data (8/16 bit).

Some of the routines which fall into this class are:

- (1) CALL "IDENT", a1, a2.

This is an important routine and is required by all programs using the interface rack. It IDENTifies all the function boards in the rack and creates tables in memory which can be accessed by the interrupt software to indentify which board has generated a particular interrupt. It also initializes the interrupt system by disabling all board interrupts and the CPU maskable interrupt.

The arguments a1 and a2 allow the user to output an identification table either on the VDU (a1) or on a printer (a2). The arguments set flags which either enable or disable the output stream, 1 for enabling, 2 for disabling.

(2) CALL"WRITE8", t, n, p, d

CALL"WRIT16", t, n, p, d

These two routines perform essentially the same function of writing a word represented by d to the address specified by t, n, p; the difference being that in the former case d is an 8-bit byte and in the latter a 16-bit byte. In the latter case the eight higher bits are sent to address t, n, p+1.

(3) CALL"READ8", t, n, p, X

CALL"READ16", t, n, p, X

These two routines are similar to the two previous ones except that the integer is read from the address specified and where the former is of 8-bits and the latter 16, and where the higher eight bits are read from address t, n, p+1.

(4) CALL"STROBE", t, n

This function provides the start signal to conversion devices and timers such as the analogue-to-digital convertor by writing a zero in the address location t, n, 4. We could do this by the WRITE8, t, n, 4, 0 command but the former is faster because in the latter two parameters need not be specified.

(b) Special Purpose Routines

These are routines which will only access a particular kind of board and that type is subsumed in the command. Since the type of

board is not specified, it being supplied by the routine, the specific purpose is faster. Some of these routines are:

(1) CALL"INADC", n, VARADR(X)

This performs a conversion in the ADC number n and stores the result in the variable X. This routine, like all special purpose routines, is a combination of general purpose routines but the former's greater compactness means it is executed more quickly. Thus this command could also be written as:

CALL"STROBE", 4, n

CALL"READ16", 4, n, 0, VARADR(X)

The STROBE command initializes the conversion in board type 4 (the ADC), the n^{th} one from the left. The READ16 command reads the 16-bit conversion from board type 4, number.n, port 0. In our system we have a 12-bit ADC, therefore the top four bits will be zero.

(2) CALL"XLINE", n, x, y, 0

This command moves the pen of the X/Y plotter controlled from the n^{th} graphics controller board to the coordinates x, y. The fourth parameter determines whether the pen is up or down, 0 for up and 1 for down.

(3) CALL"XCHAR", n, VARADR(T\$)

With this routine we are able to write the characters contained in the string T\$ with the X/Y plotter.

(4) CALL"WAIT", d

This routine waits for d 10ms intervals before continuing with the program. We could use this to allow an experiment to

stabilize.

(5) CALL "TIMER", n, d

The TIMER call sets a type 12 eight-decade timer board to count in units of d ms. Activation occurs during a call to the TIMER. SETTR can be used either to set the single shot or repeat mode of the timer board.

(6) CALL "SETTR", t, n, TR, CB

This routine allows us to set the interrupt trigger source and spare control bit as specified by TR and CB. The former specifies four trigger sources (0 to 3), the latter is a single bit and their values will depend on the type of board.

In the next chapter we will present some of the programs that have been developed during the course of this work.

Chapter Five

The Programs Developed

A Preamble

A number of programs have been developed during the course of this work and in this chapter we will discuss them. The programs themselves are listed in Appendix 6; flow diagrams are presented in the chapter where necessary. The language used is BASIC with additional routines for the interface as presented in the previous chapter.

B The Programs

(a) In chapter two the wall-jet theory was presented and we saw that we are able to calculate values for various parameters, namely $\beta^{2/3}$ which is a function of the geometry of the electrode system; N_o , the collection efficiency, which is the fraction of the electrochemically produced species reaching the ring. Values of β_J can also be calculated with corresponding values of M and r_J . A program has been written for making these calculations (A6-1); specific values for these parameters for a given concentration of substrate can be determined and the theoretical titrations plotted. This is particularly useful when a new electrode is being tested since we can readily test theory with experiment. This is important since they do not always agree. For example, the collection efficiency is theoretically independent of the flow rate but in practice, as we shall see, it does in fact depend on the flow rate. A set of theoretical calculations are shown in Table 5.1. This program is only involved with theoretical calculations and therefore it does not involve the interface rack or any of its commands.

(b) As described in chapter three a process for cleaning the electrodes was developed which previously was controlled manually from the Oxford box. With the system described in the previous chapter we can now automate this process and a program has been written to perform this task (A6-2). It is a simple program but readily shows how the interface commands are used and as an example we will go through this program line by line. The boards we require are the timer and a DAC to provide the voltages to the electrode.

LINE10 The IDENT routine identifies the boards in the rack and sets up the table in memory and also initializes the interrupt system.

LINE 12 initializes the timer board such that one unit of time corresponds to 1s (1000 ms).

LINE 13 sets the timer board (type 12, number 1) to the single-shot mode (CB = 1), internally generated TR = 0.

LINE 20 This statement writes a 0 into board type 1, number 1 and port 0; type 1 is the two 12-bit DAC and port 0 is the first of the two DACs (port 2 is the second). Thus we are outputting 0V to the first DAC, which will be connected to the electrode being cleaned.

LINE 30 This statement causes a delay of 10s (1000 10ms intervals) so as to allow the electrode surface to stabilize.

As we saw the cleaning process involves holding the electrode at 1.55V for 10s, 0.95V for 30s and -0.20V for 30s and that this process should be repeated several times; five times was often the case but this can be readily changed.

LINE 60 This asks the user how many cycles are required.

LINES 70- These constitute a FOR....NEXT loop performing the cycle.
240

LINE 80 The statement outputs 1.55V (1550mV) to the electrode.

LINES 90- These statements provide the 10s delay required, LINE 100
110
 provides the start signal to the timer (reading a 0 to
 type 12, number 1, port 4); LINE 101 produces the 1s wait
 (1000ms) and this loop, is performed 10 times (J=1 to 10).

LINES 130- These statements hold the electrode at 0.95V for 30s in a
160
 similar way.

LINES 180- These statements hold the electrode at 0.20V for 30s.
210

LINE 260 The cleaning process now over, the electrode is returned
 to zero volts.

LINES 120, 170, 220, 230, 250. These statements allow the user to
 see how far the process has progressed.

(c) We will now look at a titration program; many of these were written as the work developed incorporating greater sophistication and flexibility - we will discuss one typical one.

As discussed in chapter one the titration is performed by ramping a disc current which generates bromine by oxidizing bromide which travels downstream to the ring electrode where it is reduced back to bromide so generating a ring current which is measured. The ratio of the ring to disc currents constitutes the collection efficiency, N_o , in the absence of a substrate. However in the presence of a substrate such as As^{3+} or phenol the bromine is removed chemically such that initially no ring current is observed but as the disc current is increased the bromine is generated in sufficient quantities that it

begins to reach the ring. The result is that the collection efficiency is shifted to higher disc current values. We then saw that the concentration of the substrate can be calculated in two different ways - either from the intercept of the collection efficiency through the disc current axis or by an analysis of the titration curve. Thus we need to provide a current ramp at the disc electrode and we need to measure a current at the potentiostatted ring electrode. In practice it is found that we obtain better titration curves if we use a decreasing disc current (29) and so we initially sweep upwards quickly (anodic direction) and then slowly reduce the current to zero.

The X/Y plotter can be used for obtaining a hardcopy of the titration curve; a printer (Epson MX-80F/T) can be used for recording the values of the respective disc and ring currents and any calculations.

Thus the boards required are a DAC (with two ports for the disc and ring), an ADC for measuring the ring current, the X/Y graphics controller board, the XROM containing the character set routines and the timer board. The one DAC output is connected to the disc input of the electrochemical control box, the other to the ring input; the ADC is connected to the output of the box.

The program TI138 is presented in Appendix A6-3 and a flow diagram in Figure 5.1.

LINES 10- These statements are setting up the rack and initializing
300 the boards, defining the various arrays, defining the colour coding of the VDU, plotting out the axes and printing the headings.

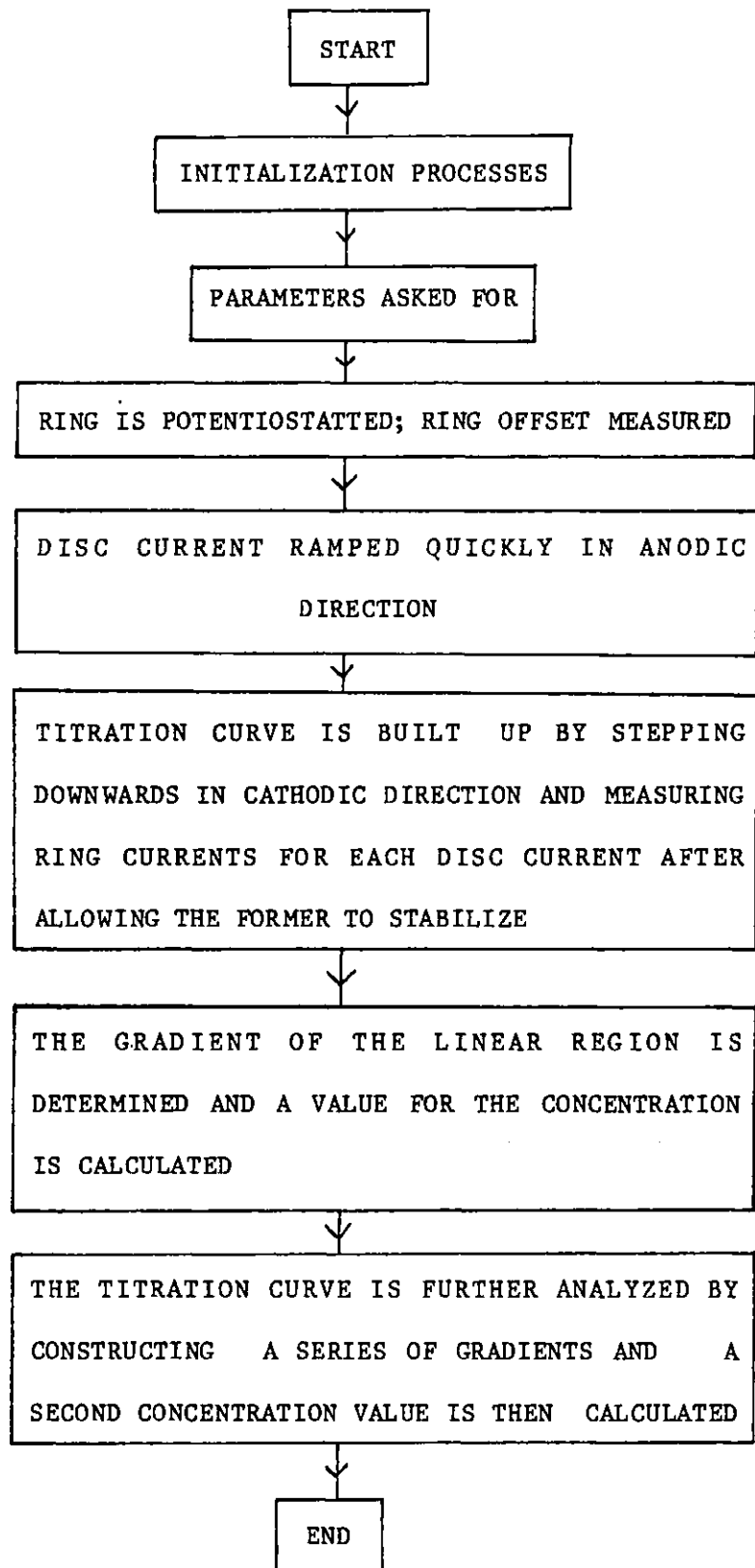


Figure 5.1 The Titration Experiment Flow Diagram

LINE 320 The maximum disc current in μA is asked for; the program can be modified so as to set the lower value, though usually it is kept at zero.

LINE 330 The disc current is generated by stepping up or down and consequently we must define the step size.

LINE 340 We must allow for the number of electrons transferred in the reaction between the substrate and the electrochemically produced species - this is the value n in chapter two. For the reaction with arsenic the value of n is 2 since we have an oxidation of As^{3+} to As^{5+} .

LINES 350, 390 FY and FX are scale factors for plotting the readings in hardware.

LINES 370, 380 The current values are given in μA ; the ADC output is in mV. $V = IR$ and so to make the conversion we multiply the given currents by 10 since the resistor in the galvanostat is 10 kohms.

LINES 430, 440 The ring is potentiostated at -0.45V .

LINES 450-540 The disc is held at zero volts during which 250 measurements of the ring current are made using the INADC command. An average is then determined and this constitutes a ring offset (variable K).

LINES 550-590 These statements generate the quick upward ramp of the disc current.

LINES 600-1210 The downward sweep is now performed, usually descending to zero current, in steps, definable by the user, but often set to a value of $5\mu\text{A}$. At LINE 870 the new disc current is set; LINES 880 to 920 generate a 2s delay to

allow the ring current to stabilize (this is important as will be seen in the next chapter); LINES 930 to 1000 perform the analogue-to-digital conversion, in this case 360 conversions are made and the average found. The variable X is used for plotting the point on the VDU.

Part of the titration curve is the linear section which is used in one of the calculations of the concentration and it is necessary to determine the gradient of this section. The program takes points within defined limits and which lie on this linear section to calculate this gradient; the variables LC and CL at LINES 650 and 660 are these limits. At LINE 820 the points are plotted on the VDU; the third argument of the plot routine is the colour code and thus we can plot the points used in the gradient calculation in a brighter colour and so ensure we have the correct limits. LINES 690 to 710 and 1110 to 1210 contain the statements which perform the calculation of the gradient, the correlation coefficient and the ring current offset using the equations of linear regression which are given in Appendix A5. LINES 1010 to 1080 allow us to determine a base line for the titration curve.

LINES 1220-These values that have been calculated are now plotted.
1620

The concentration is then calculated (LINE 1570), using the equation, equation 1.23 rearranged:

$$C = \frac{N_o i_D}{1.6 \beta^{2/3} k n F v^{-5/12} D^{2/3} a^{-1/2} r^{3/4} v_F^{3/4}} \quad (5.1)$$

where N_0 is the measured gradient, i_D is the disc current offset (at zero ring current). The line of gradient 0.134 is also plotted which is the point where any titration curve for this electrode system should enter the linear section.

LINES 2480-2920-The values for the disc and ring currents are then printed out and also their ratio. Also printed out are the various parameters and results obtained for a permanent record, including the concentration of the substrate, temperature (recorded manually) and the time between changing the disc current and measuring the new ring current.

Previously it was shown that we are able to determine the concentration by constructing lines with varying gradients and which intercept the titration curve. These gradients are then plotted against their respective disc current intercepts and from the gradient of the line so obtained we can calculate a value for the concentration. This is of particular importance for those points whose ring to disc current ratio lie below the value at which the titration curve enters the linear region since we are unable here to use the first method. This is important for those curves where the linear region cannot be recorded; in addition these values provide verification for the theoretical model. The latter half of this program is concerned with constructing these gradients and subsequently finding the concentration.

In chapter two we arrived at the expression:

$$i_R = N_O i_D - \beta^{2/3} M. \quad (2.83)$$

Since $N' = i_R/i_D$ we can write

$$N' i_D = i_R = N_O i_D - \beta^{2/3} M$$

and so

$$i_D/M = \frac{\beta^{2/3}}{N_O - N'} \quad (5.2)$$

Rearranging and substituting for M we obtain:

$$i_D = \frac{1.60knF\nu^{-5/12}D^{2/3}a^{1/2}r^{3/4}V_F^{3/4}\beta^{2/3}C}{N_O - N'} \quad (5.3)$$

where N' is the ratio of the ring to disc current and is the gradient of the analysis lines. Thus we can find the concentration, C, from a plot of i_D against $(N_O - N')^{-1}$. This operation is performed by the LINES 3270 to 4560.

LINES 3270- The various headings and axes are drawn.
3510

LINES 3520- The value of $(N_O - N')^{-1}$ is calculated for each of the
3700
disc currents within the the limits defined by the user;
eg the ring disc current ratio must not exceed 0.0134.

LINES 3710- These points are then plotted on the X/Y plotter.
3790

LINES 3860- Various parameters are calculated, the gradient,
4560
correlation coefficient and the two intercepts which
should be zero; from the gradient the concentration is
determined. These values are printed out as are the disc
current and $(N_O - N')^{-1}$ values. The gradient is also
drawn on the X/Y plotter.

A number of titration programs have been written, each with a varying degree of sophistication and hence greater flexibility. For routine analysis the program can be modified such that all the parameters are built in. The disadvantage of this technique is that it is a batch analysis approach and as we have seen it was considered desirable to develop a continuous mode of analysis and consequently the autotitration technique was developed. However it should be added that the titration technique with microprocessor control can be made continuous since we can readily modify the program to continuously repeat itself. This will have the disadvantage of each analysis taking a considerable amount of time (typically one minute) since a complete titration curve is required, but the concomitant advantage is greater accuracy because a complete titration curve is analyzed, whereas in the autotitration technique only one point on the titration curve is used, although the average of a large number of measurements can be taken.

C The Autotitration Technique

A technique for a fast and continuous on-line analysis for phenols and cresols in water was required and as we have seen the autotitration technique using the wall-jet ring-disc electrode is a potential system for such an operation. As we saw in chapter one an analogue method has been developed in this laboratory (29) whereby the disc current is continually adjusted such that the ratio of ring to disc current remains constant and from the value of the disc current the concentration can be determined knowing the value of their ratio; that is to say we continually move up and down a gradient of the ring-disc current plot depending on the variation in the concentration of

the substrate under analysis. An aim in this project was to effect this approach adopting a digital method using the microprocessor. This was achieved in the following manner.

Initially an arbitrary disc current is generated, a ring current is measured and their ratio calculated. Knowing the theoretical value of the collection efficiency, N_o , calculated from the three electrode radii using the program previously described, we are able to calculate a new disc current such that its value and that of its respective measured ring current will have the desired ratio. This is diagrammatically shown in Figure 5.2. The equation for calculating the new disc current is:

$$I = \frac{(IR - (N_o \cdot ID))}{(G - N_o)} \quad (5.4)$$

where I is the new disc current, ID is the previous disc current, IR is the previously measured ring current and G is the required gradient of analysis. Thus we can readily change the analysis gradient from the program whereas in the analogue method can only be altered by changing two resistors. The optimum value for this gradient is the one which lies at start of the linear region of the titration curve (0.0134 for the electrode used in this work) since it is at this point there is the greatest sensitivity, the value of the ring current has been maximized with respect to the disc current, ie the point at which the reaction boundary just completely covers the ring electrode (see Figure 1.8). For greater values of disc current the percentage difference between the disc and ring current decreases. However it is sometimes necessary, as will be seen later, to have greater values for the analysis gradient.

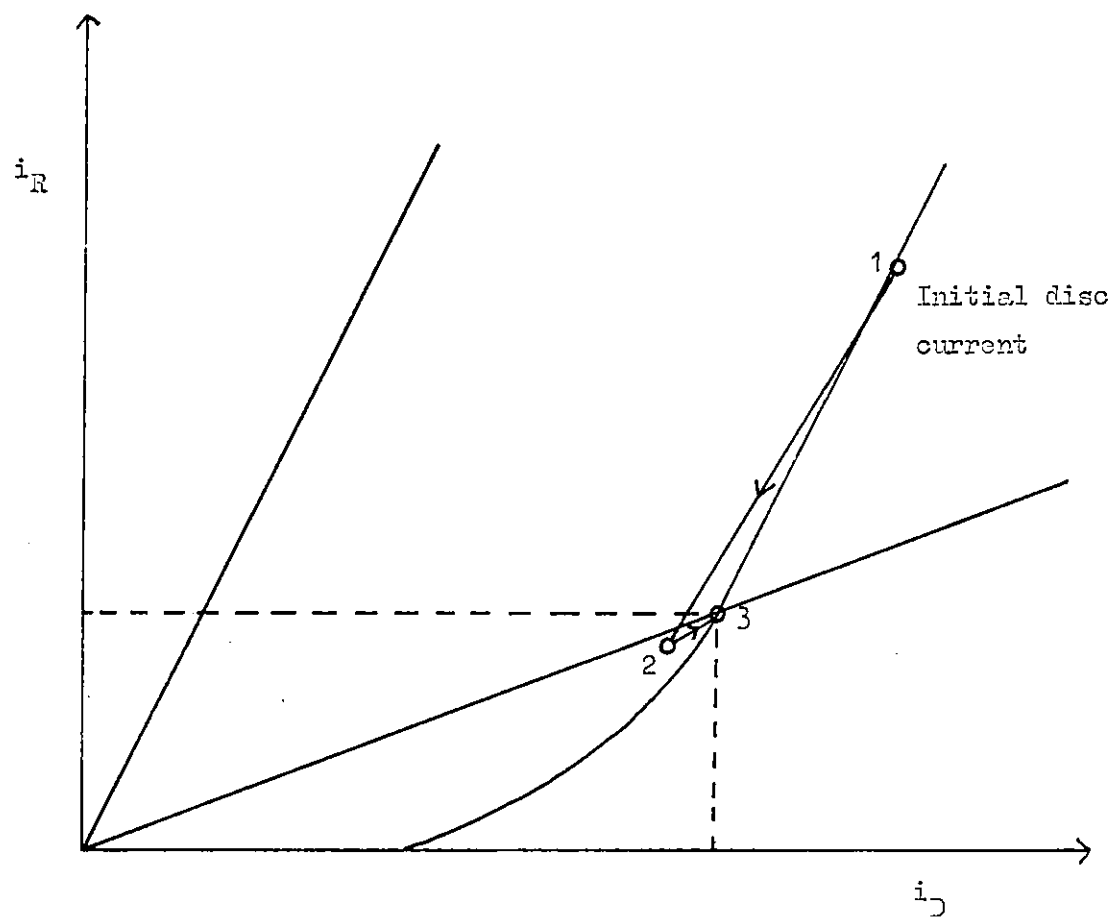


Figure 5.2 The autotitration technique

We are also readily able to change the time interval between each change in disc current and this is important as will be seen later. This compares favourably with the analogue method where a change in time interval is effected by a change in capacitance.

It is also advantageous to be able to determine acceptable limits above and below the desired analysis gradient, eg $0.0134 \pm 1\%$, since the closer to the gradient we set them the longer it will take to determine the appropriate disc current. Any reading we obtain will still be a valid one and we are able to use the data acquired, it is simply that it may not lie on the analysis gradient we have set. Whether or not the time factor is important depends on the desired accuracy and the variation in concentration with time. The faster the latter varies the greater the sampling frequency must be if we are to determine accurately a concentration profile. It is possible to vary the flow rate of the solution passing through the cell but as we will see there are limits to this.

The boards required for the basic autotitration program are the same for the titration experiment, namely the ADC, the DAC, and the timer board. In addition the two graphics boards can be used when a hardcopy of the concentration profile is required. As we saw in chapterthree we can also control the peristaltic pump using another DAC but we had tubing problems and so flow rates were measured manually.

As with the titration experiment a number of autotitration programs were developed according to need and one such one will now be presented. In order to test this technique a program was written (see Appendix A6-4) which analyzed a succession of solutions and the known concentrations were compared with the experimentally determined ones.

(d) A flow diagram for the program AUTOTD can be seen in Figure 5.3.

LINEs 10-400 The system is initialized, the board table is constructed and the headings and axes are drawn.

LINEs 410-790 The various parameters are set: the analysis gradient, the acceptable limits as a percentage of the gradient, the number of concentrations to be tested, the flow rate, the initial disc current, the time interval between each sampling, the number of measurements for each concentration, the temperature and the number of electrons transferred. The collection efficiency must also be given, either the theoretical value or the one previously measured for the system. These values will all be built into the program for the fully automated system; they are then printed out.

LINEs 800-860 The ring current is measured at zero disc current.

LINE 1080 The value of the concentration of the next sample is entered.

LINE 1140 The absolute value of the new disc current is taken since occasionally a negative value for the new disc current is obtained, and it is then outputted from the DAC.

LINE 1160 This statement provides a safeguard such that if the new disc current is greater than 200 μ A the program is aborted.

LINE 1170 The delay before the ring current is generated to allow it to stabilize.

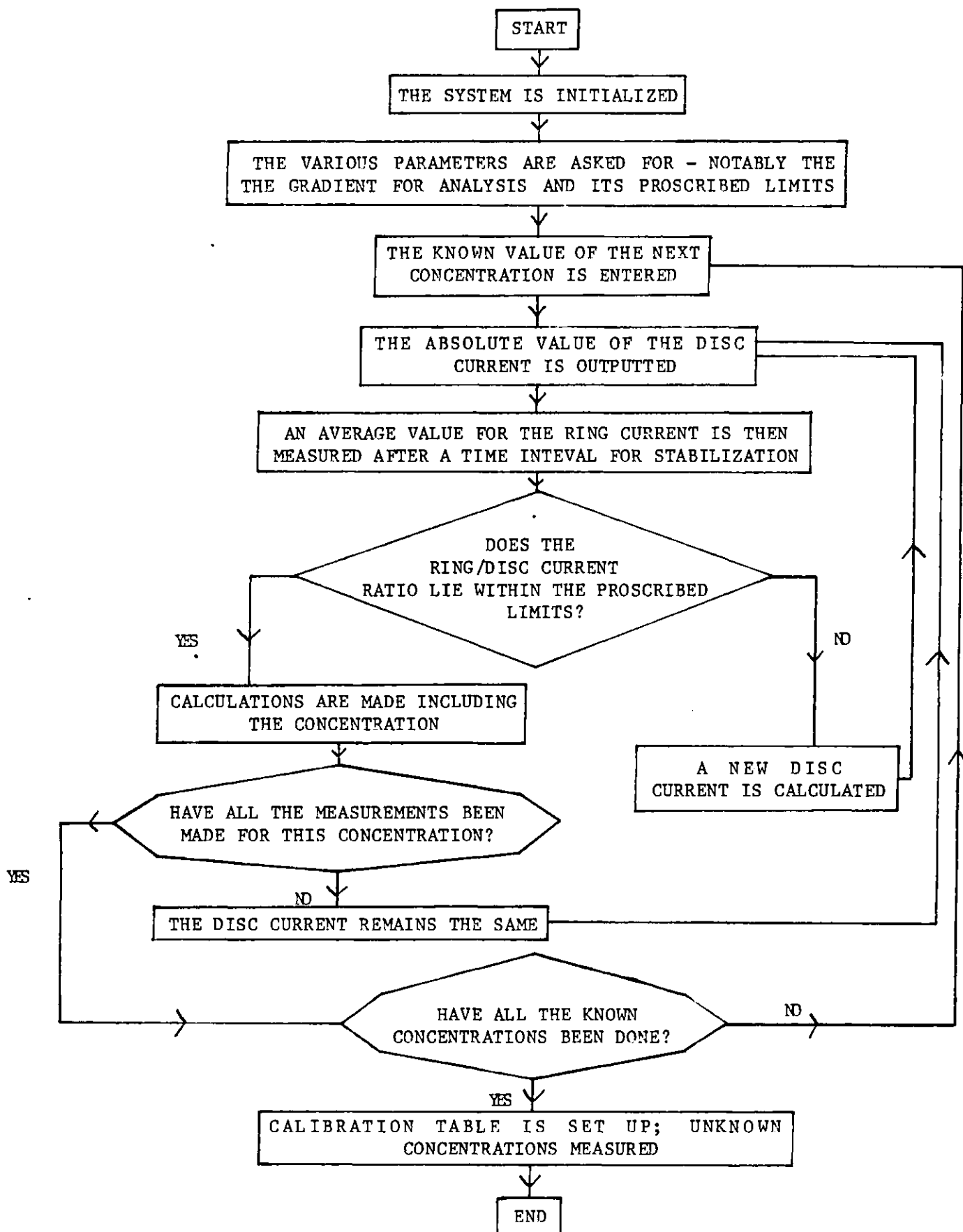


Figure 5.3 Autotitration Flow Diagram

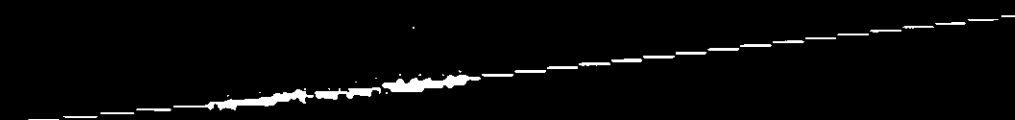
LINES 1180- 200 measurements of the ring current are made and their
1250 mean determined.

LINES 1260- If the ring/disc current ratio falls within the
2520 prescribed limits the point is plotted in the lower half
of the VDU screen in a bright colour and the
concentration is calculated which is then used to build
up concentration profile in the upper half of the VDU
screen - this process can be seen in Photograph 5.1;
this profile is also recorded on the X/Y plotter. The
respective ring and disc currents are printed out, as
are their ratio and calculated concentrations. It should
be noted that in performing the concentration
calculation the value of N' used is the ring/disc
current ratio and not the analysis gradient. When the
prescribed number of measurements of the concentration
have been made their mean is calculated and printed out.
The new disc current remains the same as the previous
one.

If, however, the ring/disc current ratio lies
outside the proscribed limits a new disc current is
calculated (LINE 1630) using equation 5.4 and is
outputted from the DAC board; after the time interval the
ring current is measured - this process is repeated
until the ring/disc current ratio lies within the
prescribed limits. In such a way the concentration of
all the samples is measured.

In addition the respective known and measured
concentrations can be compared by drawing a graph.

CONCENTRATION IS 77.84 UMM



THE NEW DISC CURRENT IS 51.74 μ A

VOLUME FLOW RATE (ml/s)? 0.07

INITIAL DISC CURRENT (μ A)? 80

TIME DELAY BETWEEN EACH SAMPLING (s)? 3

■

Applying linear regression the gradient, correlation coefficient and the two intercepts can be determined. This could be used to establish a calibration curve and the program was written such that solutions of unknown concentration could then be analyzed and their concentrations determined from this curve.

We can see that this program can be readily modified such that a continuous analysis can be performed and a concentration profile recorded for a solution passing through the electrode cell.

D The Rise-Time Experiment

It was felt necessary that we should determine the time it took for the ring current to stabilize since this would determine how quickly we would be able to record titration curves and perform autotitrations. It was hoped that the time taken would be small so as to be able to perform swift analyses.

A program was written to perform this task whereby the disc current is held at a steady value and the ring current is continuously measured. The disc current is then instantaneously stepped to a second value, which can be either higher or lower, while the ring current continues to be measured. The initial ring current measurements are averaged to provide an initial ring current; the final ring current is found from a final set of ring currents. The rise-time is then taken as being the time elapsing between stepping the disc current and for the ring current to reach a certain fraction of the final current, less the initial ring current, in our case $(1 - e^{-1})$. The program (TIME10) for performing this experiment is presented in Appendix A6-5 but it should be noted that some of the routines vary from those

previously given since these experiments were performed using the Mark I interface system whose routines were of a slightly different format. The early titration work was also done on the Mark I interface system but the programs were modified for the Mark II system.

As before the boards required are the DAC, ADC, timer and graphics boards if a hardware copy is required. A schematic diagram of the rise-time curve is given in Figure 5.4.

(e) The Rise-Time Program.

LINES 10-180 The system is initialized, the board table is constructed, the headings and axes are drawn.

LINES 200-280 The initial and final disc currents and the ring potential are asked for; the initial disc current and ring potential are outputted and the system waits for them to stabilize.

LINES 290-310 An array of 1 by 600 has been set up and the first 100 points are given the value of the required disc potential to generate the desired initial disc current. The remaining points are given over to producing the final disc current.

LINES 320-370 Using real time an initial time is noted and the disc potential values are successively applied and immediately the ring current is measured (LINE 350) and, once finished, the time of the completion is noted. By subtracting the initial time, the time required for the 600 points to be scanned can be obtained.

LINES 380-420 The average ring currents for the first and last fifty points are calculated (S1, S2).

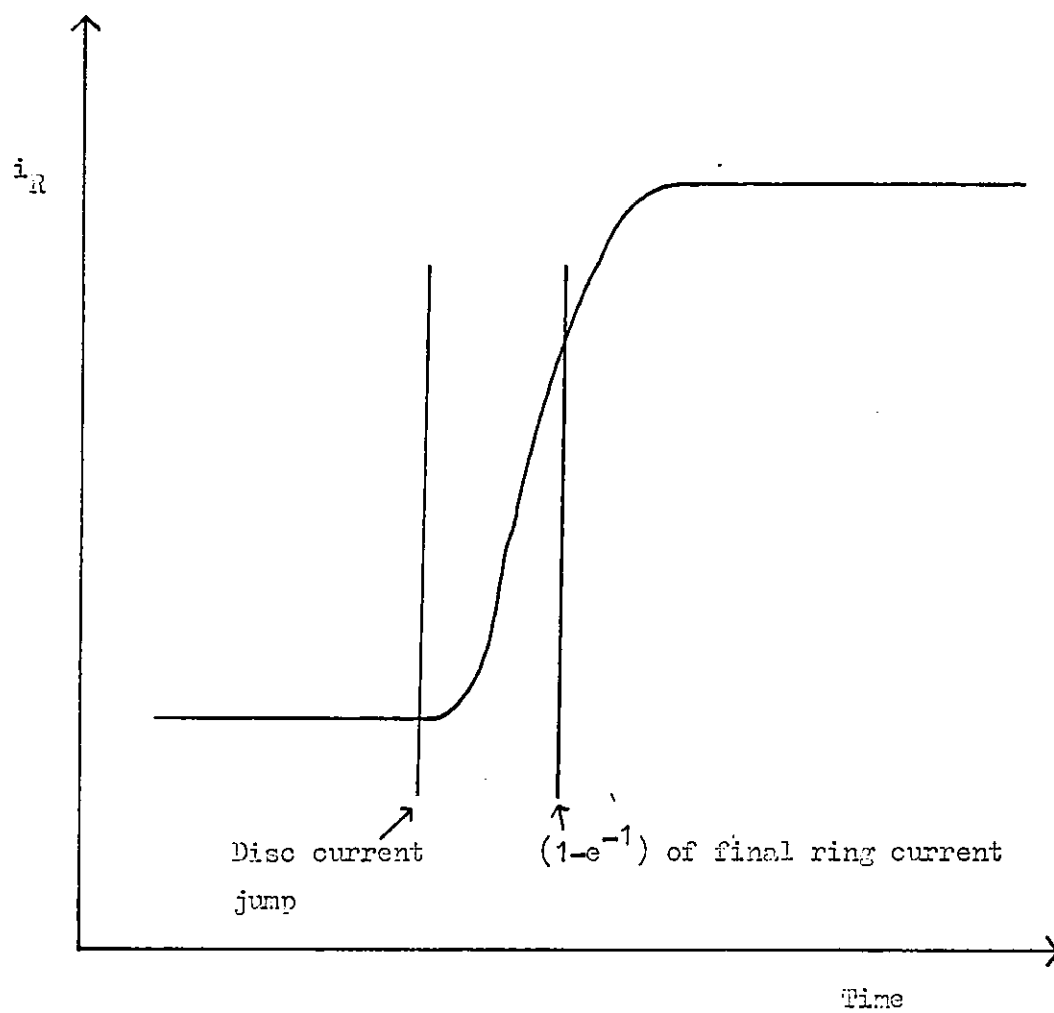


Figure 5.4 A schematic diagram of the rise-time plot

LINES 430- The time taken for the curve to be obtained is converted
640 into seconds; the time lapse from the measurement of the first point to each of the successive ones is determined (LINES 540 to 640) and they, with their respective ring currents, are plotted on the VDU and the X/Y plotter. Also determined is the first point to be in excess of the desired fraction $(1 - e^{-1})$ of the final ring current (LINES 580, 590).

LINES 650- Two lines are drawn, the first indicating the point at
750 which the disc current is stepped, and the second indicating the point where the ring current has reached the required fraction of the final ring current; subtracting these two times (LINES 740, 750) gives us the rise-time.

LINES 760- The rise-time, initial and final disc currents and the
END flow rate are printed out.

We have seen here the main types of programs used but they were variously modified to perform variously defined tasks as required.

Chapter Six

Results and Discussion

A Preamble

Having described the experimental apparatus, both the electrochemical and the microcomputer and interface parts, and having presented in the previous chapter the types of programs developed in this work for performing the various tasks required, we will now turn our attention to the results obtained and the degree to which the system was successful in achieving the desired aims.

Before proceeding to titration curves some initial experiments must be done in order to determine the optimum working conditions for the electrode system and how well the hydrodynamics are obeyed. The particular wall-jet ring-disc electrode used in this work was first used by Brett (27) who performed the following preliminary experiments.

The wall-jet cell had the following dimensions:

$$r_1 = 3499 \pm 2 \mu\text{m}$$

$$r_2 = 3738 \pm 6 \mu\text{m}$$

$$r_3 = 3999 \pm 8 \mu\text{m}$$

leading to:

$$N_o = 0.1155 \quad (\text{equation 2.66})$$

$$\beta^{2/3} = 0.193 \quad (\text{equation 2.64})$$

The nozzle diameter, a , was 0.343 mm.

Deoxygenation was not necessary so the system can be used in the push

mode.

(1) A conclusion arrived at from the theory in chapter two was that electrodes always receive fresh solution from the impinging jet and none from the recirculation of the solution already in the cell. This arises since the theory predicts that velocity component perpendicular to the electrode is directed away from the electrode at the electrode surface for all r . Thus an initial experiment in the verification of the theory would be to determine whether this prediction is correct.

In order to do this a platinum wire was inserted into the cell, such that about 1.5 cm lay along the the back of the cell with the tip just short of the nozzle. A 10 mM $K_4Fe(CN)_6$ solution in 0.4M K_2SO_4 was used since the couple involved ($Fe^{2+}-Fe^{3+}$) is reversible and well-behaved. The wire was potentiostatted at +0.5V vs SCE to generate ferricyanide and the electrode under test was potentiostatted at 0V to as to reverse the reaction should any ferricyanide reach it. The electrode current was measured with varying wire positions and experimental conditions, wire potential ranging from 0.0 to 0.5V, flow rates ranging from 0.015 to 0.125 ml s⁻¹. In all cases the electrode current remained at zero whereas a diffusion limiting current is of the order of 1 mA. Consequently we can conclude that the electrode always receives fresh solution.

(2) Next to be considered is the effect the distance between the nozzle and the electrode wall has on the behaviour of the cell. The theory has assumed an infinite size for the cell volume so that any experiments concerned with the verification of the wall-jet theory should preferably be carried out with the cell volume as large as

possible. However the larger the cell volume the greater the dead space and therefore the greater the response time of the cell and in analytical work we want to have a short a response time as possible. Thus a balance has to be struck between these two.

Using a solution of 3mM $K_4Fe(CN)_6$ in 0.4M K_2SO_4 and a flow rate of 0.091 ml s^{-1} the ring and disc currents were measured as was the collection efficiency, the results can be seen in Figure 6.1. The ring and disc currents reach their limiting values at high separations as expected; the collection efficiency is also maximized at high separation. A value of 5mm (the maximum for this particular cell) for the nozzle-electrode separation would thus be the optimum separation and it was the one used in this work. However if it were important to have a smaller dead space, if, for example, only small amounts of solution were available in an analysis, then a separation of 3.5 mm could be used since these parameters have virtually reached their final values.

By looking at the flow functions and streamlines as seen in Figures 2.2 and 2.3 we can see why this happens and why it is that these parameters are maximized at greater separations for the ring current and collection efficiency than for the disc current. The flow pattern is disrupted at a radial distance corresponding, approximately, to where the boundary layer ($\eta=6$) reaches the back wall of the cell. This layer moves further from the centre of the cell as the separation increases until it will reach the outer layer of the disc or ring electrode at which point the full and predicted limiting current will be reached. This explains why the full value of the ring current and hence collection efficiency are reached at a greater separation than that for the disc. It is therefore the back wall-

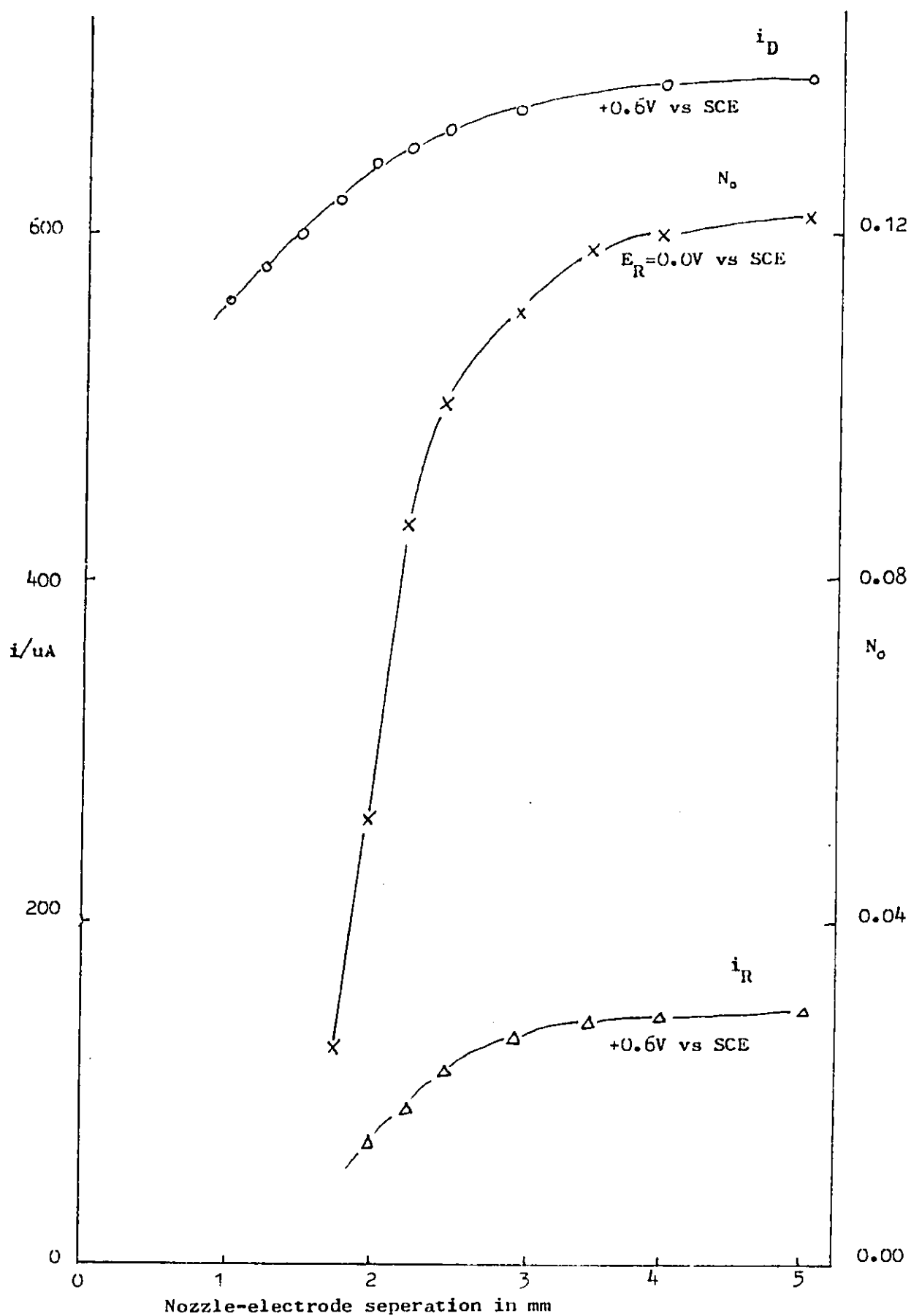


Figure 6.1 The influence of nozzle-electrode separation at the WJRDE

electrode separation that is of importance and not that of the nozzle-electrode separation.

(3) Voltammograms were measured at the ring and disc electrodes at various flow rates for the ferro-ferricyanide system and the bromide-bromine system since the latter is involved in the titration experiment. The limiting currents were plotted against $v_f^{3/4}$ (the Levich plot, see equation 1.14). The positive intercepts obtained suggested that the hydrodynamics are not being perfectly obeyed but good straight lines were obtained. These values were compared with the theoretical ones and it was found that although the disc plots were as expected the ring ones were a little higher which lead to high values of $\beta^{2/3}$. However the results obtained were sufficient to justify using this electrode system in this project.

B The Titration Experiment

(a) Initial investigations

Originally the object was to use the microcomputer and interface rack to provide signals for the modular Oxford box instead of their being produced from ramps and power supplies from within the box as previously practised. An Oxford box was built and tested manually by performing ring and disc voltammograms with the ferro-ferri cyanide system; Levich plots were obtained with good straight lines although, as with Brett, positive intercepts were obtained. The Oxford box was then connected to the microcomputer in an attempt to produce a disc voltammogram; the disc voltage was produced from the DAC board of the interface and a disc current measured by monitoring a voltage over a resistor using a ADC board. A typical disc voltammogram using a standard solution of 3mM $K_4Fe(CN)_6$ is presented in Figure 6.2 where

DISC POLAROGRAPH

11/00/00 ON 6/6/80

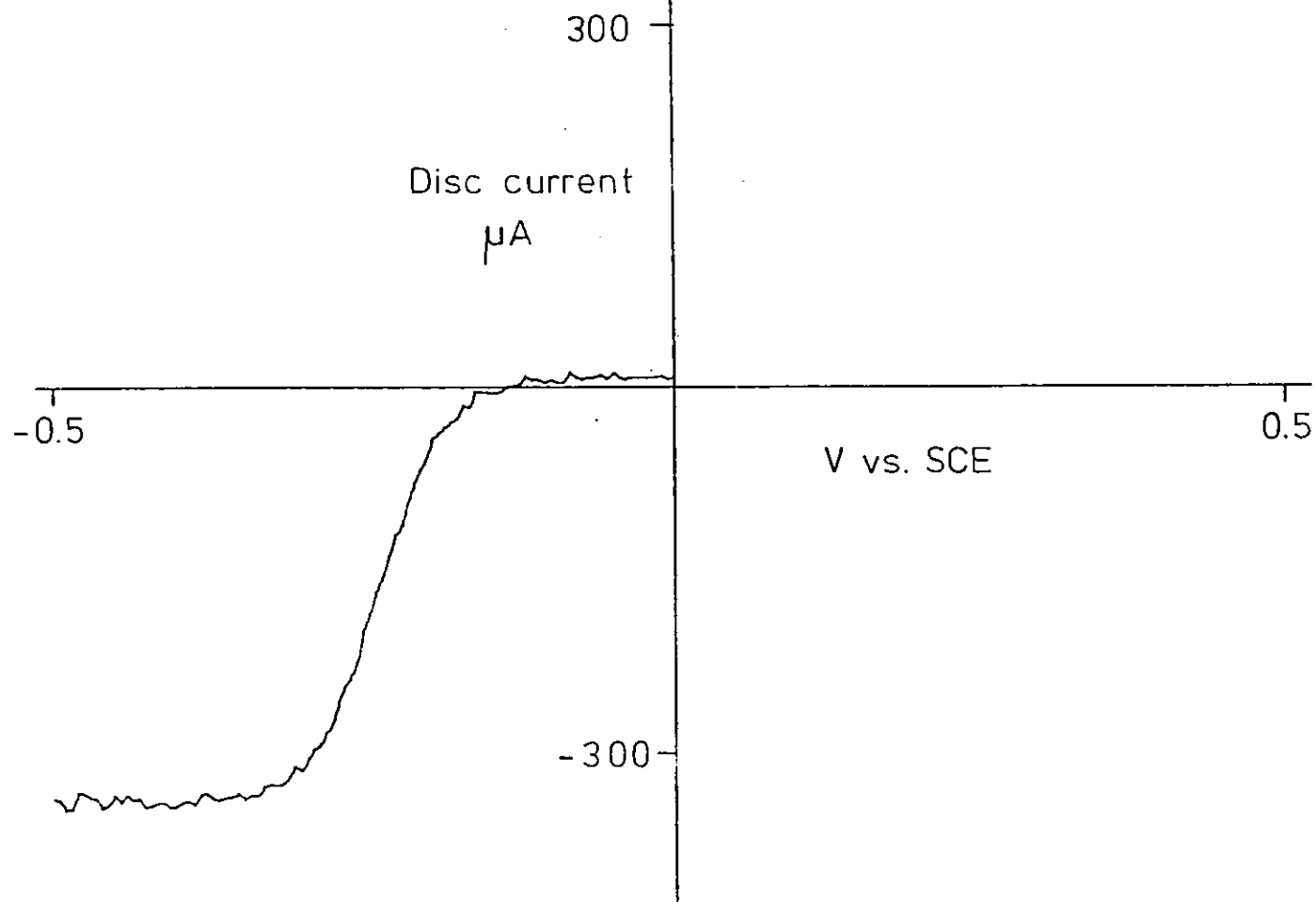


Figure 6.2 A voltammogram obtained and controlled by the microcomputer.

the disc current potential is plotted against the disc current. The rate controlled region and the diffusion controlled region can both be seen. Having successfully recorded voltammograms titration curves could now be attempted.

This experiment requires complicated circuitry which includes the galvanostat, inverter, subtractor, summing inverter and the two voltage followers; a disc current and ring potential need to be provided and a ring current measured - the former two are produced from a DAC board (which has two ports) and the latter is measured by a ADC. However after much time and effort the attempts at obtaining a collection efficiency (which uses exactly the same circuitry as the titration experiment) were abandoned since no satisfactory collection efficiency could be recorded; the Oxford box contains many connections between each of the modules, each introducing a certain amount of noise. In addition there were also problems with earth loops between the Oxford, interface and the computer. It was thus decided that a dedicated titration unit should be built, which has been described in chapter three, to replace the Oxford box which would greatly reduce the number of connections; in addition amplifiers were used which were firmly fixed on a well grounded base.

(b) The collection efficiency

Before titration curves were measured collection efficiency measurements were made in order to see if the system worked, to determine the range of flow rates that can be used and to give an idea of the lower limit of concentration that could be monitored with this system. Before the collection efficiencies were measured the electrodes were cleaned using the program described in chapter five.

A solution of 0.25M KBr in 0.5M H_2SO_4 was made up and four collection efficiencies were measured for each flow rate. The program TITRE34 was used, a ring potential of -0.45V and a maximum disc current of 100 μA . The collection efficiency is calculated from the data, as is the correlation coefficient and the disc and ring current offsets (intercepts) using the equations of linear regression (Appendix 5). Using another program the average of each of these parameters was found as well as the percentage difference between the average value and the maximum value measured (ie $((X_{\text{max}} - X_{\text{av}})/X_{\text{av}}) \cdot 100$) in order to give an idea of the constancy of the values measured. The results obtained are given in Table 6.1 and in Figure 6.3 N_0 has been plotted against the flow rate. We note that the value for N_0 increases with the flow rate from 0.115 at 0.046 ml s^{-1} to 0.130 at 0.172 ml s^{-1} . The theoretical value obtained by the wall-jet theory was 0.1155 and so fairly good agreement is obtained at the lower end of the flow rate range. The correlation coefficient is good although it reaches a maximum at the middle of the flow range at a value of about 0.1 ml s^{-1} . At about this flow rate there also occurred the minimum disc current offset value and a small ring current intercept. In the table are also given the "concentration" values which were obtained by treating the disc current offset as if it were a titration curve. This gives an idea of the lower end of the concentration range that we can monitor and from the figures we can conclude that a concentration of 2uM is a lower working limit for this system. Flow ranges outside these limits, which at the higher end would give a greater disc current offset, become unacceptable either because pulsing from the peristaltic pump becomes too great or because the hydrodynamics are not established or because they have broken down.

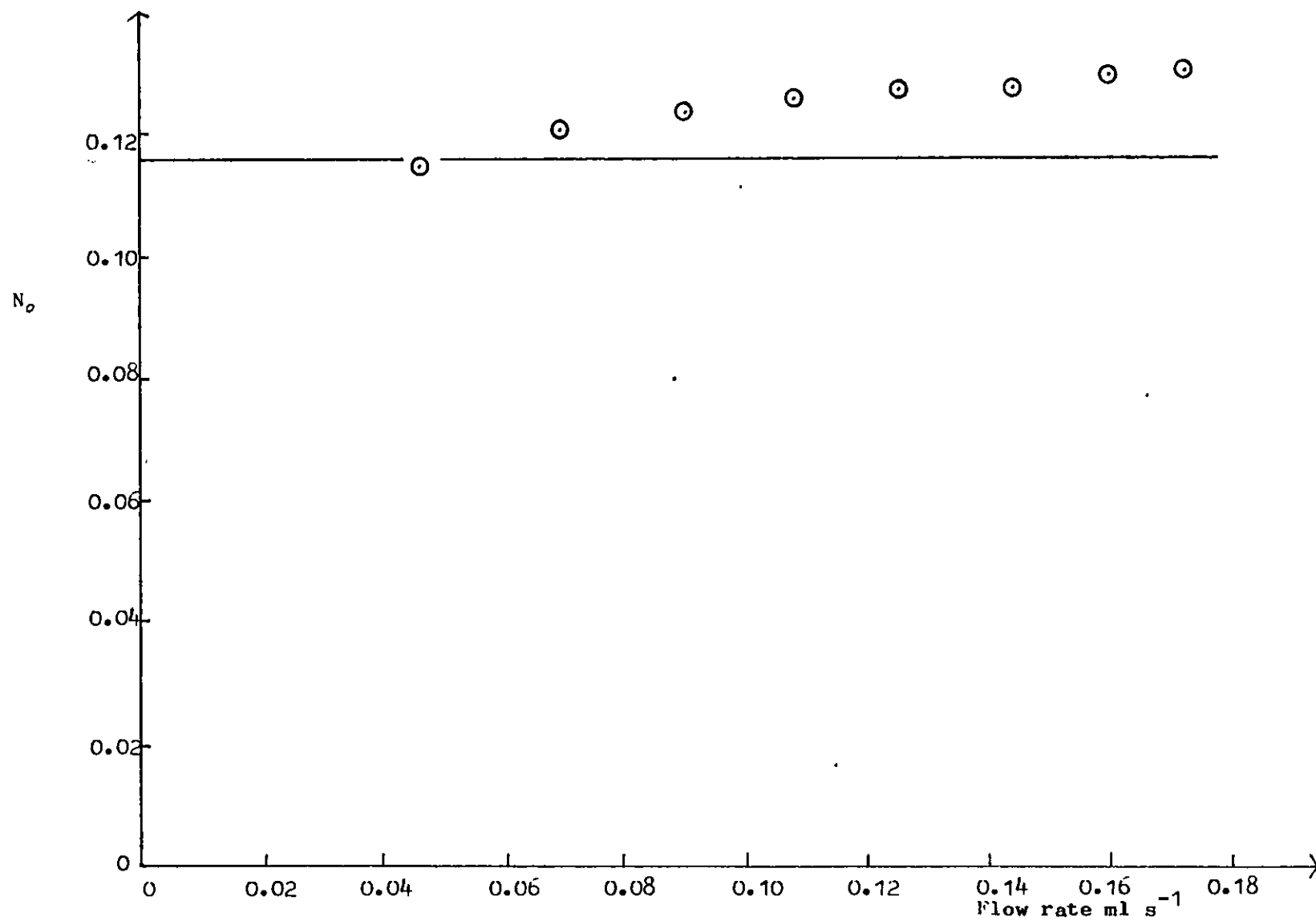
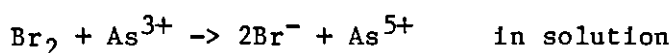


Figure 6.3 The variation in collection efficiency with flow rate.

(c) The titration experiment

The next stage is to perform a series of electrochemical titrations using the same conditions as when measuring N_0 values in the previous section. The arsenic system was the one used since it gives good, well behaved titrations curves. The bromine generated at the disc reacts with As^{3+} ; the unreacted bromine is detected at the ring:



Once more a solution of 0.25M KBr in 0.5M H_2SO_4 was used in which varying amounts of As_2O_3 were added to produce a range of As^{3+} concentrations; TITRE34 was used with the same experimental conditions.

In each run the linear region of the curve is extrapolated back to the disc current axis, as seen on the VDU, and a disc current offset is obtained. This value is used by the program to calculate a value for the concentration using equation 5.1:

$$C = \frac{N_0 \cdot i_D}{1.6 \beta^{2/3} k_n F \nu^{-5/12} D^{2/3} a^{-1/2} r^{3/4} \nu_f^{3/4}} \quad (5.1)$$

where

$$n = 2$$

$$\nu = 0.951 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$$

$$D = 9.80 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1} \quad (\text{temp. coeff.} = 1.5\%/\text{°C}).$$

In each case the temperature was recorded manually. As previously concentrations were measured over a range of flow rates. Average results were calculated from sets of three experiments and the percentage difference between the average and maximum value to

indicate constancy.

A solution containing $58.5\mu\text{M}$ As^{3+} was made up and further solutions were then prepared by quantitatively diluting this original solution. Unfortunately we were not able to prepare stronger solutions since As_2O_3 is very insoluble, but it is the lower limit that is of greater importance. Thus solutions with the following concentrations of As^{3+} were prepared: 58.5, 14.6, 5.85, 2.925 and $1.46\mu\text{M}$. Disc current increments were taken reaching a final value of $100\mu\text{A}$, though with larger concentrations it is better to have a higher final disc current to ensure that a sufficient number of points are collected within the linear region of the plot. As previously mentioned in chapter five the titration curve was collected with a decreasing disc current after being initially quickly ramped to the maximum disc current.

For each flow rate of each concentration the collection efficiency was determined, its deviation from the theoretical value, its correlation coefficient, the disc current offset, the concentration calculated from this offset using the measured collection efficiency and finally the deviation of the concentration from the known value; percentage differences were also calculated. The results are shown in Tables 6.2 to 6.6.

As with the collection efficiency measurements we note that N_o increases with the flow rate and that the correlation remains good. In general the concentration calculated decreases with an increase in the flow rate but in determining this value we have a problem in deciding which value of k to take; Matsuda (15) takes k as 0.86 but $k=1$ gives concentration values in closer agreement with the known concentration.

	Flow rate, mls^{-1}	Collection efficiency	N_o from theory	Correlation in N_o	Disc current offset (μA)	"Concentration" with $k=1$, (μM)	"Concentration" with $k=0.86$, (μM)
3	0.046	$0.114 \pm 0.66\%$	-0.8%	0.9988	$-1.88 \pm 67\%$	$-4.6 \pm 66\%$	-5.4
4	0.070	$0.121 \pm 1.18\%$	+4.5%	0.9999	$-0.84 \pm 20\%$	$-1.6 \pm 20\%$	-1.9
5	0.090	$0.124 \pm 0.70\%$	+7.3%	0.9998	$-0.27 \pm 173\%$	$-0.4 \pm 174\%$	-0.5
6	0.108	$0.126 \pm 0.35\%$	+9.1%	0.9999	$+0.31 \pm 92\%$	$+0.4 \pm 92\%$	+0.5
7	0.125	$0.127 \pm 0.45\%$	+10.2%	0.9998	$+0.67 \pm 46\%$	$+0.9 \pm 46\%$	+1.1
8	0.145	$0.128 \pm 0.37\%$	+10.6%	0.9999	$+0.29 \pm 26\%$	$+0.3 \pm 26\%$	+0.4
9	0.160	$0.130 \pm 0.13\%$	+12.4%	0.9999	$+0.54 \pm 53\%$	$+0.6 \pm 53\%$	+0.7
10	0.172	$0.130 \pm 0.75\%$	+12.8%	0.9997	$+0.63 \pm 47\%$	$+0.7 \pm 48\%$	+0.8

Table 6.1 Collection efficiencies measured in 0.25M KBr and 0.5M H_2SO_4 .

	Flow rate, mls ⁻¹	Collection efficiency	N _O from theory	Correlation in N _O	Disc current offset (μA)	Concentration with k=1, (μM)	Dev. from true conc.	Concentration with k=0.86, (μM)	Dev. from true conc.
3	0.049	0.107 ± 1.42%	-7.76%	0.9979	27.6 ± 1.76%	60.9 ± 3.20%	+4.02%	70.76	+21.0%
4	0.068	0.110 ± 1.18%	-4.53%	0.9998	33.6 ± 2.78%	59.6 ± 3.98%	+1.90%	69.31	+18.5%
5	0.089	0.113 ± 0.84%	-2.34%	0.9996	39.8 ± 1.31%	59.0 ± 2.15%	+0.84%	68.59	+17.3%
6	0.107	0.112 ± 0.59%	-2.72%	0.9997	44.5 ± 0.03%	57.3 ± 0.59%	-1.99%	66.67	+14.0%
7	0.126	0.112 ± 0.79%	-3.12%	0.9998	48.9 ± 0.37%	55.6 ± 0.99%	-5.02%	64.62	+10.5%
8	0.144	0.112 ± 0.18%	-3.33%	0.9995	53.1 ± 0.81%	54.4 ± 0.99%	-7.03%	63.24	+8.1%
9	0.164	0.112 ± 1.70%	-3.40%	0.9998	57.0 ± 0.53%	53.0 ± 2.23%	-9.46%	61.58	+5.3%
10	0.179	0.113 ± 1.21%	-2.09%	0.9997	59.8 ± 0.92%	52.8 ± 1.86%	-9.78%	61.327	+4.9%

Table 6.2 Titration curves using 58.5 μM As³⁺.

	Flow rate, mls ⁻¹	Collection efficiency	N _O from theory	Correlation in N _O	Disc current offset (μA)	Concentration with k=1, (μM)	Dev. from true conc.	Concentration with k=0.86, (μM)	Dev. from true conc.
3	0.048	0.109 ± 1.06%	-5.90%	0.9991	6.14 ± 4.48%	14.0 ± 4.05%	-4.23%	16.3	+11.3%
4	0.070	0.119 ± 0.20%	+2.72%	0.9999	8.15 ± 1.58%	15.0 ± 1.42%	+2.50%	17.4	+19.2%
5	0.091	0.117 ± 0.30%	+1.62%	0.9999	9.40 ± 0.53%	14.3 ± 0.37%	-2.27%	16.6	+13.7%
6	0.111	0.119 ± 0.14%	+2.72%	0.9999	10.6 ± 1.11%	14.0 ± 1.05%	-4.00%	16.3	+11.7%
7	0.127	0.119 ± 0.47%	+3.03%	0.9999	11.3 ± 3.73%	13.6 ± 3.58%	-7.05%	15.8	+8.1%
8	0.150	0.121 ± 0.10%	+4.57%	0.9999	13.0 ± 0.37%	14.0 ± 0.17%	-4.40%	16.2	+11.2%
9	0.170	0.121 ± 0.60%	+4.96%	0.9999	13.8 ± 1.37%	13.6 ± 1.97%	-7.21%	15.8	+7.9%
10	0.182	0.122 ± 0.14%	+5.84%	1.0000	14.7 ± 0.76%	13.8 ± 0.89%	-5.31%	16.1	+10.2%

Table 6.3 Titration curves using 14.6 μM As³⁺.

	Flow rate, mls ⁻¹	Collection efficiency	N _o from theory	Correlation in N _o	Disc current offset (μA)	Concentration with k=1, (μM)	Dev. from true conc.	Concentration with k=0.86, (μM)	Dev. from true conc.
3	0.049	0.113 ± 0.80%	-2.1%	0.9992	2.10 ± 17.3%	4.90 ± 18.21%	-16.2%	5.70	- 2.6%
4	0.070	0.120 ± 0.96%	+3.6%	0.9998	2.85 ± 12.8%	5.36 ± 13.76%	-8.4%	6.23	+6.6%
5	0.093	0.123 ± 0.28%	+6.6%	0.9998	3.74 ± 7.7%	5.89 ± 7.94%	+0.7%	6.85	+17.1%
6	0.112	0.125 ± 0.35%	+8.5%	0.9999	4.36 ± 4.4%	6.06 ± 4.36%	+3.6%	7.05	+20.4%
7	0.132	0.127 ± 0.25%	+10.2%	0.9999	4.91 ± 2.2%	6.12 ± 2.22%	+4.6%	7.12	+21.7%
8	0.150	0.129 ± 0.54%	+11.7%	0.9999	4.73 ± 2.1%	5.42 ± 2.65%	-7.3%	6.31	+7.8%
9	0.170	0.131 ± 0.40%	+13.2%	0.9999	5.73 ± 3.7%	6.07 ± 4.08%	+3.8%	7.06	+20.7%
10	0.185	0.132 ± 0.27%	+14.4%	0.9999	6.27 ± 0.9%	6.29 ± 1.40%	+7.6%	7.32	+25.1%

Table 6.4 Titration curves using 5.85 μM As³⁺.

	Flow rate, mls ⁻¹	Collection efficiency	N _o from theory	Correlation in N _o	Disc current offset (μA)	Concentration with k=1, (μM)	Dev. from true conc.	Concentration with k=0.86, (μM)	Dev. from true conc.
3	0.049	0.111 ± 0.51%	-3.90%	0.9994	1.21 ± 4.36%	2.76 ± 4.21%	-5.8%	3.21	+9.6%
4	0.072	0.118 ± 0.27%	+2.18%	1.0000	1.34 ± 9.63%	2.44 ± 9.24%	-16.5%	2.84	-2.9%
5	0.093	0.118 ± 0.71%	+2.27%	0.9999	1.70 ± 6.96%	2.56 ± 6.65%	-12.6%	2.97	+1.7%
6	0.111	0.119 ± 0.16%	+3.31%	0.9999	1.89 ± 2.97%	2.51 ± 3.06%	-14.3%	2.92	-0.3%
7	0.132	0.121 ± 0.27%	+4.50%	1.0000	2.38 ± 4.23%	2.82 ± 4.08%	-3.7%	3.27	+12.0%
8	0.149	0.122 ± 0.20%	+5.28%	1.0000	2.53 ± 3.37%	2.75 ± 3.58%	-6.1%	3.19	+9.2%
9	0.171	0.123 ± 0.32%	+6.22%	1.0000	2.87 ± 2.03%	2.84 ± 2.22%	-3.0%	3.30	+12.8%
10	0.186	0.123 ± 0.44%	+6.62%	0.9999	3.10 ± 2.71%	2.89 ± 3.16%	-1.3%	3.36	+14.8%

Table 6.5 Titration curves using 2.925 μM As³⁺.

	Flow rate, mls ⁻¹	Collection efficiency	N _O from theory	Correlation in N _O	Disc current offset (μA)	Concentration with k=1, (μM)	Dev. from true conc.	Concentration with k=0.86, (μM)	Dev. from true conc.
3	0.048	0.110 ± 1.18%	-4.85%	0.9992	0.83 ± 14.3%	1.93 ± 14.0%	+31.9%	2.24	+53.5%
4	0.071	0.012 ± 0.93%	-0.51%	1.0000	0.61 ± 38.4%	1.09 ± 37.9%	-25.5%	1.26	-13.4%
5	0.091	0.118 ± 0.23%	+1.98%	0.9999	1.13 ± 23.9%	1.72 ± 24.0%	+17.9%	2.00	+37.2%
6	0.111	0.119 ± 0.19%	+3.12%	0.9999	1.31 ± 18.7%	1.73 ± 18.9%	+18.7%	2.02	+38.0%
7	0.130	0.120 ± 0.09%	+3.93%	0.9999	1.31 ± 16.3%	1.56 ± 16.3%	+7.0%	1.82	+24.4%
8	0.147	0.121 ± 0.32%	+4.69%	0.9999	1.47 ± 19.7%	1.61 ± 19.3%	+10.2%	1.87	+28.2%
9	0.167	0.122 ± 0.20%	+5.75%	1.0000	1.56 ± 20.6%	1.56 ± 20.8%	+7.1%	1.82	+24.6%
10	0.182	0.123 ± 0.10%	+6.42%	1.0000	1.67 ± 17.3%	1.59 ± 17.4%	+8.6%	1.84	+26.2%

Table 6.6 Titration curves using 1.46 μM As³⁺.

The percentage differences become more consistent at higher flow rates since higher disc currents will be recorded corresponding to the $v_f^{3/4}$ disc current offset dependency.

For analytical purposes we can obviate this problem by calibrating known concentrations against the measured disc current offset. We can do this by plotting the disc current offset against $v_f^{3/4}$ for each concentration and then plotting the $(\text{gradient})^{-1}$ of these graphs against the concentration. In Table 6.7 are given the gradients, correlation coefficients, intercepts and disc current offsets for these plots at various concentrations and in Table 6.8 the requisite parameters for the graph of concentration of arsenic against $(\text{gradient})^{-1}$; this graph can be seen in Figure 6.4. Both intercepts are about 1% of the maximum value and the correlation coefficient is 0.99988. Alternatively we can simply plot the concentration against the disc current offset for a given flow rate; such a plot is given in Figure 6.5 at a flow rate of 0.1 ml s^{-1} .

From these results we see that the relationship between the disc current offset and the flow rate is in good agreement with the wall-jet theory, ie there is a $v_f^{3/4}$ dependency on the disc current offset, though the value of concentration derived depends on the value of k that is chosen.

In addition we have seen that the system, both the hardware and the software, is capable of controlling these electroanalytical experiments and of producing reliable results. The program could be modified to record disc current offsets at various known concentrations and build up a calibration curve in memory; disc current offsets could then be measured for unknown concentrations and

Conc. (μM)	Gradient	Correlation	X-intercept	Y-intercept
58.5	$5.3 \cdot 10^{-3}$	0.9991	8.57	-0.045
14.6	0.021	0.9987	1.44	-0.030
5.85	0.044	0.9875	-0.23	0.010
2.93	0.088	0.9903	-0.16	0.014
1.46	0.157	0.9330	-0.03	0.005

Table 6.7 The results from plotting disc current offsets
against $V_f^{3/4}$ for various As^{3+} concentrations

Conc. (μM)	Gradient	(Gradient) $^{-1}$
58.5	0.00529	189.1
14.6	0.02112	47.4
5.85	0.04403	22.7
2.92	0.08825	11.3
1.46	0.15676	6.4

$$\text{Gradient} = 3.20$$

$$\text{Correlation} = 0.9999$$

$$\text{X-intercept} = -0.681$$

$$\text{Y-intercept} = 2.17$$

Table 6.8 The results from plotting the arsenic concentration
against the reciprocal of the gradients of disc
current offset against (flow rate) $^{3/4}$

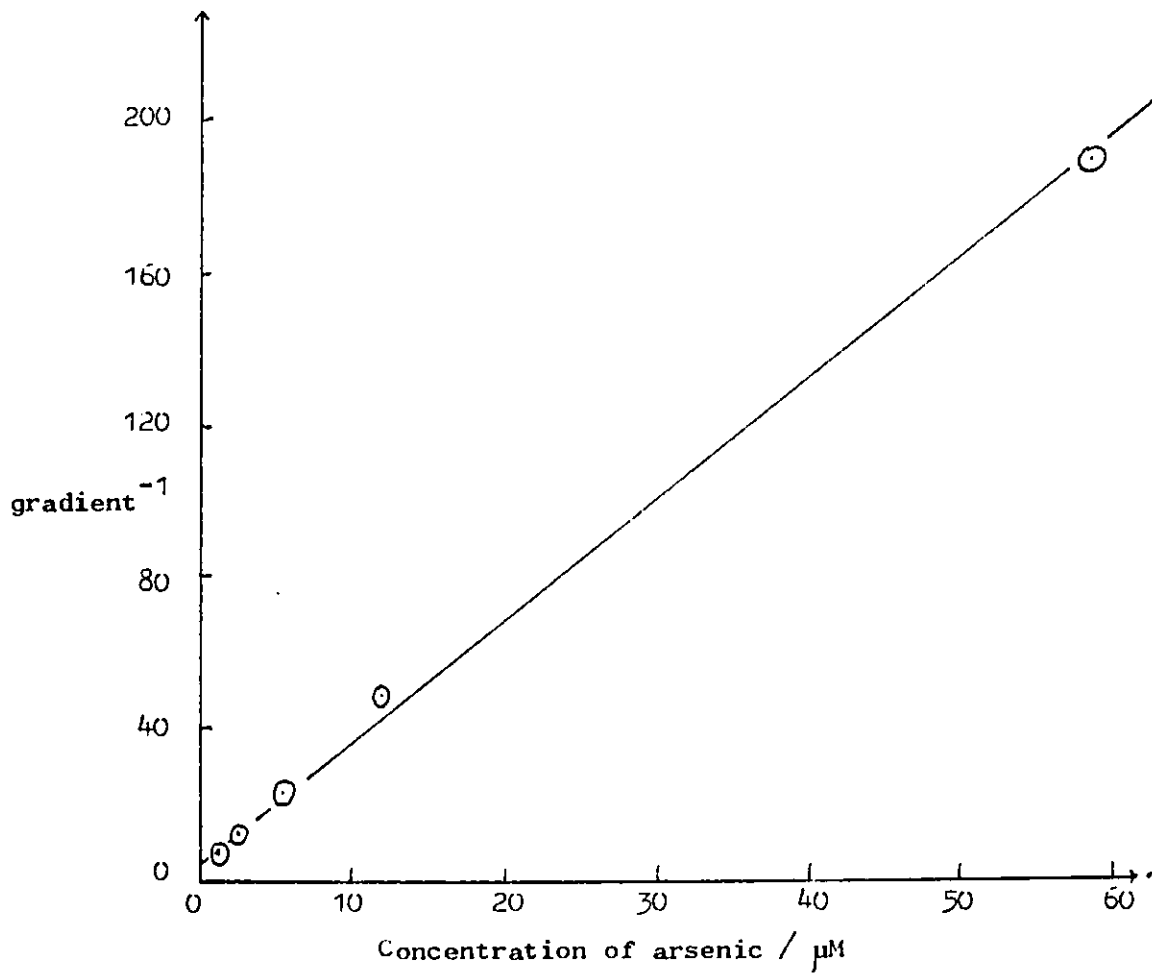


Figure 6.4 Plot of As^{3+} concentration against gradient⁻¹

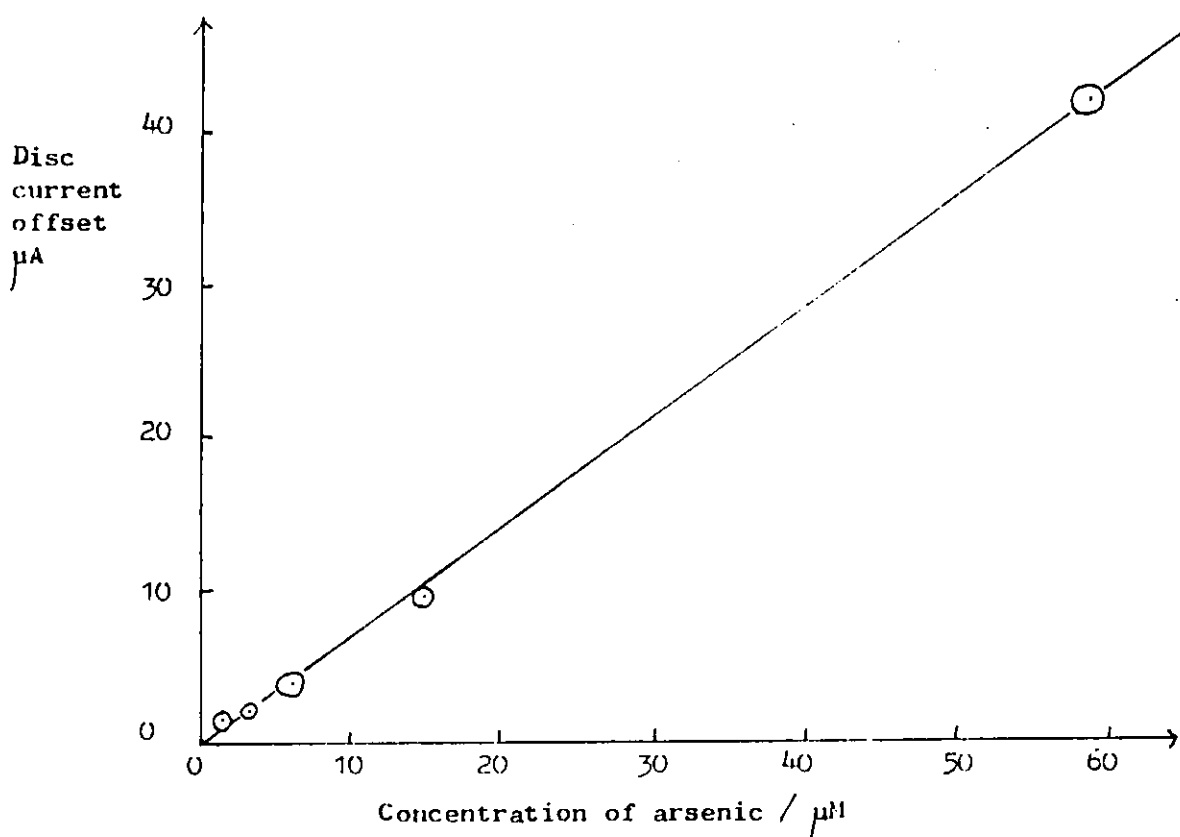


Figure 6.5 Plot of As^{3+} concentration against i_D at a flow rate of 0.1 ml s^{-1}

their concentration values determined.

C The Response Time at the Ring

The automation of the titration technique had now been achieved but the aim was to develop an on-line continuous analysis technique whereas the titration technique is essentially a batch analysis technique. As previously mentioned the latter can be made to be continuous by having the program continually repeat itself but it is a time consuming process since a whole titration curve must be recorded, taking, typically, one minute, although for this reason greater accuracy should result.

However when time is a constraint, such as analyzing the elutant from a liquid chromatograph, we must be able to measure concentrations more quickly and to do this the autotitration technique was developed. However before doing this it was felt necessary to measure the ring response to changes in the disc current. Ideally we should like any changes in the ring current to be instantaneous such that if we were to increase the disc current we would wish to see zero time elapse before the ring current changes. In practice this does not occur and it was decided to investigate this time lag and the factors which influenced it.

In order to do this the rise time program was developed as discussed in chapter five where rise times could be measured for various changes in the disc current. The flexibility of the program made it possible to alter the disc current in various ways. In all cases a standard solution of 0.25M KBr in 0.5M H_2SO_4 was used; the disc oxidizes the bromide to bromine and the ring reduces the bromine back to the bromide. Thus the time is being determined between jumping

the disc current and the establishing of the new ring current. The shorter the time taken the more quickly we will be able to perform the autotitration.

Two sets of experiment were done; in all cases the disc current is held at an initial value and the ring electrode is potentiostatted at -0.45V and a ring current is continuously measured. The disc current is then stepped, the change in ring current is measured and the rise time constant is determined (the time taken to arrive at $(1 - 1/e)$ of the final value). The first vertical line on the plot of time against ring current is the point at which the disc current was stepped and the second indicates the rise time constant.

(1) Experiments were done in which the disc current was stepped by varying amounts from a variety of initial currents and in both directions.

(2) Experiments were done in order to determine the dependency of the rise times on the flow rate.

(1) In this category the following experiments were performed:

(a) stepping the disc current from $0\mu\text{A}$ to a final value ranging from 10 to $80\mu\text{A}$; see Table 6.9 and Figure 6.6.

(b) stepping the disc current from an initial current varying from 80 to $10\mu\text{A}$ to a final value of $0\mu\text{A}$; Table 6.10 and Figure 6.7.

(c) stepping the disc current downwards in $5\mu\text{A}$ intervals; see Table 6.11 and Figure 6.8.

In experiments (a) and (b) we see that the rise times remain fairly constant, i.e. they are independent of the disc current jump, and that they are approximately the same in both the anodic and cathodic directions; from the figures we can conclude that allowing 2s for the ring current to stabilize will be sufficient for all changes in the

Final current (μA)	Rise time(s)	Final current (μA)	Rise time(s)
80	0.853	30	0.894
70	0.873	20	0.830
60	0.649	10	0.911
50	0.854	5	1.44
40	0.874		

Table 6.9 Rise times - stepping the disc current from 0 μA to varying final disc current values

Initial current (μA)	Rise time(s)	Initial current (μA)	Rise time(s)
10	0.824	50	0.704
20	0.704	60	0.785
30	0.744	70	0.744
40	0.725	80	0.744

Table 6.10 Rise times - stepping the disc current from varying initial values to 0 μA

Initial current (μA)	Final current (μA)	Rise time (s)
85	80	0.366
75	70	0.331
65	60	0.366
55	50	0.366
45	40	0.570
35	30	0.639
25	20	0.283
15	10	0.406
5	0	0.483

Table 6.11 Rise times - stepping the disc current downwards in 5 μA increments

Flow rate (mls^{-1})	Rise time (s)	Flow rate (mls^{-1})	Rise time (s)
0.022	3.517	0.116	0.426
0.047	1.339	0.119	0.365
0.068	0.873	0.152	0.345
0.089	0.629	0.157	0.243
0.106	0.487		

When plotting rise time against $(\text{flow rate})^{-1}$:

Gradient = 0.083 X-intercept = 3.65
Correlation = 0.9985 Y-intercept = -0.30

Table 6.12 Rise times - stepping the disc current from 0 to 80 μA at varying flow rates

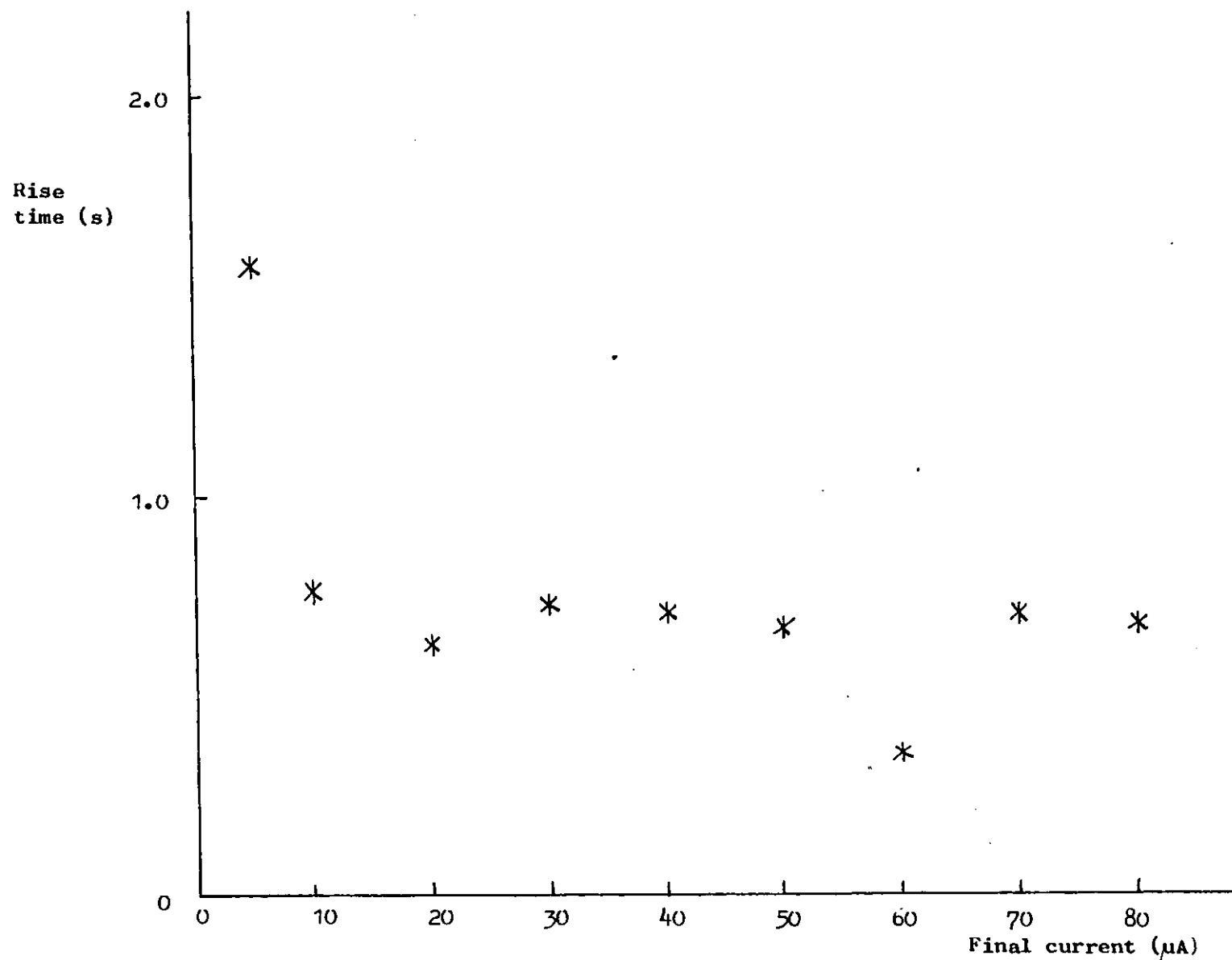


Figure 6.6 Rise times - stepping the disc current from 0 μA to a range of final values.

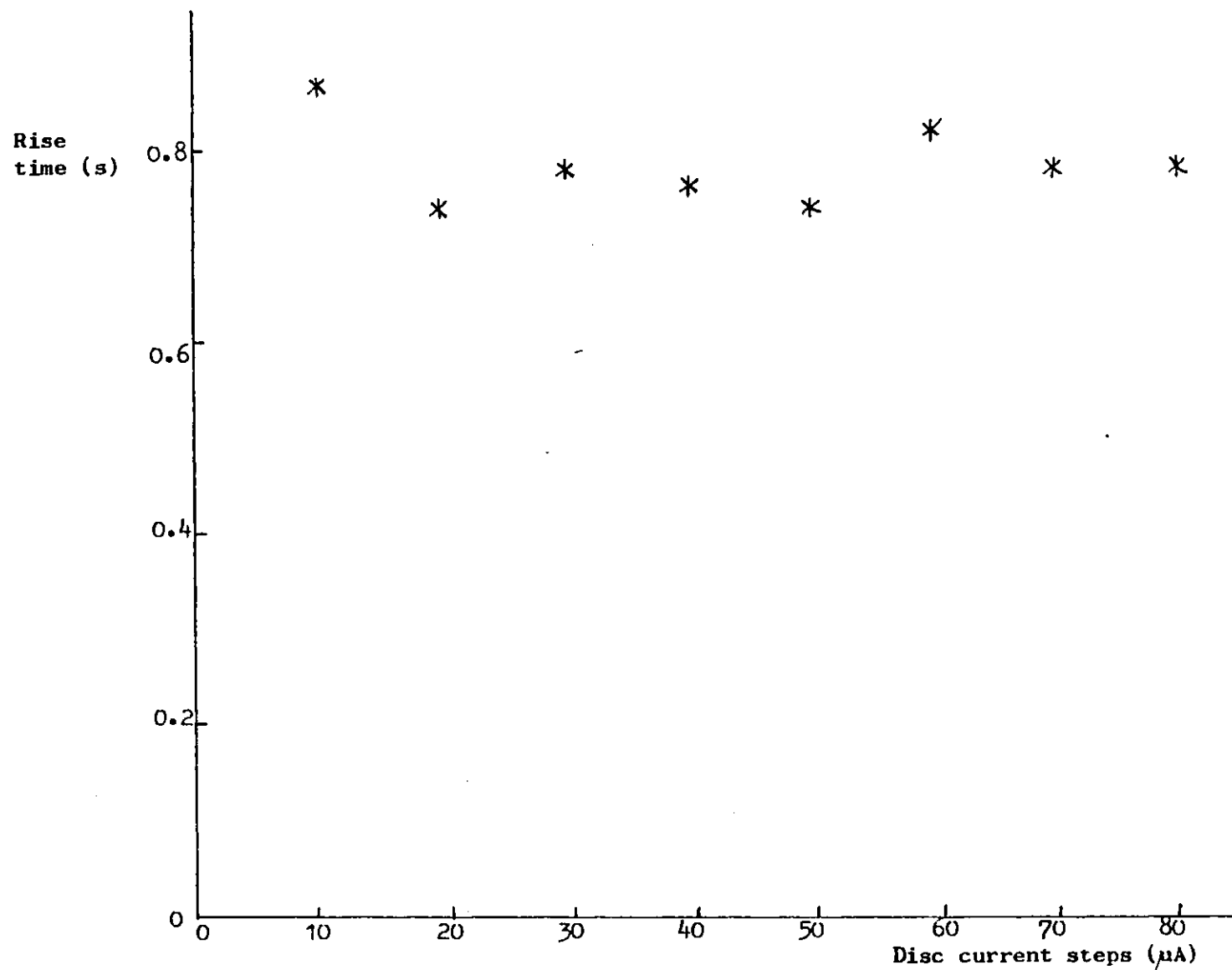


Figure 6.7 Rise times - stepping the disc current to 0 μA from a range of initial disc currents.

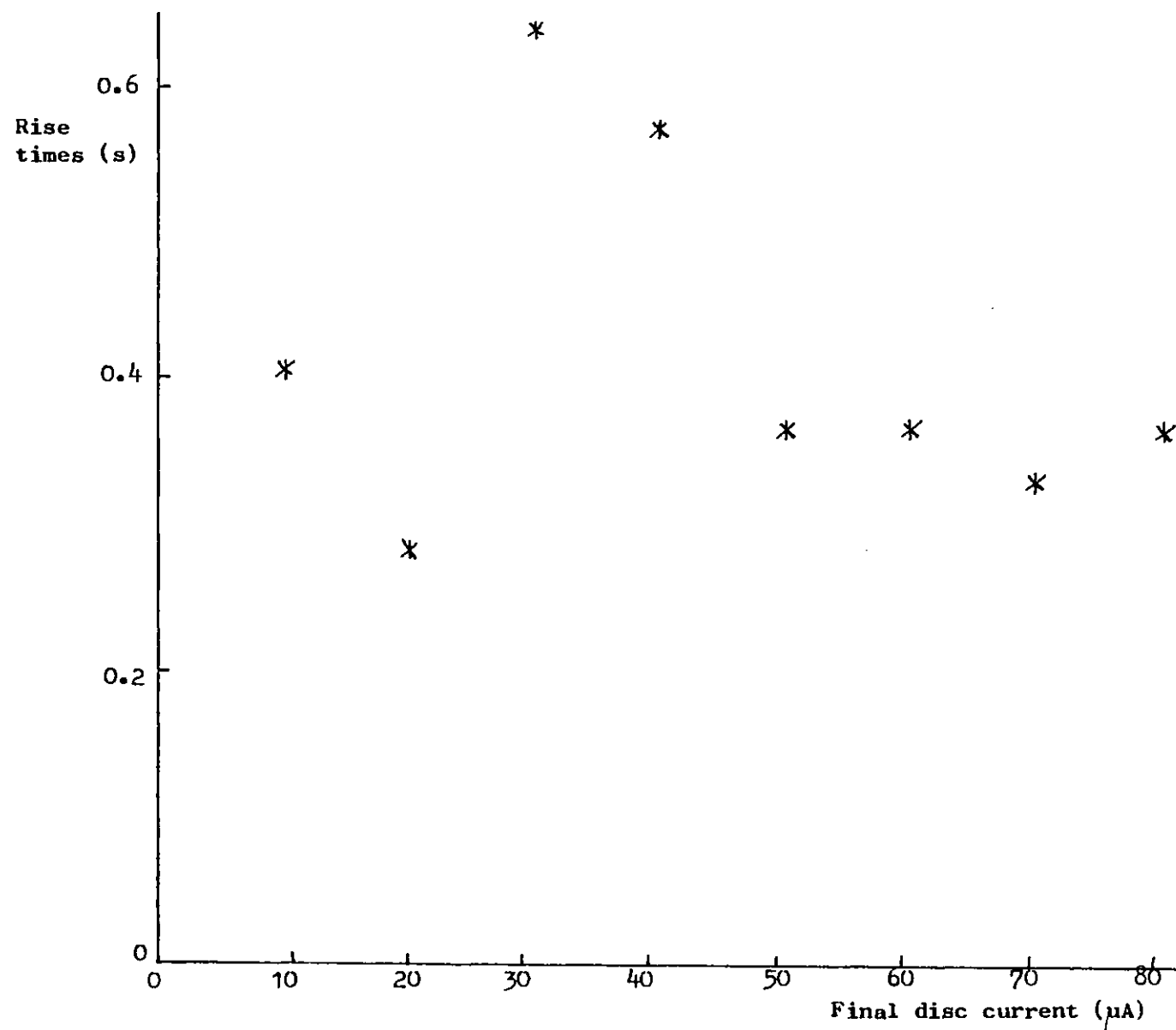


Figure 6.8 Rise times - stepping the disc current downwards in $5\ \mu\text{A}$ increments.

disc current. The importance of this will be seen when we discuss the autotitration experiments.

Similarly experiment (c) shows that waiting 2s before making each new ring current measurement in the titration experiment is sufficient time for the ring current to stabilize.

(2) In this category the disc current was stepped from 0 to 80 μ A at varying flow rates, ranging from 0.022 to 0.157 ml s⁻¹; see Table 6.12 and Figure 6.9. In Figures 6.10 to 6.12, as examples, are some of the hardcopies of the rise time plots as obtained on the X-Y plotter. These rise times were then plotted against the reciprocal of the flow rate as shown in Figure 6.13 and we note a reasonably straight line is obtained (correlation coefficient = 0.9985) and a strong dependency of the rise time on the flow rate. This we would expect since the faster the flow rate the more quickly the solution will travel from the disc current to the ring current, ie higher flow rates will favour quicker analyses. In each case we also note that there is a small time lapse between the disc current being stepped and the there being any change in the ring current. This corresponds to the generated bromine passing across the insulating gap between the disc and ring electrode. Thus in designing a new cell for a fast autotitration system it would be expedient to minimize this gap.

From these rise time results we see that it is important when developing the autotitration technique to ensure that we allow enough time for the ring current to stabilize before measuring it. This factor will be the one to determine the rate at which we will be able to record autotitrations though we have seen that we are able to minimize it. This innate time constraint also means that we are able to do the programming in BASIC rather than the much faster assembly

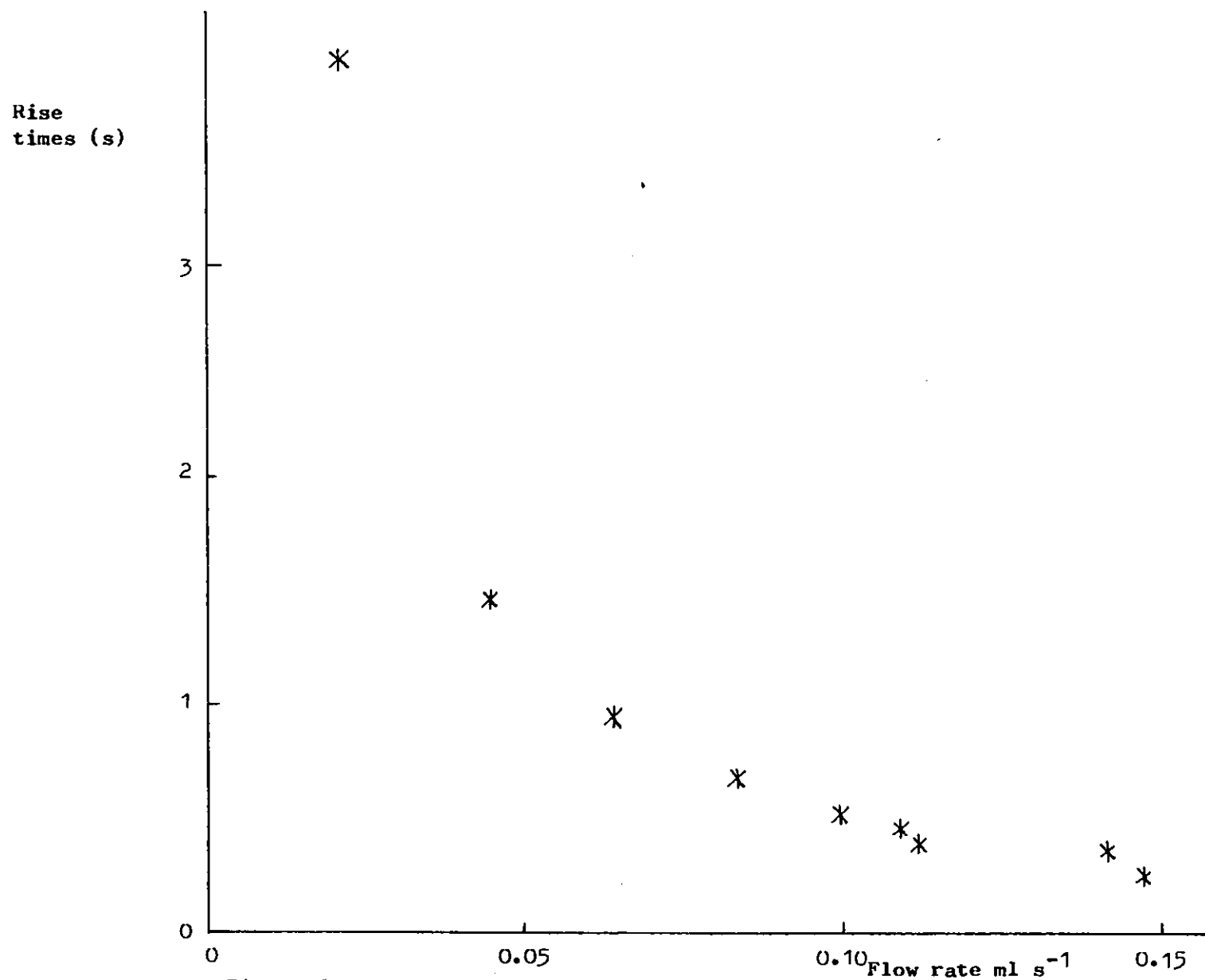


Figure 6.9 Rise times - the variation of rise time with flow rate.

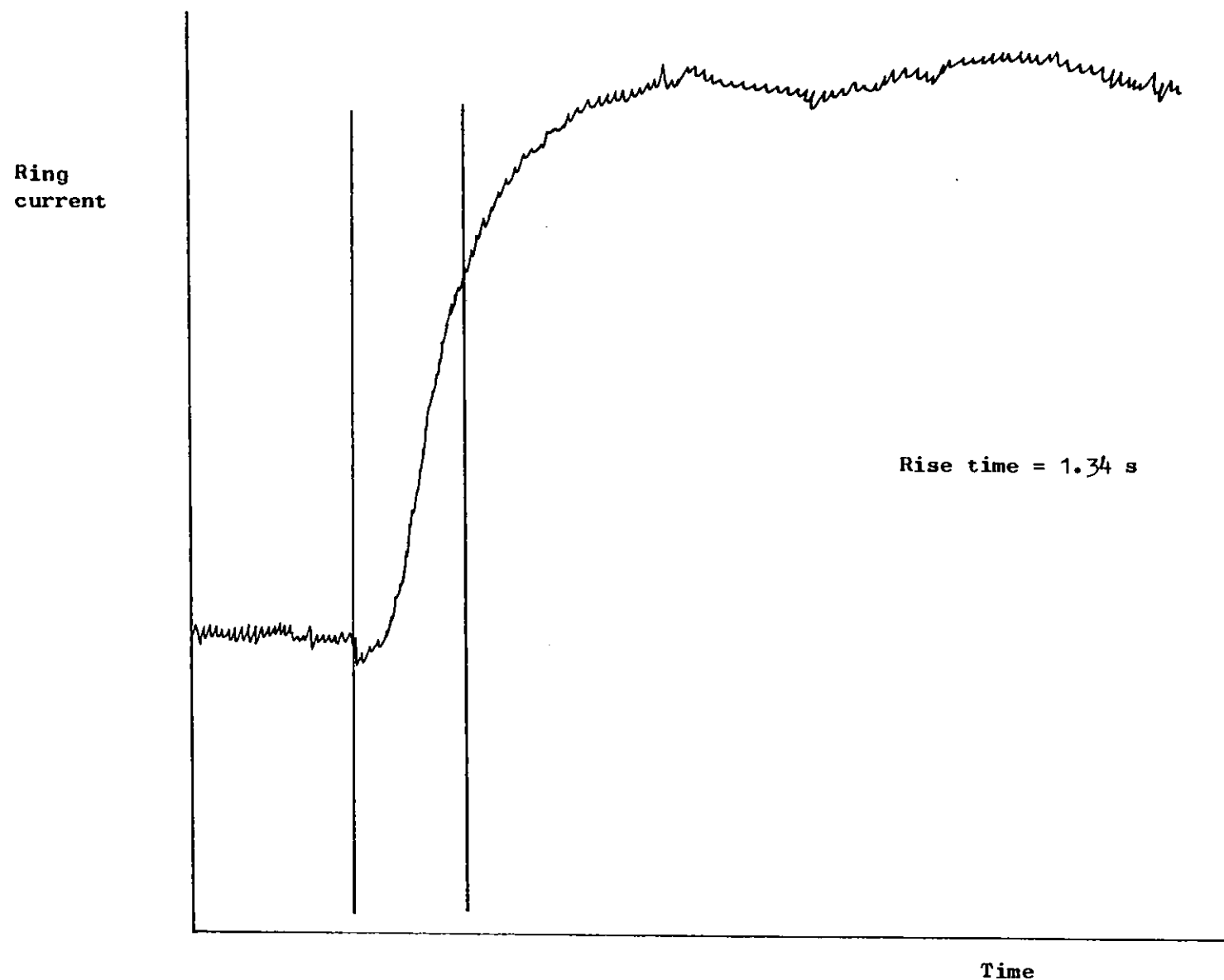


Figure 6.10 Rise time plot at flow rate 0.047 ml s^{-1} ; note the pulsing caused by the peristaltic pump.

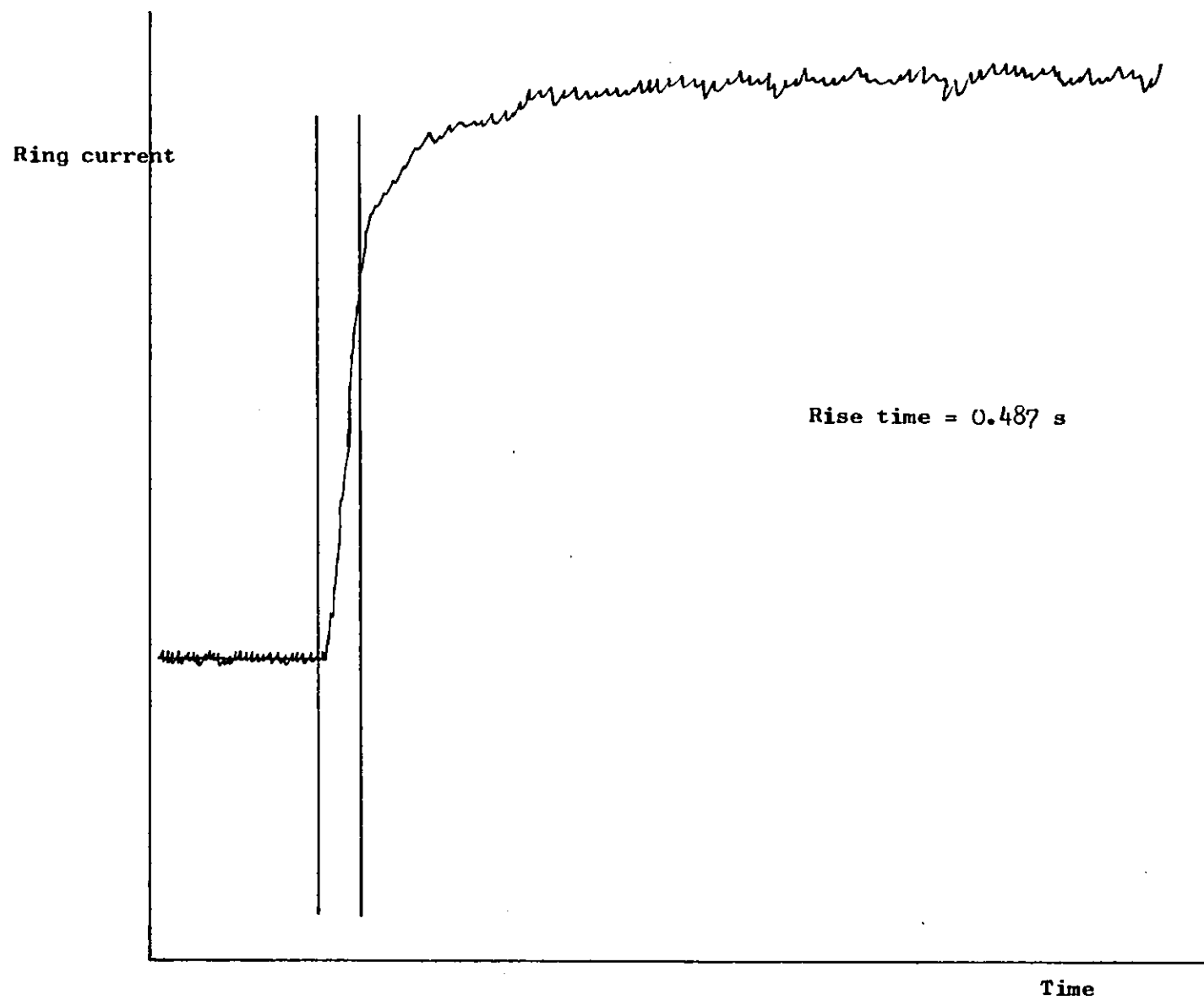


Figure 6.11 Rise time plot at flow rate 0.106 ml s^{-1}

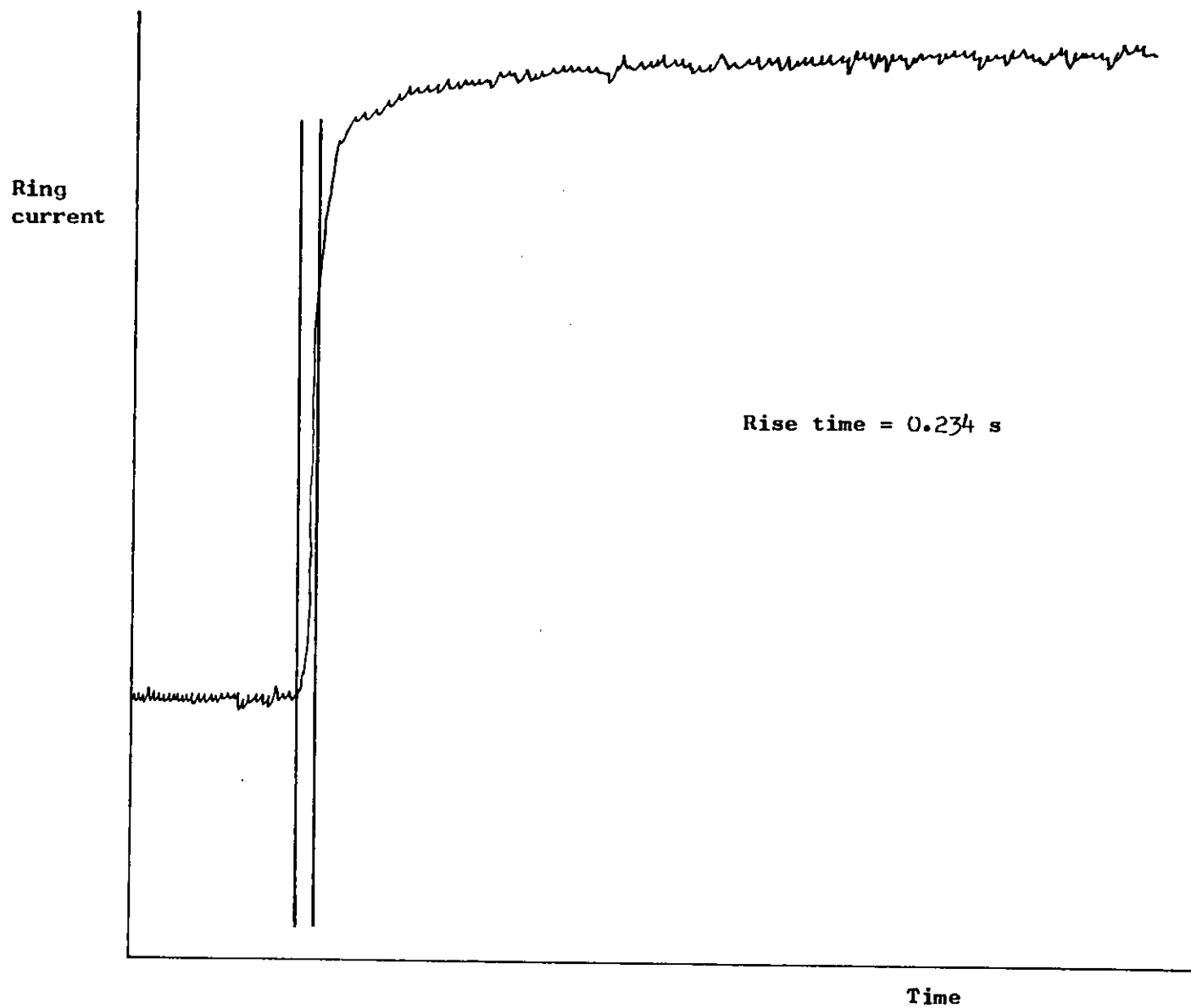


Figure 6.12 Rise time at flow rate 0.157 ml s^{-1}

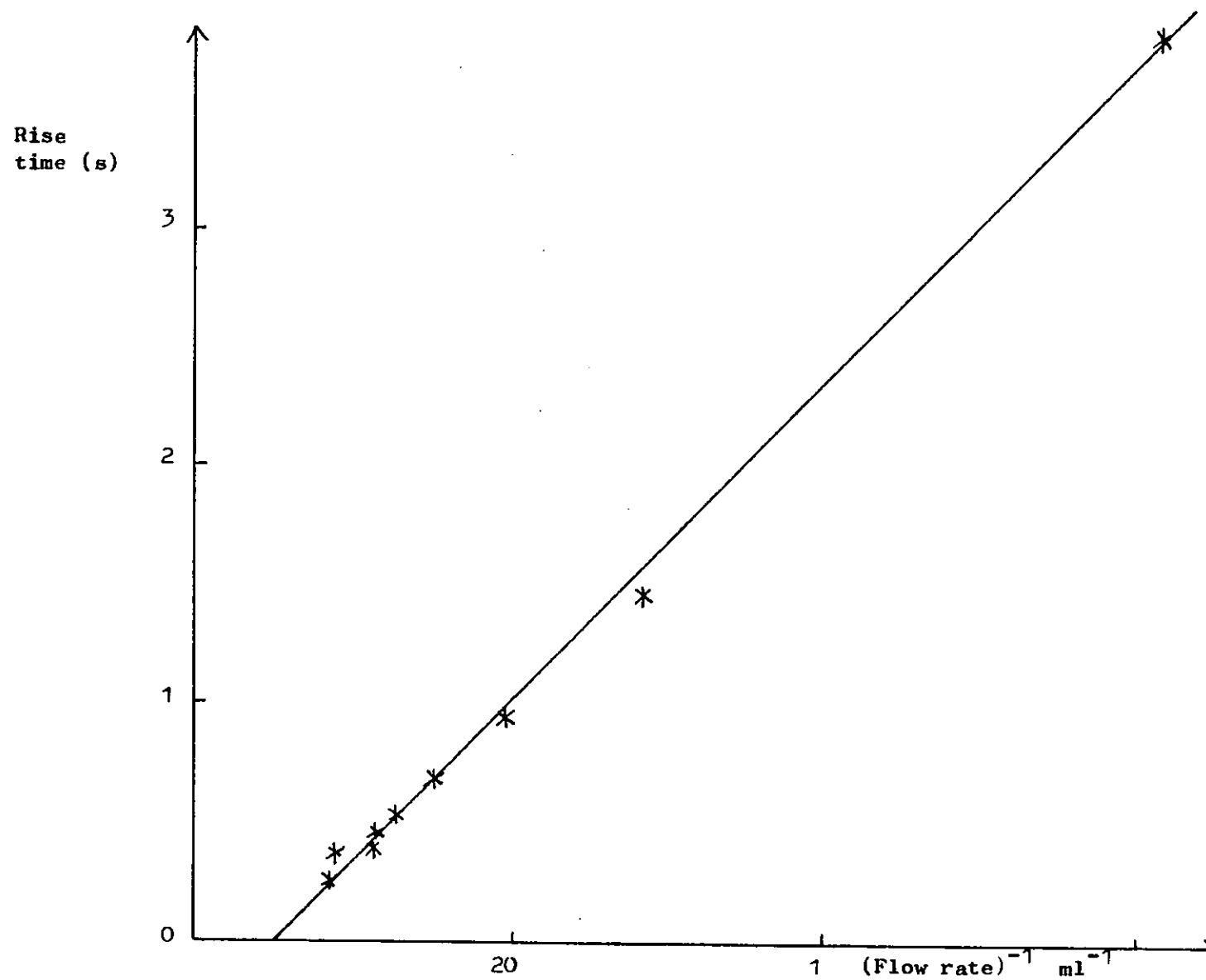


Figure 6.13 The plot of rise times against (flow rate)⁻¹; disc current jump: 0 to 80 μ A.

code.

D The Autotitration Experiment

(a) The Arsenic Calibration

The autotitration technique, as mentioned in chapter one, was first developed by Wood (29) in the analogue mode and in this work we have developed it in this digital mode using the interface and microprocessor. The process by which this is done and the program written to perform the task have been explained and presented in chapter five. Essentially the disc current is continually being varied such that the ring/disc current ratio always lies on a specific gradient within proscribed limits and the value of the disc current is a function of the bulk concentration of the substrate. The new disc current outputted from the DAC is given by:

$$I = \frac{(IR - (N_o \cdot I_D))}{(G - N_o)} \quad (5.4)$$

where I is the new disc current, ID the previous one, IR is the previous ring current and G is the gradient of analysis. Sometimes the change in disc current is large, as when there is a large change in the concentration, and in this case it is important that the time taken for the ring current to stabilize is still within the limits set. But as we saw in the previous section the rise times remain fairly constant for all disc step values.

If the new ratio lies outside the prescribed limits for the analysis gradient a new disc current is outputted as calculated using equation 5.4 - if it does lie within the limits the concentration is calculated using equation 5.3 rearranged:

$$C = \frac{i_D (N_o - N')}{1.6knFv^{-5/12}D^{2/3}a^{1/2}r^{3/4}v_f^{3/4}\beta^{2/3}} \quad (6.1)$$

To test this system the arsenic reaction was used since it provides us with good, well-behaved titration curves. A range of arsenic solutions (20.37, 17.83, 15.3, 12.7, 10.2, 5.1, 2.55, 1.29 μM) were prepared in a solution of 0.25M KBr and 0.25M H_2SO_4 (pH0) and the program AUTOD was used. For each concentration ten valid measurements were made, ie ten which lay within the prescribed limits of the analysis gradient, and that for each point 200 conversions were made, and for each the concentration was calculated; the disc and ring currents and their ratio are also determined. These are then averaged for each concentration. A calibration curve of true concentration against measured concentration is then calculated and using the equations of linear regression the gradient, correlation coefficient and the two intercepts are then calculated. Solutions can then be analyzed and their concentration determined from the calibration curve as well as from theory. In the results presented the same solution used for determining the calibration curve were then analyzed to test how well the system worked - the results are shown in Table 6.13. The analysis gradient taken was 0.0134 which is the most sensitive one and lies at the beginning of the linear region of the titration curve; the prescribed limits were $\pm 3\%$. There was a two second delay for the ring current to stabilize; the flow rate was 0.1389 ml s^{-1} . We notice that the calculated values of the concentration are higher than they should be - this will largely be the result of the collection efficiency being higher than 0.1155, the theoretical value which was

True conc. (μM)	Disc current (μA)	Ring current (μA)	Ring/Disc ratio	Measured conc. (μM)	Conc. from calib. (μM)
20.4	30.8	0.411	0.01335	29.6	-
17.8	27.9	0.370	0.01328	26.8	-
15.3	24.4	0.324	0.01331	23.4	14.4 - 5.75%
12.7	20.7	0.277	0.01340	19.9	12.6 - 0.79%
10.2	17.2	0.229	0.01332	16.6	10.1 - 0.69%
5.1	10.0	0.132	0.01327	9.6	5.2 + 1.18%
2.6	6.8	0.091	0.01330	6.6	2.5 - 2.35%
1.3	4.6	0.061	0.01318	4.5	1.1 -17.05%

On plotting true against measured concentration we obtain:

Gradient = 1.33 X-intercept = $-2.24 \mu\text{M}$

Correlation = 0.9997 Y-intercept = $2.97 \mu\text{M}$

Table 6.13 The autotitration experiment calibrated using As^{3+} with an analysis gradient of $0.0134 \pm 3\%$. In the last column is given the concentration as determined from the calibration curve and the deviation from the true value.

True conc. (μM)	Disc current (μA)	Ring current (μA)	Ring/Disc ratio	Measured conc. (μM)	Conc. from calib. (μM)
20.4	37.2	1.86	0.05011	30.6	18.1 -11.3%
15.3	29.1	1.46	0.05015	23.9	15.2 - 0.9%
10.2	17.8	0.89	0.05008	14.7	8.6 -16.1%
5.1	12.3	0.62	0.04996	10.1	5.2 + 1.4%
2.0	7.1	0.35	0.05013	5.1	2.3 +14.2%

On plotting true against measured concentration we obtain:

Gradient = 1.36 X-intercept = $-1.98 \mu\text{M}$

Correlation = 0.9949 Y-intercept = $2.68 \mu\text{M}$

Table 6.14 Arsenic calibrations of the autotitration experiment using a gradient of analysis of $0.05 \pm 1\%$.

used, since as we saw earlier the measured values of N_0 are often greater than the theoretical value since we have a cell of finite volume.

This is reflected in the calibration gradient of true against measured concentration of 1.33 and a concentration coefficient of 0.9997 and it can be seen in Figure 6.14. The values of some of the same concentrations were then analyzed and the concentrations determined from the calibration curve are in fairly close agreement with the true concentrations.

The experiment can easily be done with other analysis gradients but as previously mentioned the sensitivity is lessened. Such results for the analysis gradient $0.05 \pm 1\%$ are shown in Table 6.14; here the calibration curve only has a correlation coefficient of 0.9949 with correspondingly less good results in the concentrations determined from his curve. Presented in Figure 6.15 is a concentration profile for the analysis, produced directly from the experiment, showing the concentrations calculated from the disc current and N' . The second set of readings are then used to determine the concentration from the calibration curve.

(b) Autotitration with controlled flow rates

As discussed in chapter three the peristaltic pump was modified such that it could be controlled from the interface rack. The autotitration program was modified such as to record autotitrations at various flow rates. A solution of $20.4 \mu\text{M As}^{3+}$ was used and for each flow rate a set of 15 "valid" measurements were recorded and the average calculated. Unfortunately we cannot simply calibrate the flow rate since it varies for a given potential outputted depending on the state of the tubing. Thus in this experiment the disc current measured

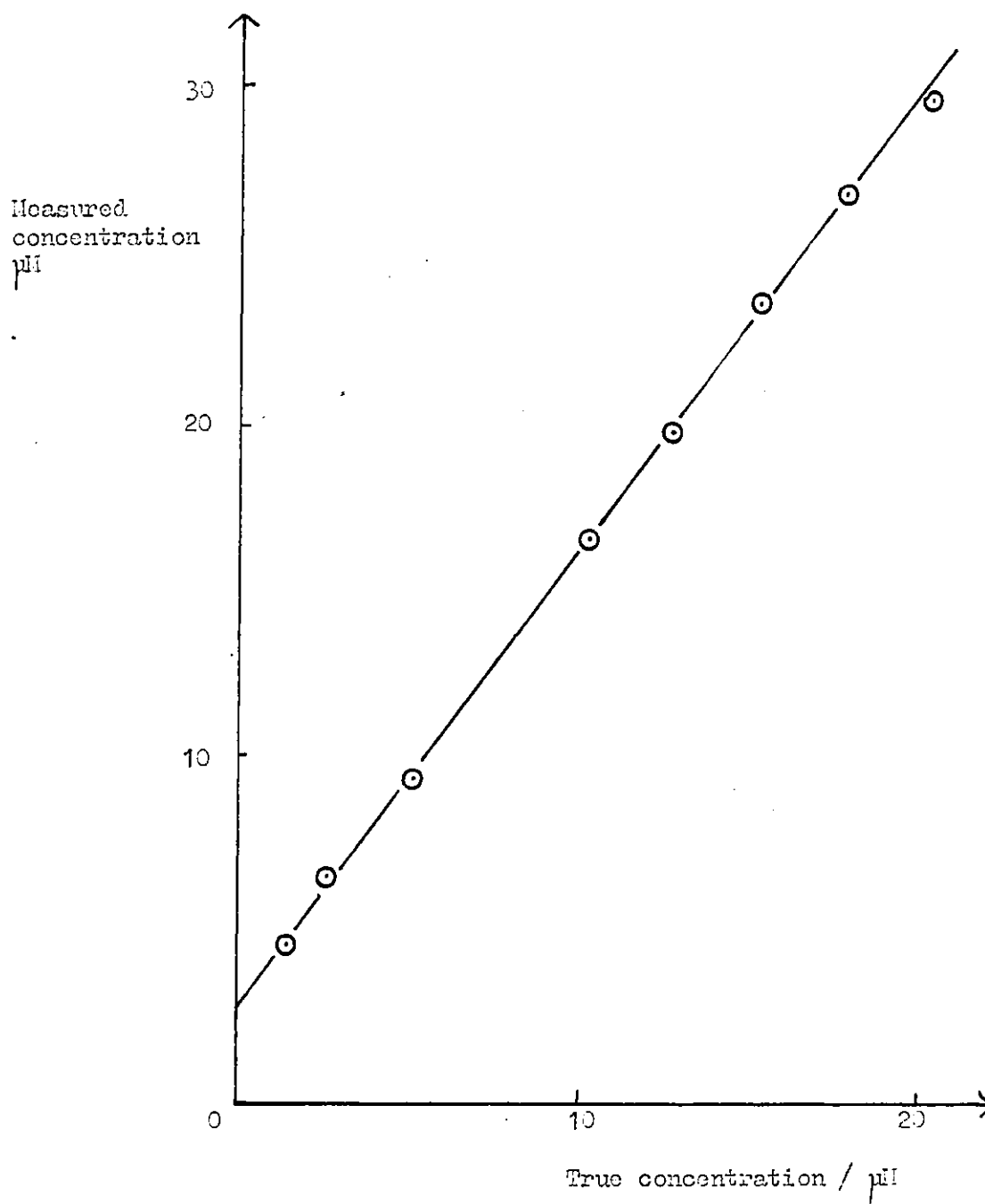


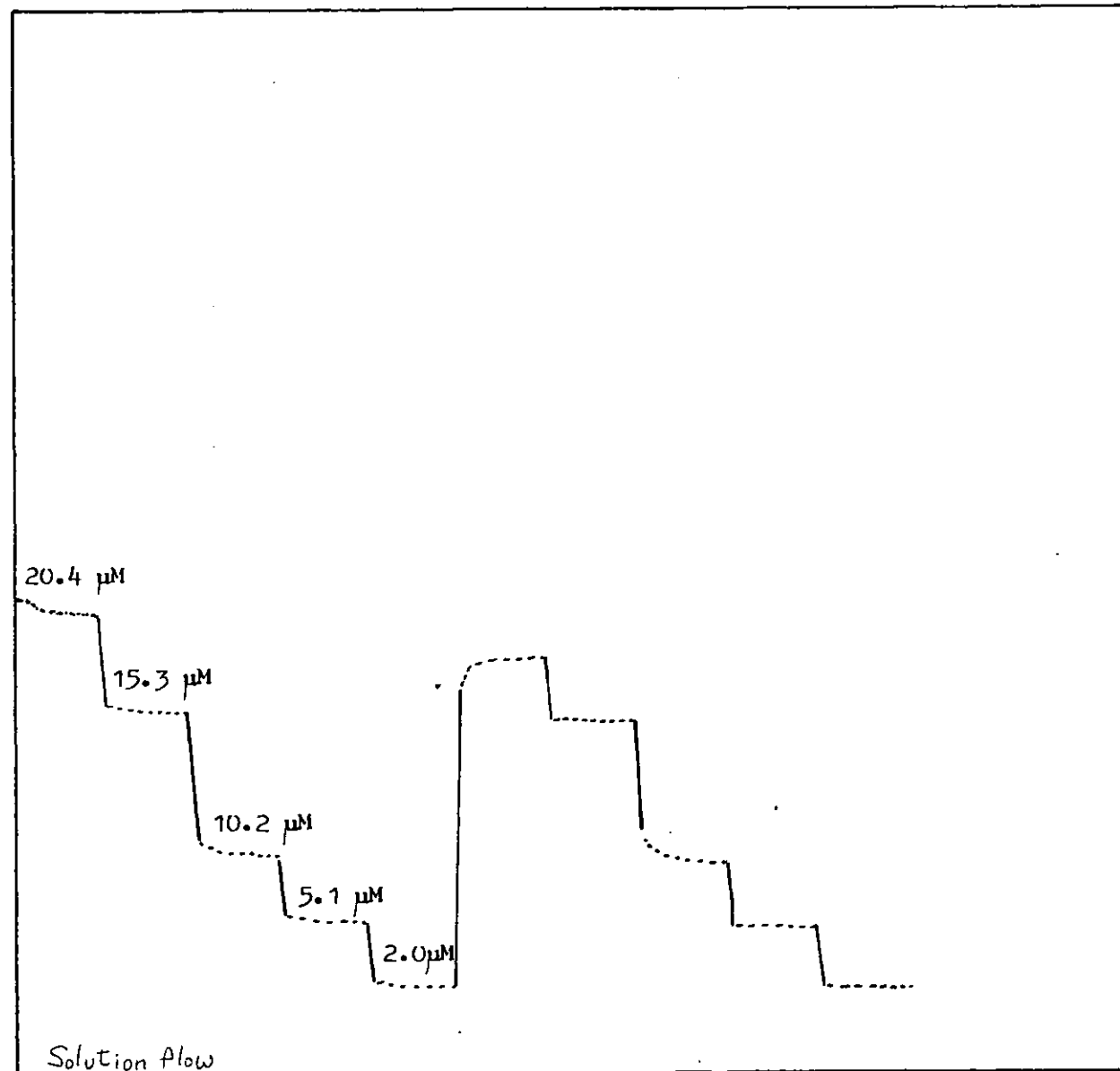
Figure 6.14 The autotitration experiment calibrated with the arsenic-bromine system.

Figure 6.15

The concentration profile for the arsenic calibration.

The first set of readings are used to generate the calibration curve from which concentration determinations can be made for subsequent solutions.

Concentration



(Pump potential) ^{3/4}	Disc current (μA)	Ring current (μA)	Ring/Disc ratio
2038	23.8	3.14	0.0132
2164	27.1	3.66	0.0134
2288	26.3	3.87	0.0131
2410	32.0	4.27	0.0133
2529	37.0	4.86	0.0131
2647	39.1	5.33	0.0136
2763	40.7	5.27	0.0129
2877	43.1	5.79	0.0134
2990	45.0	5.93	0.0131

On plotting the (pump potential)^{3/4} against disc current we obtain:

Gradient = 0.0228

Correlation = 0.9939

X-intercept = 997 (mV)^{3/4}

Y-intercept = -22.3 μA

Table 6.15 The autotitration experiment with the flow rate controlled from the interface rack; 20.4 μM As³⁺ was used and an analysis gradient of 0.0134.

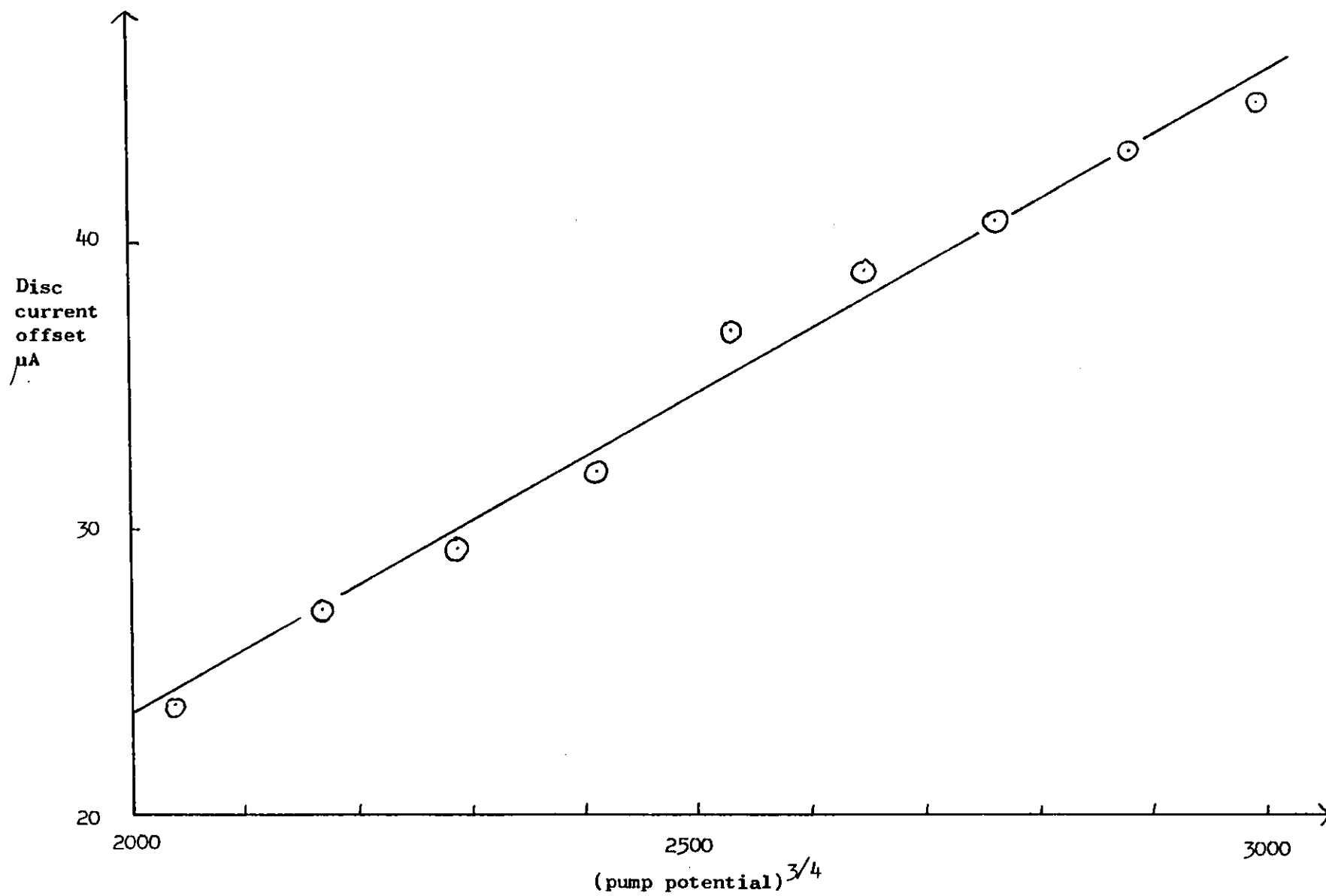


Figure 6.16 The plot of disc current offset against the $(\text{pump potential})^{3/4}$

was plotted against (pump potential)^{3/4}; the results and graph obtained are given in Table 6.15 and Figure 6.16 respectively. The correlation coefficient is 0.9939 which suggests that such a system could be developed. The actual flow rate could be determined by weighing using scales with a BCD output.

E Phenol and p-Cresol

(a) Titrations

Having tested the system with the well-behaved $\text{As}^{3+} - \text{Br}_2$ reaction we were now in a position to ascertain how well phenol and p-cresol would behave. The necessary requirement for a well-behaved titration curve is that the rate of reaction between the bromine and the substrate is fast ($k_2 > 10^5 \text{ M}^{-1}\text{s}^{-1}$) so that there is a well defined reaction boundary (see Figure 1.12 and 1.13). However for phenol this is not the case since $k_2 = 1.8 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1}$ (37). Wood (38) made some preliminary investigations into the diffusion layer titration of phenol using the RRDE and found them to have two regions which are schematically shown in Figure 6.17.

At low disc currents the concentration of bromine generated at the disc is much lower than that of the phenol and so first order kinetics results. The gradient of this region was found to increase with the rotation speed - this was because the bromine reaches the ring more quickly and consequently there is less time for the reaction with the phenol.

As the disc current is increased the amount of bromine increases until its concentration is comparable to that of the phenol and consequently second order kinetics arise and the second region of the titration curve. In this region the ring current decreases with

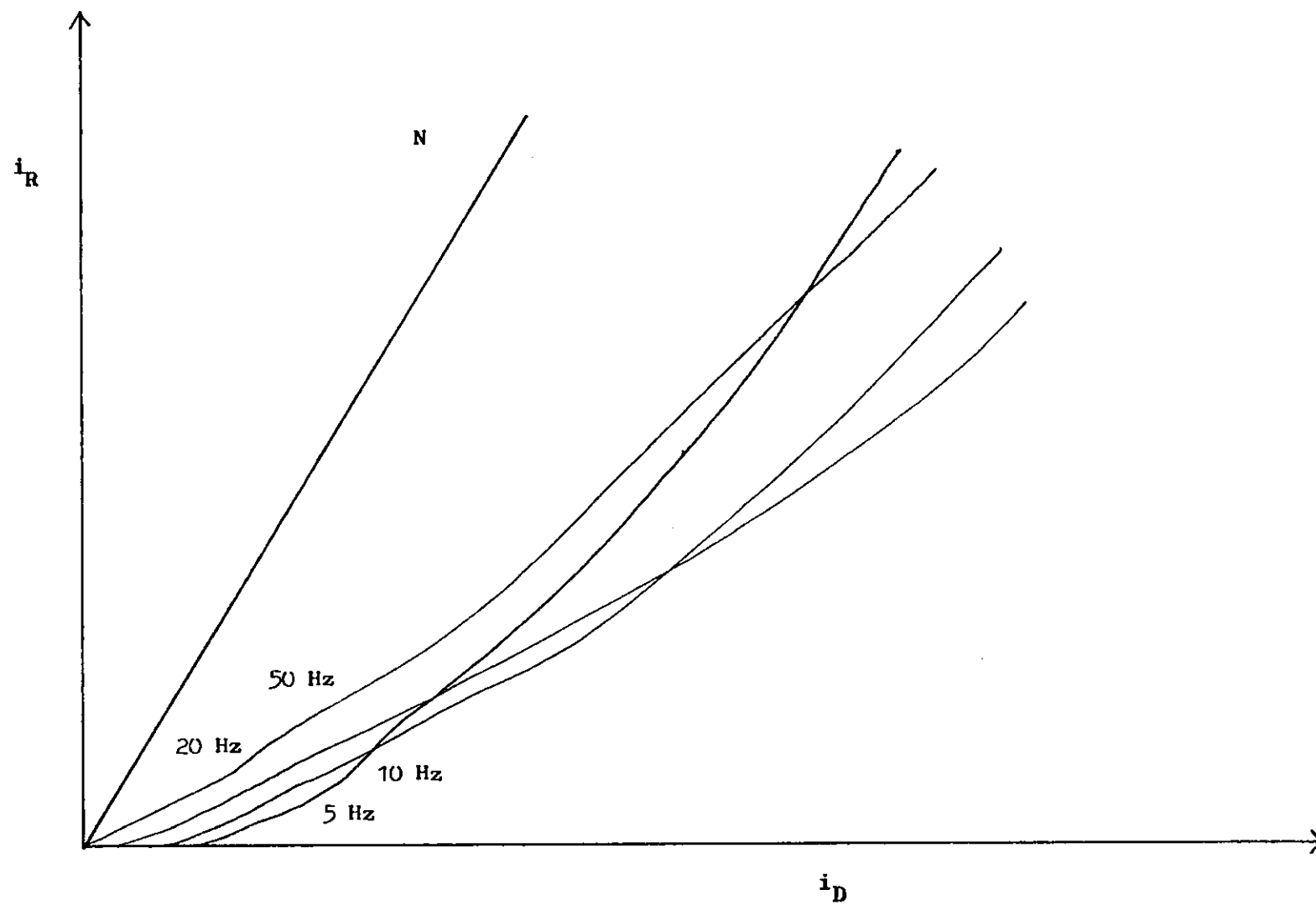


Figure 6.17 Schematic RRDE titration curves for the bromination of phenol.

increasing rotation speed since more phenol is being pumped to the electrode where the ring and disc current are related by:

$$i_R = N_O i_D - H \beta^{2/3} \quad (6.2)$$

where H is the equivalent to M in the WJRDE system. It is thus at higher disc currents that we approach the theoretical value for N_O and where it is therefore best to determine concentrations.

A set of titration curves were recorded over a range of concentrations - 1.0 to 60.0 μM phenol in 0.25M KBr and 0.5M H_2SO_4 (pH0) - and for each concentration 3 titration curves were recorded with a maximum disc current of 120 μA and step intervals of 1 μA ; the flow rate was 0.0901 ml s^{-1} and the results are given in Table 6.16 and Figure 6.18a and a typical titration curve is shown in Figure 6.20. Due to the insufficiently fast kinetics we do not obtain the ideal shape for the titration curve and at low disc currents a ring current is recorded. We note that the values of N_O are higher than the theoretical value as with arsenic and that the linear regions have correlation coefficients of typically 0.998. The calculated values for the concentration are too low but the graph of true against measured concentration (gradient 0.7500) gives a reasonably straight line with a correlation coefficient of 0.9986 which suggests that concentrations could be determined by comparison with known concentrations and with a lower limit of detection of 5 μM . The calculated concentrations are too low at high concentration because of the slow reaction rate between the phenol and the bromine allowing the latter to reach the ring before it would otherwise have done. The results indicate a lower limit of detection of 10 $\mu\text{M} \pm 5\%$.

True Conc. (μM)	Disc current offset (μM)	N_o	Correlation coefficient	Measured conc. (μM)
1.0	1.6 $\pm 40\%$	0.139	0.9981	3.4
2.0	2.5 $\pm 12\%$	0.145	0.9984	5.6
4.0	2.9 $\pm 21\%$	0.142	0.9984	6.2
6.0	3.6 $\pm 21\%$	0.138	0.9993	7.6
8.0	3.4 $\pm 24\%$	0.140	0.9984	7.1
10.0	5.1 $\pm 0.3\%$	0.136	0.9978	10.5
20.0	8.7 $\pm 5.7\%$	0.136	0.9984	17.8
40.0	16.5 $\pm 1.9\%$	0.130	0.9985	32.5
60.0	26.0 $\pm 6.5\%$	0.122	0.9962	48.2

On plotting true against measured concentration we obtain:

Gradient = 0.750

Correlation = 0.9986

X-intercept = $-3.76 \mu\text{M}$

Y-intercept = $2.82 \mu\text{M}$

Table 6.16 Titration results for varying phenol concentrations in 0.25M KBr and 0.5M H_2SO_4 (pH0). The flow rate was 0.0901 ml s^{-1} .

True conc. (μM)	Disc current offset (μA)	No	Correlation coefficient	Measured conc.		Corr. coef.
				1 (μM)	2	
2.0	0.6	0.129	0.9997	1.0	-	-
2.0	0.6	0.130	0.9995	1.0	-	-
	0.6	0.123	0.9996	1.0		
3.9	1.7	0.128	0.9997	2.6	2.7	0.7214
3.9	1.8	0.129	0.9997	2.8	3.2	0.6789
	1.7	0.129	0.9997	2.7	3.0	0.7002
7.8	2.9	0.125	0.9994	4.3	4.5	0.8291
7.8	2.7	0.126	0.9996	4.2	4.5	0.8343
7.8	3.1	0.127	0.9994	4.8	4.6	0.7999
	2.9	0.126	0.9995	4.4	4.5	0.8211
13.7	5.4	0.122	0.9995	8.2	12.9	0.7385
13.7	5.1	0.123	0.9996	7.6	16.8	0.4009
	5.2	0.122	0.9996	7.9	14.8	0.5697
29.4	11.1	0.116	0.9993	15.7	19.3	0.9779
29.4	11.5	0.119	0.9996	16.7	21.2	0.9852
	11.3	0.118	0.9995	16.2	20.8	0.9816
49.0	16.9	0.110	0.9986	22.7	28.1	0.9834
49.0	18.2	0.112	0.9990	24.8	31.7	0.9869
	17.5	0.111	0.9988	23.8	29.9	0.9852

On plotting the true against measured concentration (1) we obtain:

$$\text{Gradient} = 0.518$$

$$\text{Correlation} = 0.9964$$

$$\text{X-intercept} = 1.58 \mu\text{M}$$

$$\text{Y-intercept} = -0.82 \mu\text{M}$$

Table 6.17 p-Cresol titrations in 0.25M KBr and 0.5M H_2SO_4 at a flow rate of 0.121 ml s^{-1} . For each concentration the final set of values are the average for that concentration. Concentration 1 is determined from the disc current offset and concentration 2 from the $(N_0 - N')^{-1}$ values.

These results can be compared to those for p-cresol obtained at a flow rate of 0.1205 ml s^{-1} which are shown in Table 6.17 and where the graph of true against measured concentration can be seen in Figure 6.18b. A straight line of correlation coefficient 0.9964 and gradient 0.965 is obtained allowing the possibility of calibration with a lower detection limit of $2 \text{ }\mu\text{M}$. However we are not able to draw a direct comparison between phenol and p-cresol since these experiments were done at two different flow rates and as we will see this is an important factor.

A second set of experiments were run with p-cresol where for a concentration of $49.03 \text{ }\mu\text{M}$ the concentration was measured for a range of flow rates. The results can be seen in Table 6.18 and the graph in Figure 6.19. Initially the disc current offset increases with flow rate as expected since more p-cresol is being brought to the electrode but at about 0.1 ml s^{-1} the disc current offset begins to fall away, with a correspondingly greater decrease in the measured concentration. This is because the reaction between the aromatic and the bromine is not sufficiently fast for the bromine to be removed before reaching the ring electrode. We conclude from this that when titrating for these aromatics we must choose the optimum flow rate.

For this concentration we observe that concentration measured at a flow rate of 0.0901 ml s^{-1} is considerably higher than at 0.1205 ml s^{-1} $38.43 \text{ }\mu\text{M}$ as compared with $23.67 \text{ }\mu\text{M}$, which is now more comparable for the results we obtained for phenol. We also observe that there is not very good agreement between the values of concentration obtained from the disc current offset and the $(N_0 - N')^{-1}$ values; this is a result of the non-ideality of the titration curves.

Flow rate(mls ⁻¹)	Disc current offset(μ M)	N _o	Measured conc. (μ M)		Corr. coef.
			1	2	
0.063	16.9	0.114	38.4	42.8	0.9762
0.090	21.4	0.119	38.4	47.8	0.9924
0.116	17.7	0.112	23.9	30.6	0.9895
0.141	17.1	0.111	20.8	26.5	0.9905
0.161	16.0	0.111	17.4	22.7	0.9989
0.185	14.5	0.111	14.2	19.0	0.9987
0.208	11.7	0.111	10.6	14.5	0.9847
0.233	14.0	0.115	12.0	19.2	0.9508

Table 6.18 p-Cresol titrations (49.0 μ M), with varying flow rates; concentration 1 was determined from the disc current offsets and concentration 2 from $(N_o - N')^{-1}$ calculations.

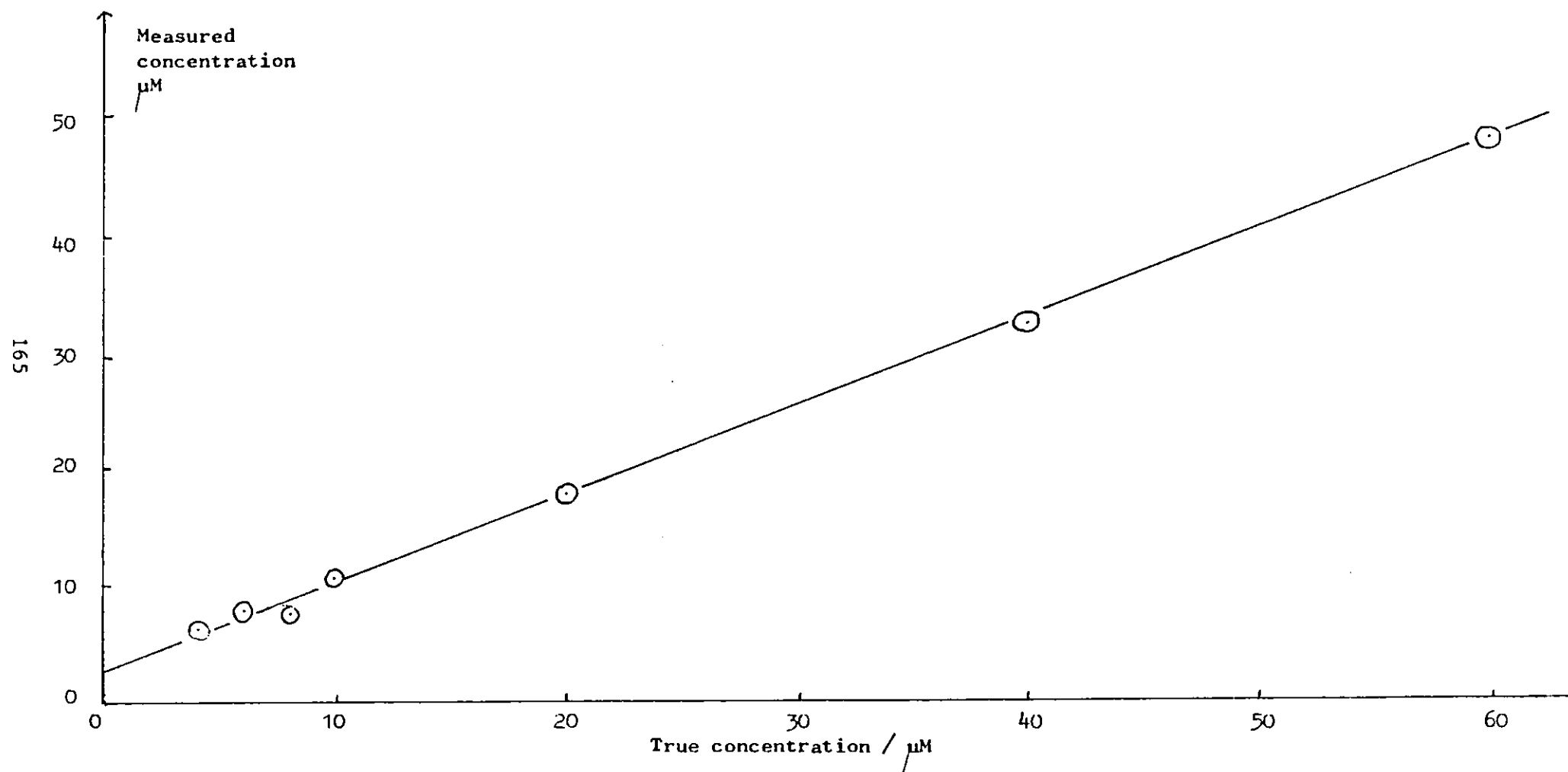


Figure 6.18 a The plot of true against measured concentration for phenol.

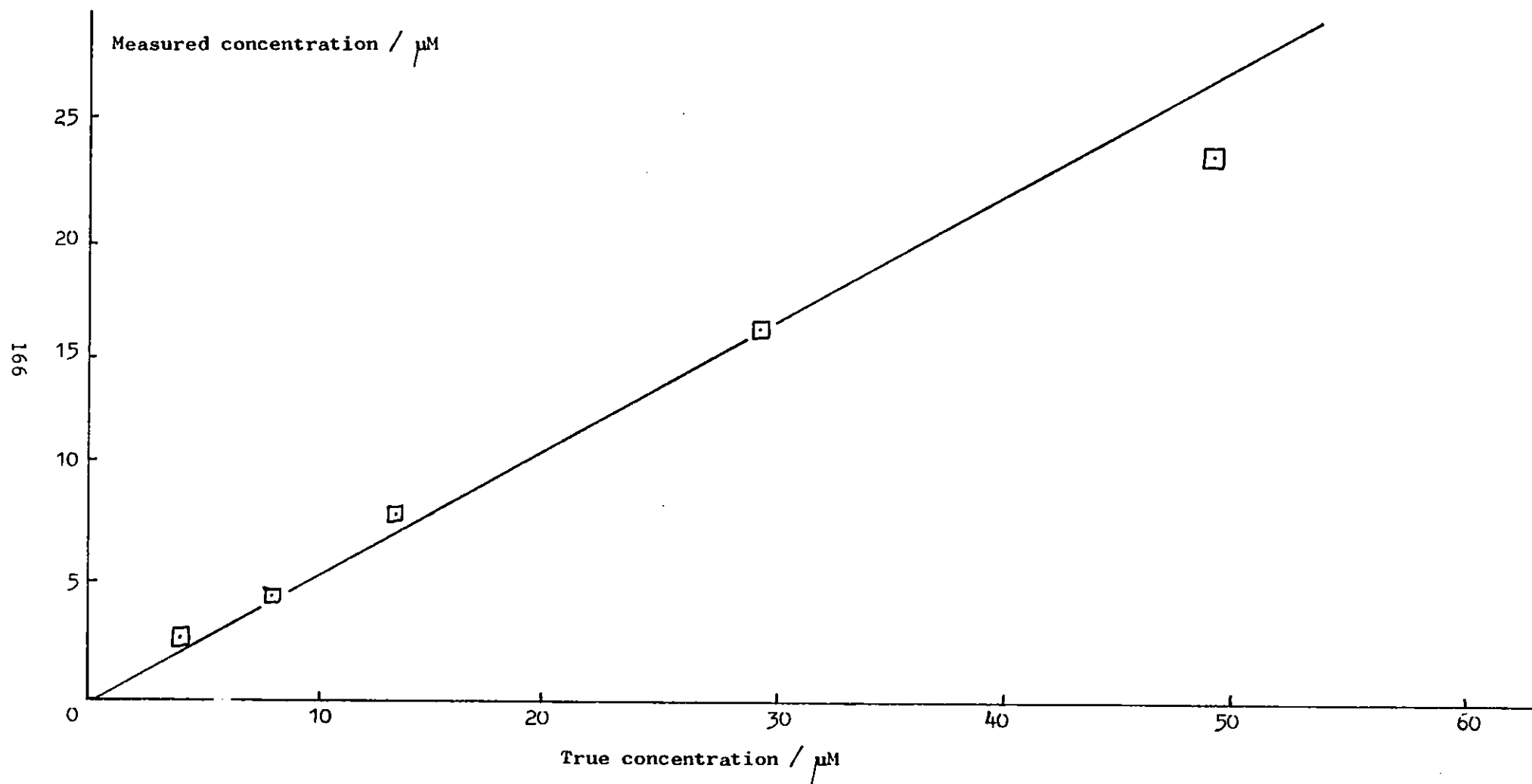


Figure 6.18b The plot of true against measured concentration for p-cresol at pH 0.

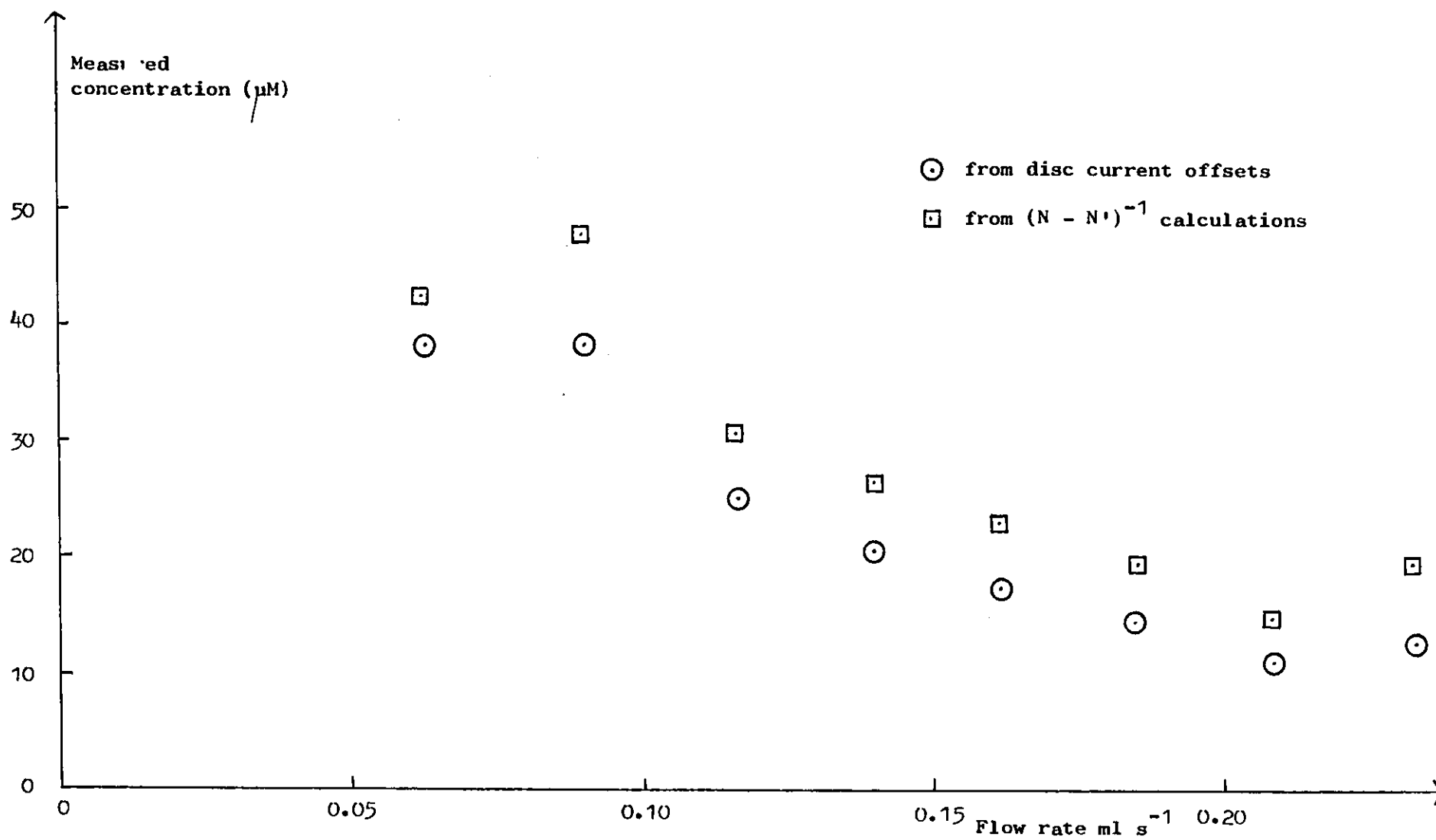


Figure 6.19 The plot of flow rate against measured concentration for $49.0 \mu\text{M}$ p-cresol.

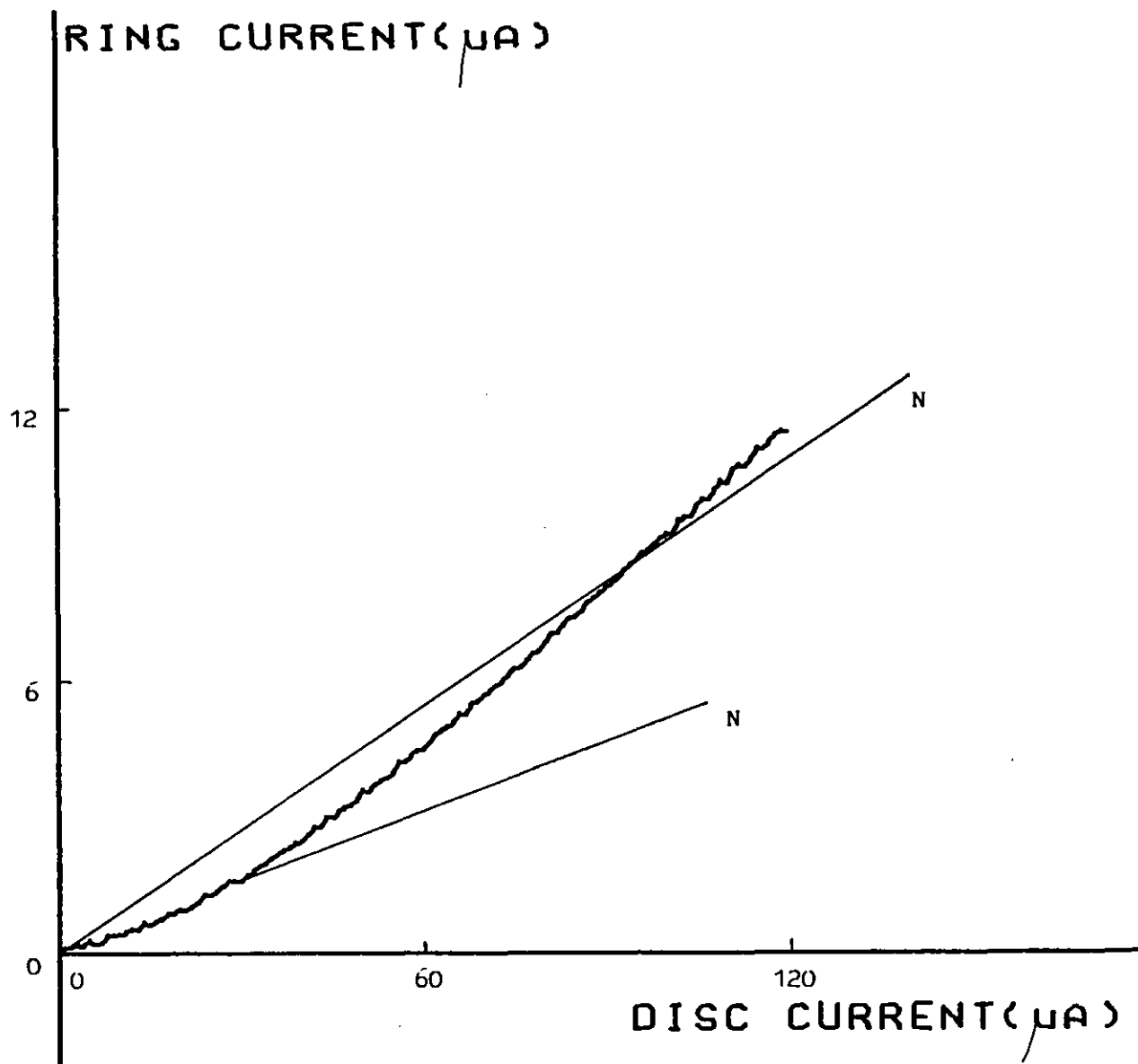


Figure 6.20 A titration curve for 60 μM phenol at pH 0; because of the non-ideality in shape autotitrations can only be done at high N.

(b) Autotitrations

Since well-behaved titration curves were not obtained for aromatics under these conditions it was very difficult to perform autotitrations; this can be best seen in Figure 6.20. At the optimum analysis gradient of 0.0134 analyses were impossible since the analysis gradient lies very close to the early part of the titration curve resulting in a whole range of "valid" measurements - thus autotitrations were only possible at high concentrations with high, and consequently less sensitive, analysis gradients; for example, using p-cresol concentrations of 49.03, 29.42 and 13.73 μM and an analysis gradient of 0.1 $\pm 6\%$ we were able to obtain a calibration curve with a correlation coefficient of 0.962.

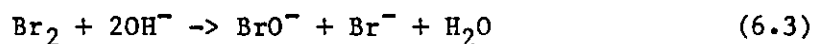
Clearly, if we are going to be able to develop a sensitive technique for analyzing aromatic substrates it is imperative to increase the reaction kinetics with the bromine and so produce better titration curves. It would also be advantageous if we were able to activate the ring such that two or three bromines were substituted so that larger disc current offsets were obtained for a given concentration. In order to do this we decided to perform the analyses at pH 9.2 instead of pH 0. This would result in the formation of the phenylate ion ($\text{C}_6\text{H}_5\text{O}^-$) which would be more susceptible to attack from the bromine, in the form of the bromate ion BrO^- , and so increase the reaction kinetics since the ring is now more nucleophilic. There is also the possibility that two or three bromines will be substituted. However the oxidation of bromide at a platinum electrode is inhibited by phenol where the radical ($\text{C}_6\text{H}_5\dot{\text{O}}$) is formed in an anodic charge transfer adsorption process (39); both increases in phenol concentration and pH increase the potential at which inhibition

occurs.

(i) Titrations at pH 9.2

Solutions were buffered at pH 9.2 using a 0.025M solution of Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in 0.5M KBr which doubles as a background electrolyte.

A further problem at this pH is that deoxygenation is necessary and this was done by outgassing with oxygen-free argon before each experiment:



Titration curves were then recorded for concentrations of phenol ranging from 50.0 down to 7.0 μM and some representative examples are shown in Figures 6.21 to 6.23; the results are given in Table 6.19. We immediately see that the shape is much closer to the ideal titration curve suggesting that we now have faster reaction kinetics; a plot of true concentration against disc current offset is shown in Figure 6.24. We observe there is a disc current offset of 7.89 μA which must be due to unremoved oxygen. Such an intercept is also seen in the plot of true concentration against measured concentration but we are able to derive a gradient which would suggest a calibration approach. The measured concentration at 20 μM are somewhat high and this would seem to be the result of a high value for the collection efficiency. We also note that at higher concentrations the values obtained are less consistent and this is most probably a consequence of the inhibition of bromide oxidation at these phenol concentrations. Now that the ideal titration has been restored we obtain better agreement between

Figure 6.21 a

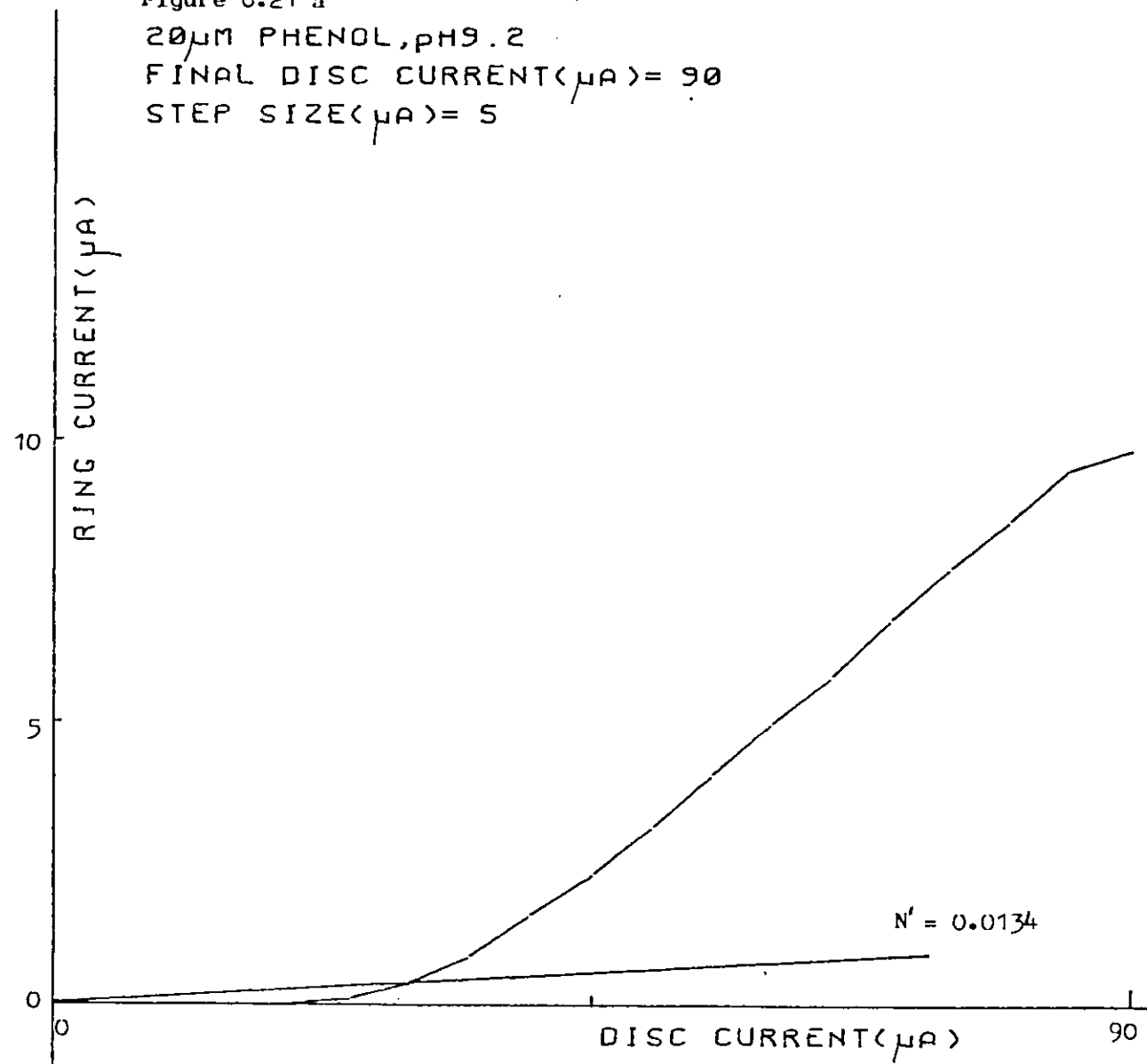
20 μ M PHENOL, pH 9.2FINAL DISC CURRENT (μ A) = 90STEP SIZE (μ A) = 5

Figure 6.21 b

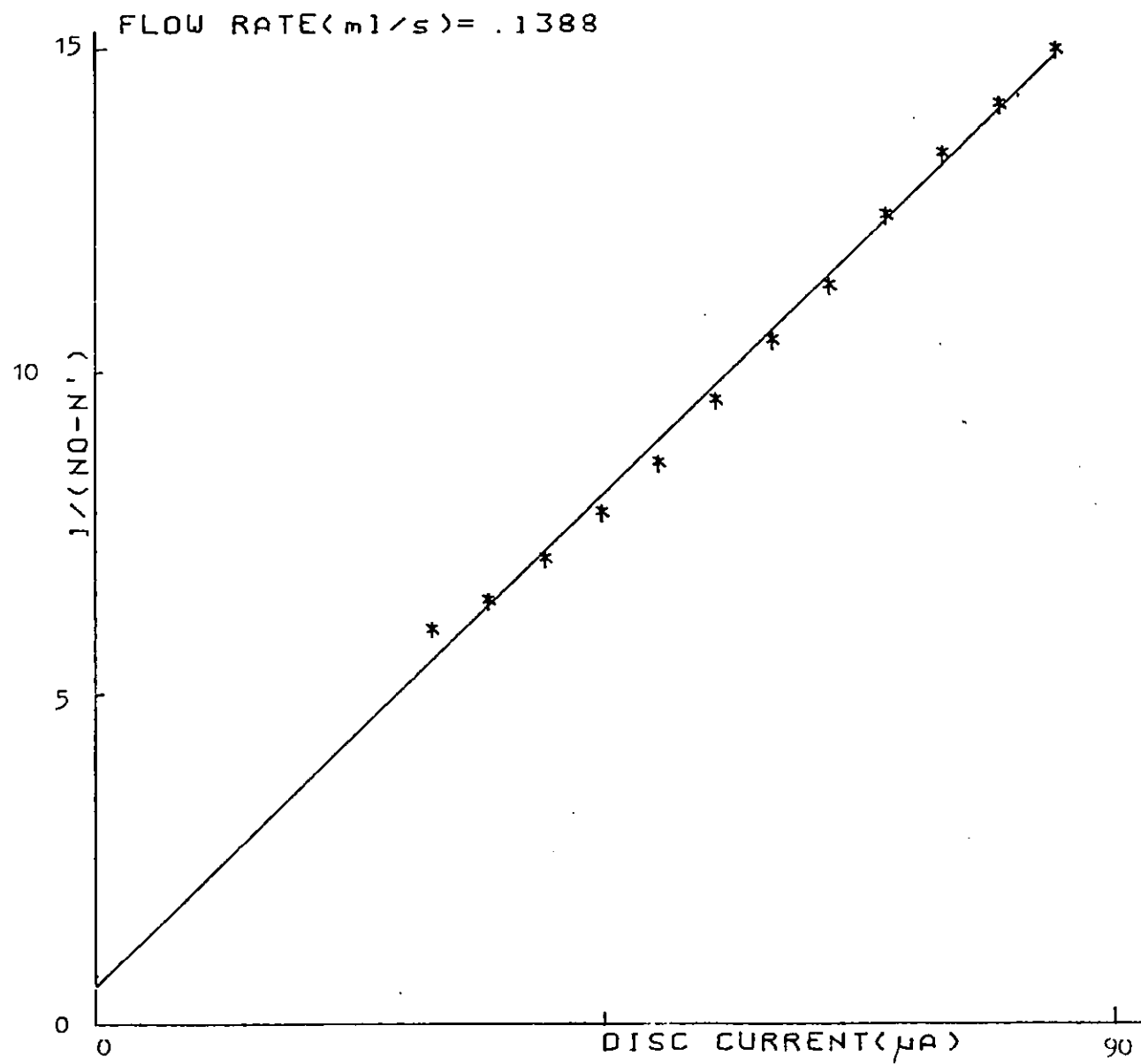


Figure 6.22 a

35 μ M PHENOL, pH 9.2
FINAL DISC CURRENT (μ A) = 100
STEP SIZE (μ A) = 5

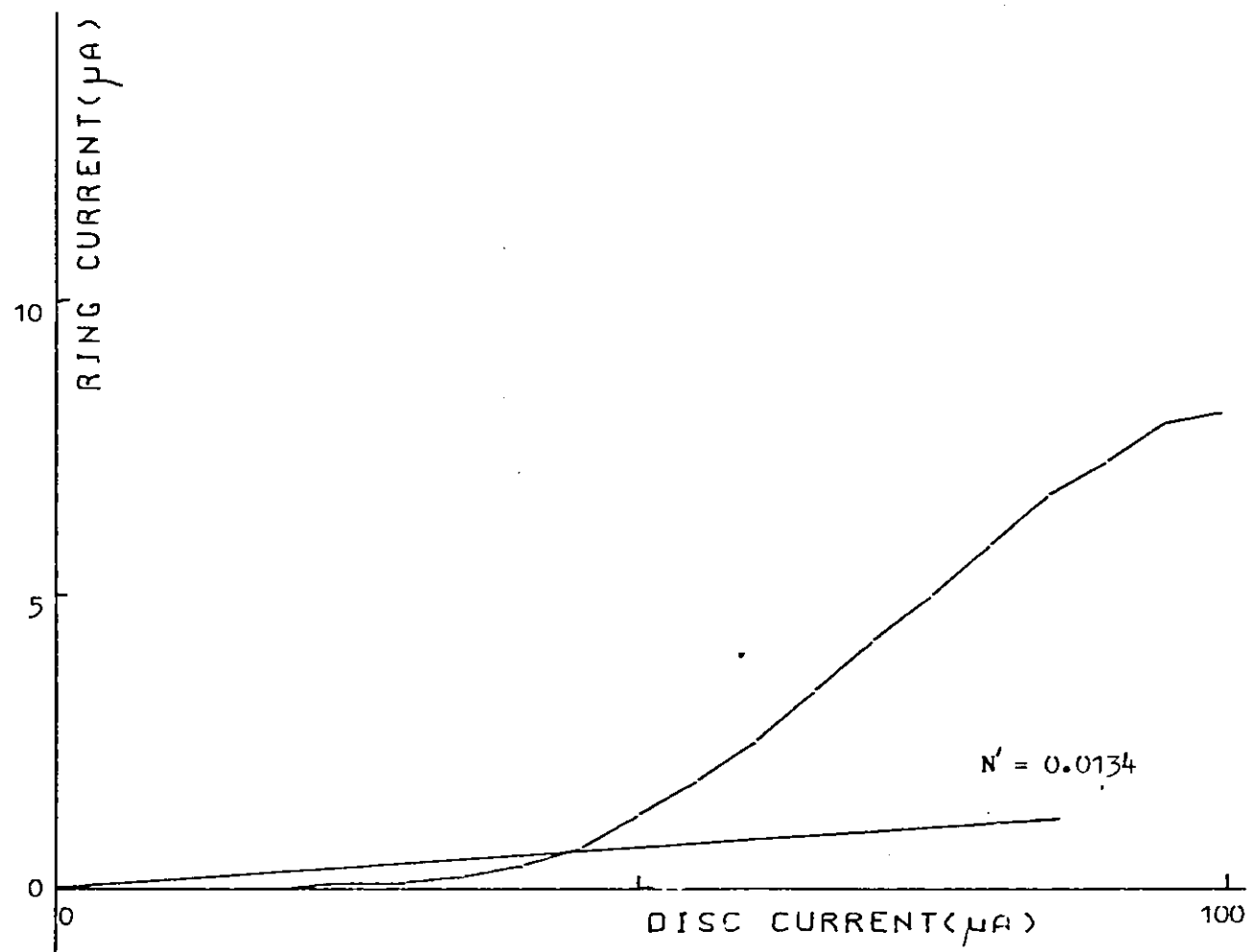


Figure 6.22 b

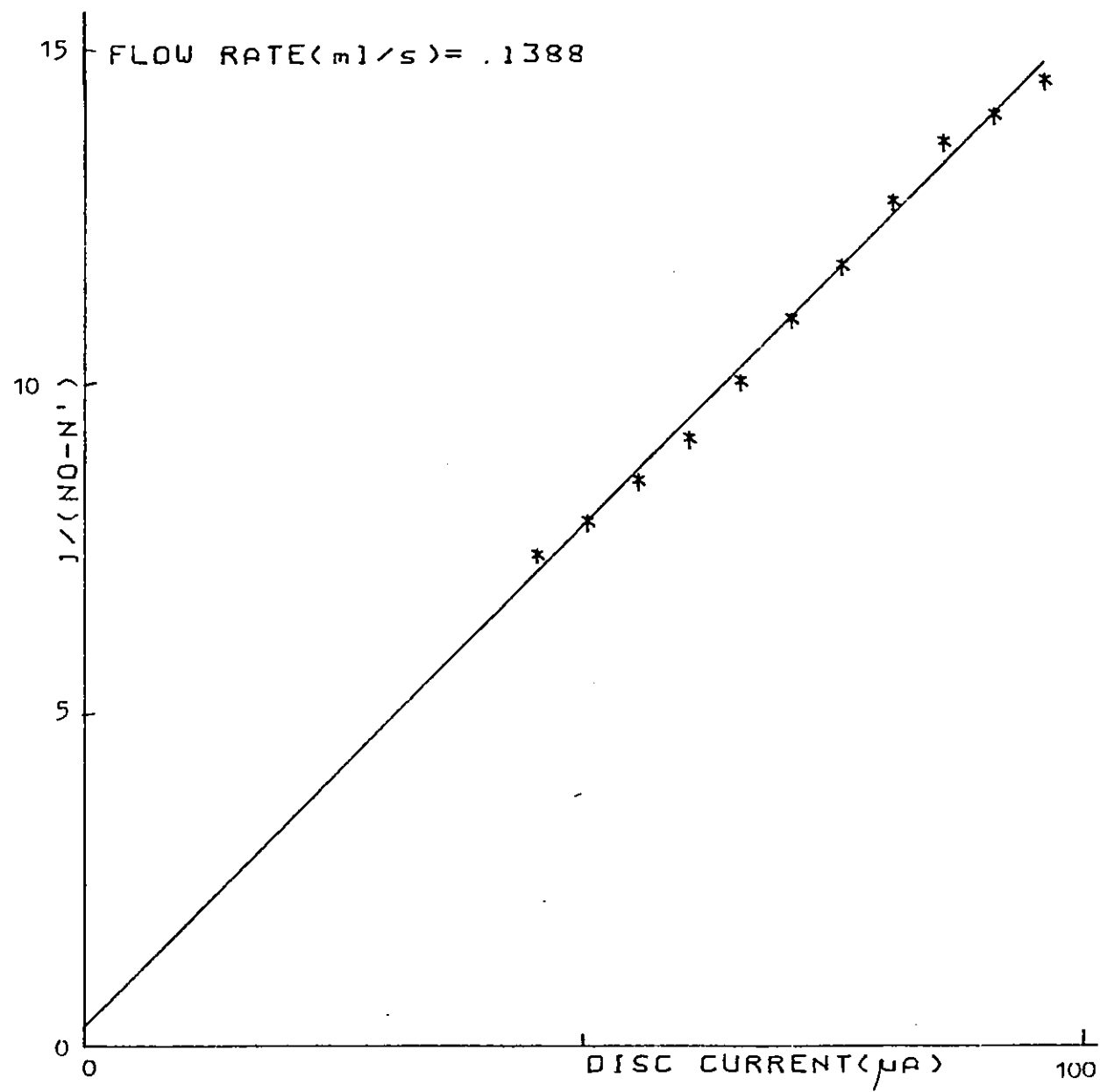


Figure 6.23 a

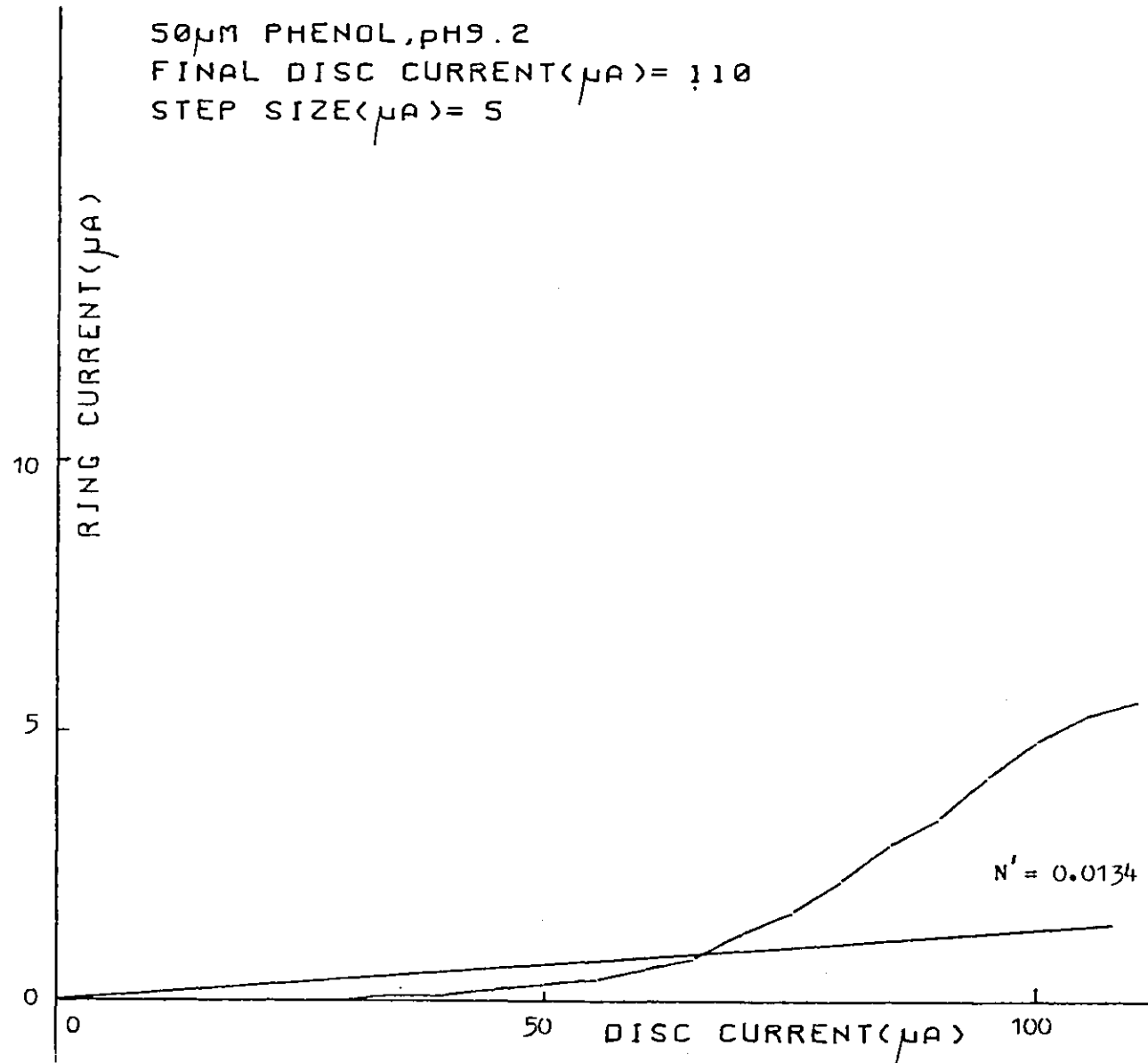
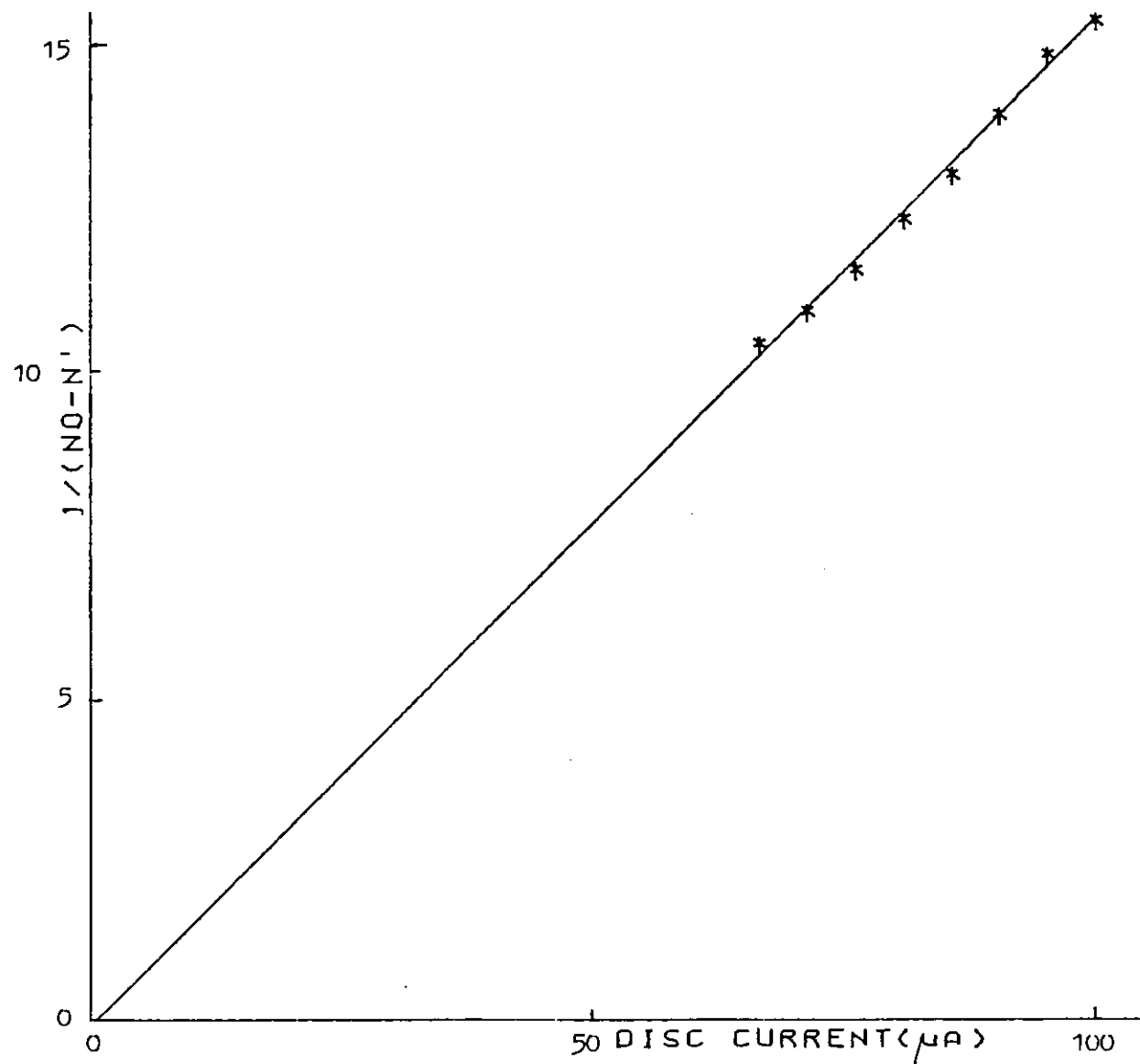


Figure 6.23 b

FLOW RATE (ml/s) = .1388



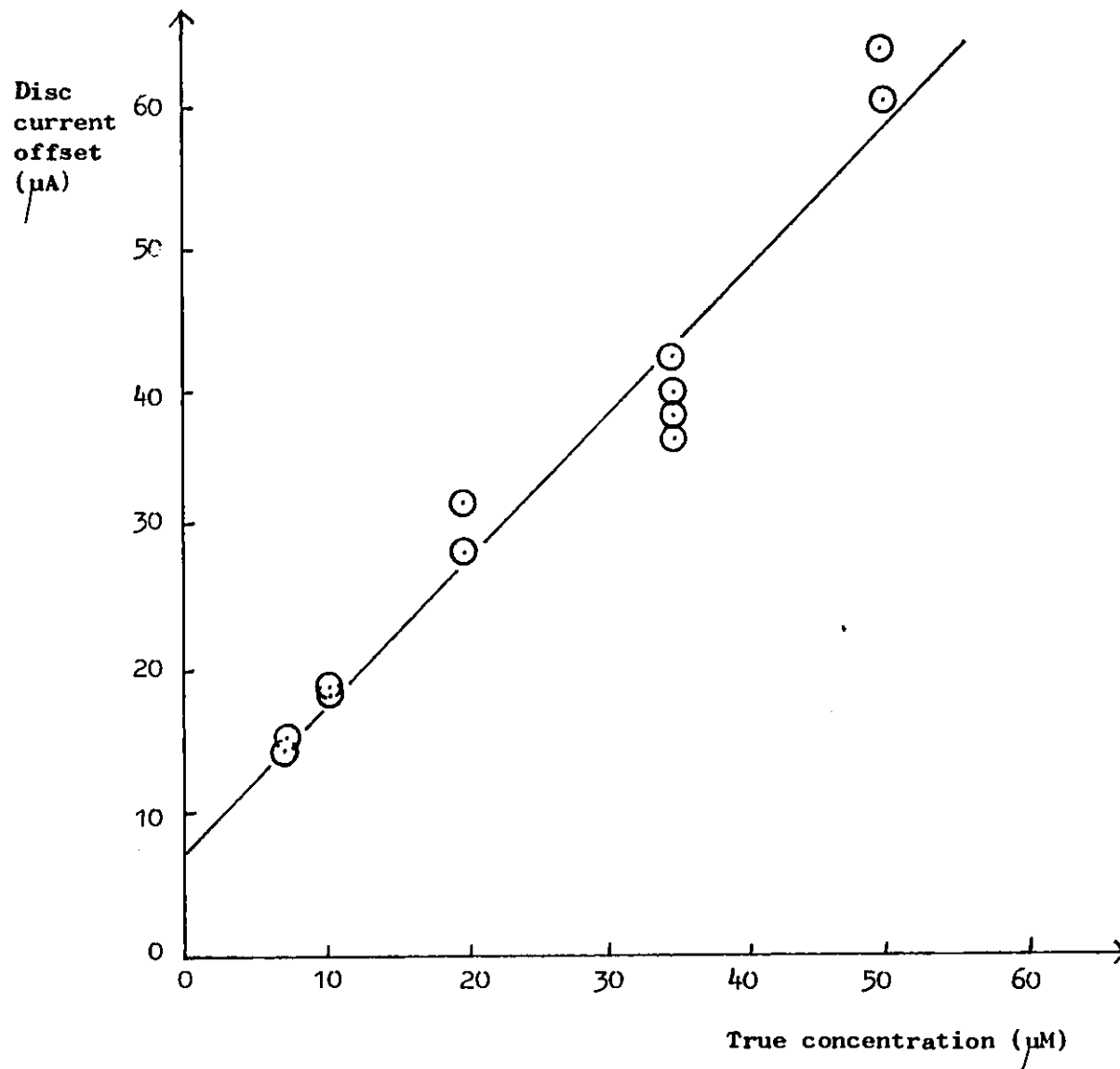


Figure 6.24

The plot of phenol concentration
against disc current offset
at pH 9.2.

True conc. (μM)	N_o	Correlation coefficient	Disc current offset (μA)	Measure conc. (μM) 1	2	Corr.
50.0	0.101	0.9976	63.8	70.5	-	-
50.0	0.113	0.9984	60.3	74.9	75.1	0.9970
	0.107	0.9980	62.1	72.7	75.1	0.9970
35.0	0.124	0.9860	36.3	49.3	50.5	0.9417
35.0	0.132	0.9899	37.9	54.9	56.4	0.9593
35.0	0.138	0.9949	39.8	60.3	62.0	0.9795
35.0	0.147	0.9990	42.5	68.5	70.7	0.9966
	0.135	0.9925	39.1	58.2	59.9	0.9693
20.0	0.175	0.9982	28.3	54.3	56.0	0.9986
20.0	0.177	0.9997	31.8	61.8	66.4	0.9972
	0.176	0.9990	30.1	58.1	61.2	0.9979
10.0	0.159	0.9999	18.7	32.6	33.7	0.9993
10.0	0.158	0.9999	19.1	33.0	34.1	0.9993
	0.158	0.9999	18.9	33.3	33.9	0.9993
7.0	0.148	0.9999	15.1	24.6	25.2	0.9993
7.0	0.147	0.9999	14.9	24.0	24.7	0.9992
	0.148	0.9999	15.0	24.3	24.9	0.9993

On plotting the true against measured concentration and taking the lower three concentrations we obtain the following values:

$$\text{Gradient} = 2.57$$

$$\text{Correlation} = 0.9992$$

$$\text{X-intercept} = -2.69 \mu\text{M}$$

$$\text{Y-intercept} = 6.91 \mu\text{M}$$

Table 6.19 Phenol titrations with varying concentrations at pH 9.2 and with a flow rate of 0.1389 ml s^{-1} . For each concentration the final is the average for that concentration. Concentration 1 is determined from the linear region of the titration curve, while concentration 2 is determined from the $(N_o - N')^{-1}$ calculations.

the concentration calculated from the disc current offset and that from $(N_0 - N')^{-1}$ calculations.

A further set of experiments were done where titration curves were recorded for 10 μM phenol over a range of flow rates from 0.0909 to 0.2310 ml s^{-1} ; the results are given in Table 6.20 and the plot of $(\text{flow rate})^{3/4}$ against disc current offset in Figure 6.25. The offset increases with flow rate once more and we obtain a reasonably straight line though at higher flow rates the plot rounds off suggesting that the reaction boundary is still not clearly defined. We also observe more consistent measurements as we have a relatively low concentration of phenol and therefore comparatively less bromide oxidation inhibition.

Again there is good agreement between the concentrations calculated from the disc current offset and those from $(N_0 - N')^{-1}$. The concentrations decrease for higher flow rates and this is most probably due to there being less time for the reaction between the bromine and the phenol and thus not all the phenol has time to react.

We are now in a position of being able to obtain a bromine number for phenol, that is the number of bromines the phenol reacts with as compared to that with arsenic, by plotting the disc current offsets for arsenic against those for phenol. We can determine the disc current offsets for As^{3+} concentrations of 50.0, 35.0, 20.0, 10.0 and 7.0 μM from the calibration results for arsenic we obtained. The results can be seen in Table 6.21 and a graph in Figure 6.26. The gradient of 1.17 indicates a bromine number of 1 for phenol, i.e. 1 bromine is substituted into the aromatic ring. Thus increasing the pH increases the rate of reaction but not by so much that further bromines are substituted. The large intercept is most probably due to

unremoved oxygen.

(ii) Autotitration at pH 9.2

Having established that at pH 9.2 faster, second order kinetics for the bromination of aromatics are achieved it was now possible to perform a satisfactory autotitration experiment. This was done with a set of phenol concentrations of 50.0, 35.0, 20.0, 10.0, 7.0, 4.0 and 2.0 μM and using an analysis gradient of $0.0134 \pm 1\%$. The results are given in Table 6.22 and a plot of the true against measured concentration in Figure 6.27. Again the calculated concentrations are too high but the values obtained from the calibration are better, having error limits of 10% and a lower limit of detection of 10 μM . Once more we observe the graph rounding off at higher concentrations suggesting that there is bromide oxidation inhibition. In Figure 6.28 there is a concentration profile for the analysis.

F Future Work

From the results obtained we can note firstly that it is possible to develop an electroanalytical system where an electrochemical experiment can be controlled by a microcomputer and an interface system. The collection efficiency and titration experiments with the arsenic-bromine system showed its ability to record titration curves, by providing and measuring voltages, from which the concentration could be calculated by determining the disc current offset. This system was then calibrated and calibration curves with correlation coefficients of 0.9998 were obtained. These curves allowed arsenic to be detected down to a lower limit of $3 \mu\text{M} \pm 3\%$. Prior to the introduction of microprocessors this procedure could only be done manually and in a batch mode but with this system it is possible to

Flow rate	N _O	Correlation coefficient	Disc current offset (μA)	Measured conc. (μM)		Corr. coef.
0.091	0.155	0.9999	16.4	38.2	37.0	0.9961
0.091	0.157	0.9999	15.9	37.6	40.1	0.9880
	0.156	0.9999	16.2	37.9	38.5	0.9921
0.118	0.155	0.9998	18.8	36.2	36.6	0.9970
0.118	0.157	0.9998	18.5	36.1	36.3	0.9971
	0.156	0.9998	18.7	36.2	36.4	0.9971
0.139	0.159	0.9999	20.1	35.0	35.1	0.9981
0.139	0.162	0.9999	19.7	34.9	35.0	0.9985
	0.160	0.9999	19.9	34.9	35.1	0.9983
0.161	0.159	0.9999	21.2	33.0	33.0	0.9998
0.161	0.158	0.9999	21.9	33.8	33.6	0.9994
	0.158	0.9999	21.6	33.4	33.3	0.0006
0.183	0.158	0.9999	24.1	33.9	33.8	0.9992
0.183	0.159	0.9999	24.5	34.8	34.5	0.9995
	0.159	0.9999	24.3	34.4	34.2	0.0004
0.208	0.158	0.9998	26.0	33.1	32.8	0.9989
0.208	0.151	0.9994	25.4	31.1	31.0	0.9952
	0.155	0.9996	25.7	32.1	31.9	0.9971
0.213	0.148	0.9995	26.5	31.1	31.0	0.9973
0.231	0.143	0.9973	26.1	27.9	27.2	0.9873
0.231	0.144	0.9977	25.9	28.0	27.0	0.9792
	0.144	0.9975	26.0	27.9	27.1	0.9833

On plotting (flow rate)^{3/4} against the disc current offset we obtain:

Gradient = 64.5

Correlation = 0.9880

X-intercept = -0.086 (ml s⁻¹)^{3/4}

Y-intercept = 5.54 μA

Table 6.20 Phenol titration results with varying flow rates, concentration 10.0 μM at pH 9.2.

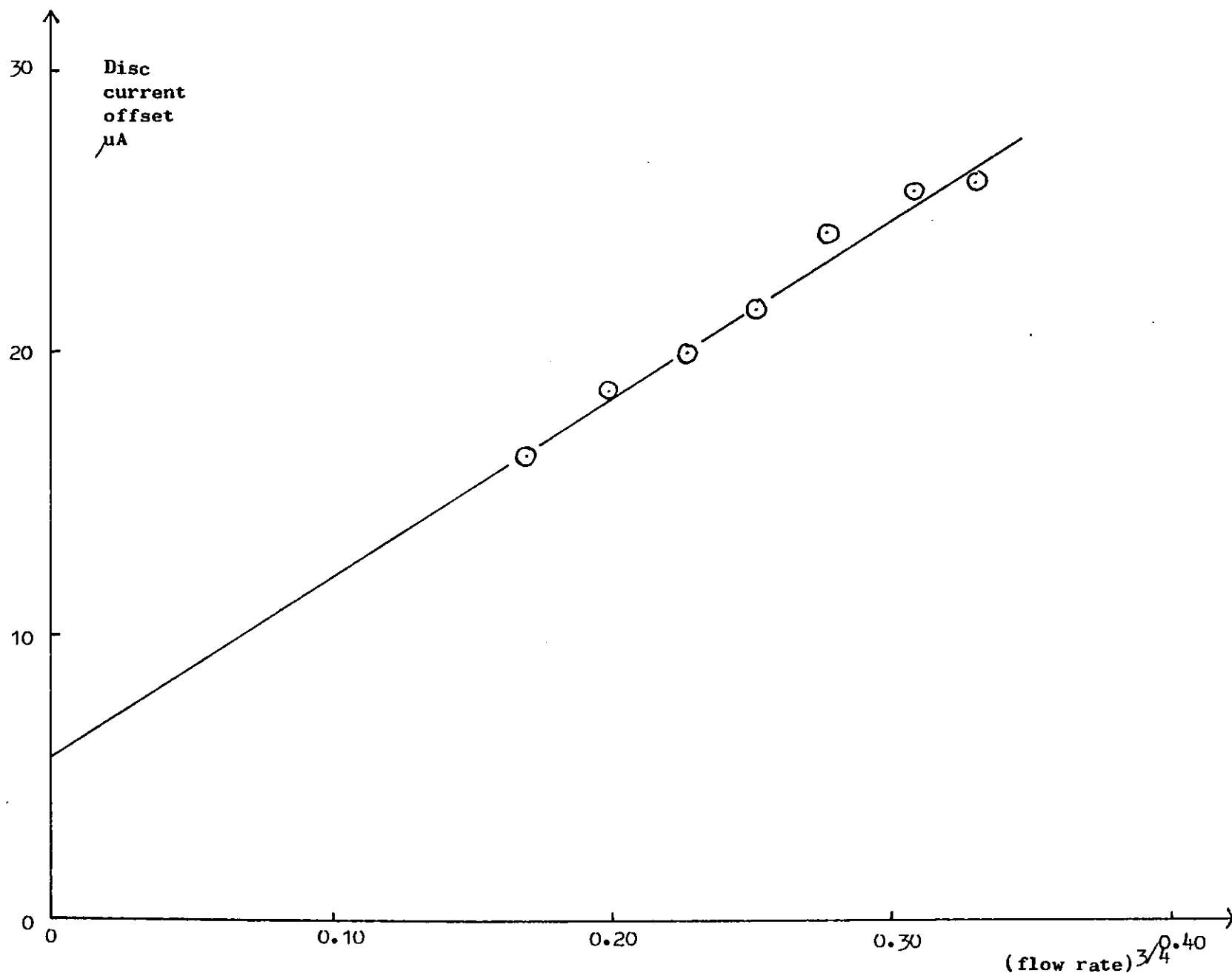


Figure 6.25 The plot of disc current offset against (flow rate) $^{3/4}$ for phenol at pH 9.2.

Concentration (μM)	Disc current offsets (μA)	
	As^{3+}	Phenol
50.0	43.7	62.1
35.0	30.5	39.1
20.0	17.3	30.1
10.0	8.6	18.9
7.0	5.9	15.0

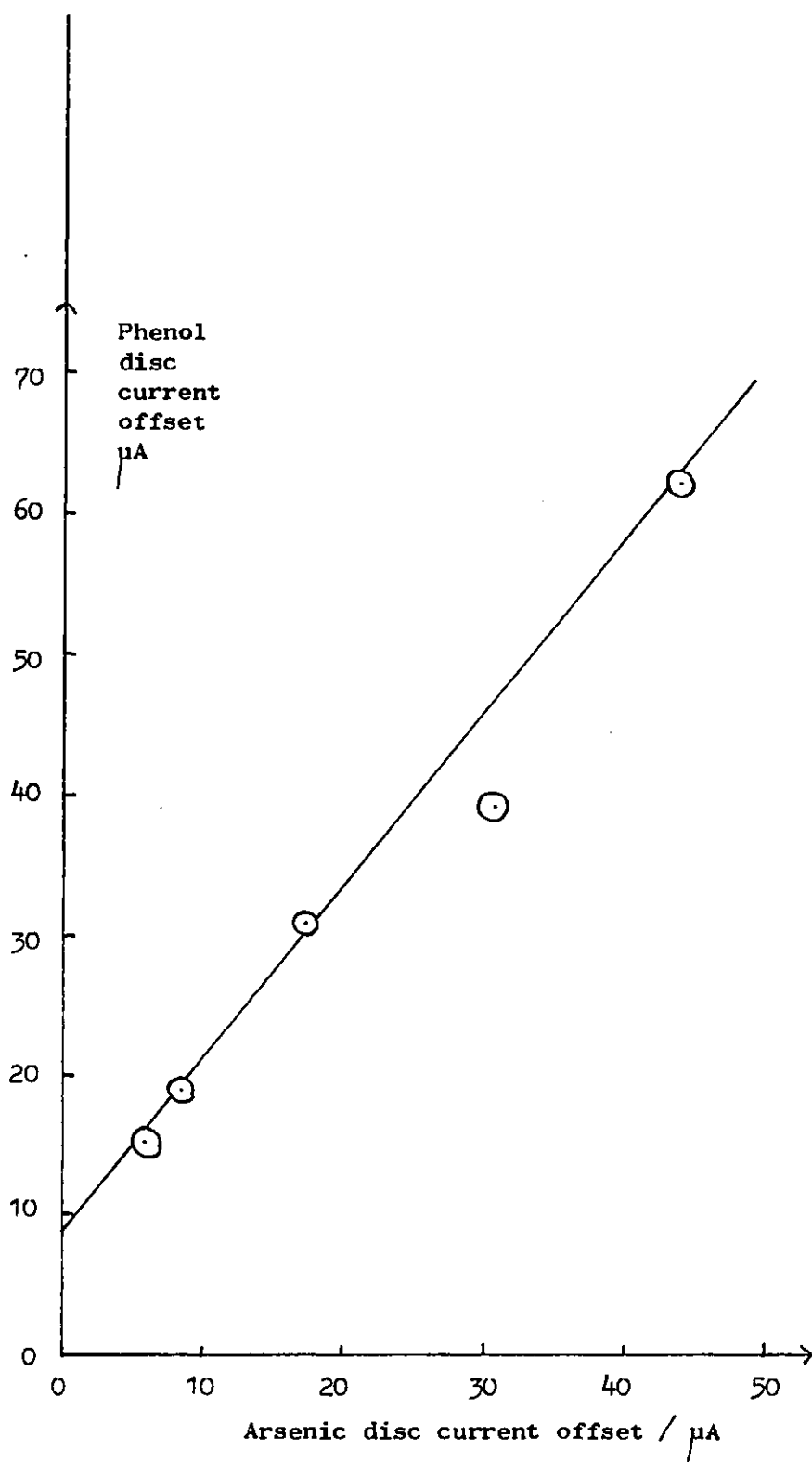
On plotting the disc current offset for As^{3+} against that for phenol we obtain:

Gradient = 1.17
Correlation = 0.9881
X-intercept = $-6.95 \mu\text{A}$
Y-intercept = $8.16 \mu\text{A}$

Table 6.21 The determination of the bromine number for phenol.

Figure 6.26 The plot of disc current offsets for arsenic against phenol at a flow rate of 0.1389 ml s^{-1}

The gradient of 1.17 indicates a bromine number of 1 for phenol.



True conc. (μM)	Disc current	Ring current	Ring/Disc ratio	Measured conc. (μM)	Conc. from calib. (μM)
4.0	9.7	0.128	0.01339	10.8	1.89 - 52.8%
7.0	15.4	0.205	0.01339	17.2	6.04 - 13.7%
10.0	20.3	0.272	0.01340	22.8	10.20 + 2.00%
20.0	36.0	0.482	0.01342	40.3	22.94 + 14.7%
35.0	53.6	0.717	0.01339	60.0	39.21 + 12.0%
50.0	69.6	0.933	0.01340	78.0	53.08 + 6.20%

On plotting true concentration against the measured concentration we obtain:

$$\text{Gradient} = 1.45$$

$$\text{Correlation} = 0.9966$$

$$\text{X-intercept} = -5.07 \mu\text{M}$$

$$\text{Y-intercept} = 7.40 \mu\text{M}$$

On plotting the true concentration against the concentration derived from the calibration curve we obtain:

$$\text{Gradient} = 1.12$$

$$\text{Correlation} = 0.9976$$

$$\text{X-intercept} = 1.10$$

$$\text{Y-intercept} = -1.23$$

Table 6.22 The autotitration of phenol at pH 9.2 with an analysis gradient of $0.0134 \pm 1\%$ and a flow rate of 0.139 ml s^{-1}

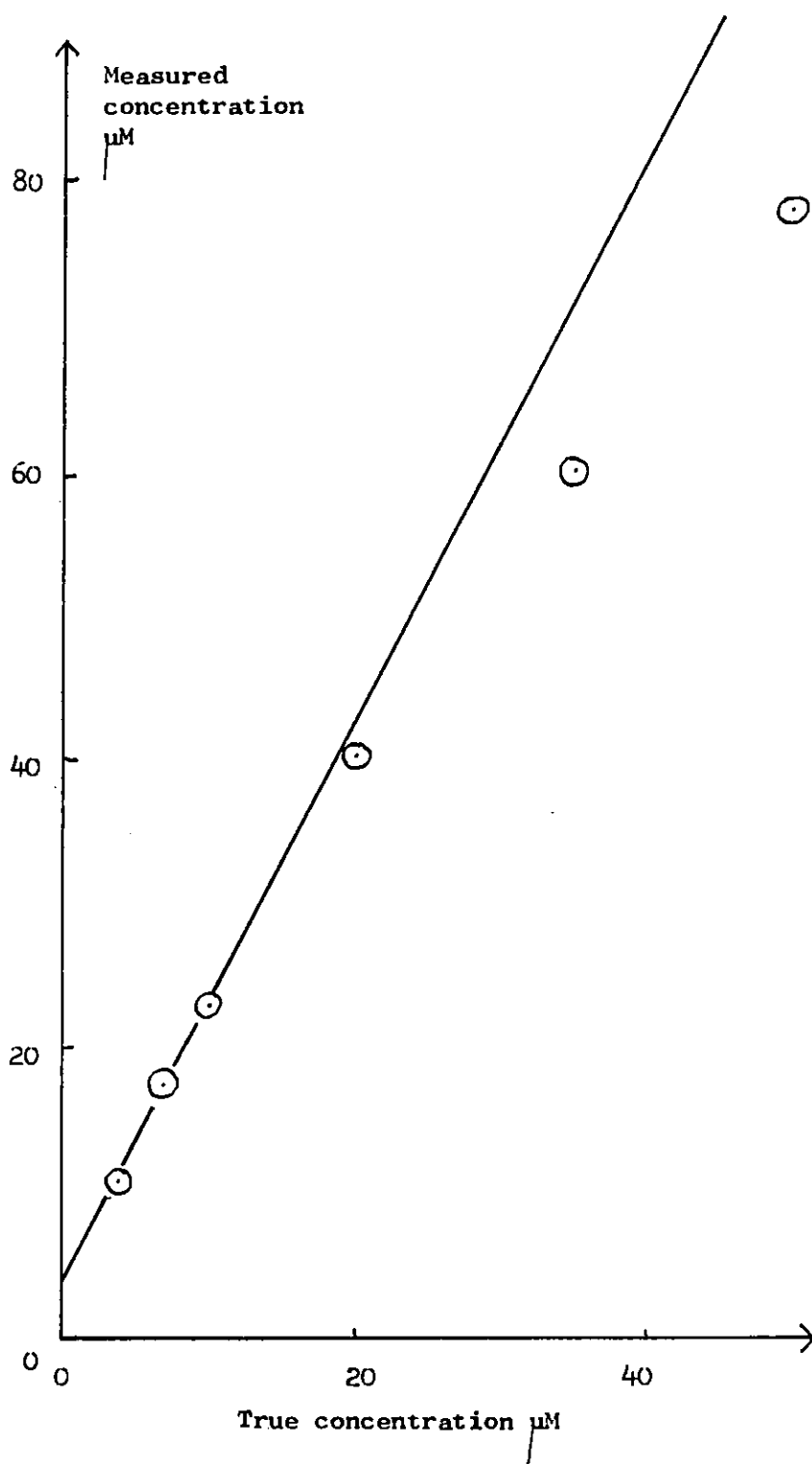


Figure 6.27 The autotitration of phenol at pH 9.2.

Concentration

187

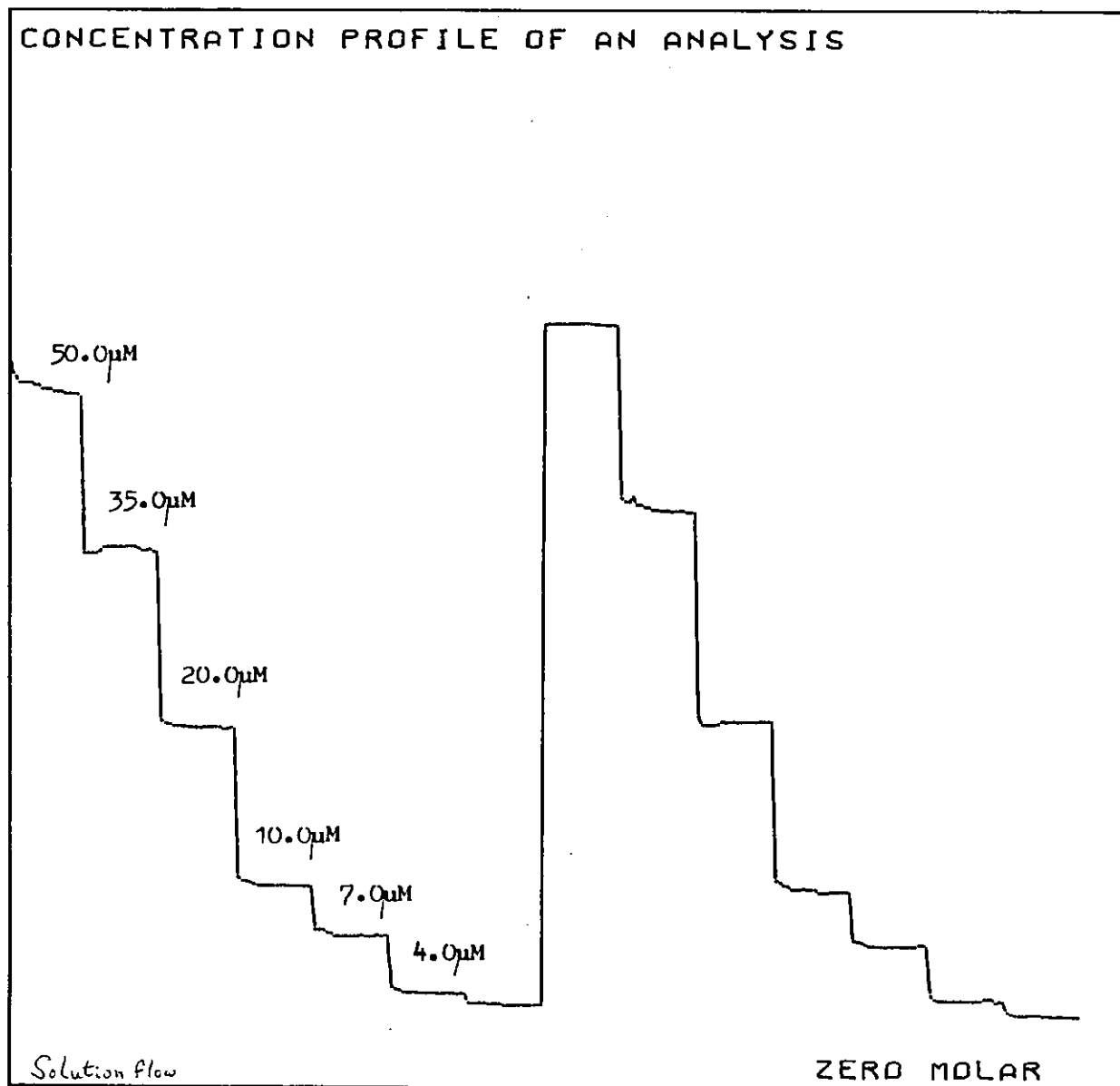


Figure 6.28

The autotitration profile
for phenol at pH 9.2.

automate the process. A program could be written to record disc current offsets for a range of standard known concentrations at a given flow rate and a calibration curve could be stored in memory. Then solutions of unknown concentration could be analyzed and their concentrations determined from the calibration curve. Furthermore the system could be recalibrated at various intervals so as to obviate any problems of electrode poisoning.

The concentration was also calculated from the disc current offset following on from the wall-jet theory. The concentrations calculated were in fairly good agreement with the true concentrations at higher concentrations but there were problems on the value of k to be taken; in addition it was found that the collection efficiency varied with the flow rate as the result of the finite size of the cell.

Since this analysis process is rather slow because complete titration curves must be recorded the digital autotitration experiment was developed; calibration curves were measured from which concentrations of unknown solutions could be determined with a lower detection limit for arsenic of $5 \pm 3\% \mu\text{M}$. An analysis point can be measured every 2s and such a system could be used in analyzing the elutant from a liquid chromatogram. This delay time is inherent to the system as was found by the rise time experiments and is a function of the time taken for the ring current to stabilize. It was found that this time was a function of the flow rate such that high flow rates required the smallest time delay. However at high flow rates there is a breakdown in hydrodynamics in the cell - thus a compromise flow rate must be established.

When titrating the aromatics phenol and p-cresol it was found

that non-ideal titration curves were obtained as the consequence of insufficiently fast kinetics between the bromine and the aromatics; titrations were possible with a lower limit of 10 μM for phenol which is in reasonable agreement with Rauwel and Thevenot (40) who recorded a lower limit of 7 μM for phenol. However autotitrations were only possible at higher concentrations, greater than 20 μM , using high, insensitive values for the analysis gradient. Titration curves were then recorded at a higher pH value (9.2 from 0.0) where it was found that faster kinetics gave rise to better titration curves. We were now able to perform autotitrations down to 4.0 μM but we found there were deviations at higher concentrations due to the bromide oxidation inhibition at higher phenol concentrations - this problem arose at concentrations above 20 μM . Thus when analyzing solutions above 20 μM a medium of pH 0 should be used and when below 20 μM a medium of pH 9.2. However the Laboratory of the Government Chemist wish to be able to determine concentrations at least two orders of magnitude lower. One way we might improve our system would be to use ADC boards with an integration ADC which is the most accurate method. Although it is the slowest this would not matter since we must wait for the ring current to stabilize.

Future work would also include the development of a better pumping system; already mentioned has been the use of a BCD output balance for determining flow rates. We should also like to be able to produce a pulse-free solution flow so as to be able to dispense with the resistive coil tube and capacitative glass bulb. This would also make deoxygenation easier since there is less opportunity for oxygen to be re-introduced. Such a system could be developed using syringe drives which could be controlled from the microcomputer via the

interface. With the additional use of solenoid valves, which control the solution flow and which in turn are controlled from the microcomputer via the power rack, the determination of calibration curves followed, by the analysis of unknown solutions, could be fully automated.

G Conclusions

Although the apparatus developed was unable to achieve the detection limits required by the Laboratory of the Government Chemist, we have seen that electroanalytical experiments can be readily automated using a microprocessor and that this can be done with great versatility. Using the titration unit a collection efficiency and titration experiment can easily be done; by simply changing parameters in the program the experimental conditions can be readily altered; by simply changing the program we can then perform the rise time experiment.

Thus it can be seen that there is much potential for automating both analytical and investigative experiments. For example, proteins could be detected which have previously been separated on a chromatographic column. This separation occurs at various pH values although the titration must take place at pH 9.2. Using the microprocessor and the interface rack it would be possible to perform the titration but also to check that the pH of the elutant and the solution to be analyzed are always at the correct pH values. Once again, using solenoid valves and solution reservoirs the pHs can be maintained.

By changing the electrochemical unit different experiments can then be performed. An example would be anodic stripping voltammetry, a

technique that has been studied in this laboratory (27), in which positively charged species, usually a metal ion, is plated on to an electrode from which it is then stripped by changing the potential in the anodic direction. This results in a burst of current which can be measured. Selectivity can be achieved when more than one metal is present by selecting a deposition potential and so plating only one metal, or, if the metals have differing stripping potentials, by looking at the various stripping peaks. This experiment could be automated by potentiostatting the electrode at various potentials and then measuring a succession of currents. Another related experiment is anodic stripping voltammetry with collection in which the stripped metal ions are collected at a downstream electrode.

Further afield microelectrode systems could be automated by microprocessors such as in vivo studies; for example, continuously monitoring electrochemical changes in a rat's brain or the human stomach.

Appendix One - Useful Mathematical Relations

Most of these functions are taken from the Handbook of Mathematical Functions (30).

- (1) The Laplace transform $f(s)$ of a function $F(t)$ is defined as

$$\bar{f}(s) = \mathcal{L} F(t) = \int_0^{\infty} e^{-st} F(t) dt \quad (\text{A1.1})$$

$$F(t) = \mathcal{L}^{-1} \bar{f}(s) \quad (\text{A1.2})$$

The convolution theorem states that

$$\mathcal{L}^{-1} f(s)g(s) = \int_0^t F(u)G(t-u)du \quad (\text{A1.3})$$

(2) The Gamma function $\Gamma(z) = \int_0^{\infty} t^{z-1} e^{-t} dt \quad (\text{A1.4})$

- (3) The Beta function

$$B(a,b) = \frac{\Gamma(a)\Gamma(b)}{\Gamma(a+b)} = B(b,a) \quad (\text{A1.5})$$

- (4) The incomplete Beta function

$$B_x(a,b) = \int_0^x t^{a-1}(1-t)^{b-1}dt \quad (\text{A1.6})$$

(5) $I_x(a,b) = B_x(a,b)/B(a,b) = 1 - I_{1-x}(b,a) \quad (\text{A1.7})$

$$(6) \quad F(x) = \frac{1}{B(1/3, 2/3)} \int_0^x \frac{dt}{t^{2/3}(1+t)} \quad (A1.8)$$

$$G(x) = \frac{1}{B(2/3, 1/3)} \int_0^x \frac{dt}{t^{1/3}(1+t)} \quad (A1.9)$$

$$\text{and} \quad F(x) = 1 - G(1/x) \quad (A1.10)$$

(7) In this section we show that

$$I_x(2/3, 1/3) = G(x/1-x) \quad (A1.11)$$

From the equations A1.5, A1.6 and A1.7

$$I_x(2/3, 1/3) = \frac{1}{B(2/3, 1/3)} \int_0^x t^{-1/3}(1-t)^{-2/3} dt$$

Substituting $t = \zeta / (1+\zeta)$

this becomes

$$\begin{aligned} I_x(2/3, 1/3) &= \frac{1}{B(2/3, 1/3)} \int_0^{\frac{x}{1-x}} \frac{d}{1^{1/3}(1+)} \quad (A1.12) \\ &= G(x/1-x) \end{aligned}$$

Appendix Two Derivation of Equation 2.27

Consider the normalized variables

$$\chi = \left(\frac{9}{8}\right)^{1/3} \left(\frac{C}{D}\right)^{1/3} \rho^{7/8} z$$

$$\xi_n = \rho^{9/8} - \left(\frac{r_{n-1}}{r_3}\right)^{9/8}$$

$$\chi_n = \frac{c_\infty - c_n}{c_\infty} \quad (2.26)$$

The rules for partial differentiation show that, since that $\chi = f(z, \rho)$

$$\left(\frac{\partial c}{\partial z}\right)_\rho = \left(\frac{9}{8}\right)^{1/3} \left(\frac{C}{D}\right)^{1/3} \rho^{-7/8} \left(\frac{\partial c}{\partial \chi}\right)_\rho \quad (A2.1)$$

$$\begin{aligned} \left(\frac{\partial c}{\partial \rho}\right)_z &= \left(\frac{\partial c}{\partial \rho}\right)_\chi + \left(\frac{\partial c}{\partial \chi}\right)_\rho \cdot \left(\frac{\partial \chi}{\partial \rho}\right)_z \\ &= \left(\frac{\partial c}{\partial \rho}\right)_\chi - \frac{7}{8} \left(\frac{9}{8}\right)^{1/3} \cdot \left(\frac{C}{D}\right)^{1/3} \cdot \frac{z}{\rho^{5/4}} \cdot \left(\frac{\partial c}{\partial \chi}\right)_\rho \end{aligned} \quad (A2.2)$$

Substituting equation A2.1 into A2.2 gives

$$\left(\frac{\partial c}{\partial \rho}\right)_z = \left(\frac{\partial c}{\partial \rho}\right)_\chi - \frac{7}{8} \frac{z}{\rho} \left(\frac{\partial c}{\partial z}\right)_\rho$$

Equation 2.25

$$\frac{z}{\rho^{11/4}} \left(\frac{\partial c}{\partial \rho}\right)_z + \frac{7}{8} \frac{z^2}{\rho^{15/4}} \left(\frac{\partial c}{\partial z}\right)_\rho = \frac{D}{C} \frac{\partial^2 c}{\partial z^2} \quad (2.25)$$

becomes

$$\frac{z}{\rho^{11/4}} \left(\frac{\partial c}{\partial \rho} \right)_\chi = \frac{D}{C} \frac{\partial^2 c}{\partial z^2} \quad (\text{A2.3})$$

and with the normalized variables of equation 2.26 it then becomes:

$$\chi \frac{\partial y_n}{\partial \xi^n} = \frac{\partial^2 y_n}{\partial \chi^2} \quad (2.27)$$

Appendix Three - Evaluation of Equation 2.62

The collection efficiency, N_o , for the WJRDE is given by:

$$N_o = \frac{2\theta_1^{-2/3}}{3} \int_0^{\theta_3} \xi_3^{-1/3} I_{\frac{\theta_1}{1-\xi_3}}(2/3, 1/3) d\xi_3 \quad (2.62)$$

Integrating by parts and using the fact that $\theta_1 + \theta_2 + \theta_3 = 1$ we arrive at:

$$N_o = \frac{\theta_3}{\theta_1} \frac{2/3}{I_{\frac{\theta_1}{1-\theta_3}}(2/3, 1/3)} - \frac{1}{B(2/3, 1/3)} \int_0^{\theta_3} \frac{\xi_3^{2/3} d\xi_3}{(\theta_2 + \theta_3 - \xi_3)^{2/3} (1 - \xi_3)} \quad (A3.1)$$

Using the substitution $\xi = \xi_3^{-1}$, the integral becomes

$$\begin{aligned} & \int_{\theta_3^{-1}}^{\infty} \frac{d\xi}{[(\theta_2 + \theta_3)\xi - 1]^{2/3} (\xi - 1)} \\ &= \int_{\theta_3^{-1}}^{\infty} \frac{d\xi}{[(\theta_2 + \theta_3)\xi - 1]^{2/3}} \left[\frac{1}{(\xi - 1)} - \frac{1}{\xi} \right] \quad (A3.2) \end{aligned}$$

This may be evaluated as two separate integrals. Taking the first and putting $t = 1/(\xi - 1)$ it becomes

$$\int_0^{\frac{\theta_3}{\theta_1 + \theta_2}} \frac{dt}{t^{1/3} [(\theta_2 + \theta_3) - \theta_1 t]^{2/3}}$$

and further substitution with $\phi = \theta_1 t / (\theta_2 + \theta_3)$ yields

$$\frac{1}{\theta_1^{2/3}} \int_0^{\frac{\theta_1 \theta_3}{(\theta_1 + \theta_2)(\theta_2 + \theta_3)}} \frac{d\phi}{\phi^{1/3} (1-\phi)^{2/3}} \quad (A3.3)$$

an incomplete Beta function (equation A1.6). The second integral uses the substitution $\phi = 1/\zeta(\theta_2 + \theta_3)$ to give

$$\int_0^{\frac{\theta_3}{\theta_2 + \theta_3}} \frac{d\phi}{\phi^{1/3} (1-\phi)^{2/3}} \quad (A3.4)$$

Combining equations A3.3 and A3.4 we arrive at equation A6.2 which is therefore

$$B(2/3, 1/3) \left[\theta_1^{-2/3} I \frac{\theta_1 \theta_3}{(\theta_1 + \theta_2)(\theta_2 + \theta_3)} (2/3, 1/3) - I \frac{\theta_3}{\theta_2 + \theta_3} (2/3, 1/3) \right]$$

The expression for N_0 is therefore

$$\begin{aligned}
N_o &= I \frac{\theta_3}{\theta_2 + \theta_3} (2/3, 1/3) + \frac{\theta_3}{\theta_1}^{2/3} I \frac{\theta_1}{\theta_1 + \theta_2} (2/3, 1/3) \\
&\quad - \theta_1^{-2/3} I \frac{\theta_1 \theta_3}{(\theta_1 + \theta_2)(\theta_2 + \theta_3)} (2/3, 1/3) \quad (A3.5)
\end{aligned}$$

Using the fact that

$$I_x(2/3, 1/3) = G(x/1-x) \quad (A1.11)$$

this can be written as

$$N_o = G\left(\frac{\theta_3}{\theta_2}\right) + \left(\frac{\theta_3}{\theta_1}\right)^{2/3} G\left(\frac{\theta_1}{\theta_2}\right) - \theta_1^{-2/3} G\left(\frac{\theta_1 \theta_3}{\theta_2}\right) \quad (2.63)$$

Appendix Four - Differentiation of Equation 2.90

The equation to be differentiated is

$$\frac{M}{i_D} \theta_J^{-1/3} = \frac{-3\theta_1^{2/3}}{2} \frac{\partial}{\partial \theta_J} \left[G\left(\frac{\theta_J}{\theta_2}\right) + \left(\frac{\theta_J}{\theta_1}\right)^{2/3} G\left(\frac{\theta_1}{\theta_2}\right) - \left(\frac{\theta_1 + \theta_2 + \theta_J}{\theta_1}\right)^{2/3} G\left(\frac{\theta_1 \theta_J}{\theta_2(\theta_1 + \theta_2 + \theta_J)}\right) \right] \quad (2.89)$$

From Appendix 1

$$G(x) = \frac{1}{B(2/3, 1/3)} \int_0^x \frac{dt}{t^{1/3}(1+t)} \quad (A1.9)$$

$$\frac{dG}{dx} = \frac{1}{B(2/3, 1/3)} \frac{1}{x^{1/3}(1+x)} \quad (A4.1)$$

Taking the equation 2.90 in constituent parts

$$(a) \quad \frac{\partial}{\partial \theta_J} G\left(\frac{\theta_J}{\theta_2}\right) = \frac{1}{B(2/3, 1/3)} \frac{\theta_2^{1/3}}{\theta_J^{1/3}(\theta_2 + \theta_J)} \quad (A4.2)$$

$$(b) \quad \frac{\partial}{\partial \theta_J} \left[\left(\frac{\theta_J}{\theta_1}\right)^{2/3} G\left(\frac{\theta_1}{\theta_2}\right) \right] = \frac{2}{3\theta_1^{2/3}\theta_J^{1/3}} G\left(\frac{\theta_1}{\theta_2}\right) \quad (A4.3)$$

$$\begin{aligned}
(c) \quad \frac{\partial}{\partial \theta_J} & \left[\left(\frac{\theta_1 + \theta_2 + \theta_J}{\theta_1} \right)^{2/3} G \left(\frac{\theta_1 \theta_J}{\theta_2 (\theta_1 + \theta_2 + \theta_J)} \right) \right] \\
&= - \frac{2}{3 \theta_1^{2/3} (\theta_1 + \theta_2 + \theta_J)^{1/3}} G \left(\frac{\theta_1 \theta_J}{\theta_2 (\theta_1 + \theta_2 + \theta_J)} \right) \\
&\quad - \frac{1}{B(2/3, 1/3)} \frac{\theta_2^{1/3}}{\theta_J^{1/3} (\theta_1 + \theta_2 + \theta_J)} \quad (A4.4)
\end{aligned}$$

Substituting these relations into equation 2.89 gives

$$\frac{M}{i_D} = - G \left(\frac{\theta_1}{\theta_2} \right) + \left(\frac{\theta_J}{\theta_1 + \theta_2 + \theta_J} \right)^{1/3} \cdot G \left(\frac{\theta_1 \theta_J}{\theta_2 (\theta_1 + \theta_2 + \theta_J)} \right) \quad (2.90)$$

Appendix Five - The Equations of Linear Regression

For $y = mx + c$

$$\text{Gradient } m = \frac{\sum xy - \frac{\sum x \sum y}{N}}{\sum x^2 - \frac{(\sum x)^2}{N}}$$

$$\text{Intercept } c = \frac{1}{N} (\sum y - m \sum x)$$

$$\text{Correlation coefficient } r = m \frac{\sigma_x}{\sigma_y}$$

Standard deviations

$$\sigma_x^2 = \frac{\sum x^2}{N} - \left(\frac{\sum x}{N} \right)^2$$

$$\sigma_y^2 = \frac{\sum y^2}{N} - \left(\frac{\sum y}{N} \right)^2$$

$$\sigma_m^2 = \frac{1}{N-2} \left(\frac{\sigma_y^2}{\sigma_x^2} - m^2 \right)$$

$$\sigma_c = \sigma_m \left(\frac{\sum x^2}{N} \right)^{1/2}$$

Appendix 6-1 Theoretical calculations program

```

5 HJ=0
20 DIM RJ(40),BJ(40),N(40),MI(40),ID(40),IR(40)
30 GRAPHO
40 PRINT"CALCULATION OF COLLECTION EFFICIENCY,NO"
50 PRINT"THE THREE RADII VALUES (uM)"
60 INPUT"R1";R1
70 INPUT"R2";R2
80 INPUT"R3";R3
90 A=(R2/R1)^(9/8)-1
100 B=(R3/R1)^(9/8)-(R2/R1)^(9/8)
110 B2=B^(2/3)
120 X=A/B
130 GOSUB 250
140 AB=F
150 X=A
160 GOSUB 250
170 AA=F
180 X=(A/B)*(1+A+B)
190 GOSUB 250
200 A2=F
210 NO=1-AB+B2*(1-AA)-((1+A+B)^(2/3))*(1-A2)
220 PRINT"B2/3 IS";B2
230 PRINT"COLLECTION EFFICIENCY IS";NO
240 GOTO 270
250 F=(0.1378322239*LOG(((1+X^(1/3))^3)/(1+X)))+(0.4774648293*ATN((2*X^(1/3)-1)/(SQR(3))))+1/4
260 RETURN
270 INPUT"NUMBER OF GRADIENTS REQUIRED";N
280 D=N-1
290 L=R3-R2:ST=L/D
300 PRINT"      Rj          Bj"
310 FOR I=0 TO D
320 RJ(I)=R2+I*ST
330 BJ(I)=(RJ(I)/R1)^(9/8)-((R2/R1)^(9/8))
340 PRINT RJ(I),BJ(I)
350 NEXT I
360 INPUT"CONTINUE";G
370 IF G>0 THEN 20
380 PRINT"      Bj          N'          M/ID"
390 X=A:GOSUB 250:A3=F
400 FOR I=1 TO D
410 X=A/BJ(I)
420 GOSUB 250
430 AJ=F
440 X=((1+A+BJ(I))*A)/BJ(I)
450 GOSUB 250
460 BJ=F
470 N(I)=1-AJ-((1+A)/(1+A+BJ(I))^(1/3))*(1-BJ)
480 X=((1+A+BJ(I))*A)/BJ(I)
490 GOSUB 250
500 BI=F
510 MI(I)=1-A3-((BJ(I)^(1/3))/(1+A+BJ(I))^(1/3))*(1-BI)
520 PRINT BJ(I),N(I),MI(I)
530 NEXT I

```

```

540 PRINT
555 INPUT"CONCENTRATION OF SAMPLE";CN
556 INPUT"VOLUME FLOW RATE";VF
560 PRINT"    ID(uA)          IR(uA)"
563 M=CN*1.6*1*2*96487*6.957*4.579*10^(-4)*5.4*0.4549*VF^(0.75)
570 FOR I=1 TO D
580 H=1/MI(I):ID(I)=H*M
590 IR(I)=ID(I)*N(I)
600 PRINT ID(I)*1000,IR(I)*1000
610 NEXT I
620 PRINT
630 PRINT"FOR A CONCENTRATION OF";CN;" Molar"
640 INPUT"CONTINUE";G
650 IF G>0 THEN 20
660 GRAPH1
665 IF HJ=100 THEN 720
666 HJ=100
670 CALL"RESOLUTION",0,2
680 CALL"OFFSET",0,-10
690 CALL"PLOT",310,0,2
700 CALL"LINE",0,0,2
710 CALL"LINE",0,190,2
720 FOR I=1 TO D
730 P=ID(I)*6*1000:Q=IR(I)*180*1000
740 CALL"PLOT",P,Q,2
750 NEXT I
760 J=P+100
770 K=Q+(NO*180*100)/6
780 CALL"PLOT",P,Q,2
790 CALL"LINE",J,K,2
800 GRAPH0
810 CALL"PLOT",0,0,2
820 ER=120
830 ET=ER*NO*180/6
840 CALL"LINE",ER,ET,2

```

Appendix 6-2 The cleaning program

```
10 CALL"IDENT",0,0
12 CALL"TIMER",1,1000
13 CALL"SETTR",12,1,0,1
20 CALL"WRIT16",1,1,0,0
30 CALL"WAIT",1000
60 INPUT"HOW MANY CYCLES REQUIRED";C
70 FOR I=1 TO C
80 CALL"WRIT16",1,1,0,1550
90 FOR J=1 TO 10
100 CALL"STROBE",12,1,4
101 CALL"SWAIT",12,1
110 NEXT J
120 PRINT"END OF  FIRST PART"
130 CALL"WRIT16",1,1,0,950
140 FOR K=1 TO 30
150 CALL"STROBE",12,1,4
151 CALL"SWAIT",12,1
160 NEXT K
170 PRINT"END OF SECOND PART"
180 CALL"WRIT16",1,1,0,-200
190 FOR L=1 TO 30
200 CALL"STROBE",12,1,4
201 CALL"SWAIT",12,1
210 NEXT L
220 PRINT"END OF  THIRD PART"
230 PRINT"THIS IS THE END OF";I;"CYCLE"
240 NEXT I
250 PRINT"END OF CLEANING "
260 CALL"WRIT16",1,1,0,0
270 END
```

Appendix 6-3 A titration program

```

10 REM T
20 POKE&39EA,6
30 ZZ=0
40 RA=0
50 ZX=0
60 FF=0
70 VV=0
80 CALL"IDENT",0,0
90 CALL"WRIT16",1,1,0,0
100 CALL"WAIT",1000
110 CALL"TIMER",1,1000
120 CALL"SETTR",12,1,0,1
130 CALL"SETTR",4,1,1,0
140 CALL"XSET",1,0,12,0
150 CALL"XSPEED",1
160 CALL"XMODE",1,1
170 DIM
Y(1100),X(1100),R(1100),G(100),H(100),IR(100),N(100),M(30),W(30),YY(300)
180 PRINT FRE(1)
190 CO$="10uM PHENOL,pH9.2"
200 PRINT#2,CHR$(14)"TITRATION CURVE VALUES"
210 PRINT#2,
220 PRINT#2
230 PRINT#2,CO$
240 PRINT#2
250 CALL"RESOLUTION",0,2
260 CALL"OFFSET",0,-15
270 CALL"COLOUR",3,200
280 CALL"COLOUR",1,150
290 CALL"COLOUR",2,100
300 CALL"PLOT",0,-15,2
310 CALL"LINE",0,175,2
320 CALL"PLOT",0,0,2
330 CALL"LINE",310,0,2
340 CALL"XLINE",1,-2048,-1800,0
350 CALL"XLINE",1,2047,-1800,1
360 CALL"XLINE",1,-2048,-2048,0
370 CALL"XLINE",1,-2048,2047,1
390 X$="DISC CURRENT( $\mu$ A)"
400 Y$="RING CURRENT( $\mu$ A)"
410 CALL"XLINE",1,0,-1950,0
420 CALL"XCHAR",1,VARADR(X$)
430 CALL"XSET",1,0,12,6
440 CALL"XLINE",1,-1900,0,0
450 CALL"XCHAR",1,VARADR(Y$)
460 CALL"XSET",1,0,12,0
470 GRAPH1
480 IF ZZ=9 THEN 490
490 DC=90
500 DC$=" ^---$ (DC)"
510 SS=5
520 SZ$=STR$(SS)
530 NE=2
540 CP=49

```

```

550 FY=4
560 CALL"XLINE",1,-1700,1900,0
570 CALL"XCHAR",1,VARADR(CO$)
580 FD$="FINAL DISC CURRENT(uA)="
590 SS$="STEP SIZE(uA)="
600 CALL"XLINE",1,-1700,1750,0
610 CALL"XCHAR",1,VARADR(FD$)
620 CALL"XLINE",1,200,1750,0
630 CALL"XCHAR",1,VARADR(DC$)
640 CALL"XLINE",1,-1700,1600,0
650 CALL"XCHAR",1,VARADR(SS$)
660 CALL"XLINE",1,-550,1600,0
670 CALL"XCHAR",1,VARADR(SZ$)
680 CALL"XSPEED",1
690 IF FY=0 THEN FY=1
700 DC=DC*10
710 SS=SS*10
720 FX=DC/200
730 GOTO 750
740 INPUT"Offset obtained from the collection      efficiency curve at
this flow rate(uA)";CE
750 CE=0
760 INPUT"RING";RV
770 CALL"WRIT16",1,1,2,RV
780 JJ=0
790 LC=40
800 CL=800
810 FOR N=1 TO 250
820 CALL"WRIT16",1,1,0,0
830 CALL"INADC",1,VARADR(J)
840 J=-J
850 JJ=JJ+J
860 NEXT N
870 K=JJ/250
880 FOR I=0 TO DC STEP DC/10
890 CALL"WRIT16",1,1,0,I
900 CALL"STROBE",12,1,4
910 CALL"SWAIT",12,1
920 NEXT I
930 A=1: SX=0: SY=0: XY=0: X2=0: Y2=0
940 FOR I=DC TO 0 STEP -SS
950 GOSUB 1220
960 II=-2
970 IF FF=0 THEN 1050
980 IF (J-K)<LC THEN 1050
990 IF (J-K)>CL THEN 1050
1000 II=-3
1010 A=A+1
1020 SX=SX+I: SY=SY+J
1030 XY=XY+(I*J)
1040 X2=X2+(I*I): Y2=Y2+(J*J)
1050 Y(I)=(J-K)/4.385508754
1060 FF=1
1070 Y(I)=Y(I)/10

```

```

1080 J=INT((J-K)/FY)
1090 X(I)=I
1100 X(I)=X(I)/10
1110 CALL "PLOT",X,J,II
1120 X=X*20-2048
1130 J=J*20-1800
1140 IF VV=0 THEN 1170
1150 CALL "XLINE",1,X,J,1
1160 GOTO 1190
1170 CALL "XLINE",1,X,J,0
1180 VV=1
1190 IF X=0 THEN 1200
1200 NEXT I
1210 GOTO 1360
1220 CALL "WRIT16",1,1,0,I
1230 MT=2
1240 FOR RW=1 TO MT
1250 CALL "STROBE",12,1,4
1260 CALL "SWAIT",12,1
1270 NEXT RW
1280 M=0
1290 FOR L=1 TO CP
1300 CALL "INADC",1,VARADR(J)
1310 J=-J
1320 M=M+J;NEXT L
1330 J=M/CP
1340 X=INT(I/FX)
1350 RETURN
1360 AS=0:T=0
1370 FOR I=0 TO 60
1380 IF Y(I)=0 THEN 1410
1390 T=T+Y(I)
1400 AS=AS+1
1410 NEXT I
1420 RA=999
1430 E=T/AS
1440 A=A-1
1450 IF A<4 THEN 1870
1460 M=((XY-(SX*SY/A))/(X2-(SX*SX/A)))
1470 C=(SY-M*SX)/A
1480 XS=SQR((X2/A)-(SX*SX/(A*A)))
1490 YS=SQR((Y2/A)-(SY*SY/(A*A)))
1500 R=M*XS/YS
1510 GR=M/4.38551
1520 SM=((YS*YS)/(XS*XS)-(M*M))/(A-2)
1530 IF SM>0 THEN 1560
1540 ZX=99
1550 SM=ABS(SM)
1560 SM=SQR(SM)
1570 PRINT "S. DEV. OF M =";SM
1580 N$="
1590 PLOT 4,48,N$
1600 PLOT 4,48,"COLL. EFF. =" +STR$(GR)
1610 PM=GR

```

```

1620 PLOT 4,45,N$
1630 PLOT 4,45,"CORR. COEFF.="+STR$(R)
1640 X=(K-C)/M
1650 X2=X
1660 TX=INT(X/FX)
1670 INPUT"CONTINUE";G
1680 IF G>0 THEN 4490
1690 CALL"PLOT",TX,0,-1
1700 X1=X
1710 Y=M*2000+C
1720 Y=INT(Y-K)/FY
1730 XG=INT(2000/FX)
1740 CALL"LINE",XG,Y,-1
1750 PRINT"X OFFSET =" ;X2/10;" uA"
1760 IF ZX=99 THEN PRINT"SM WAS NEGATIVE"
1770 PRINT"Y OFFSET IS";E;"uA"
1780 PLOT 4,42,N$
1790 PLOT 4,42,"X OFFSET      =" +STR$(X2/10)+" uA"
1800 UB=X2/10
1810 PZ=(X2/10)+(E/GR)
1820 PLOT 4,39,N$
1830 PLOT 4,39,"ADJUSTED X OFFSET="+STR$(PZ)+"
1840 II=PZ/1000-CE/1000
1850 GOTO 1870
1860 II=X2/10000-CE/1000
1870 INPUT"TIME TAKEN FOR 10 ml (s)";FR
1880 FR=10/FR
1890 PRINT FR
1900 INPUT"TEMPERATURE";TE
1910 IF A<4 THEN 1950
1920 CC=II*GR/(NE*FR^0.75*1.6*0.86*96487*6.957*4.579*10^(-
4)*5.4*0.4549*0.193)
1930 PLOT 4,36,N$
1940 PLOT 4,36,"CONC OF As3+=" +STR$(CC)+" Molar"
1950 CALL"PLOT",0,0,1
1960 GX=2000:GY=2000*0.0134*4.38551*FX/FY
1970 CALL"LINE",GX,GY,2
1980 IF A<4 THEN 2810
1990 INPUT"CONTINUE";G
2000 IF G>0 THEN 4490
2010 PR=GR*6/7
2020 FOR W=1 TO 8
2030 U=W/10
2040 N(W)=PR*U
2050 N(W)=N(W)*6/7
2060 H(W)=N(W)*2000/7
2070 RT=2000/7
2080 P=(1/X)-(N(W))/(PR*X)
2090 P=1/P
2100 IF P>295 THEN 2120
2110 H=P*N(W)*6
2120 H(W)=GR*U
2130 N(W)=(10/X2)-(H(W))/(GR*X2/10)
2140 N(W)=1/N(W)

```

```

2150 NEXT W
2160 GRAPH0
2170 PRINT"      NO      IS ";GR
2180 PRINT" N'      CURRENT INTERCEPT"
2190 FOR T=1 TO 20
2200 IF N(T)=0 THEN 2220
2210 PRINT H(T)      ;N(T)
2220 NEXT T
2230 FOR F=1 TO 13
2240 PRINT:NEXT F
2250 INPUT"CONTINUE";G
2260 IF G>0 THEN 4490
2270 CALL"RESOLUTION",0,1
2280 GRAPH1:CALL"OFFSET",-15,-15
2290 CALL"PLOT",-15,0,-1
2300 CALL"LINE",293,0,-1
2310 CALL"PLOT",0,-15,-1
2320 CALL"LINE",0,172,-1
2330 A=0: SX=0: SY=0: XY=0: X2=0: Y2=0
2340 FOR B=1 TO 8
2350 IF H(B)=0 THEN 2440
2360 Y=GR-H(B): Y=1/Y
2370 J=N(B)
2380 GOSUB 2710
2390 Y=Y*10
2400 Y=INT(Y)
2410 J=INT(J)
2420 CALL"PLOT",Y,J,-1
2430 Y=Y/10
2440 NEXT B
2450 A=8
2460 GD=(XY-(SX*SY)/A)/(X2-(SX*SX)/A)
2470 CT=(1/A)*(SY-GD*SX)
2480 GX=(X2/A)-(SX/A)*(SX/A)
2490 GY=(Y2/A)-(SY/A)*(SY/A)
2500 TY=((GY/GX)-(GD*GD))/(A-2)
2510 IF TY>0.0 THEN 2530
2520 TY=-TY
2530 TY=SQR(TY)
2540 GY=GY^0.5
2550 GX=GX^0.5
2560 CF=GD*GX/GY
2570 GD=GD/10
2580 Z=-CT/GD
2590 INPUT"CONTINUE";G
2600 IF G>0 THEN 4490
2610 CALL"PLOT",Z,0,-1
2620 D=GD*2000:CALL"LINE",2000,D,-1
2630 GD=GD*10
2640 A$="      "
2650 PLOT 7,48,A$
2660 PLOT 7,48,"GRADIENT      "+STR$(GD)
2670 PLOT 7,45,A$
2680 PLOT 7,45,"INTERCEPT  "+STR$(CT)

```

```

2690 GRAPH0
2700 GOTO 2760
2710 XY=XY+Y*J
2720 SX=SX+Y:SY=SY+J
2730 X2=X2+Y*Y:Y2=Y2+J*J
2740 A=A+1
2750 RETURN
2760 CO=GD/(1.6*0.86*NE*96487*6.957*4.579*10^(-
4)*5.4*0.4549*0.193*FR^0.75*1000)
2770 PLOT 7,42,A$
2780 PLOT 7,42,"CONC.OF As3+="+STR$(CO)+" Molar"
2790 INPUT"CONTINUE";G
2800 IF G>0 THEN 4490
2810 PRINT#2," DISC( $\mu$ A) RING( $\mu$ A) RING/DISC"
2820 PRINT"VALUES OF RING AND DISC CURRENTS ( $\mu$ A)"
2830 PRINT"Y(I) X(I)"
2840 PP=DC
2850 FOR I=0 TO DC
2860 IF Y(I)=0 THEN 2970
2865 Y(I)=Y(I)-E
2870 PRINT Y(I),X(I)
2880 R(I)=0
2890 IF X(I)=0 THEN 2940
2900 R(I)=Y(I)/X(I)
2910 YH=R(I)*10000:YH=INT(YH)/10000
2920 YU=Y(I)*100:YU=INT(YU)/100
2930 GOTO 2960
2940 R(I)=0
2950 YU=Y(I)*100:YU=INT(YU)/100
2960 PRINT#2,TAB(3)X(I),TAB(15)YU,TAB(27)YH
2970 NEXT I
2980 ZZ=9
2990 INPUT"CONTINUE";G
3000 IF G>0 THEN 250
3010 CALL"RESOLUTION",0,2
3020 CALL"WRIT16",1,1,0,0
3030 CALL"WRIT16",1,1,2,0
3040 PRINT#2
3050 PRINT#2
3060 PRINT#2,"FINAL DISC CURRENT( $\mu$ A) =",DC/10
3070 PRINT#2,"FLOW RATE(ml/s) =",FR
3080 PRINT#2,"RING POTENTIAL(mV) =",RV
3090 IF A<4 THEN 3160
3100 PRINT#2,"COLLECTION EFFICIENCY =",GR
3110 PRINT#2,"CORRELATION COEFFICIENT=",R
3120 PRINT#2,"X-OFFSET ( $\mu$ A) =",UB
3130 PRINT#2,"CONCENTRATION ( $\mu$ M) =",CO
3140 PRINT#2,"ADJUSTED X-OFFSET( $\mu$ A) =",PZ
3150 PRINT#2,"ADJUSTED CONCENTRATION =",CC
3160 PRINT#2,"Y-OFFSET ( $\mu$ A) =",E
3170 PRINT#2,"DISC STEP SIZE( $\mu$ A) =",SS/10
3180 PRINT#2,"MEASURING TIME (s) =",MT
3190 PRINT#2,"TEMPERATURE (C) =",TE
3200 PRINT#2,"ELECTRONS TRANSFERED =",NE

```

```

3210 PRINT#2,"CONVERSIONS PER POINT =",CP
3220 CALL"WRIT16",1,1,0,0
3230 CALL"WRIT16",1,1,2,0
3240 GRAPH0
3250 PRINT
3260 REM GRACONC
3270 PRINT"PROGRAMME FOR PLOTTING A GRAPH OF          TITRATION INTERCEPTS
AND CARRYING OUT    THE CONCENTRATION CALCULATIONS"
3280 PRINT
3290 INPUT"CONTINUE";G
3300 IF G>0 THEN 4490
3310 X$="DISC CURRENT( $\mu$ A)"
3320 Y$="1/(N-N') "
3330 U$="RING=-450mV"
3340 F$="FLOW RATE(ml/s) ="
3350 CALL"XLINE",1,1900,-1900,0
3360 CALL"XLINE",1,-1900,-1900,1
3370 CALL"XLINE",1,-1900,1900,1
3380 CALL"XLINE",1,0,-2000,0
3390 CALL"XCHAR",1,VARADR(X$)
3400 CALL"XSET",1,0,12,6
3410 CALL"XLINE",1,-1930,0,0
3420 N$="1/(NO-N') "
3430 CALL"XCHAR",1,VARADR(N$)
3440 CALL"XSET",1,0,12,0
3450 CALL"XLINE",1,-1800,1950,0
3460 CALL"XCHAR",1,VARADR(F$)
3470 FR=FR*10000:FR=INT(FR)/10000
3480 FR$=STR$(FR)
3490 CALL"XLINE",1,-500,1950,0
3500 CALL"XCHAR",1,VARADR(FR$)
3510 XX=0:YY=0:XM=0:YM=0
3520 FOR I=1 TO DC
3530 IF X(I)=0 THEN 3660
3540 IF Y(I)/X(I)<0.0134 THEN 3660
3550 IF X(I)<0.8*UB THEN 3660
3560 IF X(I)<XX THEN 3580
3570 XX=X(I)
3580 IF X(I)>XM THEN 3600
3590 XM=X(I)
3600 R(I)=Y(I)/X(I)
3610 Y(I)=1/(PM-R(I))
3620 IF Y(I)<YY THEN 3640
3630 YY=Y(I)
3640 IF Y(I)>YM THEN 3660
3650 YM=Y(I)
3660 NEXT I
3670 IF A<4 THEN 3710
3680 XS=XX-XM:YS=YY-YM
3690 XF=3800/XS*YF-3800/YS
3700 T$="*"
3710 FOR I=1 TO DC
3720 IF X(I)=0 THEN 3790
3730 IF R(I)<0.0134 THEN 3790

```

```

3740 IF X(I)<0.8*UB THEN 3790
3750 XP=X(I)*XF-(1900+32)
3760 YP=Y(I)*YF-(1900+52)
3770 CALL "XLINE",1,XP,YP,0
3780 CALL "XCHAR",1,VARADR(T$)
3790 NEXT I
3800 MX=XM*XF-1900
3810 NX=XX*XF-1900
3820 XO=O*YF-1900
3830 MY=YM*YF-1900
3840 NY=YY*YF-1900
3850 YO=O*XF-1900
3860 Z1=O:Z2=O:Z3=O:Z4=O:Z5=O:N=0
3870 LL=1
3880 UL=PP
3890 FOR I=1 TO DC
3900 IF I=DC THEN 4000
3910 IF X(I)=0 THEN 4000
3920 IF R(I)<0.0134 THEN 4000
3930 IF X(I)<0.8*UB THEN 4000
3940 Z1=Z1+X(I)*Y(I)
3950 Z2=Z2+X(I)
3960 Z3=Z3+Y(I)
3970 Z4=Z4+X(I)*X(I)
3980 Z5=Z5+Y(I)*Y(I)
3990 N=N+1
4000 NEXT I
4010 GR=(Z1-(Z2*Z3)/N)/(Z4-(Z2*Z2)/N)
4020 IX=(Z2-(1/GR)*Z3)/N
4030 IY=(Z3-GR*Z2)/N
4040 DX=Z4/N-(Z2/N)*(Z2/N)
4050 DX=SQR(DX)
4060 DY=Z5/N-(Z3/N)*(Z3/N)
4070 DY=SQR(DY)
4080 CC=GR*(DX/DY)
4090 GR=1/GR
4100 PRINT "GRADIENT IS";GR
4110 PRINT "X INTERCEPT IS";IX
4120 PRINT "Y INTERCEPT IS";IY
4130 PRINT "CORRELATION COEFFICIENT";CC
4140 CT=GR/(1.6*0.86*NE*96487*6.957*4.579*10^-
4*5.4*0.4549*0.193*FR^0.75*1000)
4150 PRINT "CONCENTRATION IS ";CT;" Molar"
4160 GR=1/GR
4170 IF XI<0 THEN 4250
4180 GZ=IX*XF-1900
4190 CALL "XLINE",1,GZ,-1900,0
4200 DC=(DC-50)/10
4210 GQ=(DC-IX)*GR
4220 GZ=DC*XF-1900
4230 GE=GQ*YF-1900
4240 CALL "XLINE",1,GZ,GE,1
4250 GR$=STR$(GR)
4260 IX$=STR$(IX)

```

```

4270 IY$=STR$(IY)
4280 CC$=STR$(CC)
4290 CT$=STR$(CT)
4300 PRINT#2,
4310 PRINT#2,
4320 PRINT#2," DISC( $\mu$ A)          RATIO          1/(NO-N')"
```

DISC(μ A)	RATIO	1/(NO-N')
4330 DC=DC*10		
4340 FOR I=1 TO DC		
4350 IF X(I)=0 THEN 4410		
4360 IF R(I)<0.0134 THEN 4410		
4370 IF X(I)<0.8*UB THEN 4410		
4380 R(I)=R(I)*10000:R(I)=(INT(R(I)))/10000		
4390 Y(I)=Y(I)*100:Y(I)=(INT(Y(I)))/100		
4400 PRINT#2,TAB(3)X(I),TAB(15)R(I),TAB(27)Y(I)		
4410 NEXT I		
4420 PRINT#2,		
4430 GR=1/GR		
4440 PRINT#2,"CONCENTRATION IS (Molar)=";CT		
4450 PRINT#2,"THE GRADIENT =" ;GR		
4460 PRINT#2,"CORRELATION COEFFICIENT =" ;CC		
4470 PRINT#2,"X-INTERCEPT =" ;IX		
4480 PRINT#2,"Y-INTERCEPT =" ;IY		
4490 CALL"WRIT16",1,1,0,0		
4500 CALL"WRIT16",1,1,2,0		
4510 PRINT#2		
4520 PRINT#2		
4530 PRINT#2		
4540 PRINT#2		
4550 GRAPH0		
4560 END		

Appendix 6-4 An autotitration program

```

10 REM AUTOTD
20 REM CALIBRATIVE ON-LINE ANALYSIS
30 POKE &39EA,6
40 CALL"IDENT",0,0
50 CALL"SETTR",4,1,1,0
60 CALL"TIMER",1,1000
70 CALL"SETTR",12,1,0,1
80 CALL"XSET",1,0,12,0
90 CALL"XSPEED",1
100 CALL"XMODE",1,1
110 PRINT
120 PRINT
130 PRINT"Continuous analysis using the          auto-titration
technique"
140 CALL"XLINE",1,-2048,-2048,0
150 CALL"XLINE",1,2047,-2048,1
160 CALL"XLINE",1,2047,2047,1
170 CALL"XLINE",1,-2048,2047,1
180 CALL"XLINE",1,-2048,-2048,1
190 W$="CONCENTRATION PROFILE OF AN ANALYSIS"
200 CALL"XLINE",1,-2000,1900,0
210 CALL"XCHAR",1,VARADR(W$)
220 D$="ZERO MOLAR"
230 CALL"XLINE",1,900,-2000,0
240 CALL"XCHAR",1,VARADR(D$)
250 CALL"XLINE",1,-2048,-2048,0
260 CALL"WRIT16",1,1,0,0
270 PRINT#2,CHR$(14)"ANALYSIS USING AUTO-TITRATION TECHNIQUE"
280 CALL"WAIT",1200
290 PRINT FRE(1)
300 CALL"RESOLUTION",0,2
310 CALL"OFFSET",0,-15
320 CALL"COLOUR",3,200
330 CALL"COLOUR",1,150
340 CALL"COLOUR",2,100
350 CALL"PLOT",0,-15,2
360 CALL"LINE",0,175,2
370 CALL"PLOT",0,0,2
380 CALL"LINE",310,0,2
390 GRAPH1
400 L$="PHENOL,pH9.2"
410 INPUT"ANALYSIS GRADIENT";AG
420 INPUT"PERCENTAGE ACCURACY";PA
430 INPUT"HOW MANY CALIBRATION POINTS";CP
440 INPUT"VOLUME FLOW RATE (ml/s)";V
450 INPUT"INITIAL DISC CURRENT ( $\mu$ A)";I
460 INPUT"TIME DELAY BETWEEN EACH SAMPLING (s)";ST
470 INPUT"NUMBER OF POINTS PER CONCENTRATION";DD
480 DIM CO(CP),NC(CP)
490 INPUT"TEMPERATURE";TE
500 INPUT"NUMBER OF ELECTRONS TRANSFERED";NE
510 GT=ST*100
520 PE=AG*PA/100
530 UL=AG+PE:LL=AG-PE

```

```

540 N=0.115479:RV=-450:GOTO570
550 INPUT"COLLECTION EFFICIENCY";N
560 INPUT "RING VOLTS IN mV";RV
570 CALL"WRIT16",1,1,2,RV
580 JJ=0
590 DG=0
600 PRINT#2,
610 PRINT#2
620 PRINT#2,L$
630 PRINT#2,
640 PRINT#2,
650 PRINT#2," ANALYSIS GRADIENT      =";AG
660 PRINT#2," PERCENTAGE ACCURACY    =";PA;" %"
670 PRINT#2," RING POTENTIAL          =";RV;" mV"
680 PRINT#2," COLLECTION EFFICIENCY=";N
690 PRINT#2," VOLUME FLOW RATE        =";V;" ml/s"
700 PRINT#2," INITIAL DISC CURRENT    =";I;"  $\mu$ A"
710 PRINT#2," SAMPLING TIME INTEVAL=";ST;" s"
720 PRINT#2," TEMPERATURE             =";TE;" C"
730 PRINT#2," ELECTRONS TRANSFERED   =";NE
740 PRINT#2,
750 PRINT#2,
760 PRINT#2," DISC ( $\mu$ A)    RING ( $\mu$ A)    Ir/Id    CONCENTRATION ( $\mu$ M)"
770 PRINT#2,"-----"
780 PRINT#2,
790 LC=60
800 FOR ZV=1 TO 250
810 CALL"WRIT16",1,1,0,0
820 CALL"INADC",1,VARADR(J)
830 JJ=JJ+J
840 NEXT ZV
850 K=JJ/250
860 K=-K
870 CALL"PLOT",0,0,2
880 FG=300*AG*4.385507854*7/6
890 CALL"LINE",300,FG,2
900 I=I*10
910 CALL"PLOT",300,70,2
920 CALL"LINE",10,70,2
930 CALL"LINE",10,160,2
940 FOR HJ=80 TO 160 STEP 10
950 CALL"PLOT",11,HJ,2
960 CALL"LINE",300,HJ,2
970 NEXT HJ
980 CALL"PLOT",301,70,2
990 CALL"LINE",301,160,2
1000 HH=0
1010 TP=0
1020 AF=0
1030 EP=0
1040 CH=10
1050 IF HH=0 THEN 1080
1060 INPUT"UNKNOWN CONCENTRATION";FG$
1070 GOTO 1120

```

```

1080 INPUT"NEW CONCENTRATION";GF
1090 AF=AF+1
1100 NC(AF)=GF
1110 FG$=STR$(GF)
1120 PRINT#2
1130 PRINT#2"CONCENTRATION(uM) =";FG$
1140 I=ABS(I):CALL"WRIT16",1,1,0,I
1150 TP=TP+1
1160 IF I>2000 THEN 1920
1170 CALL"WAIT",GT
1180 RC=0
1190 FOR P=1 TO 200
1200 CALL"INADC",1,VARADR(J)
1210 RC=RC+J
1220 NEXT P
1230 R=RC/200
1240 R=-R
1250 R=R-K
1260 PI=2
1270 IF R/(4.385508754*I)<UL AND R/(4.385508754*I)>LL THEN PI=3
1280 IF PI=3 THEN TY=99
1290 Z=R/6:Q=I/7
1300 CALL"PLOT",Q,Z,PI
1310 R=R/4.385508754
1320 NP=R/I
1330 I=I/10000
1340 CN=(I*(N-
NP))/(V^0.75*1.6*NE*0.86*96487*6.957*5.4*0.4549*4.579*10^(-4)*0.193)
1350 NJ=CN*10^6:NJ=INT(NJ*100):NJ=NJ/100
1360 IF TY=0 THEN 1540
1370 EP=EP+1
1380 CF=CN*10^(5)*9+70
1390 CALL"PLOT",CH,CF,3
1400 QT=(CF-70)*38-2048
1410 QS=(CH-10)*14-2048
1420 CALL"XLINE",1,QS,QT,1
1430 CH=CH+1
1440 DG=DG+1
1450 PLOT 5,59,H$
1460 PLOT 5,59,"CONCENTRATION IS"+STR$(NJ)+" μM"
1470 IF HH=0 THEN 1490
1480 NJ=NJ/ZG+XI
1490 NP=INT(NP*100000):NP=NP/100000
1500 ZZ=R/10:ZZ=INT(ZZ*1000):ZZ=ZZ/1000
1510 FF=I*1000:FF=INT(FF*100):FF=FF/100
1520 PRINT#2,TAB(2)FF;TAB(15)ZZ;TAB(27)NP;TAB(40)NJ
1530 DA=DA+FF:RA=RA+ZZ:NA=NA+NP:CA=CA+NJ
1540 TY=0:I=I*10000
1550 IF R/I>UL THEN 1630
1560 IF R/I<LL THEN 1630
1570 GOTO 1670
1580 GRAPH0
1590 GOTO 1630
1600 INPUT"COLLECTION EFFICIENCY";N

```

```

1610 INPUT"INITIAL DISC CURRENT";I
1620 INPUT"INITIAL RING CURRENT";R
1630 I=(R-N*I)/(AG-N)
1640 GY=INT((I/10)*100):GY=GY/100
1650 PLOT 6,4,E$
1660 PLOT 6,4,"THE NEW DISC CURRENT IS"+STR$(GY)+"  $\mu$ A"
1670 IF DG=DD THEN 1690
1680 GOTO 1140
1690 DA=DA/DD:RA=RA/DD:NA=NA/DD:CA=CA/DD
1700 CO(AF)=CA
1710 PRINT#2,"-----"
1720 DA=DA*100:DA=(INT(DA))/100
1730 RA=RA*1000:RA=(INT(RA))/1000
1740 NA=NA*100000:NA=(INT(NA))/100000
1750 CA=CA*100:CA=(INT(CA))/100
1760 PRINT#2,TAB(2)DA;TAB(15)RA;TAB(27)NA;TAB(40)CA
1770 PRINT#2,"-----"
1780 PRINT#2
1790 IF AF=CP THEN 2270
1800 INPUT"READY FOR NEXT CONCENTRATION";G
1810 IF G>0 THEN 2200
1820 DG=0
1830 DA=0:RA=0:NA=0:CA=0
1840 GOTO 1050
1850 INPUT"DISC CURRENT";ID
1860 INPUT"RING CURRENT";IR
1870 N=0.1155
1880 I=(IR-N*ID)/(0.0134-N)
1890 PRINT"NEW DISC CURRENT";I/10
1900 GOTO 1850
1910 END
1920 GRAPH0
1930 PRINT"ABORTED SINCE NEW DISC CURRENT IS ABOVE 200 $\mu$ A AT";I/10;" $\mu$ A"
1940 CALL"RESOLUTION",0,2
1950 END
1960 U$="ANAL.GRAD.="
1970 CALL"XSET",1,0,0,16
1980 CALL"XLINE",1,-2000,1700,0
1990 CALL"XCHAR",1,VARADR(U$)
2000 AG$=STR$(AG)
2010 CALL"XLINE",1,-850,1700,0
2020 CALL"XCHAR",1,VARADR(AG$)
2030 H$=" PER.ACC.="
2040 CALL"XLINE",1,-350,1700,0
2050 CALL"XCHAR",1,VARADR(H$)
2060 PA$=STR$(PA)
2070 CALL"XLINE",1,1000,1700,0
2080 CALL"XCHAR",1,VARADR(PA$)
2090 CALL"XLINE",1,-2000,1500,0
2100 CALL"XCHAR",1,VARADR(L$)
2110 PLOT 5,15,Z$
2120 PLOT 5,15,"END OF ANALYSIS"
2130 PRINT#2,
2140 PRINT#2,

```

```

2150 PRINT#2,"      THE TOTAL NUMBER OF READINGS TAKEN WAS";TP;". "
2160 PRINT#2,
2170 PRINT#2,
2180 PRINT#2,
2190 PRINT#2,"                                END OF ANALYSIS"
2200 CALL"WRIT16",1,1,0,0
2210 CALL"WRIT16",1,1,2,0
2220 GOTO 2240
2230 CALL"XLINE",1,-2048,-2048,0
2240 GRAPH0
2250 END
2260 REM *****
2270 Z1=0:Z2=0:Z3=0:Z4=0:Z5=0
2280 FOR OI=1 TO CP
2290 Z1=Z1+NC(OI)
2300 Z2=Z2+CO(OI)
2310 Z3=Z3+NC(OI)*CO(OI)
2320 Z4=Z4+NC(OI)*NC(OI)
2330 Z5=Z5+CO(OI)*CO(OI)
2340 NEXT OI
2350 ZG=(Z3-(Z1*Z2)/CP)/(Z4-(Z1*Z1)/CP)
2360 YI=(Z2-ZG*Z1)/CP
2370 XI=(Z1-(1/ZG)*Z2)/CP
2380 XS=(Z4/CP)-(Z1/CP)*(Z1/CP)
2390 YS=(Z5/CP)-(Z2/CP)*(Z2/CP)
2400 XS=SQR(XS):YS=SQR(YS)
2410 ZC=(ZG*XS)/YS
2420 PRINT#2:PRINT#2
2430 PRINT#2,"CALIBRATION GRADIENT          = ";ZG
2440 PRINT#2,"CALIBRATION X-INTERCEPT (μM)= ";XI
2450 PRINT#2,"CALIBRATION Y-INTERCEPT (μM)= ";YI
2460 PRINT#2,"CALIBRATION CORRELATION CO.= ";ZC
2470 HH=1
2480 PRINT#2,"-----"
2490 AF=0
2500 DG=0
2510 DA=0:RA=0:NA=0:CA=0
2520 GOTO 1050

```

Appendix 6-5 A rise time program

```

10 REM TIME10
20 CALL"IDENTIFY";0
30 CALL"XLINE",1,-2040,-1800,0
40 CALL"XLINE",1,-2040,2047,1
50 CALL"XLINE",1,-2040,-1800,0
60 CALL"XLINE",1,2047,-1800,1
70 CALL"XSET",1,0,0,16
80 T$="TIME(s)"
90 C$="CURRENT( $\mu$ A)"
100 CALL"XLINE",1,1250,-1700,0
110 CALL"XCHAR",1,VARADR(T$)
120 CALL"XLINE",1,-1900,1900,0
130 CALL"XCHAR",1,VARADR(C$)
140 L$="NO TITRANT"
150 CALL"XLINE",1,300,-100,0
160 CALL"XCHAR",1,VARADR(L$)
170 CALL"XLINE",1,-2040,-1800,0
180 DIM S(600),Y(600),V(600),T1(3),T2(3)
190 INPUT"GALVANOSTAT RESISTOR (kohms)";R
200 INPUT"START CURRENT ( $\mu$ A)";C1
210 INPUT"FINAL CURRENT ( $\mu$ A)";C2
220 V1=R*C1:V2=R*C2
230 INPUT"RING VOLTAGE (mV)";RV
240 CALL"WRITE16",1,2,2,-RV
250 CALL"WRITE16",1,2,0,-V1
260 GRAPH1
270 CALL"WAIT",16000
280 CALL"WRITE8",3,1,2,&F6
290 FOR I=0 TO 600
300 IF I>99 THEN V(I)=V2 ELSE V(I)=V1
310 NEXT I
320 CALL"RTIME",1,VARADR(T1(0))
330 IF T1(1)>45 THEN 320
340 FOR I=0 TO 600
350 CALL"WRITE16",1,2,0,-
V(I):CALL"STROBE",3,1,3:CALL"READ16",3,1,0,VARADR(Y(I))
360 NEXT I
370 CALL"RTIME",1,VARADR(T2(0))
380 S1=0:S2=0
390 FOR K=0 TO 49
400 S1=S1+Y(K):S2=S2+Y(K+551)
410 NEXT K
420 S1=S1/50:S2=S2/50
430 IF S1<S2 THEN SA=S1-100 ELSE SA=S1+100
440 IF S2>S1 THEN SB=S2+100 ELSE SB=S2-100
450 X=0
460 CALL"RESOLUTION",0,2
470 CALL"OFFSET",0,0
480 TH=T2(0)-T1(0):TS=T2(1)-T1(1)
490 TM=T2(2)-T1(2):TT=T2(3)-T1(3)
500 IF TH<0 THEN TH=TH+100
510 IF TS<0 THEN TS=TS+60
520 IF TM<0 THEN TM=TM+60
530 TD=TM*60+TS+TH/100

```

```

540 FOR I=0 TO 600
550 S(I)=I*TD/600
560 Y=INT(192*((Y(I)-SA)/(SB-SA)))
570 IF X>0 THEN 600
580 F=(Y(I)-S1)/(S2-S1)
590 IF F>0.632 THEN X=I
600 CALL"PLOT",I/2,Y,2
610 XX=(I/2)*13-2040
620 YY=Y*18-1100
630 CALL"XLINE",1,XX,YY,3
640 NEXT I
650 CALL"PENUP",1
660 CALL"PLOT",50,0,2
670 CALL"LINE",50,192,2
680 CALL"PLOT",X/2,0,2
690 CALL"LINE",X/2,192,2
700 CALL"XLINE",1,-1390,-1800,0
710 CALL"XLINE",1,-1390,1656,1
720 CALL"XLINE",1,(X/2)*13-2040,-1800,0
730 CALL"XLINE",1,(X/2)*13-2040,1656,1
740 T=S(X)-S(100)
750 IF T<0 THEN T=T+60
760 PRINT"RISE TIME =" ;T;" SECONDS"
770 R$="RISE (s) ="
780 CALL"XLINE",1,100,-400,0
790 CALL"XCHAR",1,VARADR(R$)
795 T=T*1000:T=(INT(T)/1000)
800 RT$=STR$(T)
810 CALL"XLINE",1,1260,-400,0
820 CALL"XCHAR",1,VARADR(RT$)
830 S$="START (μA) ="
840 CALL"XLINE",1,100,-550,0
850 CALL"XCHAR",1,VARADR(S$)
860 C1$=STR$(C1)
870 CALL"XLINE",1,1260,-550,0
880 CALL"XCHAR",1,VARADR(C1$)
890 F$="FINAL (μA) ="
900 C2$=STR$(C2)
910 CALL"XLINE",1,100,-700,0
920 CALL"XCHAR",1,VARADR(F$)
930 CALL"XLINE",1,1260,-700,0
940 CALL"XCHAR",1,VARADR(C2$)
950 RV$="RING (mV) ="
960 V$=STR$(RV)
970 CALL"XLINE",1,100,-850,0
980 CALL"XCHAR",1,VARADR(RV$)
990 CALL"XLINE",1,1340,-850,0
1000 CALL"XCHAR",1,VARADR(V$)
1010 G$="FLOW(ml/s) ="
1020 CALL"WRITE16",1,2,0,0
1030 CALL"WRITE16",1,2,2,0
1040 INPUT"TIME TAKEN FOR 10cc TO FLOW (s)";TK
1042 FF=10/TK
1045 FF=FF*1000:FF=(INT(FF)/1000)

```

```

1050 FF$=STR$(FF)
1060 CALL "XLINE",1,100,-1000,0
1070 CALL "XCHAR",1,VARADR(G$)
1080 CALL "XLINE",1,1260,-1000,0
1090 CALL "XCHAR",1,VARADR(FF$)
1100 CALL "XLINE",1,-2048,-2048,0
1105 GOTO 1530
1110 PF=0
1120 INPUT "POSITION";P$
1130 IF PF=0 THEN 1150
1140 CALL "PLOT",P/2,Y,2
1150 PF=1
1160 IF P$="" THEN P=P+1:GOTO 1220
1170 IF P$="-" THEN P=P-1:GOTO 1220
1180 IF P$="END" THEN 1260
1190 P=VAL(P$)
1200 IF P<0 THEN P=0
1210 IF P>600 THEN P=600
1220 PRINT P;S(P)
1230 Y=INT(192*((Y(P)-SA)/(SB-SA)))
1240 CALL "PLOT",P/2,Y,3
1250 GOTO 1120
1260 INPUT "START POINT";SP
1270 GRAPH0
1280 IF SP>500 THEN 1260
1290 SX=0:SY=0:X2=0:Y2=0:XY=0:N=0
1300 FOR I=SP TO SP+100
1310 SX=SX+I:SY=SY+(Y(I))
1320 X2=X2+(I*I):Y2=Y2+(Y(I)*Y(I))
1330 XY=XY+(I*Y(I))
1340 N=N+1
1350 NEXT I
1360 GOSUB 1480
1370 PRINT "GRADIENT";M
1380 PRINT "S.D. M ";SM
1390 FOR J=SP+1 TO 500
1400 SX=SX+101:SY=SY-Y(J-1)+Y(J+100)
1410 XY=XY-((J-1)*Y(J-1))+((J+100)*Y(J+100))
1420 X2=X2-((J-1)*(J-1))+((J+100)*(J+100))
1430 Y2=Y2-(Y(J-1)*Y(J-1))+((Y(J+100)*Y(J+100)))
1440 GOSUB 1480
1450 IF ABS(M)<SM THEN PRINT J;M/SM;((S(J)-S(100))/(S(P)-S(100)))
1460 NEXT J
1470 STOP
1480 M=((XY-(SX*SY/N))/(X2-(SX*SX/N)))
1490 XS=(X2/N)-(SX*SX/(N*N))
1500 YS=(Y2/N)-(SY*SY/(N*N))
1510 SM=SQR(((YS/XS)-(M*M))/(N-2))
1520 RETURN
1530 CALL "WRITE16",1,2,0,0
1540 CALL "WRITE16",1,2,2,0
1550 GRAPH0
1560 END

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