

SOME STUDIES IN ELECTROANALYTICAL CHEMISTRY
AND THEIR APPLICATION TO
CONTINUOUS ANALYSIS

by

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ABSTRACT

A system for continuous analysis by automated stripping voltammetry was developed. The potentiostat, ramp generator and current read out unit were constructed from operational amplifiers and the various stages of the analysis were controlled by a cam timer. Samples were deoxygenated and processed using continuous flow principles. The slowly dropping mercury electrode and glassy carbon electrode, mercury plated in situ, were both used in a variety of flow cells to determine the optimum conditions for the operation of the system. Derivative output was used to increase the sensitivity and reduce the interference from one ion on the determination of another.

A procedure was developed for the determination of lead in blood using the automated anodic stripping system after a manual ashing stage. By using a longer electrolysis step the apparatus was sufficiently sensitive to be used for the simultaneous determination of copper, lead and cadmium in the ppb range in natural water samples. The electrochemistry of selenium at the mercury electrode was studied and a semi automated cathodic stripping procedure used for its determination in dilute nitric acid over the concentration range 0.2 to 6×10^{-6} M (0.02 to 0.5 ppm). Pulse and phase selective a.c. stripping voltammetry were found to increase the sensitivity and selectivity of stripping voltammetry. Integration of the output signal was investigated in an attempt to increase the precision of stripping voltammetry but no improvement was found. Studies showed that variation in the deposition stage was

responsible for most of the variation in stripping voltammetry and this could be reduced by the use of both controlled stirring of the solution and the slowly dropping mercury electrode.

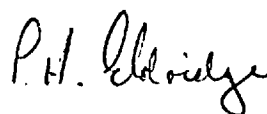
The polarographic reduction of naphthaldehydes and their semicarbazone derivatives was investigated. A system for the determination of the semicarbazone derivatives using continuous flow polarography was constructed. An analytical method for the determination of the cyanide ion by pulse polarography was developed. The continuous flow polarographic analyser was improved by the use of a chemical method to remove oxygen from the sample and a short, controlled drop time electrode.

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CHAPTER 1: INTRODUCTION

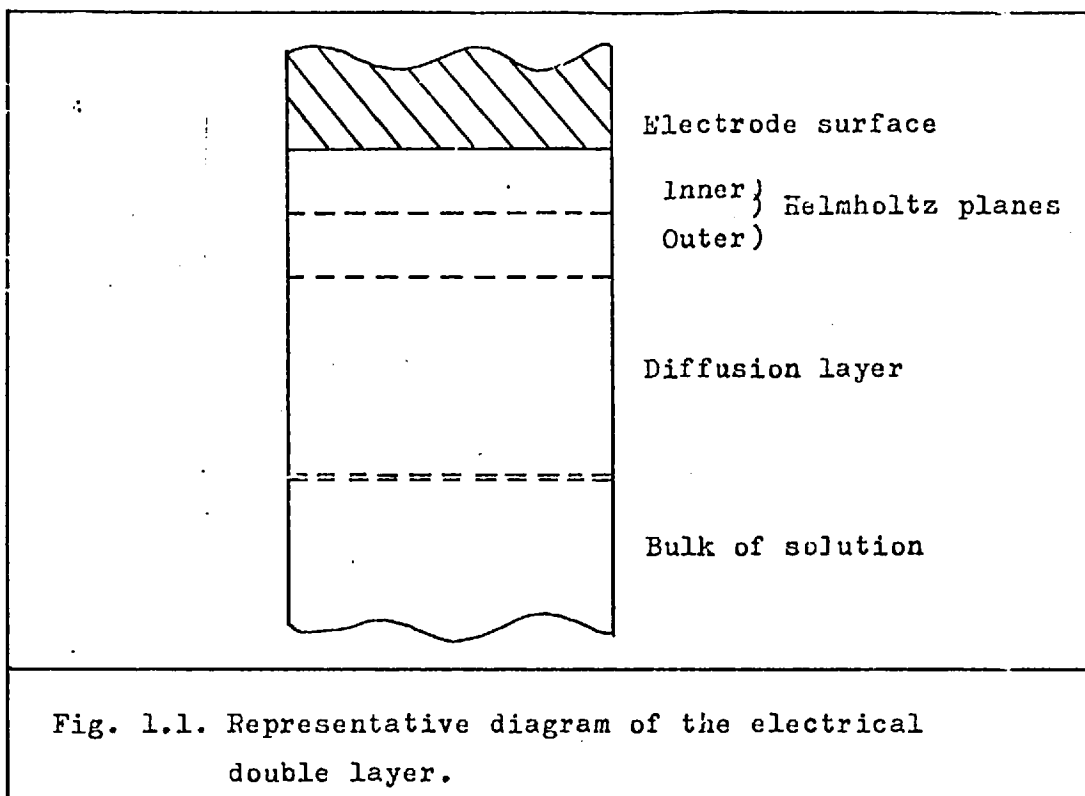
In the past decade, the field of trace analytical chemistry has grown considerably. This has been due to the development of more sophisticated methodology by both university and industrial research to suit more demanding requirements in many areas for the control of trace composition. The nuclear power and semiconductor industries and river authorities can be taken as examples. During the same period there has been increasing use made of automated or mechanised methods of analysis for both major and trace components. At the present time, most of the commercially available automated systems use a spectrophotometer, flame photometer or atomic absorption spectrophotometer as the analytical sensor.

This thesis presents the design and evaluation of some voltammetric systems for use as sensors in continuous flow conditions. Such sensors could have possible application to continuous flow analysers. In this chapter there will be a brief survey of the electrochemical techniques used in the experimental work. The reasons for the automation of the analytical process will be stated, followed by a brief description of some analysers which have been developed. The experimental work is divided into two parts. The first part deals with the application of stripping voltammetry to continuous analysis in chapters two to six. The application

of other voltammetric methods is dealt with in part two. In chapter seven the polarographic determination of a range of naphthaldehydes via their semicarbazone derivatives will be discussed together with their application in the continuous polarographic determination of aromatic aldehydes. The determination of the cyanide ion by pulse polarography is presented in chapter eight.

Voltammetric Methods of Analysis

Electroanalytical chemistry received an early start in 1801 when Cruikshanks (1) showed that lead, copper and silver could be qualitatively determined after electrodeposition from solution. During the 19th century the work of Faraday, Kohlrausch, Nernst and others established much of the theoretical background of electrochemistry. The lack of suitable electrodes was overcome by Heyrovský in 1922 by the application of the dropping mercury electrode (DME) to voltammetry (2) resulting in what is now known as polarography (3). This was the first readily polarised micro-electrode with a regularly renewed surface of controllable area. Since then, the polarographic technique has been further developed and used for investigations into physical chemical properties and in analytical determinations. Polarography and its related techniques are now among the most versatile, moderate cost methods available for both organic and inorganic analysis (4) although it has been suggested that electroanalytical methods in general are underrated at present (5).



Electrochemical Reactions

The theory of electrochemical reactions has been well documented (6-10) but a brief description is necessary as a background to the experimental work.

The basic electrochemical system in all the methods to be discussed consists of two electrical conductors (electrodes), which may be either metals or semiconductors, in electrical contact with each other via an ionic conductor, the electrolyte. Electrochemical reactions may be defined as electron exchange reactions at an electrode, such a process leading to oxidation or reduction. The electrical current due to the transfer is termed the faradaic current.

Between the bulk of solution and the electrode occurs

the interface known as the electrical double layer, as shown in fig. 1.1. The reaction of interest and main potential drop occur in this layer. It consists of an array of charged particles and/or oriented dipoles. Its actual nature depends on such factors as the solvent, adsorption phenomena, the nature and concentration of supporting electrolyte and potential. A consequence of the electrical double layer is that it acts as a capacitor. A typical value of this capacitance is $30 \mu\text{F}.\text{cm}^{-2}$ for a DME. Variations in electrical potential cause the charging or capacitive currents observed in voltammetry and polarography.

Transport of the active species to the electrode surface can occur by three processes; a) migration of charged species due to attraction between the ions and the electrode, b) convection due to density gradients, vibrations, shocks and stirring, c) diffusion between the bulk of the solution and the electrode surface where the concentration of active species is depleted because of the electrode reaction. The addition of a large excess of supporting electrolyte virtually eliminates migration. Diffusion is normally the only method of transport under quiet conditions. The effect of convection is to reduce or continuously renew the diffusion layer.

Equations describing the shape of current/potential curves have been derived for both reversible and irreversible oxidation/reduction systems. Generally the shape is given by the rate of the electron transfer reaction and diffusion to the electrode.

For quantitative purposes measurement of the faradaic

current is important as it can be related to the concentration of the substance undergoing reaction. Thus the practical limit of sensitivity of any voltammetric method is reached when the faradaic current cannot be resolved from the capacitive current.

Electrodes

The electrode at which the reaction of interest takes place is designated the working electrode. This electrode should be readily polarised and inert over the potential range of interest. In Faraday's time mercury was found to offer the advantages of chemical nobility, high hydrogen overvoltage and ease of purification. Since then it has been widely used as an electrode material. In the DME these properties are combined with a periodically renewed surface of definite geometric shape. This electrode, developed by Lippmann (11) and Kucera (12), consists of a glass capillary of 0.01 to 0.1 mm bore connected to a mercury reservoir. Mercury flows through the vertical capillary and emerges in the form of drops.

Many modified forms of the DME have been produced. The Smoler (13) capillary has the plane end bent through 90° so that it is vertical rather than horizontal. Drawn out capillaries have been used for very long drop time electrodes (14). Capillaries with conical rather than plane ends offer less shielding of the mercury drop which is useful in stripping voltammetry (15) and in phase sensitive a.c. polarography where shielding alters the phase of the faradaic current (16).

Tapered and bulb capillaries have been suggested to combat capillary response associated with solution creepage between the mercury thread and capillary bore (17). Teflon capillaries have been used for polarography in hydrofluoric acid (18). The streaming mercury electrode has been used in research on electrode processes and offers a constant area, rapidly renewed surface (19).

Stationary electrodes have the advantage of constant surface area which eliminates problems associated with the periodic fluctuation in charging current. The main disadvantage is irreproducibility caused by deactivation of the surface through adsorption effects. The various types of stationary mercury electrodes are dealt with in the section on stripping voltammetry.

The potential range of the mercury electrode is limited in both positive and negative directions. The cathodic potential is limited by cations in solution or the solvent itself. In dilute acid solutions reduction of H_3O^+ occurs at about -1.0 V vs saturated calomel electrode (SCE) whilst in neutral or alkaline solutions of tetra-alkylammonium ions reduction of the solvent occurs at -2.7 V. At positive potentials mercury is oxidised to mercury (I) or (II), the potential depending upon the stability of the complex formed between the mercury ions and the anions in solution. Weakly complexing anions such as perchlorate allow potentials as positive as +0.4 V to be reached.

To investigate reactions that occur at more positive

potentials other electrode materials must be used. Adams (20) has given a comprehensive review of the great variety of solid electrodes used in voltammetry and has discussed their fabrication and usage. Alder et al (21) have evaluated a range of electrode materials for voltammetry. Platinum is the most commonly used material in the anodic region but cannot be used cathodically. Oxygen trapped in pores limits the use of carbon but this can be overcome by the use of specially prepared electrodes (22-25). These electrode materials offer a wider potential range than platinum. The other platinum group metals do not offer any additional advantages over platinum and, with the possible exception of boron and tungsten carbides, the carbides, sulphides and nitrides investigated (21) were not satisfactory.

The reference electrode is required to produce a steady potential with which the potential of the working electrode may be compared. Meites (26) gives the following characteristics required by an ideal reference electrode:-

- i) ease of preparation from readily available materials.
- ii) rapid attainment of accurately reproducible potential.
- iii) invariance of potential with time.
- iv) negligible thermal hysteresis.
- v) low polarisability.

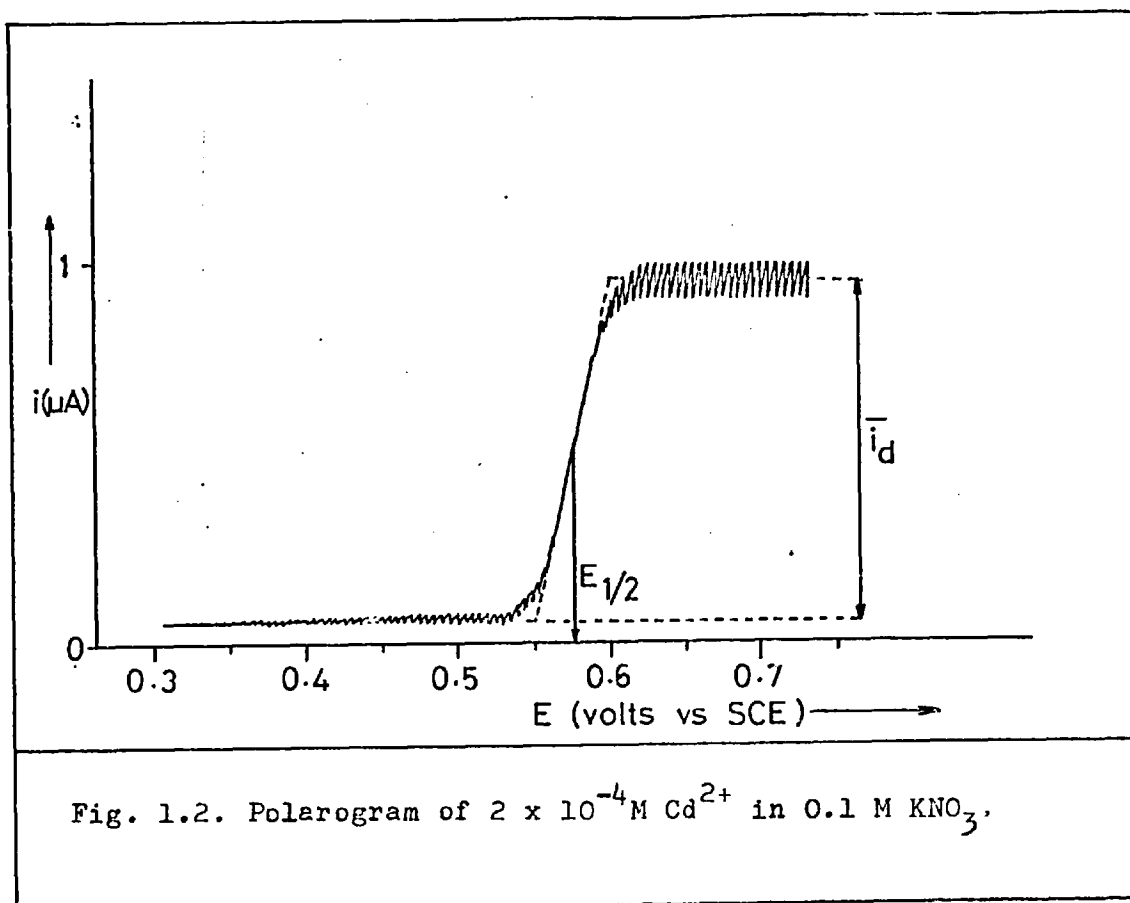
There are several reviews on reference electrodes for use in aqueous (27) and non aqueous (28) solvents. The most widely used reference electrodes in aqueous voltammetry are the mercury/mercurous chloride/saturated potassium chloride, SCE, and the

silver/silver chloride/saturated potassium chloride electrodes. Both these electrodes satisfy the above requirements for an ideal electrode. Calomel electrodes with 0.1 or 1 M potassium chloride are often used. They have similar properties to the SCE with the advantage of a smaller temperature coefficient. In the literature the SCE is the standard against which electrode potentials are reported. In non aqueous solvents care is taken to avoid the introduction of water. The use of a non aqueous bridge between the electrochemical cell and aqueous reference electrode introduces problems of slow leakage of water and of variable liquid junction potentials. The use of a silver/silver chloride/tetramethylammonium chloride reference electrode in anhydrous acetonitrile has been recommended.

In modern instruments incorporating a potentiostat, a third, counter electrode is used (29). This electrode is not involved in the electrochemical reaction of the species of interest but serves to take the cell current allowing the reference electrode to operate at almost zero current which eliminates the effect of polarisation. This electrode does not have to meet the stringent requirements of working and reference electrodes and normally any inert conducting material may be used. e.g. A silver counter electrode in an electrolyte containing chloride ions forms insoluble silver chloride.

DC Polarography

This method consists of applying a slow linear potential ramp across a DME and suitable reference electrode in solution



and plotting the current/potential curve or polarogram. A typical polarogram or polarographic wave is shown in fig. 1.2. Once the reduction potential of the cadmium has been reached the charge transfer reaction occurs and the electrode is no longer ideally polarised. The cadmium is termed the depolariser. The mechanism of the reaction is diffusion controlled and above a certain potential, where the rate of reduction of the cadmium ions is equal to their rate of diffusion from the bulk of solution, a limiting current will be attained. Ilkovic (30) has solved an equation for the magnitude of the limiting current for a diffusion controlled faradaic process at the DME assuming planar diffusion to the electrode. The mean diffusion current during the life of a drop

is given by:-

$$\bar{i}_d = 607 \, n \, c \, D^{1/2} \, m^{2/3} \, t^{1/6} \, \mu A \quad \dots\dots\dots 1.1$$

where n = no. of electrons transferred
 c = concentration (mM.L^{-1})
 D = diffusion coefficient ($\text{cm}^2.\text{s}^{-1}$)
 m = mercury flow rate (mg.s^{-1})
 t = drop time (s)

Owing to the small thickness of the diffusion layer compared with the drop radius this is a good approximation. Although more accurate equations, which consider spherical diffusion, have been devised (31,32) the differences are of smaller magnitude than the experimental error and insignificant in analysis. For a given set of experimental conditions the Ilkovic equation reduces to the analytically useful form:-

$$\bar{i}_d = kc \quad \dots\dots\dots 1.2$$

Polarographic waves are also seen which depend on kinetic (33), adsorption (34) and catalytic (35) processes to define the limiting current. These currents are distinguished by their dependence upon the mercury reservoir height. A study of these currents can be of great importance in the elucidation of electrode processes but there are few analytical applications.

The polarographic reduction of inorganic ions is normally a simple diffusion controlled charge transfer reaction and is widely used for analysis in the concentration range 10^{-3} to 10^{-5} M. Analytical selectivity is given by the characteristic half wave potential of each ion. Two waves can be resolved if the half

wave potentials differ by at least 100mV. However the measurement of one wave in the presence of a larger prewave from another species is difficult. A wide range of anions and organic ligands forming mercury complexes may also be determined.

The simplest organic electrode processes are observed in non aqueous aprotic solvents where reversible one electron transfer reactions result in the formation of stable radical ions (36). However in aqueous or semi aqueous solvents the reactions are influenced by the participation of protons, adsorption of depolariser on the electrode, inhibition from products and hydrogen bonding with the solvent. The majority of polarographic reductions of organic compounds are irreversible and result in bond fission. Detailed accounts of organic polarography (37,38) show its uses for the study of electrode reactions. As a method of analysis it is applicable to the determination of functional groups. Its use in organic chemistry and such related fields as biochemistry, pharmacology and agricultural chemistry is growing rapidly.

Linear Potential Sweep Voltammetry

If, instead of a DME, a stationary electrode is used in a quiet solution and a current/voltage curve or voltammogram is plotted a peak shaped response is seen. Initially the current increases due to reaction of the depolariser. However the diffusion layer becomes depleted and the current decays to a small limiting value. For a reversible reaction at a plane electrode, the peak current is given by the Randles-Ševčík equation (39,40) with the

constant derived by Nicholson and Shain (41).

$$i_p = 2.687 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} c \quad \mu A \quad \dots\dots\dots 1.3$$

where A = electrode area (cm^2)

v = scan rate (V.s^{-1})

The peak potential is related to the half wave potential by (42):

$$\text{Reduction} \quad E_p = E_{1/2} - 29/n \text{ mV} \quad \dots\dots\dots 1.4$$

$$\text{Oxidation} \quad E_p = E_{1/2} + 29/n \text{ mV} \quad \dots\dots\dots 1.5$$

The faradaic current is seen from equation 1.3 to be dependent on $v^{1/2}$. However the charging current is proportional to v^2 which limits the sensitivity of the technique at high scan rates. Slow scan rates give an improvement in sensitivity over classical polarography.

If the electrode is rotated or the solution stirred the diffusion layer is disturbed and a similar wave to that formed in polarography will be obtained. A derivative output (di/dE) can improve selectivity and give a five to ten times increase in sensitivity.

Cyclic Voltammetry

A development of the above technique has been to apply a triangular wave potential to the electrode (41). This allows the study of the oxidation of the products of a chemically reversible reduction. For a reversible system, cathodic and anodic peaks of equal magnitude and separated by $58/n$ mV are obtained. For reactions influenced by kinetics (41-43) and adsorption (44-46) these relationships no longer apply and

hence the use of cyclic voltammetry in studying these reactions. No routine analytical methods have been suggested.

Tast and Pulse Polarography

With d.c. polarography it becomes difficult to discriminate between the small faradaic current and larger capacitive current below about 10^{-5} M. The capacitive current decays at a faster rate than the faradaic and in tast polarography (47) the current is sampled towards the end of the drop lifetime. A controlled drop time DME synchronised with the current sampler is used. This method gives a useful increase in sensitivity of one order of magnitude.

Pulse polarography (17,49) relies on this same method of minimisation of capacitive current. A voltage pulse, synchronised with the controlled DME is applied to the electrode. The difference between the current sampled before the voltage pulse and at the end of the pulse is measured. The applied waveform, current sampling points and relative faradaic and capacitive currents are shown in fig. 1.3a. Theoretical equations for the pulse polarographic response and its dependence on diffusion, kinetic and catalytic currents have been given by Brinkmann et al (50). Fig. 1.3b shows normal and differential pulse polarograms. The peak shape of the latter is particularly useful when resolving mixtures and detection limits of 2×10^{-8} M for reversible and 5×10^{-8} M for irreversible reactions are possible. A consequence of the sampling method is that very dilute supporting electrolytes can be used. The limit of

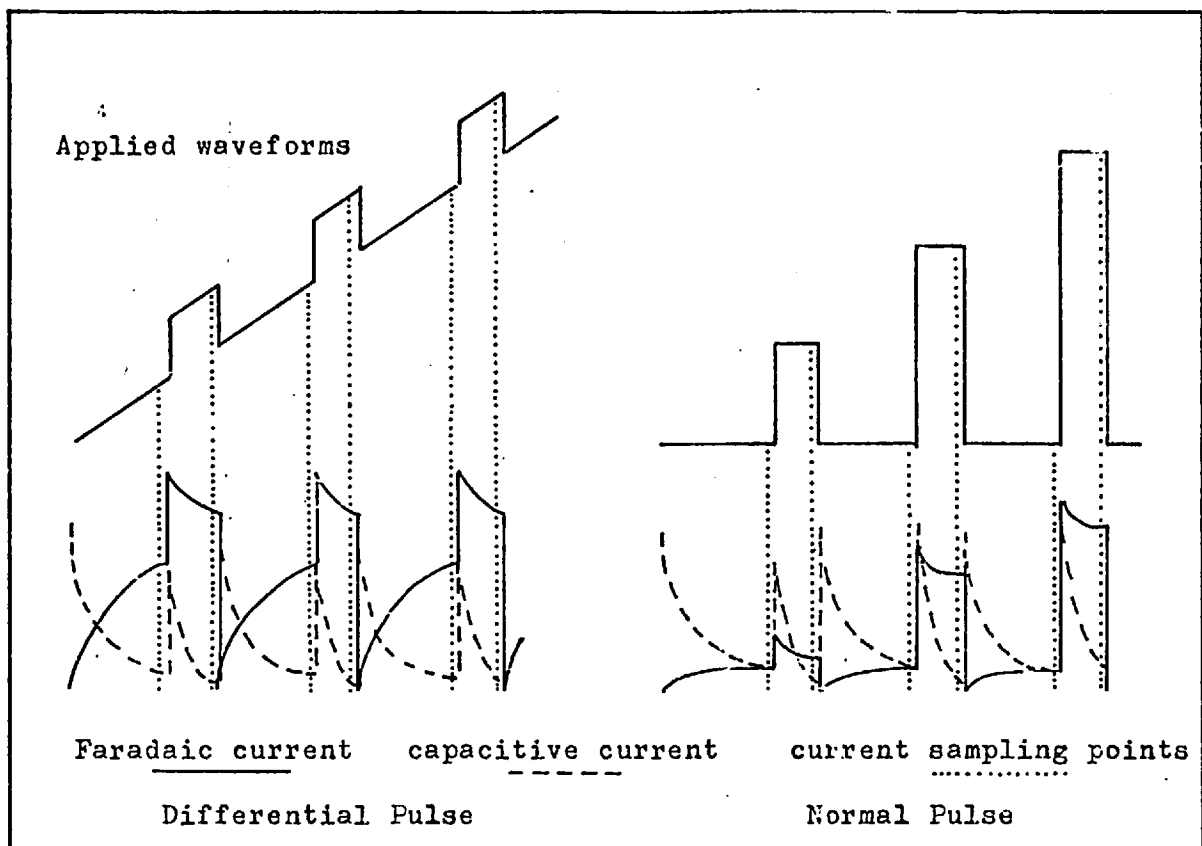


Fig. 1.3a. Pulse polarography - applied waveforms, current sampling points and response.

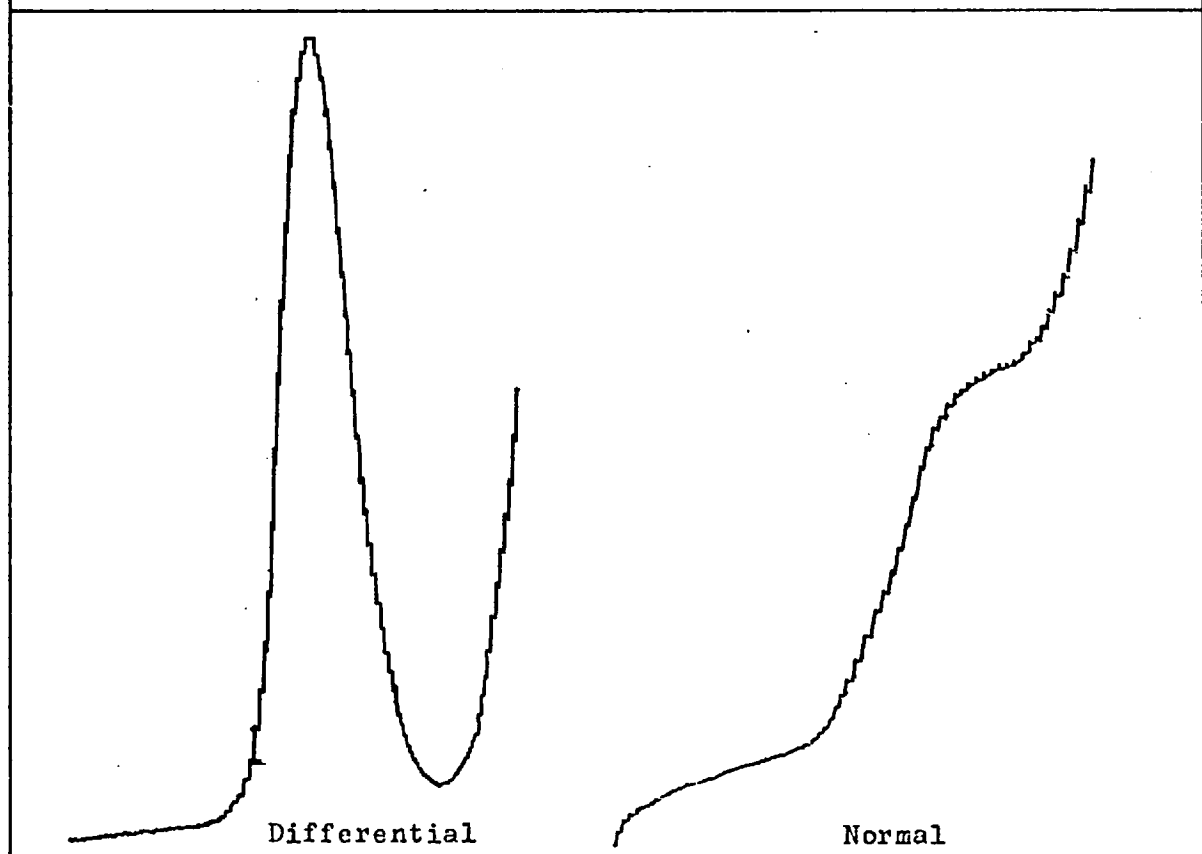


Fig. 1.3b. Pulse polarograms.

detection is controlled by the capillary noise (17). The original equipment was very complex and bulky but now with the availability of small, relatively inexpensive microcircuits this is becoming a practical trace analytical method.

AC. Polarography

This technique (51) involves the superimposition of a small sinusoidal a.c. voltage upon a d.c. ramp applied to the electrode. The alternating current flowing through the cell is plotted versus the applied d.c. potential. In the presence of a reversibly reduced species a symmetrical peak shaped response is obtained. The faradaic current consists of a mixture of the harmonics of the a.c. frequency, the fundamental predominating. The general theory, circuitry and results have been given by Smith (10). For a simple reversible reaction the peak fundamental response is given by:-

$$i_p = \frac{n^2 F^2 A c}{4 R T} (f D)^{1/2} \Delta E \sin \pi/4 \quad \dots\dots\dots 1.6$$

where f = frequency of applied a.c. voltage (Hz)

ΔE = amplitude of applied a.c. voltage ($\leq 8/n$ mV)

Smith (10) has given equations describing the wave shape but for analytical purposes it is sufficient to know that the peak occurs at $E_{1/2}$ and the width of the peak at half amplitude is $90/n$ mV. The response depends on the rapid exchange of reduced and oxidised species and thus no response is given by irreversible reactions. Systems in which the rate of electron transfer is slow or which have coupled chemical reactions have been considered and do not adhere to equation 1.6.

Because of the large background response due to the capacitive current simple a.c. polarography is less sensitive than d.c. polarography. However the faradaic process can be compared with a complex resistance/capacitance impedance. It is found that the capacitive current leads the applied voltage by 90° whereas the faradaic current leads by approximately 45° . By the use of a phase sensitive detection system (52) the capacitive current may be virtually eliminated. This is most effective with a hanging mercury drop electrode (HMDE). It has been shown that phase sensitive a.c. polarography at this electrode is useful down to 10^{-8} M (53). With the DME the capacitance of the double layer varies with the drop growth and because of the complex nature of the response the phase angle changes during the drop growth. For this reason complete removal of capacitive current at this electrode is not yet possible.

This has the advantage of better reproducibility and resolution than d.c. polarography. There are many applications to inorganic analysis. Many organic species show an a.c. response (54). The use of short controlled drop times in a.c. and d.c. polarography has been suggested (55) and shown to give advantages of faster analysis together with better reproducibility. However it has been calculated that the ratio of faradaic to capacitive current in d.c. polarography with a DME of controlled drop time of 0.1 s is about ten times that of the same DME of natural drop time 5 s (56). This would, therefore, be expected to give a reduced sensitivity for a.c. polarography as has been

noticed in d.c. polarography (57).

Higher harmonics than that of the applied signal are produced due to the non linearity of the faradaic process (10). The amplitude of the harmonic components is roughly proportional to the inverse power of the harmonic. The number of peaks in the response is equal to the harmonic number. These signals have received considerable attention as their study can give data on coupled chemical reactions. Analytically an advantage of the higher components is that the capacitive current is eliminated so that the second harmonic is more sensitive than the fundamental harmonic using the DME. However the complex shapes of higher harmonics make resolution of mixtures more difficult and for this reason Bond (58) considers that second and third harmonics offer no advantages over the fundamental harmonic for a general analytical technique.

Intermodulation a.c. polarography is a technique in which two a.c. signals of frequencies f_1 and f_2 are applied to the cell and the current measured at frequency $f_2 - f_1$ (59). The response is similar to second harmonic polarography but it requires more complex instrumentation (56). Another method of removal of the capacitive current has been to use a small amplitude triangular instead of sine wave (61). Theoretically the capacitive response should give a square wave current output which is removed by full wave rectification and use of a tuned amplifier. Other a.c. polarographic techniques have been proposed such as amplitude modulation, radio-frequency, frequency

modulated (17) and multiplex mode polarography (62).

The study by a.c. polarography of substances showing adsorption-desorption phenomena is tensammetry (52). Changes in the double layer caused by adsorption give rise to the response. Two peaks, corresponding to the adsorption and desorption potentials, are normally observed. These can be used for the polarographic determination of a wide range of organic compounds under specific conditions.

Square Wave Polarography (60)

By using a square instead of sine wave and an electronic sampling circuit use can be made of the faster rate of decay of the capacitive than faradaic current. A useful response down to 10^{-8} M has been reported. However the circuitry required is more complicated than that for pulse polarography and high concentrations of supporting electrolyte are necessary to lower the cell resistance.

Stripping Voltammetry

The detection limits of the methods described previously are determined by the discrimination of the faradaic current from capacitive current, capillary noise or electronic noise. The technique of stripping voltammetry was brought about by research into increasing the sensitivity of polarography without using complex instrumentation. In its simplest form it combines the high sensitivity of linear potential sweep voltammetry at a stationary electrode with an electrolytic concentration step.

Electrolytic stripping was originally used for such

determinations as the thickness of tin coatings on copper wires (48). Zbinden (63) determined the concentration of dissolved copper by electrolytic deposition onto a platinum electrode followed by anodic stripping. Interest in the technique really began after several authors had reported its sensitivity and selectivity for trace metal ions concentrated on platinum (64) and mercury (60,65-68) electrodes. Concentrations in the range 10^{-6} - 10^{-9} M can be analysed with reasonable precision and with only the simplest of polarographic equipment. There have been several reviews discussing the theory, methodology and applications (15,69-74). The review by Brainina (71) covers only thin film stripping at solid electrodes. In general the method is applicable to the determination of any species which can be concentrated at an electrode and then stripped by an appropriate voltage scan. At present it is the most sensitive electroanalytical method and for the determination of a wide range of metals is only surpassed by neutron activation analysis in detection limits.

Initially it was only thought to be applicable to amalgam forming metals by concentration at a mercury electrode and subsequent anodic stripping, ASV. The formation of insoluble films on an electrode and subsequent stripping is now of interest (71). Film stripping voltammetry, FSV, as this is known, includes both the cathodic stripping, CSV, of insoluble mercury compounds with anions or the cathodic deposition and anodic stripping of metal films or other insoluble compounds on a solid electrode.

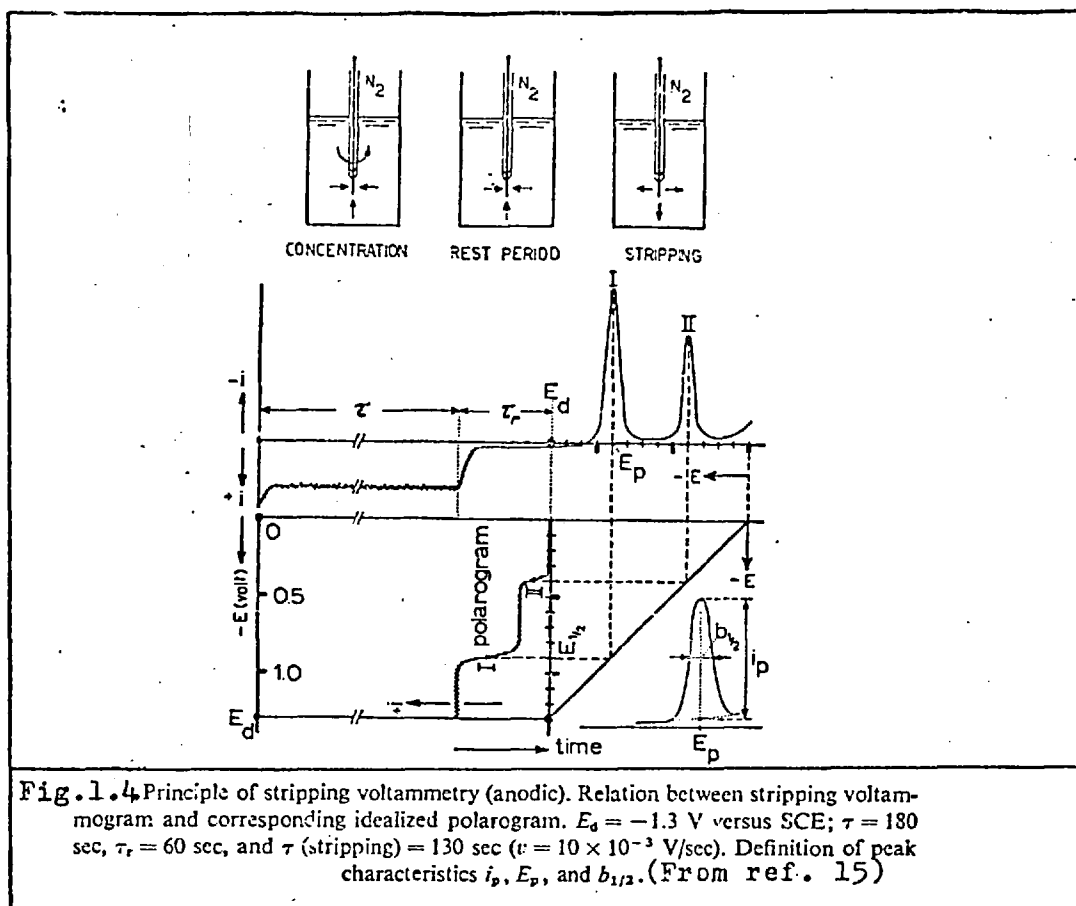


Fig. 1.4 shows the three stages in an ASV determination together with the current response and the peak characteristics. The shape of the voltammogram varies with the type of electrode used and the voltage scan rate. The three stages and response in CSV are similar although there are some important differences in shape to be discussed later.

Theoretical

The concentration of material on the electrode is the step which defines the sensitivity and reproducibility of this method. The choice of the electrodeposition potential, E_d , is not critical and can be any point on the plateau of a normal voltammetric curve. In mixtures, selective deposition is achieved by the choice of a potential at which one ion is deposited but

not the other(s). Overpotential phenomena may arise in very dilute solutions because of the higher concentration of metal in mercury electrodes.

Mass transport to the electrode determines the concentration step. In the case of the HMDE the limiting current for an amalgam forming reaction has been defined by the following semi-empirical equation (75).

$$i_l = (4\pi r n F D c + k n r^2 D^{2/3} c U^{1/2}) \times 10^{-3} \text{ A} \quad \dots\dots\dots 1.7$$

where r = radius of mercury drop (cm)
 k = empirical constant
 U = rotation speed of stirrer (rpm)

This assumes that no depletion of the solution takes place during electrolysis. If the electrolysis process is maintained for τ s, the amalgam concentration, c_a , is given by:-

$$c_a = \frac{3 i_l \tau}{4 \pi r^3 n F} \text{ mM.L}^{-1} \quad \dots\dots\dots 1.8$$

Similarly for a mercury film electrode (MFE):-

$$c_a = \frac{i_l \tau}{A n F} \text{ mM.L}^{-1} \quad \dots\dots\dots 1.9$$

where l = thickness of film (cm)

After the deposition step it is normal to have a rest period during which the solution comes to rest, the current falls to a low value (depletion of diffusion layer) and the deposit becomes homogeneous.

The theory of the anodic stripping step from the HMDE with linearly changing potential resembles that developed by

Randles and Ševčík for voltammetry with linear potential sweep. Reinmuth (76) has considered the case for a reversible process with semi-infinite diffusion and derived the following experimentally verified equation.

$$i_p = nD_r^{1/2} \tau c (k_1 r n^{1/2} v^{1/2} - k_2 D_r^{1/2}) \quad \dots\dots\dots 1.10$$

where D_r = diffusion coefficient of metal in amalgam ($\text{cm}^2.\text{s}^{-1}$)

k_1, k_2 are empirical constants

The second term in the brackets is the spherical contribution, and can amount to 20 per cent of i_p . At small values of v ($< 20 \text{ mV.s}^{-1}$) a correction for finite electrode volume is necessary. Generally a scan of 2 to 10 mV.s^{-1} is used at which proportionality between i_p and c is maintained. At higher sweep rates, tailing of the peaks occurs because of the slow rate of diffusion of the metal from the amalgam. Faster scan rates do not increase the sensitivity because the capacitive current is proportional to v .

There are important differences in the case of stripping from mercury films. Roe and Toni (77) derived an equation relating the peak current to the concentration in the mercury film using the approximation that the mercury film had negligible thickness:-

$$i_p = \frac{n^2 F^2 A l c_a v}{\exp RT} \quad \dots\dots\dots 1.11$$

This equation was about 4 per cent in error with experimental results. An exact treatment has been made by de Vries (78,79) which considers the diffusion of material within a mercury film of finite thickness. The results indicated several important differences from those predicted by the Randles-Ševčík theory

which were experimentally verified. A list of these, together with predicted values in brackets, is given below:

- i) $i_p \propto v$ for $l < 25\mu$ ($i_p \propto v^{1/2}$)
- ii) $B_{1/2} = 38$ mV at low values of l and v , asymptotically approaching 102 mV at high values of v and l . (102 mV)
- iii) $(E_p - E_{1/2})$ asymptotically approaches +14.3 mV at high values of v and l . (+14.3 mV)

Other features are:

- iv) i_p independent of l for $v < 5 \text{ mV.s}^{-1}$
- v) $B_{1/2}$ independent of v for $l < 4\mu$

The use of a fast scan rate increases the peak current but does not lower the actual sensitivity or resolution if a very thin mercury film is used.

Nicholson (80) has considered the process of reversible anodic dissolution of a metal film from the surface of an inert solid electrode, using the assumption that the film forms an incomplete monolayer on a statistically homogeneous surface and that the activity of the layer is determined by the part of the surface occupied. Brainina (71) has used the same assumptions for an irreversible process and has considered thick layers. These predict that i_p is proportional to the amount of metal on the electrode and hence to the metal ion in solution. Similar predictions are given (71) for the dissolution of films by CSV.

Electrodes

The majority of work in stripping voltammetry has been carried out with mercury, either in the form of a drop or film (15).

As well as the advantages discussed earlier, mercury will amalgamate with a good range of metals producing solutions with only weak intermetallic bonds. This allows the selective determination of mixtures possible.

Although the spherical mercury drop has the smallest surface area to volume ratio of any geometric shape thus minimising sensitivity, its area can be reproduced accurately which accounts for its wide use.

Mercury drops have been hung from inert metal contacts previously mercury wetted. Platinum, gold and nickel have all been used as metal contacts. Problems that may arise with these electrodes are due to the amalgamation of the metal contact. High concentrations of these metals may cause effects such as intermetallic compound formation e.g. PtSb, PtSn and PtZn, and the lowering of the hydrogen overpotential. These have been shown to be negligible under normal conditions when a fresh mercury drop is used for each determination. In the Kemula type (68) HMDE the drop is extruded from a capillary by means of a micrometer screw. This eliminates interference from substrate metals. The mercury reservoir allows the formation of several drops without problems associated with the removal of the electrode from the cell. However there are several practical disadvantages:-

- i) back diffusion of amalgam into capillary
- ii) good thermostating of the reservoir is required to give a constant drop size

iii) creeping of solution and evolved hydrogen in the capillary
cause drop instability

iv) air in the reservoir causes drop instability.

Two methods of refilling the mercury reservoir without moving the electrode have been suggested (81,82) which will also stop the introduction of air into the reservoir. The sessile mercury drop electrode, SMDE, in which the drop is supported from below, is considerably more stable than the hanging versions especially under conditions of high pH, very negative potentials or strong convection. DMEs of long drop time have very reproducible areas and are very simple to use but the very small electrode area at the initial stage of growth limits the sensitivity attainable. There have been a few applications to stripping voltammetry(83-86).

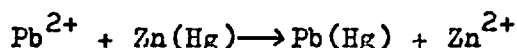
Mercury film electrodes were originally prepared on platinum, gold, silver or nickel substrates by either immersion in mercury or electrodeposition. Films of thickness between 1-200 μ could be prepared. Electrodeposition gives some control over the thickness. Because of the low hydrogen overpotential of these metals it is necessary to ensure complete coverage with the mercury. This is hampered by the presence of oxides on the metal surfaces and many cleaning procedures have been suggested. One relatively successful method (87) for platinum involves the production of a layer of platinum black on the electrode surface. The relative instability of platinum black oxide allows the electrode to be reproducibly coated with mercury. Problems with mercury film electrodes arise through intermetallic

compound formation and lowering of the hydrogen overpotential because of dissolution of the substrate in the mercury. Because of the large surface area of substrate to mercury volume this is more important than in the HMDE. The electrodes are difficult to keep in an active state especially when exposed to air. The MFE prepared on nickel plated platinum is reported to be more stable than when prepared on platinum (88).

A composite graphite/mercury electrode (89) overcomes some of these problems. Spectroscopy grade graphite was vacuum impregnated with paraffin wax to fill the pores as suggested by Nicholson (90), carefully polished and then mercury plated by electrolysis. Microscopic examination of the surface has shown that 10 per cent of the mercury formed drops of 10 μ diameter while the rest was present as extremely small droplets. After consideration of the high hydrogen overpotential and sharpness of the stripping peaks of metal ions, it was proposed that the plating and stripping occurred at the smaller drops which were assumed to be on the most active sites on the graphite surface. It has been shown that these films were less prone to oxidation (91). Florence (92) has suggested the use of the polished glassy carbon electrode, mercury plated in situ, as a reproducible film electrode. He was able to produce and use films of mercury as thin as one monolayer on this material. Reproducible results in stripping voltammetry were obtained when films of between 0.001 - 0.01 μ thickness were electrodeposited on the electrode in situ with the ions to be analysed. Complete resolution of

cadmium, indium and lead was shown to be possible. The results were in agreement with the theory and, because of the thin mercury film, the value of $E_{1/2}$ only increased from 32 to 42 mV over the scan range 3 to 80 mV.s⁻¹. The first anodic scan on a mercury layer was found to give a lower peak than in subsequent electrolysis/stripping cycles. This observation has not been reported in work on mercury films on other substrate materials. Simultaneous pre-electrolysis and mercury film formation has also been suggested by adding mercury oxynitrate to a test solution (93).

Film electrodes are considered to be superior to drop electrodes in terms of sensitivity and selectivity (94,95). Generally, drop electrodes are more reproducible although films prepared on carbon substrates are promising. Thin films have been found to be insensitive towards zinc in a wide range of electrolytes but no explanation has been suggested to account for this (96). The higher concentrations of metals amalgamated with the mercury in films can result in the greater effect of displacement reactions occurring between the solution and amalgam in the analysis of mixtures (15). Reactions such as:



increase the amalgam concentration of lead at the expense of zinc.

The same problems of irreproducible production of mercury films on solid electrodes apply to stripping voltammetry of films of other metals on solid electrodes. Deposition and stripping

of metals and sparingly soluble compounds of variable oxidation state ions have been accomplished on solid electrodes of platinum (64,90), gold (97), silver (98) and carbon (71). Platinum and gold, with their low hydrogen overpotential, are only suitable for the determination of ions of the more electropositive metals such as mercury, silver and gold (on platinum). The various carbon forms which can be used over a very wide potential range have been used as electrodes for both the noble and other metal ions. Paraffin wax (24,99,100) and epoxy resin (101) impregnated carbon electrodes have been successfully used. More recently the use of non porous pyrolytic graphite (102) and glassy carbon forms has been reported (103-105). The carbon paste electrode has been used to some extent over a long period of time (22,106), but still receives attention. Chulkina et al (107) have studied the influence of the composition of the paste on the efficiency of anodic stripping at the nanogram level. Monien et al have shown the use of this electrode material for the determination of tin (108) and antimony (109).

A comparative investigation (23) into the use of the various carbon electrodes showed that wax impregnated and carbon paste were the most reproducible as adsorption or a possible decrease in the number of active sites on the electrode surface gave non repetitive results for pyrolytic and glassy carbons. However in view of other reports showing the advantages of glassy carbon it appears that preparation of the electrode surface is of great importance with these materials (105).

The nature of the deposited layer can cause problems during the stripping step. For even simple one component analysis, multiple stripping peaks have been observed. One explanation is the formation of several monolayers all having different activities which will then be stripped at specific potentials (97,110). Formation of intermetallic bonds between the electrode and film can produce a more strongly bound layer on the electrode. This has been shown to cause difficulties in the ASV determination of mercury on platinum where the compound PtHg_4 is formed on the surface (111). The PtHg_4 might also be expected to give a lower limit to the thickness of mercury films which can be used for the stripping analysis of other ions. The deposited metal does not form a homogeneous layer on the electrode as in amalgams which can cause problems in stripping. The simultaneous analysis of mixtures on solid electrodes is difficult due to the formation of strong, intermetallic bonds. (In amalgams these are considerably weakened). However, by use of the platinum ring-disc electrode system, selective deposition and stripping of a mixture $10^{-5} - 10^{-8}$ M in Cu^{2+} and Ag^+ may be achieved by suitable adjustment of the disc potential (112).

The shape of the response in FSV differs from that of amalgam stripping. The rising part of the response is similar to that of stripping from mercury films, but when the film has been depleted the current drops sharply to the base line.

Experimental

Cells used in stripping voltammetry are similar to

polarographic cells but require provision for stirring the solution and/or rotating the electrode. Normally the solution is stirred with a synchronous stirrer during the pre-concentration step. There is some evidence that better reproducibility can be obtained by rotating the electrode (113). Uniform conditions of temperature and stirring are essential to ensure reproducible mass transfer to the electrode. The effect of temperature has been studied and electrodeposition at 100°C was found to increase the sensitivity by an order of magnitude (114). When electrolysis involves negative potentials, oxygen must be eliminated as its presence both distorts the base line and causes oxidation of the deposited material (115). The impurities in the electrolyte and mercury can limit the useful sensitivity. Removal of metallic impurities from electrolytes can be achieved by electrolysis (116,117). Organic impurities can affect the deposition step through adsorption onto the electrode. They can be removed by ashing or exposure to ultra violet radiation. The use of low concentrations of electrolytes in potentiostatted cells lowers the influence of impurities.

Normally stripping is carried out under quiet conditions. Kemula (74) reports an increase in peak current of 80 per cent when stripping into stirred solutions. With the HMDE, stirring reduces tailing of the response. The signal:noise ratio is not improved because of the noisier base line. Although a calibration graph may be used for quantitative analysis, the method of standard additions is more frequently used so that the conditions

of analysis of standard and sample are identical. The sluice method (118) allows a set volume of oxygen free standard solution to be added easily. The resolution of peaks and effects of impurities can, in some cases, be improved by the method of medium exchange between pre-concentration and stripping (119). Koster and Ariel have devised a flow cell (120) to overcome the difficulties of sample carry over and oxygen interference involved in this method.

Ladanyl et al (121) have reported a method of "rapid electrolysis and slow stripping" for which they claim good sensitivity to 2×10^{-6} M Cd^{2+} , Pb^{2+} and Cu^{2+} in aerated solutions. The pre-concentration step involved electrolysis at 6 to 8 V, 15 mA in 0.02 M H_2SO_4 for 60 seconds. This potential was not maintained by a potentiostat and it was surprising that a HMDE exhibited stability under such conditions.

Differential or subtractive techniques have been used in stripping analysis. Kemula has used two identical electrodes in the same solution but electrolysed for different times (74). This removed the capacitive current and effects of materials not directly accumulated by electrolysis, such as traces of oxygen and surfactants.

Eisner and Mark (122) explored the possibility of separating the test solution from the electrode, in pure electrolyte, by a thin, semi permeable, ion exchange membrane. Because of the long equilibration time and slow transport through the membrane, satisfactory analysis was not possible. They were able to

pre-concentrate ions of interest in pieces of membrane. In a separate cell the ions were then transferred to an electrode by electrolysis and stripped normally. Berge and Kunkel (123) were successful in separating a test solution and mercury pool electrode by a cellulose acetate membrane. This offers possibilities of analysis of solutions containing organic material which may cause adsorption problems at conventional electrodes.

These techniques have all considered pre-concentration for a set time producing only partial depletion of the ion(s) of interest from the solution. By using a small volume of solution and electrolysis for a time sufficient to give complete deposition of the ion(s), errors arising from small variations in electrolysis time, potential, stirring rate and temperature can be eliminated (124). The sample volumes of 50-100 μ l used in this cell are comparable with those used in non-flame spectroscopic analysis.

Other Stripping Techniques

Stripping with linear potential sweep from the HMDE is limited in sensitivity by the scan rate that can be employed and limited in selectivity by the slow rate of diffusion from within the drop. A small gain in these is given by the use of a derivative output (125). The use of other stripping methods has been investigated to improve sensitivity and selectivity.

Two methods of chronopotentiometric stripping have been devised by Kemula (74). The first was to electrolyse at a fixed potential with a resistance in the order of 10^8 ohms between the electrodes. After a suitable electrolysis time the fixed

potential was disconnected and the change in voltage with time across the cell followed by a high impedance voltmeter. The response consisted of potential steps, the time for a step being proportional to concentration. The alternative method was, after electrolysis, to apply a high voltage (~ 100 V) across the electrodes through a 10^{10} ohm resistor. Again the variation in cell potential with time was followed, the conditions this time being constant current. More precise measurements of trace lead in the presence of a hundred fold excess of cadmium were possible than with linear potential sweep stripping. A disadvantage was the time taken for the stripping step.

By applying a small amplitude sine wave to the d.c. voltage ramp and a phase sensitive detection system (as described in the section on a.c. polarography) the capacitive current and effects of irreversibly reduced interferences can be eliminated (126-130). This has been shown to give an increase in sensitivity of about one order of magnitude. The effects of variations in such parameters as frequency and amplitude of the a.c. potential on the stripping peak were the same as in a.c. polarography. The resolution was also similar so that ions with half wave potentials differing by 50 to 60 mV could be easily resolved. Although the influence of irreversibly reduced species was eliminated, oxygen has been shown to react with amalgams and give a distorted response for zinc due to zinc hydroxide formation.

A similar increase in sensitivity and selectivity can be achieved by using square wave voltammetry (17,131). The

disadvantages are the complex instrumentation and high electrolyte concentrations required. Recent advances in electronics and the use of potentiostats capable of compensating for solution resistance could make this a viable technique. The Japanese workers have also applied amplitude modulated radio frequency (132) a.c. techniques to stripping voltammetry at a mercury film electrode.

The technique of pulse polarography has been applied to stripping analysis (133,134) and offers the same advantages as a.c. and square wave stripping without the necessity of high electrolyte concentrations. The advantages gained by the use of low electrolyte concentrations outweigh the cost of the complex instrumentation. By the use of large scale production and integrated circuits, a compact pulse polarograph is now available commercially (Model 174, Princeton Applied Research Corp., Princeton New Jersey, U.S.A.). This instrument can be used for stripping analysis and for many elements is several orders of magnitude more sensitive than spectroscopic equipment costing three times as much.

Applications

The wide range of cations and anions which have been determined by the various forms of stripping analysis are well documented by the reviews (15,69,70). In aqueous solutions, a wide range of amalgam forming metals may be determined at mercury electrodes. A similar range, also including the noble metals, can be determined on the graphite electrode. The technique is

suitable in the concentration range 10^{-5} - 10^{-10} M. Sample pretreatment depends on its nature. The most widely used application is in the analysis of 10^{-4} - 10^{-6} per cent of metallic impurities in "pure" chemicals, metals, semi conductors, ceramics, etc. High concentrations of alkali and alkali earth metals can often be tolerated and the simultaneous analysis of several ions is possible so that prior separations may not be necessary. There have been many reports on the applications of ASV published since the last reviews. The majority of these describe chemical separation procedures from various matrices followed by normal ASV at the electrodes described previously, and are not included here. The use of ASV for analysis of natural waters and biological specimens is discussed in chapters 3 and 4.

The technique of CSV, used initially for the determination of halides at the HMDE, can be applied to the analysis of other anions forming insoluble mercury compounds (71). As well as the inorganic anions this includes many organic compounds such as oxalate, succinate, dithizonate, diethyl-dithiophosphate, dithiocarbamide (135), dithiocarbamates (136) and 2-mercaptobenzo-thiazole. Recently the analysis of Pb^{2+} by deposition as PbO_2 on a platinum electrode from perchlorate media followed by cathodic stripping into acetate buffer has been studied (137). Other recent reports of the use of CSV include Fe^{III} (138), UO_2^{2+} and WO_4^{2-} (139).

Some organic compounds may be concentrated by adsorption

at one potential followed by a desorption stripping step. This has been used for the analysis of methylene blue at a graphite electrode (140) and triphenyl tin at a mercury film electrode (141).

ASV at the HMDE has been shown to be possible in mixed ethanol/water (114) and the non aqueous solvents, dimethyl formamide (143), propylene carbonate (144) and CHCl_3 (145). The characteristics of amalgam electrodes in molten electrolytes have been studied (146) and the ASV determination of nickel, silver and lead in a molten electrolyte has been reported (147).

Instrumentation

Recent advances in analytical instrumentation have followed the tremendous growth in electronics in the past twenty years. Much of this has involved the application of operational amplifiers to control and measurement circuits.

An operational amplifier is a differential input, wideband (d.c. to 1 MHz), high gain (10^8) amplifier. These are represented in circuit diagrams as shown in fig. 1.5a. The response is given by:-

$$e_o = A(e_b - e_a) \quad \dots\dots\dots 1.12$$

where A = open loop gain

In many circuits, the positive non inverting input is grounded and input and output impedances are used as in fig. 1.5b. Often the connection between the positive input and earth is omitted in circuit diagrams. The output is then given by:-

$$e_o = -(Z_f/Z_i)e_b \quad \dots\dots\dots 1.13$$

The amplifier may be used for carrying out many different

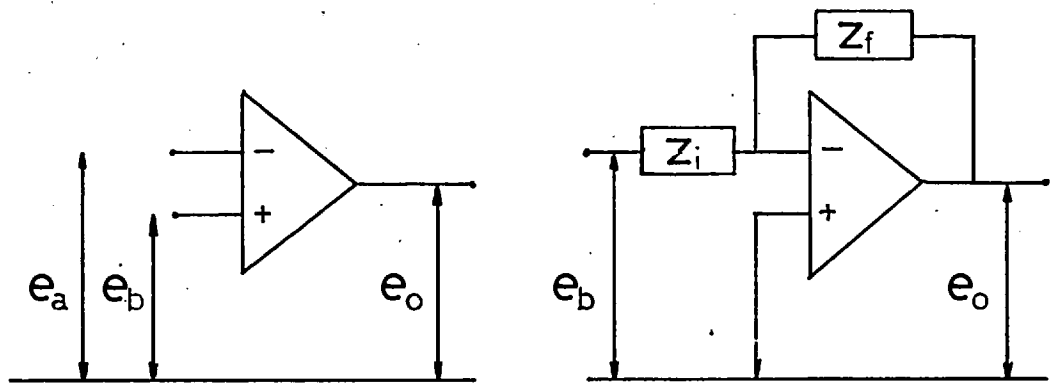


Fig. 1.5a. Circuit representation of an operational amplifier

Fig. 1.5b. Op amp in inverting configuration.

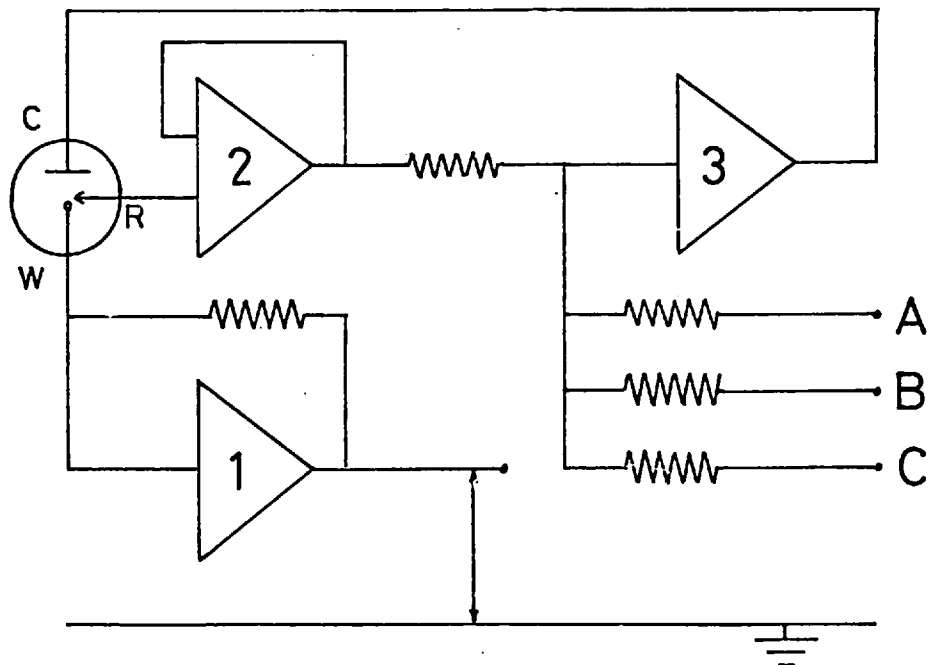


Fig. 1.6. Multi-amplifier potentiostat circuit.

functions by a suitable choice of components in this circuit (148-151). Originally these amplifiers were designed for use in analogue computers where they perform standard mathematical operations; integration, differentiation and logarithmic transformations. Early amplifiers used valve circuits but they are now available either as discrete transistorised components encapsulated in epoxy resin (as used in this thesis) or as integrated devices. These newer amplifiers have made instruments more reliable, cheaper and physically smaller than the original designs.

An analogue approach has been applied to electrochemistry by Booman (152), DeFord and Kelley (29). A recent review has covered the basic theory and use of operational amplifiers (153). A variety of circuits have been developed for established electroanalytical techniques such as d.c. (29), a.c. (10), square wave (154) and pulse (155) polarography.

The heart of most electroanalytical systems is the circuit which controls the electrode potential, termed the potentiostat. Fig. 1.6 shows the most common configuration of a multi-amplifier potentiostat (148). Amplifier 1 maintains the working electrode at earth potential by means of the feedback resistance, and provides a current to voltage conversion. Amplifier 2 is a high input impedance unity gain follower coupled to the potential control amplifier 3 which, through the counter electrode, maintains the reference electrode potential equal and opposite to the sum of potentials from signal sources A, B and C. These

signal sources may be various d.c. levels, a.c. signals, pulse trains, etc. This circuit draws no current from the reference electrode and partially compensates for the resistance of the solution. This allows the use of many organic solvents or low electrolyte concentrations. Refinements to this circuit have included positive feedback (156) to compensate for resistance between the working and reference electrodes. Other circuits may be used for the signal sources and processors to isolate the desired component of the cell current.

An important step in recent work has been the interfacing of electroanalytical instrumentation with computers to get both automatic control of the experiment, data processing and storage of results. Perone (157) has given a comprehensive survey of the applications of on-line computers in the chemical laboratory and has suggested future aims for computerised instrumentation. Analogue to digital conversion can be carried out by a variety of methods (158). Recent work has concentrated on digitised current sampling and data processing for the removal of background response and resolution of overlapping polarographic waves (159).

Automated Analytical Systems

In this thesis the application of some electrochemical techniques to continuous analysis is presented. It is therefore appropriate to consider the reasons behind the increasing demands for mechanised or automated* systems and the approaches that

* The term "automatic" normally refers to a process involving feedback control (160). At present the majority of analytical systems are not automated in this sense although this word appears in their description.

have been made. This has arisen from two directions (161-165):-
(a) the large workloads of routine samples facing hospital, water authority, industrial and other laboratories; and (b) the more rigid analytical control required of many chemical processes.

The greatest expansion in workload over the past ten years has been in the hospital clinical chemistry laboratories. This has been due to larger hospital populations, preventive medicine programmes and the increasing use of clinical assays for diagnostic purposes (166). In the U.S.A., where automated clinical analysis began fifteen years ago, a recent estimate put the workload of these laboratories at 5×10^8 tests annually (167). The workload in the United Kingdom, initially less than in the U.S.A., is now sufficient to warrant automated systems. A typical 600 bed teaching hospital, such as St. George's, London, performs 10^5 tests annually. There is now considerable literature on the use of these systems and many new or improved methodologies are being developed (168).

A similarly increased workload has resulted from the more demanding specifications being required for industrial products and from the close control of fertilizer, water, soil, etc needed in modern agriculture. Systems similar to those used in hospitals have been applied to meet these workloads (169).

For the most efficient operation of a chemical process plant it is necessary to maintain as close analytical control as possible. This ensures that all phases of the process are working within tolerances and reduces the amount of "off specification"

material produced. These requirements have led to the advent of "on-line" analysis as reviewed by Siggia (163). Sampling and analysis by either manual or the methods discussed in the previous paragraph have the disadvantages of time of analysis and sampling errors. Human errors are inherent in manual methods. On-line analysis by continuous sensors can be used to give rapid measurement. This is especially useful when the sensors can be coupled with automatic process control systems which are being increasingly used in industries such as petrochemicals (170).

The decision to automate depends on a combination of such factors as relative overall costs, time saved, personnel requirements and the possibility of more standardised precision and accuracy. In clinical and research laboratories, time and personnel requirements are usually the major factors, whereas in industry the overall improvement in economy is of prime concern.

The main market for commercial analysers has been in the hospital laboratories. Table 1.1 lists some of the available instruments for clinical laboratories and divides them into two classes by their mode of operation:-

a) Discrete analysers which mechanically reproduce the normal chemical steps on separate individual samples. These analysers are often very complex which has resulted, initially, in unreliable operation in many cases. Once these problems have been solved, large systems such as the Multichannel 300 (Vickers Medical Engineering Ltd., Basingstoke, England) offer very high workload capabilities. Discrete analysers offer great potential for

Table 1.1. Automated Clinical Laboratory Instruments			
Machine	Number of tests or channels.	Samples rate/hour.	Cost (£) approx.
Auto-Analyzer	1/6	20/80	5,000+
SMA 12/60	12	60	35,000
SMAC (Technicon Corp.)	20/40	150/200	100,000
C-4 (Perkin Elmer)	4	30/60	10,000
Mark-X (Hycel Corp.)	10	40	30,000
Auto Chemist (A.G.A. Corp.)	24	135	200,000
Automatic Clinical Analyser (Du Pont Corp.)	30	45/90	30,000
M-300 (Vickers Ltd.)	20	300	70,000
GeMSAEC (Union Carbide)	1	120	12,000

kinetic methods of analysis such as enzyme assays. The high precision of instruments such as the one made by L.K.B. Instruments, Croydon, Surrey, outweighs the cost of the complex mechanical system. Analysers based on the centrifuge principle of Anderson (164) are likely to have increasing use now that suitable rapid loading systems are in the final stages of development.

b) Continuous analysers are based on the use of a peristaltic pump and a gas segmented stream. The various stages of analysis are performed on the continuously flowing stream. The original concept by Skeggs (165) has been commercially developed as the Auto Analyser (Technicon Corporation, Tarrytown, N.Y.). Since its introduction, the versatility of this instrument has been expanded to cover a wide range of applications. Where samples are present as a flowing stream such as in water quality monitoring and industrial plants analysers based on continuous flow have an advantage. However because of its simplicity and reliability, the Auto Analyser is by far the most common analytical system used in laboratories in which the samples are present in discrete vials such as hospital laboratories.

Any analytical method consists of the following operations:-

- i) sampling; ii) chemical processing; iii) analytical measurement;
- iv) display of the analytical signal including data processing.

These operations, as performed in continuous analysers, are discussed below.

i) Sampling:- Liquid or gaseous samples may be passed directly to the processing system. Various methods for the dissolution

of solids have been suggested. The most common is that of Docherty (171) which uses a sample divider, an automatic dispensing balance and high speed homogeniser. Anodic dissolution has been shown to be feasible for metal samples (172). In batch analysis the samples are collected in "cups". A sampler withdraws solution from each cup in turn and pumps it to the chemical processing system. By means of a wash solution between each sample and gas segmentation of the stream, cross contamination of samples is minimised.

ii). Chemical Processing:- This stage consists of chemically preparing the sample for analytical measurement of the particular species or property required. Blaedel and Laessig (161) have discussed many continuous processing units. Many modules are available for the Auto Analyser so that operations from simple mixing and heating to Kjeldhal digestions are possible. It is preferred to make both chemical processing and analytical measurement as simple as possible to ensure maximum reliability. The various separation steps such as dialysis, chromatography, distillation and solvent extraction have been used in continuous analysis. The development of a relatively cheap, pulseless pumping system would lead to better control of these stages, especially solvent extraction. The Technicon Mark 3 pump uses a mechanism to produce regular pulses but does not remove them. The use of multiple piston pumps increases mechanical complexity and cost. A non pulsing flow controller has been described (173) with a similar per channel cost as a peristaltic pump but no indication of how a sample might be analysed was given. An advantage of a

mechanised system is that it is not necessary for any particular stage to proceed to completion (or equilibrium). Provided that the flow rate is constant, any stage will proceed by a definite fraction when the next stage is commenced or the measurement taken.

iii) Analytical Measurement:- The majority of commercial analysis systems are based on the mechanisation of relatively slow and tedious manual methods giving a colour reaction and spectrophotometric measurement step. Although these have been shown to be very versatile and reliable they often have limitations such as speed, sensitivity and selectivity. Considerable effort has been made over the last few years to adapt other analytical sensors to overcome these limitations or widen the range of applications. The majority of physicochemical analytical techniques have been used for continuous measurement and are reviewed by Siggia (163) and Blaedel and Laessig (161).

iv) Display of Analytical Signal and Data Processing:- Simple systems display the analogue signals from the sensor on a recorder chart. A measurement is taken when the response reaches a steady level and this can be related to concentration via a calibration graph. For routine applications with established methods it is possible to record results on chart paper directly calibrated in concentration terms. In clinical blood analysis the Technicon SMA 12/60 system records the results of twelve tests on one sample in concentration terms on one sheet of paper together with the range of normal values which can then be used by a doctor in his diagnosis. Although this type of system has been widely used there are several practical drawbacks. It is difficult to ensure

exact phasing of all the results on the chart paper, technician time is wasted manually correcting for drift and the rate of analysis is limited by the necessity to reach 'steady state' conditions. To overcome these limitations on-line control of single and multi-channel analysers by small computers has been introduced. Such systems make use of peak recognition by monitoring sensor output signals, automated measurement of throughput time, calibration curves and regularly spaced standards to correct for drift.

Kinetic Parameters

Skeggs (165) made continuous flow analysis possible by the introduction of bubble segmentation of the liquid stream which reduced longitudinal mixing of samples within the system. The ideal square wave signal is deformed by mixing between segments and in the non segmented parts of the stream producing the characteristic peak, fig. 1.7a. Normal methods are based on the attainment of steady state response. Samples are interspaced with blank solutions to minimise interaction between samples, usually termed 'carry over'. The sampling time (t_s) and wash time (t_w) determine the sampling rate. The time required for the sample to undergo chemical processing and reach the sensor is the delay time (t_d).

Thiers (174) has investigated the shape of rise and fall curves of such systems and shown that, to a first approximation, these consist of an exponential phase, (1st order kinetics) produced by the unsegmented stream, and a lag phase produced by the segmented part of the systems. He introduced the terminology 'half wash

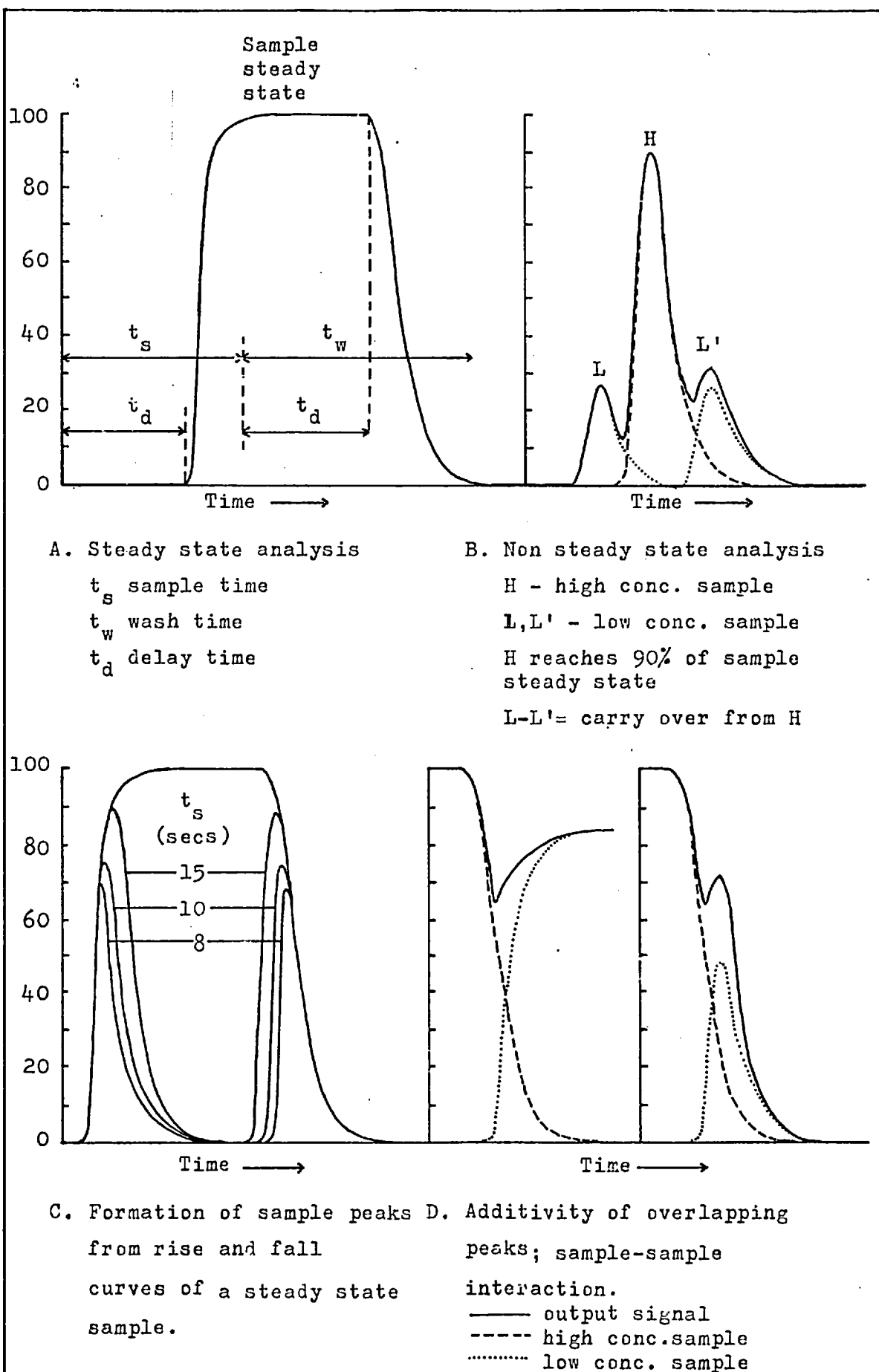


Fig.1. 7. Continuous analysis - recorder charts. From ref.174.

time' ($W_{1/2}$) and 'lag phase time' (L) and showed how they could be utilised to evaluate and optimise the performance of any continuous flow system or component. In practice, $W_{1/2}$ makes a larger contribution than L.

If t_s and t_w are so short that the response does not reach steady state, traces such as fig. 1.7b are formed. The term ' % steady state' is given to such peaks. Carry over and variations in peak height because of timer errors are observed but faster rates of analysis are possible under such conditions. Thiers (174) showed that such peaks were formed by additive superimposition of rise and fall curves as shown in fig. 1.7c. Thiers (175) later produced a mathematical model to account for interactions in the bubbled stream. A more exact treatment has been given by Begg (176) who showed that $W_{1/2}$ and L were a measure of the same phenomenon and could be better described by an expression relating the fluid transfer from one segment to the next per unit length of tube.

Walker (185) has developed a simple model to account for the deformations occurring in the non-segmented stream and shown how these could be removed electronically by the technique of curve regeneration. The basis of this analog technique is that the final height of the peak can be predicted from the slope of the rise portion of that peak. A simple operational amplifier circuit is used to add a constant proportion of the slope to the existing signal. This type of approach reduces carry over without modification to the flow system.

The work of Thiers and Begg has been applied in the Technicon SMAC and similar systems which segment the liquid stream from sample cup to sensor in order to minimise carry over. Curve regeneration systems are also available commercially (Fisons Instruments, Weir Electronics) but an equivalent mathematical operation could be built in to on-line computer installations for multichannel operation. Both techniques permit sampling rates of up to 200 samples/hour, similar to the faster discrete analysers.

PART I: THE APPLICATION AND EVALUATION OF STRIPPING VOLTAMMETRY
TO CONTINUOUS ANALYSIS

Introduction

There has been increasing demand in recent years for simple, low cost methods of quantitative analysis for trace levels of heavy metals in a wide range of materials. Many sensitive and selective spot tests have been developed for qualitative measurement using either a specific colour or fluorescence for positive identification. These methods have been replaced by the quantitative measurements made possible by the wide range of instrumental techniques now available. Table 2.1 gives an outline comparison of several parameters which could be used in deciding on a method of trace metal analysis. Although there would be variations for specific elements, atomic absorption and fluorescence are very comparable to pulse polarography and anodic stripping voltammetry except that equipment and operation costs for the latter are lower. For some purposes very little sample preparation or prior concentration steps are necessary. Other advantages of stripping voltammetry are that it is free from fire risks and only requires simple supplies of electricity and high purity nitrogen or argon. One scan may be sufficient to determine several ions in a solution. A disadvantage is that the electrolysis step limits the rate of analysis.

The simplest form of stripping analysis only requires the use of a polarograph and electrode assembly. This fact and the simplicity of construction of equipment by laboratory staff has

Table 2.1. A comparison of methods for trace metal analysis

Key 1 = low - 5 = high or wide

Method	Range of application	Sensitivity ($M\ l^{-1}$)	Selectivity	Costs	Operator requirements	Application to Continuous Analysis
Colorimetry	4	$10^{-5} - 10^{-6}$	2	1	1	yes
Fluorimetry	3	$10^{-7} - 10^{-8}$	3	2	2	yes
Mass spec.	5	10^{-4}	5	4	5	no
Arc/spark emission	4	10^{-4}	4	3	4	no
Flame emission	1	10^{-6}	4	1	2	yes
A. A. S.	4	$10^{-6} - 10^{-7}$	4	3	3	yes
A. F. S.	3	$10^{-7} - 10^{-8}$	5	3	3	yes
X-ray fluorimetry	4	10^{-3}	4	4	5	no
N. A. A.	5	$10^{-9} - 10^{-10}$	5	5	4	no
Polarography	4	10^{-5}	2	1	3	yes
Pulse polarography	4	10^{-5}	4	2	3	yes
A. S. V.	3	$10^{-8} - 10^{-9}$	4	1	3	?

meant that an instrument made specifically for stripping voltammetry was not available commercially until recently. This instrument (177) incorporates one or more modules each containing four potentiostats coupled with a d.c. voltage sweep generator and current amplifier. The cells used are based on the composite mercury/graphite electrode (89) and have some advantages over hanging drop mercury electrodes as described previously. Although manually operated, the machine is suited to batch analysis of samples in sequence, as up to twelve cells may be connected at one time. Thus the electrolysis step does not necessarily limit the analysis rate but a high degree of operator involvement is required.

In view of the many steps involved in stripping voltammetry surprisingly little work has been done on the automation of this technique. Neeb and Sauer (178) devised a semi-automated instrument in which a piston burette was used to form mercury drops on an inverted capillary mounted in a conventional cell. The operations of electrode formation, stirring and voltage sweep were automated. An analysis cycle included a flushing step to remove mercury in the capillary which may have been contaminated with amalgam from a previous sample. Detection limits of 10^{-6} M Cd^{2+} and Tl^{+} , 5×10^{-7} M Cd^{2+} and Cu^{2+} were reported using a 60 second electrolysis step.

Another system has been reported by Tamba and Vantini (179) in which the working electrode, a mercury pool, was renewed either mechanically or electrochemically. During electrolysis the test solution was allowed to flow over the electrode surface at a

controlled rate. Stripping was performed into a blank electrolyte solution. More reproducible results were obtained using a glass electrode support than with one made from Teflon. A few quantitative results were given for test solutions of between 10^{-6} M and 5×10^{-4} M and it was stated the equipment was suitable for the analysis of Pb^{2+} at 10^{-8} M.

A fully automated system for stripping voltammetry was reported by Booth et al (180) and used for the determination of the triphenyl tin cation in the range 2×10^{-8} M to 2×10^{-7} M. A thermostatted cell with separated reference electrode was employed with a rotating mercury plated platinum wire electrode. Each stage of analysis was controlled by a cam operated cycle timer and the instrument could be left unattended for several hours. The instrument was used for the determination of triphenyl tin, a fungicide, in potatoes via a manual extraction procedure. Although no provision was made for sample changing, this work showed the advantages of automating the many stages involved in this type of analysis. The electrode performed satisfactorily for up to eight hours providing it was kept in an oxygen free environment.

No reports of the application of stripping voltammetry to continuous analysis in flowing streams have appeared in the literature although the method, in view of its relatively low cost, simplicity and selectivity, ought to be considered for this type of analysis. This may be because the method requires deoxygenation and electrolysis steps, the latter disadvantage being overcome by pulse, square-wave and phase sensitive a.c.

polarography which have comparable sensitivity.

Instability of the hanging mercury drop electrode has been a further practical disadvantage of stripping voltammetry. The long drop time DME possesses the advantages of accurately reproducible electrode shape and surface area compared with other electrodes. A DME of 60 seconds drop time was used by Macchi (83) for the analysis of Zn^{2+} in brine. One of 12 minutes drop time has recently been reported and used for the analysis of Cd^{2+} in HCl by a.c. stripping voltammetry (86).

Preliminary work on the use of this type of electrode for continuous analysis by stripping voltammetry has been carried out by Booth (85). He compared the performance of this electrode in two types of flow cell. The first was a simple flow cell in which the electrode was positioned within a 2mm tube and was compared with a larger volume cell incorporating a magnetic stirrer. Electrode instability made the first cell impractical to use. The cell incorporating a magnetic stirrer gave good results but was unsuitable for the analysis of small samples. The cam operated cycle timer (180) was used to control each stage and batch analysis of samples containing 10^{-6}M Cd^{2+} , Pb^{2+} and Zn^{2+} was demonstrated.

Whilst the present work was in progress the use of a stripping voltammetry system for the continuous analysis of mercury in effluent was reported (181). The working electrode was glassy carbon, the surface of which was renewed electrochemically each cycle by keeping the electrode at 1.0V for a set period after

the stripping step. The system was used continuously for several months.

The work presented here describes the use of the long drop time DME and mercury plated glassy carbon electrode in an automated system for both anodic and cathodic stripping voltammetry.

CHAPTER 2: THE DEVELOPMENT OF A SYSTEM FOR CONTINUOUS ANALYSIS
BY STRIPPING VOLTAMMETRY

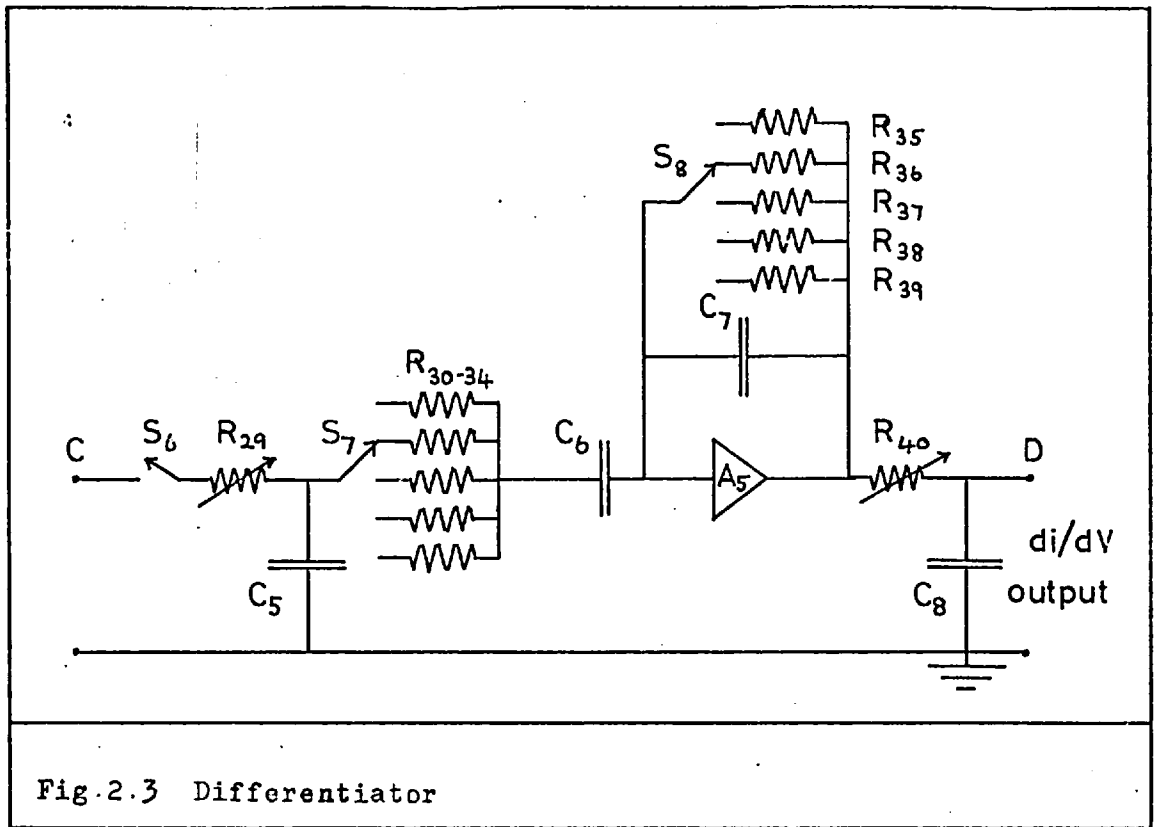
2.1 Experimental

2.1.1 Stripping voltammetry unit

This unit, constructed from operational amplifiers, was a modified version of an earlier system (180). The potentiostat circuit was based on a circuit given by Smith et al (10) and is shown in fig. 2.1. The capacitors C_1 , C_2 and C_3 were required to prevent the circuit from oscillating. A high input impedance amplifier was used for the reference voltage follower amplifier A_2 so that the d.c. current drawn was less than 10^{-11} A. The output of A_2 and other signals were fed to the summing point of A_1 through 100 K resistors R_1 to R_4 . The d.c. level was supplied at a point A, the ramp voltage at B and external signals could be applied to point C. A_3 was a current follower and produced a voltage output proportional to the current flowing through the cell to the working electrode. This voltage was selected by S_1 , and the feedback resistors R_7 to R_{11} , to give current ranges in multiples of ten from a range of 0 to 1 μ A to a range of 0 to 10 mA for 10 V output. Controls for baseline zero and slope offset were provided. The latter was of use to partially offset the capacitive current and the current due to dissolved oxygen. Fig. 2.2 shows the circuit for the variable d.c. potential and ramp generator. A 0 V to ± 2 V potential was obtained from a 1 K, ten turn Heliopot in series with a 6.5 K resistor across the 15 V supply and it was connected with A_1 via point A. The d.c.

ramp was produced by integration of a constant current using A_4 and C_4 . Scan rates of 25 mV.s^{-1} and greater were chosen so that a chopper stabilised amplifier, as used in high accuracy polarographs, was not necessary. The zero drift of A_4 was offset by applying a current to the input via R_{19} and the potential divider R_{18} . The latter resistor was adjusted to give minimum drift with S_4 in the mid position. The constant current to be integrated was obtained from the 15 V supply by the potential divider, R_{20} and R_{21} , and the selection of a suitable resistor, R_{22} to R_{27} , by S_5 . The resistor values selected ensured that the integrator current was less than 10^{-3} times that in the potential divider. Nominal scan rates of 25, 50, 100, 250, 500, 1000 and 2000 mV.s^{-1} were available. The d.c. level and ramp voltages were displayed on voltmeters V_1 and V_2 . S_4 provided a scan, hold and reset sequence. In the hold position only the zero offset current was supplied to the integrator whilst in the reset (electrolysis) position C_4 was discharged through R_{28} . This resistor was chosen to limit the discharge current to 20 mA so that the capacitor was not damaged.

In order to investigate the use of derivative stripping voltammetry the circuit shown in fig. 2.3 was incorporated in the unit. This was based on the circuit of Perone and Mueller (42) and uses A_5 in the current follower mode preceded by C_6 . The resistor capacitor networks, $R_{29}C_5$, $S_7R_{30-34}C_7$ and $R_{40}C_8$ act as low pass filters and were necessary to prevent oscillation of the circuit. The sensitivity of the derivative output could be varied in multiples of ten by the feedback circuit S_8R_{35-39} .



S_6 isolated this part of the circuit when not required.

A_2 was a FET input, Analog Devices 141A (Analog Devices, Kingston-upon-Thames), whereas the others were general purpose type PF85AU (Philbrick Nexus Research Inc., Chichester). All other components were obtained from Radiospares Ltd., London. A stabilised power supply, model ED56 (Coutant Electronics, Reading), was used to provide 0 and $\pm 15V$ for the operational amplifiers and potential dividers.

The circuit was constructed on five 5" x 3" Veroboard panels each of which held one operational amplifier and associated components. These boards and the power supply were housed in a metal cabinet 10" x 8" x 8". Power supply to the boards and connections to the switches and variable controls on the cabinet

front panel were made with edge connectors. Care was taken in the design to eliminate earth loops and screened leads were used to connect the electrodes to the unit. The unit and recorder were powered from a 240V Advance Voltstat.

2.1.2 Control assembly

The various operations in the automatic stripping process were controlled by a cam operated cycle timer (type TCP, Appliance Components Ltd., Maidenhead). The original 1/12 rpm motor was replaced by two low rpm motors and gears which provided 50 and 200 s cycle times. Ten adjustable switches were provided which gave make or break switching. The unit was housed in a metal cabinet with sockets on the front panel for connection to the switches. Most of the cam switches were simply connected in the power supply leads of various units. e.g. the magnetic stirrer and chart recorder motor. The Servoscribe recorder pen lift was an electromagnetic device operated from a 24V transformer within the cam cycle timer. Control of the stripping voltammetry unit was made by putting S_4 (fig. 2.2) in the scan position and connecting the cam switch across S_4 . During electrolysis S_4 and hence C_4 is shorted through R_{28} keeping the d.c. voltage constant. On opening the cam switch a ramp of required duration was obtained. The voltage scan was dependent upon both scan rate and duration of opening of the switch.

2.1.3 Display of signal

The stripping voltammograms were displayed on a Servoscribe Y/T recorder (Smiths Industries, London). This instrument has

a full scale response time of 1 second. When a faster response was required a Brians model 22000 XY plotter was used. This has response of 115 cm.s^{-1} . A Hewlett Packard model 141B storage oscilloscope with 142A time base (horizontal sensitivity 0.8 to 2.5 V cm^{-1}) and 1401A dual trace amplifier (0 to 450 KHz , 10^{-3} to 10 V cm^{-1}) was used to display stripping voltammograms at fast scan rates to check the response of the recorders. In each case the electrode response was displayed on the Y axis. The d.c. ramp voltage was used to provide the time base for the oscilloscope and XY recorder.

2.1.4 Electrodes

Glass capillaries of 0.08 and 0.02 mm bore were obtained in 30 cm lengths from Plowden and Thompson Ltd. (Stourbridge, Worcs.). The 0.02 mm capillaries gave drop times of 50 to 80 seconds for mercury heads of between 70 and 30 cms . As an alternative the constricted capillary proposed by Yamazaki (14) was prepared from 0.08 mm capillary by careful heating. These could be prepared to have any desired drop time. The capillaries were ground by hand to a taper point on an oil stone. It was found necessary to keep mercury flowing during grinding to prevent blockages from forming. A solenoid fitted with an arm acts as a mechanical drop controller when momentarily energised by the cam cycle timer. By shielding the mercury reservoir, connecting tubing and top part of the DME with aluminium foil connected to the instrument earth, the 50 Hz mains noise on the output was reduced to approximately $1/10$ its original level.

A glassy carbon electrode was prepared by sealing a 5 mm length of 2 mm diameter glassy carbon into glass tubing with epoxy adhesive. After grinding to remove excess adhesive the surface was polished with fine diamond paste. After polishing the surface was black and lustrous without surface irregularities when observed under x 50 magnification.

The reference electrode was normally a separated 1 M KCl/calomel electrode of approximately 1 cm² surface area. This electrode was normally downstream of the cell to prevent contamination of the test solution with impurities in the electrolyte. A Technicon T connector, type AO, with a plug of agar/1 M KNO₃ was used in the cell pull through tube to separate the reference electrode from the test solution.

2.1.5 Flow cell assemblies

The various flow cells were constructed from clear Perspex. This material was relatively simple to machine and allowed observation of the electrodes. Connections to the AutoAnalyser manifold were made with 2 mm o.d. glass tubing or alternatively Technicon polythene connectors housed in 4 mm o.d. Tygon tubing fitted into 4 mm holes in the cells. The working electrodes were fitted to the cells with Tygon sleeving. This allowed simple alteration to position and enough flexibility for operation of the drop timer.

Cell 1 shown in fig. 2.4 was a modification of Booth's original design (85). The modifications are the addition of a drainage hole linked to the peristaltic pump to continuously

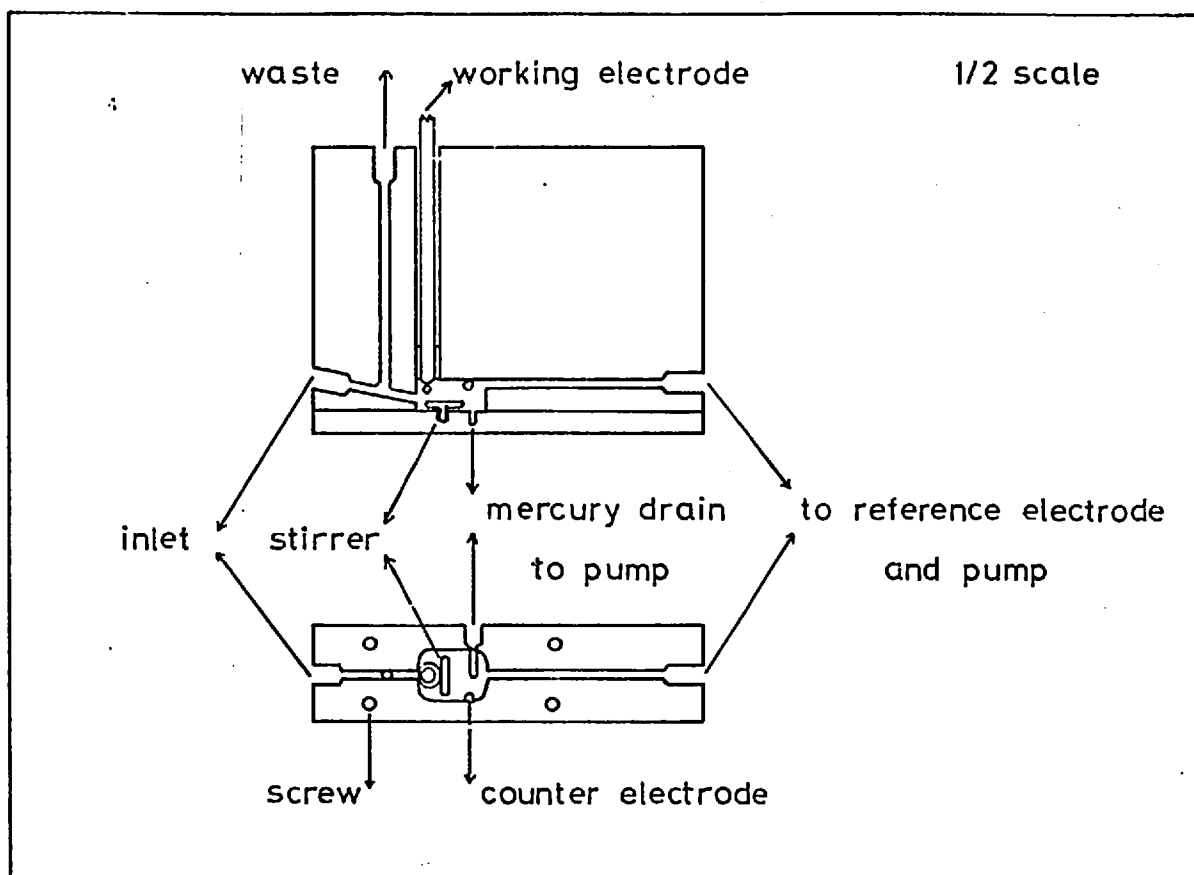


Fig. 2.4. Flow cell with magnetic stirring - 1.

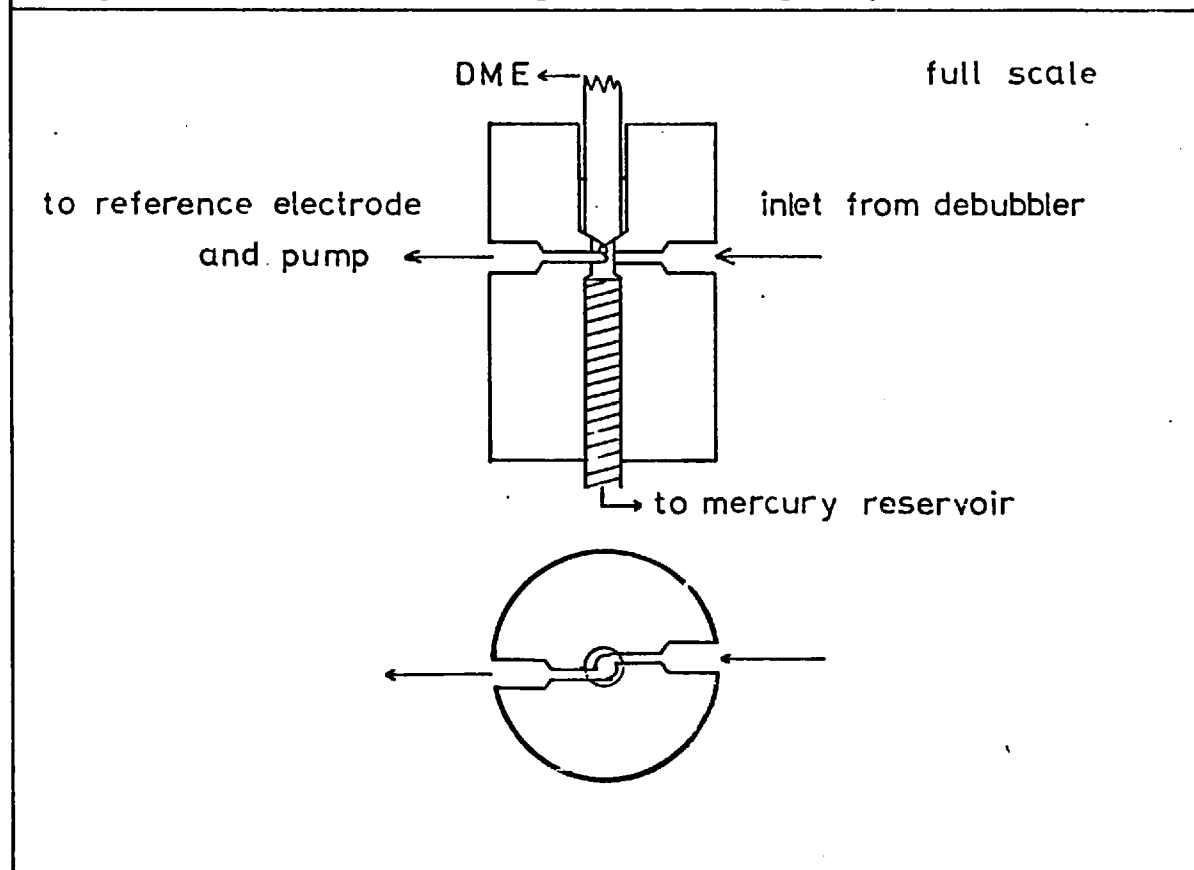


Fig. 2.5. Flow cell with vortex mixing - 2.

remove waste mercury, a silver bead counter electrode, a pivoted stirrer and a reduction in volume from 2.4 to 1.2 cm³. The stirrer bar was constructed from 5 mm lengths of soft iron wire sealed in 1 mm o.d. glass tubing. The pivot was a 2 mm length of glass sealed to the centre of the stirrer. The stirrer was pivoted so that the end of the stirrer bar was directly under the DME and approximately 1 mm below the mercury drop. The cell was positioned over a magnetic stirrer driven by a synchronous motor.

Although one type of polarographic flow cell has been shown to be unsatisfactory for stripping voltammetry (85) the simplicity of this type of cell, compared with a magnetically stirred cell, made further study necessary. Cell 2 shown in fig. 2.5 was constructed to investigate vortex type flow in a small volume cell. Waste mercury from the working electrode fell onto the mercury pool counter electrode which was connected to a reservoir of large surface area to provide an approximately constant height. This cell was also used as a two electrode system with the reference electrode and cell pull through connected to the vertical outlet, the horizontal outlet being blocked off. Cell 3, a completely self contained cell, is shown in fig. 2.6. This cell was designed to give a vortex type flow of solution around the central electrode. An annular mercury pool counter electrode was kept isolated from waste mercury from the DME. Vycor glass, saturated with 10 % KNO₃ provided electrical connection to the integral 1 M calomel reference electrode. Solution was pulled through the cell by the peristaltic pump through two tubes. Most

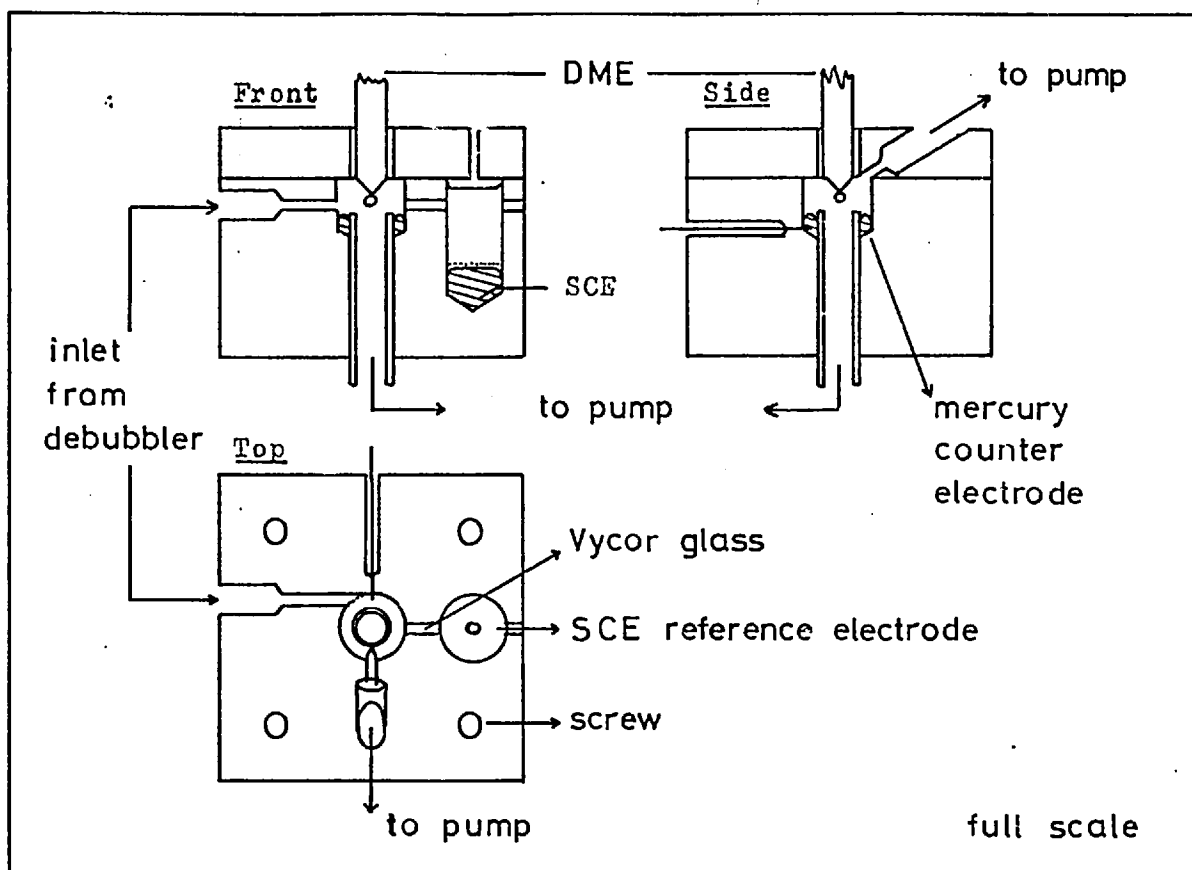


Fig. 2.6. Flow cell with integral reference electrode - 3.

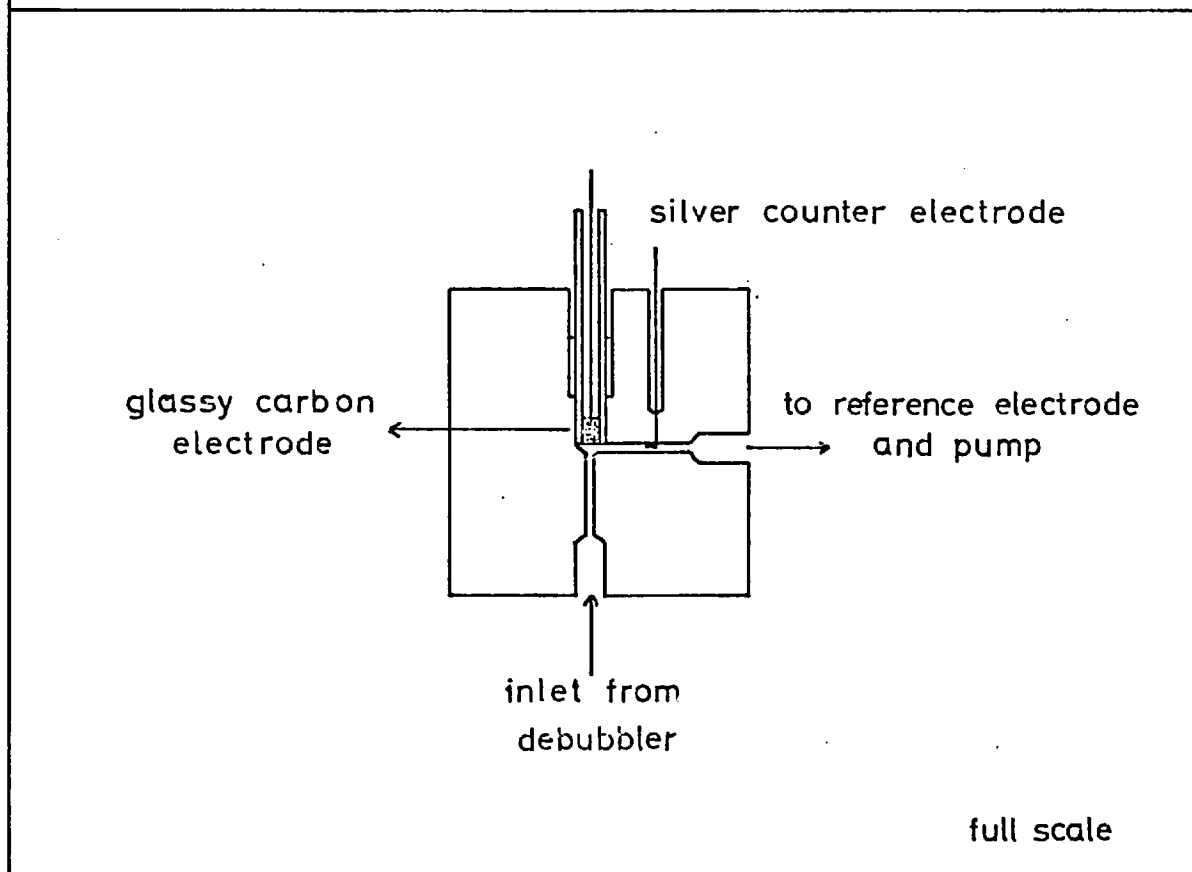


Fig. 2.7. Flow cell with glassy carbon electrode.

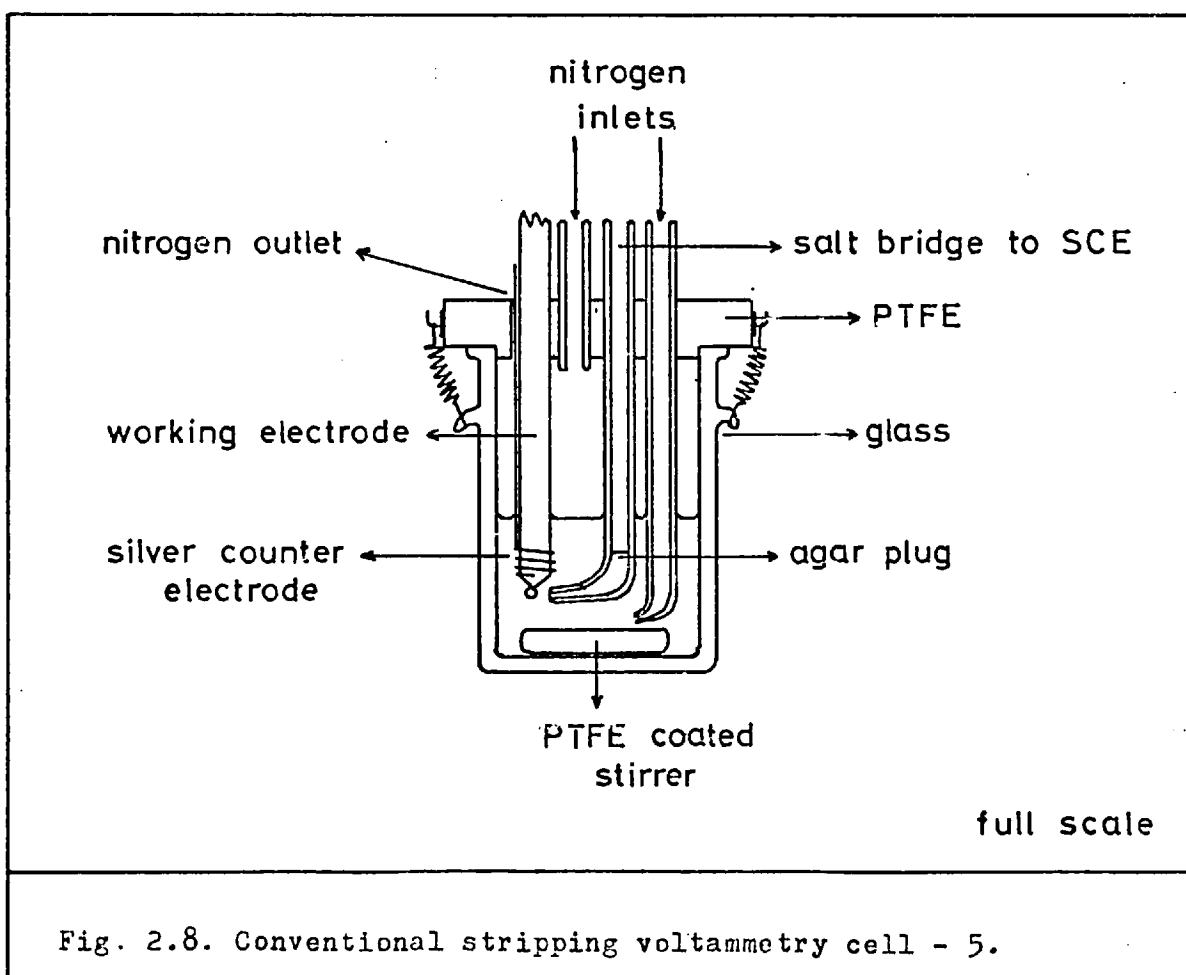
of the test solution and waste mercury was flowed through the bottom exit. The second outlet was fitted so that any gas bubbles entering or forming within the cell were quickly removed.

The glassy carbon electrode was fitted in the cell shown in fig. 2.7. Both reference and working electrodes were downstream to prevent contamination of the test solution.

A conventional cell shown in fig. 2.8, incorporating silver wire counter and separated calomel reference electrodes and a magnetic stirrer, was used to test the working electrodes before connection to the flow cells. 10 ml aliquots of solution were used in this cell.

2.1.6 AutoAnalyser manifold

A standard Technicon Mk. 1 peristaltic pump with associated



tubing and glassware was used for the construction of flow systems. A jacketed mixing coil, thermostatted at 25°C, was used to provide temperature control. Fig. 2.9 shows manifold designs for the various cells. The flow rates were altered in some experiments, as discussed later, keeping the same ratios of sample:electrolyte:nitrogen. A Technicon sampler Mk. 2 was modified to allow the sample solution to be deoxygenated with nitrogen before aspiration. This was done by fitting two probes to the sampler arm so that whilst one cup was being sampled, nitrogen was passed through the next cup in line. The wash reservoir was repositioned with spacers so that the nitrogen probe cleared the sampler housing when in the "wash" position. The samples were placed in 10 ml cups and covered with Parafilm. A hole, approximately 3 mm diameter, was made in the cover where the probes entered the cup. Similarly the wash reservoir was kept covered and deoxygenated with nitrogen. Water, for sampler wash, and electrolyte solution were stored in polythene bottles and kept deoxygenated during use with a stream of nitrogen.

2.1.7 Reagents

Mercury: Triple distilled analytical reagent grade was used. This was cleaned after use by air oxidation under 10 % nitric acid for 24 hours, washed with water, dried, filtered and distilled in vacuo.

Water: This was distilled from Pyrex glass. Measurements by atomic absorption spectrophotometry gave less than 10^{-8} M Pb^{2+} .

Nitrogen: Oxygen free grade (B.O.C.) was used.

Electrolytes: Analytical reagent grade potassium chloride and

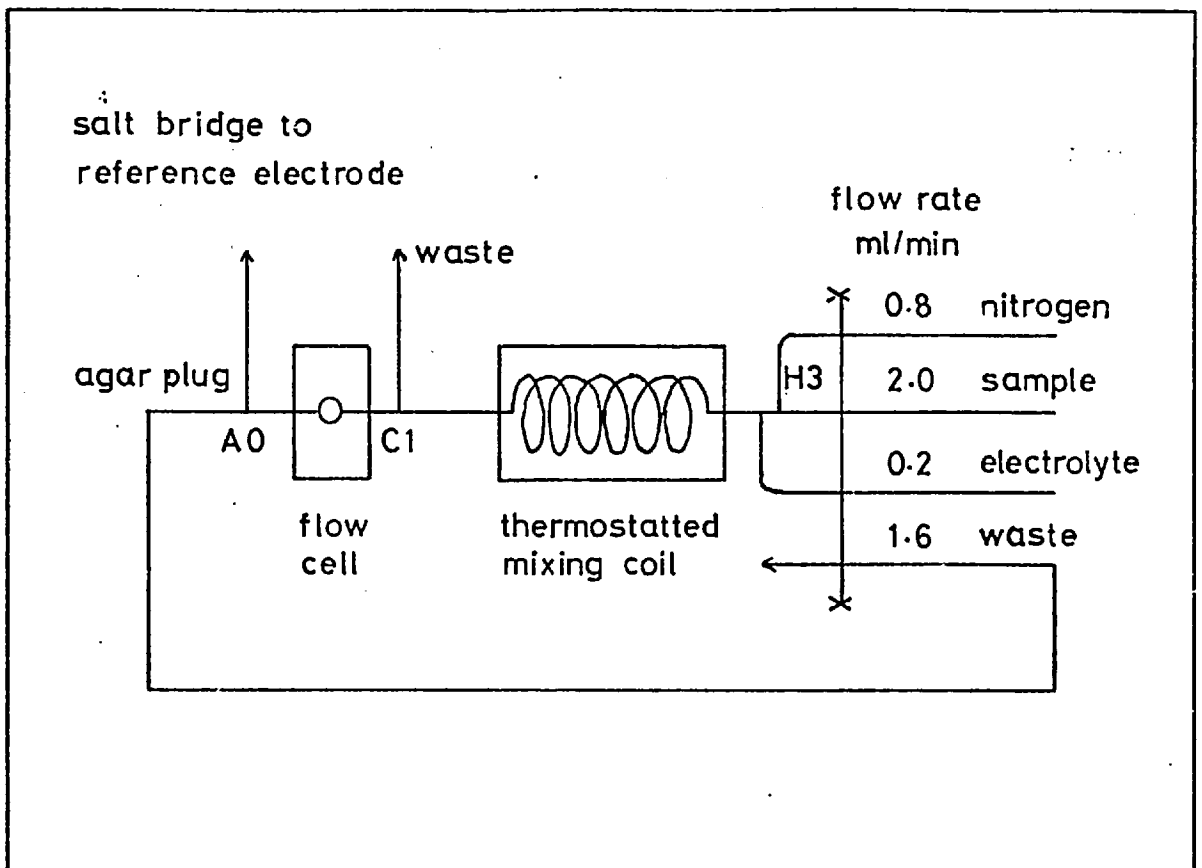


Fig. 2.9a. Autoanalyser manifold - single exit flow cell.

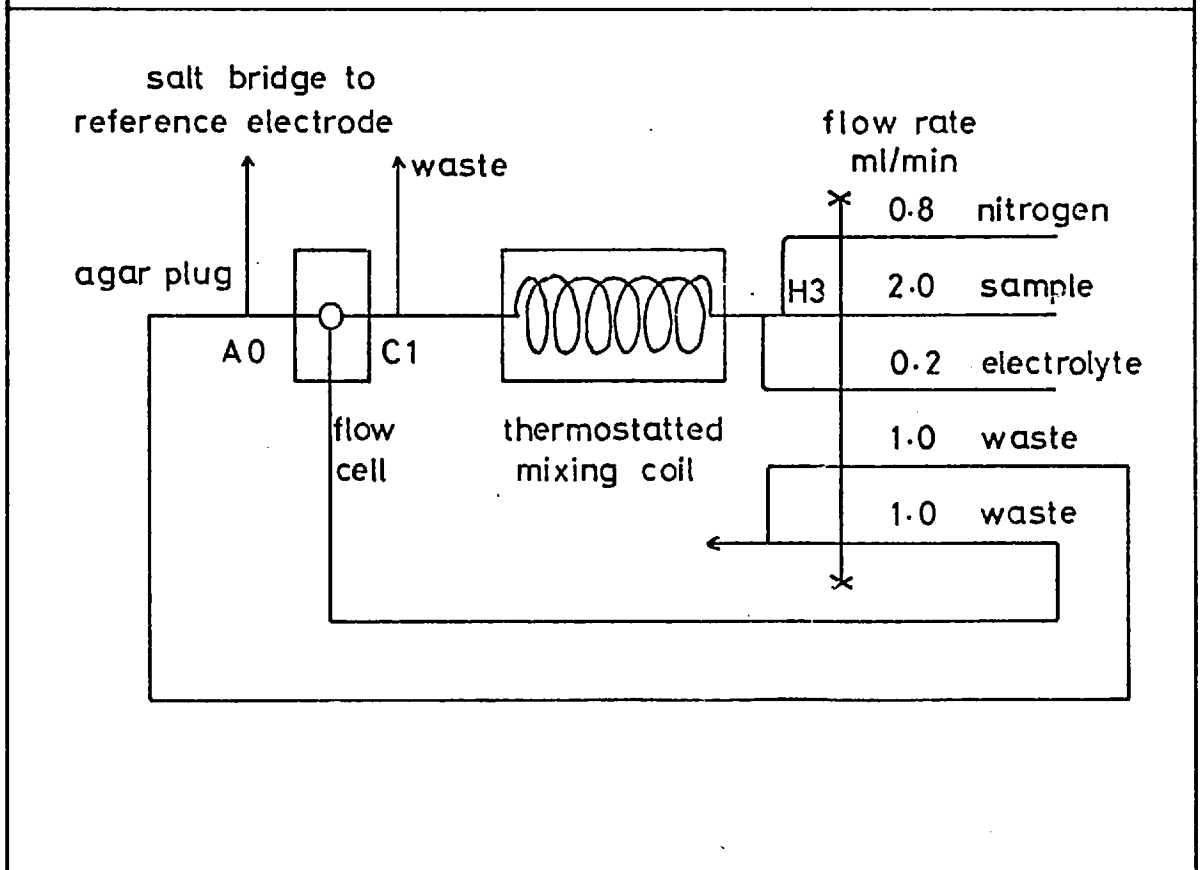


Fig. 2.9b. Autoanalyser manifold - twin exit flow cell.

nitrate were purified of traces of lead by electrolysis of saturated solutions of these salts as described by Barker (184). When required for cathodic stripping voltammetry, the potassium nitrate was electrolysed to remove trace chloride.

All other reagents were of analytical reagent grade. 10^{-3} M stock solutions of the ions to be measured were diluted immediately before use. Acid washed containers were used to store all solutions. Dilute solutions were prepared and stored in containers that had been equilibrated with a solution of the same composition for 24 hours.

2.2 Evaluation of the system for anodic stripping voltammetry

2.2.1 Calibration

The stripping voltammetry unit was calibrated by the use of a range of 1 % tolerance resistors as dummy cells. The reference and counter electrodes were joined together. The voltage output from 1.0 V applied across the dummy cell was then calibrated in terms of cell current for each sensitivity setting. Stripping peaks were measured by the method given by Barendrecht (15).

2.2.2 The long drop time DME

This electrode was initially used in cell 5 to establish the optimum conditions for its use. The cam sequence for automation is shown in fig. 2.10. It was found necessary to interrupt stirring during the stripping step as voltammograms obtained with stirring were poorly defined. A single 12" length of 0.02 mm bore capillary could only be used for drop times of

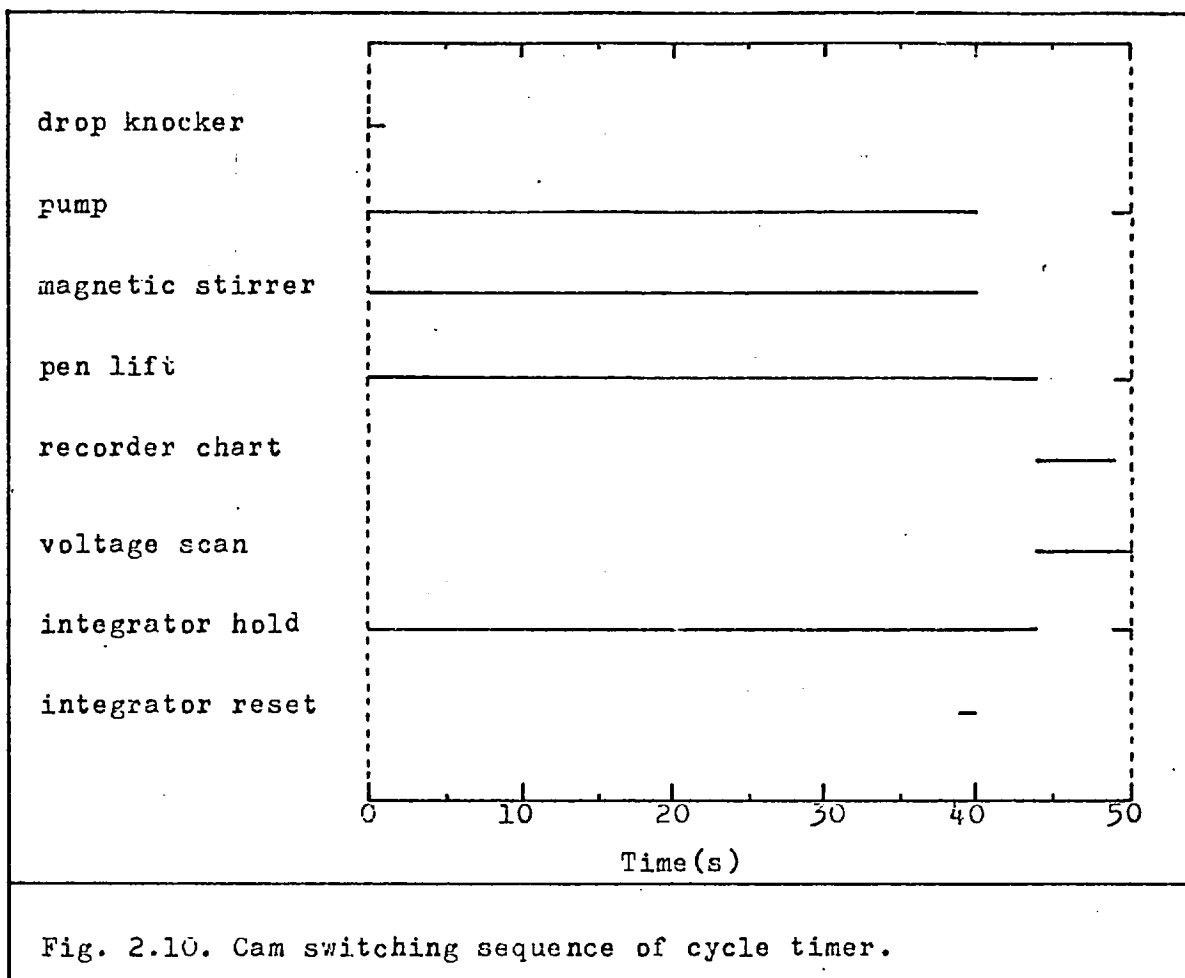


Fig. 2.10. Cam switching sequence of cycle timer.

less than 80 seconds. The use of several lengths of capillary in series for slower drop times did not give satisfactory results. The larger diameter, constricted bore capillaries produced a more stable electrode with a lower incidence of drop failure. The pointed capillaries gave approximately 10 % greater peak current compared with a convential blunt end. This was presumably due to the decreased shielding of the electrode surface. The main advantage of the pointed tip was that small air bubbles did not become trapped under the electrode.

The work of Booth (85) was repeated using cell 1 with the manifold of fig. 2.9b and cam sequence of fig. 2.10. The electrolyte was diluted by a factor of approximately 10 and the sample by a factor of 1.1. Test solutions were deoxygenated in

and aspirated directly from their containers. The sampler was only used for batch analysis. Actual electrolyte and sample concentrations, not cell concentrations, are used. The natural drop time of the electrode was adjusted to be ten seconds longer than the cycle time. The electrode was used directly in line with the entrance to the cell and the stripping voltammograms were independent of flow rate up to the maximum rate used of 4.0 ml.min^{-1} . Many of the variables such as electrolysis potential and time, delay time, voltage scan, scan rate, etc. were interrelated and the results obtained depended on the choice made. The sum of electrolysis, delay and scan times was equal to or less than the cycle time.

The stripping peak current for each ion was independent of electrolysis potential above a certain minimum. These values, using 10^{-1} M KNO_3 electrolyte, are:-

Ion	Cu^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}
Minimum electrolysis potential V vs 1 M calomel electrode	-0.10	-0.50	-0.70	-1.20
Stripping peak potential V vs 1 M calomel electrode	+0.03	-0.35	-0.57	-0.96

Thus the electrolysis potential and scan were kept to a minimum to encompass the ion(s) of interest. The scan voltage was dependent on the preset scan rate time. Fig. 2.11 shows a chart record of continuous stripping voltammetry of $10^{-6} \text{ M Pb}^{2+}$ in 10^{-1} M KNO_3 . Table 2.2 shows a comparison of 50 and 200 second cycles when using a constricted capillary DME for the determination of $10^{-6} \text{ M Pb}^{2+}$ in 10^{-1} M KNO_3 . The actual current increased by 7.5:1 compared to the 4:1 increase in electrolysis time using

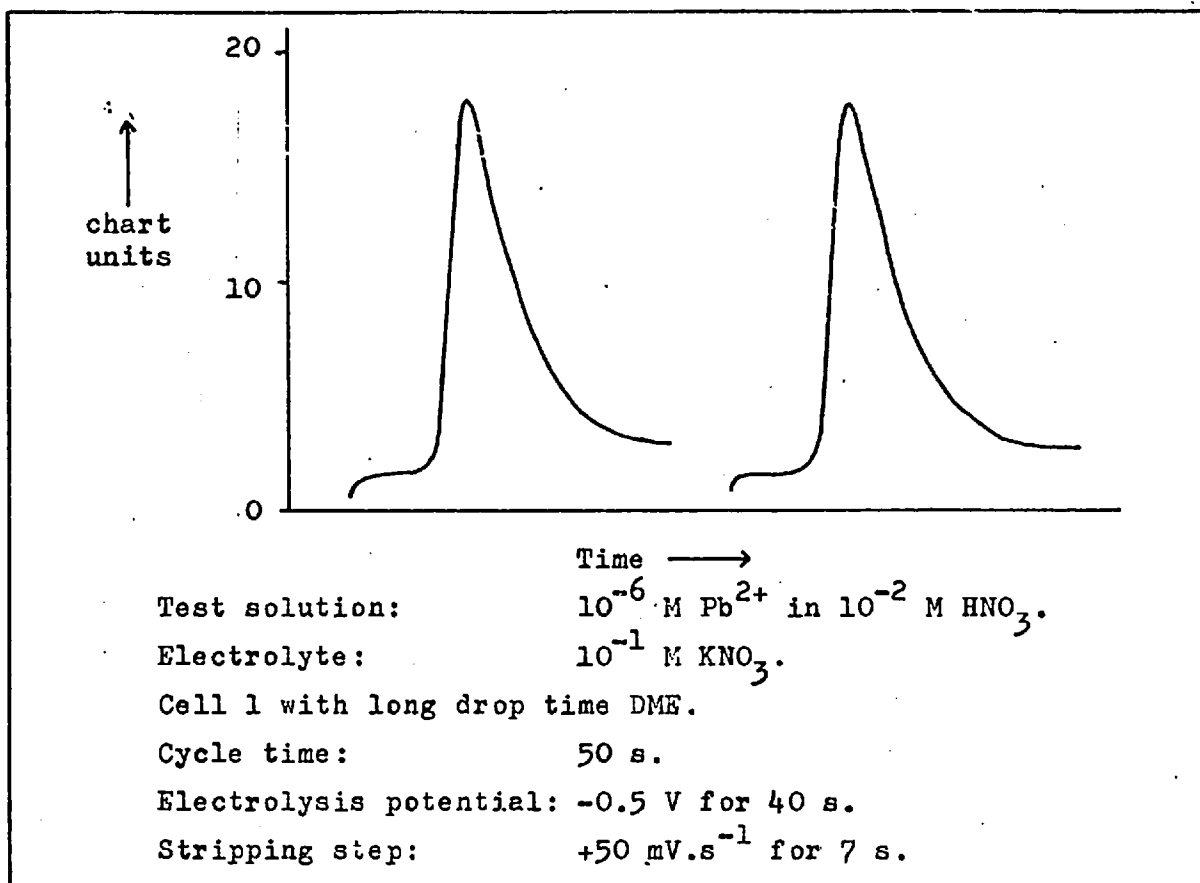


Fig. 2.11. Continuous flow stripping voltammograms.

Concentration ($\times 10^6$ M)	50 s cycle		200 s cycle	
	i_p (μA)	relative standard deviation	i_p (μA)	relative standard deviation
0	0.008	25	0.063	12
1	0.022	5	0.172	4
2	0.038	5	0.295	4
3	0.050	4	0.400	3
4	0.064	5	0.485	4
5	0.080	3	0.600	2

Table 2.2. Comparison of 50 and 200 s cycle timers.

the longer cycle time but the actual reproducibility of measurement was only improved 2:1. The shorter cycle time required less sample and gave faster analysis and was therefore used for all tests unless otherwise mentioned.

Fig. 212 shows the effect of scan rate on the determination of 10^{-6} M Pb^{2+} in 10^{-1} M KNO_3 from an electrolysis potential of -0.60 V for 40 s. The results of all three recorders is shown for comparison. Theoretically, i_p is proportional to the square root of the scan rate. The rate of recorder response affected the response when compared with the oscilloscope but for rates of 100 mV.s^{-1} and less the Servoscribe recorder was satisfactory providing the chart peaks were less than 50 % f.s.d.. The XY recorder was suitable for scan rates of up to 500 mV.s^{-1} . The baseline current was significant at high scan rates. This was due to both capacitive current and residual oxygen (115). The baseline slope control provided a linear ramp compensation but the baseline was often curved. By keeping the voltage scan to a minimum, as indicated above, a satisfactory correction could often be made. Table 2.3 shows the variation in peak width at half height with both concentration and scan rate obtained with this electrode. This width could be used to give a measure of the resolution of the method. At scan rates of 50 mV.s^{-1} or less the width was a minimum and independent of concentration. An increase in scan rate increased the width and could be expected to decrease resolution. It was also noticed that above a scan rate of 50 mV.s^{-1} the width increased with concentration.

The effect of electrolyte concentration was investigated

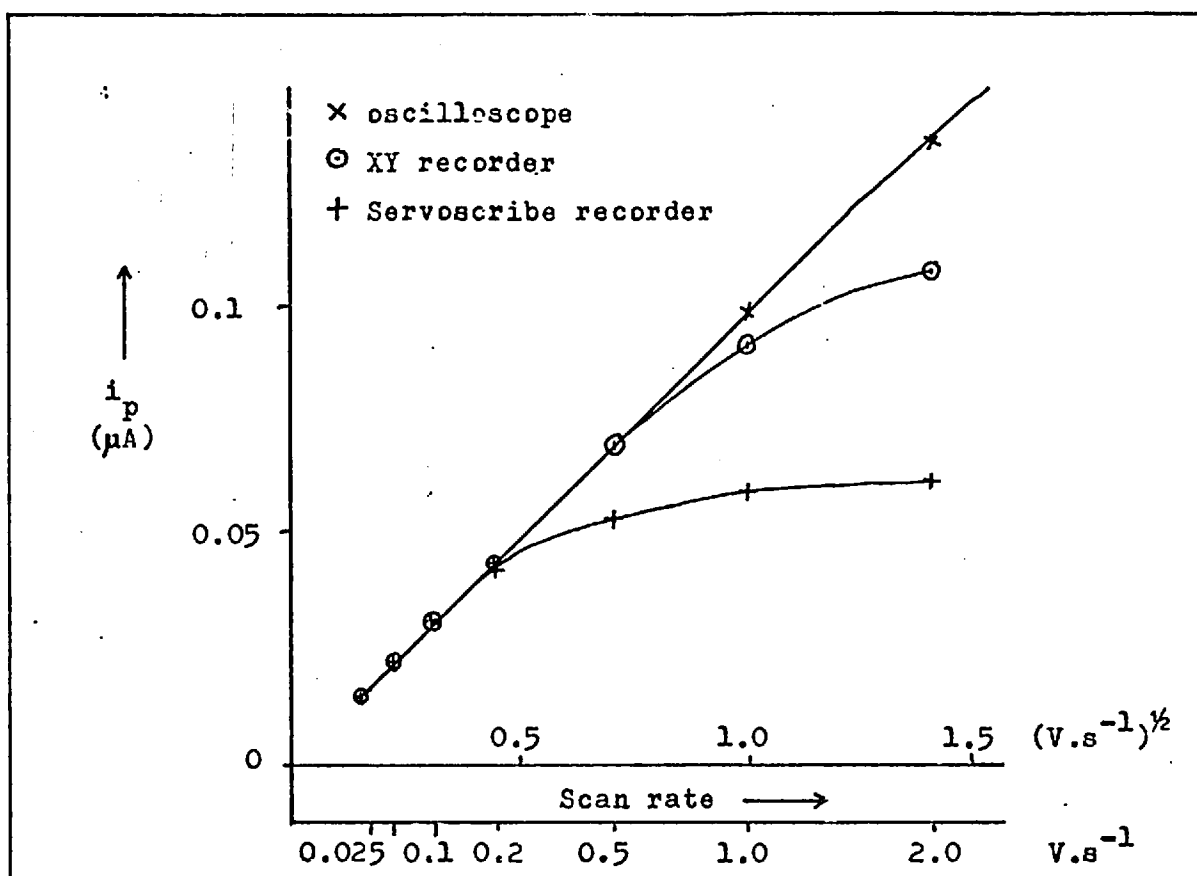


Fig. 2.12. Dependence of peak height on scan rate.

Width at half height $B_{1/2}$ (mV)					
Scan rate ($mV.s^{-1}$)	25	50	100	200	500
Conc. ($\times 10^{-6}$ M)					
0.5	100	100	100	130	150
1	100	100	100	130	150
2	100	100	110	130	175
5	100	100	110	130	175
10	100	100	130	150	-

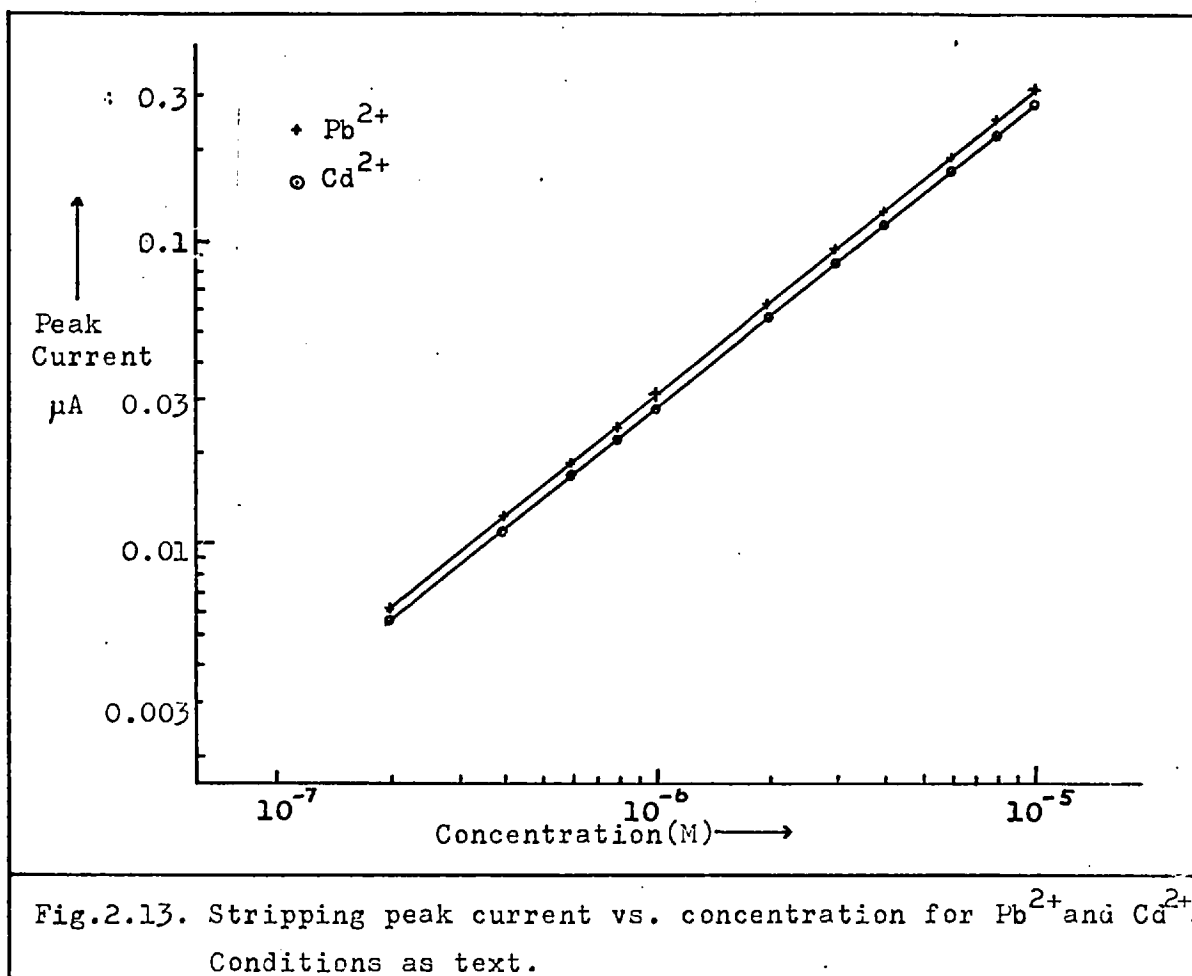
Pb^{2+} in 10^{-2} M KNO_3 . Electrolysis at -0.6 V.
 50 s cycle time. XY recorder.

Table 2.3. Variation of peak width with scan rate and concentration.

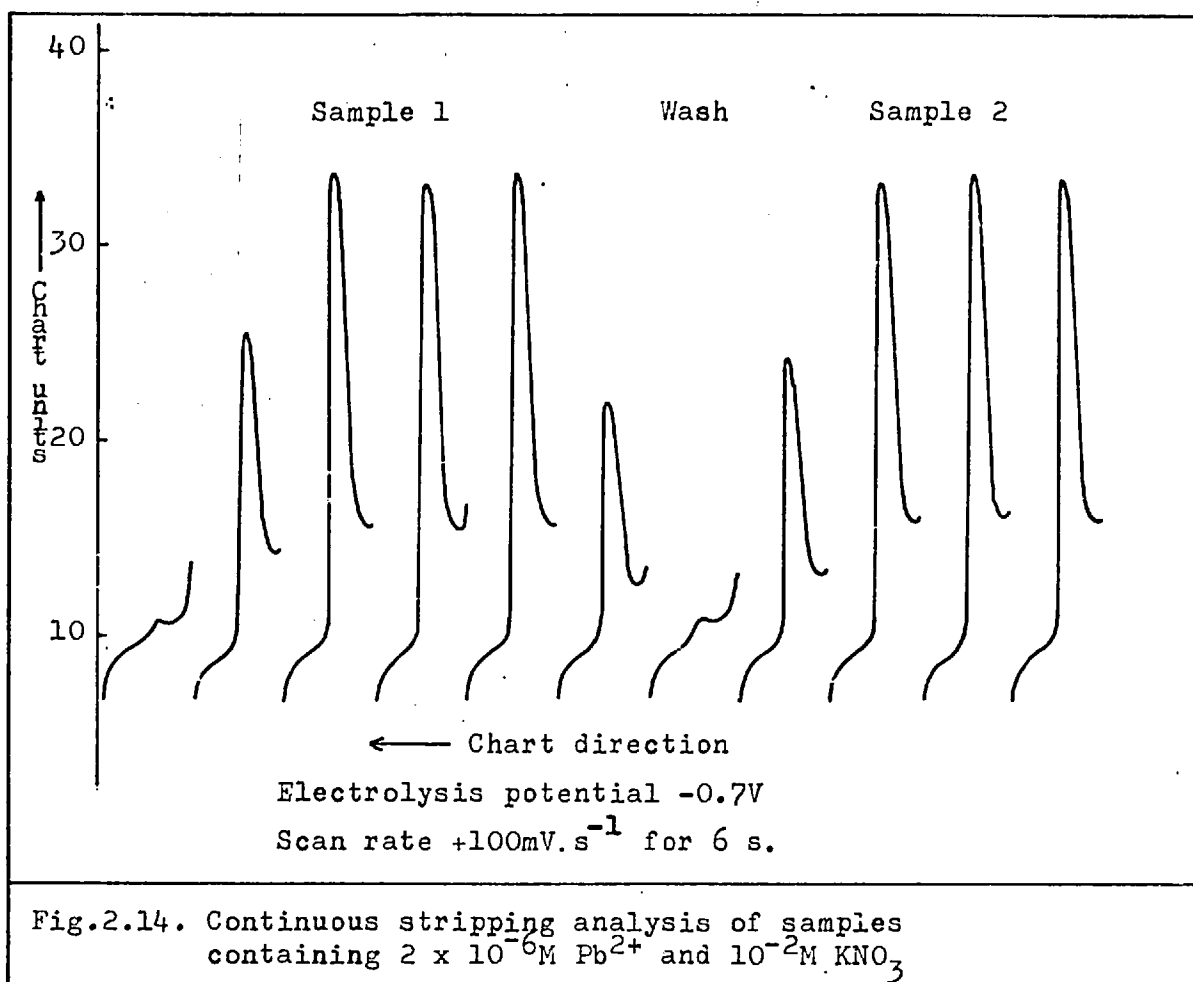
using the cell in both two and three electrode configurations. For two electrode work the reference and counter electrode inputs to the stripping voltammetry unit were both connected to the reference electrode. Using two electrodes and 10^{-6} M Pb^{2+} test solution the stripping voltammograms deteriorated when the electrolyte concentration within the cell was less than 2×10^{-2} M for both KCl and KNO_3 . This limit was lowered to 10^{-3} M when using the three electrode configuration. At 10^{-2} M analytical reagent grade KCl and KNO_3 contained approximately 3×10^{-7} M Pb^{2+} and purification by electrolysis was necessary. After electrolysis 10^{-1} M KNO_3 contained less than 10^{-8} M Pb^{2+} , as measured by anodic stripping voltammetry with a Kemula HMDE and, after concentration by evaporation, atomic fluorescence spectroscopy.

Fig. 2.13 shows the relationship between stripping peak current and concentration for Pb^{2+} and Cd^{2+} in 10^{-1} M KNO_3 obtained on this equipment using continuous aspiration of the sample, electrolysis at -0.8 V for 40 s and a scan rate of 100 mV.s^{-1} . A standard deviation of $\pm 5\%$ was observed for fifty measurements at the 10^{-6} M level for both Pb^{2+} and Cd^{2+} . The limit of detection, 2 x standard deviation of background current, was 5×10^{-8} M but a more practical lower limit was 2×10^{-7} M.

When using the sampler at a rate of 10 per hour with a sample:wash ratio of 2:1 and the manifold as fig. 2.9b, the sample received four minutes deoxygenation before aspiration. This was found to be the minimum time sufficient for analysis of test solutions in the concentration range 5×10^{-7} - 10^{-5} M. The sampler was not in sequence with the cam timer and thus at the rate



chosen there were four cycles in which test solution was flowing into the cell for a complete cycle. Because of the large volume of this cell two cycles were required to ensure that the cell was completely flushed. Thus a satisfactory analysis was expected from two cycles out of five cycles performed on each sample. Normally three cycles gave similar stripping peaks except when one sample was preceded by a sample of ten times or greater concentration when carry over reduced the number of satisfactory analysis cycles to two. Fig 2.14 shows a typical record of analysis of samples containing 2×10^{-6} M Pb^{2+} . Using sampling rates of less than $2 \text{ ml} \cdot \text{min}^{-1}$ resulted in increased carry over between samples.



This cell was a miniaturised form of a conventional cell and the sensitivity available is favourable considering the short electrolysis times and electrode area. For batch analysis this cell was limited in use to relatively large samples of more than 10 ml.

Cell 2 represented a trial flow cell to investigate "non stirred" stripping voltammetry. Initially this was used without a counter electrode. The same long drop time DME was used as before. It was found necessary to stop the pump during the stripping step as the pump pulses caused current fluctuations. Fig. 2.15 shows the dependence of peak current on cell flow rate during electrolysis for a sample of $5 \times 10^{-6} \text{M Pb}^{2+}$. High flow rates did not cause a

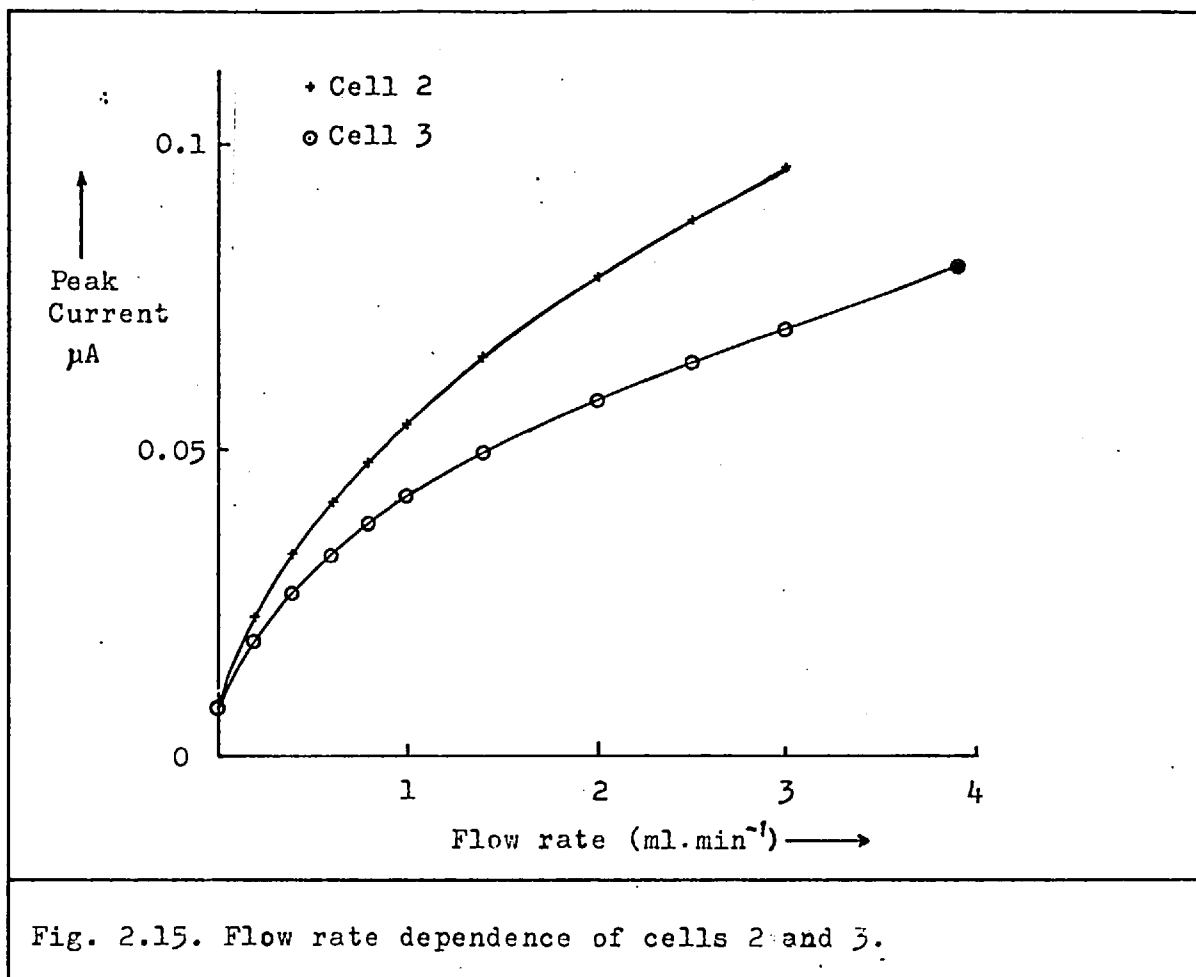


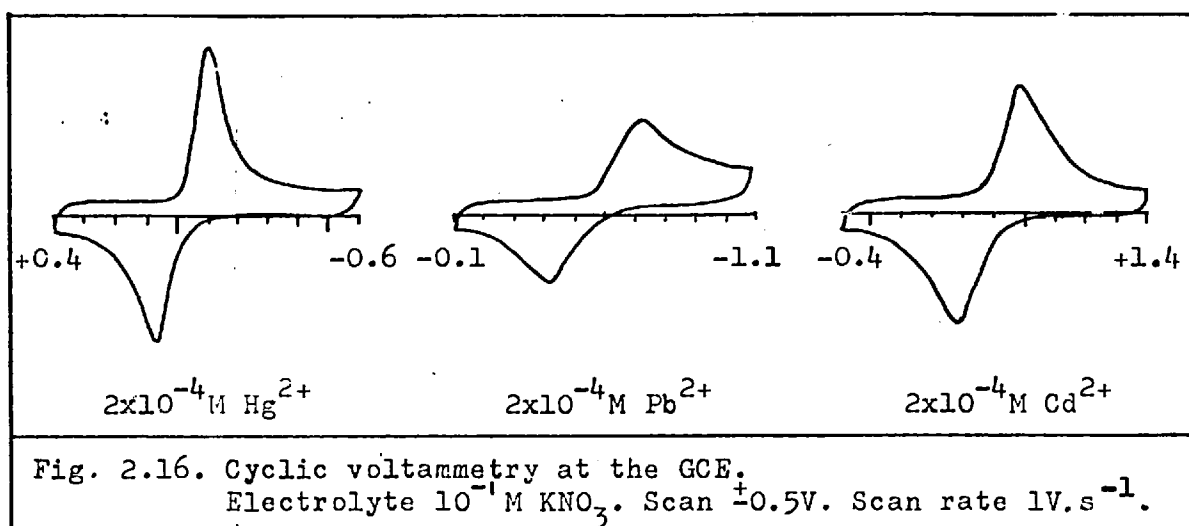
Fig. 2.15. Flow rate dependence of cells 2 and 3.

great increase in sensitivity but did cause a high incidence of premature drop fall. Bubbles of gas entering this cell were not easily removed. When used in the three electrode mode, bubbles were normally removed by the flow past the reference electrode. Pressure fluctuations within the system due to both pump pulses and variations in the debubbler waste often caused the counter electrode level to rise and fall. The use of pulse suppressors, a length of fine tubing, in sample, flow cell return and nitrogen lines reduced this effect but the results were not completely satisfactory.

Cell 3 was designed as an improvement to cell 2 and included an integral reference electrode. The dry Vycor glass was sealed

in the cell with epoxy resin and then soaked in 1 M KNO_3 . The cell was then kept filled with 1 M KNO_3 when not in use so as to prevent the Vycor glass from drying out. No problems were experienced with this material. The larger volume of this cell produced a slower flow of solution past the electrode which would account for the lower sensitivity of this cell. The flow rate dependence is shown in fig. 2.15. Gas bubbles were readily removed from the cell by the top exit line without causing interference with the electrode. The electrode stability was good and if pulse suppressors were used in sample, flow cell return and nitrogen lines the pump could be left running during the stripping step. The characteristics of electrolysis potential, peak width and potential were similar to those found for cell 1 using the long drop time DME. The stripping peak current was proportional to concentration over the range 4×10^{-7} M to 10^{-5} M for Pb^{2+} and Cd^{2+} . The sensitivity of this cell was approximately one third that of cell 1 depending on the cell flow rate. A practical limit of detection was 4×10^{-7} M Pb^{2+} for a flow rate of 1.0 ml. min^{-1} . The reproducibility was assessed by a standard deviation of $\pm 4.5\%$ obtained from 50 determinations on 2×10^{-6} M Pb^{2+} in 10^{-1} M KNO_3 .

When using this cell for batch analysis the sampling rate of 10 per hour was limited by the time required for deoxygenation of the sample. The volume required to wash the sample through the cell was much less than cell 1 allowing the use of lower sample flow rates and hence sample volume. 1.0 ml. min^{-1} was the lowest flow rate that could be used to maintain sensitivity.



2.2.3 The glassy carbon electrode

Because of the relatively low selectivity, complexity and failure rate of the DME it was necessary to investigate a mercury film electrode or solid electrode for continuous analysis. The glassy carbon electrode was reported to have better selectivity, sensitivity and reproducibility when mercury plated and used for stripping analysis (92) than other substrate materials. For these reasons it was chosen as a material to be studied. To determine the characteristics of this electrode for stable operation the conventional, magnetically stirred cell 5 was used. Cyclic voltammograms for 2×10^{-4} M Hg^{2+} , Pb^{2+} and Cd^{2+} in 10^{-1} M HNO_3 were obtained on a Chemtrix polarograph and are shown in fig. 2.16. The anodic peaks were increased after electrolysis at potentials more negative than the reduction potentials but the results were erratic. If the electrode was cleaned between cycles with a tissue, reproducible results were obtained. It has been claimed that by electrochemically cleaning the electrode at +1.0 V between cycles, reproducible results could be obtained (181). With the glassy carbon electrode used in this study, electrolysis at +1.0 V for

5 minutes produced a dull electrode surface and erratic response. Polishing with a diamond paste was necessary to restore the surface and performance. The irreproducibility of results and necessary electrode cleaning step made this electrode unsuitable for continuous analysis.

The work reported by Florence (92) was repeated in cell 5 using the cam cycle timer to control each stage of analysis. The electrode was mercury plated in situ by adding a known volume of 10^{-3} M Hg^{2+} in 10^{-2} M HNO_3 to the 10^{-2} M KNO_3 electrolyte containing Pb^{2+} or Cd^{2+} . After electrolysis at -0.8 V for 40 seconds the electrode was scanned to 0 V at 100 mV.s^{-1} and the peak characteristics recorded. Similar results to those reported by Florence were obtained. For added Hg^{2+} concentrations above 10^{-5} M the peak current, potential and width at half amplitude were almost independent of Hg^{2+} concentration. Similarly the second and subsequent cycles on the same solution showed an increase in peak amplitude over the first peak. This was shown not to be due to re-accumulation of material stripped from the electrode by starting to stir the solution one second before the end of the scan. After the first cycle there was no apparent change in peak parameters for up to 50 consecutive cycles on the same solution. If the potential scan was terminated at $+0.5$ V so that the mercury layer was also stripped off every scan was similar to the first.

The manifold diagram and cam sequence for the use of this electrode in cell 1 is the same as those shown in figs. 2.9b and 2.10 without the need for a drop controller. Many of the results obtained with this electrode were similar to those obtained with

the long drop time DME. The response was independent of flow rate. The stirrer had to be stopped during stripping and similar minimum electrolysis potentials were required. For maximum sensitivity the electrode was positioned 0.5 mm above the end of the stirrer. Three procedures for mercury plating the electrode in situ were studied. The first involved using an electrolyte containing 10^{-1} M KNO_3 , 10^{-2} M HNO_3 and 5×10^{-4} M Hg^{2+} and a sample solution of 2×10^{-6} M Pb^{2+} . Each cycle consisted of electrolysis at -0.6 V and a voltage scan of 100 mV.s^{-1} to +0.5 V each cycle. The stirrer was switched on for the last 0.2 V of scan to remove oxidised material from the vicinity of the electrode before recommencing electrolysis. Results for one hundred consecutive cycles were obtained. The second method used the same electrolyte, sample solution, electrolysis potential and scan rate but the scan was terminated at -0.2 V so that the mercury film was not removed but continued to be deposited. Again the data from one hundred consecutive scans was recorded. Finally the electrode was mercury plated using the electrolyte and conditions of procedure two and a water sample. The electrolyte was replaced by deoxygenated 10^{-1} M KNO_3 , 10^{-2} M HNO_3 and the sample by deoxygenated 2×10^{-6} M Pb^{2+} . One hundred consecutive cycles using the conditions of procedure two were recorded. The results are given in table 2.4. The first procedure requires the use of a large voltage scan to remove the mercury film. Procedures two and three gave very similar response but the latter produced a more consistent baseline response and was adopted for further work. The only attention the electrode required was cleaning with soft tissue before use.

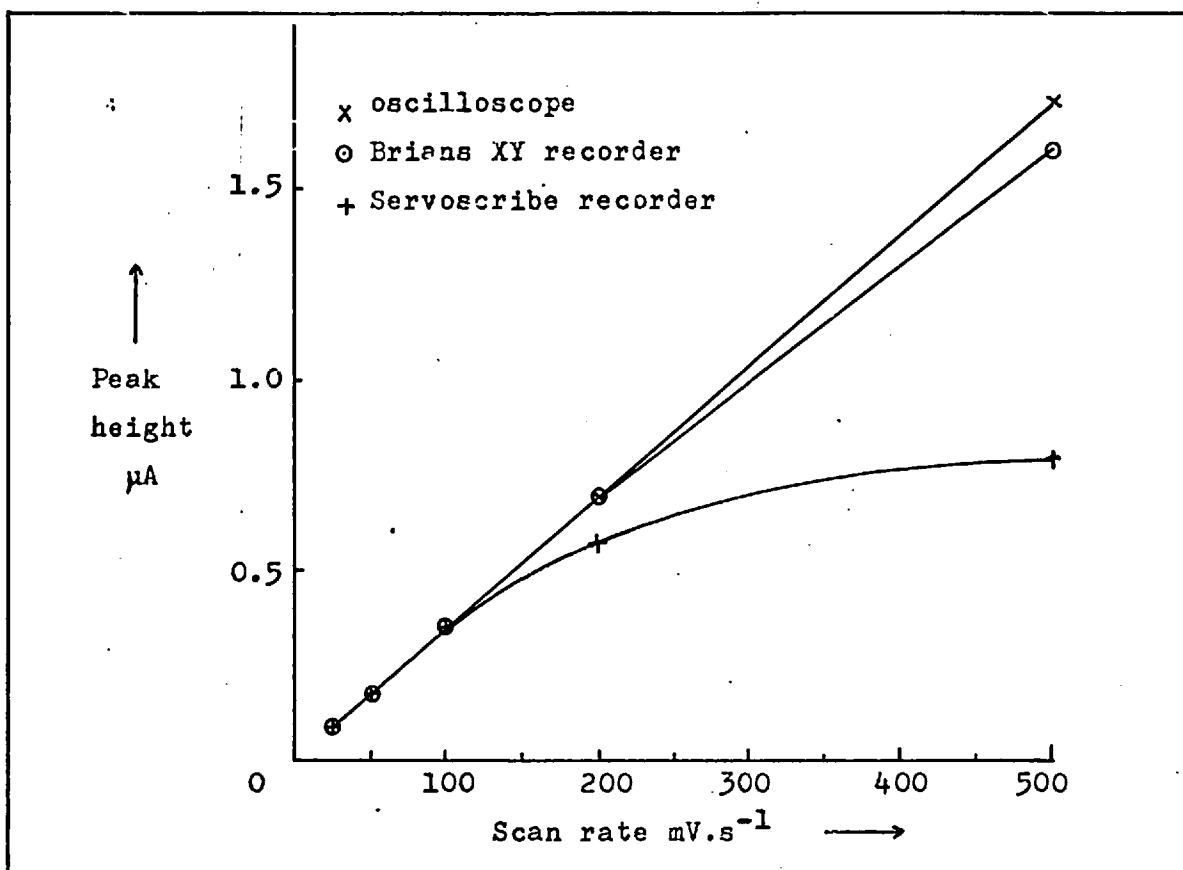


Fig.2.18. Dependence of peak height on scan rate for $10^{-6} \text{ M Pb}^{2+}$ on the mercury plated GCE. See text for conditions.

	Method		
	1	2	3
Mean peak current $\bar{i}_p$ (μA)	0.32	0.36	0.40
Relative standard deviation (%)	4	8	3
$\bar{i}_p$ peaks 1 - 20 (μA)	0.33	0.38	0.40
$\bar{i}_p$ peaks 80 - 100 (μA)	0.32	0.34	0.40
$\beta_{1/2}$ peaks 1 - 20 (mV)	45	45	45
$\beta_{1/2}$ peaks 80 - 100 (mV)	45	45	45

$\beta_{1/2}$ = peak width at half height.

$10^{-6} \text{ M Pb}^{2+}$ in 10^{-2} M HNO_3 ; electrolysis at -0.6V ; 50 s cycle time; scan rate 100 mV.s^{-1} XY recorder.

Table 2.4. Comparison of methods for the use of the GCE,mercury plated in situ. See text for details of the procedure.

Fig. 2.18 shows the relationship between peak current and scan rate for 10^{-6} M Pb^{2+} after electrolysis at -0.7 V for 40 seconds. The results of all three recorders is shown for comparison. The results obtained with the storage oscilloscope up to 500 mV.s^{-1} were proportional to scan rate. The response time of the servo recorders is responsible for deviation at higher scan rates. The peak width at half height dependence on scan rate is shown in table 2.5 using the XY recorder. These widths were very much less than those obtained with the mercury drop electrode and the selectivity possible with this electrode made analysis of mixtures of ions reduced at potentials of 50 mV apart or greater possible. Fig. 2.19 shows a stripping voltammogram obtained from a mixture of 10^{-6} M Cu^{2+} , Pb^{2+} and Cd^{2+} after electrolysis at -0.8 V for 40 seconds and scan to 0 V at $+100\text{ mV.s}^{-1}$. A standard deviation of $\pm 3\%$ on ten successive determinations of 10^{-6} M Pb^{2+} and $\pm 4\%$ for 10^{-7} M Pb^{2+} was found. The actual peak current was 12 times that of the DME for the same conditions but the background noise was only twice that of the DME. The practical limit of detection was 2×10^{-8} M for the conditions of fig. 2.19. The concentration dependence is shown in fig. 2.20 for Cu^{2+} , Pb^{2+} and Cd^{2+} . Using the 200 second cycle with 170 seconds electrolysis the peak current was increased four times compared with the 50 second cycle and the limit of detection was lowered to 5×10^{-9} M.

When used for batch analysis this cell had the same characteristics observed previously with the DME but with the increased sensitivity shown above. Residual oxygen in solutions deoxygenated by the sampler limited the minimum measurable concentration to 2×10^{-7} M.

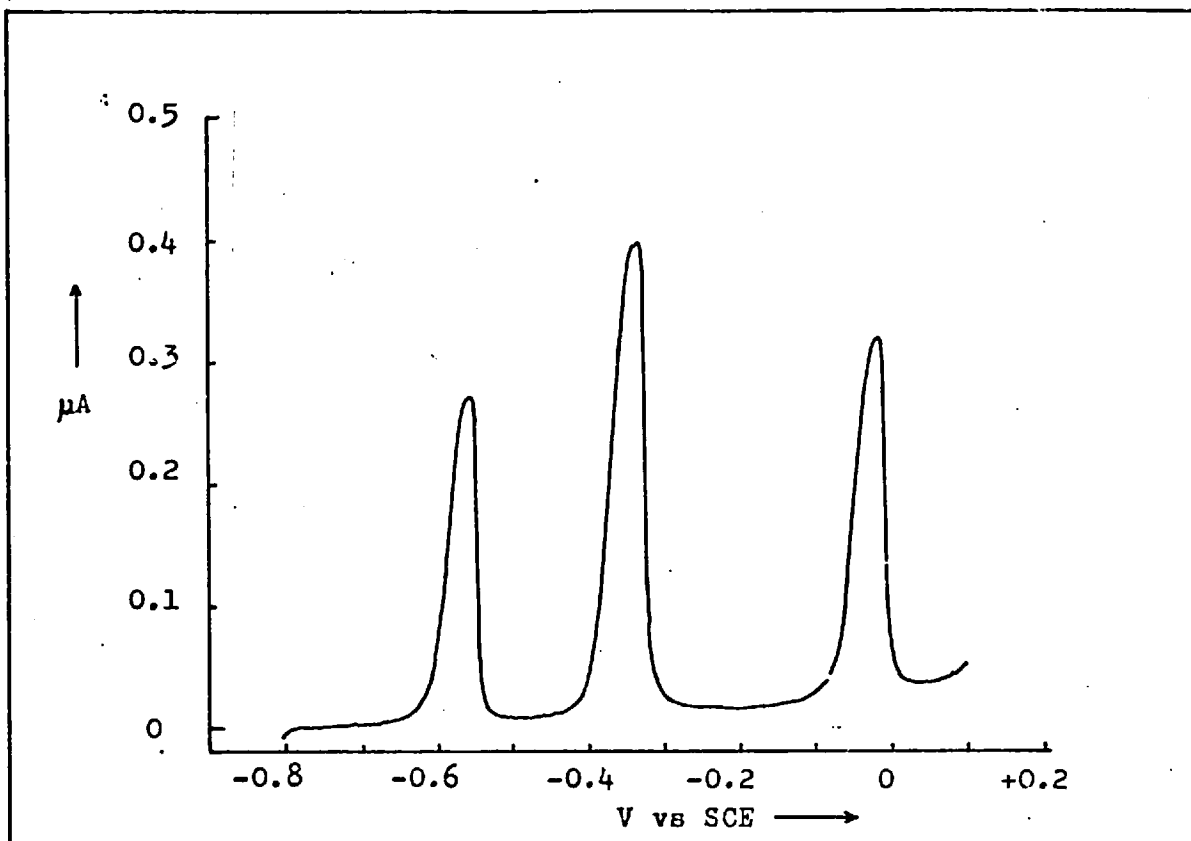


Fig.2.19. Simultaneous anodic stripping voltammetry of 10^{-6} M Cu^{2+} , Pb^{2+} and Cd^{2+} on the mercury plated GCE.

Width at half height $\beta_{1/2}$ (mV)					
Scan rate (mV.s^{-1})	25	50	100	200	500
Conc. ($\times 10^6 \text{M}$)					
5	36	38	46	70	100
2	36	36	44	64	100
1	36	38	44	60	90
0.5	36	36	44	60	90
0.2	36	36	44	60	90
Pb^{2+} in 10^{-2} M KNO_3 . electrolysis at -0.7 V, 50 s cycle time, XY recorder.					
Table 2.5. Variation of peak width with scan rate and concentration for the mercury plated GCE.					

The electrode was used in the unstirred cell 4 to investigate the use of a simpler system. The manifold design a cam sequence are the same as in figs. 2.9a and 2.10 without the need for a drop controller or magnetic stirrer. The electrode was mercury plated in situ using the method described previously and the voltage scan arranged so that the mercury layer was not removed. The solution flow was stopped during the stripping step by switching off the pump motor with the cam timer. The flow was restarted just before the end of the scan to remove oxidised material from the cell and prevent accumulation. Fig. 2.21 shows the effect of flow rate on peak current for 2×10^{-6} M Pb^{2+} in 10^{-1} M KNO_3 and 10^{-2} M HNO_3 . Because of the small volume of the cell a fast flow of solution over the electrode surface was obtained and the sensitivity was only a factor of two less than the stirred cell. The other electrode characteristics were similar to those obtained in the stirred cell. Standard deviations of $\pm 4\%$ for 10^{-6} M Pb^{2+} and $\pm 5\%$ for 10^{-7} M Pb^{2+} were obtained.

This cell was used for batch analysis at a sampling rate of 10 per hour. The size of this cell enabled it to be flushed out by only 0.05 ml of solution but a flow rate of $0.5 \text{ ml} \cdot \text{min}^{-1}$ was necessary to give good sensitivity. Thus the minimum sample requirement was 2.5 ml. Again residual oxygen limited the practical detection limit to 2×10^{-7} M.

2.3 Standards

It is common practice in stripping analysis to determine concentrations by the standard additions technique. In this

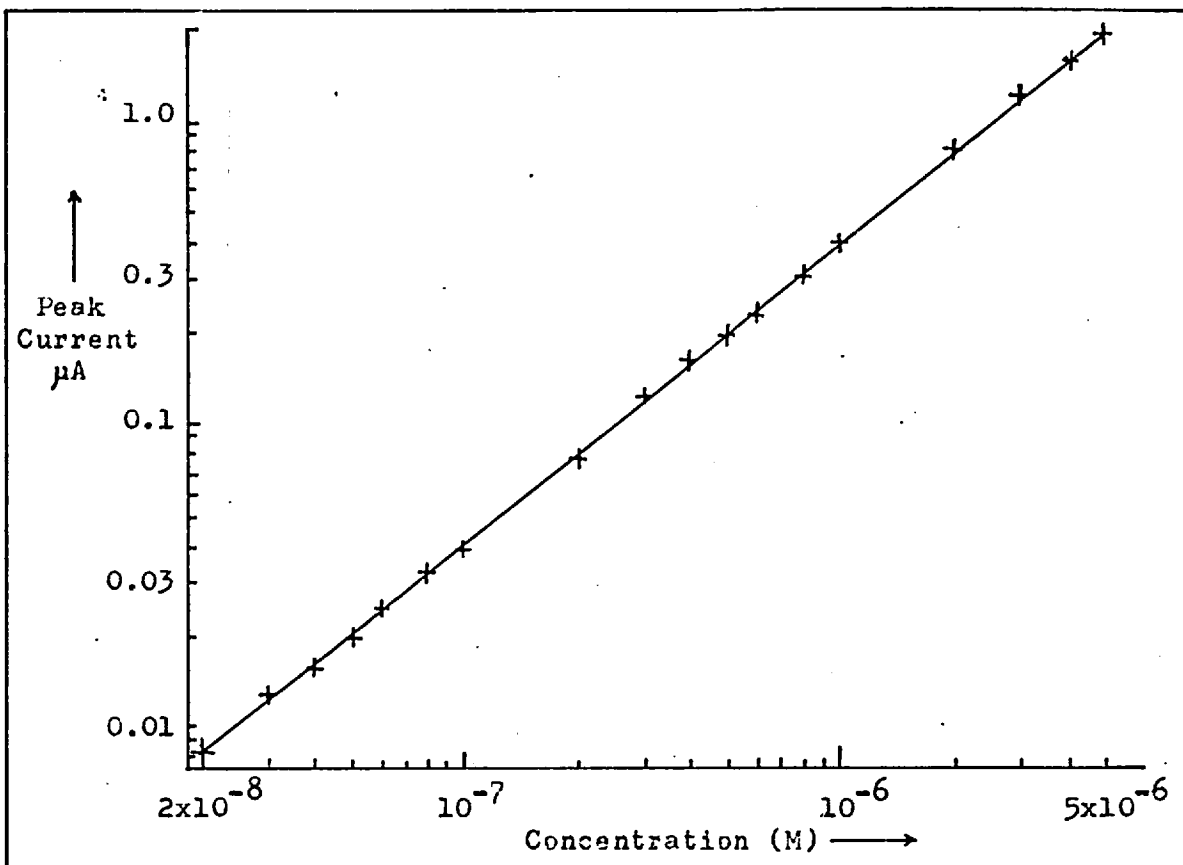


Fig.2.20. Stripping peak current vs concentration for Pb^{2+} on the mercury plated GCE. See text for details.

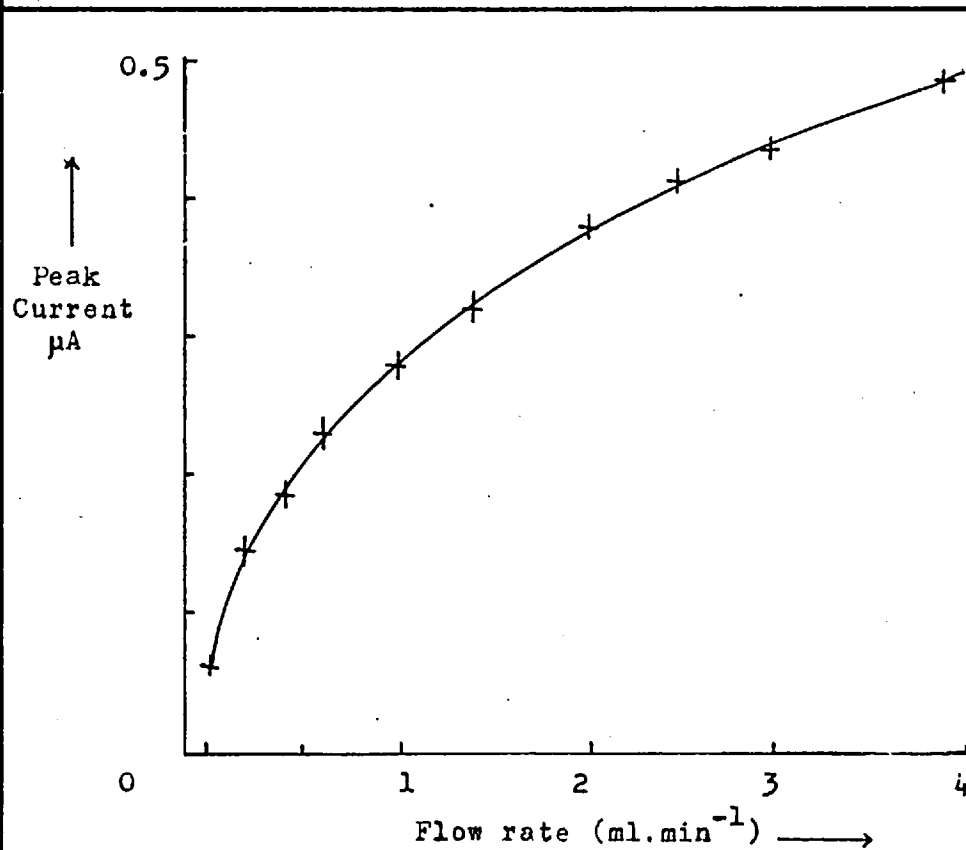


Fig.2.21. Flow rate dependence of cell 4.

method the sample is analysed before and after the addition of a known quantity of standard. The sample concentration is calculated by proportion. This method works well in completely ionised solutions. If the sample contains complexes of the ion to be analysed which are not reduced at the electrode during electrolysis the standard may alter the equilibrium between ion and complex and give an incorrect analysis. Thus the standard addition method is only suitable for analyses of completely ionised solutions. If the sample and standard are analysed separately the concentration of electroactive species only in a sample may be determined. This has been of use in the determination of trace metal species in natural waters (208). Samples and standards were analysed separately in this study.

2.4 Derivative stripping voltammetry

The use of derivative output for improving the resolution of overlapping waves and increasing sensitivity in linear sweep voltammetry is well established. It has been reported that derivative output gives a five fold increase in sensitivity of anodic stripping voltammetry (125) and an improvement in resolution.

The results obtained with the long drop time DME in this chapter show considerably less sensitivity and resolution than the mercury plated glassy carbon electrode. Although both electrode systems gave similar reproducibility it was suspected that electrode poisoning materials in real samples might affect the mercury film electrode more than the DME. Derivative output was

a simple technique and was investigated as the improvements in sensitivity and resolution were expected to give results comparable to the mercury film electrode.

This signal output was investigated using the long drop time DME in cell 3 with the manifold of fig. 2.9b and cam sequence of fig. 2.10 as in section 2.2.1. The derivative amplifier was set up by choosing a sensitivity on the current amplifier A_3 in fig. 2.1 to give a stripping peak of 0 to 1 V amplitude and a suitable derivative sensitivity by switches S_7 and S_8 in fig. 2.3. R_{29} and R_{40} in fig. 2.3 were adjusted in parallel until the amplifier just stopped oscillating. The sensitivity of the derivative output depended on both concentration of analyte and scan rate. Fig. 2.22 shows normal and derivative stripping voltammetry of a mixture of 2×10^{-6} M Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} in 10^{-1} M KNO_3 in this system. To evaluate the derivative traces the peak to peak height was measured. Absolute values were not obtained and results are given in arbitrary units. The sensitivity and concentration dependence of both normal and derivative outputs for Pb^{2+} in 10^{-1} M KNO_3 were compared using the flow system described, a cycle time of 50 seconds, electrolysis at -0.7 V for 40 seconds and scan to 0 V at 100 mV.s^{-1} . The results obtained, in table 2.6, show that the reproducibility of each method was comparable but the practical limit of detection was 1×10^{-7} M for Pb^{2+} using the derivative technique compared with 4×10^{-7} M for normal stripping.

The effect of overlapping of adjacent stripping peaks was evaluated by measuring one ion at a set concentration in the presence of varying proportions of another. Pb^{2+} and Cd^{2+} were

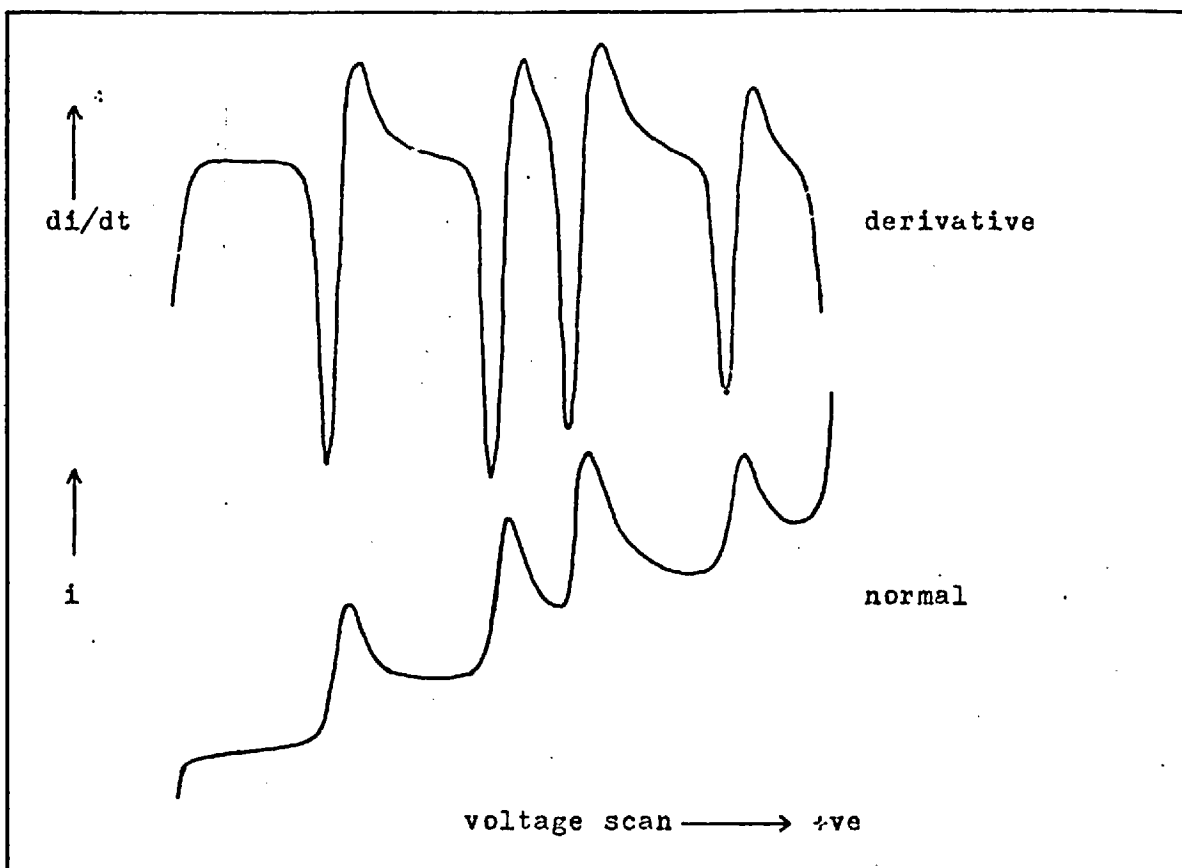


Fig.2.26. Normal and derivative stripping voltammograms of a mixture of 2×10^{-6} M Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} in 10^{-2} M KNO_3 .

Concentration $\times 10^6$ M	Peak Current		Relative standard deviation %	
	Normal μA	Derivative scale units	Normal	Derivative
0.1	-	4	-	30
0.2	0.010	9	25	12
0.5	0.016	22	10	5
1.0	0.030	41	5	4
2.0	0.058	76	5	4
5.0	0.160	184	4	4
10.0	0.310	320	3	3

Table 2.6. Comparison of normal and derivative A.S.V. Concentration dependence and reproducibility.

used under the conditions of fig. 2.22. The effect of preceding and succeeding waves was measured and tabulated in table 2.7. Derivative output gives an improvement in resolution but a quantitative value for this improvement is not obtainable.

2.5 Methods of oxygen removal

The procedure of oxygen removal from sample and reagents by nitrogen was an adaptation of manual methods. It was shown that when using the small volume flow cells the sampling rate of 10 per hour was limited by the time taken to deoxygenate the sample. In order to increase the sampling rate other methods of deoxygenation were required. Two alternative methods were studied.

2.5.1 Continuous flow deoxygenation

The manifold for this system used with cell 1 is shown in fig. 2.23. The sample was added to a deoxygenated electrolyte, segmented with nitrogen, and mixed in a twenty turn coil. After the coil the solution was debubbled and immediately segmented with nitrogen. Three such cycles of nitrogen segmentation were used to investigate whether the nitrogen would remove sufficient oxygen from the sample. The addition of 10^{-2} % Triton X-100, a surface active agent, prevented surges of solution within the manifold.

Oxygen concentrations within the cell were measured by using a DME of 3 second drop time and measuring the current at -0.4 V. The efficiency of this method was compared with the original system by comparing relative oxygen concentrations from

continuous aspiration of aerated and deaerated samples after zero, one, two and three deoxygenation cycles. The ratio of nitrogen: liquid flowing in the manifold was the maximum that could be used for the debubblers to function adequately. By using the Technicon H2 connector in a vertical plane with nitrogen for segmentation entering by the lower limb, smaller segments were produced with a larger liquid surface area:volume ratio which was expected to improve deoxygenation. The efficiency of deoxygenation is summarised in table 2.8. The oxygen free sample was water which had been deoxygenated with nitrogen for ten minutes and stored under nitrogen.

Table 2.8. Comparison of continuous flow and other methods of oxygen removal.	
No. of deoxygenation cycles	i (0.4 V) μ A
0	2.2
1	0.55
2	0.32
3	0.21
Sample deoxygenated in sampler cup	0.018
Oxygen free sample	0.001

A report on the effect of oxygen on stripping voltammetry has suggested the gases used for deoxygenation should contain less than 10^{-2} % oxygen to give a cathodic current at -0.4 V in the electrolyte of less than 0.005 μ A. The manufacturer's quoted maximum oxygen concentration for the nitrogen used in this study was 10^{-3} % and gave the very low residual current

at -0.4 V shown in table 2.8. From the polarographic data, the continuous flow method of oxygen removal was not satisfactory for stripping voltammetry. A comparison of stripping voltammograms of 5×10^{-6} M Pb^{2+} in deaerated and aerated samples using three deoxygenation cycles showed a high background current and distorted peak for the aerated sample. Any interference from the addition of surface active agent was not studied.

2.5.2 Chemical oxygen removal

Sodium sulphite can be used in polarography to reduce oxygen in alkaline solutions. Lead interferes with this process but its simplicity made its use in continuous analysis of interest.

The rate of oxygen removal by sodium sulphite was studied by following the reduction in cathodic current at -0.4 V in cell 5 using the 3 second drop time DME. 1 ml of saturated Na_2SO_3 was added to 10 ml of 0.1 M NaOH in the cell, mixed by a magnetic stirrer and a current vs time graph was plotted. The current was reduced from 2.0 μA to less than 0.005 μA in approximately 100 seconds. On the basis of this result two 20 turn mixing coils were added to the manifold of fig. 2.9b between the sample inlet and thermostatted mixing coil to increase the delay time to 110 seconds. The electrolyte was saturated Na_2SO_3 resulting in a final concentration of approximately 2×10^{-1} M in the flow system. Using the 3 second drop time DME in cell 1 the residual current at -0.4 V was 0.003 μA whilst sampling aerated distilled water. Samples of Zn^{2+} in 10^{-3} M HNO_3 were used to evaluate the system for anodic stripping voltammetry with the long drop time

DME. The conditions used were a 50 second cycle time, electrolysis at -1.2 V and a scan rate of 100 mV.s^{-1} for 5 seconds.

Satisfactory stripping voltammograms with a linear concentration dependence were obtained over the range 10^{-6} to 10^{-5} M. Stripping peaks were not obtained for Cu^{2+} , Pb^{2+} and Cd^{2+} in this medium.

This method simplified the system required for continuous flow stripping voltammetry by allowing the use of an unmodified sampler and increased sampling rates. However several metal ions did not give stripping peaks with the electrolyte used. A recent report (186) has suggested the use of ascorbic acid to remove the interference due to dissolved oxygen in the anodic stripping analysis of several metal ions in solution.

2.6 Conclusions

The system described here removed many of the manipulative steps required in this analytical technique. The long drop time DME worked reliably and gave reasonable precision. Extra sensitivity and resolution was achieved by the use of derivative output or the mercury coated GCE.

The system had several practical disadvantages. The long electrolysis step limited the analysis rate. The modified sampler was cumbersome in operation and did not remove sufficient oxygen from the sample to enable full use to be made of the sensitivity of the technique.

CHAPTER 3: A SEMI-AUTOMATED PROCEDURE FOR THE DETERMINATION OF
LEAD IN BLOOD

3.1 Introduction

There are a number of trace elements found in human tissues which do not have any known or suspected biochemical function (187). Some of these elements are known to be contaminants and are toxic if present in abnormally high concentrations. In particular, lead poisoning from atmospheric, water and food contamination has caused much concern (188-190). There is a wide divergence of opinion regarding the main source of the body intake of lead but now this metal and other trace pollutants are subject to rigid controls. The accepted normal levels of lead in blood are between zero and 0.32 ppm. Symptoms of lead poisoning may appear above a level of 0.8 ppm. There are two main population groups at risk from lead poisoning. These are workers in industries associated with the production or use of lead and lead compounds (191) and children with pica (192). Any analytical procedure for the determination of lead in blood should preferably be capable of analysing large numbers of small samples with the minimum of effort.

The recommended procedure for the determination of blood lead involves the destruction of the organic matter, complexation of the lead with dithizone and spectrophotometric measurement (193,194). Polarography (195) and emission spectrography (196) have been used but the methods have not gained wide acceptance. Atomic absorption spectrophotometry has been studied by many

workers because of the selectivity of this method (197-199) although its sensitivity for lead is not high. A rapid extraction procedure, not involving acid digestion, has been developed (200) but no confirmatory results have been published. Donovan and Feeley (198) have compared atomic absorption after both acid digestion and dry ashing with the recommended procedure (194) and obtained good correlation. An important advance has been made with the introduction of the Delves cup technique (199). This method requires 10 μ l of blood and a minimum of preparation enabling one operator to analyse one hundred samples per day. Flameless atomic absorption has been used for blood lead analysis on micro samples (201) and may supersede the Delves method once its reliability and freedom from interferences have been established.

Newberry and Christian (142) reported the use of anodic stripping voltammetry for the determination of several metals in biological samples after dry ashing and dissolution of the ash in water. This offered the advantage that contamination of the test solution by impurities in acid reagents and electrolytes was eliminated. Other workers have used acid digestion, ashing and dissolution of the ash in an electrolyte before analysis by stripping voltammetry (202-206). A semi micro technique has been reported by Roschig and Matschiner (207) in which modifications of the ashing step and electrolyte composition were made to improve the precision of the method.

In this chapter a semi automated procedure for the determination of lead in 5 ml blood samples is presented. The

sample was prepared by dry ashing in a silica crucible, the ash dissolved in an electrolyte of hydrochloric and ascorbic acids and the resulting solution analysed using the automated stripping voltammetry equipment described in chapter 2. The recovery of the ashing step was found to be close to 100 % so that aqueous calibration standards were used.

3.2 Experimental

3.2.1 Apparatus

The automated stripping voltammetry equipment described in chapter 2 was employed. The component parts were the Technicon sampler with modification for deoxygenation of the sample, the manifold as in fig. 2.9b without the addition of an electrolyte, the flow cell as in fig. 2.6 and the long drop time DME. The timer was set to give 40 seconds electrolysis, 2 seconds delay and 5 seconds scan. The stripping voltammetry unit was set for an electrolysis potential of -0.7 V and 100 mV.s^{-1} scan rate. The derivative output was displayed on the Servoscribe recorder. 20 ml silica crucibles were cleaned in boiling aqua regia for one hour before use. Other glassware was acid washed and coated with Repelcote. A laboratory muffle furnace was calibrated with a thermocouple for the temperature range $400\text{--}600\text{ }^{\circ}\text{C}$.

3.2.2 Reagents

The sulphuric and hydrochloric acids were B.D.H. Aristar grade. The ascorbic acid was B.D.H. Analar grade. Other reagents were as described in chapter 2.

3.2.3 Samples

Blood for transfusion was obtained from the National Blood

Transfusion Service. Out of date stock was used. This contained A.C.D. (citric acid, sodium citrate and dextrose) to prevent clotting. Standard additions of Pb^{2+} were made to aliquots of the blood to simulate actual samples.

3.2.4 Standards

Standards were prepared daily from 10^{-3} M Pb^{2+} stock solution by serial dilution with a solution of 2 M HCl containing 1 % ascorbic acid. Four standards ranging from zero to 5×10^{-6} M (0 to 1 ppm) were used and analysed with each group of samples.

3.2.5 Procedure

5 ml of a blood sample was evaporated to dryness in a 20 ml silica crucible over a steam bath. The crucible was heated over a low flame to volatilise as much of the organic matter as possible. The crucible was then heated in the muffle furnace at 550°C for 6 hours. 2 ml of hydrochloric acid were added and the residue was slowly evaporated to dryness. Finally the ash was dissolved in 2 ml of 2 M HCl and this solution was transferred to a 5 ml volumetric flask. The crucible was then rinsed with a further 2 ml of 2 M HCl. 0.2 gm ascorbic acid was added to the flask and the extract made up to 5 ml with 2 M HCl. Sample extracts and standards were loaded in 8 ml Technicon sample cups and covered with Parafilm. The automated analytical procedure is described in chapter 2. At least three stripping voltammograms were obtained on each sample. A reagent blank was carried out by following this procedure but omitting the sample.

3.3 Results and discussion

In the methods published by Philips and Shain (119) and

Roschig and Matschiner (140), ascorbic acid was added to reduce the interference of Fe^{3+} by reducing it to Fe^{2+} . Fig. 3.1 shows the stripping voltammograms of a 0.2 ppm standard, a sample prepared as described and the same sample prepared without the addition of ascorbic acid. Also included is a stripping voltammogram of the sample after dry ashing and dissolution of the residue in water as described by Newberry and Christian (142). The addition of ascorbic acid was essential to give well defined stripping voltammograms. Dissolution of the ash in water did not give satisfactory stripping voltammograms. The reagent blank was less than 0.05 ppm. A calibration curve is given in fig. 3.2. The residual current in the zero standard represents impurities in the hydrochloric acid, ascorbic acid, water and mercury.

Table 3.1 shows the recovery of additions of Pb^{2+} to an ashed sample measured by comparison with the standard solutions. The results indicate that there were no interferences from other components of the ashed sample. Table 3.2 shows the recovery of standard additions of Pb^{2+} to a blood sample which was analysed by the procedure given. The recovery was less than, but close to, 100 % . This loss could have been due to frothing, volatilisation or adsorption on to the silica vessel during ashing. Platinum vessels could not be used for the ashing procedure because traces of this metal give large residual currents in stripping voltammetry. Table 3.3 gives a comparison of results for five samples analysed using both aqueous standards and the addition method. The two methods gave comparable results. The former was much simpler and less time consuming than the latter

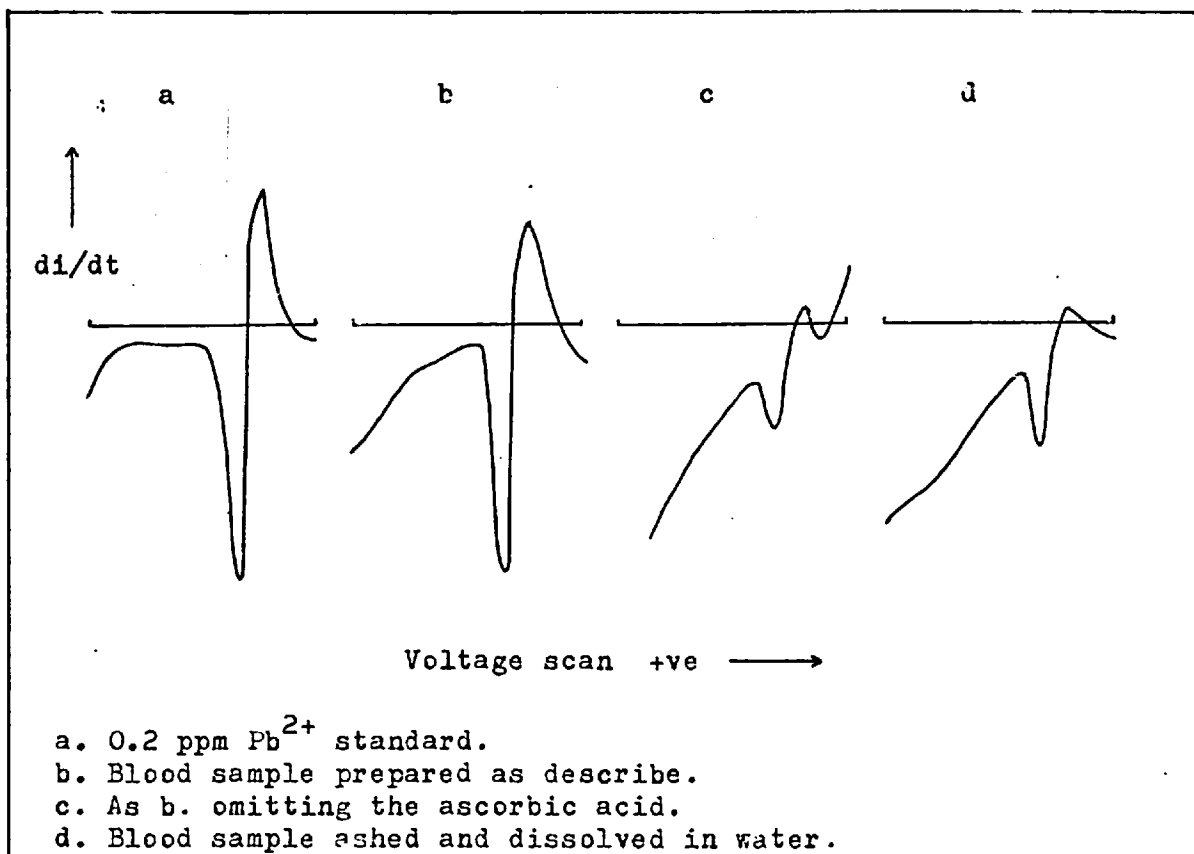


Fig.3.1. Stripping voltammograms of extracts of blood samples.

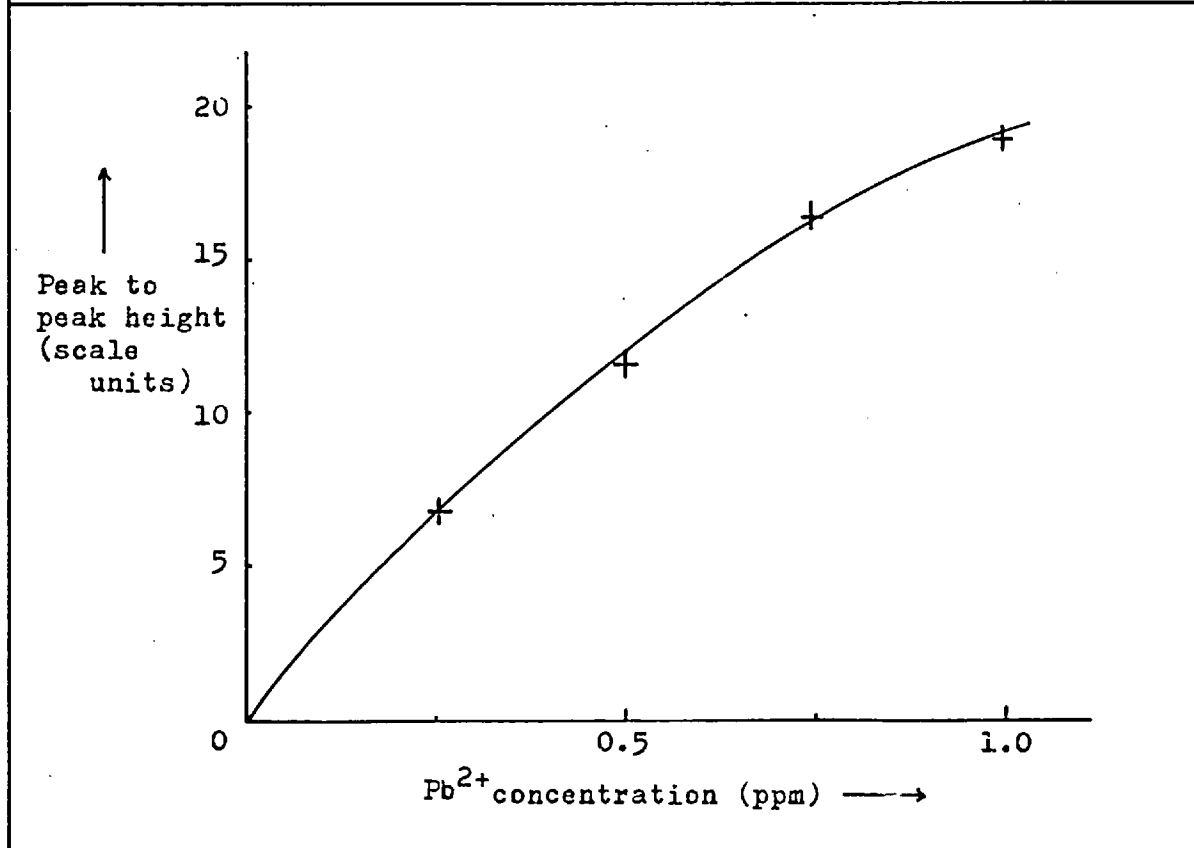


Fig.3.2. Calibration curve for Pb^{2+} in blood.

Pb ²⁺ added (ppm)	Pb ²⁺ found (ppm)				% recovery
0	0.10	0.08	0.10	0.08	-
0.25	0.32	0.38	0.35	0.35	104
0.50	0.55	0.60	0.55	0.57	95
0.75	0.82	0.85	0.80	0.85	96
1.0	1.10	1.10	1.15	1.12	103

Table 3.1. Recovery of Pb²⁺ added to an ashed sample..

Pb ²⁺ added (ppm)	Pb ²⁺ found (ppm)				% recovery
0	0.10	0.08	0.10	0.08	-
0.25	0.35	0.30	0.32	0.32	92
0.50	0.55	0.57	0.55	0.55	93
0.75	0.80	0.85	0.85	0.80	98
1.0	1.05	1.05	1.05	1.07	95

Table 3.2 Recovery of Pb²⁺ added to a blood sample.

Sample	Pb ²⁺ concentration (ppm)		Ratio
	Standard addition	Aqueous standards	
1	0.15	0.15	1.00
2	0.09	0.08	0.88
3	0.31	0.29	0.93
4	0.83	0.76	0.92
5	0.26	0.28	1.08

Table 3.3 Comparison of calibration by aqueous standards and the standard addition method.

Sample	Mean Pb ²⁺ conc. (ppm)	Number	Relative std. deviation (%)
1	0.08	10	14
2	0.28	10	8
3	0.70	10	5

Table 3.4 Reproducibility of the method.

and used less sample. In practice a recovery check would have to be carried out with each group of samples.

The reproducibility of the method was determined at three concentrations by analysing ten aliquots of each sample. The mean of three stripping voltammograms on each sample was used for calculation of the standard deviation as shown in table 3.4. The reproducibility was comparable to results achieved by other reports (193,194,197-201).

3.4 Conclusions

The dry ashing procedure described gave consistent results and required less operator skill than acid digestion and solvent extraction methods. The recovery experiments showed that the procedure was suitable for this type of analysis where high accuracy is not required. The automated system for stripping voltammetry was suitable for the analysis of ten samples per hour, giving three results for each sample. The effect of interferences was not studied but could be expected to be limited to amalgam forming metals with deposition and dissolution potentials close to those of Pb^{2+} , such as Cd^{2+} and Tl^{+} . These elements are not normally present in blood in concentrations above 0.01 ppm.

When compared to the recommended method (194) and atomic absorption (197) this method has the advantage of simple ashing and extraction steps. The stripping voltammetry equipment was inexpensive compared to atomic absorption spectrophotometers. Short electrolysis times were possible because the reproducibility of electrode area and timing reduced error.

The Delves cup (199) and flameless atomic absorption techniques (200) are much simpler, faster and use smaller samples than the method presented here. However further work, especially utilising the higher sensitivity achieved with thin film electrodes, may extend this method to the simultaneous determination of several metals in smaller blood samples.

CHAPTER 4: AN EVALUATION OF THE ANALYSIS OF CADMIUM, LEAD AND
COPPER IN NATURAL WATERS BY CONTINUOUS FLOW STRIPPING
VOLTAMMETRY

4.1 Introduction

The concentrations of heavy metal ions in natural waters are required for geochemical, biochemical and pollution control surveys. Both the total elemental concentration and a measure of the active species can be necessary in these studies (208). The accepted concentrations of heavy metals are in the range 10^{-8} to 10^{-9} M (209) but these levels have, in many cases, been almost at the limit of detection of the methods used. Direct, multi element analysis at this level is generally only possible by neutron activation analysis or anodic stripping voltammetry (table 2.1). The former method requires access to an intense neutron source and counting equipment, the cost of which may not be justified. Atomic absorption and fluorescence normally require preconcentration by ion exchange resins (210) or solvent extraction (211). A disadvantage of spectroscopic methods of analysis is that there may be interferences due to matrix effects from high concentrations of elements such as sodium, calcium and potassium.

Anodic stripping voltammetry has the advantage that analysis may be carried out without the addition of any reagents. This makes possible the direct analysis of electroactive species in solution and reduces the possibility of contamination. Whitnack (212) has investigated the application of polarography to the analysis of sea water. Since then several groups have published

reports on the simultaneous determination of several ions in fresh water (15,213) and sea water (206,214-217) by stripping voltammetry at the hanging mercury drop electrode. Electrolysis times of between five and thirty minutes and slow scan rates were used in these reports. Macchi (83) has described the determination of Zn^{2+} in brine by using a dropping mercury electrode of 68 seconds drop time. Electrolysis for 60 seconds was followed by a voltage scan of 380 mV.s^{-1} . Florence (206) has used the glassy carbon electrode, mercury plated in situ, to determine several metals simultaneously in sea water. The high selectivity of this electrode system was advantageous for multi element analysis. A disadvantage of the method was the addition of mercuric nitrate and nitric acid to the sample before analysis.

This chapter describes an attempt to overcome the problems of long electrolysis time and control of the various stages of the procedure by using the apparatus described in chapter 2. The mercury coated glassy carbon electrode was chosen because of the sensitivity and selectivity achieved with this electrode when compared with the long drop time mercury electrode. Several samples were analysed by the method suggested and its use for screening of water samples is discussed.

4.2 Experimental

4.2.1 Apparatus

The automated stripping voltammetry equipment described in chapter 2 was used with the following amendments.

a. Samples and standards were deoxygenated in polythene bottles

- and aspirated directly.
- b. Manifold as fig. 2.9b without the addition of electrolyte.
 - c. Flow cell as fig. 2.4 with the glassy carbon electrode.
 - d. Timer set for a 200 second cycle.
 - e. Output from the stripping voltammetry unit was displayed on the Brians 2200 recorder. This was used in the Y/T mode.

4.2.2 Reagents

All acids were B.D.H. Aristar grade. Other reagents were as described in chapter 2.

4.2.3 Samples

Samples were collected in polythene containers which had been acid washed and well rinsed. Samples of surface water were taken from the Thames estuary, the Solent, the River Thames and a lake in a London park. Laboratory tap water was collected after it had been allowed to flow for thirty minutes. In the laboratory the samples were acidified to less than pH 2 by the addition of 4 ml of 0.5 M HNO_3 per 100 ml of sample. Particulate matter was allowed to settle for 24 hours before analysis. Samples were analysed within 5 days of collection.

4.2.4 Standards

10^{-3} M stock solutions of Pb^{2+} , Cd^{2+} and Cu^{2+} were prepared in 10^{-2} M nitric acid. Working standards were prepared from these stock solutions by serial dilution with 10^{-2} M nitric acid. The working standards were prepared daily in acid washed, Replacote treated flasks and transferred to polythene bottles which had equilibrated with standard solutions of similar concentrations.

Standard additions to sample solutions were made by transferring aliquots of standards to a known volume of sample with a syringe burette.

4.2.5 Procedure

The electrode was polished before use with tissue paper. The mercury film was prepared by sampling a deoxygenated solution containing 10^{-5} M Hg^{2+} and 10^{-2} M nitric acid for 10 minutes with the electrode potential set at -0.2 V. An aliquot of the sample was deoxygenated by nitrogen for 10 minutes and then aspirated directly into the system from the container. A nitrogen atmosphere was maintained above the sample whilst it was being aspirated. The electrolysis potential was -0.8 V applied for 185 seconds with stirring. The stirrer was stopped for 5 seconds before the stripping step. The electrode potential was scanned from -0.8 V to 0 V at 100 mV.s^{-1} . Blanks, standards and samples were each aspirated for 15 minutes with a 30 second water wash between each one. Up to four stripping voltammograms were obtained on each sample. Standard solutions were analysed along with each group of samples in order to prepare calibration graphs. Standard additions were made to samples to check recoveries.

4.3 Results and discussion

Previous reports of sea water analysis by anodic stripping voltammetry have considered the identification of the stripping peaks. The samples used only gave stripping peaks at the potentials shown in table 4.1. Standard additions of Cd^{2+} , Pb^{2+} and Cu^{2+} were used to identify the peaks and were the only elements found using the procedure described.

Sample	E_p vs S.C.E.		
	Cu^{2+}	Pb^{2+}	Cd^{2+}
Sea water	-0.13	-0.42	-0.57
Tap water	-0.24	-0.45	-0.60
River water	-0.22	-0.43	-0.58
Lake water	-0.22	-0.41	-0.58

Table 4.1. Stripping peak potentials of Cu, Pb and Cd in natural water samples.

- a. 1% HCl blank.
- b. Sea water sample.
- c. As b plus 1% HCl.

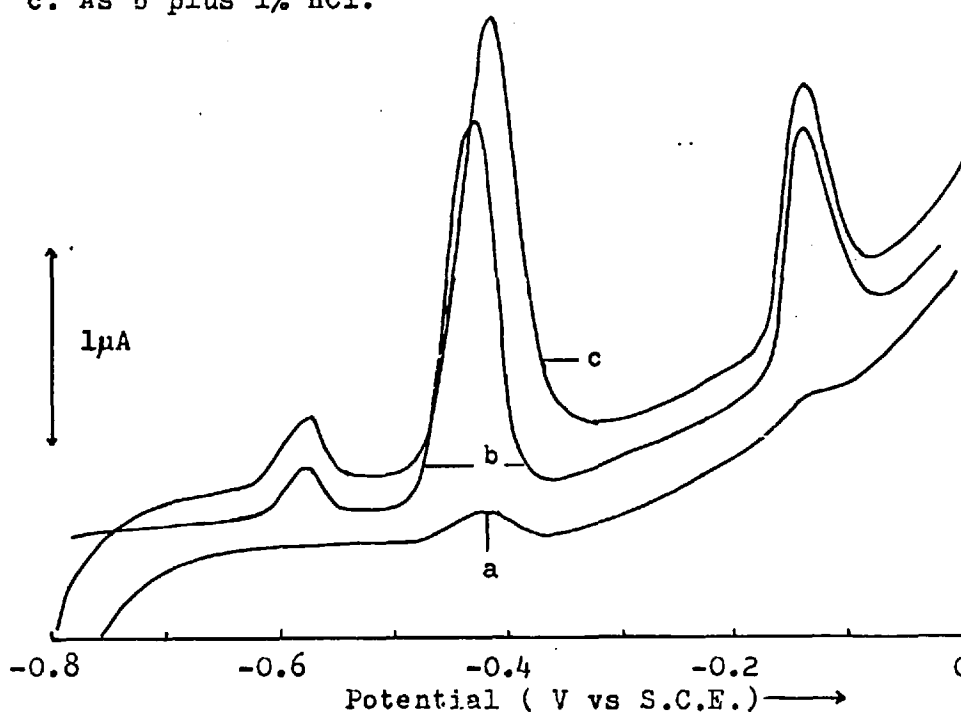


Fig.4.1. Stripping voltammograms of a sea water sample.

Fig. 4.1 shows stripping voltammograms of a sea water sample before and after the addition of acid together with a 2×10^{-2} M HNO_3 blank. There was a delay of approximately 70 hours between sampling and analysis. The deoxygenated, non acidified sample had a pH of 7.8. Standard additions of Pb^{2+} to samples of sea water did not give 100 % recovery when compared to the analysis of standards in 10^{-2} M HNO_3 . If the sample was acidified to pH 2 as described in the procedure the recoveries were close to 100 % as shown in table 4.2. Similar effects were observed for Cu^{2+} and Cd^{2+} . This observation may have been due to one or more of the following causes; dissolution of particulate matter by an added acid, breakdown of complexed species to the simple electroactive ions and loss of material to the container walls. An aliquot of sea water was filtered through a Whatman No 1 paper and then acidified according to the normal procedure. There was no reduction in the increase in peak heights upon acidification compared with another non-filtered aliquot. This eliminated the possibility that dissolution of suspended particulate matter had caused the increase. Three equal aliquots of a fresh tap water sample were stored in polythene bottles. The first was acidified with 0.5 M HNO_3 . The acidified and one other aliquot were analysed for Pb^{2+} every two days, comparing peak heights with standards in 10^{-2} M HNO_3 . After two weeks the third aliquot was acidified with 0.5 M HNO_3 , well mixed and compared with the other two. The results are shown in table 4.3 and indicate that there was considerable loss of Pb^{2+} by either loss to the container walls or precipitation. The addition of HNO_3 to bring the pH to 2 was sufficient to return

Sample	% recovery		
	non- acidified	acidified	
1	90	95	
2	98	101	
3	90	93	
4	85	104	
Mean	91	98	
Difference between methods statistically significant for p=0.02			
Table 4.2. % recovery of Pb ²⁺ added to sea water samples. (Addition equivalent to 5x10 ⁻⁸ M Pb ²⁺)			
Day	Stripping peak height vs 2x10 ⁻⁷ M standard		
	Sample 1	Sample 2	Sample 3
1	0.25	0.21	0.21
3	0.24	0.19	
5	0.24	0.16	
7	0.26	0.15	
9	0.25	0.13	
11	0.24	0.13	0.24
13	0.26	0.11	
15	0.24	0.10	
Table 4.3. Loss of Pb ²⁺ on storage.			

the concentration to the original level. It was decided to acidify all samples on receipt in the laboratory by the addition of 4 ml of 0.5 M HNO_3 per 100ml of sample to ensure that all of the elements of interest remained in solution. This reduced the calibration errors caused by the incomplete recovery of standard additions made to neutral samples and enabled the use of calibration standards to be made. By using high purity acid the reagent blanks were low. The method had a linear calibration for each element over the concentration range 5×10^{-9} to $5 \times 10^{-7} M$. This procedure was then used for the analysis of a set of samples

Sample	Concentration ($\times 10^8$ M)					
	Copper		Lead		Cadmium	
	Conc.	c.v.	Conc.	c.v.	Conc.	c.v.
Sea Water Thames Estuary	22	3	4.5	6	1.0	20
Sea Water Solent	18	3	2.5	8	<0.5	-
River Water Thames	6.0	6	3.0	8	<0.5	-
Tap Water	5.0	8	3.7	6	<0.5	-
Lake Water	8.0	6	2.0	10	<0.5	-
Table 4.4. Analysis of natural water samples.						

producing the results given in table 4.4. These are of the same order of magnitude as reported elsewhere (206,208,217). The coefficients of variation were obtained from ten successive stripping peaks on each sample and show the precision obtainable by a semi automated procedure. The determination of Cd^{2+} and Pb^{2+} in sea water at pH 2 and 7 by anodic stripping voltammetry has been shown to be free from interferences (206,217). By using an electrolysis potential of -0.8 V no zinc was deposited which would have interfered with the determination of Cu^{2+} by inter-metallic compound formation on the electrode. No effects were noticed which could be attributed to poisoning of the mercury film.

4.4 Conclusions

The method presented here uses relatively simple apparatus

for the simultaneous determination of three metal ions in natural waters over the concentration range 5×10^{-9} to 5×10^{-7} M (1 to 100 ppb). The analysis rate was approximately 4 per hour because of the long electrolysis time required. This rate is comparable to that achieved by the MASA system (177) if the analyses are done in duplicate. The cam timer system automated most of the operations required.

In view of the storage problems found with neutral samples, direct analysis would have to be made in the field. The apparatus described here is simple, rugged and could be developed into a portable system.

CHAPTER 5: THE DETERMINATION OF SELENIUM BY CATHODIC STRIPPING
VOLTAMMETRY

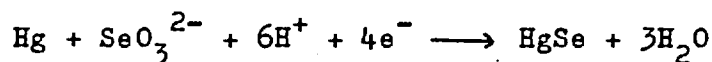
5.1 Introduction

Selenium is known to be an important trace element in both plants and animals. Past investigations have shown that selenium levels range from 0.005 to 0.5 ppm in animal tissue and 0.005 to 50 ppm in plants (182). Both inorganic and organic selenium compounds are toxic above the normal trace levels and 5 ppm of selenium in foods and 0.5 ppm in milk is reported as being potentially hazardous (183). The role selenium plays in the biochemistry of animals and its toxicity is not fully understood. It has been found that many plants concentrate the element from soils. Among the common foods wheat, when grown in soils containing 2 ppm selenium, has been shown to concentrate it to a level of 30 ppm. To effectively study the biological activity of this element an accurate analytical system is required with a sensitivity of 0.005 ppm (218). Such a system should be capable of rapid, repetitive analysis if used for surveys.

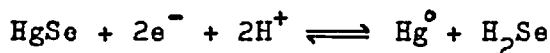
For low level selenium determinations there are only a few available methods. Neutron activation analysis and isotope dilution spark source mass spectroscopy have been used in several methods for accurate trace determinations (218-220). However these methods require facilities not generally available to a routine analytical laboratory. Fluorimetry has been used successfully to 0.01 ppm but is subject to interferences and a high blank at this level due to the complicated sample preparation..

Atomic absorption has a detection limit of 1 ppm with a conventional air/acetylene flame (221) but in a recent report, using a 1 metre long heated tube furnace and a peristaltic pump system for automated sample delivery, a detection limit of 0.1 ppb is claimed (222). Colorimetry and X-ray fluorescence have not yet shown sufficient sensitivity to be of use at the concentrations of interest.

The polarographic oxidation of the selenide ion has been reported to be similar to that of the sulphide ion (223). The reduction of the anion SeO_3^{2-} has been suggested as the basis of the polarographic analysis of selenium (183,223,224). The following mechanism has been proposed.



irreversible wave, $E_{1/2} = +0.05$ V at pH 1 in HBr electrolyte



reversible wave, $E_{1/2} = -0.56$ V

Above pH 3 a third wave is observed and has been attributed to the direct reduction of SeO_3^{2-} to Se^{2-} . Oscillographic polarography shows three waves in aqueous hydrobromic acid at -0.25 V, -0.41 V and -0.51 V (224). The first and third waves were reported to be due to reduction whilst the second wave was due to adsorption. This adsorption wave could be used for the determination of selenium above 0.01 ppm. This was used in a method for the determination of selenium in plants. The plants were digested by wet oxidation with a 1:1 mixture of nitric and perchloric acids. Hydrochloric and ascorbic acids were added to precipitate selenium. After washing with water the precipitate

was dissolved in aqueous hydrobromic acid saturated with bromine. Carbon dioxide was used to remove the bromine and oxygen from the solution before the polarographic determination.

In cases of selenium poisoning bromobenzene is given to cause fast elimination of the element in the urine. Monitoring the concentration of selenium in urine can be used to follow the cure. Faulkner et al (225) have suggested acidification of the urine with sulphuric acid followed by direct polarography. However the concentrations could be lower than that determinable by direct polarography. Analytical reagent grade sulphuric acid contains 2 to 3 ppm selenium and hence its addition would not be recommended.

Stripping voltammetry can have a high sensitivity and the instrumentation required is relatively inexpensive. The insolubility of the HgSe formed by reduction of SeO_3^{2-} in acid media was considered potentially useful in developing a method for the determination of selenium by cathodic stripping voltammetry. This chapter describes the development of a method for the determination of selenium as SeO_3^{2-} by cathodic stripping voltammetry and the use of the automated system described in chapter 2 for cathodic stripping.

5.2 Experimental

5.2.1 Apparatus

For the preliminary work of establishing the conditions for analysis the stripping voltammetry unit described in chapter 2 was controlled manually. The conventional, magnetically

stirred cell shown in fig. 2.8 was used with a Kemula type hanging mercury drop electrode. 10 μ l and 100 μ l Hamilton syringes were used to transfer aliquots of stock selenium to the cell. The Brians XY recorder was used to record stripping voltammograms. Cyclic voltammograms were obtained using the equipment built by Jee (56).

The automated equipment consisted of a flow manifold as fig. 2.9b with the addition of 1 M KNO_3 electrolyte, the flow cell as fig. 2.4 and the slow dropping mercury electrode of 60 seconds drop time. The timer was set to give 45 seconds electrolysis, stirring for the first 40 and 2.5 seconds scan. The electrolysis potential was set at -0.45 V and the scan rate at -100 mV.s^{-1} .

5.2.2 Reagents

All chemicals used were analytical reagent grade. Water was distilled using Pyrex glass apparatus. A stock solution containing 1000 ppm selenium (1.27×10^{-2} M) as H_2SeO_3 was prepared by dissolving 250 mg selenium in 50 ml hot 70 % nitric acid, cooling and diluting to 250 ml with water.

5.2.3 Procedure

For manual operation, 10 ml of electrolyte solution containing 10^{-1} M KNO_3 and 10^{-2} M HNO_3 was added to the cell and deoxygenated for 5 minutes with a stream of nitrogen. An aliquot of the stock selenium solution was transferred to the cell with a syringe. The solution was mixed by bubbling nitrogen through it for a few seconds. A mercury drop of surface area 0.03 cm^2

was grown on the electrode. The conditions of electrolysis potential, time, scan rate, etc. were chosen as required and the voltammograms recorded.

For semi automated operation, the sample solution containing 10^{-1} M KNO_3 , 10^{-2} M HNO_3 and a known concentration of selenium was deoxygenated in a polythene bottle as described in chapter 4. The sample was then aspirated directly from the bottle into the system and the stripping voltammograms recorded. By aspirating samples for five minutes each, at least three voltammograms could be obtained free from interferences from other samples.

5.3 Results and discussion

Cyclic voltammograms of 6×10^{-4} M SeO_3^{2-} in 0.1 M KNO_3 and 0.1 M HNO_3 showed two irreversible reduction waves with peak potentials at -0.62 V and -0.1 V as shown in fig. 5.1.

Electrolysis at +0.2 V for 30 seconds in a non stirred solution showed no change in the waves on scanning cathodically.

Electrolysis at -0.3 V produced a considerable increase in the wave at -0.62 V, the increase being proportional to electrolysis time.

To establish which peaks could be used for cathodic stripping, scans were made on a solution of 6×10^{-6} M SeO_3^{2-} from a range of potentials. Fig. 5.2 shows the voltammograms obtained by scanning cathodically immediately after formation of the mercury drop electrode. At this concentration the wave at -0.1 V was not observed. The wave at -0.62 V in the cyclic

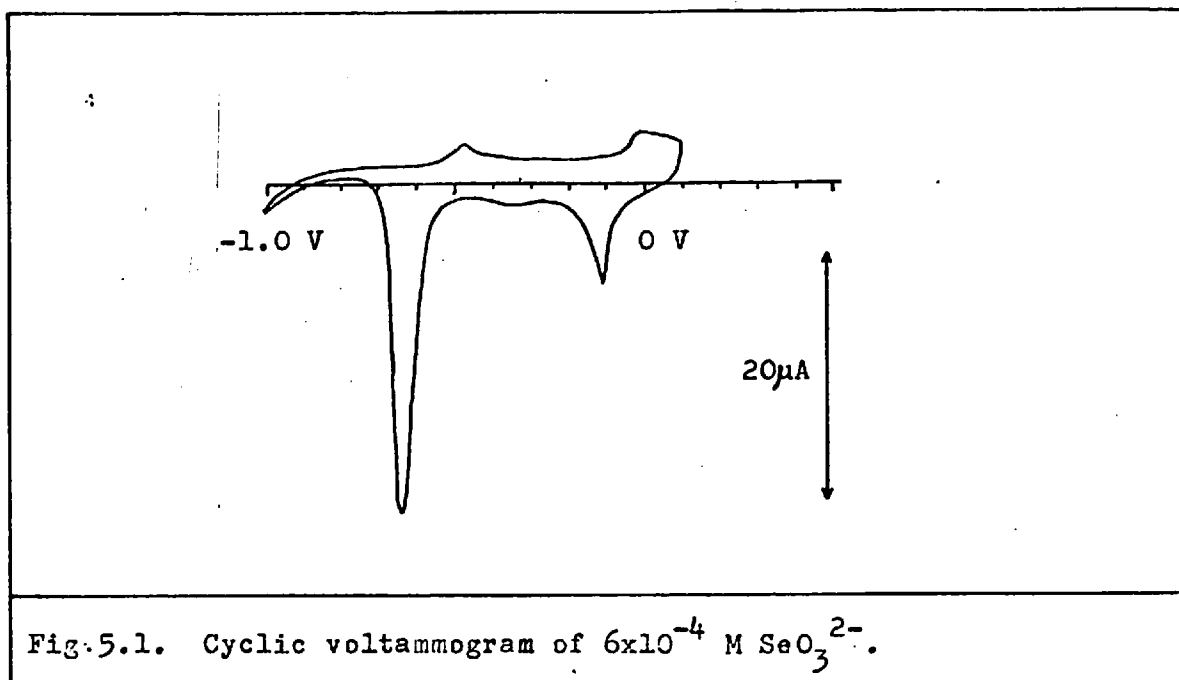
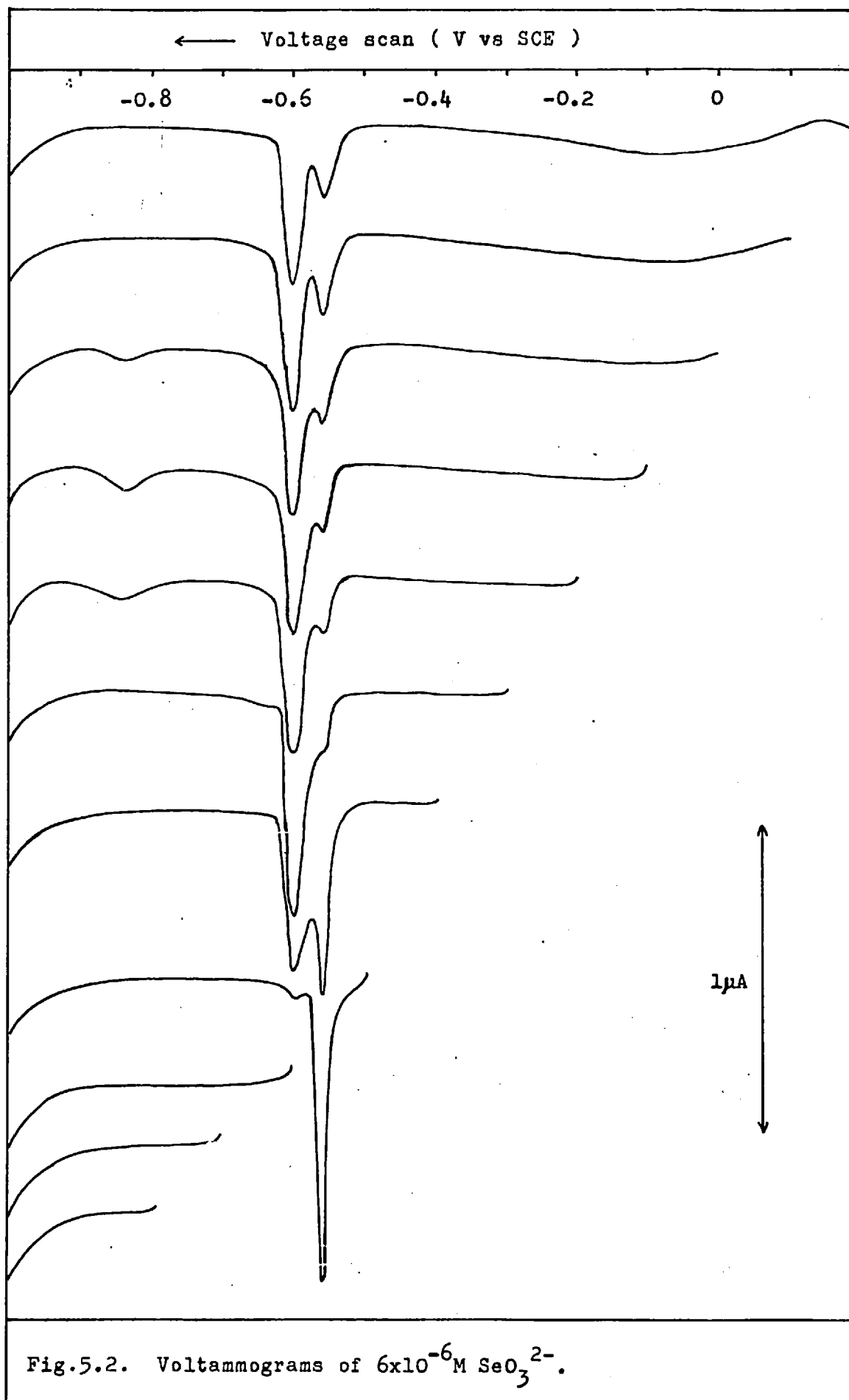


Fig.5.1. Cyclic voltammogram of 6×10^{-4} M SeO_3^{2-} .

voltammogram was split into two with peaks at -0.56 V and -0.60 V. The ratio of these two peaks varied with initial potential. A small peak at -0.84 V was present in scans starting from potentials of 0 V to -0.2 V. The voltammograms in fig. 5.3 were obtained after 60 seconds electrolysis, with stirring, at the initial potential of each scan. The wave at -0.56 V was only present as a small inflexion on the wave at -0.60 V. The latter wave was increased after electrolysis at potentials between -0.2 V and -0.5 V with a maximum at -0.45 V. The peak at -0.84 V was increased after electrolysis between 0 V and -0.5 V with a maximum increase at -0.2 V. Electrolysis at potentials of -0.3 V to -0.5 V split this wave into a minor peak at -0.82 V and the main peak at -0.88 V.

The effect of electrolysis time on the stripping peaks of 6×10^{-6} M SeO_3^{2-} was studied after electrolysis at -0.2 V. The results are presented in table 5.1. The more cathodic wave



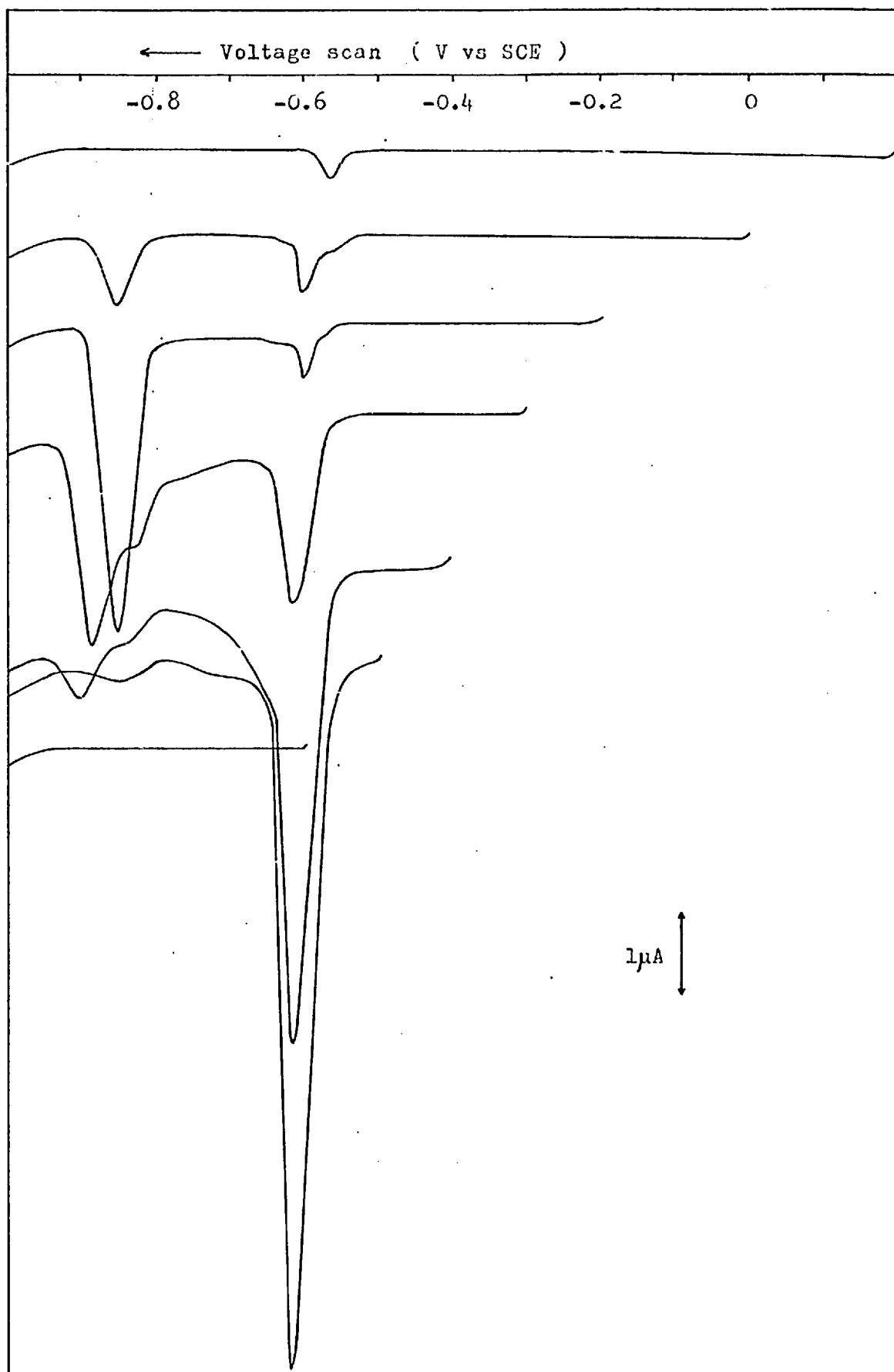


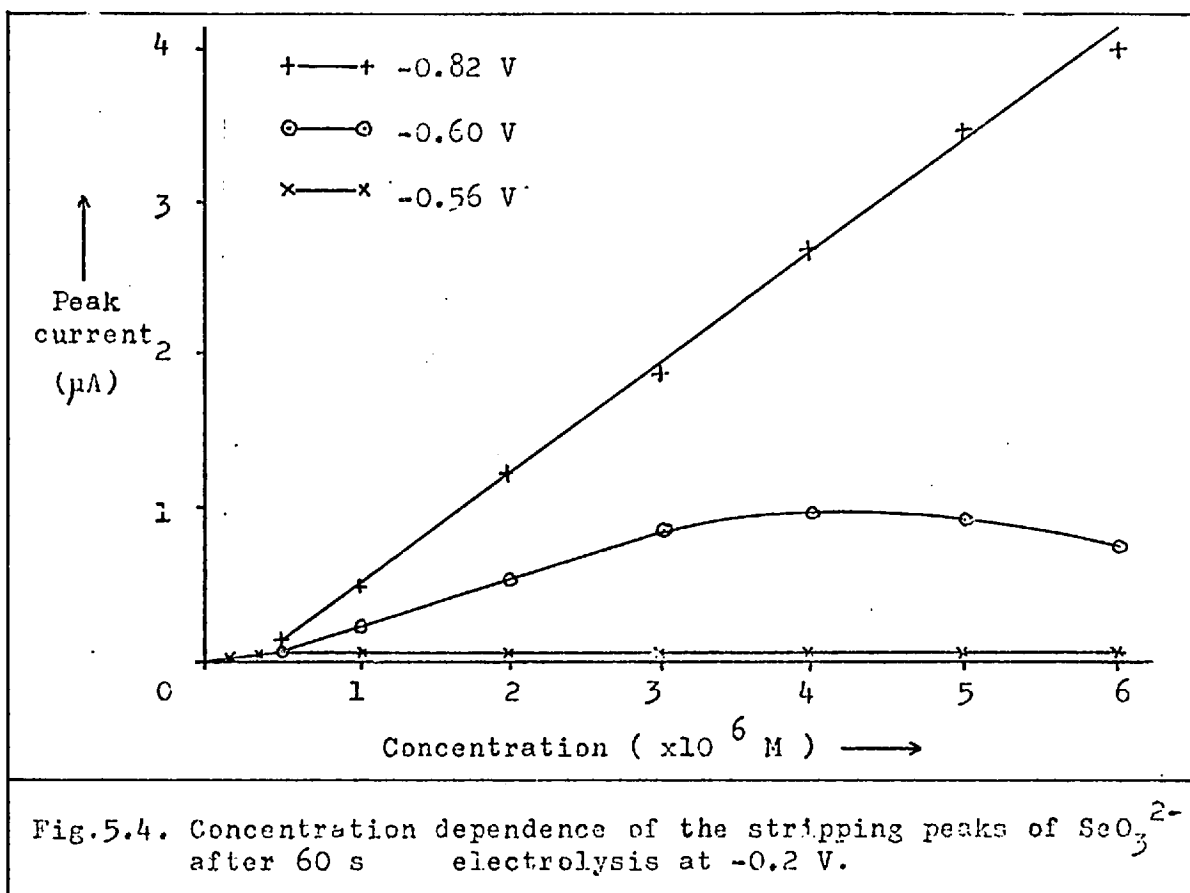
Fig.5.3. Stripping voltammograms of SeO_3^{2-} .
60 s electrolysis at the start potential.

Electrolysis time (s)	Peak current (μA)	
	0.60 V	0.82 V
0	1.0	0.15
15	3.0	1.4
30	2.5	4.4
60	1.5	7.9
120	1.2	13.3

Table 5.1. Effect of electrolysis time at -0.2 V on the stripping peaks of 6×10^{-6} M SeC_3^{2-} .

showed a linear dependence of peak current on time but the peak potential was not independent of time. The peak potential of the wave at -0.60 V was almost independent of electrolysis time. The peak current was dependent upon both time and concentration.

Fig. 5.4 shows the concentration dependence of the stripping peaks after electrolysis at -0.2 V for 60 seconds over the range 0 to 6×10^{-6} M. The peak potential of the cathodic wave at -0.84 V was independent of concentration. The peak current of this wave was linearly dependent upon concentration over the range 5×10^{-7} M to 6×10^{-6} M. At concentrations below 3×10^{-7} M this wave was not present. Electrolysis for 300 seconds reduced this lower limit to 1×10^{-7} M. Similarly the wave at -0.60 V was only present above 3×10^{-7} M, the peak current being linearly dependent on concentration



up to 3×10^{-6} M. The peak current of this wave reached a maximum at 4×10^{-6} M before decreasing at higher concentrations. The peak current of the wave at -0.56 V was dependent on concentration over the range 2×10^{-8} M to 6×10^{-7} M. Above 6×10^{-7} M the peak current was independent of concentration and the wave became merged with the wave at -0.60 V.

Electrolysis at -0.45 V for 60 seconds produced a maximum increase in the wave at -0.60 V for a 6×10^{-6} M solution. Under these conditions the wave at -0.56 V was not present. The effect of electrolysis time at this potential for a 3×10^{-7} M solution is shown in fig. 5.5 and the concentration dependence for the range 4×10^{-8} M to 6×10^{-6} M in fig. 5.6. Over the range 1×10^{-7} M to 6×10^{-6} M an approximately linear dependence was obtained.

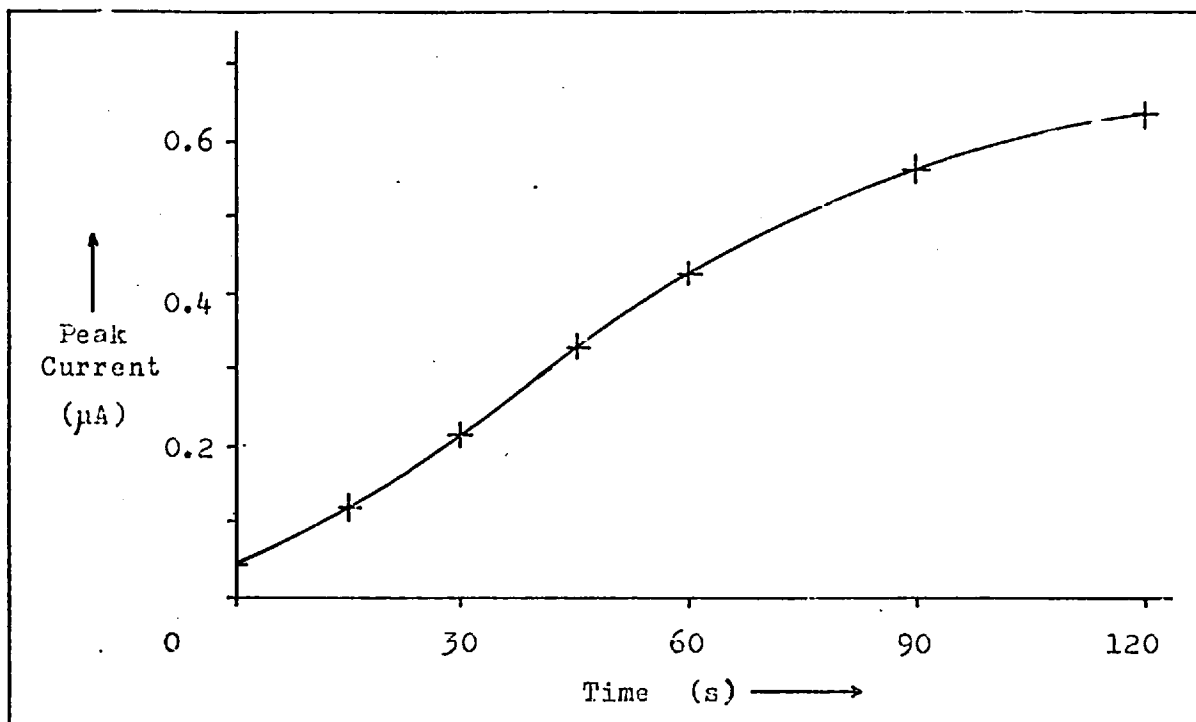


Fig.5.5. Effect of electrolysis time at -0.45 V on the stripping peak at -0.6V for 3×10^{-7} M SeO_3^{2-} .

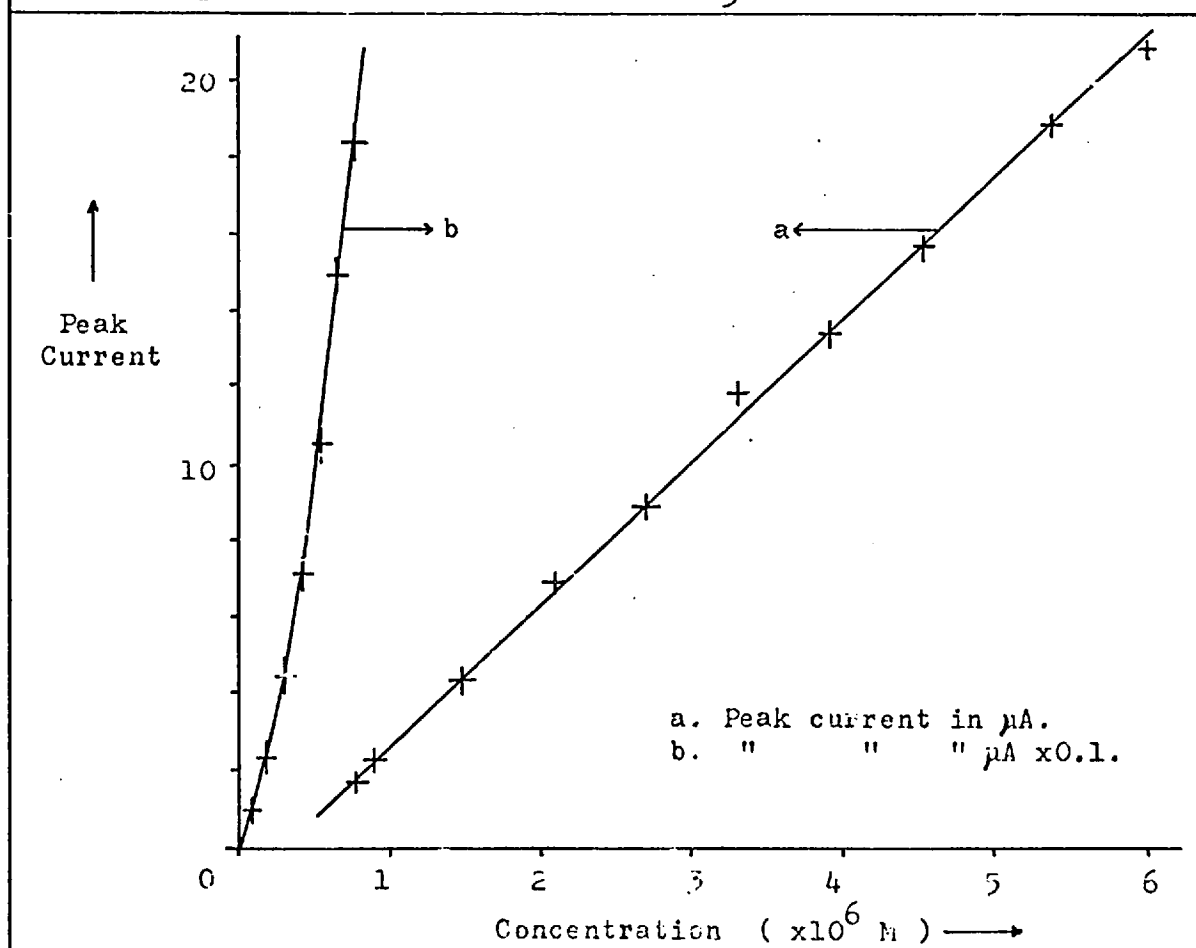
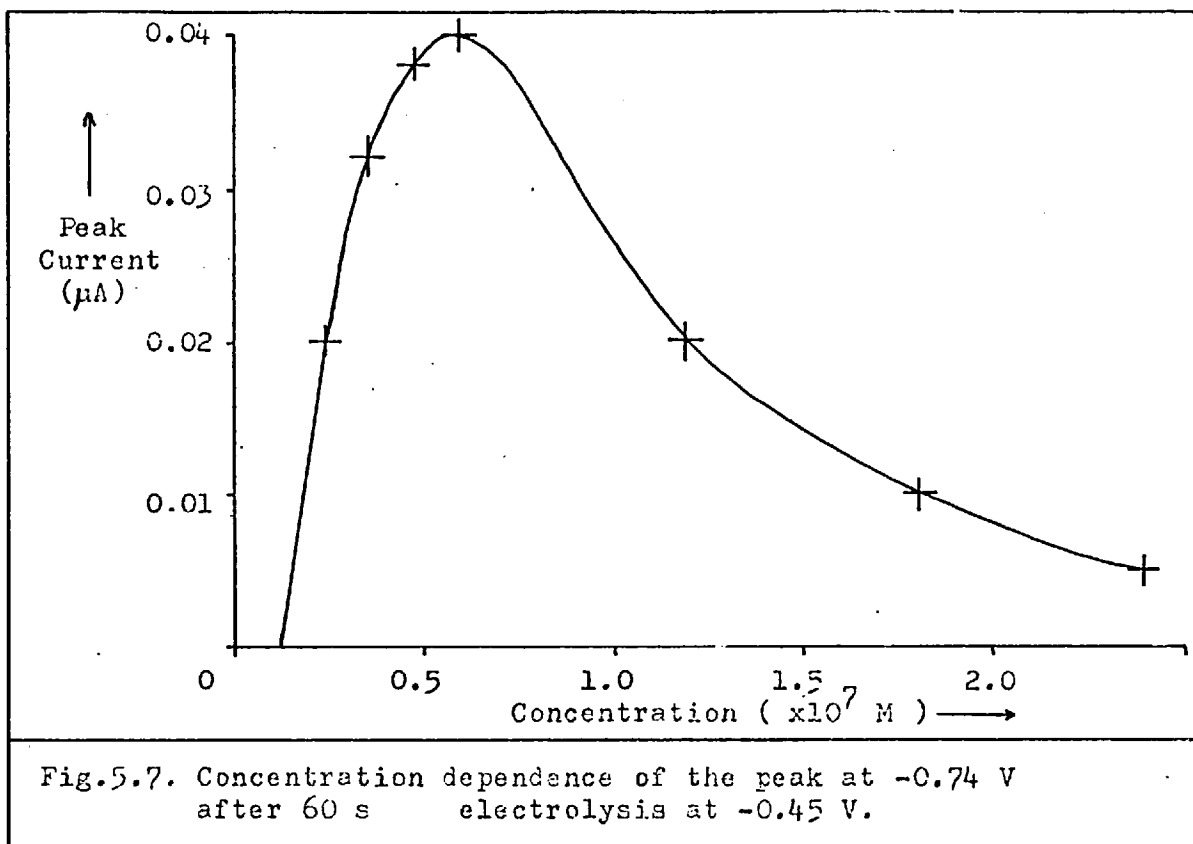


Fig.5.6. Concentration dependence of the peak at -0.60 V after 60 s electrolysis at -0.45 V.



Above 6×10^{-6} M the current increased non linearly but did not reach a maximum value as observed after electrolysis at -0.20 V. At -0.74 V a second stripping peak was observed which had a maximum peak current at a concentration of 6×10^{-8} M as shown in fig. 5.7.

Table 5.2 summarises the stripping peaks observed and the concentration ranges over which they may be used. The waves produced after electrolysis at -0.20 V had the following disadvantages:

- i) The wave at -0.84 V was masked by the other waves and was relatively insensitive.
- ii) The non linear concentration dependence of the wave at -0.60 V.
- iii) The large difference between electrolysis and stripping potentials.

Deposition potential (V vs SCE)	Stripping peak potential (V vs SCE)	Concentration range ($\times 10^6$ M)
-0.20	-0.84	0.5 - 6.0
-0.20	-0.60	0.3 - 6.0
-0.20	-0.56	0.02 - 0.6
-0.45	-0.60	0.1 - 6.0
-0.45	-0.74	0.02 - 0.06

Table 5.2. Summary of the stripping voltammetry of SeO_3^{2-} .

Electrolysis at -0.45 V overcame these problems producing a wave at -0.60 V which was linear over a wide concentration range. The wave at -0.74 V, observed below 10^{-7} M, did not exhibit a linear concentration dependence. For measurements below 10^{-7} M the peak at -0.56 V after electrolysis at -0.20 V gave a linear concentration dependence from 2×10^{-8} M to 3×10^{-7} M.

The interference of other anions on the wave of 10^{-6} M SeO_3^{2-} at -0.60 V after electrolysis at -0.45 V was studied. 10^{-3} M Cl^- , Br^- , I^- , SO_4^{2-} and SO_3^{2-} as the sodium salts did not interfere. Oxygen interfered with all the stripping waves studied and had to be rigorously excluded.

In the semi automated procedure, solutions of SeO_3^{2-} in 10^{-2} M HNO_3 were analysed. Fig. 5.8 shows a recorder trace of a series of samples, containing 1, 2 and 5×10^{-6} M SeO_3^{2-} , together with the calibration graph obtained. The recoveries of standard additions of stock SeO_3^{2-} to tap water, acidified with

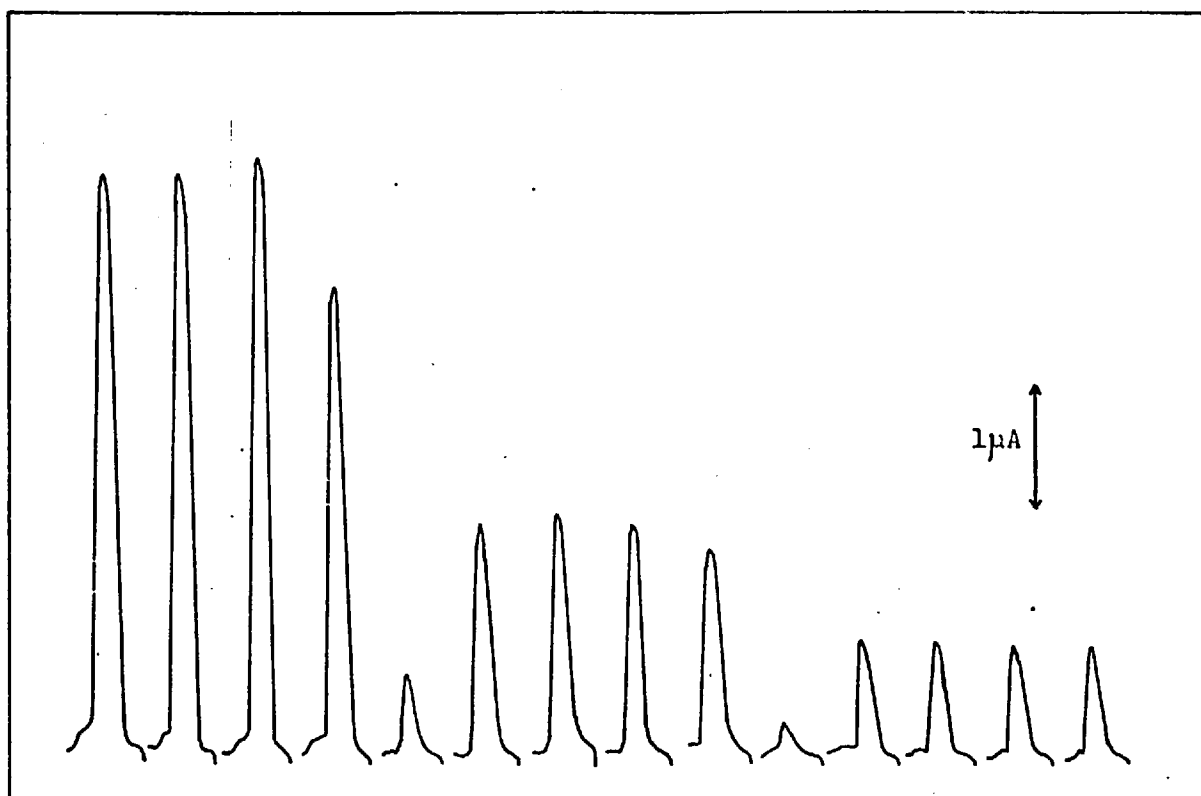


Fig.5.8a. Recorder trace, semi automated analysis of SeO_3^{2-} .

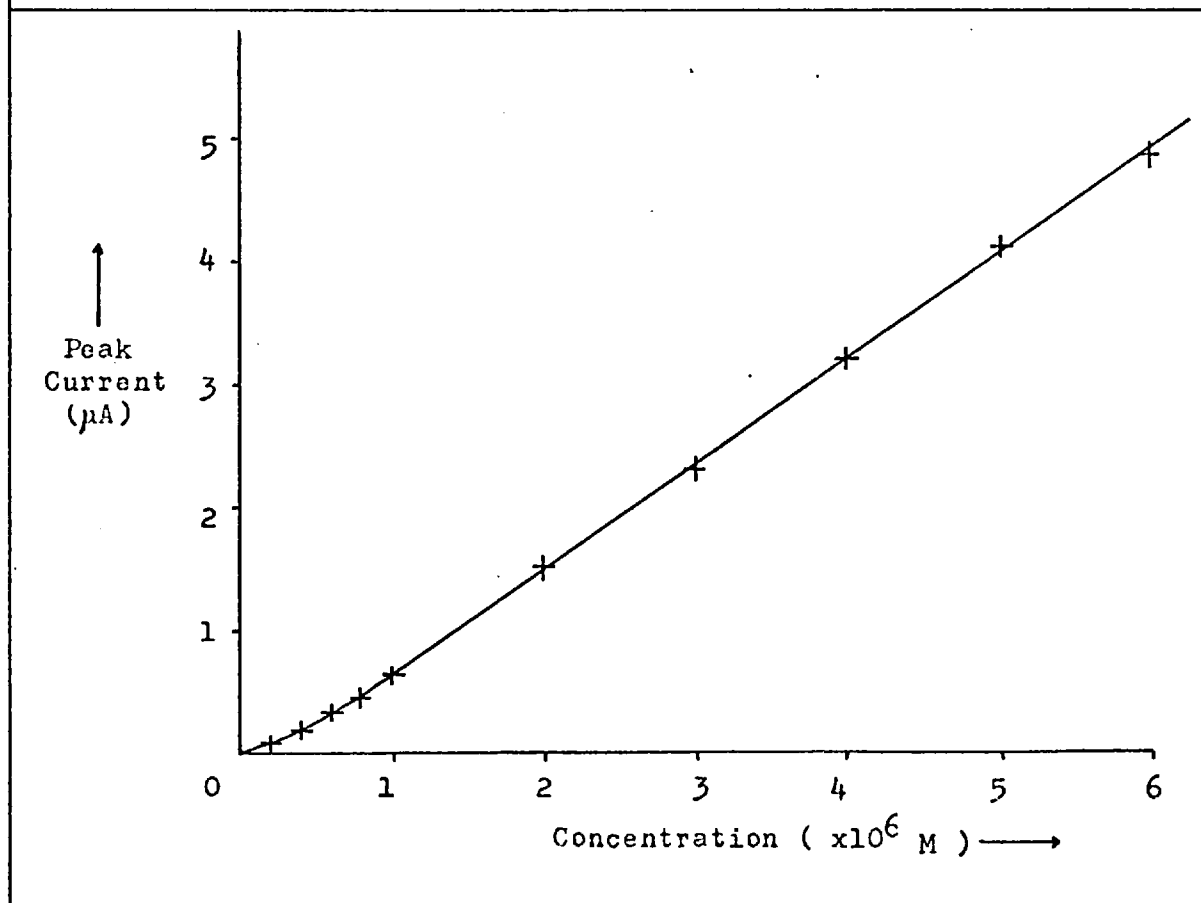


Fig.5.8b. Calibration curve, semi automated analysis of SeO_3^{2-} .

Added	Found	% recovery
0.50×10^{-6} M	0.46×10^{-6} M	92
1.0	1.02	102
2.0	2.1	105
3.0	2.9	97
5.0	4.9	98

Table 5.3. Recovery of standard additions of SeO_3^{2-} to tap water.

HNO_3 to 10^{-2} M, were measured. The results are given in table 5.3.

5.4 Conclusions

An analytical procedure for the determination of low concentrations of selenium as SeO_3^{2-} in water has been described using the technique of cathodic stripping voltammetry. Under the conditions described a linear calibration for the concentration range 0.2 to 6.0×10^{-6} M (0.02 to 0.5 ppm) was obtained. Good recoveries were obtained for standard additions of stock SeO_3^{2-} to acidified tap water indicating that the method should be suitable for the analysis of natural water samples. None of the anions studied interfered with the analysis but oxygen distorted the stripping voltammograms and had to be excluded. The electrochemical reactions involved in this work do not appear to be as simple as those reported previously for the DME. Further study of the reactions involved at the HMDE are necessary.

CHAPTER 6: PULSE AND A.C. STRIPPING TECHNIQUES; THE USE OF
PEAK AREA MEASUREMENTS FOR INCREASING THE
REPRODUCIBILITY OF ANODIC STRIPPING VOLTAMMETRY

6.1 Introduction

In chapter 2 the use of derivative output was investigated to improve the sensitivity and resolution of anodic stripping voltammetry when using a mercury drop electrode. Some improvements were gained at the expense of a more complex output signal. The application of other stripping techniques was discussed in chapter 1. Both phase selective a.c. (126-130) and differential pulse methods (133,134) increase the ratio of faradaic to capacitive current and have been shown to increase the sensitivity of stripping voltammetry by a factor of ten. These methods produce a single, symmetrically shaped peak with parameters similar to those obtained by the particular polarographic method.

The precision of stripping voltammetry is limited by both the deposition step and the current measuring system. Jee (226) evaluated the use of peak area and time integration for improving the precision of a.c. polarography at the DME. It was possible to measure peak areas with more precision than peak heights. He concluded that more reproducible results were obtained by area measurement as this method was less dependent upon the initial setting of the electrode potential and the stability of the reference electrode potential. Later work using a three electrode multifunctional polarograph (56)

showed that at high concentrations integration of the fast sweep d.c. polarographic current gave more reproducible results, but that at the 10^{-5} M level the integrated a.c. technique was superior. Integration of output signals from voltage step stripping methods has been tried (227) but the apparatus used was not sufficiently stable for comparative measurements to be made.

In this chapter pulse and a.c. stripping methods are compared. Peak area measurement was used with both these and d.c. stripping to investigate methods for improving the reproducibility of stripping voltammetry. A semi-automated system for fast sweep anodic stripping voltammetry with peak area measurement is described.

6.2 Experimental

6.2.1 Apparatus

All the apparatus used has been described in detail in chapter 2 except for the additions and modifications below.

A thermostatted water bath was used to maintain a constant temperature in both the conventional cell 5 and flow cell 1. The magnetic stirrers in cells 1 and 5 were pivoted at their centres and rotated in polythene supports. Magnetic stirring was provided by a submersible low voltage stirrer. A PAR model 174 polarograph (Princeton Applied Research Corporation, Princeton, New Jersey, USA) was used to obtain d.c., pulse and differential pulse stripping voltammograms. The multifunctional polarograph built by Jee (56) was used to compare d.c. and the

various a.c. stripping modes. An outline diagram of this apparatus is shown in fig. 6.1. Phase selective detection was added using the circuit shown in fig. 6.2. This was based on the original circuit described by Smith (10). The Brians XY recorder was used to record all the stripping voltammograms except the fast sweep a.c. voltammograms which were displayed on the Hewlett Packard storage oscilloscope as described in chapter 2. Integration was achieved by means of a voltage to frequency converter and a Harwell 2117B scaler (56). The voltage to frequency converter accepted positive voltages up to 4 V and gave output pulses of -3.5 V with a response of 1.36 Hz.mV^{-1} . The pulses were fed to the type 1 input on the scaler. The multifunctional polarograph provided a 10 V signal for inhibiting the scaler except during the voltage scans. Peak areas and recorder or oscilloscope traces were obtained simultaneously. The polarographs were run off a 240 V Advanced Instruments Voltstat voltage stabiliser. This reduced the noise present on the output signals considerably.

The PAR 174 was controlled manually as no simple connection could be made with the cam timer. The multifunctional polarograph incorporated a system for multiple cycling of drop detection, delay, voltage scan and control of the XY recorder. This enabled the instrument to be indirectly linked with the cam timer using the latter to control the drop knocker and stirrer. Unfortunately the delay times built into the polarograph were not ideal for use with the 50 or 200 second cycle times. As this polarograph had been built in modules,

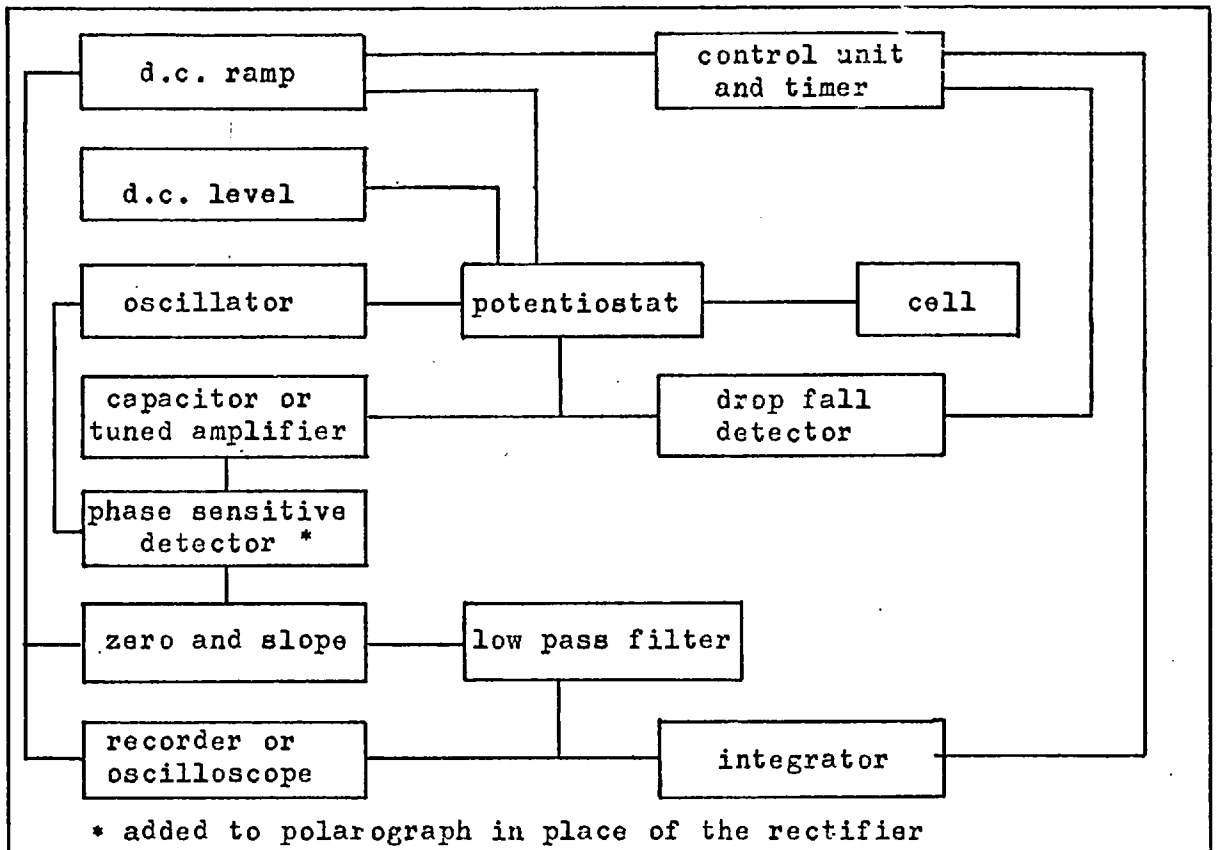


Fig. 6.1. Schematic diagram of the multifunctional polarograph.

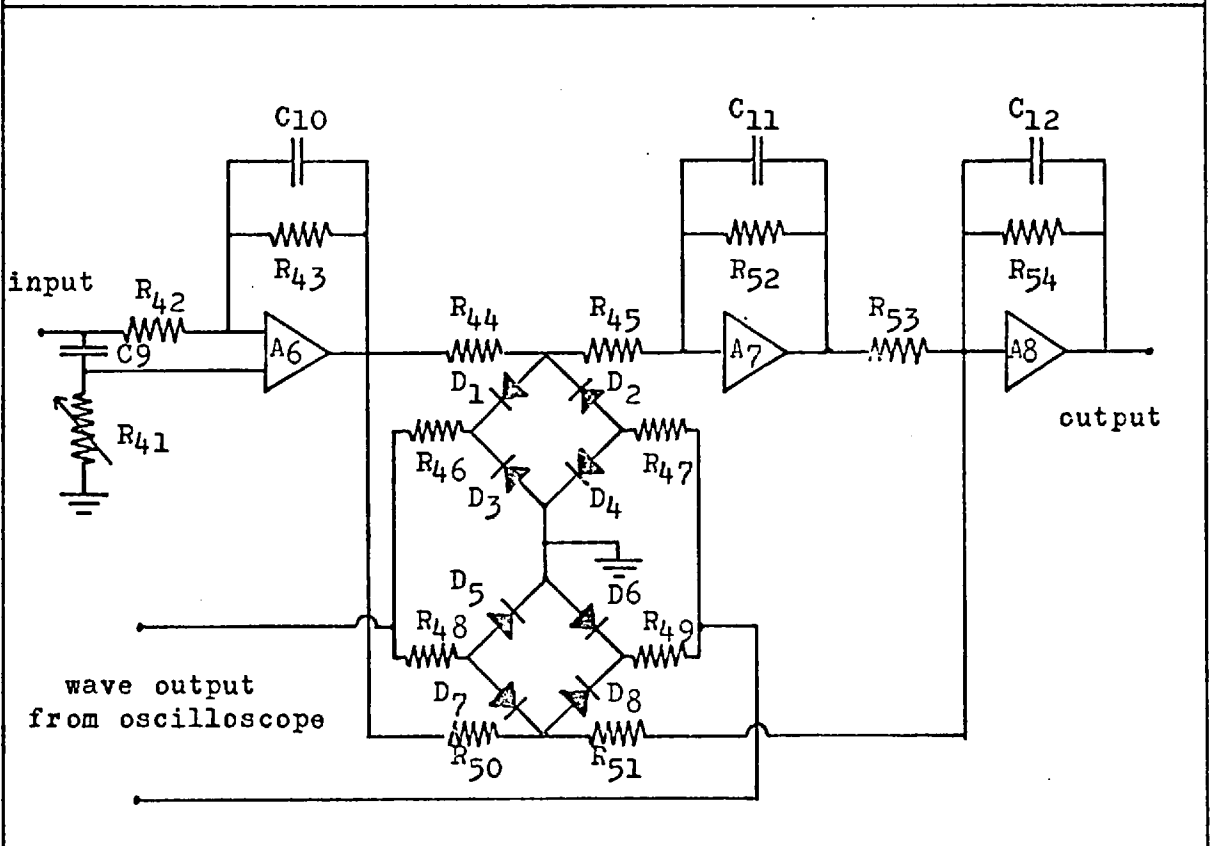


Fig. 6.2. Phase sensitive detector.

these were connected to the stripping voltammetry unit which was controlled by the cam timer. The a.c. signal from the variable frequency oscillator and attenuator was connected to the stripping voltammetry unit via point B in fig. 2.1. The output signal of this unit was then processed by the various modules as required. The cam timer was used as in fig. 2.10 with the addition of a 10 V signal applied to the scaler inhibit input except for during the voltage scan. The cam timer was also used to give a 10 V pulse to clear the scaler count before the next scan. The integrated count for each cycle was recorded manually. The continuous flow manifold was as shown in fig. 2.9b.

6.2.2 Reagents

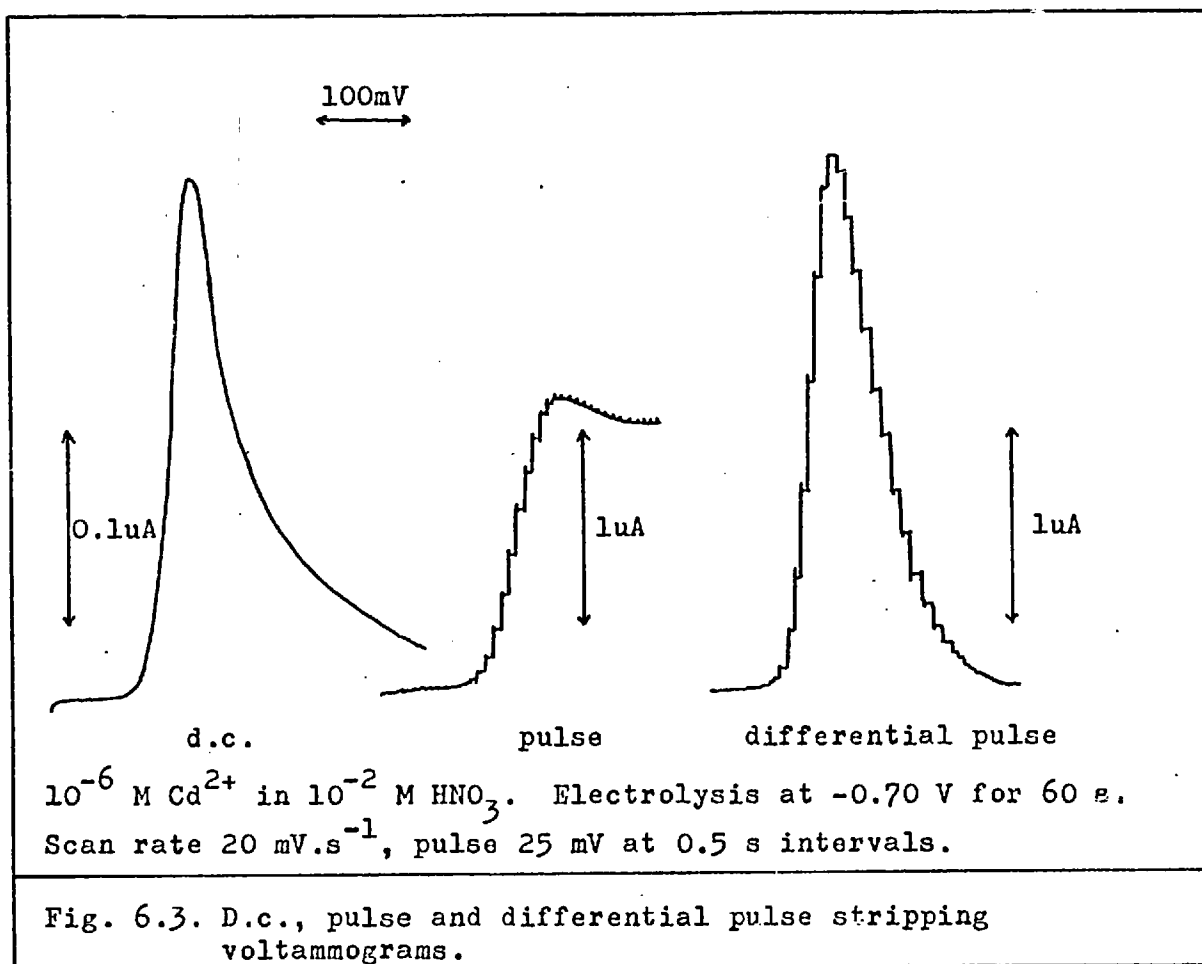
The chemicals used were as described in chapter 2.

6.2.3 Procedure

A standardised procedure was used for the comparison of d.c., a.c. and pulse stripping.

- a. Add 10 ml of solution to the cell.
- b. Deoxygenate for 10 minutes.
- c. Set electrode potential.
- d. Grow a fresh drop on the electrode.
- e. 60 seconds electrolysis with stirring.
- f. 5 seconds electrolysis without stirring.
- g. Voltage scan.

When measuring the integrated cell current the following additional steps were required.



h. After step f set the scaler baseline to 1 Hz.

j. Clear the scaler count before the voltage scan.

k. Record the scaler count at the end of the voltage scan.

Operation of the semi-automated system was as described in chapter 2. It was necessary to record manually the integrator reading after each scan.

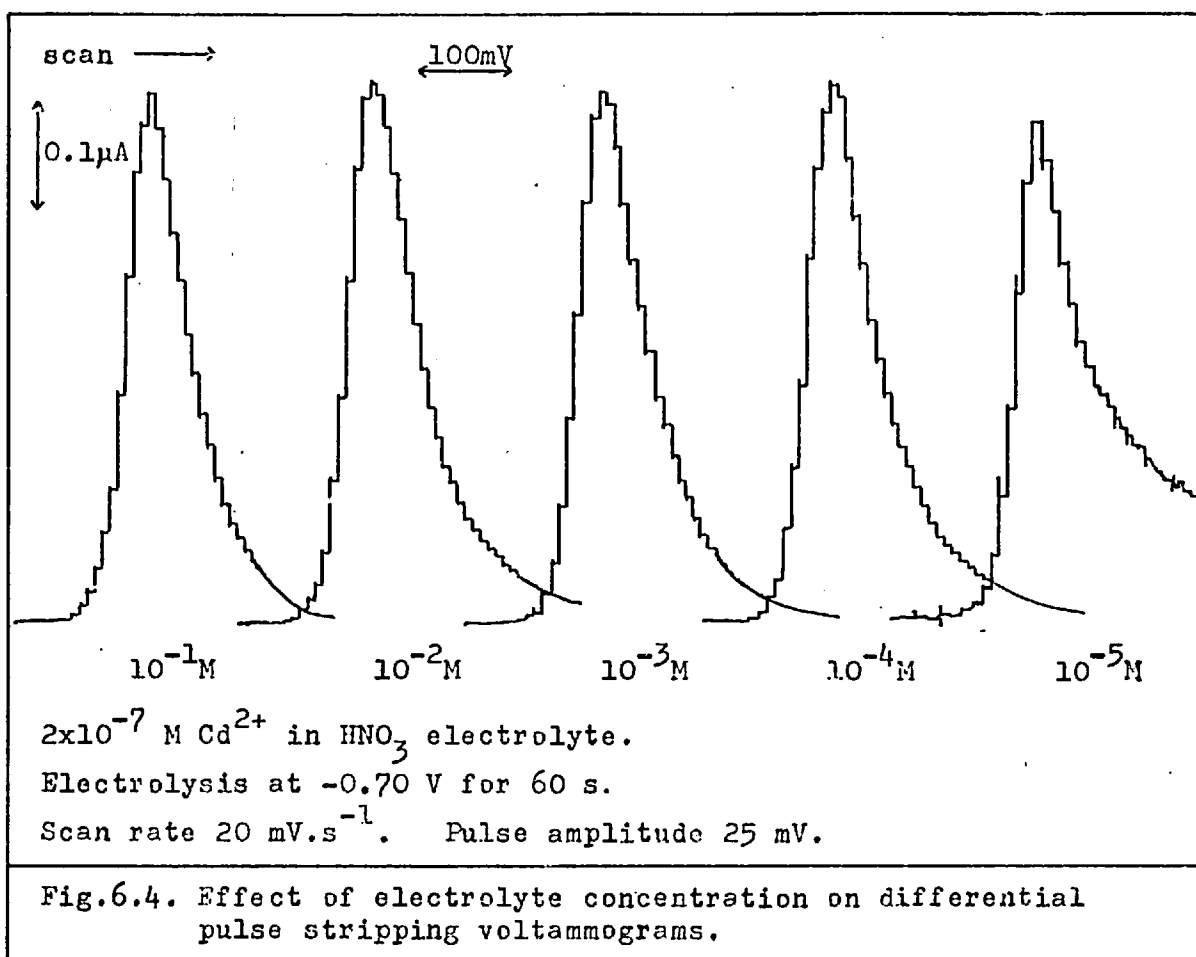
6.3 Results

6.3.1 Pulse stripping

The various parameters for pulse stripping were established using cell 5 and the Kemula type HMDE. Fig. 6.3 shows a comparison of d.c., pulse and differential pulse stripping of

10^{-6} M Cd^{2+} in 10^{-2} M HNO_3 after 60 seconds electrolysis at 0.70 V. Under these conditions the differential pulse mode gives a peak of ten times the amplitude of the d.c. mode and with similar peak width. The normal pulse mode gave a wave similar to that of normal pulse polarography which was not considered useful for further study. The fastest pulse rate of 0.5 seconds was used in all work. Slower rates reduced the definition of the stripping voltammograms. Tables 6.1 and 6.2 show the effect of pulse amplitude and scan rate on the stripping peak parameters of 10^{-6} M Cd^{2+} in 10^{-1} M KCl. The peak current was proportional to the pulse amplitude up to 50 mV. The peak width was independent of pulse amplitude up to pulses of 50 mV. The use of fast scan rates reduced the peak current and increased the measurable peak width considerably. The former observation is in contrast to d.c. stripping in which the peak current is proportional to the square root of the scan rate. At a rate of 50 mV.s^{-1} and greater, the broadening of the peak and decrease in peak current made the method less satisfactory than d.c. stripping. In table 6.3 the peak current is given versus the electrolysis time and is linear for the period measured. Fig. 6.4 shows the differential pulse stripping voltammograms for 10^{-6} M Cd^{2+} over a range of HNO_3 electrolyte concentrations. Below 10^{-4} M HNO_3 noise was present on the voltammograms which limited the working electrolyte concentration to this concentration. Similar results were found with KCl, KNO_3 and HCl. A linear dependence of peak current on concentration was found over the region 1×10^{-8} M to 1×10^{-5} M

Pulse amplitude (mV)	E_{peak} (V vs Ag/AgCl)	i_{peak} (μA)	$P_{1/2}$ (mV)
5	-0.520	0.53	93
10	-0.523	0.99	90
25	-0.530	2.44	94
50	-0.535	4.53	108
10^{-6} M Cd^{2+} in 10^{-1} M KCl. Electrolysis potential -0.70 V for 60 s. Scan rate 20 mV.s^{-1} .			
Table 6.1. Effect of pulse amplitude on peak parameters.			
Scan rate (mV.s^{-1})	E_{peak}	i_{peak}	$P_{1/2}$
1	-0.554	4.68	45
2	-0.540	4.60	55
5	-0.542	4.31	60
10	-0.535	3.45	73
20	-0.525	2.44	94
50	-0.515	1.40	180
100	-0.507	0.92	-
10^{-6} M Cd^{2+} in 10^{-1} M KCl. Electrolysis potential -0.70 V for 60 s. Pulse amplitude 25mV.			
Table 6.2. Effect of scan rate on peak parameters.			
Time (s)	E_{peak}	i_{peak}	$P_{1/2}$
0	-0.532	0.24	92
30	-0.532	1.33	90
60	-0.532	2.44	94
90	-0.532	3.52	92
120	-0.532	4.61	90
10^{-6} M Cd^{2+} in 10^{-1} M KCl. Electrolysis potential -0.70 V. Scan rate 20 mV.s^{-1} . Pulse amplitude 25 mV.			
Table 6.3. Effect of electrolysis time on peak parameters.			



Cd^{2+} in 10^{-1} M KNO_3 using the conditions of electrolysis at -0.70 V voltage scan to -0.4 V at 5 mV.s^{-1} and 25 mV pulse.

6.3.2 a.c. stripping

The conditions for a.c. stripping voltammetry were established using cell 5, the Kemula type HMDE and the multifunctional polarograph by following a similar procedure to pulse stripping. Fig.6.5 shows a comparison of d.c. and the various a.c. modes for stripping voltammetry of 10^{-6} M Cd^{2+} in 10^{-1} M KNO_3 after 60 seconds electrolysis at -0.70 V . The applied a.c. signal was 20 mV at 318 Hz . Total current a.c. was not considered useful because of the high capacitive component of the signal. Extensive electronic filtering removed much of the unwanted signal but

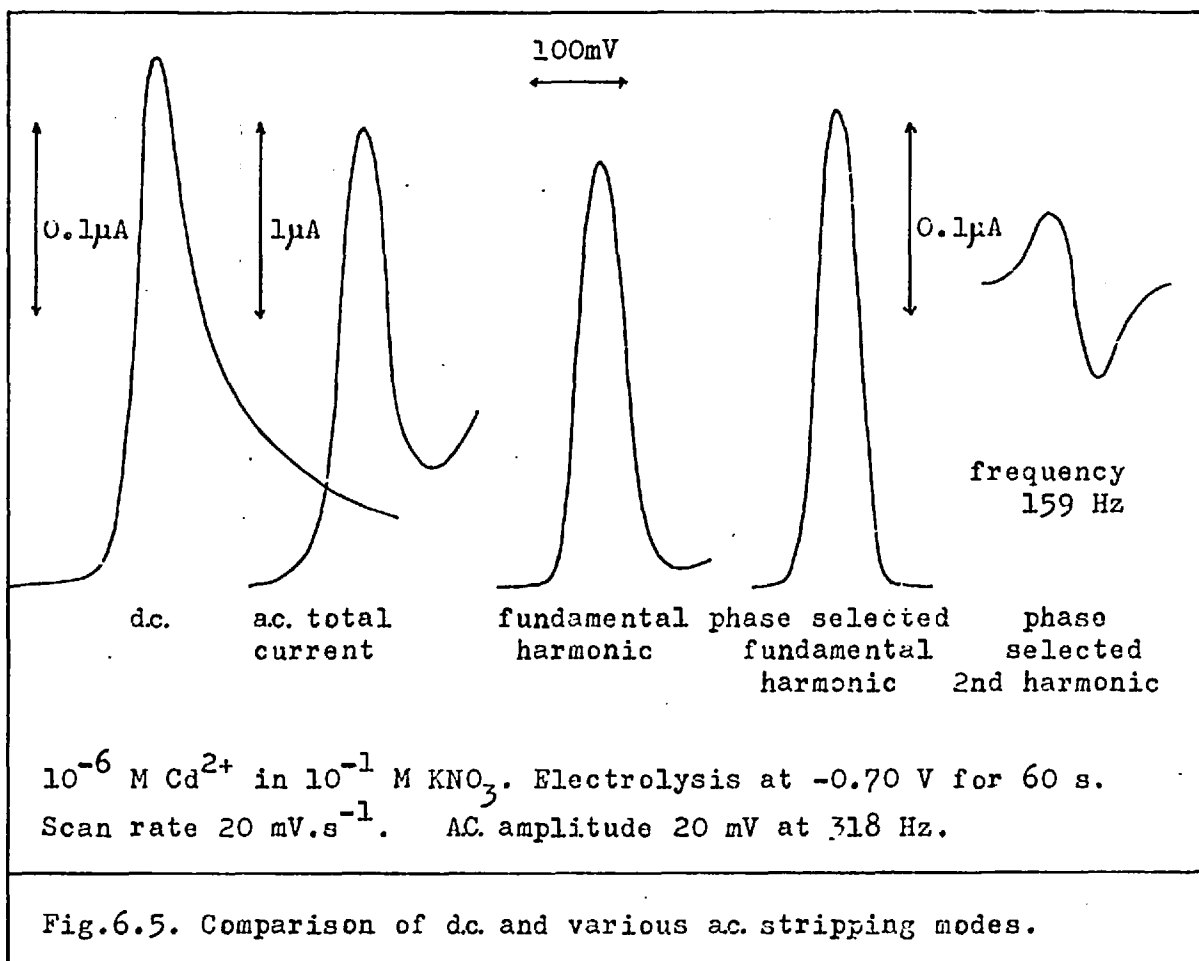


Fig.6.5. Comparison of dc. and various ac. stripping modes.

degraded the frequency response of the amplifier circuit. The fundamental harmonic response was a single, symmetrical peak. Although the 318 Hz tuned amplifier reduced much of the noise present on the total a.c. current signal the phase sensitive detector gave a further reduction and produced a horizontal baseline. Higher harmonics of the applied signal had the advantage that the capacitive current was eliminated resulting in higher sensitivity. The more complex waveforms produced were not considered useful for stripping analysis of multi-component systems or for peak area measurements.

Linearity between the applied a.c. amplitude and peak current was maintained up to 20 mV as given in table 6.4.

a.c. amplitude (mV)	E_{peak} (V vs Ag/AgCl)	i_{peak} (μA)	$\beta_{1/2}$ (mV)
2	-0.570	0.24	50
5	-0.570	0.56	50
10	-0.570	1.12	50
20	-0.570	2.4	50
50	-0.570	4.9	60
100	-0.570	6.6	85

10^{-6} M Cd^{2+} in 10^{-1} M KNO_3 . Electrolysis at -0.70 V for 60 s.
Scan rate 20 mV.s^{-1} . Frequency 318 Hz.

Table 6.4. Effect of a.c. amplitude on peak parameters.

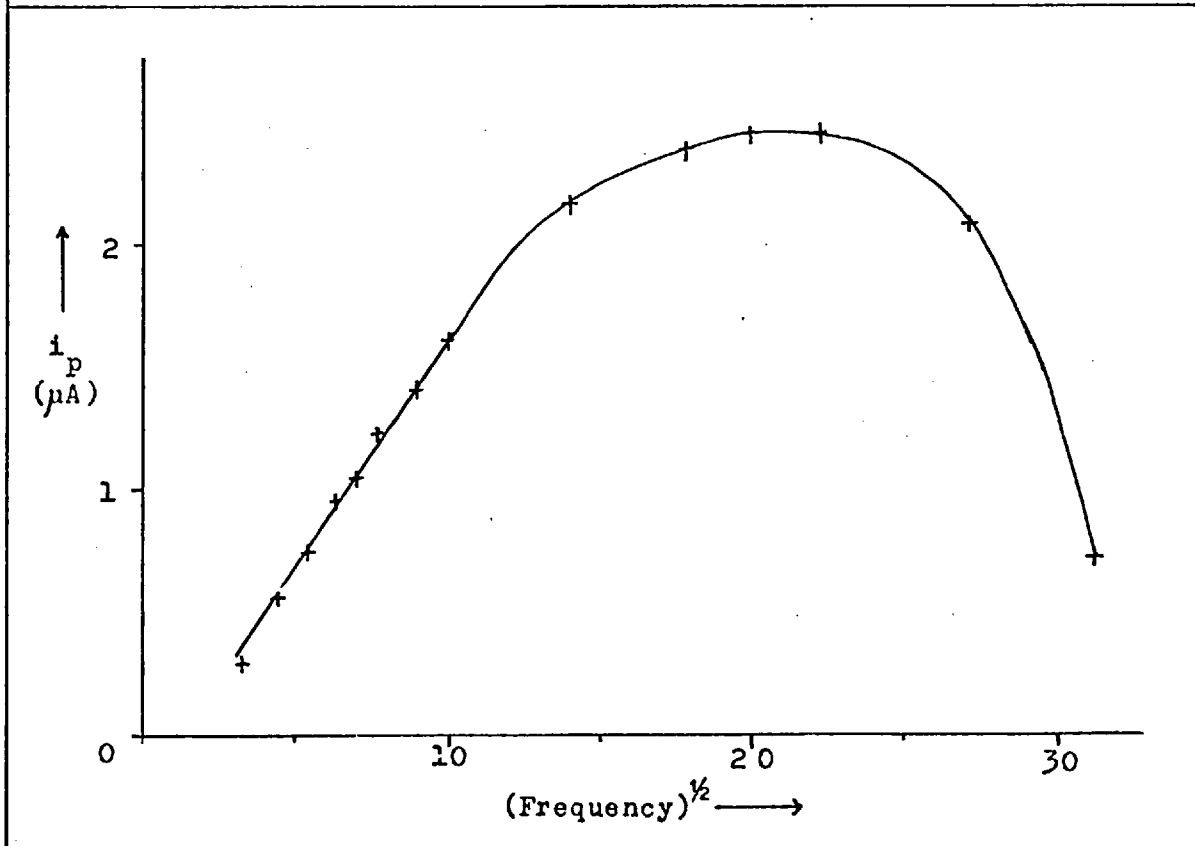


Fig. 6.6. Effect of frequency on peak parameters.

The peak width was independent of the a.c. amplitude up to 20 mV. The relationship between the applied a.c. frequency and the phase selective stripping peak current is shown in fig. 6.6. These results were dependent upon instrument settings and thus for each frequency the active electronic filtering used was limited to that necessary to reduce the noise to 0.5% f.s.d. on the recorder. I_p was proportional to the square root of the applied frequency over the range 20 to 100 Hz but reached a maximum value at 400 Hz. This deviation from linearity was due in part to the limited frequency response of the potentiostat used. 318 Hz, the frequency of the tuned amplifier, was close to the maximum and was used for subsequent work.

In contrast to both d.c. and pulse stripping the a.c. peak current and width were almost independent of scan rate over the range 5 to 500 mV.s^{-1} . Within the concentration range 10^{-2} to 1 M HCl supporting electrolyte the stripping peak parameters were constant. Lower concentrations of electrolyte caused a decrease in the peak current, a shift to more negative potentials and broadening of the peak as given in table 6.5. Using the conditions of 60 seconds electrolysis at -0.80 V in 10^{-1} M KNO_3 electrolyte, stripping at 500 mV.s^{-1} , applied a.c. signal of 20 mV at 318 Hz and measuring the phase selective fundamental harmonic response a linear calibration was found for Pb^{2+} and Cd^{2+} over the concentration range 2×10^{-8} M to 5×10^{-6} M.

6.3.3 Peak area measurements

The stability of the experimental assemblies was measured by using a dummy cell in place of the polarographic cell. For

Electrolyte Concentration (M)	E_{peak} (V vs Ag/AgCl)	i_{peak} (μA)	$\beta_{1/2}$ (mV)
1	-0.570	2.20	50
10^{-1}	-0.570	2.25	50
10^{-2}	-0.570	2.20	50
10^{-3}	-0.535	1.85	60
10^{-4}	-0.470	1.30	85
10^{-5}	-0.340	0.75	150
10^{-6} M Cd^{2+} in HCl electrolyte. Electrolysis potential -0.70 V for 60 s. Scan rate 20 mV.s ⁻¹ . A.c. amplitude 20 mV. Frequency 318 Hz.			
Table 6.5. Effect of electrolyte concentration on a.c. stripping peak parameters.			

the d.c. mode a 100 K resistor was used. A 1 μF capacitor and 100 turns of copper wire wound on a ferrite core in series with this resistor provided the necessary inductive element for pulse and a.c. stripping. Time integration was measured by setting the potentiostats at -1.0 V and counting for ten 5 minute periods. The error in scan rate and duration was measured by scanning ten times from 0 to -1.0 V at 10 mV.s⁻¹. Both the PAR 174 and multifunctional polarographs had an output variation of less than 0.2% in both time and scan integration modes.

Transport of material during the electrolysis step is an important factor affecting the reproducibility of stripping voltammetry. The magnetic stirrer in cell 5 was pivoted to give

more reproducible stirring. For comparison of stripping techniques Cd^{2+} in 10^{-1} M KCl was used. 60 seconds electrolysis at -0.70 V was followed by scanning to -0.20 V at 50 mV.s^{-1} for the d.c. and a.c. modes or 5 mV.s^{-1} for the pulse mode. A fresh aliquot of solution was used for each determination. Table 6.6 summarises the results of both peak height and area measurements for all three techniques over a range of concentrations. The pivoted stirrer reduced the coefficient of variation considerably and was used for subsequent work. Integration did not increase the precision. All three techniques were of comparable precision except for d.c. stripping below 5×10^{-7} M. Similarity between the methods at higher concentrations suggested that much of the error arose during the electrolysis step. By repeating the previous experiment for d.c. and a.c. stripping with the slow dropping mercury electrode, with manual control of the various steps, the results in table 6.7 were obtained. These show that the precision of the methods, especially at the highest concentrations, was increased although the peak currents measured were decreased by a factor of approximately three. There was less long term drift with this electrode than the Kemula type.

A linear calibration of peak area with Cd^{2+} concentration was found for both a.c., d.c. and pulse stripping over the same concentration ranges described in sections 6.3.1 and 6.3.2. The response rate of the scaler limited the scan speed in a.c. stripping to that consistent with sufficient counts to ensure precision. At 500 mV.s^{-1} the maximum scaler count for a 2

Conc. (M)	Relative standard deviation (n=10)					
	10^{-5}		10^{-6}		10^{-7}	
Technique	Height	Area	Height	Area	Height	Area
d.c.	3.9	3.5	3.7	6.0	15.2	25.6
Pulse	5.1	4.2	4.4	4.5	7.8	6.6
a.c.	3.7	3.8	3.6	4.2	6.2	6.6

Table 6.6. Precision of stripping voltammetry - hanging mercury drop electrode and pivoted stirrer.

Conc. (M)	Relative standard deviation (n=10)					
	10^{-5}		10^{-6}		10^{-7}	
Technique	Height	Area	Height	Area	Height	Area
d.c.	2.1	2.3	3.2	4.3	19.3	28.0
a.c.	2.2	2.3	2.5	2.9	7.4	9.0

Table 6.7. Precision of stripping voltammetry - slowly dropping mercury electrode and pivoted stirrer.

Pb ²⁺ (x10 ⁻⁶ M) added	Cd ²⁺ (x10 ⁻⁶ M) added	Pb ²⁺ found		Cd ²⁺ found	
		Height	Area	Height	Area
0	2.0	-	-	2.0	2.0
2.0	2.0	-	-	2.0	2.0
5.0	2.0	-	-	2.1	2.2
10	2.0	-	-	1.9	2.2
50	2.0	-	-	2.1	3.0
100	2.0	-	-	2.3	4.5
2.0	0	1.9	2.0	-	-
2.0	2.0	2.1	2.0	-	-
2.0	5.0	2.1	2.1	-	-
2.0	10	2.0	2.2	-	-
2.0	50	1.9	2.9	-	-
2.0	100	1.9	5.3	-	-

Table 6.8. Comparison of peak height and area measurements.
Interaction of a.c. stripping peaks.

electron stripping peak was approximately 500 before the scaler input became overloaded.

To enable the resolution of mixtures by stripping peak area measurements strict control of electrolysis and scan potentials was essential. Table 6.8 compares the interferences caused by Cd²⁺ and Pb²⁺ on the determination of each ion by a.c. stripping using peak height and area measurements. For the determination of Cd²⁺, electrolysis at -0.70 V followed by a scan of +0.20 V enabled measurement of the whole peak to be made. Electrolysis at -0.55 V with a scan of +0.20 V enabled measurement of the Pb²⁺ peak to be made. It was necessary to measure the total peak area to minimise errors due to variation

in the scan amplitude and cell potential. Because the total current was measured over the voltage scanned the interferences seen were considerably greater than those found by peak current measurements. These results indicate that total peak area measurements are unsuitable for the analysis of mixtures in which another peak overlaps the potential range being scanned.

Peak area measurement had the advantage of direct numerical (digital) output with possible use of a printer. Disadvantages were the poor resolution of mixtures and the necessity for simultaneous use of an oscilloscope or recorder. No increase in precision was achieved with this form of measurement compared with the recorder. At the lowest concentrations peak area measurements were less precise than peak current measurements because long term drift in the baseline current had more effect upon the former method. Significant increases in precision were achieved by the use of pivoted stirrers and the long drop time DME which reduced variations associated with the deposition step. Further increases in precision could be achieved by the use of improved temperature control and stirring or other types of transport of material to the electrode.

6.3.4 Semiautomated a.c. stripping voltammetry

In section 2.4 the use of derivative output for increasing the sensitivity and resolution of semiautomated stripping voltammetry at the long drop time DME was investigated. The detection limit was halved and up to a 5 fold excess of an ion reduced at more negative potentials could be tolerated. A.c. stripping was expected to be more sensitive than this and enable

similar resolution of mixtures to be made. Oxygen interference was considered to be less important as oxygen is irreversibly reduced at the mercury electrode. The connection of the stripping voltammetry unit to the various signal processing units in the multifunctional polarograph was given in section 6.2.

The conditions chosen for evaluation of the system were electrolyte 10^{-3} M KNO_3 , cycle time 50 seconds, electrolysis at -0.8 V for 40 seconds and scan to 0 V at 100 mV.s^{-1} . The applied a.c. potential was 20 mV at 318 Hz and the phase selective fundamental harmonic response was measured. Pb^{2+} and Cd^{2+} gave linear calibration over the range 4×10^{-8} M to 5×10^{-6} M.

In table 6.8 a comparison was made of peak height and area measurements for the resolution of mixtures of Pb^{2+} and Cd^{2+} by a.c. stripping voltammetry. Peak height measurements were not influenced by up to a 25 fold excess of another ion giving a preceding or succeeding wave.

Oxygen interfered with the a.c. stripping voltammetry of Pb^{2+} and Cd^{2+} by reducing the peak current and increasing the baseline current. This interference was similar in magnitude to that observed in d.c. stripping. For this reason the sampler system incorporating deoxygenation was not suitable when attempting to analyse concentrations below 2×10^{-7} M.

6.4 Conclusions

Differential pulse and a.c. stripping techniques were found to be an order of magnitude more sensitive than the d.c. technique. The pulse method showed highest sensitivity and narrowest peak

width at the slowest scan rates. A.c. stripping produced peaks which had both current and width almost independent of scan rate. Thus the a.c. method was more suitable for the semi-automated system than the pulse method. When using the long drop time DME the a.c. method was able to resolve mixtures better than the d.c. method. In spite of the extra complexity of the a.c. method it was only slightly more sensitive than derivative output d.c. However, a.c. had the advantage of producing a single symmetrical peak compared with the more complex output of the derivative method. D.c. stripping from the mercury plated GCE was as sensitive as a.c. with comparable resolution. Unfortunately the precision with the solid electrode was not as good as the long drop time DME.

It was found that improvements to the stirring during deposition and the use of a long drop time DME improved precision considerably. However, the relative standard deviations found were an order of magnitude greater than those found by repetitive sweep d.c. and a.c. voltammetry with the same apparatus (56) and it was concluded that the majority of the error found was in the deposition rather than the stripping stage. Closer temperature control during deposition might be expected to increase the precision further.

Integration of peak areas, when analysing for one component of a mixture, was only possible if the choice of deposition and scan potentials could be made which eliminated any current due to other components.

PART II: THE USE OF POLAROGRAPHIC TECHNIQUES AND THEIR
APPLICATIONS IN CONTINUOUS ANALYSIS

Introduction

Electrical sensors are of interest in continuous analysis as they are relatively inexpensive and can be sensitive to a wide range of both organic and inorganic species. The response is often fast and selective. Systems for the direct control of the electrochemical cell and storage of the output signal are feasible.

As early as 1913 the galvanic cell of Rideal and Evans (228) was applied to the continuous monitoring of trace oxygen in gases. Since then galvanic sensors for a wide range of gases have been devised. However, because of slow response times and lack of selectivity, these sensors are only of use in monitoring the gradual variation of one component in an unchanging mixture of others. Recently, a coulometric oxygen sensor of fast response has been developed and applied to a range of continuous analytical determinations (229).

When using either a DME or solid electrode for polarography in a liquid stream a constant flow rate is necessary to give a reproducible and steady limiting current because of the need to maintain a constant diffusion layer around the electrode. This current is proportional to the concentration of depolariser and has a logarithmic dependence on flow rate (230). The first application of polarography to continuous analysis was its use for measurement of dissolved oxygen. A wide bore DME was needed to overcome the problem of particles entering the capillary. The presence of oxygen obscures and often alters electrode

reactions. The removal of oxygen on a continuous basis is a complicating factor which may have hindered the acceptance of this measuring technique for routine work.

Blaedel and Strohl (231) have designed two flow cells for polarography using the DME. The response time to a step change in concentration was shown to be the time required to flush the cell. Blaedel considers that the DME is not entirely satisfactory because of the precautions required to ensure reliable functioning and the toxicity of mercury. The geometry of tubular electrodes is ideal for continuous analysis. The tubular platinum electrode, TPE, (232) and mercury coated TPE (233) have been suggested as sensors for continuous EDTA titrations. An evaluation of these electrodes, together with the HMDE and pyrolytic graphite electrode, for the continuous monitoring of Ca^{2+} and Mg^{2+} by titration with excess EDTA and EGTA has been made (234). Both the TPE and pyrolytic graphite electrode were found to show time dependent responses, presumably due to deactivation of the electrode surface, the mercury coated TPE gave a high background current because of residual oxygen and only the HMDE gave reproducible results. The DME can be made more suitable for continuous flow analysis by the use of a short, controlled drop time which removes the main disadvantage of its use, that of irregular drops (235).

When using d.c. polarography for continuous analysis the current at a set potential is monitored. Interferences are caused by substances with similar oxidation/reduction potentials or which give prewaves. The application of other more selective polarographic methods such as a.c. or pulse which give peak responses should give improvements in selectivity.

CHAPTER 7: THE POLAROGRAPHIC REDUCTION OF NAPHTHALDEHYDES AND
THEIR SEMICARBAZONE DERIVATIVES; THE APPLICATION OF
SEMICARBAZONES IN CONTINUOUS POLAROGRAPHIC ANALYSIS

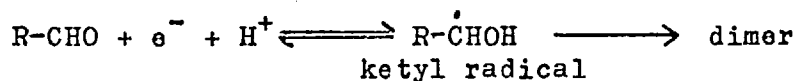
7.1 Introduction

A wide range of aliphatic carbonyl compounds which cannot be reduced directly at the DME can be reduced by conversion to azomethine or semicarbazone derivatives in situ. The reduction of aldehyde and ketone derivatives of structure $R'R''C=N-NH-R$ occurs by a 4 electron process. A survey of the mechanism has been carried out by Lund (236). Fleet and Zuman (237) confirmed this for a range of aromatic aldehyde semicarbazones and subsequently a method for the determination of a range of aldehydes was developed (238). The waves for the lower aliphatic aldehydes and ketones are not well defined and show some degree of hydrolysis. A comparison of several nucleophilic reagents has shown that Girard T (trimethylammonium acetyl hydrazide chloride) derivatives of aliphatic aldehydes give better defined waves than the corresponding semicarbazone derivative (239). The polarographic behaviour of benzaldehyde and benzoquinone semicarbazone derivatives has been described (237). The aim of this study was to compare the polarographic reduction of a range of naphthaldehydes and their derivatives so that an analytical procedure could be developed. The method was then modified for use in a continuous polarographic detector system which could have applications to automated analysis.

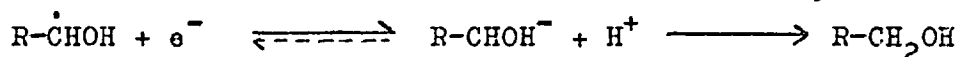
7.1.1 Theoretical

The reduction mechanism of aromatic aldehydes, including

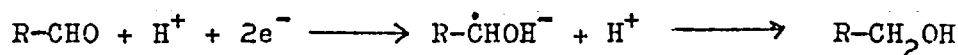
1-naphthaldehyde has been reported by Day and co-workers (240). For the first wave $dE_{1/2}/dpH$ equalled -60 mV/pH from which it was concluded that one proton was involved. Constant potential coulometry showed that one electron was transferred and that the product was a dimer. The reversibility of the reduction was shown by oscillopolarography.



For the second wave $E_{1/2}$ was only slightly dependent on pH. One electron was transferred. The slight dependence of $E_{1/2}$ on pH was explained as being due to the partial reversibility of the electron transfer and proton extraction from H_2O or H_3O^+ .

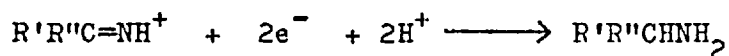
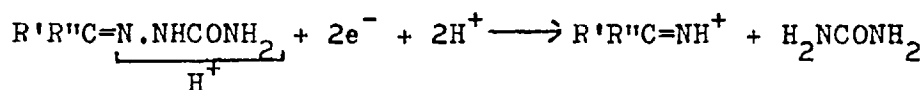
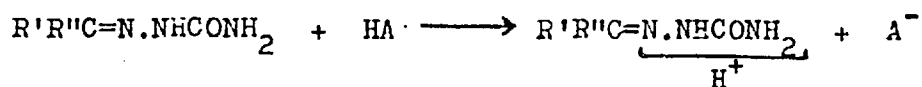


Gardner (241) has given a mechanism for the two electron wave seen at higher pH for which $dE_{1/2}/dpH$ equalled -30 mV/pH . One H^+ was taken up with the electron transfer and the ketyl radical ion extracts a proton from the solution.



Above pH 10 two separate one electron waves are seen in Ca^{2+} electrolytes whereas only a single one electron wave is seen in Na^+ electrolytes.

The mechanism derived by Fleet and Zuman for the reduction of semicarbazone derivatives in acid media involves the formation of the protonised derivative by reaction with H_3O^+ or other proton donors.



7.2 Experimental

7.2.1 Apparatus

The polarographic waves were recorded on a Radelkis polarograph, type OH-102 (Metrimpex, Hungary). A Kalousek cell with a saturated calomel reference electrode (SCE) was used. Capillary constants, measured at the potential of the SCE in 10^{-1} M KCl, were $t = 2.84 \pm 0.02$ s, $m = 1.90 \pm 0.05$ mg.s $^{-1}$ at $h = 64.0$ cm. A Chemtrix polarograph was used for cyclic voltammetry. This involved the addition of a platinum counter electrode to the cell. The AutoAnalyzer modules used consisted of a sampler, proportioning pump and associated tubing and glass fittings. The sampler was modified as described in chapter 2 to provide deoxygenation of the sample prior to analysis. The samples were presented at a rate of 40 per hour with a sample:ethanol wash ratio of 2:1. The flow through polarographic cell has been described previously (85). The DME was held in the solution stream with a calomel reference electrode downstream, separated by a porous glass cylinder. The original design of the cell was modified so that waste mercury was continuously removed. The cell and manifold design are shown in fig.7.1.

7.2.2 Chemicals

The 1-, 2- and 2-OH-1-naphthaldehydes studied were obtained from Koch Light and used without further purification. Girards reagent T, reagent grade, was recrystallised from a 9:1 ethanol: water mixture. All other chemicals were analytical reagent grade and used as obtained. 10^{-2} M stock solutions of the naphthaldehydes in ethanol were stored at 4°C. 1 M stock solutions of semicarbazide hydrochloride and Girards reagent T were prepared

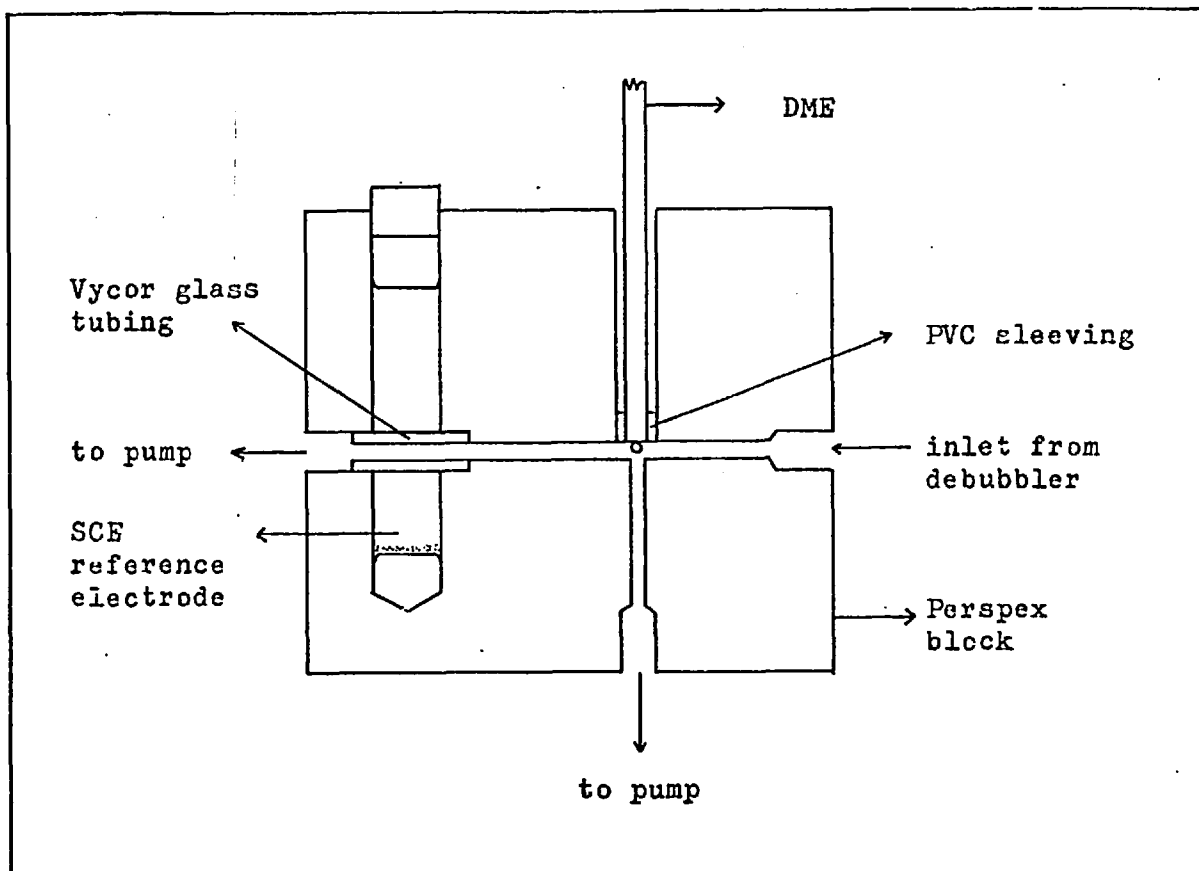


Fig. 7.1a Polarographic flow cell.

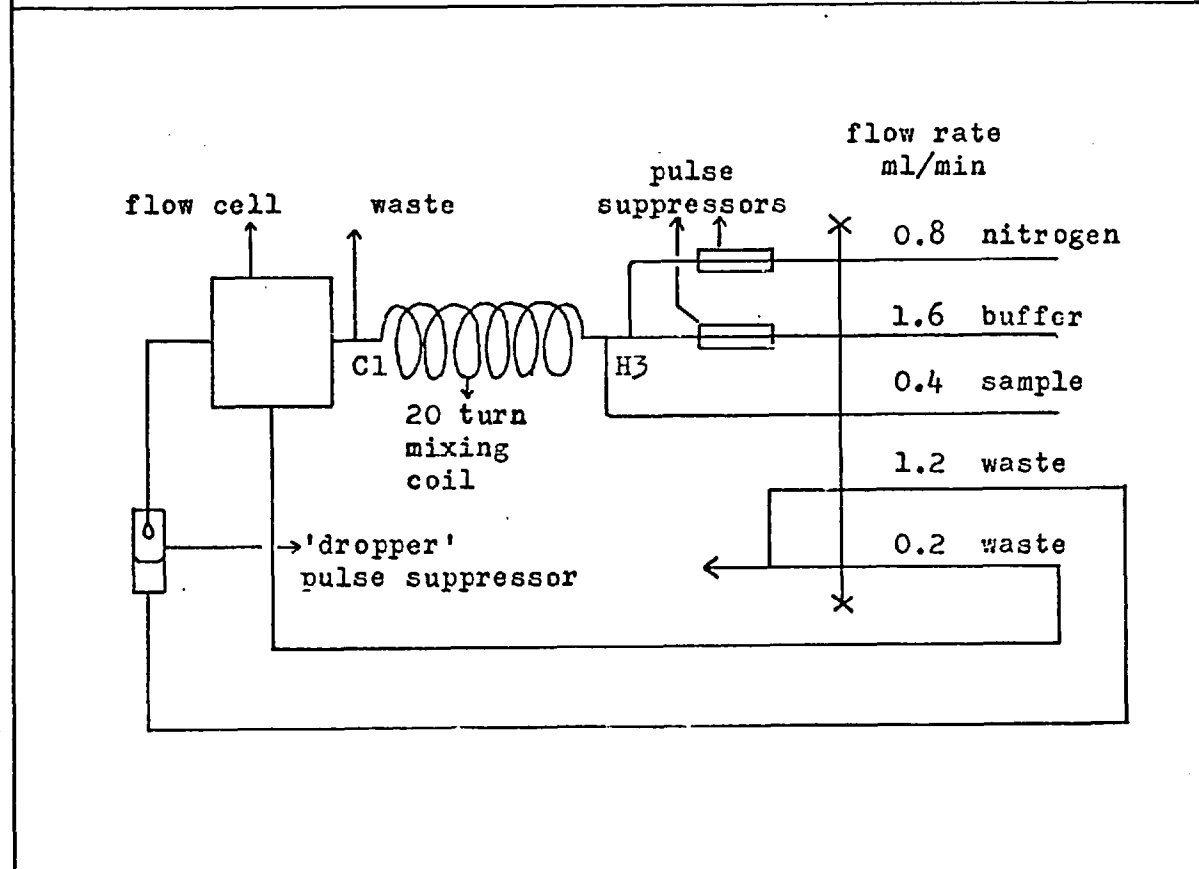


Fig. 7.1b Manifold diagram.

afresh each day. Table 7.1 lists the composition of the buffers used. The pH of these buffers was measured when diluted as directed in the method, omitting the addition of naphthaldehyde.

7.3 Analytical method

7.3.1 Manual method

To 0.2 ml of the stock naphthaldehyde solution, 4.8 ml of ethanol and 2.0 ml of buffer were added. The solution was diluted to 10 ml with distilled water and 1 drop of 1% Titron X-100 was added. To prepare derivatives 1.0 ml of 1 M semicarbazide or Girard T were added in place of 1.0 ml of ethanol. The proportions of stock naphthaldehyde to ethanol were varied, keeping the total ethanol volume constant, to obtain the concentration dependence. The proportions of ethanol:water were varied as required. The solution was then added to the cell and nitrogen was passed through it for 5 minutes to remove dissolved oxygen. The polarogram was recorded from 0 to -1.8 V versus SCE with a scan rate of $125 \text{ mV} \cdot \text{min}^{-1}$ and an instrument damping of 2 on the current response.

7.3.2 Automated method

The naphthaldehyde solution in ethanol was deoxygenated by the sampler for 1 minute prior to being aspirated. The sample was mixed with a segmented stream of 10^{-1} M acetic acid and 10^{-1} M sodium acetate buffer containing 10^{-1} M semicarbazide, 0.005% Triton X-100 and 10% ethanol. The ethanol for the sampler wash reservoir and the buffer were kept deoxygenated during use. A 20 turn coil was used to give sufficient mixing and time for the reaction forming the derivative to proceed to equilibrium. The current at an applied potential of -1.00 V versus SCE was measured.

Composition	pH*
0.5 M hydrochloric acid	1.3
0.45 M potassium chloride, 0.05 M hydrochloric acid	2.3
2 M formic acid, 0.5 M sodium formate	3.4
0.5 M formic acid, 0.5 M sodium formate	3.6
5 M acetic acid, 0.5 M sodium acetate	4.5
0.5 M acetic acid, 0.5 M sodium acetate	5.6
0.5 M acetic acid, 5 M sodium acetate	6.5
0.2 M sodium dihydrogen phosphate, 0.05 M sodium hydroxide	7.4
0.15 M sodium dihydrogen phosphate, 0.2 M sodium hydroxide	9.4
0.5 M sodium bicarbonate	10.9
0.5 M calcium chloride, saturated with calcium oxide	12.0
0.5 M sodium hydroxide	13.1
* see text	

Table 7.1 Buffer compositions

7.4 Results and discussion

The pH studies were first made on each compound in 50% ethanol. Fig.7.2 shows the polarographic waves of 1-naphthaldehyde in this solvent over a range of pH. Figs. 7.3 and 7.4 give the dependence of $E_{1/2}$ and the limiting current on pH for the naphthaldehydes studied together with the semicarbazide derivatives. The results for the naphthaldehydes follow those given by Powers and Day (240). All three compounds showed the same general behaviour as the only reduction was that of the

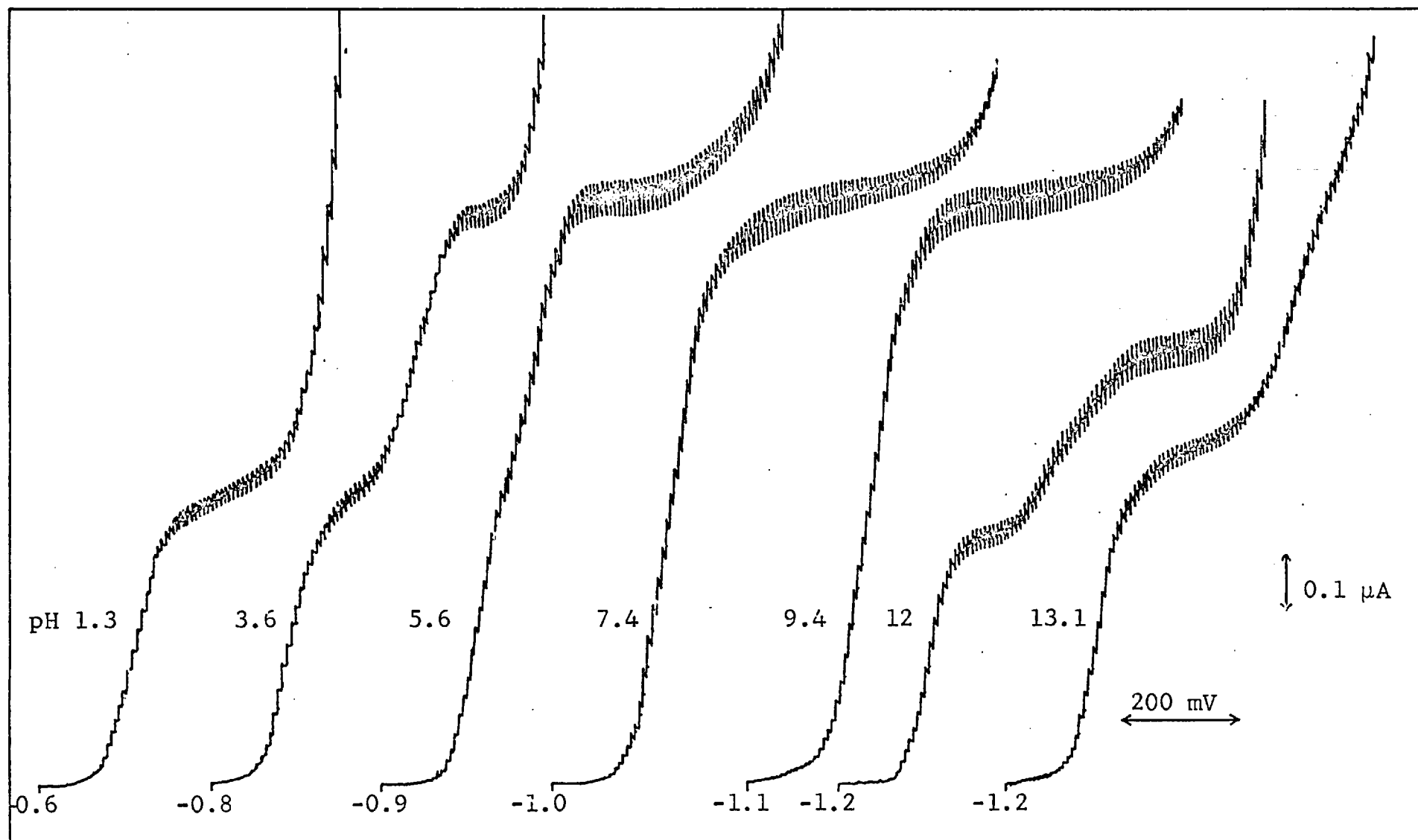


Fig. 7.2. Polarograms of 1-naphthaldehyde in 50% ethanol over the pH range 1.3 to 13.1.

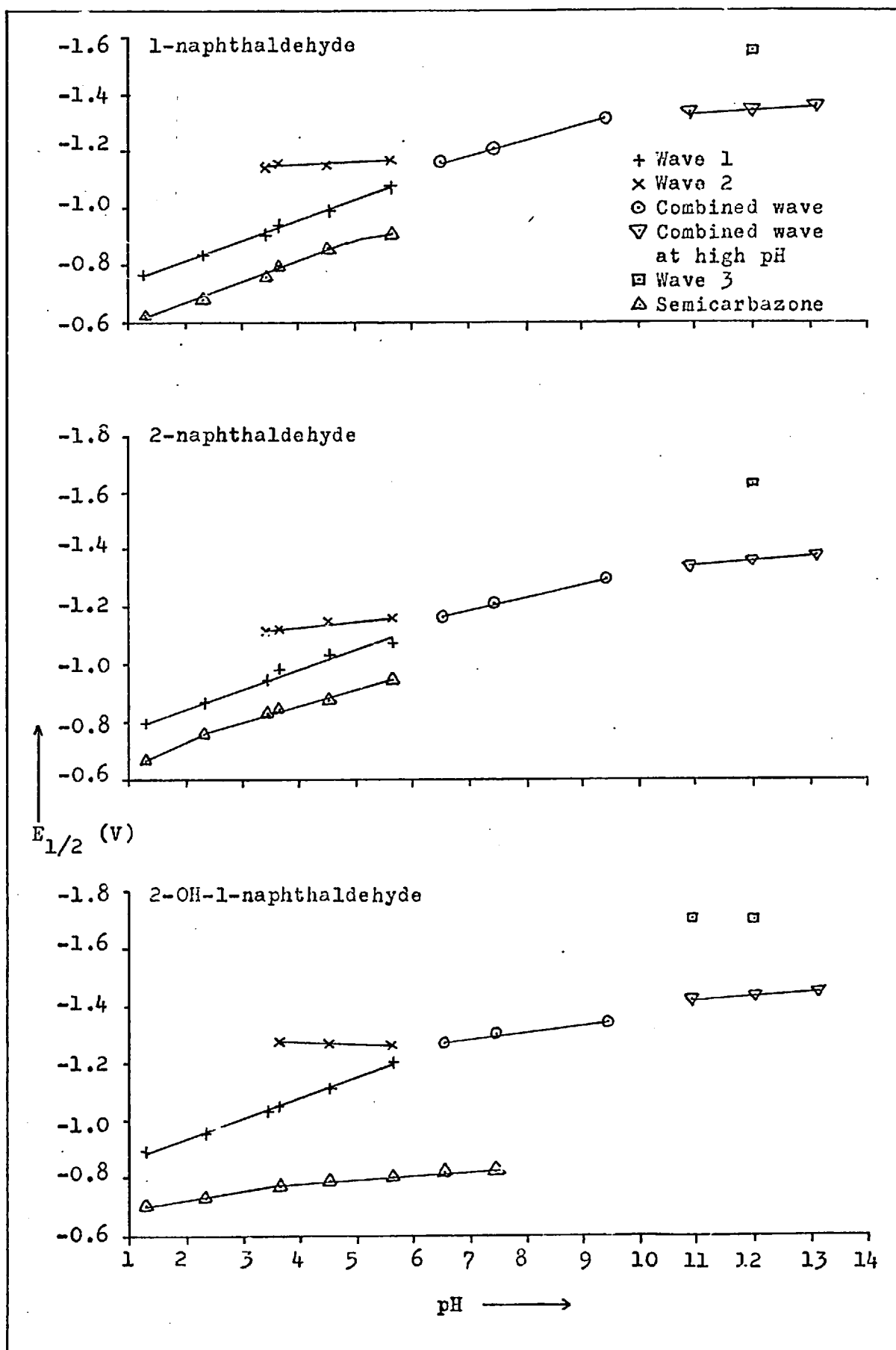


Fig. 7.3 Effect of pH on the polarographic $E_{1/2}$ of the naphthaldehydes.

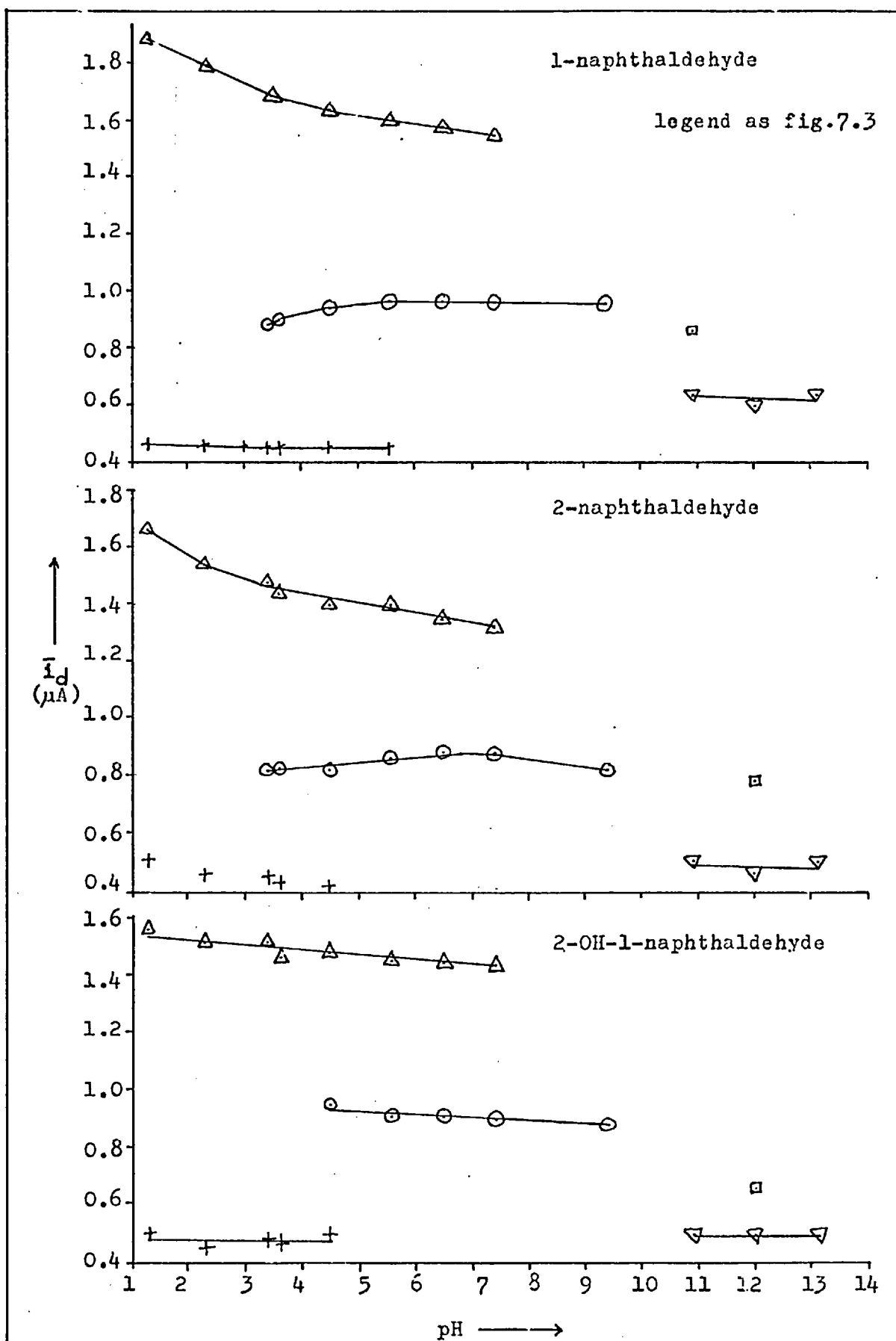
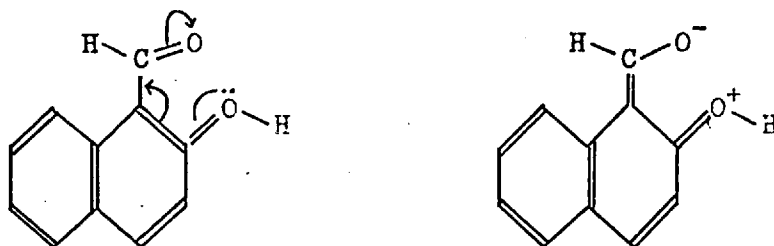


Fig. 7.4 Effect of pH on the polarographic limiting current of the naphthaldehydes.

carbonyl group. The 2-OH-1-naphthaldehyde required higher energy to be reduced and hence a more negative $E_{1/2}$ because of the electron donating (inductive) effect of the hydroxyl group which stabilises the carbonyl group:-



A decrease in the limiting current current of 2% after one hour was observed for both waves of 1-naphthaldehyde over the pH range 3.4 to 9.4. The stability in high pH solutions was difficult to estimate because of the erratic electrode response. The diffusion controlled nature of the two reduction waves of 1-naphthaldehyde at pH 4.5 was confirmed by the linear dependence of the limiting current on the square root of the corrected mercury height. Cyclic voltammetry at a slow DME of 5×10^{-4} M 1-naphthaldehyde in pH 5.6 buffer showed two partially overlapping peaks of the same height at -1.08 and -1.15 V versus SCE when scanned at 200 mV.s^{-1} . No reverse waves were seen. At higher scan rates the peaks were merged. No wave was produced on the reverse sweep even at a scan rate of 10 V.s^{-1} indicating the irreversibility of the reaction. Very little response was observed for a.c. polarography at 50 Hz.

All three of the polarographic waves observed over the pH range studied gave a linear concentration dependence over the range 2×10^{-5} to 10^{-3} M. At high pH the erratic performance of the DME limited the analytical utility.

The semicarbazone derivatives of the naphthaldehydes showed similar behaviour to that reported previously for aliphatic and

other aromatic carbonyl derivatives (237). A well defined, single diffusion controlled wave was produced over the pH range 1.3 to 6.5 as given in fig. 7.5. The half wave potential was several hundred mV less negative than the naphthaldehyde alone. The pH response of $E_{1/2}$ and the limiting current are shown in figs. 7.3 and 7.4. The diffusion current decreases with increasing pH until above pH 8 the derivative was completely dissociated and no wave was observed.

It is known that benzaldehyde semicarbazone undergoes a four electron reduction. Because of the structural similarity between benzaldehyde and naphthaldehyde it was assumed that the reduction mechanism for the semicarbazone derivative of both compounds would be similar. The limiting diffusion current was approximately 50% higher than the total of both naphthaldehyde waves. The derivatives were stable for periods of at least four hours, hydrolysis being prevented by the large excess of semicarbazide hydrochloride present.

A linear dependence of the limiting diffusion on concentration was observed over the range 10^{-5} to 10^{-3} M for the naphthaldehyde semicarbazone derivatives at pH 5.6 in 50% ethanol.

The Girard T derivatives were slow to form under the conditions used. Fig. 7.6 shows the development of the 1-naphthaldehyde derivative at pH 5.6. The $E_{1/2}$ values were less negative than the aldehyde alone but the wave was still double and of similar limiting current to the original compound.

The effect of solvent composition on the polarographic waves of 1-naphthaldehyde and its semicarbazone derivative at pH

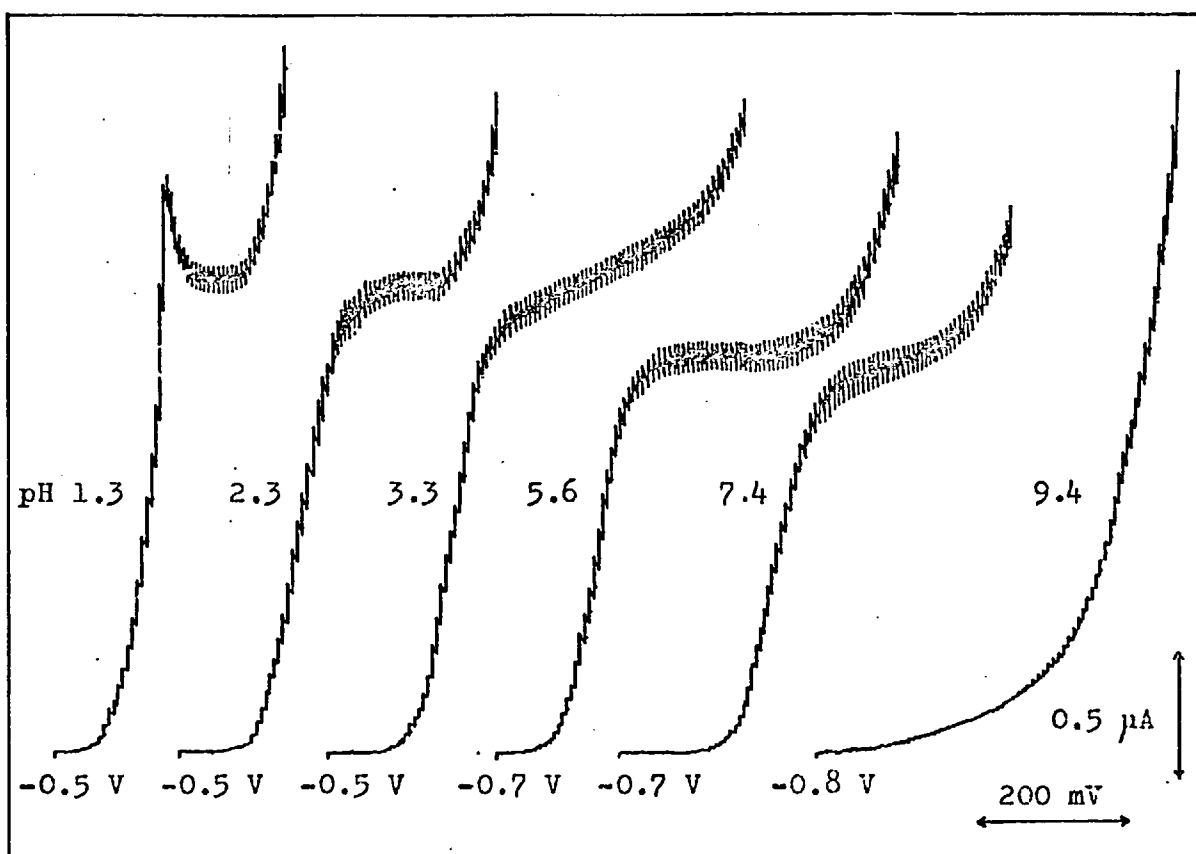


Fig. 7.5. Polarograms of 1-naphthaldehyde semicarbazone over the pH range 1.3 to 9.4.

- a. 10^{-1} M Girard T
- b. a + 10^{-4} M 1-naphthaldehyde, 1 min.
- c. b, 30 min.
- d. b, 100 min.
- e. b, 1020 min.

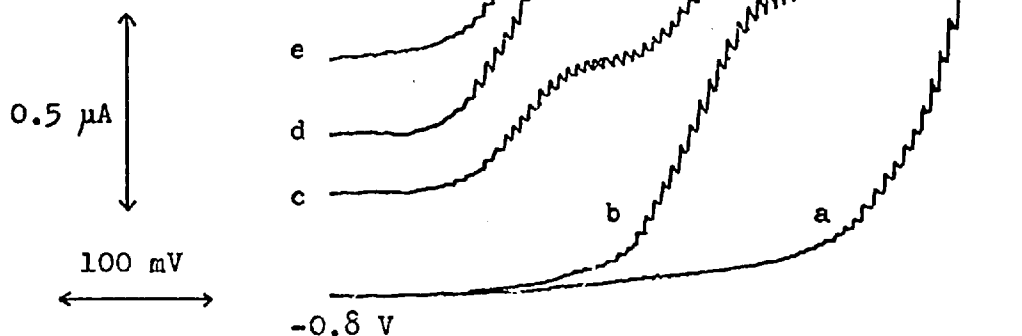


Fig. 7.6. Development of Girard T derivatives at pH 5.6.

4.5 is shown in fig.7.7. As the ethanol concentration was decreased the value of $E_{1/2}$ for each wave became less negative and the wave shape better defined. Table 7.2 gives the dependence of $E_{1/2}$ and the limiting current on solvent composition. Polarography of 1-naphthaldehyde and its semicarbazone derivative was carried out in 50% aqueous solutions of 2-methoxyethanol and 1,2-dimethoxyethane. Similar behaviour to that in ethanol was observed. The two aldehyde reduction waves were not merged in 2-methoxyethanol above pH 6.5. In 1,2-dimethoxyethane the second wave was not seen until above pH 5.6. The waves merged above pH 9 but the wave was not well defined.

The optimum pH range for the determination of the naphthaldehydes in ethanol-water mixtures was found to be 5.6 to 7.4. A pH range of 1.3 to 5.6 was suitable for the formation and determination of the semicarbazone derivatives. The advantages of derivative formation were the production of a single, larger reduction wave at less negative potentials than the double aldehyde reduction wave at an acidic pH.

The 4:1 ratio of reagent to sample in the automated system was chosen as this dilution reduced the residual oxygen concentration within the system and hence the background current to an acceptable value. At pH 5.6 and the solvent composition used the derivative waves were well defined and stable. The twenty turn mixing coil was the shortest that allowed the reaction forming the semicarbazone to proceed to equilibrium.

Considerable smoothing of the fluid flow through the cell was necessary to produce regular electrode drop time and current

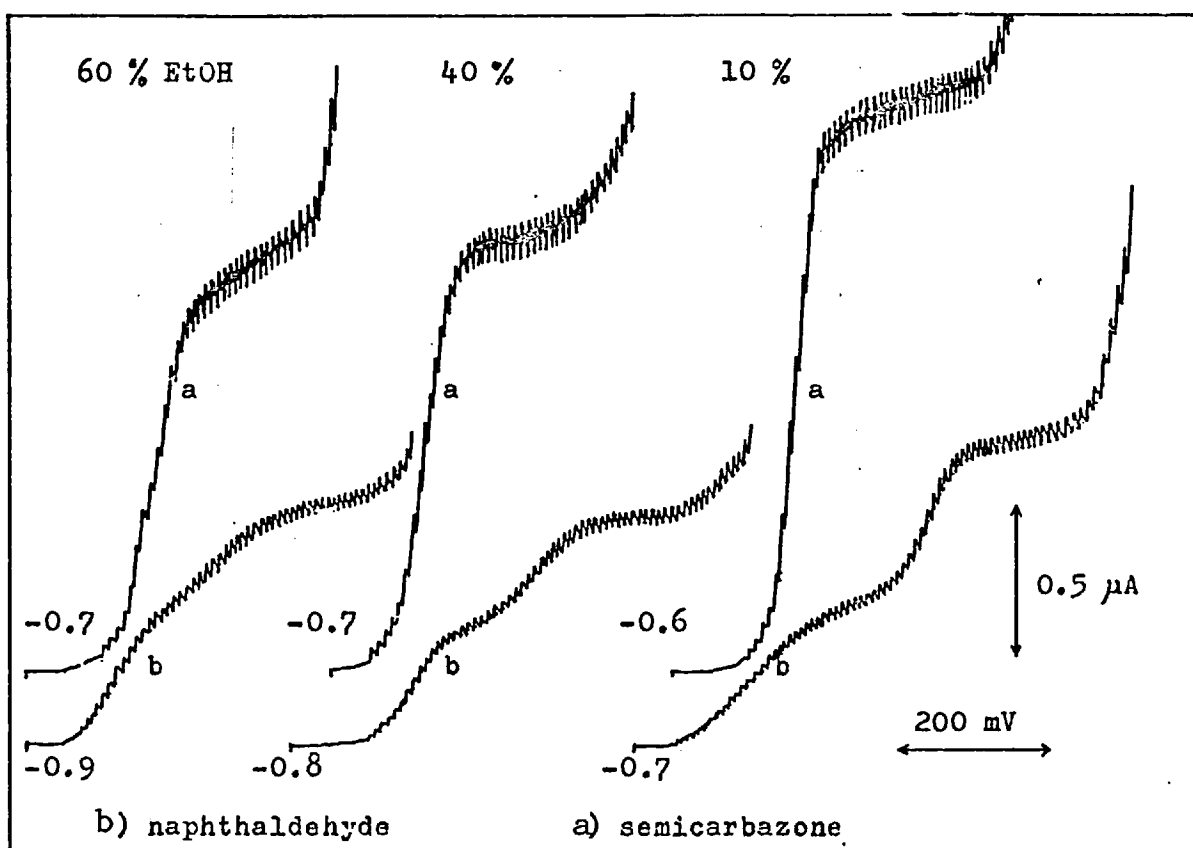
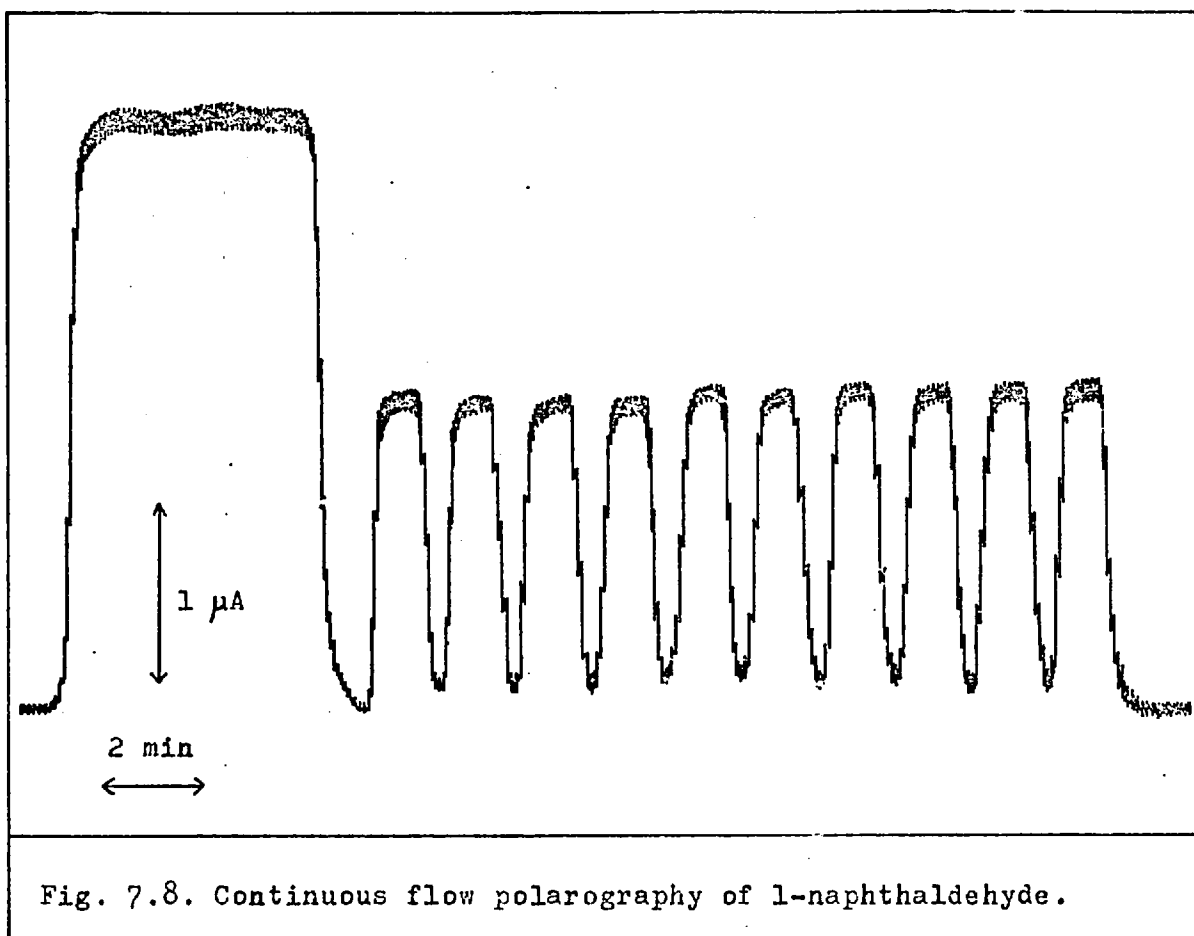


Fig. 7.7. Effect of solvent composition on the polarographic waves of 1-naphthaldehyde and its semicarbazone.

% EtOH	1-naphthaldehyde			Semicarbazone	
	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)	$\bar{i}_d$ (μ A)	$E_{1/2}$ (V)	$\bar{i}_d$ (μ A)
80	-1.05	-1.17	0.96	-	-
60	-1.02	-1.15	0.88	-0.87	1.62
50	-0.99	-1.16	0.92	-0.86	1.62
40	-0.95	-1.12	0.95	-0.85	1.65
20	-0.87	-1.10	1.10	-0.78	1.94
10	-0.87	-1.08	1.20	-0.77	2.20

Table 7.2. Variation of $E_{1/2}$ and $\bar{i}_d$ with solvent composition.



response. 5 cm lengths of 0.15 mm internal diameter tubing in the nitrogen and reagent lines, as indicated in the manifold diagram, considerably reduced pulses from the pump. To increase the smoothing a 'dropper' type of flow restrictor was added to the main pull-through line from the cell. Pulses in the other two tubes contributed only a small part of the overall irregularities in the system.

Fig. 7.8 shows the response of the cell to a continuous aspiration of a solution containing 2×10^{-3} M 1-naphthaldehyde followed by ten samples of 10^{-3} M 1-naphthaldehyde. At this sampling rate well separated peaks were obtained. The coefficient of variation on 40 peaks was 2.5%. Under the conditions used the DME gave good performance and no changes in response were

noticed. No temperature control was used in these experiments although it is known that the temperature coefficient of the diffusion current in polarography is in the range 1.5 to 2.0% per degree. The use of a thermostatted mixing coil at $25 \pm 0.1^\circ\text{C}$, as in chapter 2, gave no improvement in variation. A linear calibration of cell current with concentration was found over the range 5×10^{-5} to 5×10^{-3} M. The response of the system was similar for the three naphthaldehydes and benzaldehyde. Other compounds containing carbonyl groups would be expected to cause serious interference as the method is one of functional group analysis.

7.5 Conclusions

The polarographic behaviour of a range of naphthaldehydes has been studied from which the conditions were chosen so that a single two electron reduction wave was produced which could be used for the analytical determination of this class of compound. The use of semicarbazone derivatives for polarographic analysis has been extended to cover the naphthaldehydes. Under the conditions chosen a single four electron wave was observed which provided a more satisfactory method of analysis in acidic media. The use of a flow cell for polarography in flowing streams has been shown to be feasible for organic compounds in a mixture of water and ethanol as solvent. Reasonable precision was obtained after precautions had been taken to provide a constant solution flow within the cell.

CHAPTER 8: THE DETERMINATION OF CYANIDE BY PULSE POLAROGRAPHY

8.1 Introduction

The toxic nature of hydrogen cyanide (HCN) is well established (242) and there has been considerable public concern over the pollution caused by the disposal of cyanide containing wastes. The World Health Organisation has recommended that water with a cyanide content above 0.01 ppm (4×10^{-7} M) should be considered as unfit for human consumption (243). HCN is particularly toxic to fish if present in a concentration greater than 0.03 ppm. CN^- and heavy metal complexes with CN^- are in themselves non toxic (244).

Cyanide, in industrial waste from metal finishing or plating baths, is often in the form of the potassium salt together with some heavy metals. In the presence of water an equilibrium is set up between HCN, CN^- , H^+ and the cyanide complexes of metals such as zinc, cadmium, copper and nickel. The dissociation constant of HCN is given as 6.17×10^{-10} (245). For a total cyanide concentration of 2×10^{-5} M the following list gives the CN^- concentration at various values of pH.

pH	CN^-	HCN/CN^-
5	1.2×10^{-9} M	1.7×10^4
7	1.2×10^{-7} M	1.7×10^2
9	7.7×10^{-6} M	1.6
11	1.97×10^{-5} M	1.6×10^{-2}

At the pH values of normal water sources HCN predominates over CN^- . The equilibria set up in the presence of complex forming metals have been evaluated by calculation and the validity confirmed experimentally (246). In the case of nickel, the

transition between the predominance of HCN over complex occurs in the pH range 6 to 8 for 10^{-5} M nickel and 4×10^{-5} M total cyanide. Thus a shift in the pH value of an effluent of similar composition would cause a considerable change in the equilibrium and hence its toxicity.

The recommended methods of analysis of sewage and trade effluents for cyanide (247,248,249) are based on the methods of Aldridge (250) and Epstein (251). In these procedures the sample is acidified and distilled, collecting the evolved HCN in an alkaline solution. The CN^- content of the distillate is measured spectrophotometrically after reaction with pyridine-pyrazolone. The decomposition of relatively non toxic ferrocyanide, ferricyanide and thiocyanate during distillation is partially prevented by the addition of lead acetate (247,248). By distilling under reduced pressure in the presence of zinc acetate the decomposition can be completely prevented (244). Alternatively, if the total cyanide content is required, complex decomposition can be achieved by distillation from a mixture of phosphoric, citric and ethylenediaminetetraacetic acids (252). Montgomery and co-workers have developed a solvent extraction method for HCN (246) in which the proportion of HCN extracted was too small to disturb the HCN/CN^- equilibrium appreciably.

Recent work has concentrated on the development of methods that may be applied directly to the sample. The cyanide responsive $\text{AgI}/\text{Ag}_2\text{S}$ membrane electrode can be used for potentiometric measurements in oxidising and coloured solutions. In direct determination of CN^- activities as little as 5×10^{-5} M can

be measured with reasonable precision. The limit of detection can be lowered to 5×10^{-6} M by using the Gran's plot technique (253). Another approach has been to use a silver responsive electrode, add a small, known amount of either silver nitrate or potassium argentocyanide and monitor the equilibrium activity of the silver ion (254). This gives a detection limit of 2×10^{-5} M. The solubility of the silver iodide, used in the cyanide selective membrane, theoretically suggests a limit of 10^{-7} M for direct CN^- determination but in practice this is not achieved because of interferences and adsorption processes on the electrode surface. The electrodes are used at pH 12 to 13 to measure total cyanide activity in solution. Cations forming stable, soluble cyano complexes stronger than $\text{Hg}(\text{CN})_2$ interfere with the determination unless a masking agent such as EDTA or CDTA is employed. The electrodes are not sufficiently sensitive to be of use for direct monitoring of water unless a preliminary concentration such as distillation is used (255).

Galvanic methods for the determination of CN^- in alkaline electrolytes have been applied to the determination of HCN in air by dissolution in a continuously flowing electrolyte (256).

Polarographic methods for the analysis of CN^- are based on the complex forming anodic reaction:-



$$E_{1/2} = -0.36 \text{ V vs SCE for } 10^{-3} \text{ M } \text{CN}^- \text{ in } 10^{-1} \text{ M KOH.}$$

n varies between 2 and 4 depending on pH and CN^- concentration. However, d.c. polarography is not sufficiently sensitive for analysis below 4×10^{-5} M and interference is caused by other

species which are oxidised at similar potentials such as S^{2-} .

It was decided to investigate the possible determination of CN^- by normal and differential pulse polarography. The high sensitivity and selectivity of these techniques suggested that they might be of use for the analysis of natural water samples.

8.2 The pulse polarographic determination of CN^-

8.2.1 Experimental

8.2.1.1 Apparatus

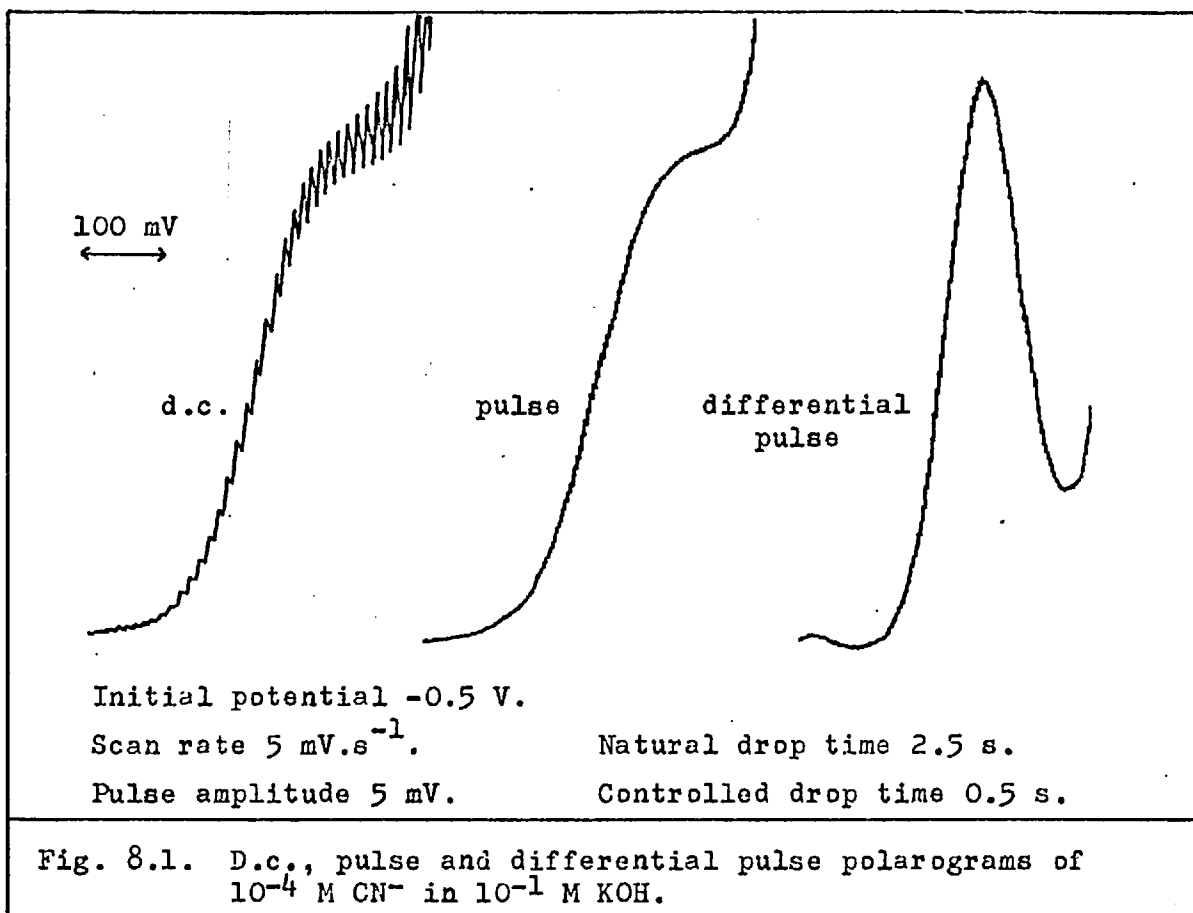
Polarograms were recorded using a PAR 174 polarograph and a Brians model 2200 XY recorder. Cell 5, described in chapter 2, was used without the magnetic stirrer. A DME with the capillary constant, measured at the potential of the SCE in 10^{-1} M KCl, $m = 1.85 \pm 0.05 \text{ mg.s}^{-1}$ at $h = 60 \text{ cm}$ was fitted in a mechanical drop knocker, PAR 172, and the drop time set to 0.5 s. The cell was immersed in a water bath regulated at $25 \pm 0.1^\circ \text{C}$.

8.2.1.2 Reagents

All reagents used were of analytical reagent grade except for the sodium sulphite which was of general reagent grade (BDH). Water was distilled from Pyrex glass apparatus and deionised before use. A stock solution of 10^{-2} M KCN in 10^{-1} M KOH was prepared and diluted for use as required.

8.2.1.3 Procedure

10 ml of electrolyte solution were added to the polarographic cell and deoxygenated with a stream of nitrogen for 5 minutes. The required volume of standard potassium cyanide solution was added, using intermediate dilutions as required. Mixing was achieved by passing the nitrogen stream for a few seconds. A



nitrogen atmosphere was maintained above the solution whilst measuring the polarograms from -0.5 to +0.1 V. Unless otherwise stated the scan rate was 2 mV.s^{-1} with a pulse amplitude of 25 mV.

8.2.2 Results and discussion

Fig. 8.1 shows d.c., pulse and differential pulse polarograms of 10^{-4} M CN^- in 10^{-1} M KOH . Removal of oxygen from the solutions was essential. Resolution of the CN^- wave from that of the OH^- of the supporting electrolyte by normal pulse polarography was similar to that achieved by d.c. polarography. The peak nature of the differential pulse response gave much better resolution than the latter methods and was used in subsequent work.

Fig. 8.2 shows differential pulse polarograms of 10^{-4} M CN^- in a range of electrolytes. The peak parameters for these are

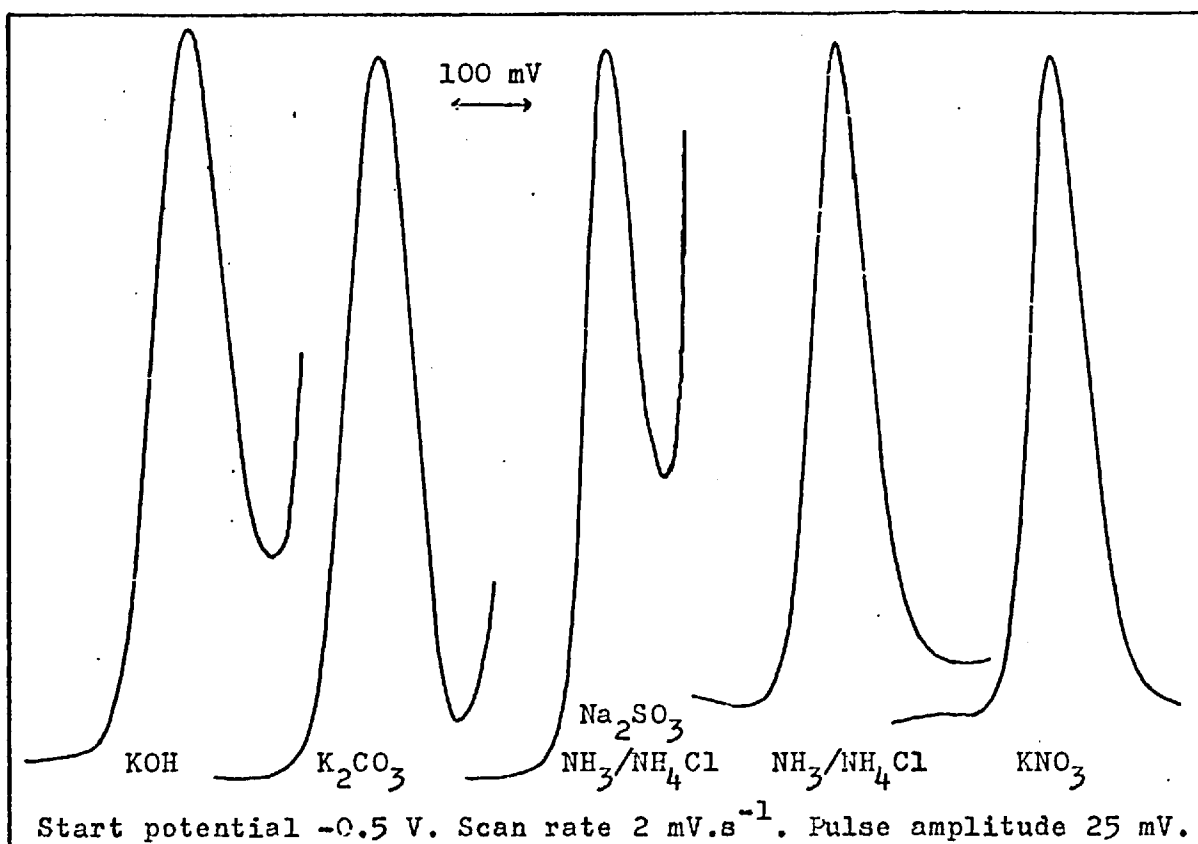


Fig. 8.2. Differential pulse polarograms of 10^{-4} M CN^- in a range of electrolytes.

Electrolyte	E_p (V)	i_p (μA)	$E_{1/2}$ (mV)
10^{-1} M KOH	-0.28	1.10	105
$10^{-1} \text{ M } K_2CO_3$	-0.29	1.10	95
$10^{-1} \text{ M } Na_2SO_3, NH_4OH$ and NH_4Cl	-0.29	1.12	80
$10^{-1} \text{ M } NH_4OH$ and NH_4Cl	-0.30	1.00	90
$10^{-1} \text{ M } KNO_3$	-0.29	1.02	80

Table 8.1. Peak parameters for CN^- in a range of electrolytes.

given in table 8.1. In KNO_3 and KCl electrolytes the peak was well defined and separated from the electrolyte oxidation wave. However, the polarograms were not stable. By passing nitrogen through the solutions for 5 minutes the peak current was reduced to 50% of its original value. A solution left in the cell for 2 hours with nitrogen passing over the surface showed approximately a 15% decrease in peak current. In both cases addition of 1 M KOH to bring the concentration to 10^{-2} M failed to restore the peak current to its original value. It was presumed that the HCN had been removed by the nitrogen. As the pH increased in 10^{-2} M K_2CO_3 and KOH electrolytes the CN^- peak became less separated from the electrolyte oxidation wave. This was because the potential at which OH^- reacts at the DME shifts by -59 mV for a decade increase in OH^- concentration (7). As SO_3^{2-} is oxidised at less positive potentials than OH^- more interference was found with this electrolyte than KOH . The CN^- peak in these electrolytes was stable on passing nitrogen through the solutions for 5 minutes.

The effect of variations in scan rate, drop time and pulse amplitude on the CN^- peak parameters are given in table 8.2. The peak current was proportional to pulse amplitude over the range 5 to 25 mV decreasing from proportionality above this. Above 25 mV the peak broadened. Variations in scan rate caused no change until a rate of above 10 mV.s^{-1} was used. The peak width reached a minimum limiting level below 2 mV.s^{-1} . The peak current increased with increasing drop time without any increase in peak width.

The effect of varying the KOH electrolyte concentration is

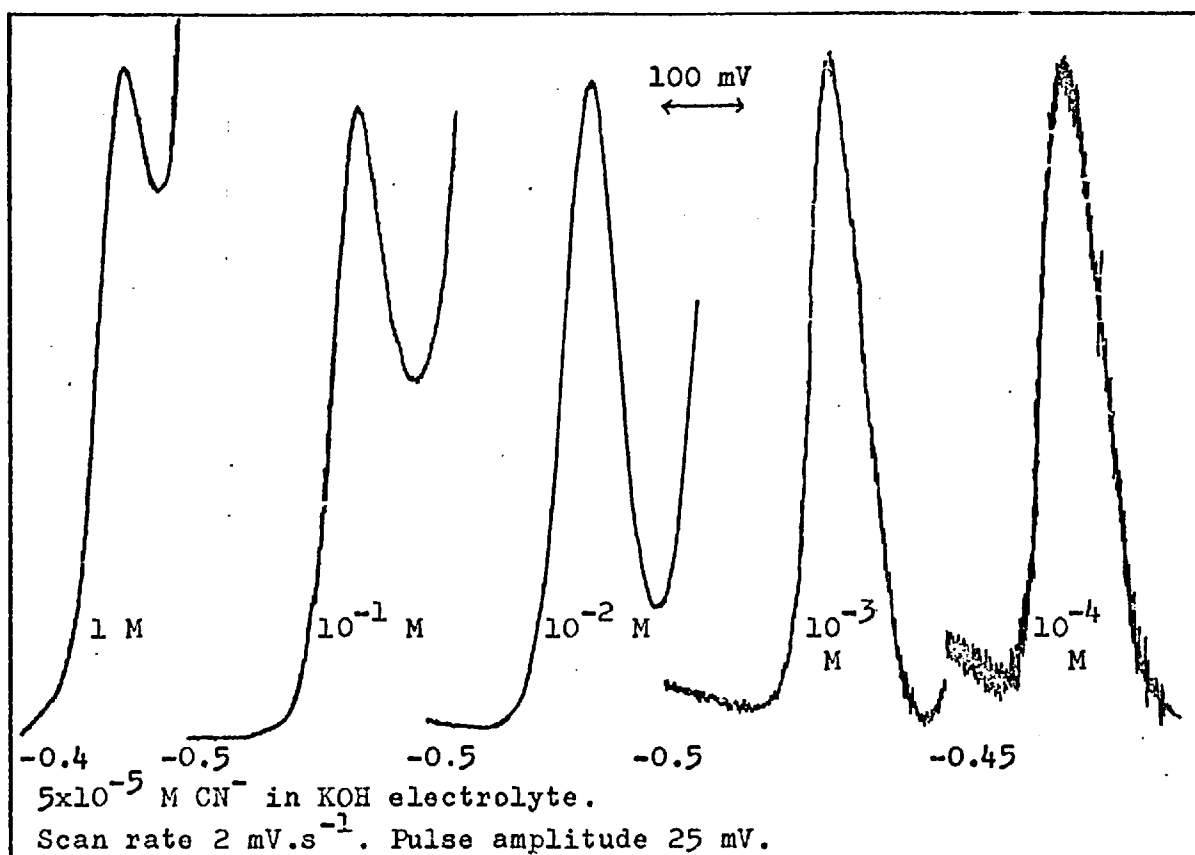


Fig. 8.3. Effect of variation in the electrolyte concentration.

Scan rate (mV.s^{-1})	Drop time (s)	Pulse amplitude (mV)	E_p (V)	i_p (μA)	$P_{1/2}$ (mV)
1	0.5	5	-0.27	0.24	105
2	0.5	5	-0.28	0.23	105
5	0.5	5	-0.27	0.24	120
10	0.5	5	-0.25	0.23	130
20	0.5	5	-0.23	0.22	-
2	1.0	5	-0.27	0.34	100
2	2.0	5	-0.27	0.43	105
2	0.5	10	-0.28	0.45	100
2	0.5	25	-0.28	1.10	105
2	0.5	50	-0.29	1.80	120
2	0.5	100	-0.32	2.80	-

Table 8.2. Effect of variations in scan rate, drop time and pulse amplitude on the peak parameters of CN^- .

shown in fig. 8.3. By using a 10^{-2} M concentration of supporting electrolyte the interference of the OH^- oxidation was reduced but lower concentrations produced noisy baselines.

In all the electrolytes investigated a linear dependence of peak current on concentration was found. The peak potential shifted in a positive direction with decreasing CN^- concentration which limited the minimum concentrations that could be measured. In 10^{-1} M KNO_3 the CN^- peak was present for concentrations of 5×10^{-7} M and above if the CN^- solution added to the electrolyte did not contain KOH. In 10^{-2} M KOH the lowest measurable concentration was 2×10^{-6} M and in 10^{-2} M Na_2SO_3 this was increased to 10^{-5} M. Heyrovský and Kuta (7) have derived an equation for the shift in $E_{1/2}$ with concentration for an anion forming complexes with mercury. The general form of this equation for a complex with n ligands of anion X is:-

$$E_{1/2} = E_{\text{Hg}}^{2+} + \frac{RT}{2F} \ln \frac{2^{n-1} K}{n[X]^{n-1}} \quad \text{where } K = \text{constant.}$$

At a neutral pH and 10^{-3} M KCN then n is equal to 2 but at a higher pH or CN^- concentration complexes with n equal to 3 and 4 are present. Thus the shift in $E_{1/2}$ would be 29, 58 or 87 mV per decade change in concentration. The shift of E_p was variable and in the region of 30 to 50 mV for the electrolytes studied.

Other anions known to give anodic polarographic waves over a potential range which might interfere with cyanide are S^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , I^- and to a lesser extent OH^- , Br^- , EDTA, CNS^- and $\text{Fe}(\text{CN})_6^{4-}$. The % effect on the peak current of 10^{-4} M CN^- in 10^{-2} M KOH caused by the addition of 10^{-4} , 10^{-2} and 10^{-1} M of some of these ions is given in table 8.3. S^{2-} caused a

	% interference		
Anion concentration (M)	10^{-4}	10^{-2}	10^{-1}
Anion			
S^{2-}	-20	-60	-
$S_2O_3^{2-}$	+5	+70	-
SO_3^{2-}	0	0	+5
I^-	0	+1	+6
Br^-	0	0	+3
CNS^-	0	0	0

Table 8.3. Interferences of some common anions on the peak current of 10^{-4} M CN^- in 10^{-2} M KOH.

considerable interference with the CN^- peak, obliterating it completely above 10^{-2} M. The $E_{1/2}$ of the reactions of all these anions at the DME shifts towards negative potentials with increasing concentration. Thus, although only $S_2O_3^{2-}$ interfered at 10^{-4} M, at higher concentrations SO_3^{2-} , I^- and to a small extent Br^- interfered. The interference caused by metal ions which form complexes with CN^- was not studied.

The recovery of CN^- added to tap water, made alkaline by the addition of 4 gm of KOH per litre was close to 100% for 2×10^{-5} and 10^{-4} M CN^- .

Although the differential pulse technique is inherently very sensitive the limiting factor in the analysis of CN^- was the interference caused by the reaction of the electrolyte.

Thus for analysis of CN^- in natural waters at the 0.01 ppm level a preliminary concentration step such as distillation is still necessary.

8.3 Continuous analysis of CN^- by pulse polarography

8.3.1 Experimental

8.3.1.1 Reagents

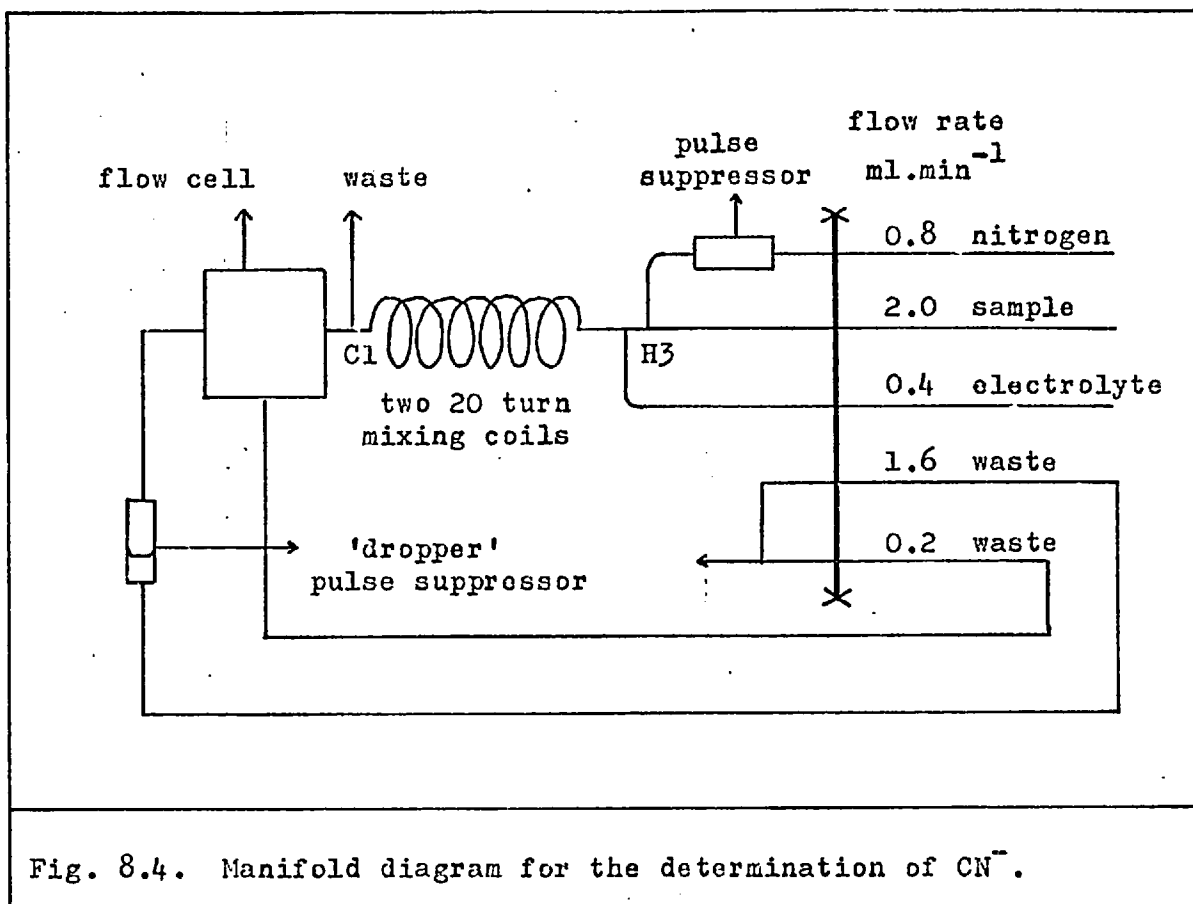
The electrolyte was 0.5 M Na_2SO_3 , 0.5 M NH_4OH and 0.5 M NH_4Cl . All other reagents were as in section 8.2.1.1.

8.3.1.2 Apparatus

The PAR 174 polarograph was used in the normal pulse mode. The output was recorded on a Smiths Servoscribe recorder. The polarographic flow cell described in chapter 7 was used with the DME and mechanical drop knocker described in section 8.2.1.2. The AutoAnalyzer modules used consisted of a sampler, proportioning pump and associated tubing and glass fittings. Temperature control was provided by immersing the mixing and delay coils in a water bath thermostatted at 25°C. The manifold diagram is given in fig. 8.4. The samples were presented at a rate of 60 per hour with a sample:wash ratio of 2:1.

8.3.1.3 Procedure

The sample stream was segmented and the electrolyte added. The stream was mixed in two 20 turn coils to give time for the reaction removing oxygen to take place. The DME potential was set to the desired potential (e.g. -0.3 V for the 10^{-5} to 10^{-4} M concentration range) and a pulse of 25 mV applied. The drop time was 0.5 s.



8.3.2 Results and discussion

The electrode potential was set at the peak potential found by differential pulse polarography for the concentration range to be measured. Figs. 8.5 and 8.6 show the recorder output for a series of samples and a calibration curve for solutions of CN⁻ in distilled water. The deviation of the calibration curve from linearity can be explained by the shift in $E_{1/2}$ with concentration. The method was more sensitive than the method described in section 8.2. This is because it involves measuring the change in current due to the CN⁻ at a single potential whereas in the differential pulse method it was difficult to separate the overlapping peaks of CN⁻ and electrolyte. Providing that the temperature and electrolyte concentration were kept

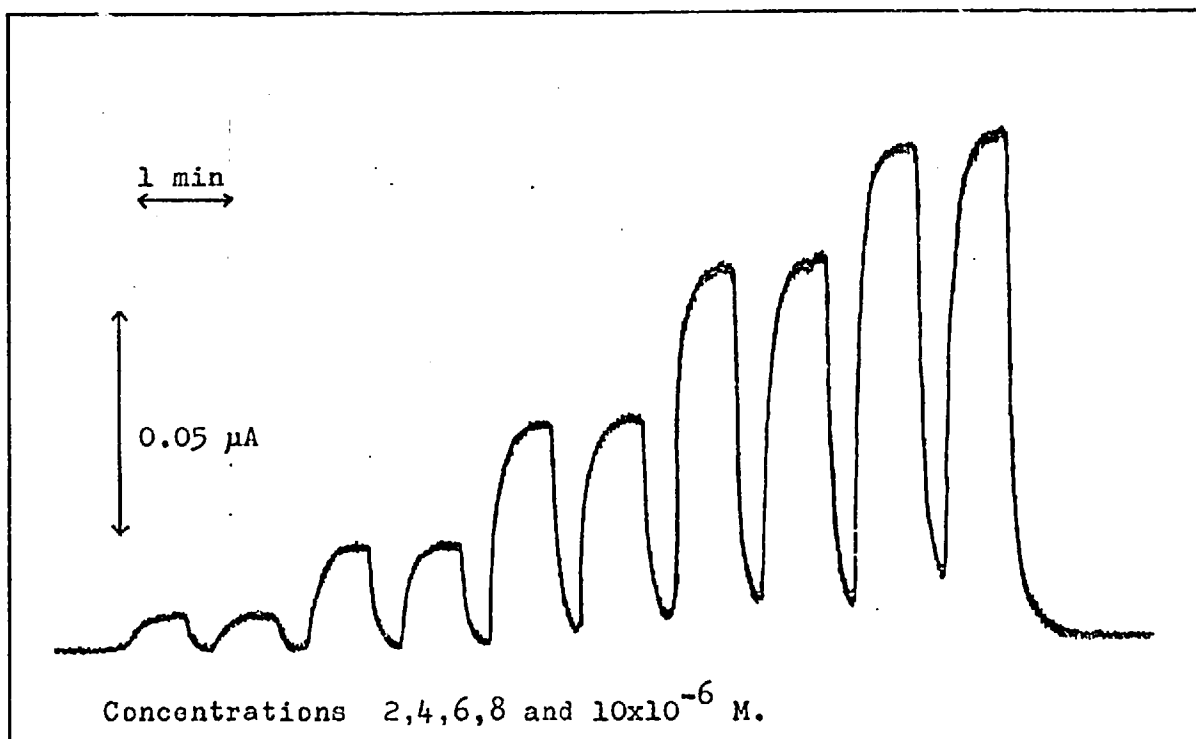


Fig. 8.5. Continuous flow pulse polarography of CN^- .

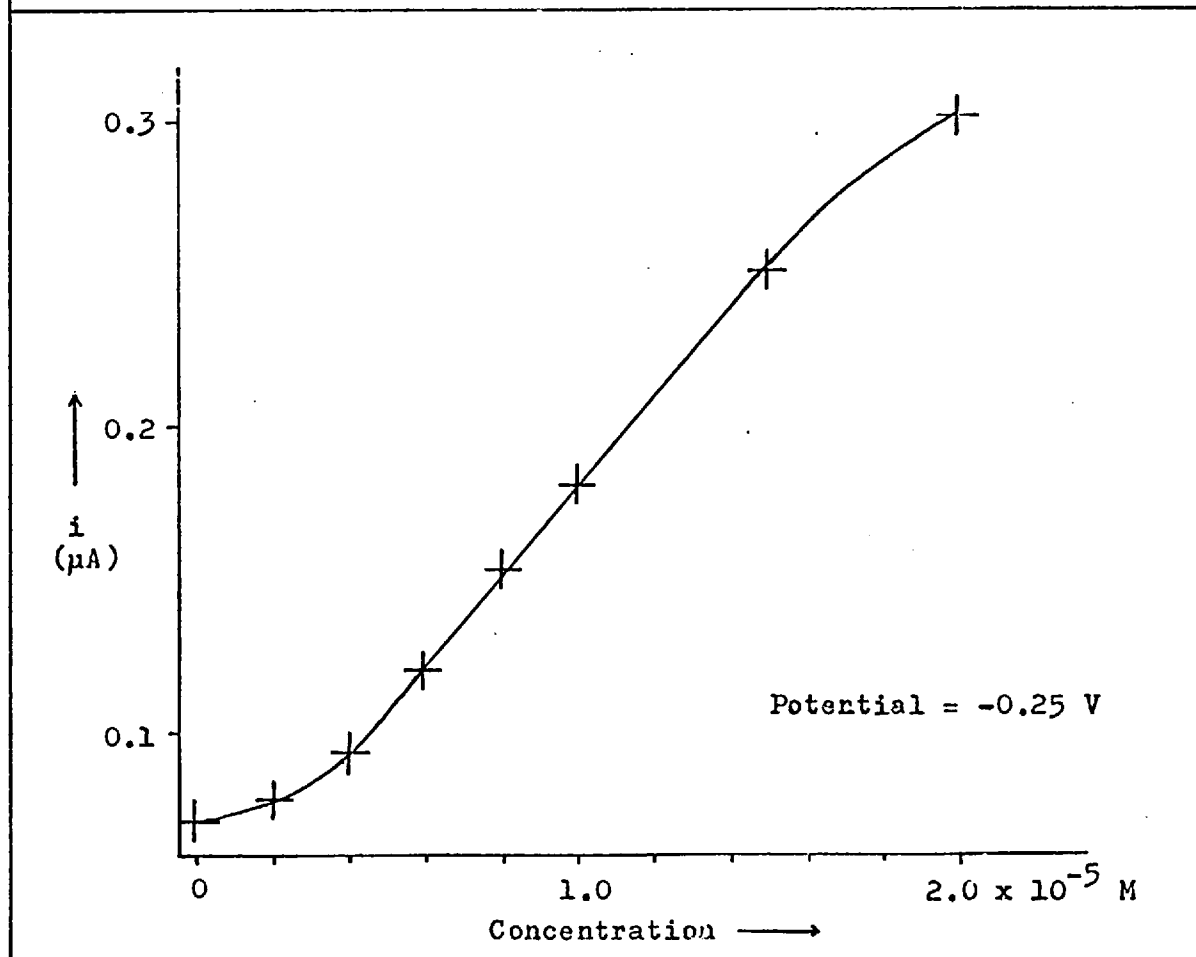


Fig. 8.6. Calibration graph for the determination of CN^- by continuous flow pulse polarography.

constant the background current was also constant and could be compensated for electronically. Capacitive damping was used to reduce the instrument switching pulses which occurred at 0.5 s intervals. The within batch reproducibility was estimated from 10 measurements of the peak current and was $\pm 1.5\%$ at 10^{-4} M and $\pm 3\%$ at 10^{-5} M.

The Na_2SO_3 electrolyte was used in preference to KOH as it enabled faster sampling rates than would have been possible using the modification for deoxygenation of the sample. It would have been necessary to make the sample alkaline before deoxygenation to prevent loss of HCN. The effect of interferences on 10^{-4} M CN^- by this method was similar to the derivative pulse method.

8.3.3 Conclusions

The system presented here was suitable for the determination of CN^- over the concentration range 10^{-6} to 10^{-4} M at the rate of 60 samples per hour. Considerable interference was caused by S^{2-} and changes in the concentration of the electrolyte. The method was not sufficiently sensitive for the determination of CN^- in drinking water at the levels recommended by the World Health Organisation. However the method could be used to provide rapid analysis of specimens after concentration by distillation.

Although this chapter has been concerned with the analysis of CN^- the method is applicable to other cations and anions.

APPENDIX COMPONENTS

Amplifiers

A ₁	PF85AU	Philbrick	Nexus
A ₂	141A	Analogue	Devices
A ₃	PF85AU	Philbrick	Nexus
A ₄	PF85AU	"	"
A ₅	PF85AU	"	"
A ₆	141A	Analogue	Devices
A ₇	141A	"	"
A ₈	141A	"	"

Capacitors

C ₁	100pF, silver mica
C ₂	0.002μF, paper
C ₃	500pF, silver mica
C ₄	2.08μF, polyester
C ₅	1μF, polyester
C ₆	50μF, electrolytic
C ₇	0.001μF, paper
C ₈	1μF, polyester
C ₉	1μF, polyester
C ₁₀	100pF, silver mica
C ₁₁	100pF, silver mica
C ₁₂	100pF, silver mica

Switches

S ₁	2 pole, 6 way
S ₂	3 pole, 4 way
S ₃	3 pole, 4 way
S ₄	2 pole, 6 way
S ₅	2 pole, 6 way
S ₆	1 pole, toggle
S ₇	1 pole, 12 way
S ₈	2 pole, 6 way

Resistors

R ₁	100K, 2% ½W oxide
R ₂	100K " " "
R ₃	100K " " "
R ₄	100K " " "
R ₅	1M, 5% carbon
R ₆	1M " " "
R ₇	10M " " "
R ₈	1M " " "
R ₉	100K, 2% ½W oxide
R ₁₀	10K " " "
R ₁₁	1K " " "
R ₁₂	1K, ten turn
R ₁₃	15K, 2% ½W oxide
R ₁₄	15K " " "
R ₁₅	50K, pot

Resistors (cont)

R ₁₆	6.5K, 5% carbon
R ₁₇	1K, ten turn
R ₁₈	50K, pot
R ₁₉	20M, 10% carbon
R ₂₀	750Ω, 1% "
R ₂₁	10Ω, 1% "
R ₂₂	2M, 5% "
R ₂₃	1M, 5% "
R ₂₄	500K, 2% ½W oxide
R ₂₅	200K " " "
R ₂₆	100K " " "
R ₂₇	50K " " "
R ₂₈	100Ω, 10% carbon
R ₂₉	50K, pot
R ₃₀	1K, 2% ½W oxide
R ₃₁	5K " " "
R ₃₂	10K " " "
R ₃₃	50K " " "
R ₃₄	150K " " "
R ₃₅	1K " " "
R ₃₆	10K " " "
R ₃₇	100K " " "
R ₃₈	1M, 5% carbon
R ₃₉	10M, 10% "
R ₄₀	50K, pot
R ₄₁	1K, ten turn
R ₄₂	10K, 2% ½W oxide
R ₄₃	10K " " "
R ₄₄	10K " " "
R ₄₅	10K " " "
R ₄₆	10K " " "
R ₄₇	10K " " "
R ₄₈	10K " " "
R ₄₉	10K " " "
R ₅₀	10K " " "
R ₅₁	20K " " "
R ₅₂	20K " " "
R ₅₃	20K " " "
R ₅₄	20K " " "

Diodes

D ₁	1N914
D ₂	1N914
D ₃	1N914
D ₄	1N914
D ₅	1N914
D ₆	1N914
D ₇	1N914
D ₈	1N914

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