1.1 Fundamentals of voltammetry

Whenever a reduction or oxidation reaction occurs at an electrode, electrons are transferred between the reactant species and the electrode. This produces a measurable current, and the more reactions (i.e. the greater concentration of reactive species), the greater the current. Hence, the measurement of currents produced by electrochemical processes involving the analyte can be used to determine concentrations.

Voltammetry is a special form of electroanalysis in which an electrical current is measured as a function of applied potential. The magnitude of the current is related to the concentration of oxidisable or reducible species in solution.

Let's consider what happens to a reducible metal ion (M^+), for example, in a solution with a pair of electrodes. The indicator electrode in this case will be a source of electrons, hence negatively charged. The reaction is shown in Equation 1.1.

$$M^+ + e \leftrightarrow M_{(s)} \hspace{5cm} Eqn\ 1.1$$

This reaction will only occur if both the following conditions apply:

* the ion is close enough to the electrode
* the voltage applied at the electrode is enough to allow the reaction to occur (the reduction potential)

Let's assume for the moment that some ions will always be close to the electrode by sheer chance. This leaves the voltage as the controlling factor for whether reaction will occur. Figure 1.1 depicts what happens to the current as we change the voltage.
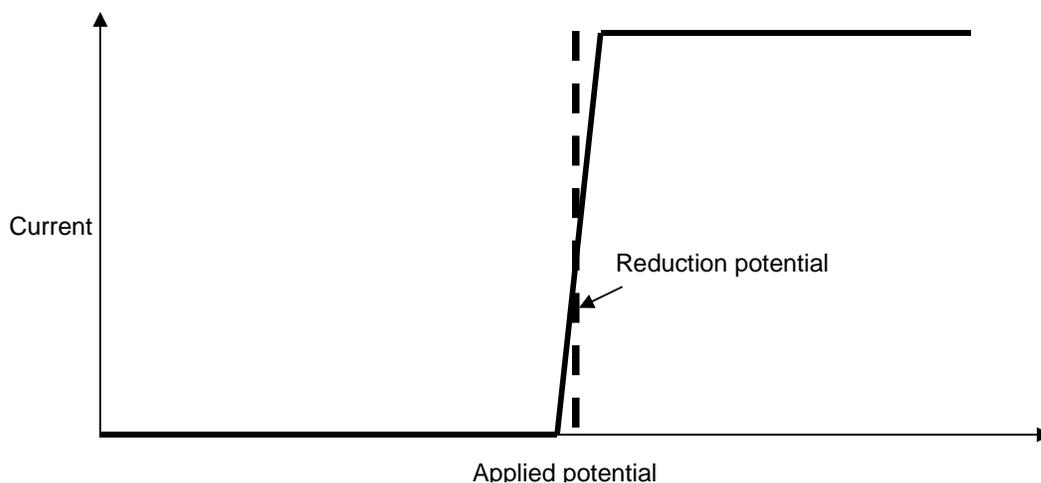
Initial potential Too low, so no reaction can occur	As potential approaches redn V, some ions react	As potential pass redn V, all ions near electrode react	After redn V, ions newly arrived near electrode react
Current is zero		Current is high	Current is high and constant
	Current is low and		

FIGURE 1.1 *Electrode reactions and current as a function of voltage*

So we produce a measurable change in current as a consequence of a voltage change: this is known as a **wave** and the whole scan a **voltammogram**.

CLASS EXERCISE 1.1

It is possible to make an analogy between spectroscopy and voltammetry, even though the measurements are very different. Complete the table below which links the two techniques.

Spectroscopy term	*Voltammetry term*
Peak	
Wavelength/frequency	
Intensity	

The voltammogram produces information useful for both quantitative and qualitative analysis:
- the wave position (voltage) is characteristic of a particular species
- the wave height (current) is proportional to concentration

Ionic movement

Ions in solution move for a number of reasons::
- diffusion (simple random motion),
- electrostatic attraction, and
- convection

It turns out that the current generated at the electrode when the reduction potential is reached is only linearly proportional to concentration, if diffusion is the only mechanism for the ions reaching the electrode. Since we usually like a linear response, we need to minimise the other two processes as much as possible.

Obviously, **not stirring the solution** during the scan and maintenance of a constant temperature should control convection. However, it is not possible to prevent electrostatic attraction between the positive ions and the negative electrode, but it can be reduced greatly by the addition of a high concentration of non-reactive ions, known as the **supporting electrolyte**. This is most commonly KCl or KNO_3 at concentrations around 0.1 M. The very high level of other ions essentially prevents the analyte ions from feeling any attraction to the electrode as shown in Figure 1.2.
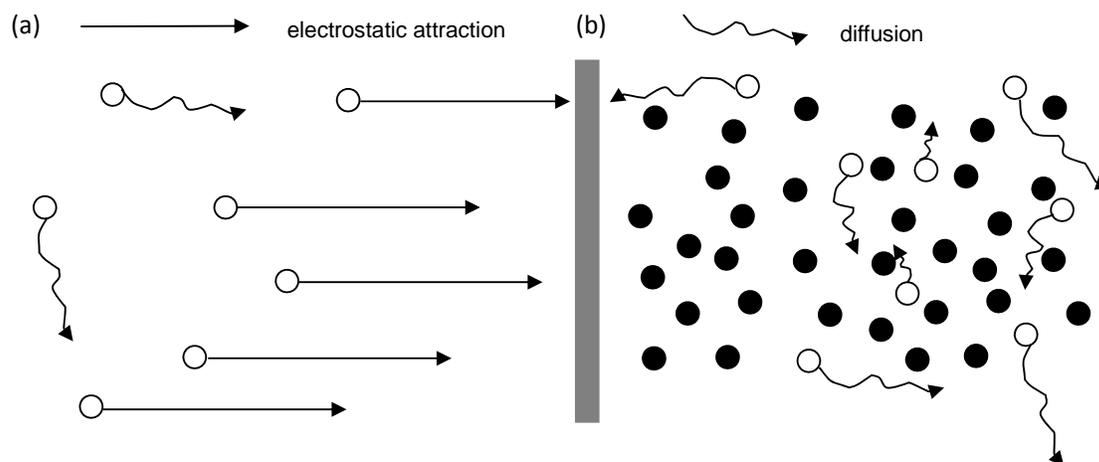

FIGURE 1.2 *Ionic transport processes (a) without and (b) with supporting electrolyte (white circles are analyte, black circles supporting electrolyte)*

The supporting electrolyte has two other functions:
- it will mask matrix interference due to different levels of background ions in different samples, because it makes the major part of the matrix in all solutions the same
- it ensures that the solution will have enough electrical conductivity to make measurements possible

One feature of voltammetry is that it only ever uses up a tiny fraction of the reducible species in the sample, under the valid assumption that the volume of the solution around the electrode is representative of the whole. This means the process is very rapid at any given voltage, and **multiple scans can be run on the one sample without changing its overall concentration**.

1.2 Polarography

Polarography is the most commonly used form of voltammetry, where one of the electrodes is made from a capillary of mercury, forming a drop at the end. This is known as a **dropping mercury electrode (DME)**. In polarography, the analysis depends on plotting a curve called a **polarogram**. The polarographic cell current produced during electrolysis is measured at various applied voltages, and a voltage vs current curve recorded, as shown in Figure 1.3.
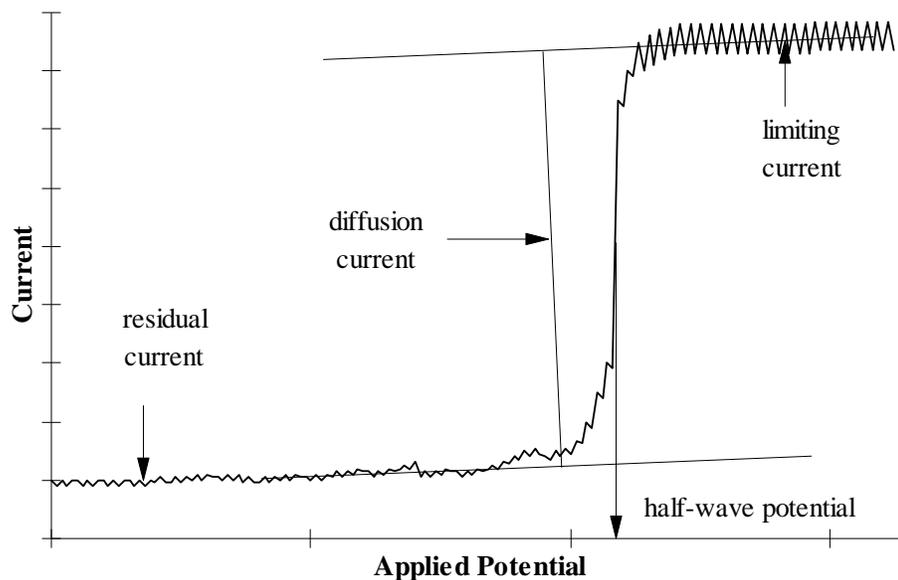

FIGURE 1.3 *A typical polarogram*

Features of the polarogram
- *residual current* – the small current before the potential at which the analyte reacts, caused by reactive species in the matrix and by the mercury drop behaving like a capacitor
- *limiting current* – the maximum current reached
- *diffusion current* – the difference between the limiting and residual, and proportional to the concentration of analyte
- *half-wave potential* – the potential half-way up the polarographic wave, which is similar to the reduction/oxidation potential, and characteristic of the species; see Table 1.1
- *current oscillations* – caused by the mercury drop which repeatedly falls off and is replenished from the capillary

TABLE 1.1 *Half-wave potentials for some common analytes*

Species	E½ (V)
Cu^{2+}	+0.04
Pb^{2+}	-0.40
Cd^{2+}	-0.64
Zn^{2+}	-1.00
Vitamin C	+0.1

CLASS EXERCISE 1.2

Measure the (a) half-wave potential and (b) diffusion current for the polarogram in Figure 1.3, given the following scale divisions.

Applied potential: each scale division is equal to 0.5 V, becoming more negative from 0 V

Current: each scale division is equal to 1 uA starting from 0.

1.3 Polarographic equipment

The equipment to record a polarogram is relatively simple:
- a cell to hold the solution
- electrodes to allow the electrochemical processes
- controller to apply the voltage to the electrodes and measure the current
- output device (screen and/or chart recorder) to produce a record of the polarogram

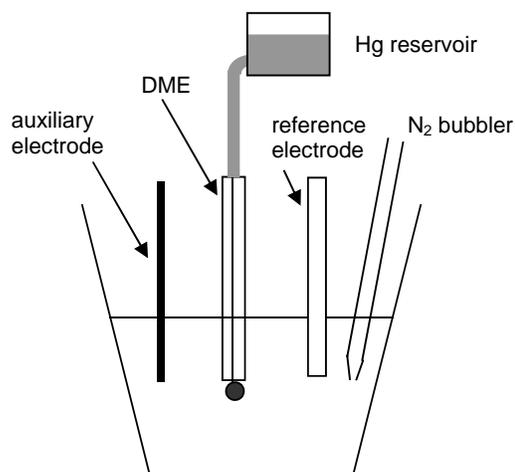A typical polarographic cell with electrodes is shown in Figure 1.4.

FIGURE 1.4 *Typical polarographic cell and electrodes*

Polarographic cell components

1. *Dropping mercury electrode* – the electrode at which the analyte reaction occurs; the drop rate is adjusted by a 'knocker', which taps the DME at a specified rate, knocking the drop off and ensuring a constant drop rate
2. *Reference electrode* – as you have met before, an electrode which maintains a constant voltage regardless of the solution and reactions occurring; usually the saturated calomel electrode (SCE)
3. *Auxiliary electrode* – provides a path through which current can flow and be measured; current and voltage cannot be measured in the same part of the circuit, so there are two circuits as shown in Figure 1.5; usually a platinum wire
4. *Nitrogen bubbler* – oxygen is the major interference in all aqueous solutions, because it produces two visible polarographic waves, at around –0.1 and –0.9 V (relative to SCE); bubbling nitrogen through the solution for 5 minutes removes the oxygen
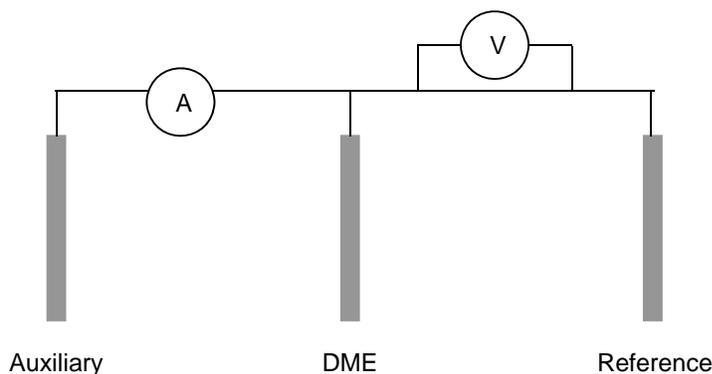

Auxiliary   DME   Reference

FIGURE 1.5 *Electrodes and circuits in polarographic cell*

Why use such a strange electrode?

The DME does not seem like the most obvious choice for an electrode. The DME has one significant advantage over solid metal electrodes such as platinum: **it presents a fresh surface to the solution every second or so**. This allows a much more reproducible control of potential than a fixed electrode, where the reduced metal (for example) becomes coated to it.

However, mercury is not a noble metal, and cannot be used in circumstances where oxidising potentials greater than about +0.4 V are required, since the mercury will be oxidised itself. In this case, a platinum or glassy carbon (graphite) working electrode must be used.

Matrix effects

The presence of complexing agents in a sample will affect the reduction of the analyte, in particular the half-wave potential. In the most extreme case, the analyte peak may completely disappear from the polarogram. For example, wine samples with known measurable concentrations of lead will not show a peak at all until the organic matrix is destroyed.

The DME has a **working voltage range of +0.4 to –1.8V**. If the reduction potential of the analyte is more positive than the oxidation potential of mercury (+0.4 V), then the mercury drop will be oxidised and not the analyte. In these cases, the DME is replaced by a Pt or graphite electrode. At potentials more negative than –1.8V, the water is reduced to hydrogen gas. Non-aqueous polarography is possible, but not very reliable.

1.3 Improvements on the polarographic process

The basic problems with the DC polarogram as it appears in Figure 1.3 are:

- *limited sensitivity* – DC polarography is limited to about 5 mg/L for most species
- *difficulty in measurement* – due to the waveform shape and the oscillations

Ideally, we would like to improve the former and get rid of the latter. This has in fact happened, through three evolutions of the technique, by changing the way that:

- the voltage changes
- the current is measured

In DC polarography, the voltage is continuously changed throughout the scan, and the current output is continuously measured.

Change 1 – Removing the oscillations

The most obvious problem is the oscillations, due to the current changes when the drop falls and a new one begins to grow. So the first change in polarographic measurement was to "digitise" the current measurement, so that a single measure per drop was taken. The measurement is timed at just before the drop falls off, as shown in Figure 1.6.
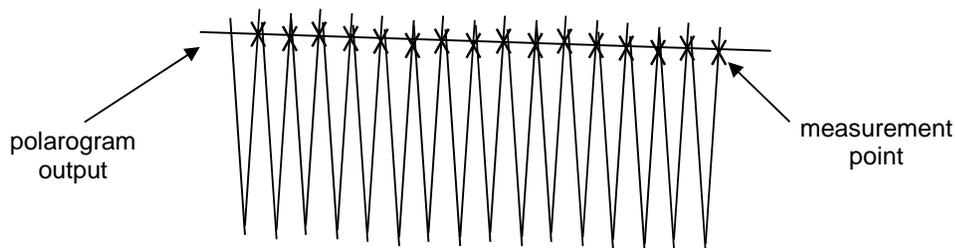

FIGURE 1.6 *Current measurement in sampled DC polarography*

The current measurement needs to be at a constant point in the drop cycle, so the only way this can be achieved is by knocking the drop off mechanically rather than allowing gravity to take effect. Typically the drop rate is once per second.

So this removes the oscillations, giving a smooth waveform, and the sensitivity (about 2 mg/L) is slightly improved, simply because it is easier to measure small diffusion currents at low concentrations without the "noise".

Change 2 – Improving sensitivity

The main reason that sensitivity is limited in these first two forms of polarography is the relatively high level of background current being detected at the DME, because it "hides" analyte response.

The matrix causes some background current – other species reacting – but once oxygen is removed, there isn't much more that can be done. However, there are two non-matrix causes of background current that can be dealt with.

The first is the **voltage changes** during the scan (and that's what the scan is, after all) cause a "charging" of the drop, meaning that it is continually receiving current that has nothing to do with species reacting at it. Only when the voltage stops changing does this charging current fade away.

What's the solution? We can't not change the voltage because then we wouldn't have a scan. However, instead of the voltage changing continuously, it is increased in a set of steps (or pulses) as shown in Figure 1.7. By ensuring that the current measurement is made just before the next pulse occurs, the amount of charging current will be at a minimum.
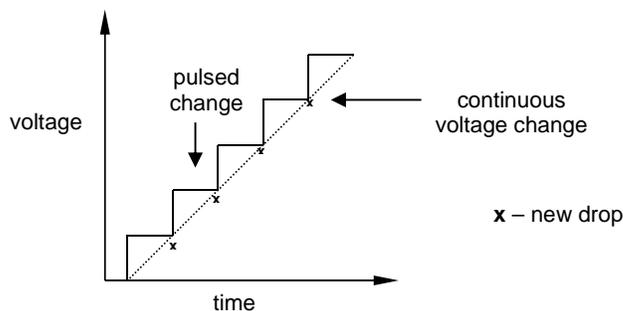
FIGURE 1.7 *Voltage changes in pulse polarography*

The other cause of background current is due to the **mercury drop** as it grows in size. Again, there is nothing that can be done to stop the drop growing, so the answer lies in the observation that the drop-growth current is greatest at the start of the drop cycle, when the drop is expanding more rapidly. Therefore, the "measure the current at the end of the drop cycle" approach which was already par tof the voltage pulse solution works perfectly here as well.

By using voltage pulses and measuring current just before the drop is knocked off, an improvement in sensitivity of roughly 10 times is achieved.

Change 3 – Changing the shape

The pulse solution described above still gives us a waveform shape, and even in its smooth form, it is not an ideal shape to make a quantitative measurement. One more step brings us to the current state of polarography which is known as **differential pulse**.

In pulse polarography, the background current is reduced but not eliminated. In differential pulse polarography, another mechanism is added. **Two current measurements** are made in each drop cycle:

- an initial current measurement before the voltage pulse, which acts as a sort of "reference" measurement, and
- after the main voltage surge at the end of the drop, which measures background current and diffusion current

The difference between the two readings is used, and gives a **peak**, rather than a wave. The sensitivity is improved two-fold on pulsed polarography.

1.4 Anodic stripping voltammetry (ASV)

A single polarographic scan only analyses a very small fraction of the solution. This is convenient because it means that the same solution can be re-analysed many times and used for standard addition. However, the measurement of current caused by diffusion of a small proportion of the analyte means that the sensitivity is limited.

The only way to reduce most or all of the analyte in the sample volume is to do it with stirring and over an extended period of time (up to 30 minutes). This is obviously not practical for a scan, because we are introducing non-diffusion current with the stirring and making the process too lengthy to be useful.

The problem is the relatively large volume of solution, from which all the ions have to be removed. This can't be solved by simply using a smaller sample aliquot: the electrodes do have to be covered after all.

Stripping voltammetry addresses these problems by:

- introducing a concentration step, which reduces all the metal ions in solution onto the electrode, and
- the voltage scan oxidises them back out again (the stripping part), as shown in Equations 1.2a and 1.2b.

Concentration $\qquad M^+ + e \Rightarrow M_{(electrode)}$ $\qquad\qquad\qquad\qquad$ *Eqn 1.2a*

Stripping $\qquad\qquad M_{(electrode)} \Rightarrow M^+ + e$ $\qquad\qquad\qquad\qquad$ *Eqn 1.2b*

The concentration step is done:

- at a fixed potential beyond the reduction potential of the most negative analyte,
- with stirring
- for at least 90 seconds

Even with this modification, not all the analyte will be reduced. Therefore, sensitivity can be increased by increasing the time given to the concentration step. Under normal circumstances, the technique achieves satisfactory results at 1 ng/L, which makes it one of the most sensitive techniques commonly available.

Species suitable for analysis by this method are limited to those which form an amalgam with mercury when reduced to the metallic form. These include copper, lead, cadmium, zinc, indium and bismuth.

CLASS EXERCISE 1.4

(a) Can you see a problem with using a DME for this analysis?

(b) What could be done to get around this problem, still using a mercury drop as the electrode?

1.5 Applications of voltammetry

Voltammetry is a somewhat under-utilised technique, given some of its advantages, which include:

- *sensitivity* – realistic detection limits for differential pulse polarography are around 50 ug/L and below 1 ug/L for ASV,
- *multi-component analysis* – provided the half-wave potentials are at least 100 mV apart,
- *equipment that is relatively simple and not particularly expensive* – typically $40,000 for a computer-controlled device capable of polarography and voltammetry,
- *a wide range of analytes* - metallic ions, non-metallic ions and organic species.

However, there are a number of disadvantages, which in some cases, outweigh the benefits, including:

- *contaminated mercury* – which can be purified by distillation with special apparatus,
- *relatively slow* – due to purging time
- *matrix interference* – due to complex formation, which can make a species not analysable because the half-wave potential is outside the measurable range

Polarography lends itself to the analysis of environmental samples for a range of significant metals, and to the analysis of low levels of alloying elements, such as copper in steel. Pre-treatment steps may be needed to remove interferences. Metals usually analysable by polarography include Cu, Zn, Cd, Pb, Ni, Fe, Sn and Co.

The food and pharmaceutical industries use polarography to analyse organic species, such as vitamin C, DDT and morphine. pH effects are considerable in polarography of organic compounds, because the great majority of redox reactions involving organic species also involve H^+ in the reaction. Various functional groups, such as OH, C=O, S-S, N=N and NO_2, are reduced or oxidised in the polarographic range.

Finally, perhaps the most significant use of voltammetry is in an electrode which measures dissolved oxygen (DO). The DO probe is not an ion-selective electrode since it relies on current, not potential, measurement. Here the oxygen is not an interference to be removed, but the analyte. Rather than scanning, the potential inside the probe is held at -0.8V, and the current is considered to be proportional to the oxygen concentration. It is similar to potentiometric gas-sensing electrodes in that a gas-permeable membrane separates the sensing electrodes from the sample. It is calibrated using a saturated solution (9 mg/L at 25°C)

What You Need To Be Able To Do

- define important terminology
- briefly describe the analytical measurement involved in voltammetry
- explain how polarography differs from voltammetry
- describe the function of equipment used in polarography and ASV
- draw a typical polarogram and identify its components
- describe and explain the need for the various pre-treatment steps in polarography
- outline how quantitative analysis is performed using polarography
- explain the changes in polarographic scan modes
- explain why ASV increases sensitivity
- outline the measurement process in ASV
- list advantages and disadvantages of each technique

Revision Questions

1. Give TWO ways that the polarogram of the solution giving the scan in Figure 1.3 would differ if the scan was run in differential pulse mode.

2. Why are three electrodes necessary for polarography?

3. What advantages does the mercury drop electrode have over alternative working electrodes?

4. You need to analyse river water for cadmium.
   (a) What needs to be added to the sample before recording its polarogram?
   (b) List the steps involved in recording the polarogram.

5. Which of the following would cause the polarogram of a 10 mg/L lead solution to give a flat line?
   (a) no initial purge
   (b) mercury electrode not dropping
   (c) wrong voltage range
   (d) scan too slow
   (e) scan too fast
   (f) no electrolyte
   (g) presence of complexing agents

6. What is the main advantage of ASV compared to differential pulse polarography?

Answer guide on following page

Answer guide

1.   It would be a peak, not a wave.

       It would be 10-20 times higher.

2.   Two circuits needed, one for current the other for voltage, since they can't be measured in the same circuit at the same time; DME common to both circuits.

3.   It provides a continuously fresh surface for the electrode, which would otherwise become electroplated and change its behaviour.

4.   (a) Add KCl to about 0.1 M.

       (b) Purge with nitrogen for 5 minutes, turn the purge off, set the Hg electrode dropping, adjust voltage to -0.4V, scan to to -0.8 V

5.   (b) (c) (f) (g)

6.   Greater sensitivity.