EMT 518:   METHODS IN ENVIROMENTAL ANALYSIS III (2 UNITS)

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SYNOPSIS

Electro-analytical method: Potentiometry, Reference electrode – Calomel, Ag/Agcl, indicator electrodes – 1st, 2nd and 3rd order, Metal Electrodes, membrane electrodes – glass electrode, types of liquid junction potential, solid state electrode, potentiometric titration, end point location in potentiometric titration –visual, plot of E/V, plot of derivative curves 1st and 2nd electrogravimetry, fixed potential, constant current, constant cathode potential coulometry: constant current coulometry, coulometric titration. Voltammetry: classical polarography, Description of dropping mercury electrode, condition for polarographic determination, qualitative and quantitative analysis conductance methods: description of limiting ionic conductance, conductance cell, conductomertic titration. Thermal methods: Thermogravimetry, differential thermal analysis (DTA)

LECTURE CONTENT

POTENTIOMETRY

Is a measurement of a given chemical species in an equilibrium system by the use of an electrode, while potentiometric titration is the technique that is used for following the changes in the concentration of chemical species as function of added titrant using an electrode. In both cases a cell is needed and a cell consists of the following:

- (1) Reference electrode (2) Liquid junction (3) Analyte solution
- (4) indicator electrode. It is also possible to have a cell without liquid junction.

REFERENCE ELECTRODE.
In carrying out a potentiometric determination the half cell potential of one electrode must be known which should be constant, reproducible and completely insensitive to the reference electrode and must be fully polarised throughout the duration of the measurement i.e the potential of the reference electrode does not change through the whole measurement.


A classical example of reference electrode is the calomel electrode.

The potential of this cell varies with chloride concentration and as such the chloride concentration must be specified in describing the electrode. The calomel electrode is most commonly used due to the ease of preparation and because of its large temp range.

INDICATOR ELECTRODE.
There are two types of indicator electrodes

(i)   Metallic indicator and (ii) Membrane indicator

(ii)   Metallic indicator electrode: Metals that are capable of reversible half reaction can be used as indicator electrode. The potentials of these metals have direct effect on the activities of the ions in solution. Metals that have been used as indicator electrode include Ag, Cd, Cu, Hg and Pb.

$Cd = Cd^{2+} + 2e^-$
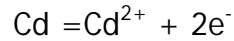
Metallic indicator electrode can either be of the 1st or 2nd order type.

For the 1st order type a metal dips into a solution of its ion and measuring the concentration of its own ion. E.g Zn dipping into Zn^{2+} solution measuring Zn^{2+}. However, some metals such as Ni, Co, Cr, Fe and W (tungsten) tends to give non reproducible potential due to formation of strains or crystal deformation in their lattice structure or as a result of oxide coating on their surface. Such metals cannot form useful indicator electrode. Therefore, when an electrode potential is directly dependent upon an ion in the electrode process it is referred to as 1st order indicator electrode. Whereas when an electrode measures the concentration of an ion not directly involved in the electrode transfer process then a 2nd order electrode result. Examples of these are metal electrodes which are also indirectly sensitive to anion that form slightly soluble precipitate with the cathode. It is usually necessary to saturate the solution with the sparingly soluble salt. A good example of 2nd order electrode is the Ag/AgCl electrode.

Half cell   AgCl saturated KCl//Ag
Half equation AgCl(s) + e------ Ag(s) + Cl-

In 2nd order indicator electrode, the ion being measured is not directly involved in the electrode transfer process. In most cases it is a metal together with its insoluble salt measuring the anion of the insoluble salt e.g Ag/IAgCl measuring Cl
Hg/HgSO$_4$ measuring SO_4^{2-}

Nerst equation gives the relation between electrode potential and chloride concentration.
$E = E^o$ Ag/AgCl $-2{,}303RT/nF$ log (Cl-)
$E = 0.22 - 0.0591$ log (Cl-)

Through this electrode is 2nd order electrode it can also be used as a lst order electrode to measurement the concentration of silver ion (Ag^+).

$Ksp = [Ag^+] [Cl-]$

Substituting into the equation

$E = E^o$ Ag/AgCl $- 2.303RT/nF$ log Ksp/Ag^+)
$E = E^o$ Ag/AgCl $- 2.303RT/nF$ log Ksp $- 2.303RT/nF$ logAg^+
$E\ E' + 0.0591$ log (Ag^+)

It is also possible to have 3rd order electrode in which the material controlling the potentials does not appear in the electronic equation. A good example of this is the redox electrode. This is made up of an inert metal dipping into a solution containing a chemical element in two different oxidation states.

The platinum wire helps in transferring electron in and out of the system, this does not appear in the electronic (equation), and in order to measure the potential of one of the oxidation state, then the other must be held constant, also the equilibrium does not change unless a reducing or oxidizing agent is added.

MEMBRANE INDICATOR ELECTRODE

For membrane electrode the half cell is represented by analyte/membrane/internal reference solution. The membrane act as a barrier between the analyte and internal reference solution and dipping inside the internal solution is an internal reference electrode. The internal reference electrode is performing the same function as an inert metal in the redox electrode. All these (membrane/internal reference solution) constitute what is referred to as indicator electrode (half cell). To complete the cell, a salt bridge is in contact with the analyte solution and depending on the nature of the electrode and the membrane. the following types of membrane electrode are recognised:

   (1) Glass membrane electrode
   (2) Liquid ion exchange electrode
   (3) Solid state or precipitate membrane electrode
   (4) Enzyme substrate membrane electrode.

GLASS MEMBRANE ELECTRODE

Glass membrane electrodes are available in the form of K^+, Ag^+, Na^+ Li^+ and H^+. The most popular one is the H^+ sensitive membrane electrode. In all cases the membrane is glass about 0.03 – 0.1mm in thickness, however, the composition of glass membrane vary from one type to another.
For example, the following composition.

The internal reference solution in all case must have the ion of interest usually in 0.1M and the counter ion for the positive ion is usually Cl- with an internal reference electrode of Ag/AgCl.

The most important advantage of glass electrode is that it can be used without interference in solution containing strong oxidant, reductant or proton. However, glass electrode for monitoring pH can be affected by the following:

   (1) Alkaline error: being sensitive to alkali metal at pH greater than 9.

(2) Acid Error: at pH less than zero, values obtained are abnormally too high.

(3) Error may normally occur as a result of dehydration of the electrode, this may cause unstable performance.

(4) Error in pH of buffer solution: any error or inaccuracy in preparation or change in composition of the buffer during storage will be reflected as error in pH measured.

SOURCE OF POTENTIAL IN GLASS MEMBRANE ELECTRODE

The internal reference solution contains the ion specie to be measured with this electrode and its concentration is fixed, so also is the activities fixed (a_2), also note that the potential of the internal reference solution is fixed and not affected by the surrounding.

$$E_{obs} = E_{int} + E_{ex} + E_{lj} + E_{membrane}$$

The potential due to the membrane is a function of the activity of the analyte solution. A glass membrane is usually soaked in water or slightly acidic solution before being used. During the period of soaking, it adsorbes moisture as shown below.

The water molecules enters the first few molecular layer of the glass and it is only on the surface layer of the glass that this phenomenon occur. This is a surface effect not exceeding more than 0.03 mm on both sides. Glass itself is made up of silicate; therefore, this reaction can take place.

$$Na^+ GL^- + H^+ \text{-------------} H^+ GL^- + Na^+$$
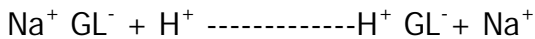
This reaction takes place to a small extent and depends on the availability of hydrogen ion. At the surface of the gel all fixed singly charged sites are occupied by H^+ and from the surface to the interior of the gel, there is a continuous increase in the number of H^+ and a corresponding decrease in the number of Na^+, however, since the field intensity of H^+ and Na^+ are not the same, then there is an imbalance when H^+ replaces Na^+ which leads to a distortion thereby inducing a potential difference (electrical potential is generated) this potential is referred to as membrane potential and this is proportional to log a_1/a_2.

LIQUID JUNCTION POTENTIAL

LJP occur due to unequal distribution of cations and anions across the boundary between two electrolyte solutions, the ions move from the more concentrated solution to the less concentrated solution. This movement depends on the mobility of the ions, and in this case that of H+ being greater than that of Cl- thereby the less concentrated solution becomes positively charged while the more concentrated solution becomes negatively charged. The charges formed tend to characterise the frequency in the mobilities of the two ions, thereby setting up equilibrium. A p.d therefore arises from this charge separation, which can be removed by introducing a more concentrated electrolytic solution e.g using Kcl as a salt b ridge which has very little p.ds in it ions mobility.

LIQUID MEMBRANE ELECTRODE

LME measures the p.d across the interface between the solution and an immiscible liquid that selectively binds with the ion being determined. It differs from glass membrane in terms of materials separating the solution with a fixed activity.

Liquid membrane electrode has been used extensively for measuring polyvalent cation, the membrane is a liquid ion exchanger (organic polymer not miscible with H_2O, not volatile with acid, basic or chelating functional group), the liquid is carried inside a plastic or glass which is porous. The nature of the functional group determines the ion to which the membrane is sensitive, for example having a long chain organosulphurous compound is highly sensitive to calcium and zinc ion but the ratio of sensitivity is in favour of calcium ion. Another example is tribenzene ring which is highly sensitive for measuring NO_3^-.

SOLID STATE PRECIPITATE ELECTRODE

There are 2 type (1) having ppt impregnated membrane serving as electrode in which the active ppt is 50% Ag-iodide which is carried by a silicone rubber.

   (2) This is referred to as synthetic single state solid state membrane. It contains lanthanide fluoride which is grown as a large crystal.

For the AgI2 electrode it can exchange both Ag^+ and I^- ions while that containing lanthanide can be used to measure F^- and S^{2-}

ENZYME ELECTRODE

These are electrodes that have enzyme built into them e.g the normal glass electrode can have incorporated into it a membrane containing the enzyme into the electrode e.g in the hydrolysis of area, instead of adding urea, an electrode is dipped inside it just like the normal ion selective electrode substrate membrane. The ammonia produced can give rise to ammonium ion (NH_4^+) since the electrode used is sensitive to NH_4^+. The concentration of the ions can be measured in order to monitor the reaction. This is referred to as an immobilised or insolubilized enzyme (i.e it is fixed).

The enzyme is immobilized in a gel layer which coats a convectional cation-sensitive glass electrode. For the ammonium ion-selective electrode, the enzyme, urease is fixed in a layer of acrylamide gel held in place around the glass electrode bulb by porous nylon netting or a thin cellophane film. The urea acts specifically upon urea in the sample solution to yield ammonium ions which diffuse through the gel layer and are sensed by the electrode.

The resulting potential is proportional to the substrate (urea) concentration in the sample solution. There are thousands of enzyme substrate combinations that would yield products measurable with ion-selective electrode. With some modification, this electrode system can be

reversed, that is, the substrate would surround the glass membrane, resulting in an enzyme sensing electrode.

POTENTIOMETRIC TITRATION

This is a titrimetric procedure in which potentiometric measurement are carried out in order to locate the equivalence point. A potentiometric titration provides different information from that of direct potentiometry. For example direct measurement with pH sensitive electrode gives the H+ concentration of an acid e.g acetic acid, whereas a potentiometric titration of the same solution give the information as to the amount of acetic acid in the sample P.T is useful for titration of coloured or opaque solution. its major disadvantage is that it is time consuming. It involves measurement of indicator potential against a convenient electrode and plotting the change of this potential against a convenient electrode and plotting the change of this potential against volume of titrants. A large potential break will occur at the equivalence point.
Also since only the potential change is required it is therefore, not necessary to know the potential of the indicator electrode.

SCHEMATIC DIAGRAM
Three methods are available for end point determination
(1) By visual inspection: this involve an appraisal of the potentiometer reading and determination of the max p.d. for example from the following results obtained in potentiometric titration of $AgNO_3$ solution against chloride solution. Determine the end point of this titration.

Vol $AgNO_3$	E
5.0	0.062
16.0	0.085
20.0	0.107
22.0	0.123
23.0	0.138
23.5	0.146
23.80	0.161
24.0	0.174
24.1	0.183
24.2	0.194
24.3	0.233
24.4	0.316
24.5	0.340
24.6	0.351
24.7	0.358
25.0	0.373
25.5	0.385
26.0	0.396

28.0   0.426

This means that the max potential difference is located between 24.3 and 24.4, therefore, the end point of this titration can be taken as the average of the two volumes i.e. 24.3 + 24.4/2 = 24.35ml.

(2) Plotting E against volume of titre: this involves a direct plot of potential against titrant volume. The mid- point in the steeply rising potion of the curve is estimated visually and a line is drawn from this point to the x-axis where the end pt is then read off.

(3) Plot of derivative Curves: there are two type of derivative curves, the 1st derivative and 2nd derivative

(a) The first derivative: this involve calculation of a drop in potential per unit change in vol of titrant and plotting against average volume, this gives a sharp max at the end –pt.

Vol	E	$\Delta E/\Delta V$	$V^1 = V_1 + V_2/2$
24.0	0.174	0.009/0.1=0.09	24.05
24.1	0.183	0.011/0.1=0.11	24.15
24.2	0.194	0.039/0.1=0.39	24.25
24.3	0.233	0.083/0.1=0.83	24.35
24.4	0.316	0.024/0.1=0.24	24.45

(b) Second derivative curve: it has been shown that the end-pt value can be estimated accurately by fixing the point where the second derivative of the voltage become zero with respect to volume i.e $\Delta^2 E/\Delta V^2$, values of $\Delta^2 E/\Delta V^2$ are calculated by subtracting corresponding data for $\Delta E/\Delta V$.

$\Delta^2 E/\Delta V^2$	$V^{11}2$
0.11-0.09	24.05+24.15/2=
0.39-011	24.15+24.25/2=
0.83-0.39	24.25+24.35/2=
0.24-0.83	24.35+24.35/2=

ELECROGRAVIMETRY

In general, electro analytical methods are based on the principle of electrochemistry i.e chemical reaction in which one or more electrons are transferred from one specie to another, such method include potentiometry, electrodeposition, electrolysis, coulometry and voltammetry.

Electro gravimetric the oldest electro analytical technique which involves deposition of a metal at an electrode of an electrolysis cell and weighing the deposit. Conditions are controlled so as to produce a uniformly smooth and adherent deposit in as short a time as possible.

The simple electrochemical cell has been referred to as spontaneous or internal electrolysis in this case an electro-gravimetric analysis can be accomplished within a short circuited galvanic cell e.g Cu^{2+} ions in solution will quantitatively deposit on a platinum cathode when an external contact is made with Zn anode immersed in a solution of Zn ions.

If this rxn is allowed to proceed to equilibrium, substantially all the copper (ii) ion are recovered from solution. Internal electrolysis is more selective than ordinary electrolysis without cathode potential control and through adequate choice of anode system, the co-deposition of many elements can be eliminated. The problem of internal electrolysis is that of internal resistance of the cell, if this is too high (if the connecting wire is thick), too long a period is required for completion of the reaction.
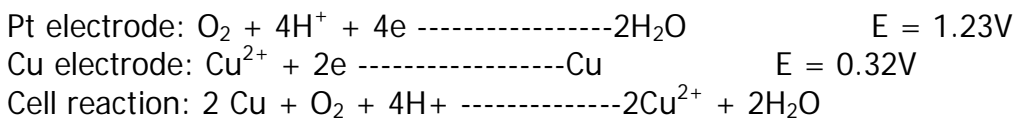
ELECTRO-SEPARATION (ELECTRODEPOSITION)

This depends on principle of electrolysis in which the electrode is serving as the precipitating agent. Consider the internal electrolysis of a galvanic cell, if the cell is now connected to an external battery i.e Eapplied (energy that is introduced into the system), so that the two e.m. fs oppose each other and if Eapplied is greater than the E-cell then the direction of current is reversed, likewise the cell reaction is reversed from the normal spontaneous reaction such that instead of Zn metal going into solution or dissolving, it is then deposited on the electrode surface.

For electrolysis to occur, a certain amount of voltage must be applied and there are certain factors that determine the amount of voltage to be applied before electro-deposition can takes place.

(1) BACK E.M.F: this is the applied potential being equal to the e.m.f arising from the electrochemical series. If an electrochemical cell is now converted to an electrolytic cell a voltage must be applied to the current flow in opposite direction to that of an electrochemical cell. The voltage that is at least equal to that of electrochemical cell is called BACK EMF in the sense that it is acting in opposition to that of ECC.

To determine what voltage must be applied to a cell so that electrolysis can take place, it is necessary to know what reaction occur at the two electrode. With this knowledge, it is then possible to calculate the potential of each electrode and thereby determine the e.m.f of galvanic cell which exerts its potential in opposition to the applied potential. For example, considered the cell

Pt electrode: $O_2 + 4H^+ + 4e$ ------------------$2H_2O$ $E = 1.23V$
Cu electrode: $Cu^{2+} + 2e$ ------------------Cu $E = 0.32V$
Cell reaction: $2 Cu + O_2 + 4H+$ --------------$2Cu^{2+} + 2H_2O$

Given that the concerns are as follows: Cu = 0.1M, O_2 = 0.2atm; H+ = 0.2M

$E_{red/ox} = E0 – 0.059log/n$ 1/reductant
$E_{pt} = 1.23 – 0.059log/1/(O2)(H+) = 1.18$
                    Log $1/(0.2)(0.2)4$
$E_{cu} = E^O – 0.059 log 1/Cu2+$
$E_{cu} = 0.34 -0.59 log 1/0.1 = 0.31$
$E_{cell} = E_{pt} – E_{cu}$
$= 1.18 – 0.31 = 0.87V$

Then compare with 1.23 – 0.34 = 0.89
This shows that, if E – applied is 0.87v the two e.m.fs cancel each other and no current flows but if E-applied exceed 0.87v the cell reaction is reversed and electrolysis of the solution takes place.

(2) **OVER VOLTAGE (OVER POTENTIAL):**   When a current flows across an electrode solution interphase , it is observed that the electrode potential changes from the reversible value it possess before the passage of current. The difference between measured potential and the reversible value is the over potential. At this point the electrodes are said to be polarised.

In anodic over potential the applied potential necessary to cause electrolysis will be a more positive value than that of the calculated voltage while for a cathodic over potential the value is more negative. Various types of over potential may occur because:

(i)   Formation of film of oxide or some other substances on the electrode surface thereby setting up resistance to passage of current across it.
(ii)   Concentration over potential: species at electrode surface are not replaced at a rate equivalent to that required by the current.
(iii)   Gas over potential: this occurs when a gas is produced during electrolysis. The gases usually constitute a resistance to the flow of current.
In all the three case above, the voltage needed to overcome these resistance is called the over voltage.
     IR DROP

This is a voltage due to circuit resistant e.g if passing a current of IA through a cell with a resistance of 0.5Ω, then an additional 0.5 volt must be applied to overcome this voltage (recall that V =IR, therefore 1 x 0.5 = 0.5).

Therefore, for electrodeposition to take place, E applied must be greater than or equal to Ecell + Eover+ E_{IR}. There are three main methods by which electrodeposition can take place:

(1) At constant cell potential
(2) At constant current
(3) At constant cathode potential.

CONSTANT CELL POTENTIAL (Fixed potential/control voltage electrolysis)

Ecell = 0.87V
Eover= 0.85
E_{IR} = 0.5, therefore Eapplied = 2.2V

Therefore, if the cell is operated at a fixed potential of 2.5V, with time there will be a decrease of Cu^{2+} ion concentration due to electro-deposition. This will affect E anode and E cathode i.e when the Cu concentration has been lowered to 10^{-6}M the theoretical cathode potential goes from 0.31V to 0.16V, whereas the value of the anode increase slightly, therefore, the overall back e.m.f increases (approx 1.0V). However, before the Cu concentration diminishes to 10^{-6}M the cathode would have been affected by what is known as concentration polarisation, this occurs as a result of Cu2+ion which can no longer be brought to the electrode surface at a sufficient rate to carry the current because of this the current therefore, drops (i.e current drops very rapidly after a few minutes of operating the electrolysis cell and eventually approaches zero as the electrolysis near completion). This decrease in the electrode potential of the cathode may cause other ions of sufficient lower potential to co-deposit and may also allow the formation of hydrogen gas, therefore, electrolysis at constant cell potential can only be employed to separate easily reduced cations from those which are more difficult to reduce than hydrogen ion. The formation of hydrogen gas can be prevented by the addition of a depolariser, for example NO^-_3 ion which will react according to the equation.

NO^-_3 + 10H+ +6e--------------NH_4^+ + $3H_2O$
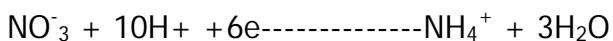
In this case a depolariser is a compd more easily reduced than hydrogen ion but more difficult to reduce than the cation of interest.

CONSTANT CURRENT
This is done by continuously adjusting the applied potential to maintain a constant current. Electrolysis at constant current is similarly affected by concentration polarization.

Since Concentration polarisation causes a decrease in current this effect can be initially off-set by increasing the applied potential, however with time the concentration of Cu become very low and forces of diffusion and electrostatic attraction cannot keep the electrode surface supplied with sufficient Cu^{2+} to maintain the desired current. Therefore, at this point the additional energy (E applied) will cause co-deposition of other reducible species and as such the contribution of Cu^{2+} to the total current become smaller and smaller.

CONSTANT CATHODE POTENTIAL

This involves the measurement of the potential of one of the working electrode (anode or cathode) against a reference electrode such that a potential impressed across the working electrode can then be adjusted to the level that it will impact the desire potential to the cathode. The p.d between the reference and cathode is measured with a potentiometer while the E applied is adjusted throughout the electrolysis by a voltage divided in order to maintain a constant cathode potential.
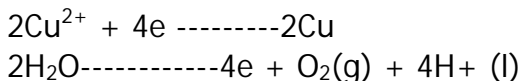
COULOMETRY

This involves measurement of quantity of electricity in coulombs required to convert the analyte to different chemical state. It obeys the first law of electrolysis and as such instead of weighing the electrodes as usually done, the quantity of electricity passed through the cell can be used to calculate the concentration of the analyte. Therefore, for a constant current of I ampere flowing for t(s), the no coulombs (q) is given by Q = It, whereas for a variable current, the number of coulombs is given by $Q=\int Idt$

There are two types of coulometry
   (1) Coulometry at constant electrode potential
   (2) Constant current coulometry

CONSTANT CURRENT COULOMETRY

A constant current is passed through the cell until an indicator signals completion of the rxn. in the case, quantity of electricity is readily measured. The method is also the basis for coulometric titration. A constant current of 1.50A was passed through a solution for 18.5minutes, calculate the grammes of Cu and O_2 deposited at the cathode and anode respectively, given cell reactions as follows.
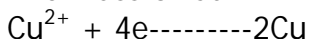
$2Cu^{2+}$ + 4e ---------2Cu
$2H_2O$------------4e + O_2(g) + 4H+ (l)

Solution
Q = It
= 1.50 x 18.5 x 60
= 1665C

From the equation
The mass of Cu
$Cu^{2+} + 4e$ ---------$2Cu$
$4F = 2\,Cu$
$2F = 1$mole of Cu
$Ic = 64/2 \times 96500$
$:1665C = 64/2 \times 96500 \times 1665 = 0.552_g$

Mass of oxygen.
$4F = 32g$ of $O2$
$Ic = 32/4F = 32/4 \times 9650$
$:1665C = 32/4 \times 9650 \times 1665$
$=0.14g$

In general, for coulometry method i.e constant current coulometry there must be 100% current efficiency i.e each faraday of electricity must bring about a chemical change corresponding to one equivalent of the analyte, however it is possible that some specie can take part in a reaction that is secondary to the electrode reaction. A good example of this is the oxidation of $Fe^{2}+$ at a Pt electrode. As the rxn proceeds the initial concentration of Fe^{2+} decreases, the anode potential rises and as such decomposition of water takes palce.

Fe^{2+} ----------Fe^{3+} $+e$
$2H_2O$ ----------$O_2 + 4H+ 4e$
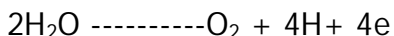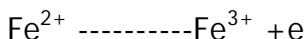
Therefore the current required to complete oxidation of Fe^{2+} to Fe^{3+} will then exceed that demanded by theory, this error can be avoided by addition of Ce3+ at the beginning of the rxn, with this Ce^{3+} is oxidized to Ce^{4+} at a lower anode potential than water. Therefore preventing the oxidation of water and as such a current efficiency, in that the Ce^{4+} produced then react with Fe^{2+} and although only a fraction of Fe^{2} is oxidized, a 100% current efficiency would have been obtained.

Ce^{3+} -----------Ce^{4+} $+e$
$Ce^{4+} + Fe^{3+}$---------$Ce^{3+} + Fe^{3+}$
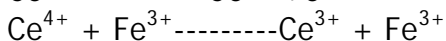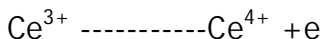
COULOMETRY TITRATION
This involves the electrolytic insitu generation of a reagent which then reacts with analyte. The end pt of which can be located by means of potentiometry, spectophtometry or by use of visual indicator.   For example generation of Fe^{2+} in solution by electrolytic reduction of Fe^{3+}, the generated Fe^{2+} is then titrated with dichromate. A typical coulometry titration apparatus, include a titration beaker and two independent circuit. 1. the generator circuit which requires a constant source of current and a pair of electrode one of which generates the titrant and the other of which is separated from the solution by a fritted glass connection serving to complete that cell.

2.   The detector circuit which consist of suitable indicator electrode, reference electrode and a potentiometer

ADVANTAGES OF COULOMETRY TITRATION
(1) There is no need for preparation or standardization of solution
(2) The problem of storage of prepared solution is eliminated.
(3) Labile reagent (reagents that are unstable) such as Cl_2 Br_2 and titanium owing to their instability are inconvenient as volumetric reagent but easily generated in coulometry titration.
(4) Very small amount of reagent can be accurately measured
(5) In similarity to volumetric analysis all the types of titrant as in volumetric analysis can be generated with 100% current efficiency at an electrode.This include oxidants, reductants, acids, bases, precipitants, complex reagents and several metal ions.

Example of reagents generated

| Reagent	Titrant generated
Na_2SO_4	H^+, OH^-
$NaCl$ (H_2SO_4)	Cl_2
$NaBr$(H_2SO_4)	Br_2
KI (H_2SO_4)	I_2
$CeSO_4$ (H_2SO_4)	Ce_4^+
$CuSO_4$ (HCl)	$CuCl_2^-$
$CrCl_3$ ($NaOH$)	CrO_4^{2-}
$Fe NH_4$ (SO_4)	
(H_2SO_4)	Fe^{3+}
$AgNO_3$ (HNO_3)	Ag^+
$TiCl_4$ (HCl)	$Ti3+$
$NaSCN$ ($HClO_4$)	SO_4^{2-}
KAg (CN)$_2$	
($NaSCN$)	CN^-

CALCULATION
(1) An apparatus was employed to determine O_2 content of a light hydrocarbon stream having a density of 0.00140g per ml, if 20litres of this gas consumed 3.13C of electricity calculate the oxygen in the sample on weight   basis in ppm.   Given that the equation for the production of O_2 is $2H_2O == O_2 + 4H^+ + 4e$
(2) Ascorbic acid (GFW = 176) is oxidized to dehydro-ascorbic acid with Br_2 according to the equation $C_6H_8O_8 + Br_2$ ---------- $C_6H_6O_8 + 2H^+ + 2Br$

A vitamin C tablet was dissolved in sufficient water to give exactly 200ml solution, a 10ml aliquot was mixed with an equal volume of 0.10KBr. If the bromine generated by a steady current of 70.4mA for a total of 6.51min was needed for the titration.

(3) The Fe in a lg sample was converted quantitatively to Fe^{3+} and titrated coulometrically with electrogenerated Ti^{3+}, if a current of 1.567mA passed for 123sec was required to reach the end – pt calculate the % of Fe in the sample.

Solution

$Q = It = 1.567 \times 10^{-3} \times = 0.1927C$

$Fe^{3+} + Ti^{3+} ----------Fe^{2+} + Ti^{4+}$
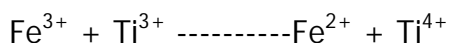
$IF = I$ mole Fe^{3+}

$Ic = 55.97/9650 = 0.1927C = 55.97/9650 \times 0.1927$

$= 0.00111766g$

% of Fe $= 0.000112/1 \times 100 =$

COULOMETRY AT CONSTANT POTENTIAL

This involves maintaining the potential of a working electrode at constant level such that quantitative reduction of analyte occurs without involvement of less reactive specie in the sample. At the beginning the current is high due to increase in concentration of analyte in the coulometry cell as electrolysis progresses but the current decreases rapidly and approaches zero as the analyte is removed from solution.

A plot of I against t and the determination of the area under the curve gives the quantity of electricity which may similarly be determined by the use of a chemical coulometer or by integration of a current time curve.

Example

The quantity of Fe^{3+} in a solution was determined by quantitative reduction to Fe^{2+} at a platinum electrode when current ceased the volume of O_2 and H_2 formed in a coulometer connected in series with the working cell was 39.3ml at 23^OC with a barometric pressure of 765 mmHg. Calculate the mg $Fe_2 (SO_4)_3$ in the solution.

Step

(1) Calculate the volume at STP

(2) Convert the volume at STP to moles

(3) Determine the equation of reaction in the coulometer

(4) Convert the mole to quantity of electricity

Step 1

The cadmium and Zn in 1.06g ore sample were the dissolved and subsequently deposited from an ammoniacal solution with a Hg cathode. When the cathode potential was maintain at -0.95V only cadmium was deposited, when the current ceased at this potential a H coulometer in series with cell was found to have evolved 44.6ml of gas (corrected water vapour) at a temperature of 21^0C and a barometric pressure of 773mmHg. The potential then rose to about -1.03V where upon Zn^{2+} was reduced. Upon completion of this electrolysis an additional 23ml of gas was produced under the same condition whereupon Zn^{2+} was reduced.

VOLTAMETRY
This is an electrolytic technique in which current/voltage relationship is display as a polarogram. Voltammetry consist of a group of electroanalytical procedures that are based upon the current voltage behaviour of an easily polarised electrode in the solution being analysed. This include

(1) Classical polograhy
(2) Differential pulse polarography
(3) Stripping polarography
(4) Rapid scan polarography
(5) Amperometry

CLASSICAL POLAROGRAPHY
This is an electrolytic technique in which current – voltage relationship is display as a polarogram. The polarographic cell consist of a small easily polarised electrode, usually the dropping mercury electrode (DME) and a large non-polarisable reference electrode so that the polarographic cell is made up of the following.

Ref electrode/salt bridge/analyte/indicator electrode/DME)

The DME is referred to as the working or indicator electrode, it is made up of mercury reservoir connected to a capillary tube. The capillary tube deliver mercury size of about 1mm in diameter (micro-electrode), the mercury drops every two seconds and as such a fresh surface of mercury is encountered such that the reaction at any point in time does not depend on the past history of the electrode. This therefore, makes the electrode reaction perfectly reproducible. Also since it is a micro electrode, the amount of current carried is very low (0-15UA).

CONDITION FOR POLAROGRAPHIC DETERMINATION
The analyte solution normally has at least 3 components:

(1) An electro-active substance i.e the analyte in question and in this case of DME, it is the substance that can be reversibly reduce for example metals, Cu, Zn, Cd.

(2) Inert salt which is not electro-active in the voltage range for which the analyte material is electro-active.   It is also referred to as "Supporting Electrolyte" this eliminates the migration current that may be due to the analyte. The supporting electrolytic is usually about a thousand times more concentrated than the analyte.

(3) This is a substance present in the order of 0.1-1% referred to as the maximum suppressor. In the absent of this substance the shape of a polarogram would be distorted by current maximum and interfere with the accurate evaluation of diffusion current and half wave potential.   Examples include high molecular wt substances such as gelatine, trixtin x-100, methyl red and several other dyes.

CREATING A POLAROGRAM

Consider a test solution of M^{n+} placed in a polarographic cell, for reduction to take place at the cathode or for current to following in a circuit, the applied e.m.f must be greater than the back e.m.f, i.e no current will flow as long as the potential is not high enough to reduce any of the electro-active substances. Therefore current will only flow when the applied potential is equal to the decomposition potential of one of the electro-active materials, therefore the value of current then increase with the applied potential.

AB is referred to as residual current, which can be due to the following:

(1) Reduction of trace impurities present in solution e.g small amount of dissolved oxygen, heavy metal ions from distilled water and impurities from supporting electrolyte.

(2) As a result of charging current or condenser current this result from a flow of electrons that charges the mercury droplet with respect to the solution. This residual current can be eliminated by analysing a blank solution, and then the actual diffusion current is the difference between the analyte's diffusion current and the blank diffusion current.

At B, the applied potential is equal to the decomposition potential of the electro-active specie in solution and as such at this point current is proportional to E-applied.

Between B and C, current increases linearly with E- applied and this portion is referred to as the diffusion current.

At C, the current no longer increases with E-applied and at CD, this represents the maximum current i.e limiting current. At this point current becomes independent of applied potential.

HALF WAVE POTENTIAL

This is a potential at which current is equal to 1/2 of diffusion current (id/2), it is represented as E1/2 and it is used for qualitative identification. A plot of E_{DME} against log i/id-i gives a straight line and E1/2 is a value of E_{Dme} when the log value of i/id-i is zero.

EFFECT OF OXYGEN ON POLAROGRAPHY

Oxygen can be easily reduced at the DME to give a peroxide, $O_2 + 2H + 2e == 2H_2O_2$ and as such a polarographic wave exist for oxygen in the range of 0 to -0.4V. The H_2O_2 formed can be further reduced in the range of apply potential greater than   -0.7V, therefore, when there is dissolved oxygen in the system, two waves exist due to oxygen which has covered the whole range of the usefulness of DME, and as such it is necessary to de-oxygenate the system.

This wave through constituting a nuisance in polarographic determination, it is the basis of oxygen probe or O_2- sensitive electrode. De- oxygenation is achieved by bubbling O_2 free nitrogen into the system to expel the oxygen.

SEPARATION OF MIXTURE

We separate many elements in a single run; the differences in their id (diffusion current) must be of the order of 0.2V

If id difference is less than 0.2V the waves overlap, it is possible to separate overlapping waves by using masking agent e.g when analysing Fe^{3+} and Cu^{2+} in a non-complexing medium, their waves overlap, however if KF is used as a background electrolyte, a complex is formed with the Fe^{3+} which delays the wave of Fe^{3+} by about 0.5V. Simultaneous determination is possible if waves are well resolve as in for example

Cu(+ 0.02V)
Pb(-0.4V)
Cd (-0.6V)
Zn(-1.0V)

QUANTITATIVE ANALYSIS

The diffusion current is directly proportional to the concentration of the reacting specie id & (M^{n+}).
The Ilkovic Equation relates the id and concentration such that we have

$$id = 607nD^{1/2} M^{2/3} t^{1/6}C$$

This equation is the basis of quantitative analysis in polarography

id = diffusion current (micro amperes, μA)

n = no of faradays per mole of reactant

D = diffusion coefficient, $cm^2 S^{-1}$

m = rate of mercury flow g/min

t = drop time, second (s)

c = concentration of the reactant in mmoles/litre.

The equation can be summarised as

id = KC. K is a constant if the medium is not changed i.e $M^{2/3} t^{1/6}$ is referred to as capillary constant and this allows comparism of id from different capillaries. To calculate K, a calibration curve of a standard solution is made or by using standard addition method.

CALCULATION

1. If the concentration of the an analyte the is 1.00 x 10 -4M and given the rate of mercury drop as 0.1194glmin and the drop time as 0.05mins, calculate the diffusion coefficient of the medium

   Solution
   C = 1.00 x 10-4 M x 103 = 1.00 x 10-1 mmoles = 0.1mmoles
   M = 0.1194g/min = 119.4/60 = 1.99mg/S =2
   T = 0.05min = 0.05 x 60 = 3s
   D = ?
   $1d = 607 \times 2^{nD1/2} M^{2/3} t^{1/6} C$
   $10 = 607 \times 2 D^{1/2} \times (1.99)^{2/3} \times 3^{1/6} \times 0.1$
   $10/01 = 607 \times 2 \times D^{1/2} \times 1.99^{2/3} \times 3^{1/6}$
   $D1/2 = 100/ 607 \times 2 \times 1.99^{2/3} \times 3^{1/6}$
   $D = (100/607 \times 2 \times 1.99^{2/3} \times 3^{1/6})^2$

2. Calculate the nickel cone in mgll on the baiss of the following data: Ni = 58.71 current in -11V 25.0ml of 0.2M Nall diluted to 50ml 8.4
   25.0ml lfo 0.2M Nall + 10ml of sample diluted to 50ml   46.3
   25.0ml of 0.2M Nall + 10ml of sample + 5ml of std
   Dilute to 50ml (2.30 x 10-2M) 68.4

   Solution
   $Id/c1 = id/c_2$
   46.3 – 8.4/ x 68.4 8.4/ x + 2.3

18

37.9 + 2.3 (37.9) = 60x

22.1x = 2.3 x 37.9

X = 3.944 x 5

X = 19.72 mmole/L

To mg/L 19.72 x 58.71

= 1`.16 x 10^3 mg/L

3. The following data are collected on 3 dropping mercury electrode.

	A	B	C
Flow rate mg/litre	1.89	4.34	3.11
Drop time, Sec	2.12	5.84	3.87
Is/c NA	2.39	4.86	3.68

Complete the data for electrode A and C

$Id/C = 607\ nD^{1/2}\ m^{2/3}\ t^{1/6}$

n =

D =

M =

T =

From B

$Id/c = 607nD^{1/2}\ m^{2/3}\ t^{1/6}$

$4.86 = 607\ x\ nD^{1/2}\ x\ 2.658\ x\ 1.3427$

$nD^{1/2} = 4.86/607\ 2.658\ x\ 1.3427$

$nD^{1/2} = (4.86/607\ x\ 2.658\ x\ 1.3427)^2$

$= (4.86/2166.3202$

$= 2.24\ x\ 10^{-3}$

AMPEROMETRY

This is an instrumental method of end point determination and it depends on polarographic behaviour of the substance in solution. The major condition used is that one of the reactants must be polarographic, a normal ploarographic cell is set-up and a potential is applied such tat a reacting material is already given a limiting current. This current is measured against the volume of the material is already given a limiting current. This current is measured against the volume of the titrant. In normal case only one polarised electrode is used and athe following situation can arise:

(1) Analyte active, titrant not active:- e.g if pb is the analyte and SO4 is added to it as the titrant indicating that lead as the analyte is active and SO4 as the titrant is not active at the applied potential, in this case 1.OV against scE

$Pb2+ + SO^{2-}4$----------------$pbSO^2$
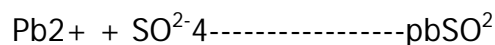
And as such the conce of pb^{2+} decreases which leads to a decrease in current observed until all the pb^{2+} is consumed.

(2) Analyte not active, titrant active:-

In this case for example when a potential of -1.6V against SCE is applied to a solution of 8 hydroxylqiunoline at this potential Mg^{2+} is not active.

(3) Both analyte and titrant are active:- e.g titrant pb2+ against chromate $(Cr_2^{2-}7)$ at -1.0V against SCE both will give polarograph wave, in such a case the current decrease to minimum then rises to maximum.

Assignment

(1) 6.480g of a rok sample to abe rich in aluminium was dissolved in 200ml of deconized distilled water. The sample was polorography using method of standard addition. The result obtained is tabulated below.

Solution	Current at -1.70V
20ml of 0.2MHCL + 20ml of H2O	10.2
20ml of 0.2MHCL +10ml sample + 10ml H2O	33.2
20ml of 0.2MHCL +10ml sample + 10ml of 6.32 x 10^{-3}M Al^{3+}	52.0

(i)   What is the % Al in the sample
(ii)   Can the sample be said to be rich in Al
(2) The Hg from a dropping electrode was collected for 6mins and found to weigh 0.72 x 10^{-2} kg. The time required for 40 drops of Hg to form was 3.7 mins when this electrode was run with a standard solution Pb^{2+} having a concentration of 2.2 x 10^{-2}M, a current of 10.55NA was observed. In the same cell, a lead solution of unknown conce produced a current of 73.05NA with a new electrode which had a drop time of 0.12mins and a flow rate of 0.2922glmin. What is the conce of the Pb^{2+} solution in mg/litre. Pb= 207.