Technical Assistance
HYDROLOGY PROJECT

World Bank & Government of The Netherlands funded

Training module # WQ - 32

Potentiometric Analysis

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with
HALCROW, TAHAL, CES, ORG & JPS

Table of contents

1. Module context

This module discusses principles of potentiometric analysis and different types of indicating electrodes used in such analysis. Modules in which prior training is required to complete this module successfully and other, available related modules are listed in the table below.

While designing a training course, the relationship between this module and the others, would be maintained by keeping them close together in the syllabus and place them in a logical sequence. The actual selection of the topics and the depth of training would, of course, depend on the training needs of the participants, i.e. their knowledge level and skills performance upon the start of the course.

No.	Module title	Code	Objectives
1.	Basic chemistry concepts	**WQ - 02**	• Convert units from one to another • Discuss the basic concepts of quantitative chemistry • Report analytical results with the correct number of significant digits.
2.	Understanding the hydrogen ion concentration (pH)	**WQ - 06**	• Discuss about the concept of pH • Calculate pH
3.	The chemistry of dissolved oxygen measurement	**WQ - 11**	• Appreciate significance of DO measurement. • Understand the chemistry of DO measurement by Winkler method.
4.	Understanding chemical oxygen demand test	**WQ - 18**	• Appreciate significance of COD measurement • Understand the chemistry of COD measurement
5.	Basic aquatic chemistry concepts	**WQ - 24**	• Understand equilibrium chemistry and ionisation constants. • Understand basis of pH and buffers • Calculate different types of alkalinity.
6.	Advanced aquatic chemistry: solubility equilibria	**WQ - 29**	• Explain the principles of chemical equilibrium • Define solubility product and explain how this relates to water quality assessment • Define the octanol-water partition coefficient and explain how this relates to water quality assessment.
7.	Advanced aquatic chemistry concepts: redox equilibria	**WQ - 30**	• Understand the principles of redox reactions • Understand the significance of redox potential measurement

2. Module profile

Title : Potentiometric Analysis

Target group : HIS function(s): Q2, Q3, Q5, Q6

Duration : One session of 45 min

Objectives : After the training the participants will be able to understand:

- the principles of potentiometric analysis
- construction of reference and indicating electrodes.

Key concepts :

- reference electrodes
- indicating electrodes

Training methods : Lecture, exercises

Training tools required : Board, flipchart, OHS

Handouts : As provided in this module

Further reading and references :

- Chemistry for environmental engineers, C. N. Sawyer, P. L. McCarty & G. F. Parkin, Mc Graw Hill, Inc., 1994
- Process chemistry for water and wastewater treatment, L. D. Benefield, J. P. Judkins & B. L. Weand, Prentice-Hall, Inc., 1982

3. Session plan

No	Activities	Time	Tools
1	***Preparations***		
2	***Introduction:*** • Review fundamentals of redox reactions, requirement of potentiometric analysis	10 min	OHS
3	***Reference Electrodes*** • As trainees about electrodes used in pH measurement • Explain different reference electrodes	10 min	OHS
4	***Indicator electrodes*** • Different types of indicator electrodes	20 min	OHS
5	***Wrap up***	5 min	

4. Overhead/flipchart master

OHS format guidelines

Type of text	Style	Setting
Headings:	OHS-Title	Arial 30-36, with bottom border line (not: underline)
Text:	OHS-lev1 OHS-lev2	Arial 24-26, maximum two levels
Case:		Sentence case. Avoid full text in UPPERCASE.
Italics:		Use occasionally and in a consistent way
Listings:	OHS-lev1 OHS-lev1-Numbered	Big bullets. Numbers for definite series of steps. Avoid roman numbers and letters.
Colours:		None, as these get lost in photocopying and some colours do not reproduce at all.
Formulas/Equations	OHS-Equation	Use of a table will ease horizontal alignment over more lines (columns) Use equation editor for advanced formatting only

Potentiometric analysis

- Review of principles of redox reactions
- Reference electrodes
- Indicating electrodes

Review (1)

- Electrode
- Half-cell
- Electrode potential
- Electrochemical cell

Review (2)

$$Zn(s) \leftrightarrow Zn^{2+} + 2e$$
$$Cu^{2+} + 2e \leftrightarrow Cu(s)$$

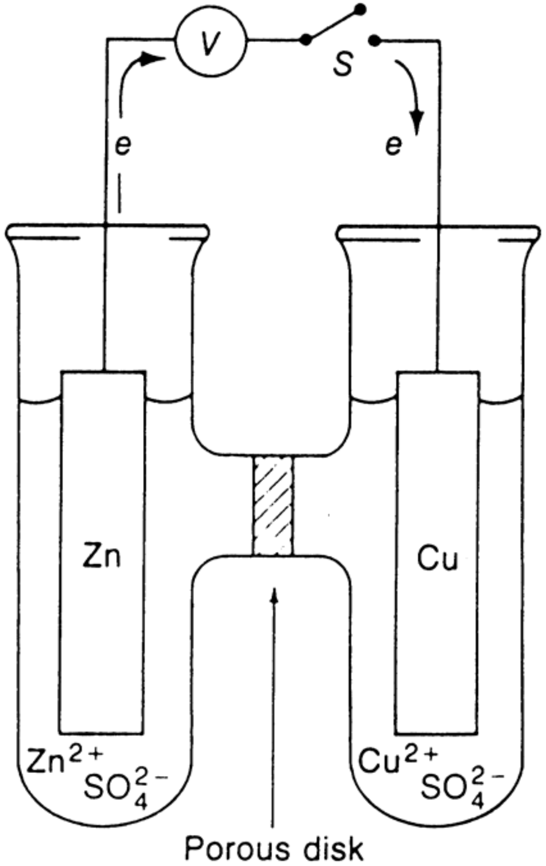


Figure 1 Galvanic cell

Review (3)

- Nernst Equation

$$aA + bB \ldots + ne \rightleftharpoons cC + dD$$

$$E = E^0 - \frac{RT}{nF}\ln\left[\frac{[C]^c[D]^d}{[A]^a[B]^b}\right]$$

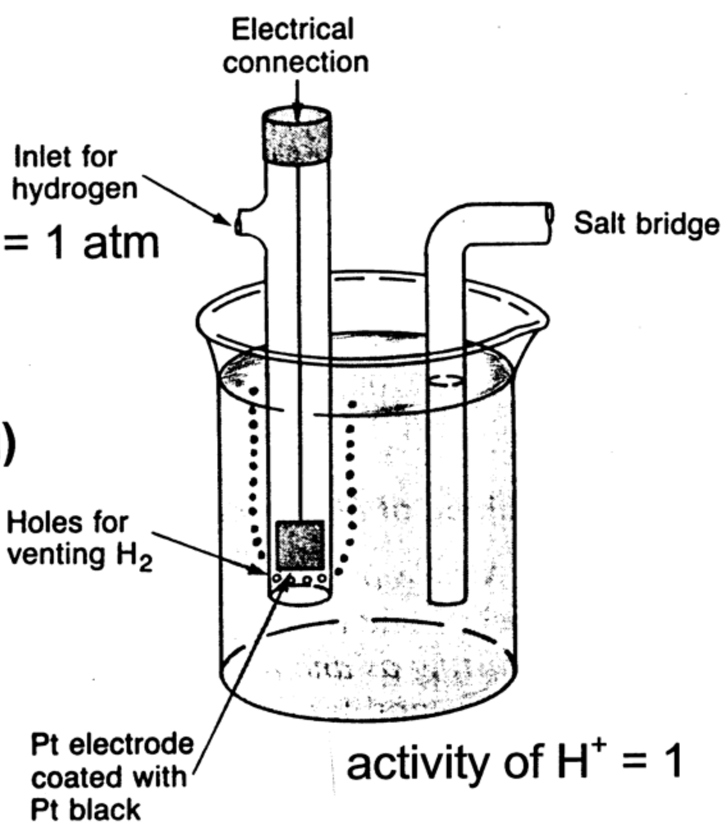
Potentiometric analysis

- Reference electrodes
    - *constant electrode potential*
- Indicating electrodes
    - *electrode potential depends on analyte concentration*
- Measurement of potential
    - *pH meter*
    - *ion meter*

Reference Electrodes (1)

pressure = 1 atm

$2H^+ + 2e \leftrightharpoons H_2(g)$



activity of H^+ = 1

Figure 2 Standard hydrogen electrode

Reference electrodes (2)

- By definition potential of hydrogen electrode is zero and acts as anode
- Inconvenient to maintain
- Hazardours

Reference Electrodes (3)

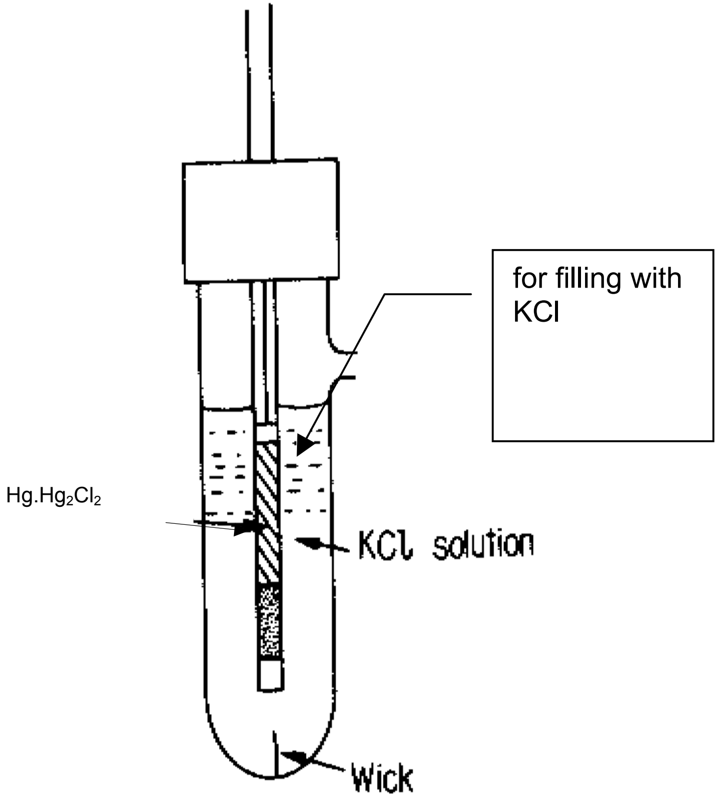


Figure 3: Schematic diagram of the Calomel reference electrode

Reference electrodes (4)

- Calomel electrode reaction

$$Hg_2Cl_2(s) + 2e \leftrightharpoons 2Hg(l) + 2Cl^-$$

- Standard potential at 25^0C

KCl	E_H
0.1N	-0.3358
1.0N	-0.3834
Saturated	-0.2444

Indicator Electrodes

- Electrode potential depends on analyte concentration
- Types of indicating electrodes
  - *Metal electrodes, type I and type II*
  - *Redox electrodes*
  - *Membrane electrodes, crystalline & liquid*

Metal Electrode: type I

- For copper electrode dipped in Cu^{2+} solution

  $$Cu^{2+} + 2e \leftrightharpoons Cu(s)$$

- $$E = E^0 - \frac{0.059}{2} \log \frac{1}{\left[Cu^{2+}\right]}$$

- E vs. log $[Cu^{2+}]$ has slope = + 0.0295

Metal Electrode: type II

- For anion which forms sparingly soluble precipitate with electrode metal.

$$AgI(s) \rightleftharpoons Ag^+ + I^-$$

$$Ag^+ + e \rightleftharpoons Ag(s)$$

$$AgI(s) + e \rightleftharpoons Ag(s) + I^-$$

- $E = E^0_{AgI} - 0.059 \log [I^-]$
- E vs. $\log [I^-]$ has slope = -0.059

Redox electrode

- Non-reactive metal electrode, e.g. platinum
- Electrode potential depends on relative conc. of reduced and oxidised specie in equilibrium

$$Fe^{3+} + e \leftrightharpoons Fe^{2+}$$

$$E = 0.77 - \frac{0.059}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Membrane Electrodes (1)

- Membrane sensitive to ion of interest
- Ion conc. within electrode is constant (std.)
- Potential depends on conc. in analyte sample

Membrane Electrode (2)

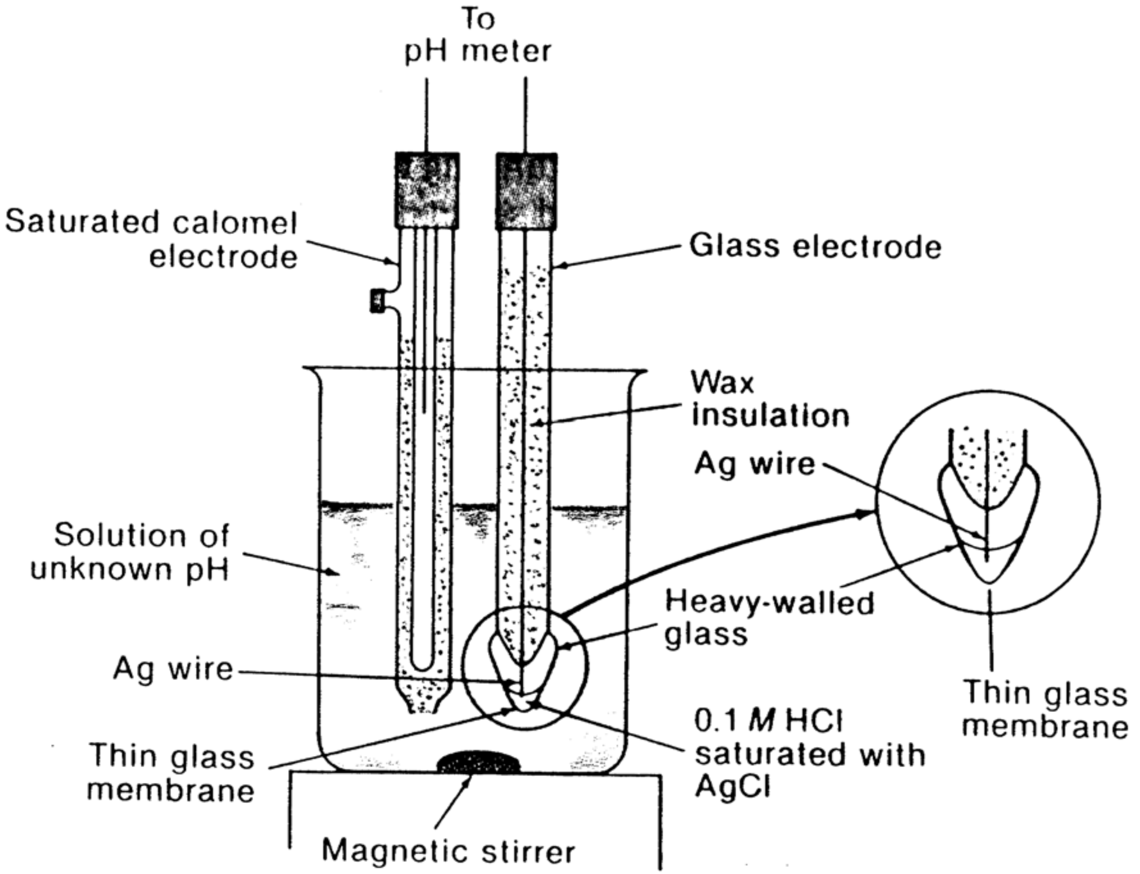


Figure 4: Glass electrode system for measuring pH

Membrane Electrode (3)

$$E_{ind} = k + 0.059 \log \frac{\left[H_a^+\right]}{\left[H_e^+\right]}$$

$$E_{ind} = K + 0.059\ pH$$

- *$[H_a^+]$ and $[H_e^+]$ = internal electrode and external analyte conc. (activity), respectively.*

- *K = constant*

Membrane Electrode (4)

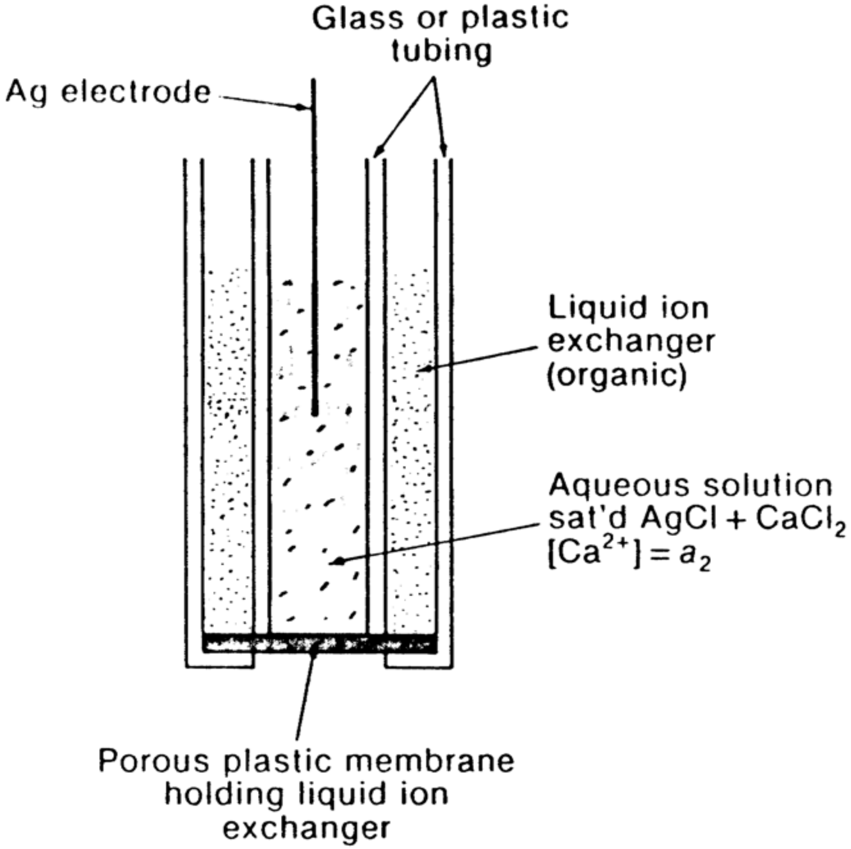


Figure 5: Liquid membrane electrode for Ca^{2+}

Probes (1)

- Respond to molecular specie
- Complete cell
- Polarographic type, need external current
- Galvanic cell type

Probes (2)

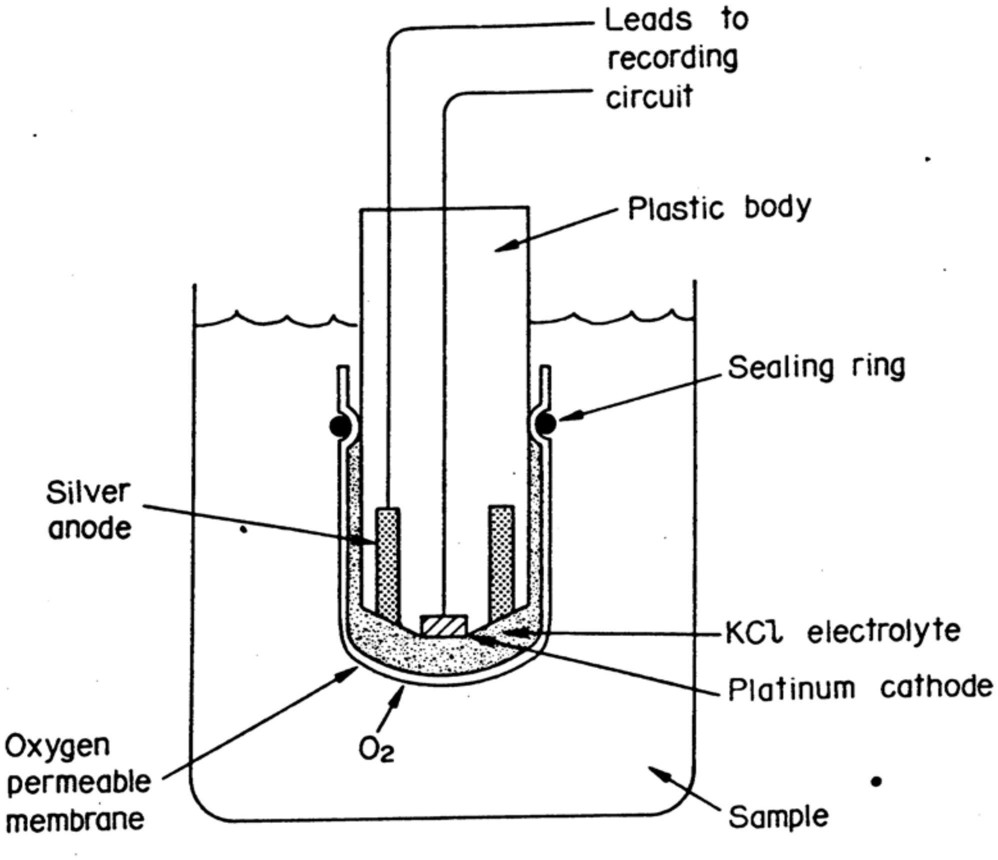


Figure 6: Schematic diagram of oxygen probe

5. Evaluation sheets

6. Handout

Potentiometric analysis

- Review of principles of redox reactions
- Reference electrodes
- Indicating electrodes

Review (1)

- Electrode
- Half-cell
- Electrode potential
- Electrochemical cell

Review (3)

- Nernst Equation

  $aA + bB \ldots + ne \rightleftharpoons cC + dD$

$$E = E^0 - \frac{RT}{nF}\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

Potentiometric analysis

- Reference electrodes
  - *constant electrode potential*
- Indicating electrodes
  - *electrode potential depends on analyte concentration*
- Measurement of potential
  - *pH meter*
  - *ion meter*

Reference electrodes (2)

- By definition potential of hydrogen electrode is zero and acts as anode
- Inconvenient to maintain
- Hazardours

Reference electrodes (4)

- Calomel electrode reaction

  $Hg_2Cl_2(s) + 2e \rightleftharpoons 2Hg(l) + 2Cl^-$
- Standard potential at 25^0C

KCl	E_H
0.1N	-0.3358
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Indicator Electrodes

- Electrode potential depends on analyte concentration
- Types of indicating electrodes
  - *Metal electrodes, type I and type II*
  - *Redox electrodes*
  - *Membrane electrodes, crystalline & liquid*

Metal Electrode: type I

- For copper electrode dipped in Cu^{2+} solution

  $Cu^{2+} + 2e \leftrightharpoons Cu(s)$
- $$E = E^0 - \frac{0.059}{2} \log \frac{1}{\left[Cu^{2+}\right]}$$
- E vs. log $[Cu^{2+}]$ has slope = + 0.0295

Metal Electrode: type II

- For anion which forms sparingly soluble precipitate with electrode metal.

  $AgI(s) \leftrightharpoons Ag^+ + I^-$

  $Ag^+ + e \leftrightharpoons Ag(s)$

  $AgI(s) + e \leftrightharpoons Ag(s) + I^-$

- $E = E^0_{AgI} - 0.059 \log [I^-]$
- E vs. log $[I^-]$ has slope = -0.059

Redox electrode

- Non-reactive metal electrode, e.g. platinum
- Electrode potential depends on relative conc. of reduced and oxidised specie in equilibrium

$Fe^{3+} + e \leftrightharpoons Fe^{2+}$

$$E = 0.77 - \frac{0.059}{1} \log \frac{\left[Fe^{2+}\right]}{\left[Fe^{3+}\right]}$$

Membrane Electrodes (1)

- Membrane sensitive to ion of interest
- Ion conc. within electrode is constant (std.)
- Potential depends on conc. in analyte sample

Membrane Electrode (3)

$$E_{ind} = k + 0.059 \log \frac{\left[H_a^+\right]}{\left[H_e^+\right]}$$

$$E_{ind} = K + 0.059\ pH$$

- *$[H_a^+]$ and $[H_e^+]$ = internal electrode and external analyte conc. (activity), respectively.*
- *K = constant*

Probes (1)

- Respond to molecular specie
- Complete cell
- Polarographic type, need external current
- Galvanic cell type

Add copy of Main text in chapter 8, for all participants.

7. Additional handout

These handouts are distributed during delivery and contain test questions, answers to questions, special worksheets, optional information, and other matters you would not like to be seen in the regular handouts.

It is a good practice to pre-punch these additional handouts, so the participants can easily insert them in the main handout folder.

8. Main text

Contents

Potentiometric Analysis

1. Introduction

Potentiometric and Conductance analyses instruments both rely on electrochemistry: the relationship between electric and chemical conditions in a solution.

The pH meter is probably the most widely used electrical method of analysis. The pH measurement is a *Potentiometric* analysis. In this method, a set of electrodes is immersed in a solution and direct measurement of difference in electrode potential (voltage) between the electrodes is carried out. From this, the concentration of an active ion may be derived (e.g. H^+).

Conductance analysis is employed for measurement of Electric Conductivity (EC). In this method, the ability of a solution to carry an electrical current is measured using two platinum electrodes in a reference cell.

Potentiometric analysis and *Conductance* analysis are two different types of analytical methods, both based on electric-chemical principles. pH and EC are two of the most common basic water quality parameters which are routinely measured. Theory and laboratory determination of EC was discussed in modules # 08 and 09. This module discusses the principles of potentiometric analysis.

2. Basic principles of redox reactions

Redox reactions and basic electrical-chemical principles were discussed in Module # 30 - "Advanced Aquatic Chemistry Concepts: Redox Equilibria". These are briefly reviewed here.

Electrode: A simple electrode is a strip of metal immersed in a solution of its own ions. A chemical change will occur at an electrode, as certain ions in solution migrate towards the electrode. The reaction occurring at the electrode is a redox-reaction, where electron transfer is involved. Thus, a potential difference is established between the metal and the solution.

Half-cell: a single electrode dipping into a solution is also known as a half-cell. Each half-cell has a specific redox reaction occurring there.

Electrode potential: The electric potential of an electrode is the potential due to electron transfer in a redox reaction occurring at the electrode. The potential is measured against a reference half-cell or electrode.

Electrochemical cell (also known as 'galvanic cell'): The combination of 2 electrodes (half-cells), creates an electrochemical cell. If a voltmeter is connected across the electrodes, it can measure the electromotive force being generated by the electrochemical cell (E_{cell}).

Cell Potential: The electrochemical cell potential, E_{cell}, is equal to the difference of the 2 electrode potentials and can be measured in volts, see Figure 1.

$Zn(s) \leftrightarrow Zn^{2+} + 2e$
$Cu^{2+} + 2e \leftrightarrow Cu(s)$

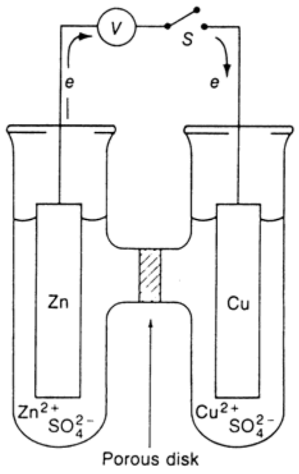

Figure 1 Galvanic cell

$$E_{cell} = E_c - E_a$$

Where:

- E_{cell} = electrochemical cell potential (volts)
- E_c = the electrode potentials of the cathode
- E_a = the electrode potentials of the anode

Nernst Equation: For the generalised half-reaction

$$aA + bB\ldots + ne \leftrightharpoons cC + dD\ldots$$

the potential is related to the ionic activity of the solutes (approximated by their concentration) by the expression:

$$E = E^o - \frac{RT}{nF}\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

Where:

- E = Electrode Potential, volts
- E^o = a constant called standard electrode potential; it is equal to E when the activities of all reactants and products are one.
- R = the Gas Constant, 8.316 J oK-1 mol-1
- T = Absolute temperature, ^{0}K
- n = number of moles of electrons that appear in the half reaction for the electrode process
- F = The faraday = 96487 coulombs
- [A], [B], [C], [D] = Active ions in the solution
- a, b, c, d = mole concentrations of the respective ions

Substituting numerical values, simplifying and converting to base-10 logarithm provides:

$$E = E^o - \frac{0.059}{n}\log\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

The Nernst equation indicates that the electrode potential varies with the log of ionic activities (concentration). In an electrochemical cell where the potential of one electrode is known (reference electrode), the measured cell potential can be related to the electrode potential at the indicator electrode. The indicator electrode potential, is in turn related to the ionic concentration of the species of interest.

If the cell potential is measured for standard solutions of the ion of interest, using its indicator electrode, and a calibration is made, the cell can be then used to measure the ion in unknown solutions.

3. Potentiometric analysis:

In order to determine the potential in an electrochemical cell, a potential measuring device and two electrodes are necessary. These two electrodes are generally referred as *reference electrode* and *indicator electrode*. The potential of the reference electrode is independent of concentration of analyte or any other ion present in the sample. Any instrument used in potentiometric methods includes:

- reference electrode,
- indicator electrode, and
- a potential measuring device(voltmeter).

3.1 Reference Electrodes

There are 3 common reference electrodes used for potentiometric analysis

- Hydrogen electrode
- Calomel electrode
- Silver – silver chloride electrode

Hydrogen Electrode

Figure 2 shows a standard hydrogen electrode. This reference electrode is used as the standard to which the potentials of all other electrodes are related. The hydrogen ion activity in a standard hydrogen-electrode is maintained at unity and the hydrogen gas partial pressure at one atmosphere. The electrode reaction is:

$$H_2(g) + 2e \leftrightharpoons 2H^+$$

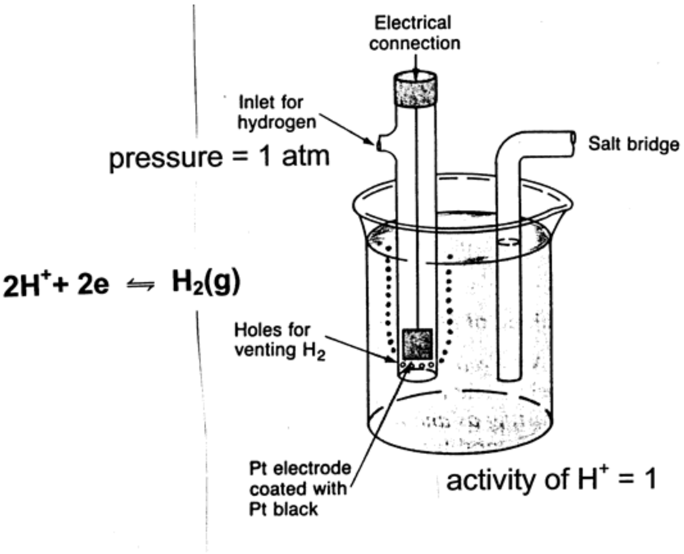

Figure 2 Standard hydrogen electrode

By convention the potential of this half-cell is assigned a value of exactly zero at all temperatures. The flowing stream of gas needed for the operation of a hydrogen electrode is inconvenient as well as hazardous. Therefore, ordinarily such an electrode is not used.

Calomel Electrode

The calomel electrode is most widely used reference electrode due to its ease of preparation and constancy of potential. The calomel electrode is the reference electrode used in the electronic pH measurement. The calomel electrode is also used in oxidation-reduction measurements, and in most other electrochemical analyses for which a stable easy-to-use reference electrode is desired. A simplified diagram of the calomel electrode is shown in Figure 3.

It has a calomel half-cell in which mercury and calomel (mercury(I) chloride) are covered with potassium chloride solution of definite concentration (0.1 M,1 M or saturated). The inner tube containing $Hg.Hg_2Cl_2$ is connected to the outer tube containing KCl through a small opening. Contact with the analyte solution is made through a porous fibre wick or a fritted disc at the bottom of the outer tube. These electrodes are referred to as the decimolar, molar and the saturated calomel electrode depending on the concentration of KCl solution. The potential of each with respect to the hydrogen electrode is given below:

Standard potentials of calomel reference electrodes at 25°

Concentration of KCl	E_H in volts
0.1 N	-0.3358
1.0 N	- 0.2824
Saturated	-0.2444

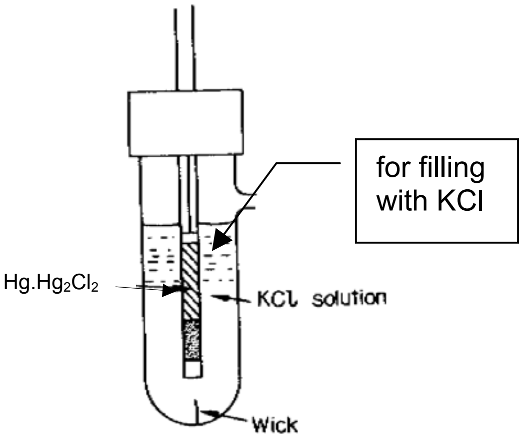

Figure 3. Schematic diagram of the Calomel reference electrode

The electrode reaction is: Hg_2Cl_2 (s) + $2e^-$ $\leftrightarrow$ 2Hg (liq) + $2Cl^-$

Silver-Silver Chloride Electrode

This electrode is another reference electrode consisting of a silver wire or a silver plated platinum electrode dipped in saturated solution of KCl in a tube. The tube is connected to analyte through a porous plug at the bottom. In practice, it is no longer commonly used and therefore is not discussed here.

3.2 Indicator Electrodes

An indicator electrode of a cell is one whose potential is dependent upon the activity (concentration) of a particular ionic specie whose concentration is to be determined. Various types of electrodes used for determination of different ions are discribed below.

Metal electrodes: A metal electrode consists of a metal in contact with its ions. For example, the half-reaction for the Cu electrode in Figure 1 is,

$$Cu^{2+} + 2e \leftrightharpoons Cu(s)$$

and the Nernst expression is written as:

$$E = E^0 - \frac{0.059}{2}\log\frac{1}{\left[Cu^{2+}\right]}$$

It is seen that the electrode potential is directly related to logarithm of inverse of concentration of Cu^{2+} ion in solution in contact with the electrode. A plot of E vs. log $[Cu^{2+}]$ would have a slope of +0.0295.

This type of electrode might be used for analysis of metals such as Ag, Cu, Hg, Pb and Cd. Metal electrodes for other elements cannot be used as they do not behave ideally and do not give reproducible results.

Another kind of metal electrode may be used for determination of an anion that forms a sparingly soluble precipitate on reaction with the electrode metal. For example, I^- can be determined using an Ag electrode. Here two equilibria are involved:

$AgI(s) \leftrightharpoons Ag^+ + I^-$
and $Ag^+ + e \leftrightharpoons Ag$

Combining the two equations one gets:

$$AgI(s) + e \leftrightharpoons Ag(s) + I^-$$

The Nernst expression for this process is:

$$E = E^0_{AgI} - 0.0591 \log [I^-]$$

The above equation shows that the potential of a silver electrode immersed in a tube containing a saturated solution of AgI is directly proportional to the logarithm of iodide concentration. A plot of E vs. log $[1^-]$ would have a slope of -0.0591.

The electrode is constructed by providing the tube containing the electrode and AgI solution with an agar plug saturated with AgI and supported on a porous disc at the bottom of the tube. This prevents the loss of AgI solution from the electrode tube and at the same time provides contact with the analyte solution.

Redox electrode:

A non-reactive metal electrode, such as platinum, may be used as indicator electrode for redox systems. Of itself, the electrode is inert; its potential depends solely on the potential of the chemical system with which it is in contact. As in the case of other indicator electrodes, it is used in conjunction with a reference electrode.

Glass membrane electrodes:

Determination of pH involves measurement of the potential developed across a thin glass membrane that separates two solutions with different hydrogen ion concentrations. Indicator glass membrane electrodes for other univalent ions, such as Na^+, K^+, NH^+_4, etc., are also available.

The glass membrane electrode and also other types of membrane electrodes, which are discussed later, are fundamentally different from metal electrodes both in design and principle. Since pH is measured routinely potentiometrically in all laboratories, glass membrane electrode for pH measurement is described in detail.

Figure 4 shows an electrode system, comprising a reference saturated calomel electrode and a glass indicator electrode, for measurement of pH. The indicator electrode consists of a thin, pH-sensititve glass membrane sealed onto one end of a heavy-walled glass or plastic tube. A small amount of dilute HCl that is saturated with silver chloride is contained in the membrane bulb. A silver wire in this solution forms an internal silver-silver chloride reference electrode. An internal calomel reference electrode may also be used within the glass electrode in place of the silver-silver chloride electrode.

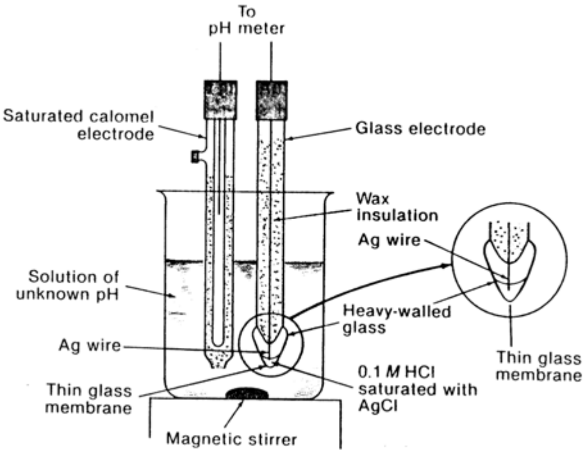

Figure 4: Glass electrode system for measuring pH

The thin glass membrane responds to pH. The process involves ion exchange reactions on the two sides of the membrane in which H^+ ions in the solutions are exchanged with monovalent cations in the glass lattice. The electrode potential established on the pH electrode is a function of H^+ ion activities of the analyte, H_a^+, and the solution within the electrode, H_e^+, on the two sides of the glass membrane:

$$E_{ind} = k + 0.059 \log \frac{\left[H_a^+\right]}{\left[H_e^+\right]}$$

since $[H_e^+]$ is constant

$$E_{ind} = K - 0.059 \text{ pH}$$

The glass membrane of the pH electrode is of 0.03 to 0.1mm thickness. It is of silicate glass within which there are singly charged cations, such as sodium and lithium, that are mobile in the lattice and are responsible for electrical conduction. The surface of the membrane is hygroscopic and must be hydrated before it will function as a pH electrode. It loses pH sensitivity after dehydration by storage. The effect is reversible, however, and the response is restored by soaking in water.

Liquid membrane electrode:

Liquid membrane electrodes have been developed for the direct potentiometric measurement of both polyvalent cations and polyvalent anions.

Figure 5 shows a schematic diagram of a liquid membrane electrode for calcium. It consists of a conducting porous membrane impregnated with a liquid ion exchanger that selectively bonds calcium ions, an internal solution containing a fixed concentration of $CaCl_2$ and a silver-silver chloride electrode. The similarity to the glass membrane electrode is obvious.

The exchange of Ca^{2+} ions at the two surfaces of the membrane differs as a consequence of the difference in Ca^{++} activity of the internal electrode solution and the external analyte. This results in the development of the electrode potential as in the case of the pH electrode.

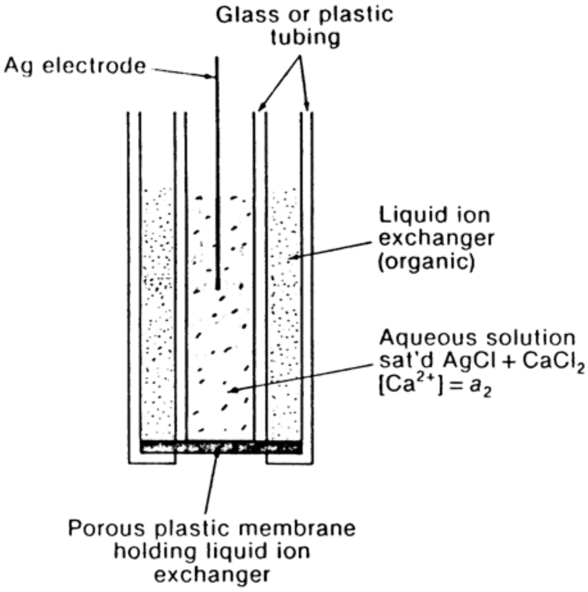

Figure 5: Liquid membrane electrode for Ca^{2+}

Crystalline membrane electrodes:

Many solid crystalline membranes, other than glass, have been developed for specific anions and cations, such as CN^-, F^-, Pb^{2+}, Cd^{2+}, etc. These also function on the same principle as the glass membrane and liquid membrane electrodes.

Gas-sensing probe:

The electrodes belonging to this class are not strictly ion electrodes because they respond to dissolved molecular species.

Further, they represent a complete electrochemical cell rather than an electrode. They are, therefore, more properly called probes.

Figure 6 shows a schematic diagram of an oxygen probe based on principle of polarography. An inert metal such as gold or platinum serves as cathode and silver is used for the anode. These are electrically connected through an electrolyte solution. The cell is separated from the sample by means of a replaceable gas permeable membrane. Any oxygen that passes through the membrane is reduced at the cathode by externally applying a potential of about 0.5 to 0.8 volt across the anode and cathode. This causes a current to flow. The magnitude of the current is proportional to the amount of oxygen in the sample.

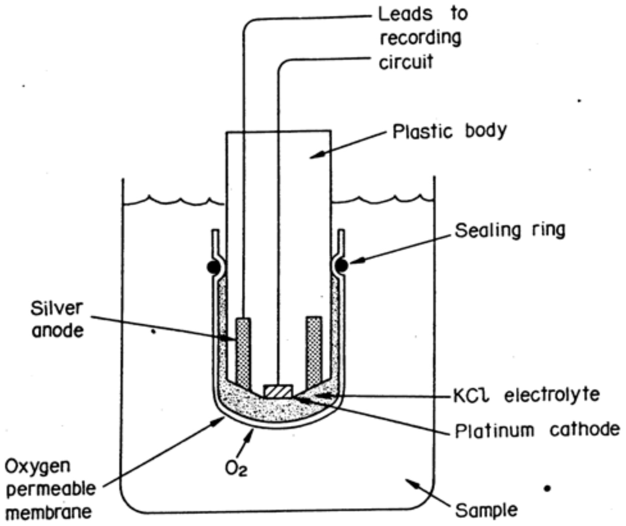

Figure 6: Schematic diagram for oxygen probe

In a galvanic cell type probe, a basic electrolyte such as KOH and a lead cathod is used in place of the inert platinum cathode. This produces enough potential to reduce the oxygen and the magnitude of the current is proportional to the dissolved oxygen concentration in the analyte solution.

3.3 Measurement of Cell potential

An instrument for potentiometric measurements must not draw any current from the cell as it will change its potential. Historically, potential measurements were performed with a potentiometer, a nul-point instrument in which the unknown potential was just balanced by a standard reference potential. At null, no electricity is withdrawn from the cell whose potential is being measured.

The potentiometer has now been supplanted by electronic voltmeters, commonly called pH meters when used for measurement of pH or ion meters when used for measurement of other ions. These meters directly read the concentration or p-concentration of the chemical specie being measured after suitable calibration.