



برنامج المسار الوظيفي للعاملين بقطاع مياه الشرب والصرف الصحي

دليل المتدرب

البرنامج التدريبي كيميائي مياه

ION SELECTIVE ELECTRODE – الدرجة الثالثة



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أهداف البرنامج التدريبي

في نهاية البرنامج التدريبي يكون المتدرب قادر على :-

- a. Identification of the principles of ISE and the application of in drinking water

ION SELECTIVE ELECTRODE

Introduction

- In recent years, a variety of membrane-type ion selective electrodes have become available commercially and show great promise as fast and efficient tools for in situ monitoring and laboratory analysis of municipal and environmental waters and waste streams.
- These Chemical sensors are miniaturized analytical devices, which can deliver real-time and on-line information on the presence of specific compounds or ions in complex samples. Usually an analyte recognition process takes place followed by the conversion of chemical information into an electrical or optical signal. Among various classes of chemical sensors ion-selective electrodes (ISE) are one of the most frequently used potentiometric sensors during laboratory analysis as well as in industry, process control, physiological measurements, and environmental monitoring.
- Ion Selective Electrodes (ISE) is membrane electrodes that respond selectively to ions in the presence of others. These include probes that measure specific ions and gases in solution. The most commonly used ISE is the pH probe. Other ions that can be measured include fluoride, bromide, cadmium, and gases in solution such as ammonia, carbon dioxide, and nitrogen oxide.
- The principle of ion-selective electrodes operation is quite well investigated and understood. An ion-selective electrode (ISE), also known as a specific ion electrode (SIE), is a transducer (or sensor) that converts the activity of a specific ion dissolved in a solution into an electrical potential, which can be measured by a voltmeter or pH meter.

1.0. Basics

- Potentiometry is an electrochemical method where the potential of an electrochemical cell is measured at equilibrium. Equilibrium means that no current is flowing in the system when the measurement is taken.
- Potentiometric analysis involves measuring a response (potential) which varies with analyte concentration, and then you need an indicator electrode which responds only to the analyte ion. The measured electrode potential is a function of the analyte ion concentration. By applying the Nernst equation, the unknown concentration can be determined.

1.1. The Nernst equation

- The technique of potentiometer involves the measurement of cell potentials under conditions of no current flow. In the electrochemical cell, if a high impedance device like a voltmeter is placed between the indicator and reference electrodes, no current will flow between the two compartments. It is possible under these conditions to measure the potential difference that exists between the two electrodes. For cells with

all reactants present at unit activity, the measured cell potential will be the standard cell potential, ($E_{o \text{ cell}}$)

- As a reminder, activity defines an “effective concentration” for a particular species, and takes into account all the interionic interactions that the ions experience in the solution, not just a count of the number of molecules of a species per liter (molarity). In real applications of potentiometry, reactant activities are seldom (read never) equal to unity, and measured cell potentials move away from those that result from the tabulated values of (E_o).
- A fundamental expression for characterizing redox systems under equilibrium conditions is the Nernst equation. One usually has encountered this expression early in their study of electrochemistry, perhaps in a general chemistry course long ago. The Nernst equation allows the calculation of relative activities of the species in a redox reaction as a function of the measured electrode potential (E) and the standard reduction potential (E_o) for the half reaction.

$$E = E_o + 2.3 \left(\frac{RT}{nF} \right) \log \text{Activity}$$

→ Slope Factor

Where

- E_o = constant for a given cell
- R = the gas constant
- T = the Temperature in Kelvin
- n = the ionic charge
- F = the Faraday constant

Theory

1.2. How does it work?

- Ion Selective Electrodes (including the most common pH electrode) work on the basic principal of the galvanic cell. By measuring the electric potential generated across a membrane by "selected" ions, and comparing it to a reference electrode, a net charge is determined. The strength of this

charge is directly proportional to the concentration of the selected ion. The basic formula is given for the galvanic cell:

$$E_{o \text{ cell}} = E_{o \text{ ISE}} - E_{\text{ref}}$$

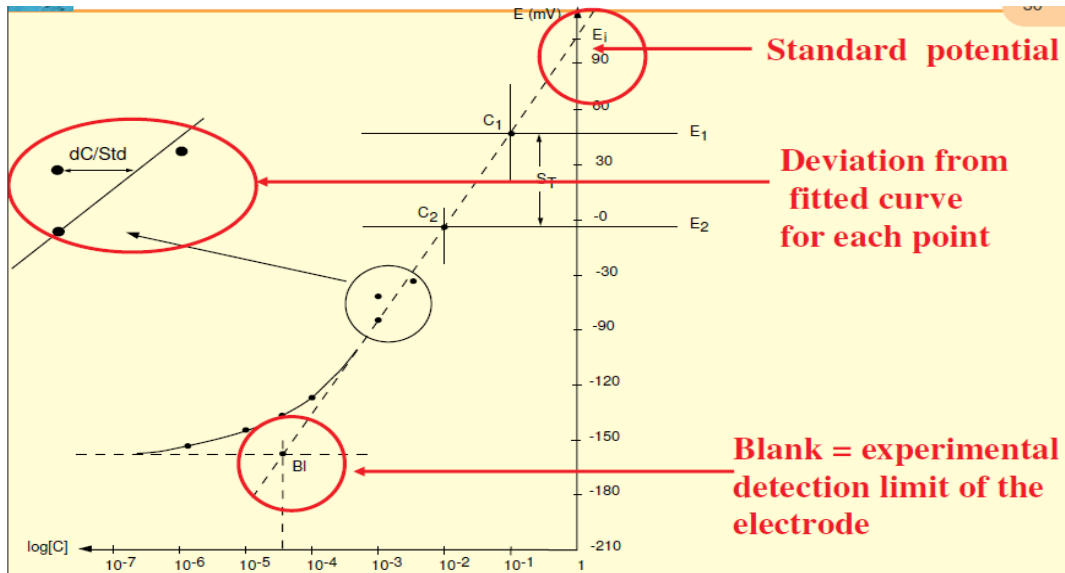
- Where the potential for the cell is equivalent to the potential of the ISE minus the potential of the reference electrode. An Ion Selective Electrode measures the potential of a specific ion in solution. (The pH electrode is an ISE for the Hydrogen ion.) This potential is measured against a stable reference electrode of constant potential. The potential difference between the two electrodes will depend upon the activity of the specific ion in solution. This activity is related to the concentration of that specific ion, therefore allowing the end-user to make an analytical measurement of that specific ion. Several ISE's have been developed for a variety of different ions.

1.3. How Does the mV Reading Correspond to the Concentration?

- Standard solutions of known concentrations must be accurately prepared. These solutions are then measured with the pH/mV meter. The mV reading of each solution is noted and a graph of concentration vs. mV reading must be plotted. Now the unknown solution can be measured. The mV value of the unknown solution is then located on the graph and the corresponding solution concentration is determined.
- Ion Selective Electrodes (including the most common pH electrode) work on the basic principal of the galvanic cell. By measuring the electric potential generated across a membrane by "selected" ions, and comparing it to a reference electrode, a net charge is determined. The strength of this charge is directly proportional to the concentration of the selected ion. The basic formula is given for the galvanic cell:

$$E_{\text{cell}} = E_{\text{ISE}} - E_{\text{ref}}$$

- The potential for the cell is equivalent to the potential of the ISE (working electrode) minus the potential of the reference electrode.



A Typical calibration curve of an ion selective electrode.

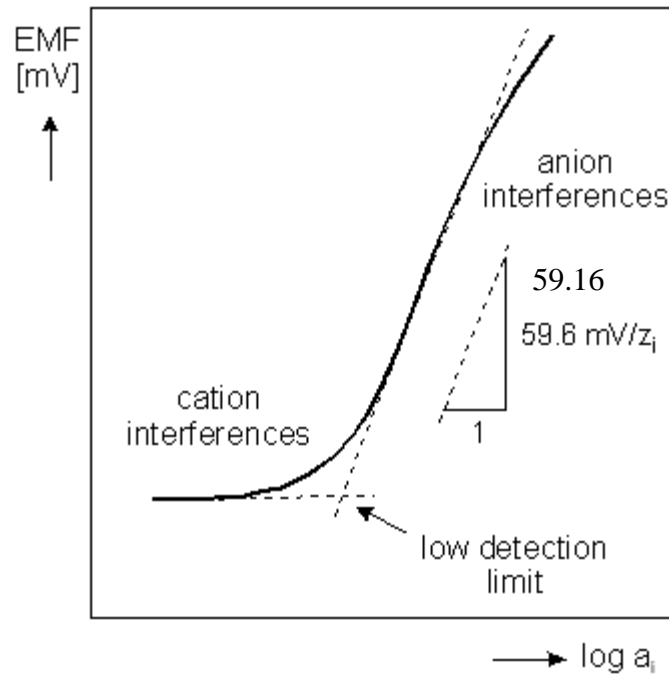
Characteristics of Ion Selective Electrode technique

- Selectivity:** Selectivity is one of the most important characteristics of an electrode, as it often determines whether a reliable measurement in the sample is possible or not. The selectivity coefficient (K_{xy}) is expressed as the logarithm of (K_{xy}). The experimental selectivity coefficients depend on the activity and a method of their determination. The ion that is to be determined is referred to as the determinant and other ions to which an electrode responds are known as interfering ions. It is possible to calculate the preference of an electrode for the determinant over the interference. This is called the selectivity of the electrode. The preference, expressed as a ratio is called the selectivity coefficient, or ratio. Each electrode has its own set of selectivity coefficients. For example:

$$K_{K^+ / Na^+} = 2.6 \times 10^{-3}$$

- Meaning that the preference for K^+ (potassium) over Na^+ (Sodium) for this electrode is 1 to 2.6×10^{-3} or 385:1. This means that the electrode is 385 times more selective to K^+ than Na^+ .
- Slope of the linear part of the measured calibration curve of the electrode.**

The theoretical value according to the Nernst equation is: 59.16 [mV/log (a_x)] at 298 K for a single charged ion or $59.16/2 = 29.58$ [mV per decade] for a double charged ion. A useful slope can be regarded as 50-60 [mV (per decade)] (25-30) [mV per decade] for double charged ion respectively).



- For example, when measuring Potassium ions, (i.e. $n=+1$), the slope factor at 298K (25°C) has a value of 59.16 mV. This is termed the Ideal Slope Factor, and means that for each tenfold change in Potassium concentration, an ideal measuring system will sense mV change of 59.16. Cleaning the electrodes after measurements maintains the electrode against system accuracy loss, which is diagnosed as a deflected slope factor value. The Table below gives the ideal slope values for monovalent and divalent anions and cations.

Ionic charge	Slope	Example
+2	29.58	Ca^{2+} , Mg^{2+}
+1	59.16	K^+ , Na^+
-1	-59.16	F^- , Cl^-
-2	-29.58	S^{2-}

- **Range of linear response:** at high and very low target ion activities there are deviations from linearity. Measurements in non-linear ranges can still be carried with no significant problems.
- **Detection limit:** Detection limit is defined by the cross-section of the two extrapolated linear parts of the ion-selective calibration curve. The observed detection limit is often governed by the presence of other interfering ions or impurities.
- **Response time:** Earlier, it was defined as the time between the instant at which the ion-selective electrode and a reference electrode are dipped in the sample solution (or the time at which the ion concentration in a solution is changed on contact with ISE and a reference electrode) and the first instant at which the potential of the cell becomes equal to its steady-state value within [1 mV] or has reached 90% of the final value. However, it should be pointed out that a single time constant does not describe the form of the electrode response function. Moreover, in many investigations the response time of the overall measuring system is determined, which influences on the response time of the ISE.

Basic Components of a potentiometric system

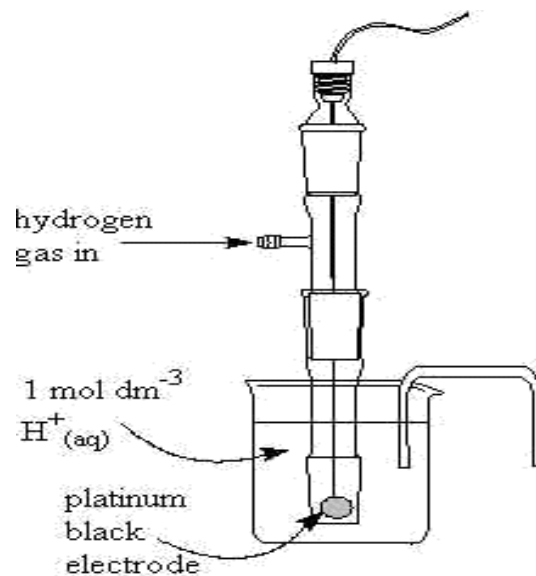
1.4. Reference Electrode: Gives reference (constant) potential in potential measurements, which is invariant with respect to solution composition. It also shows nearly no variation in the liquid junction potential from one test or standard solution to another.

- Examples of the most wide spread reference electrodes

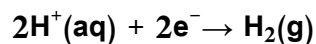
1) Standard Hydrogen Electrode

The SHE is the universal reference for reporting relative half-cell potentials. It is a type of gas electrode and was widely used in early studies as a reference electrode, and as an indicator electrode for the determination of pH values. The SHE could be used as either an anode or cathode depending upon the nature of the half-cell it is used with. The SHE consists of a platinum electrode immersed in a solution with a hydrogen ion concentration of 1.00M. The platinum electrode is made of a small square of platinum foil which is platinized (known as platinum black). Hydrogen gas, at a pressure of 1 atmosphere, is bubbled around the platinum electrode. The platinum black serves as a large surface area for the reaction to take place, and the stream of hydrogen keeps the solution saturated at the electrode site with respect to the gas. It is interesting to note that even though the ISHE is the universal reference standard, it exists only as a theoretical electrode which scientists use as the definition of an arbitrary reference electrode with a half-cell potential of 0.00 volts. (Because half-cell potentials cannot be measured, this

is the perfect electrode to allow scientists to perform theoretical research calculations) The reason this electrode cannot be manufactured is due to the fact that no solution can be prepared that yields a hydrogen ion activity of 1.00M.



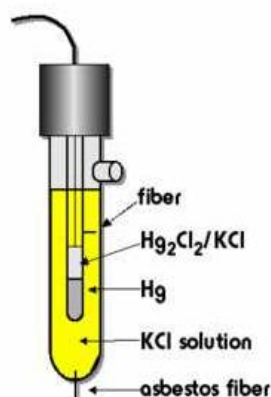
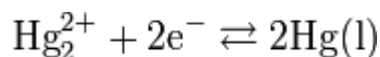
Hydrogen electrode is made by adding platinum black to platinum wire or a platinum plate. It is immersed in the test solution and an electric charge is applied to the solution and platinum black with hydrogen gas. The hydrogen-electrode method is a standard among the various methods for measuring pH. The values derived using other methods become trustworthy only when they match those measured using hydrogen electrode method. However, this method is not appropriate for daily use because of the effort and expense involved, with the inconvenience of handling hydrogen gas and great influence of highly oxidizing or reducing substances in the test solution. Its potential is sensitive to oxidants and reductants in solution. The catalytic Pt surface is poisoned by a variety of substances including As, CN⁻, H₂S and Hg. The overall reaction for a hydrogen electrode is



2) Calomel Electrode

The calomel electrode (SCE) is a reference electrode based on the reaction between elemental mercury and mercury(I) chloride. The aqueous phase in contact with the mercury and the mercury (I) chloride (Hg₂Cl₂, "calomel") is a solution of potassium chloride in water. The electrode is normally linked via a porous frit (asbestos fiber) to the solution in which the other electrode is immersed. This porous frit is a salt bridge. The calomel electrode is very practical and very robust and is one of the most common electrodes used. They are also relatively low cost. The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated

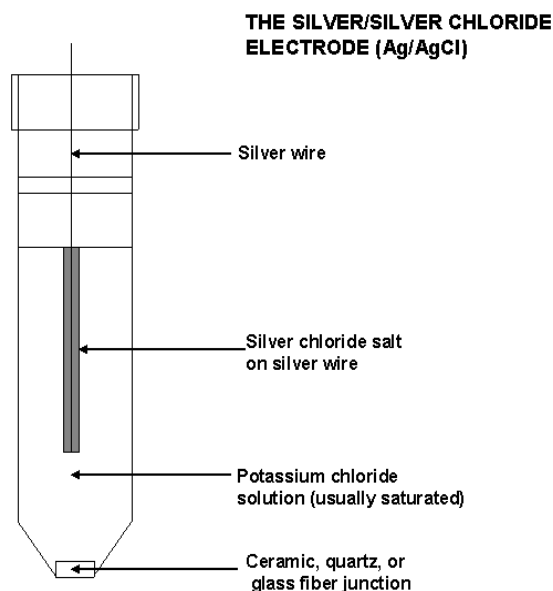
calomel electrode (SCE) and if the potassium chloride solution is 1 N, the electrode is known as normal calomel electrode (NCE) while for 0.1 N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE). The electrode is based on the following redox reaction



3) Silver-Silver chloride electrode

This is by far the most common reference type used today because it is simple, inexpensive, very stable and non-toxic. It is mainly used with saturated potassium chloride electrolyte, but can be used with lower concentrations such as 1 M potassium chloride. Note that changing the electrolyte concentration changes the potential. Silver chloride is slightly soluble in strong potassium chloride solutions, so it is sometimes recommended the potassium chloride be saturated with silver chloride to avoid stripping the silver chloride off the silver wire.

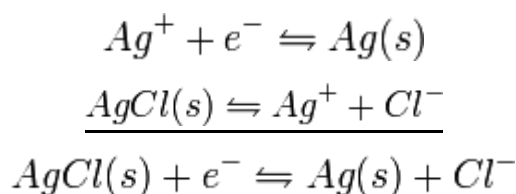
The silver-silver chloride electrode is the most common due to its ease of manufacture and its superior temperature range, actually usable even above 130°C. The electrode is a silver wire that is coated with a thin layer of silver chloride either by electroplating or by dipping the wire in molten silver chloride. When the electrode is placed in a saturated potassium chloride solution it develops a potential of 199 mV vs the standard hydrogen electrode. The potential developed is determined by the chloride concentration of the solution, as defined by the Nernst equation. The potential of the electrode remains constant as long as the chloride concentration remains constant. The silver-silver chloride reference electrode develops a potential proportional to the chloride concentration, whether it is sodium chloride, potassium chloride, ammonium chloride or some other chloride salt.



The concentration of chloride in the reference electrolyte determines the potential of the reference element. Potassium chloride is the most widely used electrolyte because **it does not generally interfere with pH** measurements and the **mobility of the potassium and chloride ions are nearly equal**. This equal transference minimizes junction potentials since the (+) potassium and (-) chloride ions move at the same rate. These ions provide the conductive path between the reference element and the sample, commonly referred to as a salt bridge.

Most of reference electrodes use a saturated KCl solution with an excess of KCl crystals. The extra KCl dissolves into the electrolyte as the potassium and chloride ions diffuse out through the liquid junction in normal use. This extra buffer of KCl extends the time before the reference cell starts to drift due to the depletion of chloride ions in the electrolyte.

The silver-silver chloride electrode simplicity of fabrication and fundamental ruggedness makes it a good candidate for many industrial applications where the electrochemical potential has to be measured or controlled. The reactions and the overall reaction of the silver/silver chloride electrode is:



1.5. Working Electrodes (Ion Selective electrodes)

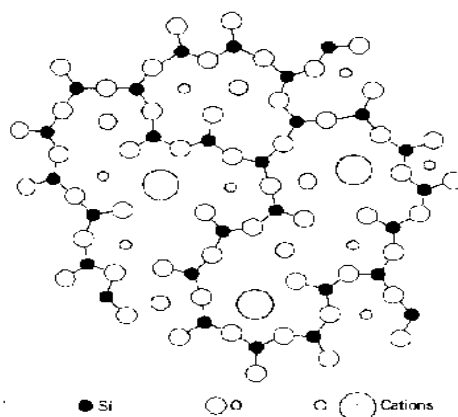
The nature of the membrane determines the selectivity of the electrode. A membrane is considered to be any material that separates two solutions. It is across this membrane that the charge develops. The term "membrane" is often confused as implying permeability. While this is true in many cases, the term here is used denote any material which the charge can develop across.

Several types of sensing electrodes are commercially available. They are classified by the nature of the membrane material used to construct the electrode. It is this difference in membrane construction that makes an electrode selective for a particular ion.

1. Glass-membrane Electrode

The most common ion selective electrode is the glass electrode that is sensitive for H^+ ions; therefore it is basically the pH electrode. It also plays the role of the core of many other ion selective electrodes.

The best known example of this type of electrodes is the glass electrode (pH electrode), in which the anionic fixed sites are created by defects in the SiO_2 membrane and the cationic vacancies due to the non silicon constituents of glass. When the glass membrane is exposed to water a thick hydrated layer is formed (5-100 nm), which exhibits improved mobility of the ions, which determine the wide linear range of the ISE calibration curve (typically 2-12 pH). The membrane is manufactured as a bulb of typical wall thickness of 0.05-0.2 mm (the optimum thickness is the result of compromise between the mechanical properties and electrical resistance). Two processes occur during the interaction of glass hydrated membrane and the sample solution (which both influence on the value of selectivity coefficient): ion-exchange and diffusion of all participating ions.



The example of another glass-membrane electrode is the sodium-selective electrode (pNa electrode). The construction of this electrode is essentially identical to that of pH electrode, with the exception of the glass used (silica with 10% Na_2O and Al_2O_3) and the fact that the inner reference solution has a fixed sodium ion activity. Interferences from hydrogen and silver cations are high, therefore the activity of such ions should be maintained some four order of magnitude less than the sodium ion activity to be measured. Although the pNa electrode is insensitive to ions other than H^+ and Ag^+ , glass membranes selective for other ions (e.g. K^+) have not been constructed.

2. Solid state membranes

Other types of membranes with fixed sites include single crystals of sparsely soluble salt and heterogeneous membranes in which the insoluble salt is incorporated in some suitable inert binder. In order to consider these layers at equilibrium it is necessary to use saturated solutions. In practice, these electrodes are applied in non-saturated solutions, so in this case the insoluble membrane slowly dissolves. Insoluble inorganic materials as: Ag_2S , CuS , CdS , PbS , LaF_3 , AgCl , AgBr , AgI and AgSCN have all been tested as cation exchange membranes, incorporated into an electrode body in the form of single crystal or compressed powder discs. These materials are ionic conductors, though the conductivity is extremely small and mainly takes place through the migration of point defects in the lattice. The response time of these membranes can be increased by incorporating aliovalent ions into the lattice (e.g. the fluoride-selective membrane LaF_3 can be doped with Eu^{2+} ions). Sensors for the detection of: Ag^+ , Cu^{2+} , Cd^{2+} , Pb^{2+} , S^{2-} , F^- , Br^- , I^- , SCN^- and CN^- ions can be constructed from such membranes. The sensitivity to ions of these electrodes arises from the dissolution equilibria at the membrane surface.

It was also proved that it is possible to fabricate sensors by directly contacting the membrane with a wire (so called coated-wire electrodes) to form an ohmic contact. Such systems are found to exhibit complex behavior (time and temperature dependences), requiring frequent re-calibration, but they are extremely simple to construct. An example is a silver-selective electrode that has been designed by attaching a wire to the back of graphite/PTFE disc, on the front side of which the silver halide is rubbed in to the surface. Another exemplary coated-wire electrode was prepared by simply coating a wire with a membrane film of PVC containing an ion-exchanger.

3. Liquid-membrane electrodes

In addition to solid membranes, immiscible liquid (organic) phases with ion-exchange properties can be used, with such phases stabilized against the external solution phase within a polymer or ceramic membrane. The main component of electroactive membrane is neutral or charged compound, which is able to complex ions reversibly and to transfer them through an organic membrane by carrier translocation. This compound is called as an ionophore or an ion carrier. There are two kinds of ionophores: charged one (usually termed liquid exchanger) and neutral carriers. They are mobile in both free and complexes forms, so the mobility of all species are part of the selectivity coefficient together with ion-exchange equilibrium. The mobile binding sites are dissolved in a suitable solvent and usually trapped in a matrix of organic polymer (gel). Ion activity measurements are performed predominantly in aqueous media, so all membrane constituents are lipophilic. Therefore, the primary interaction between the ion in water and the lipophilic membrane containing the ionophore is the extraction process.

Such a membrane is quite similar to liquid phase, because diffusion coefficients for dissolved low molecular weight ionophores are in the order of 10^{-7} - 10^{-8} cm²/S. An appropriate plasticizer is added to a membrane in order to ensure the mobility of the free and complexed ionophore. It determines the membrane polarity and provides suitable mechanical properties of the membrane. The ionophore is usually present in 1% amount (approximately 10^{-2} M), which is relatively low as compared to the glass electrode. A cation selective membrane can contain a salt of lipophilic anion and hydrophilic cation (additive), which improves performances of a membrane. Although other polymers like: polysiloxane, polystyrene, polyamide or polyimide can be used as a membrane matrix, PVC is the most widely used matrix due to simplicity of membrane preparation.

Among the ion carriers, electrically neutral ionophores have found a wide field of applications as components in ion-selective liquid-membrane electrodes, e.g. in clinical chemistry, electrophysiology, as detectors in ion chromatography, in highly selective transport processes through artificial membranes (also biological membranes). As a result of the introduction of natural as well synthetic ionophores in ion-selective membranes, ISEs for direct measurement of various cations and anions were designed.

It is worth mentioning that nowadays, reference and working electrode are sometimes merged together in what is known as a "combination electrode". The combination electrode is a complete cell, therefore a single electrode carries on the whole mission.

1.6. Ion Meter

The Ion meter is the final component of the potentiometric system that measures the potential difference in mV to concentrations or pH. The ion meter is an electronic device that was modified nowadays to put at the fingertips of the user many options that may aid and enhance his analytical

goals. Ion meters not only measure potential differences, but also they draw the calibration curves, calculate the slope value, slope percentages, and so they give the user a complete report about the calibration he's just done. Measurements are no doubt an interest point of these intelligent meters, since they may save the user's measurements and get a hard copy of the values via connection to a computer. Resolution of an ion meter is an important aspect that gives the process a fine look. Higher resolutions are no doubt more precise, yet they require more stabilization time.

Application to Drinking Water Analysis

- Ion selective electrode technique has shown a great progressive leap over the last years, so that we can now find hundreds of selective electrodes for direct measurements of different ions. As for Drinking water, it's evident now that ion selective electrodes are of an important role for the measurement of many analytes that are critical for the quality of drinking water. Of these analytes for example are fluoride, cyanide, ammonia and many others.
- The common use of ion chromatography and spectrophotometry has put many of the analytes of interest on the lists of routine analysis for these techniques, while some analytes were continuously debatable. One of the most important examples of these debatable analytes was ammonia. Ordinary spectrophotometric methods for ammonia showed somehow good results, but on the other hands most are hazardous, and the measurement range is definitely narrow. Ion chromatography, the other strong, widely used technique, measures ammonia after acidification as NH_4^+ , but also with some interference problems that obscure a precise measurement for ammonia in a drinking water sample. Ion selective electrode technique has shown a great precision for the measurement of ammonia as NH_3 , using a gas-permeable membrane electrode, that depends on the change in pH of the internal solution due to the permeation of ammonia gas through the membrane.
- The ammonia-selective electrode is highly selective, with nearly no interferences. Measurement range is very wide, typically (0.03 – 1400 mg/L NH_3). All these facts put the technique at the top of the available techniques for the measurement of ammonia, as an example. Many other analytes may be precisely analysed by the potentiometric technique that is always being developed, to reach a higher precision, for much more analytes, of which many may be utilized to keep drinking water quality under control.

Ammonia (Example):

Principle:

- The ammonia-selective electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia ($\text{NH}_{3(\text{aq})}$ and NH_4^+) is

converted to $\text{NH}_3(\text{aq})$ by raising pH to above 11 with a strong base. $\text{NH}_3(\text{aq})$ diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. The fixed level of chloride in the internal solution is sensed by a chloride ion-selective electrode that serves as the reference electrode.

- Potentiometric measurements are made with a pH meter having an expanded millivolt scale or with a specific ion meter.

Interference:

Amines are a positive interference. This may be enhanced by acidification. Mercury and silver interfere by complexation with ammonia.

Equipments

- Mettler-Toledo Sevenmulti® Ion Selective Electrode instrument.
- Ammonia selective electrode.
- Teflon-coated Magnetic stirring bars with stirrer.
- Pipette filler.

Chemical and reagents

- Deionized water.
- NaOH 10N solution.
- Stock NH_4Cl Solution: dissolve 3.819g anhydrous NH_4Cl (dried at 100 °C) in water, and dilute to 1000 mL; (1.0 mL = 1.0 mg-N = 1.22 mg NH_3).
- Standard Ammonium Chloride solution of the concentrations 0.1, 1, 10, 100 and 1000 ppm, prepared by diluting the previously mentioned NH_4Cl stock solution.
- Ammonia electrode filling solution

Procedure

(Note: These instructions are those of the Mettler-Toledo SevenMulti® Ion selective electrode instrument, and are not necessarily applicable to any other instruments).

- Switch on the Instrument by pressing the power button on the instrument.
- Press "Mode" button, then select "Ion" mode.

Calibration

- Prepare a blank & a series of standards according to the calibration range required. (Be cautious to keep all the prepared solutions at the same temperature).

- It's preferable to cover the prepared solutions with Para film to reduce ammonia gas evolution during base addition & measurement.
- In the ion mode, press the "Menu" button, then scroll down to "Ion Methods in Memory", press "Enter". Then select "Load a stored Method from Memory", press "Enter". Scroll down to NH₃, and press "Select". The system then reviews the Method information on the display screen, including the method name, measurement unit, calibration setting, calibration mode and other preset items. To load the method press "Load", then press "exit" twice until the instrument displays the standby screen, with the method label displayed at the upper right corner.
- To perform a new calibration, press "Menu", then scroll down to "calibration setting" and press "Enter", press "Enter" on option number 1. "Set calibration standard". The instrument then displays a multiple choice of concentration units, scroll down to number 4. "mg/L" and press "select". The current calibration setting are displayed, to continue using the current calibration press "Save", to modify the current calibration setting press "Edit". The instrument then displays a flashing cursor that asks the user to enter the temperature compensation value, and the concentration of the set of standards that are to be entered during calibration. Upon finishing the entrance of the standards, press "End", the instrument then displays the entered values of the calibration standards, to re-edit, press "Edit", to continue press "Save". Press then the "Exit button twice to return to the standby screen. The instrument is now ready for calibration.
- To begin calibration, add about 1 ml of 10N NaOH to 100 ml of the first calibration standard, drop the magnetic stir bar in the beaker, place the beaker on the stirrer, switch on the stirring at a low stirring speed, to homogenize the sample, yet not evolving ammonia gas, immerse the ammonia electrode and press "Cal" on the instrument panel. The instrument then displays the concentration of the standard at the lowest left corner of the screen, and the read value on the reading display. Upon stabilization, the instrument stops with a final reading on the screen. Remove then the ammonia electrode, and repeat the last step for all the calibration standards. When calibration mission is accomplished, the instrument displays the calibration curve on the screen, accompanied with the slope and slope percentage, ideally, the ammonia curve gives a slope of 59.16, slope percentage is best at 100% . Perfection decreases as it goes further. If acceptable, press "Save" to continue. The instrument is now ready for measurements.

Measurements

- Measurement of samples is more or less like calibration, just add the 1ml NaOH, stir bar, place on the stirrer, immerse the electrode, and press "Read". The instrument takes some time for stabilization. When stabilized, the instrument displays the final reading stabilized.
- Note: stabilization time increases to some extent as the sample concentration goes below 1 mg/L.

Calculation

Record sample concentration directly from instrument read out according to standard curve.

Quality control**Construction of Quality control chart.****Accuracy chart (Schewarte-chart)**

- The laboratory shall construct accuracy chart to control accuracy for the analyzing of
- Control samples by analyzing 100mg/l as CaCO₃ standard solution with each sample batch and plot the result in X chart to ensure that the results within the criteria of acceptance to continue the method.

Recovery control chart:

- The %recovery of spiked matrix is plot against time in a control chart.
- N.B: the control charts are printed every 20 readings.

Reagent Blank:

- A reagent blank or method blank consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure.
- The reagent blank is used to determine the contribution of the reagents and the preparative analytical steps to error in the measurement.
- The milliQ water or deionized water is used as reagent water. The reagent blank should be analyzed with each sample batch.

Laboratory Fortified matrix (LFM):

- One sample is select from each batch to be fortified with known concentration of nitrate standard, the fortified sample is analyzed and the sample is analyzed without fortification.

$$\% \text{ Recovery} = \frac{(\text{LFM sample result} - \text{sample result})}{\text{known LFM added concentration}} \times 100\%$$

Duplicate sample:

- At least 10% of each sample batch shall be analyzed in duplicate.

Relative percent difference (RPD)

$$RPD = \frac{(\text{sample result} - \text{duplicate result})}{(\text{sample result} + \text{duplicate result})/2} \times 100\%$$

Laboratory-Fortified Blank (LFB)

- A laboratory-fortified blank is a reagent water sample to which a known concentration of the analytes of interest has been added. A LFB is used to evaluate laboratory performance and analyte recovery in a blank matrix. As a minimum, include one LFB with each sample set (batch).

$$\% \text{ Recovery} = \frac{\text{found value}}{\text{true value}} \times 100\%$$

المراجع

• تم الإعداد بمشاركة المشروع الألماني GIZ

• و مشاركة السادة :-

- د/ سناء أحمد الإله شركة مياه الشرب والصرف الصحى بالفيوم
- د/ شعبان محمد على شركة مياه الشرب والصرف الصحى بالفيوم
- د/ حمدى عطيه مشالى شركة مياه الشرب والصرف الصحى بالغربية
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