Potentiometery

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Potentiometry is a method used in electroanalytical chemistry, usually to find the concentration of a solute in solution. In potentiometric measurements, the potential between two electrodes is measured using a high impedance voltmeter. Potentiometry is a method used in electroanalytical chemistry to measure electrochemical potential of charged particles. An electrode system is used to measure this potential and detect ions while other substances are also present. Two electrodes are placed in an analyte solution and connected to a potentiometer**.**

Principle

- This is the method in which the potential between two electrodes is measured while the electric current (usually nearly zero) between the electrodes is controlled. In the most common forms of potentiometry, two different types of electrodes are used. The potential of the indicator electrode varies, depending on the concentration of the analyte, while the potential of the reference electrode is constant. Potentiometry is probably the most frequently used electro analytical method. It can be divided into two categories on the basis of the nature of the indicator electrode. If the electrode is a metal or other conductive material that is chemically and physically inert when placed in the analyte, it reflects the potential of the bulk solution into which it is dipped. Electrode materials that are commonly used for this type of potentiometry include platinum, gold, silver, graphite, and glassy carbon.

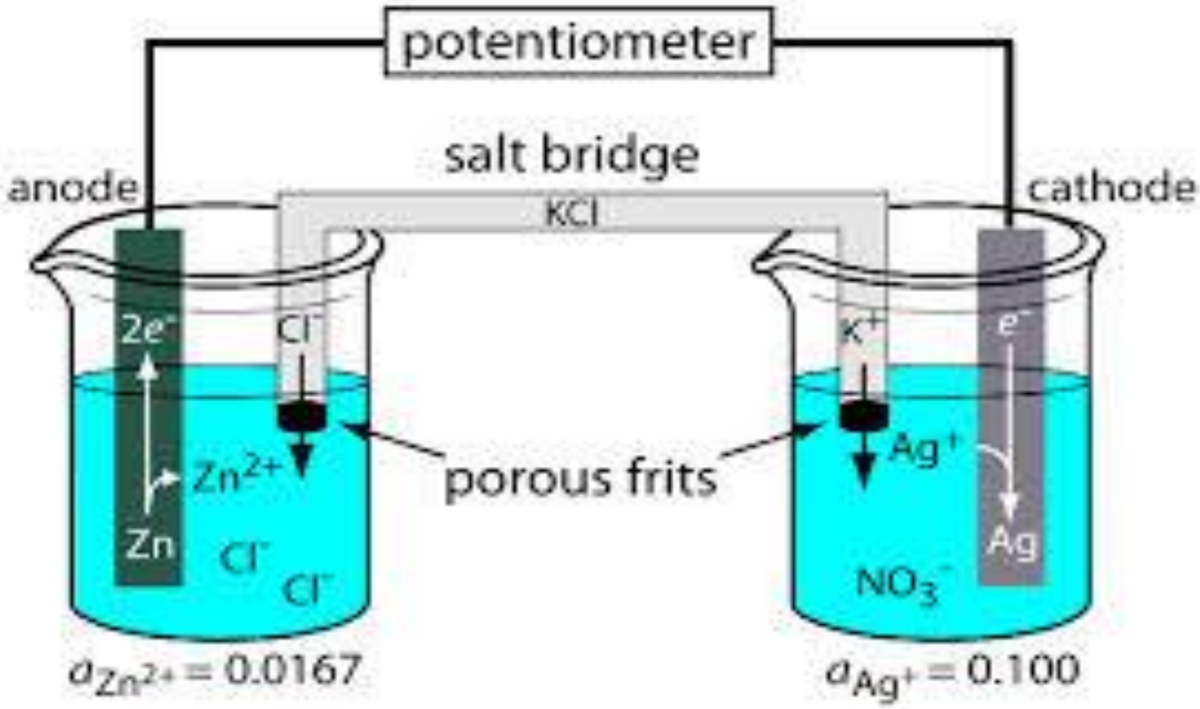
By convention, we identify the electrode on the left as the anode and assign to it the oxidation reaction; thus

$$Zn(s) \leftrightharpoons Zn^{2+}(aq) + 2e^-$$

The electrode on the right is the **cathode**, where the reduction reaction occurs.

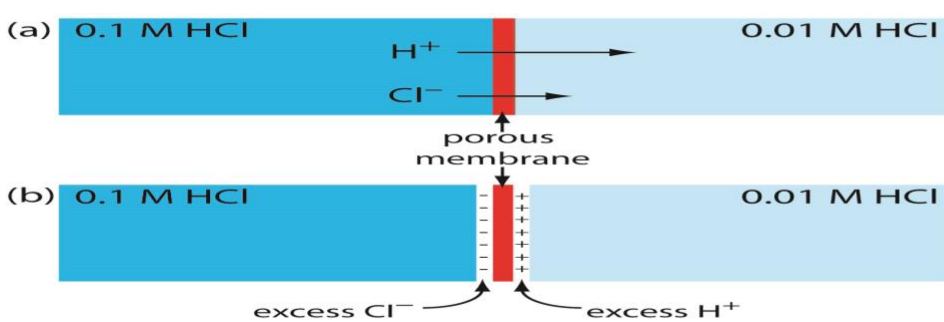
$$Ag^+(aq) + e^- \leftrightharpoons Ag(s)$$

We also define potentiometric electrochemical cells such that the cathode is the indicator electrode and the anode is the reference electrode



Junction Potentials

A **junction potential** develops at the interface between two ionic solution if there difference in the concentration and mobility of the ions. Consider, for example, a porous membrane separating solutions of 0.1 M HCl and 0.01 M HCl(fig a) . Because the concentration of HCl on the membrane's left side is greater than that on the right side of the membrane, H^+ and Cl^- diffuse in the direction of the arrows. The mobility of H^+, however, is greater than that for Cl^-, as shown by the difference in the lengths of their respective arrows. Because of this difference in mobility, the solution on the right side of the membrane has an excess of H^+ and a positive charge. Simultaneously, the solution on the membrane's left side develops a negative charge because there is an excess concentration of Cl^-. We call this difference in potential across the membrane a junction potential, which we represent as E_j.



Reference Electrodes

- In a potentiometric electrochemical cell one half-cell provides a known reference potential and the potential of the other half-cell indicates the analyte's concentration. By convention, the reference electrode is the anode; thus, the short hand notation for a potentiometric electrochemical cell is

$$E_{cell} = E_{ind} - E_{ref} + E_{j}$$

- The ideal reference electrode provides a stable, known potential so that any change in *E*cell is attributed to analyte's effect on the potential of the indicator electrode. In addition, the ideal reference electrode should be easy to make and to use.

Introduction

- Electro analytical methods have a long history of development. Ion-selective potentiometry is one of the electro analytical methods. There are some advantages of the use of Ion selective potentiometry (ISP) which is accurate, fast, economic and sensitive in relation to the standard method, UV/VIS spectroscopy. The development of potentiometric ion-selective electrodes is a very interesting field because it has a wide range of applications in determining ions in water and other mediums.
- The use of ion-selective electrodes enables the determination of ion species in a trace. Ion-selective electrodes are suitable for analysis in industry, for control processes, for physiological measurements and environmental monitoring. In recent years it was used for the determination of many ions in the food industry such as determination of calcium in milk products, fruit juice and different kinds of vegetables. In our experiment measurement of bottled water using ISP showed lower level of fluoride compared to measurement by UV/VIS spectroscopy. This results confirmed higher sensitivity of ISE in reference to UV/VIS spectroscopy

Ion-selective electrodes-example

Most ion-selective electrodes fall into one of the following classes:

1. *Glass membranes* for H^+ and certain monovalent cations (i.e. H+ electrode)

2. *Solid-state electrodes* based on inorganic salt crystals(e.g. F-electrode uses a Eu2+-doped

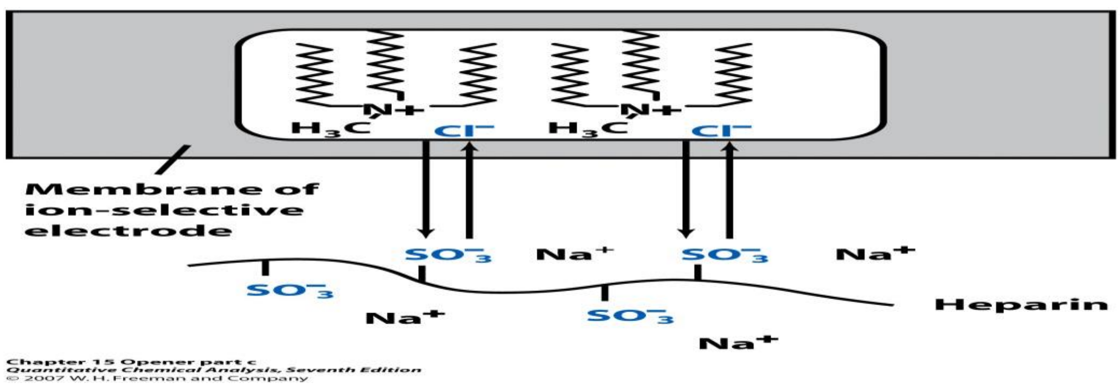
LaF3 crystal)

3. *Liquid-based electrodes* using a hydrophobic polymer membrane saturated with a hydrophobic liquid ion exchanger(e.g. Ca2+ electrode uses a liquid

chelator)

4. *Compound electrodes* with a species-selective electrode enclosed by a membrane that is able to separate that species from others or that generates the species in a chemical reaction. (e.g. CO_2 gas sensing electrode)

- Electrodes that respond selectively to specific analytes in solution or in the gas phase.
- Ion exchange between heparin and Cl^- associated with tetraalkylammonium ions in the membrane of the ion-selective electrode.

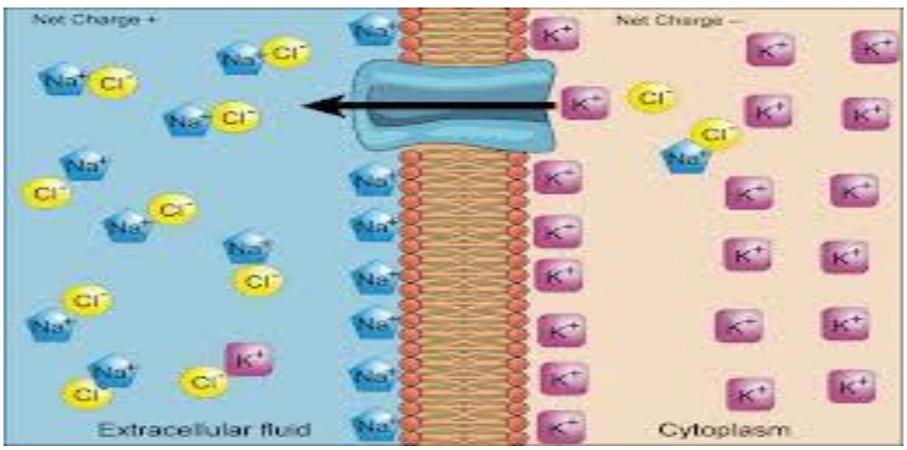


Why there is a need to use potentiometry

- When blood flow to part of the heart is interrupted, potentially lethal changes in ionic concentrations occur. To study such an event, chemists, engineers, and doctors pooled their knowledge to create flexible, miniature ion-selective electrodes that could be inserted into a beating heart. Fabrication of the device required photolithographic techniques from the microelectronics industry and polymer know-how to produce a mechanically flexible end product. Adhesion of the various layers to one another was a significant challenge in making a practical device.
- Membrane potentials are responsible for the operation of the nervous systems of living organisms. Chemists make use of Membrane potentials to construct chemical sensors for various ions in aqueous solutions. Hydrogen, sodium, potassium, and fluoride ions are routinely determined by these sensors. The pH electrode is the most common membrane sensor. It uses a glass membrane to detect H+.
- Simple concentration gradients—differential concentrations of a substance across a space or a membrane—but in living systems, gradients are more complex. Because cells contain proteins, most of which are negatively charged, and because ions move into and out of cells, there is an electrical gradient, a difference of charge, across the plasma membrane. The interior of living cells is electrically

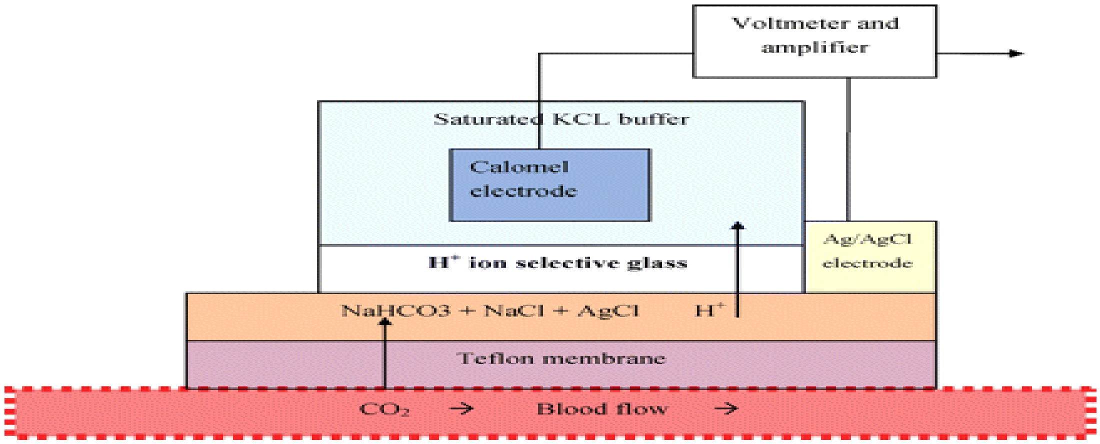
negative with respect to the extracellular fluid in which they are bathed; at the same time, cells have higher concentrations of potassium (K^+) and lower concentrations of sodium (Na^+) than does the extracellular fluid.

- Thus, in a living cell, the concentration gradient and electrical gradient of Na^+ promotes diffusion of the ion into the cell, and the electrical gradient of Na^+ (a positive ion) tends to drive it inward to the negatively charged interior. The situation is more complex, however, for other elements such as potassium. The electrical gradient of K^+ promotes diffusion of the ion *into* the cell, but the concentration gradient of K^+ promotes diffusion *out* of the cell. The combined gradient that affects an ion is called its **electrochemical gradient**, and it is especially important to muscle and nerve cells.



Respiratory gas analysis

- Respiratory gas analysis has now become a standard monitoring technique in an anesthesia in theatres, intensive care unit, and for the transfer of ventilated patients. Recommendations for Standards of Monitoring during Anaesthesia and Recovery. An appreciation of the current systems available and their design allows the user to utilize the best monitor for each situation.
- Therefore, current flows in the presence of oxygen and the current strength is directly proportional to the concentration of oxygen present, in the range of voltages used. A concentration gradient exists between the dissolved oxygen in the measured substance (usually blood) and the electrolyte solution because of the consumption of oxygen.



Equipment required "to do"
Potentiometry

- High-input impedance voltmeter
- Reference Electrode

Saturated Calomel Electrode (SCE)

Silver/Silver Chloride Electrode

- Indicator Electrode

Direct (Galvanic) electrodes

Membrane electrodes (Ion-selective)

Indirect electrodes
Reference Electrode

A galvanic cell that can monitor the quotient $[Fe2^{+}]/[Fe3^{+}]$ in the right half-cell.

The electrode potential

$$E^{+} = 0.771 – 0.05916 \log([Fe^{2+}]/[Fe^{3+}])$$

$$E- = 0.222 – 0.05916 \log([Cl^{-}])$$

$$E = E^{+} - E^{-}$$

The Pt wire is the ***indicator electrode*.**

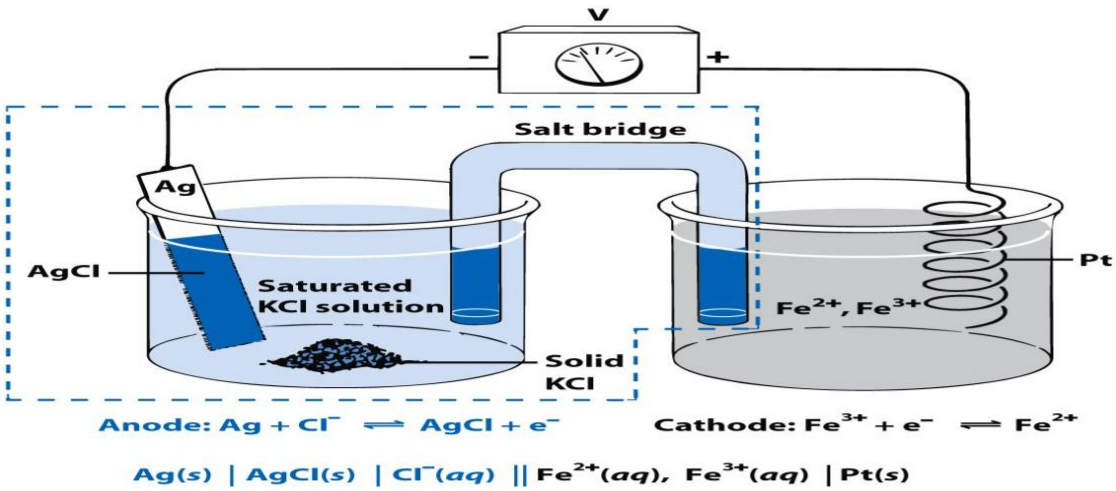


Figure 15-1
Quantitative Chemical Analysis, Seventh Edition

Silver-silver chloride electrode: a ***reference electrode***.

Silver/Silver Chloride Reference Electrode

AgCl(s) + e-   Ag(s) + Cl- (sat'd

E = 0.197 V

- Notice that the internal solution is SATURATED in Cl- vital part of any electrochemical sensing system is the reference electrode, which is a probe that is capable of measuring the potential on the solution side of an electrochemical interface.
- SILVER or silver chloride electrodes are commonly used as reference electrodes in electrophysiological studies, with ion-selective electrodes and with oxygen electrodes. It has generally been assumed that these electrodes are biologically inert. However, while studying the oxygen sensitivity of isolated arterioles, we discovered that the Ag-AgCl reference electrodes, used in conjunction with oxygen micro electrodes, exerted marked toxic effects on arteriolar vascular smooth muscle

Ion Selective Electrode

- Respond selectively to one ion.
- Do not involve redox processes.
- Features a thin membrane capable of binding only the intended ion.
- The electric potential difference across the ion-selective membrane is measured with two reference electrodes

Potentiometry: ISEs

Types of Ion Selective Electrode (based on membranes)

1. Glass membrane - pH electrode

2. Solid state (crystal) membrane

a. Single crystal mobility type

b. Solubility type

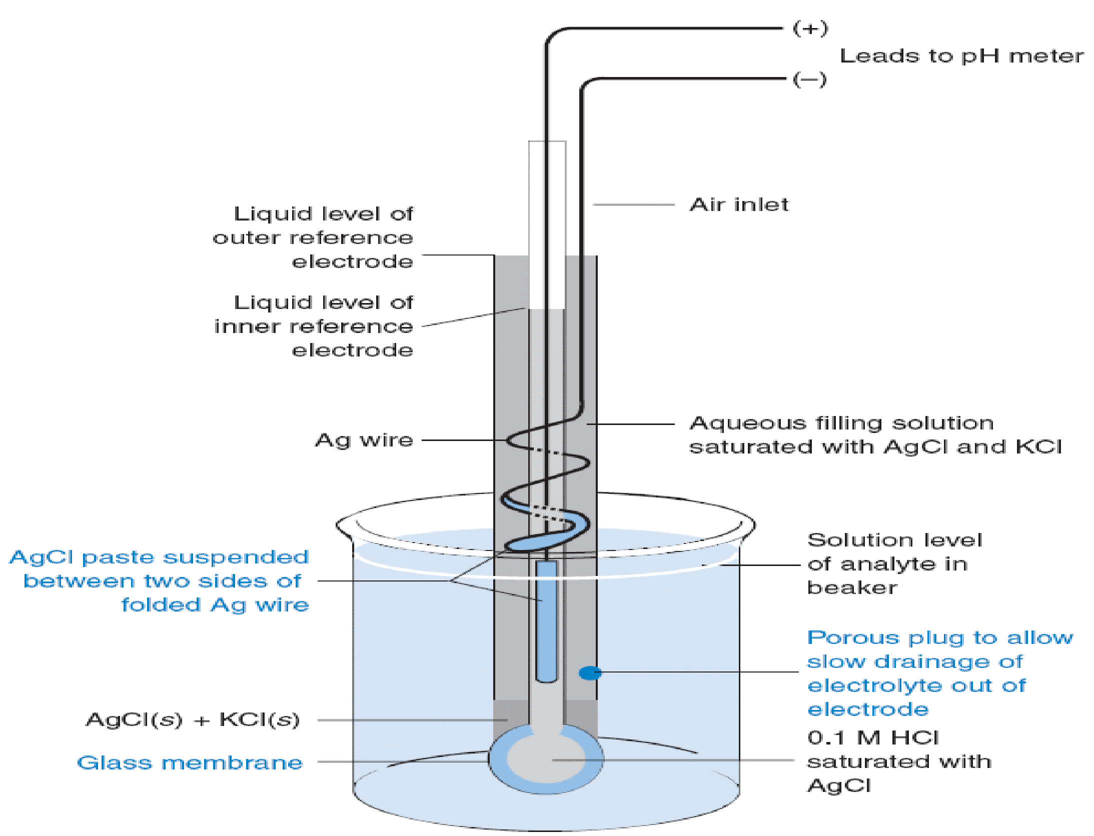
3. Liquid membrane

4. Indirect electrodes

pH measurements with a Glass electrode

- The **glass electrode** used to measure pH is the most common *ion-selective electrode.*
- A typical pH **combination electrode,** incorporating both glass and reference electrodes in one body.
- Glass combination electrode with a silver-silver chloride reference electrode. The glass electrode is immersed in a solution of unknown pH so that the porous plug on the lower right is below the surface of the liquid. The two silver electrodes measure the voltage across the glass membrane.
- The potential difference between inner and outer silver-silver chloride electrodes depends on the chloride concentration in each electrode compartment and on the potential difference across the glass membrane.
- Because $[Cl^-]$ is fixed in each compartment and because $[H^+]$ is fixed on the inside of the glass membrane, the only variable is the pH of analyte solution outside the glass membrane.

The voltage of the ideal pH electrode changes by 59.16 mV for every pH-unit change of analyte activity at 25°C.



Glass membrane selectively binds H^+

$$\underbrace{Ag(s) \mid AgCl(s) \mid Cl^-(aq)}_{\text{Outer reference electrode}} \parallel \underbrace{H^+(aq,\ \text{outside})}_{\text{H}^+ \text{ outside glass electrode (analyte solution)}} \vdots \underbrace{H^+(aq,\ \text{inside})}_{\text{H}^+ \text{ inside glass electrode}},\ \underbrace{Cl^-(aq) \mid AgCl(s) \mid Ag(s)}_{\text{Inner reference electrode}}$$

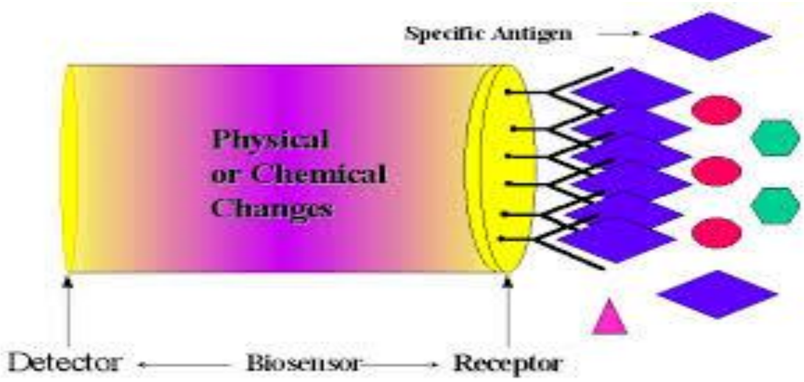
Errors in pH measurement

1. Standards.
2. Junction potential
3. Junction potential drift.
4. Sodium error.
5. Acid error.
6. Equilibration time.
7. Hydration of glass.
8. Temperature.
9. Cleaning

Pharmaceutical applications

Potentiometry used in Biosensing

- A biosensor (Figure 1)is defined by the International Union of Pure and Applied Chemistry (IUPAC) as a self-contained integrated device that is capable of providing specific quantitative or semi-quantitative analytical information using a biological recognition element (biochemical receptor), which is retained in contact direct spatial with a transduction element. Biosensing systems and methods are being developed as suitable tools for different applications, including bioprocess control, food quality control, agriculture, environment, military and in particular, for medical applications. The main classes of bioreceptor elements that are applied in environmental analysis are whole cells of microorganisms, enzymes, antibodies and DNA. Additionally, in the most of the biosensors described in the literature for environmental applications electrochemical transducers are used .
- Metabolic functions of organs are reflected in the concentrations of organic compounds or inorganic ions contained in biological fluids. Therefore, the determinations of these compounds are very important in clinical diagnosis. Various sensing systems such as biosensors have been studied. The biosensing system has great advantages of its simplicity and short measurement time compared with the conventional spectrophotometric method.



Urea biosensor

We found that a platinum electrode coated with electropolymerized insulating polypyrrole (PPy) showed a stable Nernstian response to pH. The electropolymerization process is also capable of immobilizing enzymes in combination with polyion complexes. Using this method, we fabricated a urea biosensor with urease as the enzyme for the hydrolysis of urea, which was accompanied by a pH change as follows. The biosensor shows a high sensitivity to urea. In addition, this sensor is applicable to the flow injection analysis to perform a rapid and continuous assay of urea

Creatinine biosensor

We also succeeded in applying the same system to fabricate a highly sensitive creatinine microbiosensor for diagnosis of renal, thyroid and muscular functions on the basis of the similar principle. In addition, with these results, molecular sieving effects of PIC were studied. This enables us to make a variation of sensitivity for the sensors with the PIC structure.

Glucose biosensor

Amperometric glucose sensor, which detects the hydrogen peroxide (H_2O_2) electrochemically generated by enzymatic reaction of glucose catalyzed by glucose oxidase (GOD), was fabricated. GOD is immobilized into the polyion complex (PIC) membrane. Platinum, which is known for electrocatalytic activity for the oxidation of H_2O_2, is electrode posited in the PIC membrane, and highly sensitive glucose sensor was constructed by using this technique.

Enzyme reaction: Glucose + O_2 --> Gluconolacton + H_2O_2

Electrochemical oxidation: H_2O_2 --> $2H^+ + O_2 + 2e^-$

Pharmaceutical application

An accurate potentiometric titration is proposed for the determination of norfloxacin in pure drug and in its dosage forms.

The present paper, describes the applicability of potentiometric titrations and differential potentiometric titrations of Ciprofloxacin and Gatifloxacin by titrating it with cerium(IV) in nitric acid medium using combined platinum electrode. The proposed method offers many advantages such as; sensitivity, simple, rapid. Also, it has been successfully applied for the determination of CPFX and GTFX in pure and pharmaceutical forms.

The electrode displays a good selectivity for drugs with respect to a number of common foreign inorganic and organic species. It can be used in a pH range 4.5-6.0. The membrane sensor was successfully applied to the determination of fluconazole in its capsules as well as in its recovery from blood serum and urine samples.

A simple, precise, rapid and low-cost potentiometric method for captopril determination in pure form and in pharmaceutical preparations is proposed. Captopril present in tablets containing known quantity of drug was potentiometrically titrated in aqueous solution with NaOH using a glass pH electrode.

Potentiometer play a part in the field of environmental quality, medicine and industry mainly by identifying material and the degree of concentration present.

- Food Analysis
- Study of biomolecules and their interaction
- Drug Development
- Crime detection
- Medical diagnosis (both clinical and laboratory use)
- Environmental field monitoring
- Quality control
- Industrial Process Control
- Detection systems for biological warfare agents.