EXPERIMENT 14

pH determination of liquids and dispersed systems

OBJECTIVE

To determine the pH of the different pharmaceutical liquids and dispersed systems.

Discussion

- A pH meter is a device used for potentiometric pH measurements.
- It is an electronic instrument measuring the pH (acidity or alkalinity) of a liquid.

Discussion

- The pH probe measures the pH as the activity of hydrogen cations surrounding a thin-walled glass bulb at its tip.

Discussion

- The circuit of a simple pH meter usually consists of operational amplifiers in an inverting configuration, with a total voltage gain of about -17.
- The inverting amplifier converts the small voltage produced by the probe (+0.059 volt/pH) into pH units, which are then offset by seven volts to give a reading on the pH scale.

Discussion

- For more precise measurements, a three buffer solution calibration is preferred (pH 7, pH4 and pH 10).

Discussion

- The probe is rinsed with distilled water or deionized water to remove any traces of the solution being measured, blotted with a clean tissue to absorb any remaining water which could dilute the sample and thus after the reading, and then quickly immersed in another solution.

Discussion

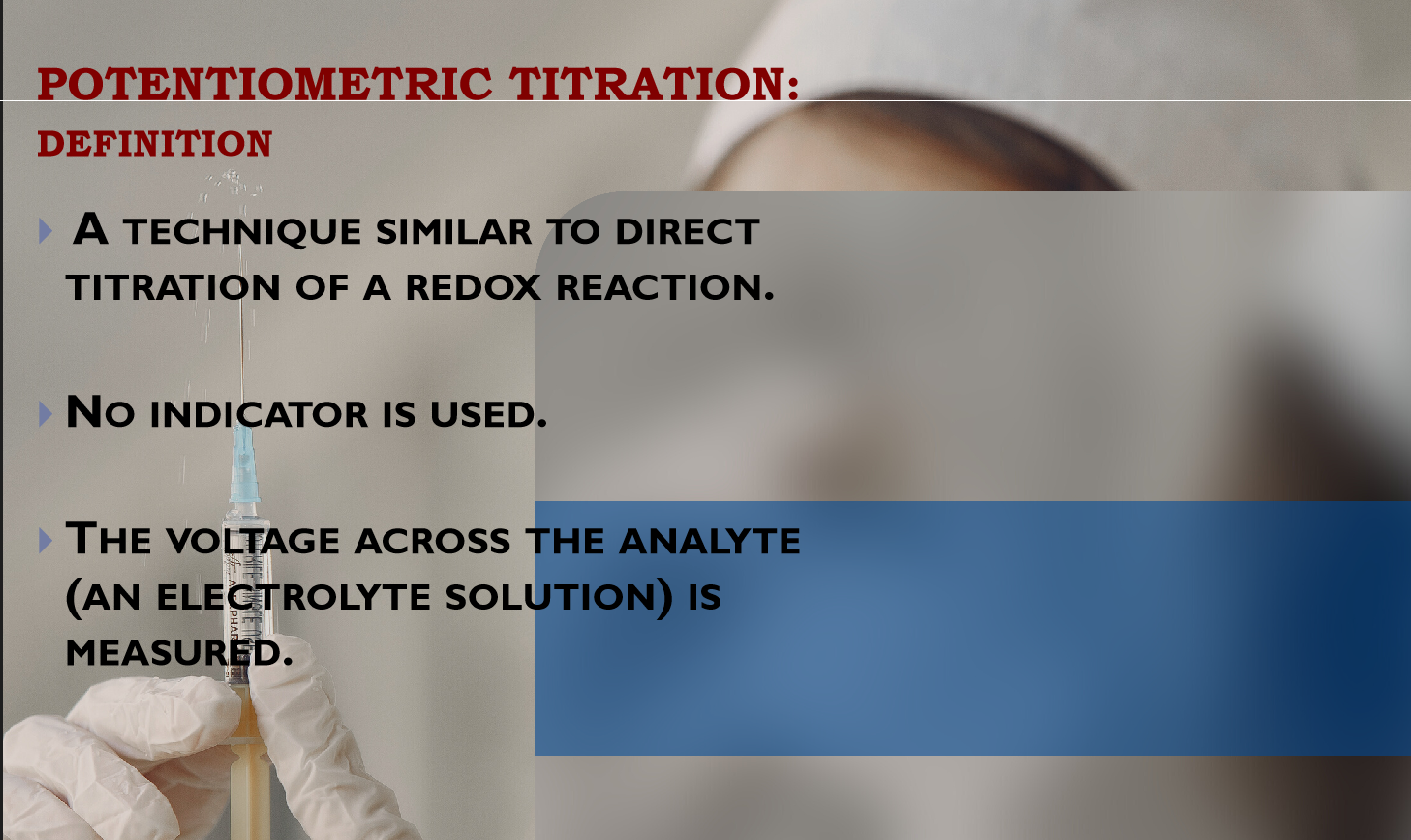
- A glass electrode alone (i.e., without combined reference electrode) is typically stored and immersed in an acidic solution of around pH 3.0.

Discussion

- pH can be measured using either pH indicators (like phenolphtalein) in a form of solution or using a pH strips- or using potentiometric method.

Discussion

- In potentiometric methods you measure potential difference between known reference electrode and the measuring pH electrode.
- Potential of the pH electrode depends on the activities of hydronium ions.



POTENTIOMETRIC TITRATION:

DEFINITION

- A TECHNIQUE SIMILAR TO DIRECT TITRATION OF A REDOX REACTION.
- NO INDICATOR IS USED.
- THE VOLTAGE ACROSS THE ANALYTE (AN ELECTROLYTE SOLUTION) IS MEASURED.

POTENTIOMETRIC TITRATION: DEFINITION

To do this, 2 electrodes are used;

1. neutral electrode
2. standard reference electrode

The voltage is recorded, at intervals, as the titrant is added.

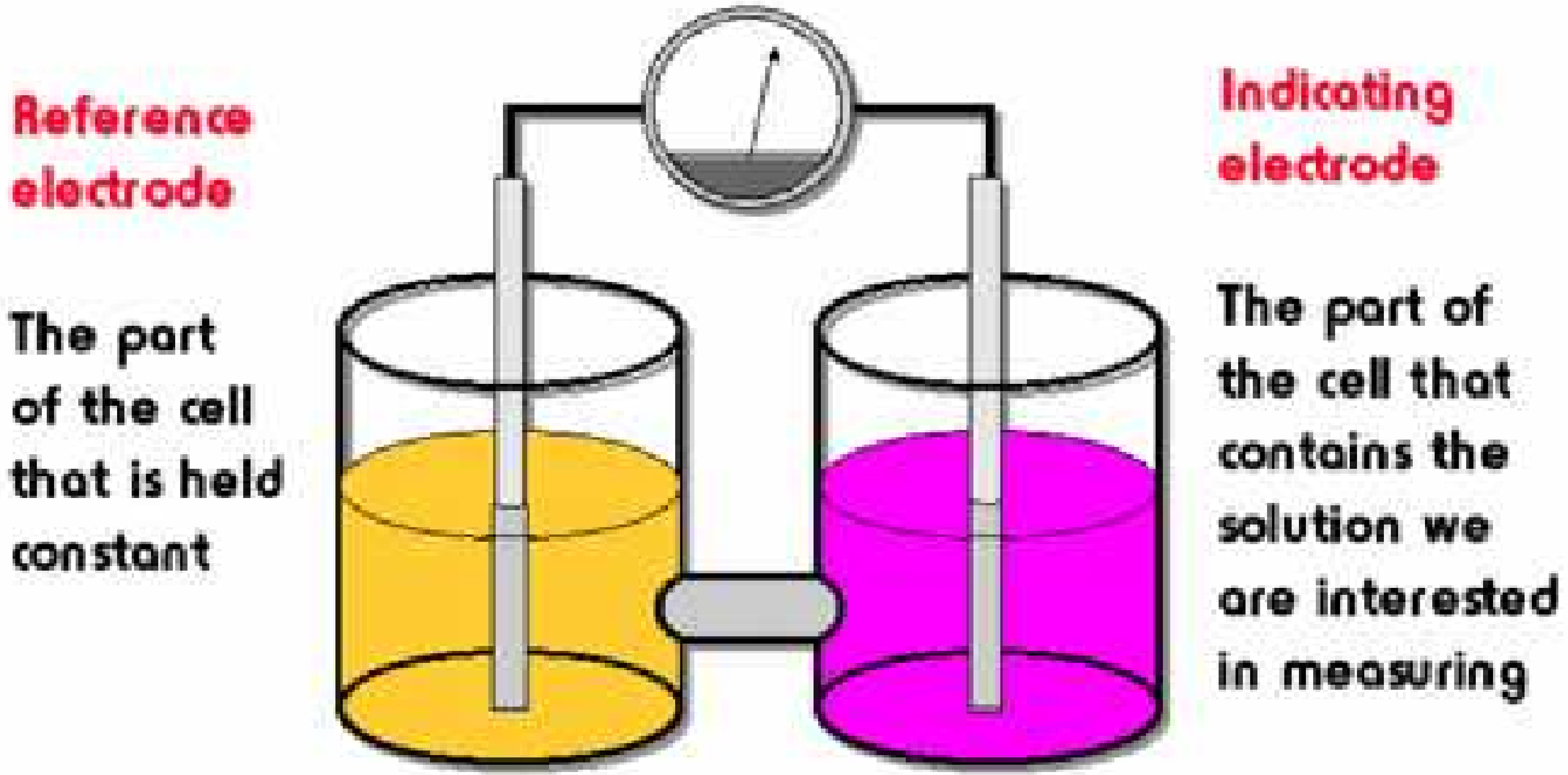
Potentiometric Titrations

- The monograph in the USP and NF usually designate the electrode pair which is to be used for a particular potentiometric titration.
  - Assay of Phenmetrazine Hydrochloride NF
    - Analyte – chloride
    - Titrant – 0.1 N silver nitrate
    - Indicator electrode - silver electrode
    - Reference electrode – mercury calomel electrode

Application

- pH Measurement
- When hydrogen ion concentrations are determined with a laboratory device such as a potentiometer or an electric instrument such as pH meter equipped with a suitable electrodes, one actually measures the activity of H+ rather than the concentration.

Potentiometric methods



POTENTIOMETRIC TITRATION:

DEFINITION

- A GRAPH OF **VOLTAGE** AGAINST THE **VOLUME ADDED** IS PLOTTED AND THE ENDPOINT OF THE REACTION IS HALFWAY BETWEEN THE **JUMP** IN VOLTAGE.

POTENTIOMETRIC TITRATION

- This method relies on the measurement of E_{cell} for quantitative analysis.

- The difference between the E values for the 2 halves of the cell gives rise to the E_{cell} .

Reference electrodes

Hydrogen electrode (SHE)

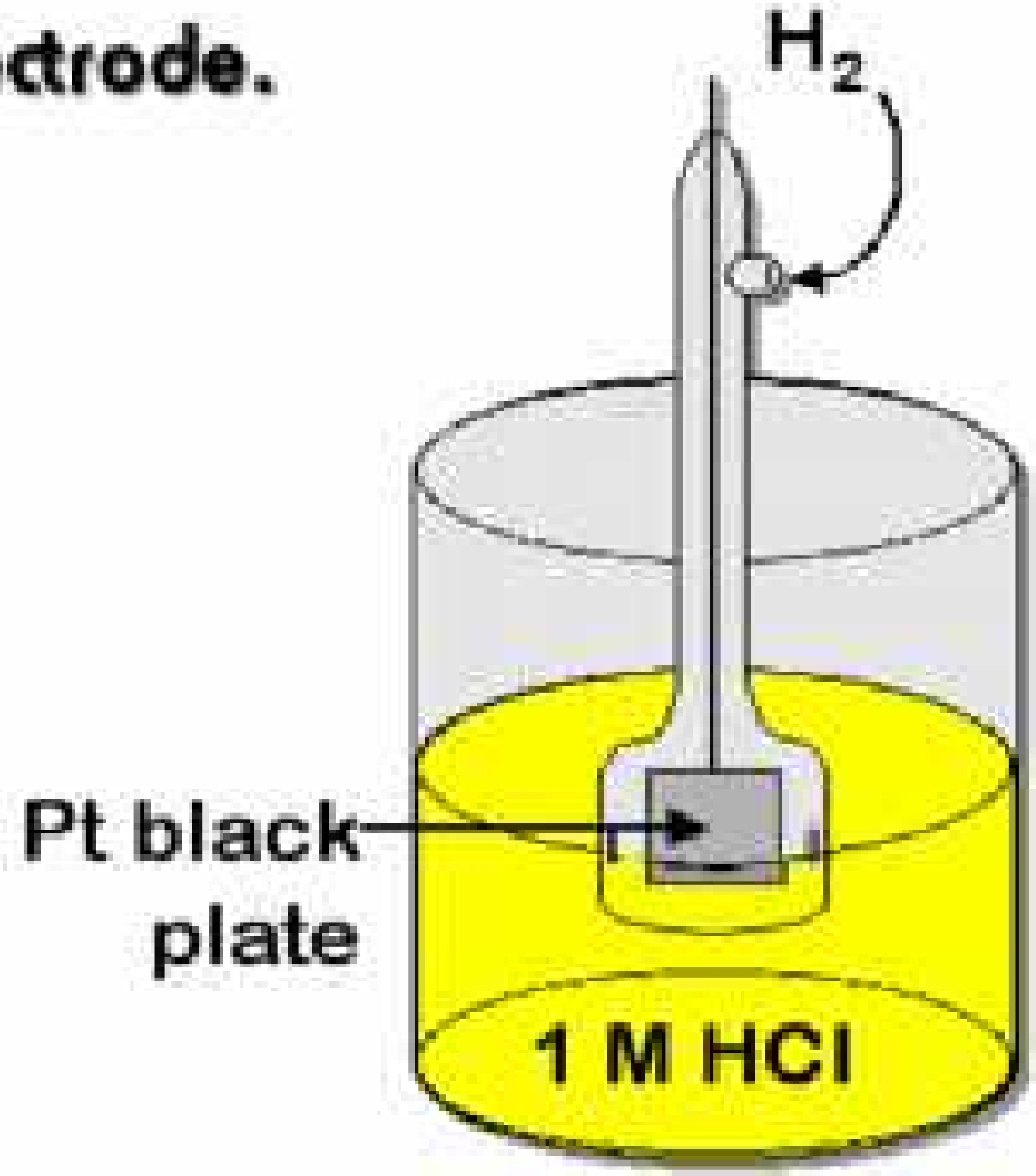
The ultimate reference electrode.

Difficult to work with.

H_2 is constantly bubbled into a 1 M HCl solution

Pt / H_2 (1atm), 1M H^+ //

E^o = 0.000000 V



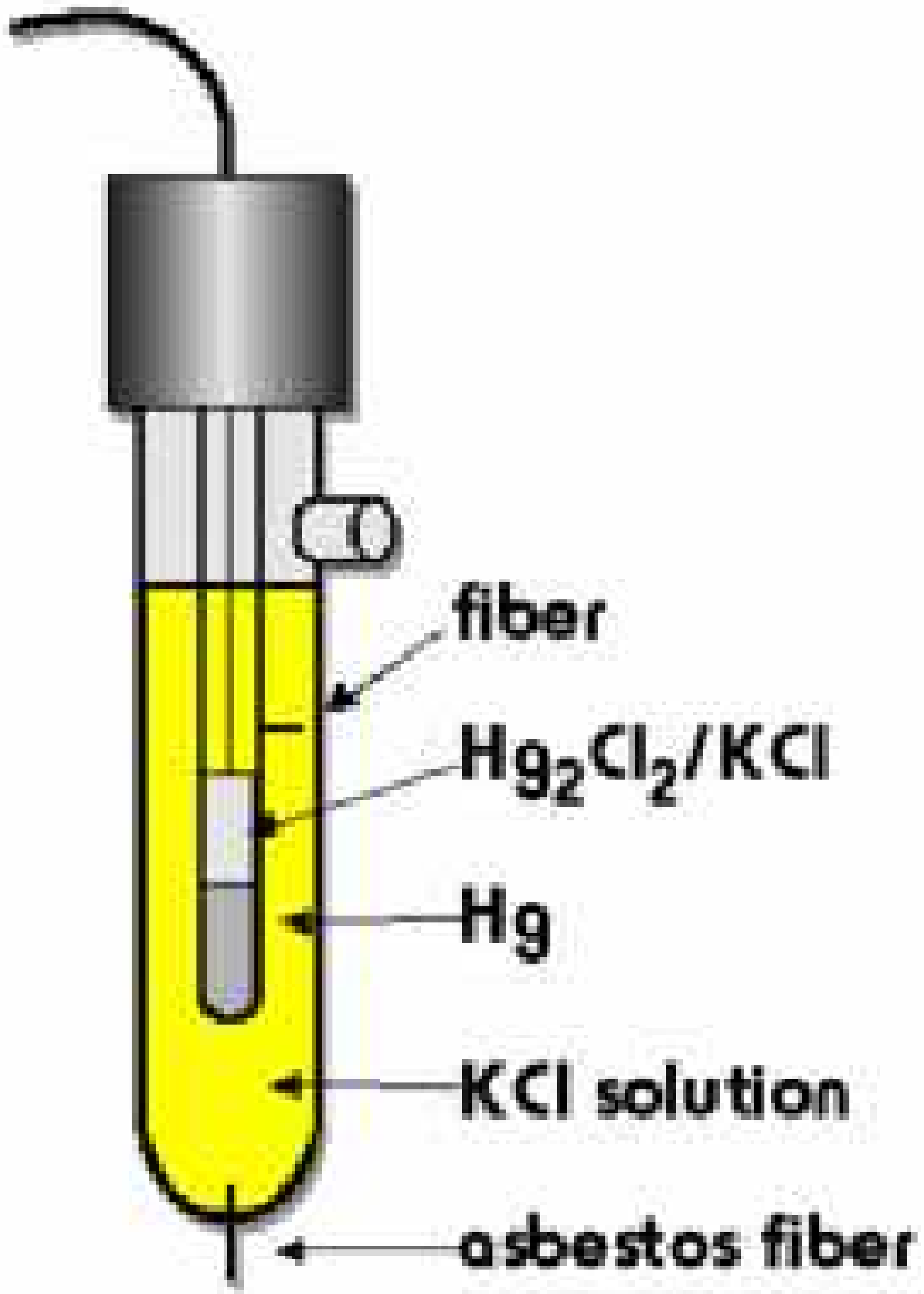
Reference electrodes

Calomel electrode (SCE)

A much more common reference electrode.

$Hg \,/\, Hg_2Cl_{2(sat)}, KCl \,//$

Chloride is used to maintain constant ionic strength.



Reference electrodes

Calomel electrode

Different KCl concentrations can be used.

0.1 M - least temperature sensitive

Saturated - easier to make and maintain.

E = 0.2444V 25°C

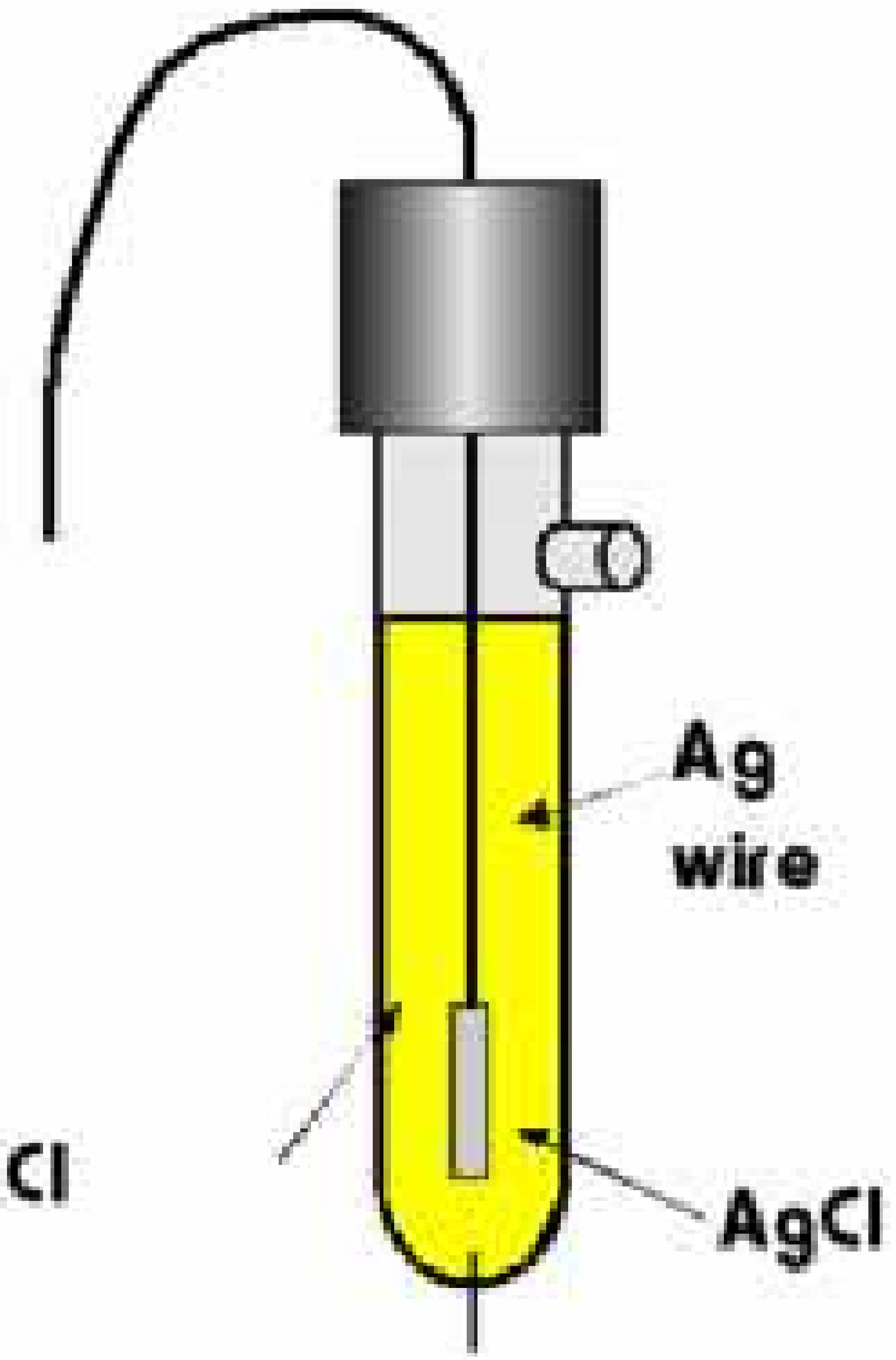
The electrode may be separate or built into the sensing electrode - combination electrode.

Reference electrodes

Ag/AgCl

Another common reference electrode.

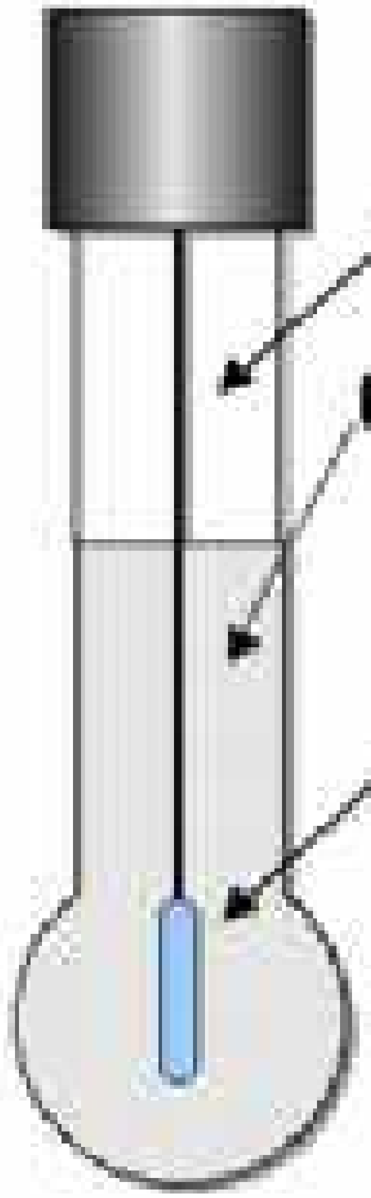
Easier to produce a combination electrode.



Membrane electrodes

A potential difference is created across a membrane that can be measured.

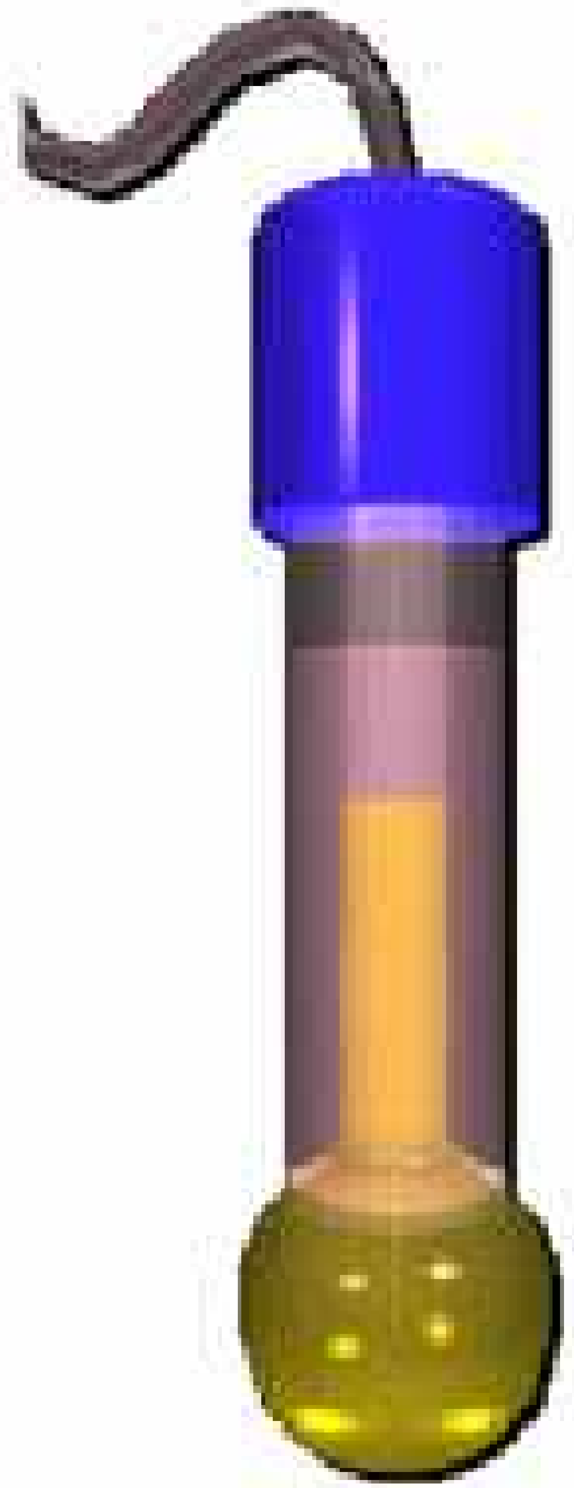
There is no change in the solution or actual contact.



pH electrode

- first discovered
- still the most significant
- relies on a glass membrane.

pH electrode



Combination electrode

The reference electrode is inside of the pH electrode.

pH electrode

Combination electrode

The reference electrode is inside of the pH electrode.

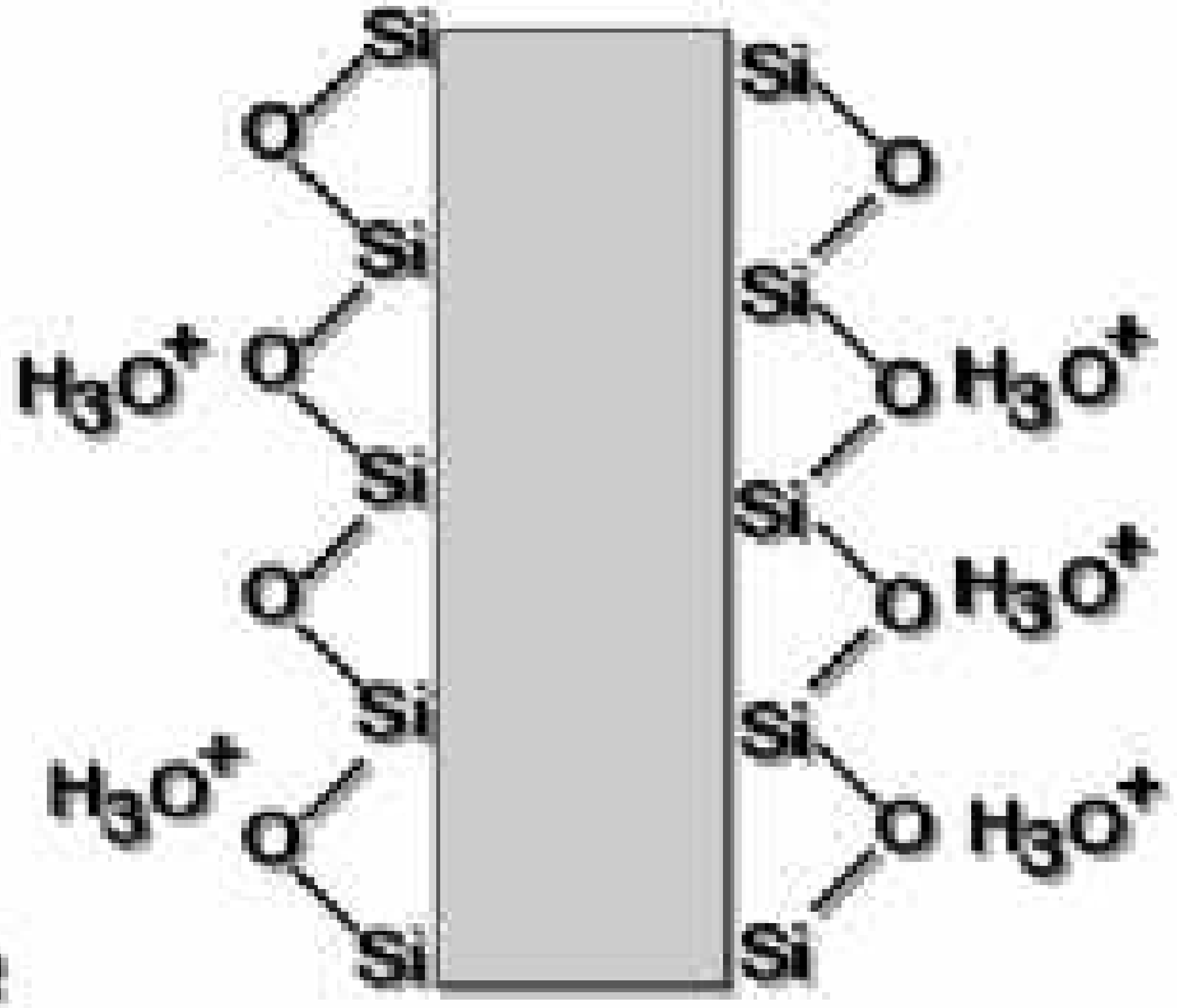
Membrane electrodes

H_3O^+ partially populates both the inner and outer SiO_2 surfaces.

The concentration difference results in a potential across the glass membrane.

A special glass is used:

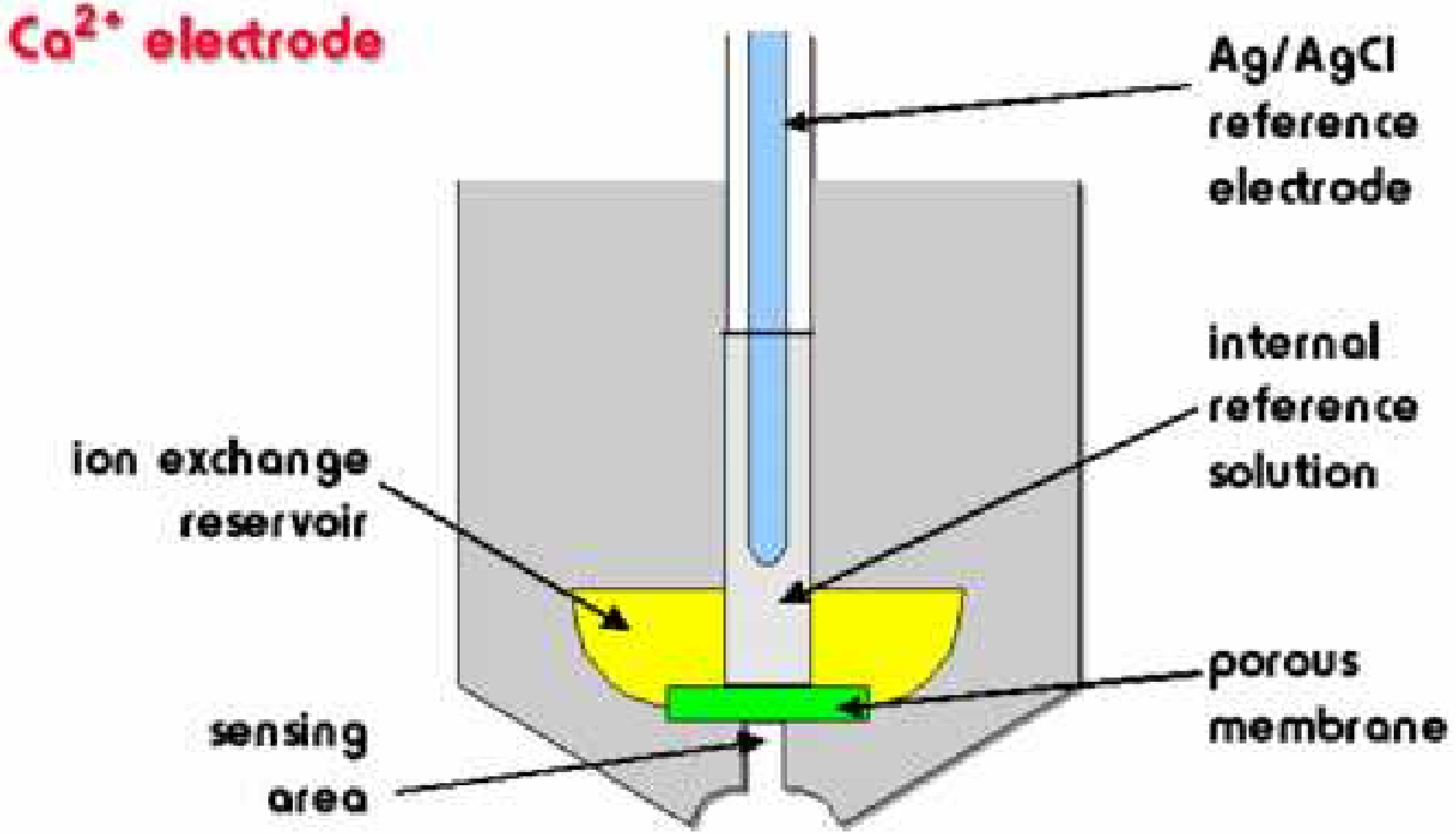
22% Na_2O, 6% CaO, 72% SiO_2



Liquid membrane electrodes

- Similar to a pH electrode except the membrane is an organic polymer saturated with a liquid ion exchanger.
- Interaction of this exchanger with target ions results is a potential across the membrane that can be measured.
- The Ca^{2+} electrode is one of the best examples.

Liquid membrane electrodes



Solid state electrodes

A very popular type of ion specific electrode.

As easy to maintain as a pH electrode.

F^- electrode

The original solid state

Works by creating defects in a LaF_3 crystal.

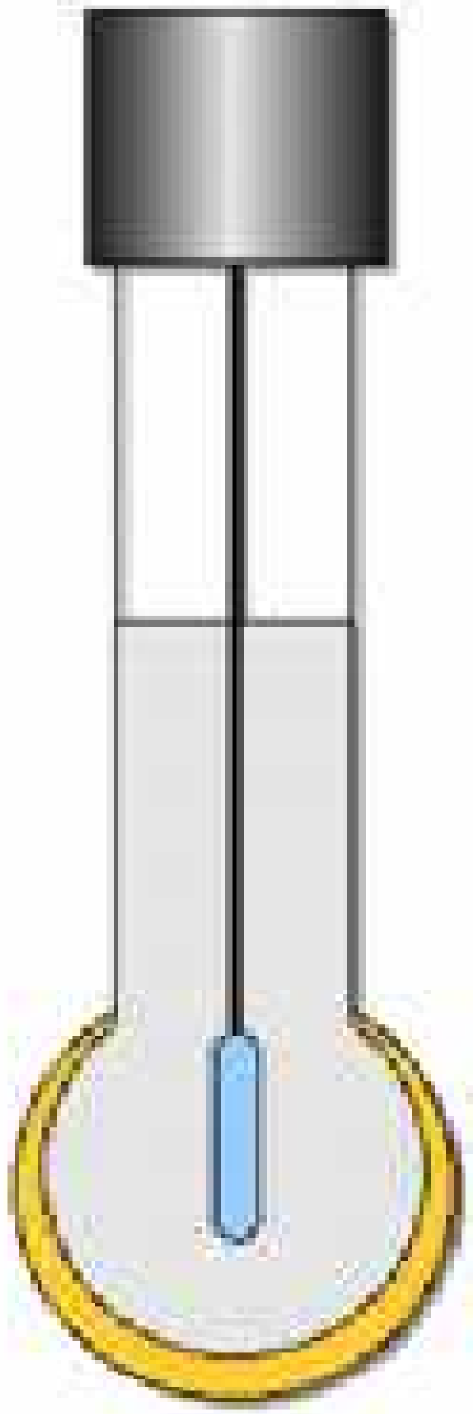
Other solid state electrodes work based on the presence of a primary absorbed ion.

Enzyme electrodes

In this example, a normal pH electrode is coated with a urease impregnated gel.

Urea will permeate the gel where the enzyme will attack it, resulting in the formation of ammonium.

The resulting change in pH can be measured.

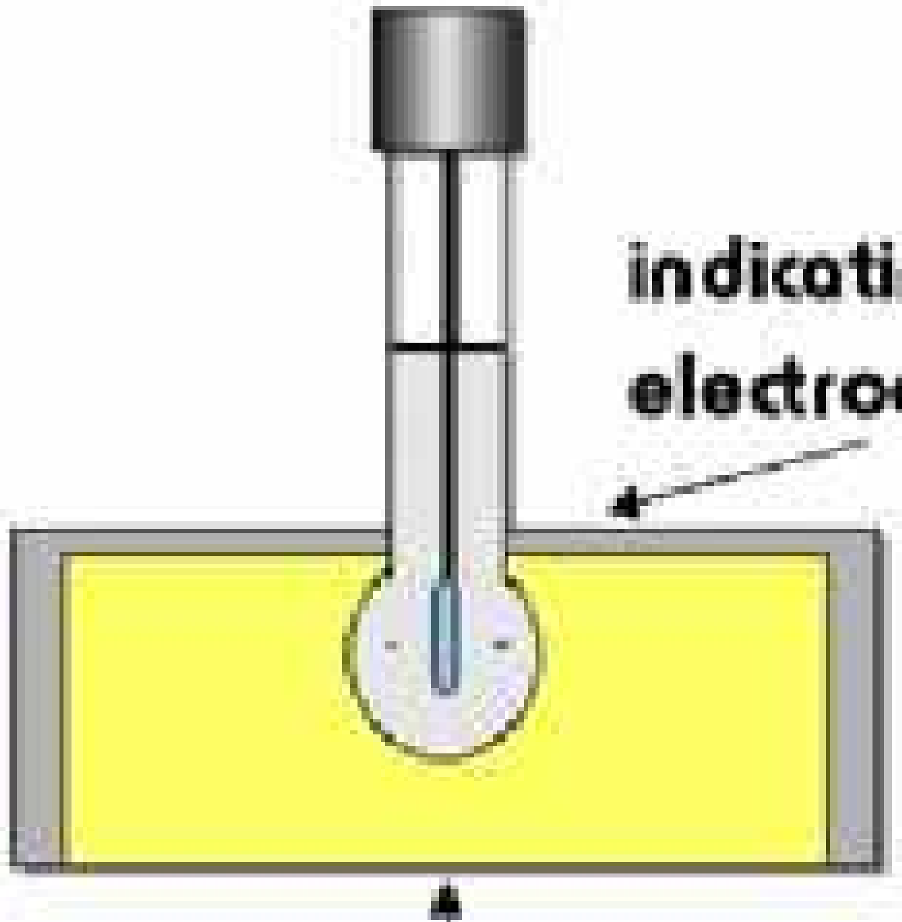


Gas sensing electrodes

Here, an indicating electrode is placed into a specific solution.

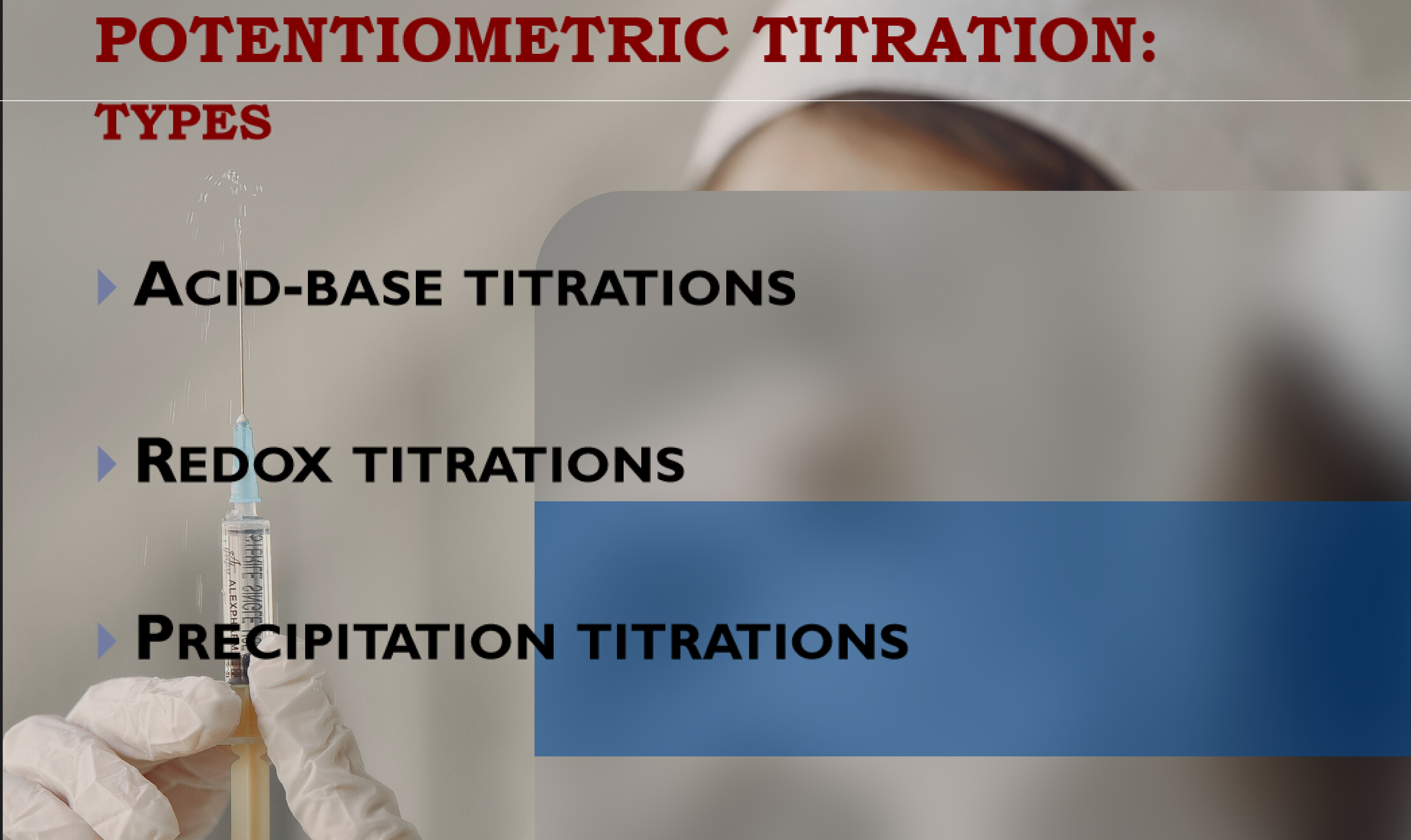
On the opposite side, there is a permeable membrane.

Permeation of the target analyte results in an equilibrium change that we can measure.



POTENTIOMETRIC TITRATION:

TYPES



- Acid-base titrations
- Redox titrations
- Precipitation titrations

MATERIALS

- Distilled water
- Lotion
- Oral solution
- Suspension
- Syrup, any brand
- Beaker, 250mL
- pH meter
- Squeeze bottle
- Tissue paper

OPERATING PROCEDURE

a)Calibration of the pH Meter

i.Condition the electrode as described in the manufacturer's instructions.

ii.Rinse the electrode (glass probe) and area around it twice with distilled water using a squeeze bottle and blot it dry with a soft tissue after each rinse. Rinse into a discard beaker or sink, not into the pH buffer solution and do not touch the electrode with your fingers.

iii.Turn the pH meter ON (by pressing the ON/OFF button). Push the CAL button to indicate that you will be calibrating the instrument.

iv.Immerse the electrode in the pH 7 buffer solution, making sure that the electrode is entirely immersed. Do not immerse the instrument further than what is necessary.

a)Calibration of the pH Meter

v. Gently stir the buffer solution with the electrode and wait for the display value to stabilize. Once the reading has stabilized, press the HOLD/CON button to accept the value and compute the calibration. If the electrode is still immersed in the buffer, the display will read the same value as the pH of the buffer (pH 7, 4, or 10).

vi. Remove the electrode from the buffer solution, rinse the electrode with distilled water and dry with soft tissue.

vii. Repeat step 3 to 9 using pH 4 and then using pH 10 buffer.

viii. Set the electrode aside; then, turn the meter OFF by pressing the ON/OFF button.

ix. Pour the buffer solution into their labeled bottles and cap them tightly.

a) pH Measurement

i. Rinse the electrode and the surrounding area with distilled water using a squeeze bottle. Blot the area dry with a soft tissue.

ii. Fill up a clean, dry 250mL beaker to the 50mL line with the sample to be tested.

iii. Immerse the electrode in the sample. Be sure that the entire electrode is immersed, but avoid immersing it any further that what is necessary.

iv. Stir once and then let the display value stabilize.

v. Once the display value is stable, read the pH value and record it.

a) pH Measurement

vi. Repeat steps 1 to step 5 for another trial of the same sample as a quality control check. The two pH values should agree to within 0.2 which is the accuracy of this technique.
vii. Rinse the electrode with distilled water, blot it dry with soft tissue and repeat step 1 to step 6 for another sample.
viii. After the test, turn the instrument OFF.