

**Pathways to precision in
soil analysis: advancing
soil laboratories in Latin
America and the
Caribbean**

**Caminos hacia la
Precisión en el Análisis de
Suelos: avance de los
Laboratorios de Suelos
en América Latina y el
Caribe**

Soil pH determination

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WORKSHOP
SANTIAGO - CHILLÁN | CHILE
8-11 APRIL 2024

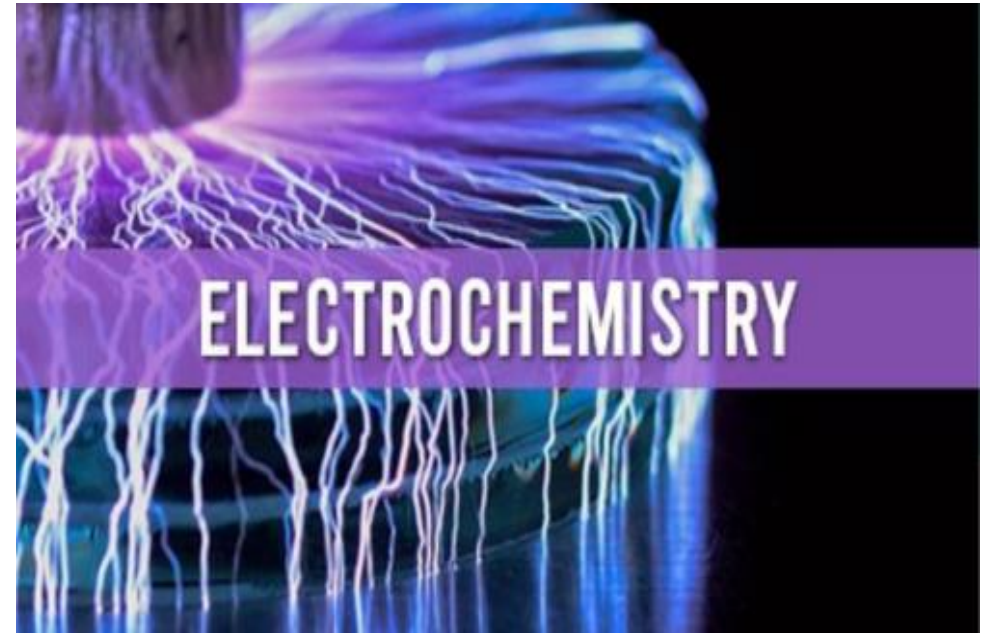


Basic concepts

- Soil pH and EC are electrochemical determinations.
- Basic concepts on these subjects are fundamental for properly measuring soil pH and EC determinations.
- We will revise the most basic concepts.

What is the electrochemistry

Electrochemistry: branch of chemistry that studies electricity **generation** through chemical reactions and the **use** of electrical parameters (intensity, etc.), for chemical analysis.



Types of cells

(1) Galvanic cells or batteries present spontaneous reactions, generating electricity.

(2) Electrolytic cells require an external electrical source (consume energy), so that a reaction can occur.

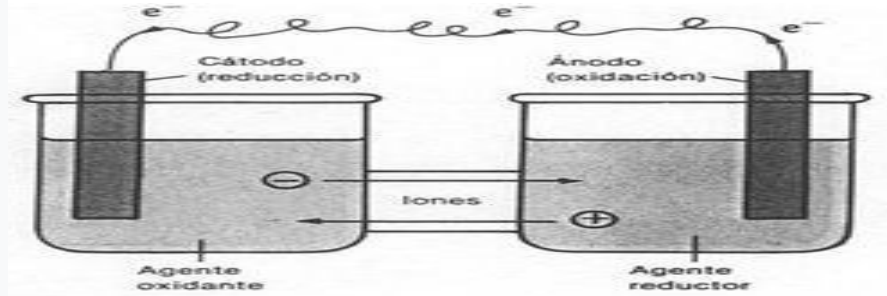


Figura 18.5
Esquema de una batería (celda galvánica).

Ánodo: Electrodo en donde se verifica la oxidación.
Cátodo: Electrodo en donde se verifica la reducción.

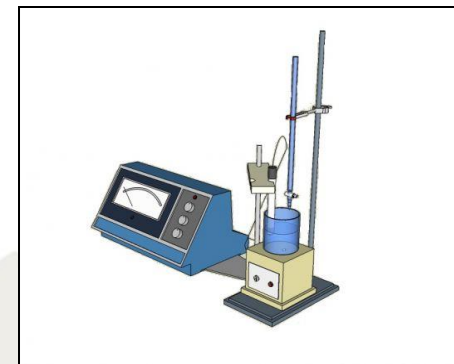


Three types of measurements:

- **Direct relationship** between concentration and an electrical parameter (potential**, intensity, resistance, conductivity**, capacitance, amount of current).
- Relationship between electrical parameters and the **end point** of a titration (potentiometric titration).
- **The analyte** is converted by the action of electric current to a **form that can be determined gravimetrically**.

Electrometric techniques for soil and plan analysis

- ❖ Potentiometric titrations (Cl⁻, F⁻, etc.....)
- ❖ Conductometry (salt concentration in soil and solutions)
- ❖ Conductimetric titrations
- ❖ Direct relation: potentiometry (pH. specific ions, electrons, redox pot....)



What is potentiometry

It is an electrochemical analytical method based on the measurement of the potential differences between electrodes (one sensitive to an ion and another used as a reference) immersed in the same solution



Potentiometric measurement

- ❖ Potentiometric measurements of ion concentration in solution are based on the similarity in the response predicted by the Nernst equation for Oxidation-Reduction (redox) reactions.
- ❖ In measurements made with ion specific electrodes (e.g. pH), there are no redox reactions.

Potentiometric measurement

- ❖ **“Attention”**: the only relation between the Nerst equation (NE) and the measurement of specific ions in solution is that NE explains changes in electric potential; there is a similarity in the response“. In potentiometric measurements there is no oxidation-reduction reactions.

Nernst Equation

$$E = E^0 - \frac{RT}{nF} \ln(Q)$$

donde:

E es el potencial corregido del electrodo.

E^0 el potencial en condiciones estándar (los potenciales se encuentran tabulados para diferentes reacciones de reducción).

R la constante de los gases.

T la temperatura absoluta (escala Kelvin).

n la cantidad de electrones que participan en la reacción.

F la constante de Faraday (aproximadamente 96500 C/mol).

$\ln(Q)$ es el logaritmo neperiano de Q que es el cociente de reacción.

Así para la reacción: $a^*A + b^*B \rightarrow c^*C + d^*D$, la expresión de Q es:

Nernst Equation

For reaction $aA + bB \longrightarrow cC + dD$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Q = equilibrium constant in redox equations

Nernst Equation

- The Nernst Equation was developed to explain the potential changes in the redox reactions.
- There is not electron exchange in measurements conducted with sensitive electrodes.

Soil pH and specific ions measurement

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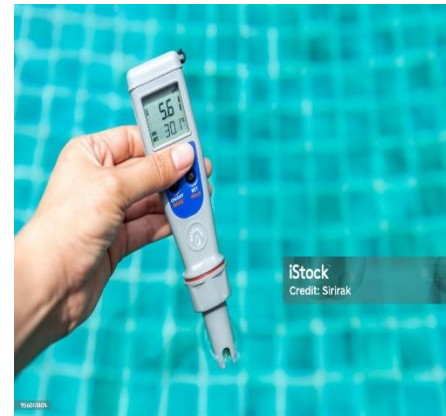
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Potenciometric techniques

Potentiometric techniques are electrometric techniques used to measure specific ions, such as soil pH and concentration of specific ions in soil solution.



Electrochemical determinations in soils

- Potenciometric
 - pH
 - Specific ions (Cl^- , NO_3^- , F^- , NH_4^+ , etc.)
 - End point of a reaction (titration)
 - Redox potential in waterlogged soils
- Conductimetric
 - Electrical conductivity (soil affected by salts)

Measurement of specific ions, what should I know?

- General principles of electrometry
- The Nernst Equation
- To know what is a cell
- To know that is an electrode
- To know what is a sensitive electrode
- To know how a sensitive electrode works
- To know what is a reference electrode
- To know how this works

Potentiometry: basic definition

- ❖ **Electrodes Cell:** Array of two externally connected electrodes and an electrolyte.
- ❖ **Electrode:** Ion-selective electrodes (ISEs) are potentiometric sensors that include a selective membrane to minimize matrix interference.
- ❖ **Electrolyte:** Ionic substance that is capable of conducting electric current when in contact with electrodes.

To measure soil pH and specific ions

Electrodes Cell: arrangement of two electrodes, one **sensitive** and one **reference**.

A **sensitive electrode** changes electrical potential in contact with ions.

Change of potential is a function of ion concentration.

To measure soil pH and specific ions

- ❖ The **reference electrode** does not change its potential.
- ❖ It allows us to see the change in the potential of the sensitive electrode.
- ❖ The electrode's cell potential changes (mV) according to the prediction of the Nernst Equation.
- ❖ A properly calibrated cell allows to know the change in concentration of an ion.

The soil pH

The determination of specific ion (as H^+) by potentiometric techniques consists of measuring the change in potential experienced by a sensitive electrode to changes of concentration of the interest ion, which forms a cell with the reference electrode that is insensitive to the interest. This electrode maintains a constant potential.

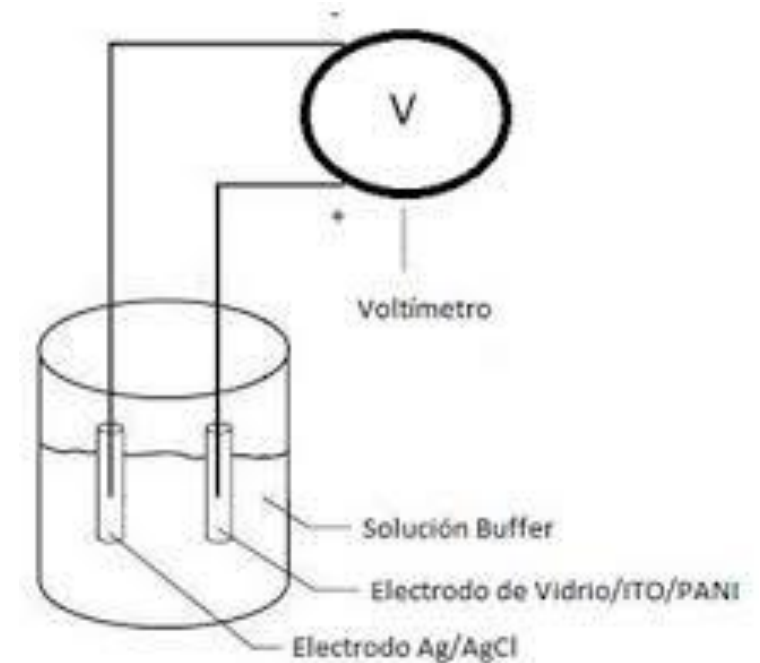
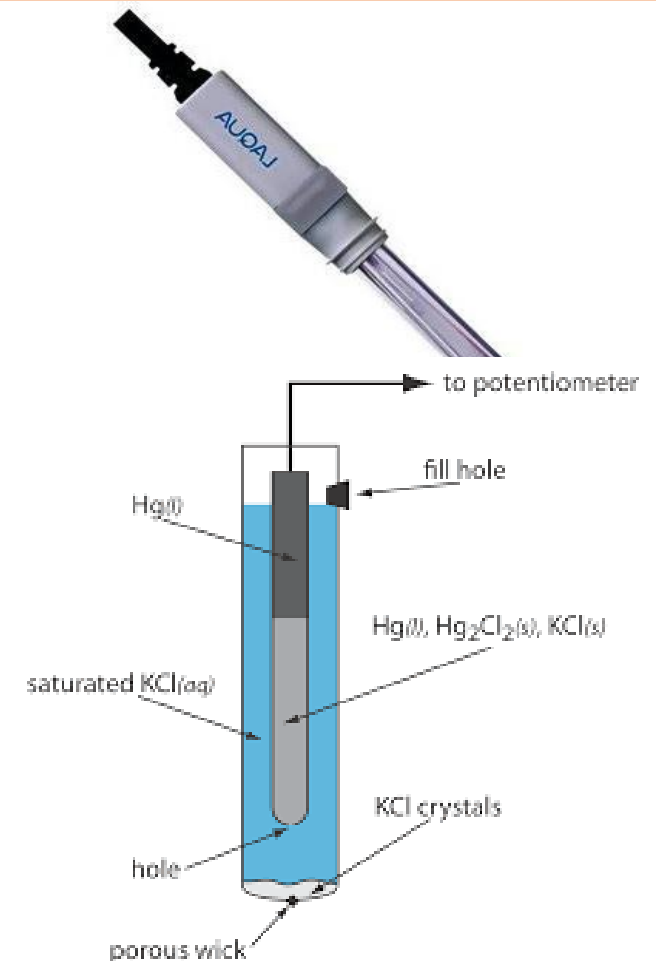


Figura 2. Celda electroquímica

Components of the cell to measure pH

Glass membrane electrode: changes potential due to changes on the glass membrane surface with the activity of H^+ ions.

Reference electrode: does not change potential with the activity of the ions. It can be made of calomel (Hg/Hg_2Cl_2) or $Ag/AgCl$. Commonly, sensitive, and reference electrodes are combined on a single stem.



Nernst equation and pH determination

$$E_{\text{obs}} = E_c + (2.3 RT/nF) \ln aH^+$$

E_{obs} = cell observed potential

E_c = reference potential + fixed and stable potentials

R = universal gas constant

T = temperature in Kelvin

N = number of e-exchanged in the redox reactions

F = Faraday constant

2.3 = conversion factor from \ln to \log

aH^+ = proton activity

Nernst equation and pH electrode

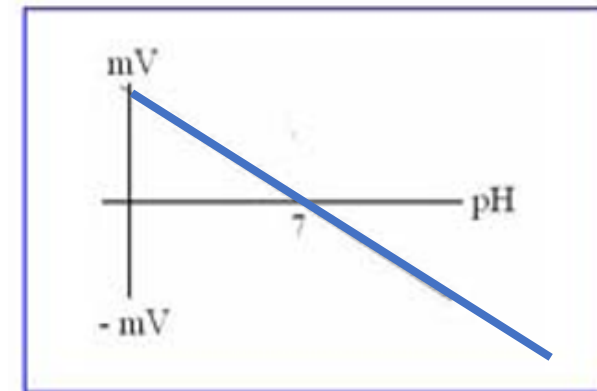
$$E_{\text{obs}} = E_c + (2.3 RT/nF) \ln a_{\text{H}^+}$$

The Nernst equation gives the slope of the pH curve vs the change of potential. It is a characteristic of the type of glass membrane.

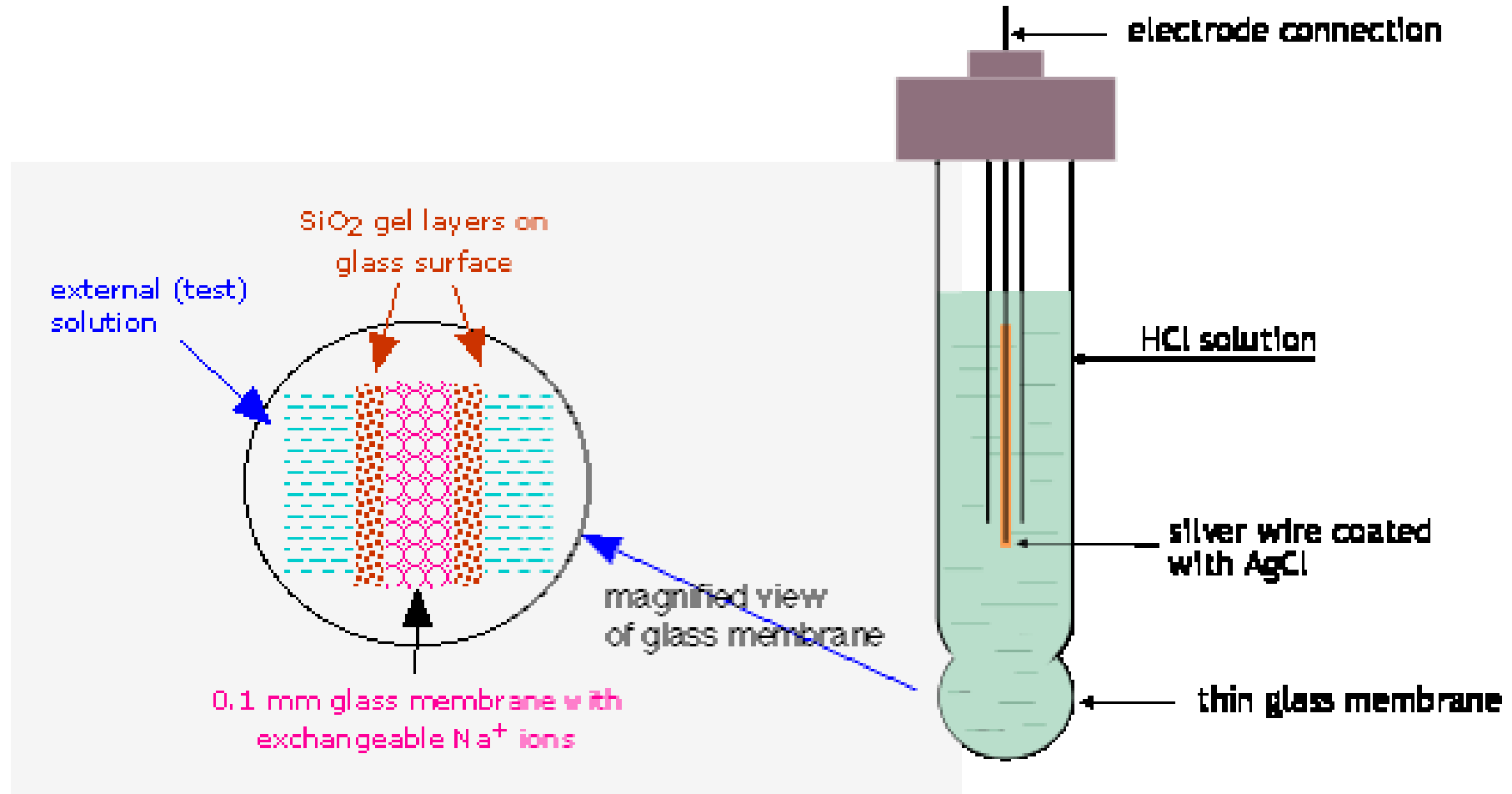
If $n=1$ (case of H^+) in the Nernst equation the value of $2.3 RT/nF = 0.0591$ volt = 59.1 mV.

If $n=2$ (case of Ca) the change of potential is 59.1 mV/2.

If $n=3$ (case of Al) the change of potential es 59.1 mV/3



Glass electrode



Potential of pH electrode

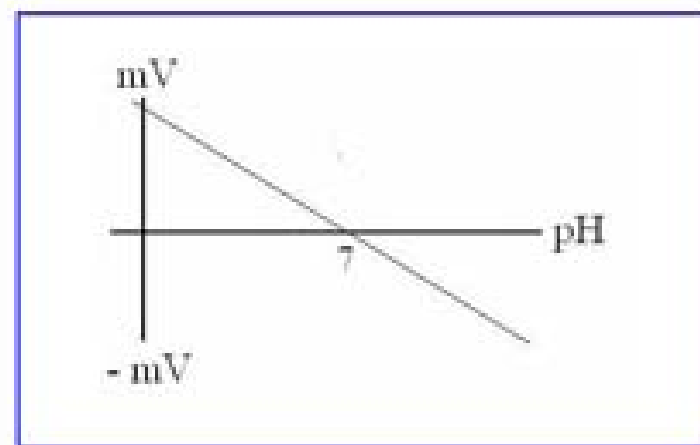
pH is the way of expressing the concentration of H^+ ions in the solution

$$E = E_0 + 2.3 \frac{RT}{F} \cdot (\log a_{H^+})$$

$$pH = -\log a_{H^+}$$

$$2.3 \frac{RT}{F} = k \cdot T \quad (\text{is called the Nernst factor, or slope factor})$$

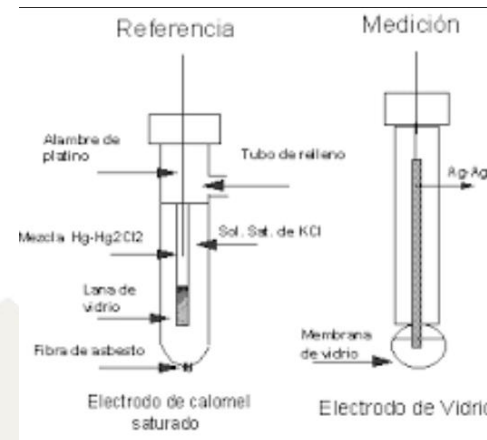
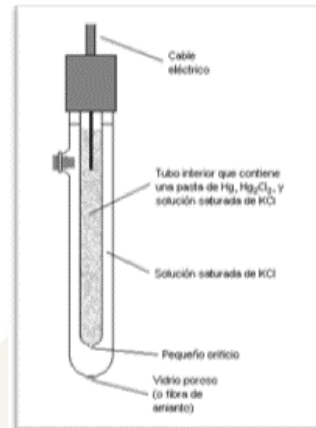
$$E = E_0 - k \cdot T \cdot pH$$



Equation of a straight line

To determine soil pH or a specific ions

- A cell (two electrodes, one sensitive, and one reference) is required.
- Each electrode generates its own potential.
- The sensitive electrode changes its potential as a function of ion concentration.
- The reference electrode does not change its potential when the concentration of the ion in the solution is changed.
- The cell potential = algebraic sum of electrode potentials.



Summary

- To make potentiometric measurements, a cell is required.
- Cell = arrangement of two electrodes.
- $E_{\text{cell}} (\text{potential}) = E_{\text{elec1}} + E_{\text{elec2}}$.
- The cell measures the change of the potential (Δ), therefore:

$$\Delta E_{\text{cell}} = \Delta E_{\text{elec1}} + \Delta E_{\text{elec2}}$$

- If the $\Delta E_{\text{elec2}} = 0$, then:

$$\Delta E_{\text{cell}} = \Delta E_{\text{elec1}} + 0$$

Determination of the soil reaction

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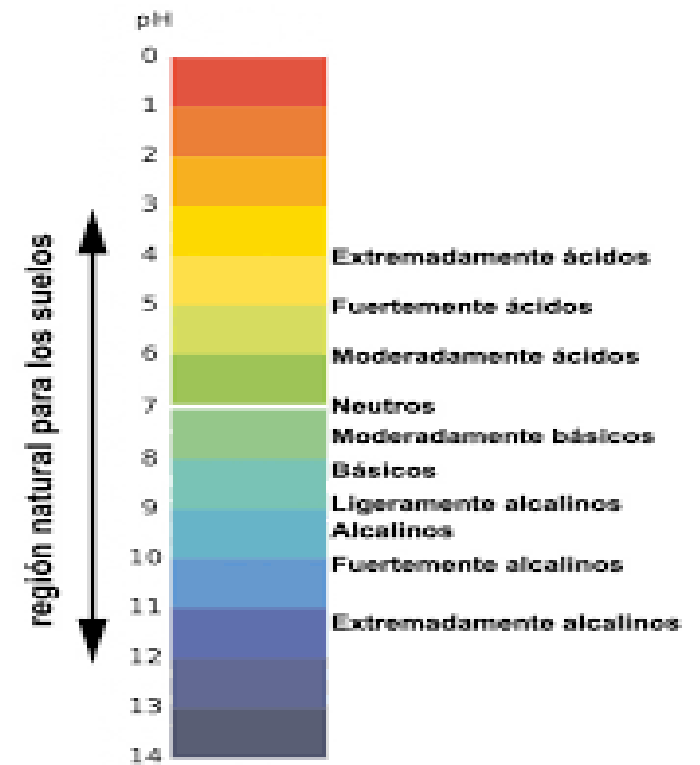
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What is the soil reaction?

- ❖ Sol reaction refers to the presence of acidic or alkaline cations in soil solution in equilibrium with the solid phase.
- ❖ Main acidic cations present on the solid phase surface and soil solution (H^+ and Al^{3+}).
- ❖ Main basic cations OH^- , $CO_3^{=}$, HCO_3^-

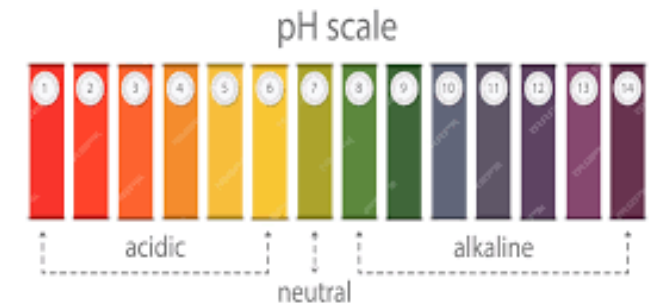


The soil reaction is due to:

- The amount of H^+ ions in the solution is in equilibrium with the solid phases.
- Most H^+ comes from the hydrolysis of Al present in the solution.
- The H^+ ions are expressed in moles L^{-1} .

How soil reaction is measured?

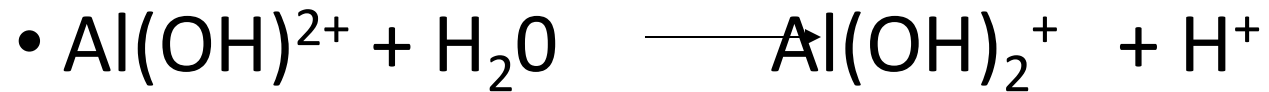
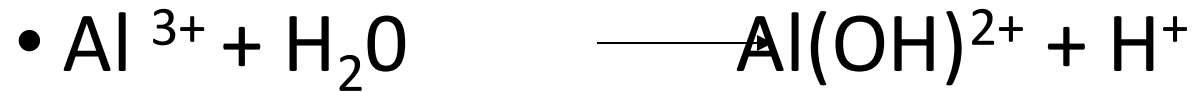
- 1.- With an indicator substance that changes color (qualitative).
- 2.- With pH meter (quantitative).
- 3.- A pH meter is a millivoltmeter coupled to a cell (reference and sensitive electrodes). The cell changes potential as the H^+ ions in the soil suspension change, compared to a estándar.
- 4.- There are technical difficulties that must be understood.



H⁺ ions: origin in the soil solution

- Most Al³⁺ comes from Al oxides and hydroxides (oxy hydroxy Al) in different states of crystallization and from alumino-silicates (clay minerals and primary minerals), which undergo some degree of decomposition or weathering.
- H⁺ also comes from organic functional groups dissociating (Ex, R-COOH → R-COO⁻ + H⁺).
- The dissociation of acids is directly proportional to the added acid to the soil to reduce CaCO₃ concentration. Ex. H₂SO₄.
- From the transformation of NH₄⁺ in fertilizers to NO₃⁻.

Principal sources of H⁺



- 3 moles of H⁺ are created for each mole of Al(OH)₃

How soil reaction is expressed?

Qualitative expression: v.g., classes of soil reaction

Quantitative expression: pH units (p function)

p función: $pX = -\log [X]$

Qualitative classes of soil reaction

- Acid reaction
- Neutral reaction
- Basic reaction

¿What is the "p" function (pX)?

- Function p expresses the concentration of ions in solution (moles L⁻¹) or K equilibrium, etc.
- Function pX

$$pX = \log \frac{1}{X} \quad \text{ó} \quad pX = -\log X$$

if X=H

$$pH = \log \frac{1}{H} \quad \text{ó} \quad pH = -\log H$$

if X=Ca

$$pCa = \log \frac{1}{Ca} \quad \text{ó} \quad pCa = -\log Ca$$

What is pH?

- Sorensen (1909):

$$\text{pH} = \log \frac{1}{a_{\text{H}^+}}$$

$$a = \gamma \times C$$

“a” and “ γ ” are the activity and de activity coefficient

In diluted solutions, as the soil solution

$$\gamma \approx 1$$

then “a” is similar to C

then

$$\text{pH} = \log \frac{1}{[\text{H}^+]}$$

pH scale

The pH scale was arbitrarily set at 14 degrees. It is based on the dissociation constant of water ($K_w=10^{-14}$)

- $K_w = [H^+] [OH^-] = 10^{-14}$

The función **p** of the above expression is:

$$-\log K_w = \{-\log [H^+] \} + \{-\log [OH^-] \} = -\log 10^{-14} \quad (x - 1)$$

$$pK_w = pH + pOH = 14$$

What is potentiometry?

- ❖ Analytical technique to measure the concentration of ionic species as a function of the change in potential experienced by a sensitive electrode to that species.
- ❖ Sensitive electrodes (glass membranes, ion exchange resins, solid state crystals, and heterogeneous electrodes) experience potential changes induced by a change in the activity of a specific ion in a solution.
- ❖ Potential change is interpreted by analogy with changes predicted by the Nernst equation.

Why a pH electrode change 0.059 volts when the concentration of H^+ changes 10 times

If the constant values are substituted into:

$$E = E_o - RT/nF \ln aX$$

and \ln transformed to \log , and being $X=H^+$, F = Faraday constant (96.406 J/V), R universal k of ideal gases (8.31 J/mol °K), and T temperature (298 °K) and the factor to convert \ln to \log 2.303

If $n=1$ then the RT/nF value is 0.059 V for every 10-fold change in $[H^+]$

$$E = E_o - 0.0591 \log aH^+ \text{ or } E_o - 0.0591 \text{ pH}$$

What is the voltage change for each pH

If the constant values are substituted into

$$E = E_o - RT/nF \ln aX$$

and Ln transformed to log, and being $X=H^+$, F = Faraday constant (96.406 J/V), R universal k of ideal gases (8.31 J/mol °K), and T temperature (298 °K) and the factor to convert Ln to log 2.303.

If $n=1$ then the RT/nF value is 0.059 V (59 mV) for every 10-fold change in $[H^+]$

$$E = E_o - 0.0591 \log aH^+ \text{ or } E_o - 0.0591 \text{ pH}$$

Para explicar verbalmente en inglés durante la práctica

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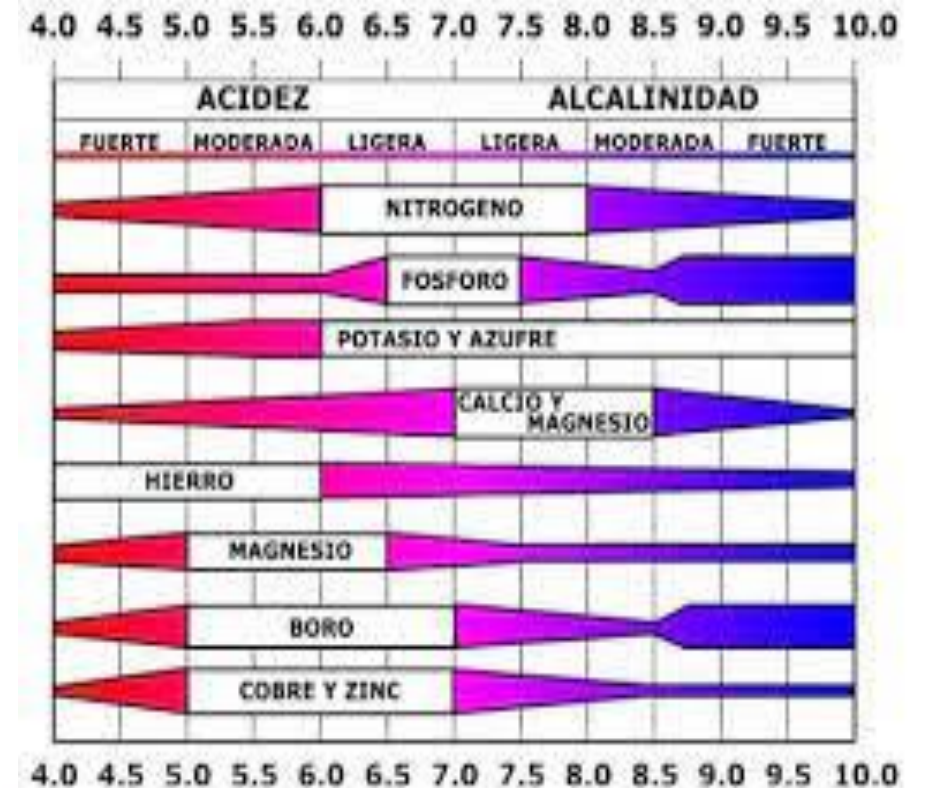
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Por qué nos interesa el pH del suelo

- pH del suelo se relaciona con:
 - Adaptabilidad de los cultivos a cierto pH
 - Disponibilidad de nutrientes
 - Ciertas enfermedades relacionadas con pH suelo



El pH en el suelo

- Mide la actividad de los iones (H^+) en solución de suelo en equilibrio con fase sólida
- Ph mportante en la producción de cultivos y en la química del suelo:
 - disponibilidad de nutrientes y de sustancias tóxicas
 - actividad y naturaleza de las poblaciones microbianas
 - actividad de ciertos pesticidas
- Variación del pH:

$$pH = \log \frac{1}{[H^+]} = -\log [H^+]$$



Al aumentar la actividad de los iones H^+ en la solución,
disminuye el valor del pH del suelo

El pH en el suelo

- pH regulado por: monómeros y polímeros de hidroxialuminio, materia orgánica y (en los suelos alcalinos) carbonato no disueltos
- Condición de equilibrio cuando se adiciona ácido o base

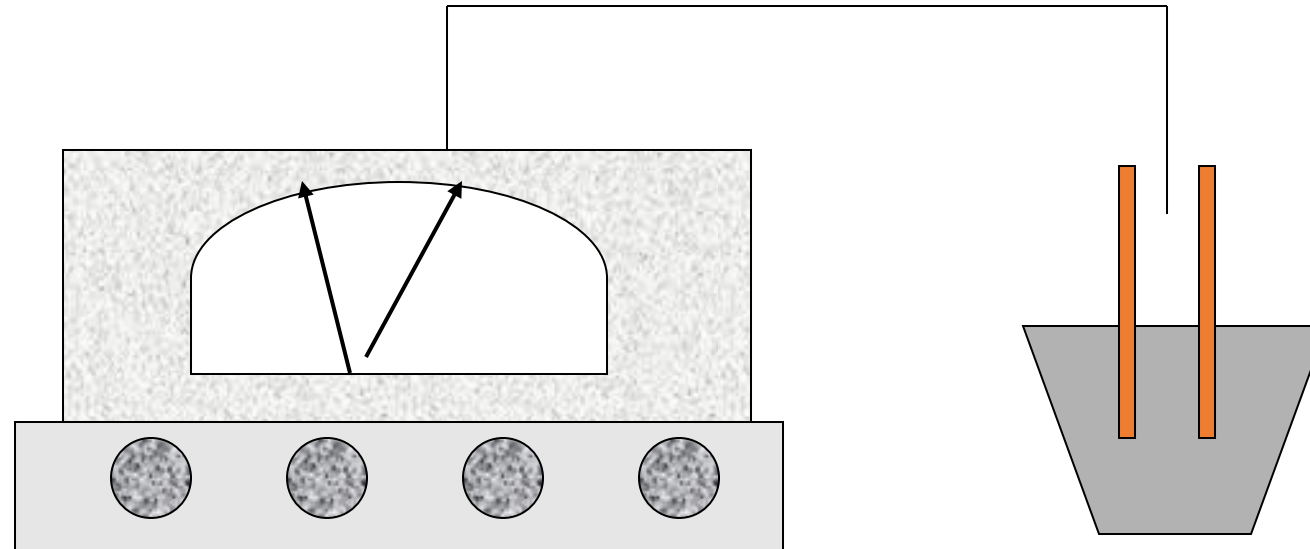


capacidad reguladora del suelo
(mantener el equilibrio original)

- límites de pH del suelo 4 a 8

Medida del pH

Medida Directa: Potenciómetro "pH metro"



Mide la concentración de iones H^+ en una solución, usando un **electrodo INDICADOR (vidrio)** y uno de **REFERENCIA (Ag/AgCl ó calomelano)**, introduciendo ambos en la solución de pH desconocido, previa calibración

Componentes "pH metro"

electrodo de indicador
(vidrio)

- * [ácido] fija en el interior
- * responde a la $[H^+]$

electrodo de referencia
(Ag/AgCl, calomelano)

- * voltaje independiente de la $[H^+]$

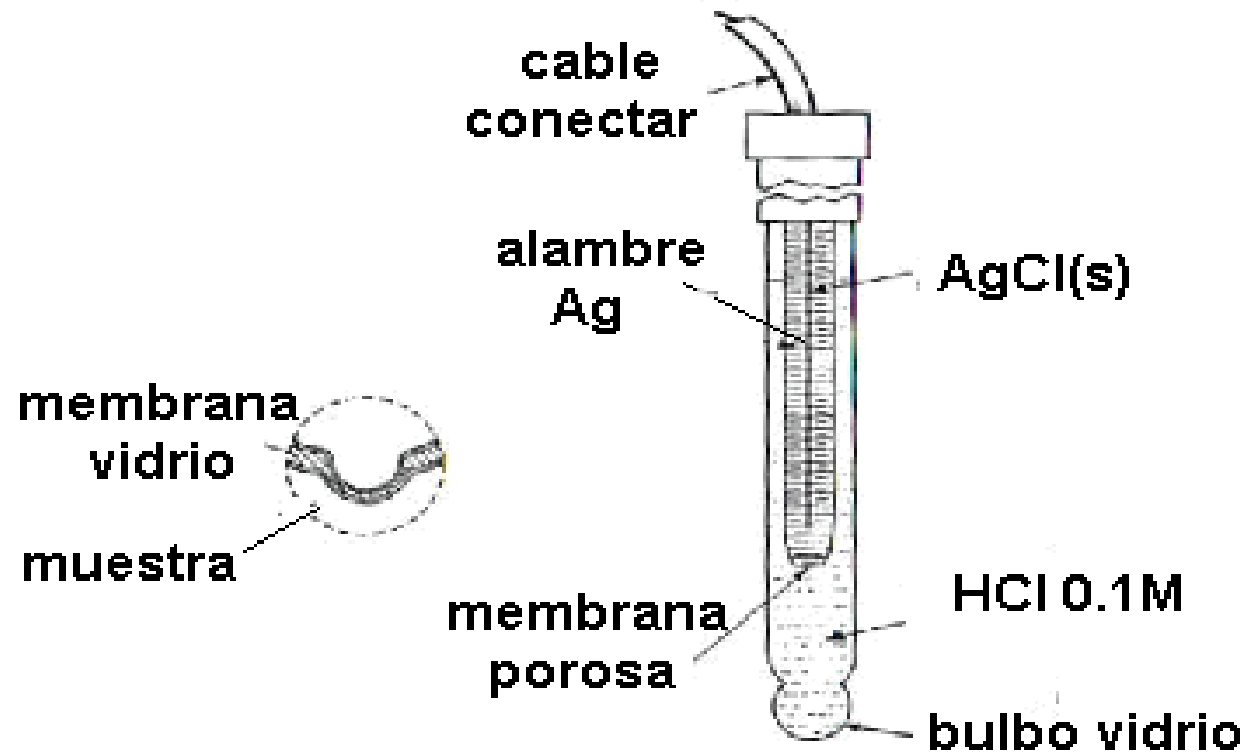


cambio voltaje respecto de un estándar de calibración

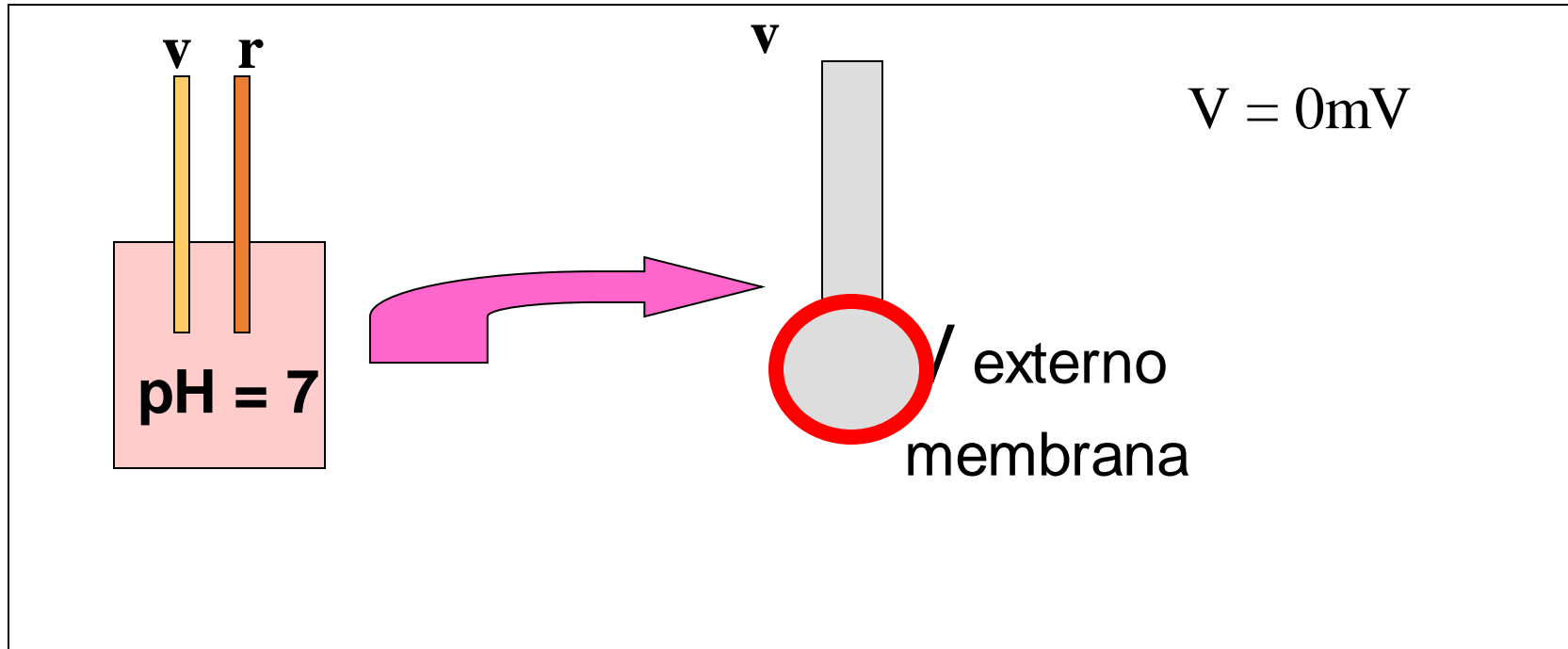
Electrodo indicador (vidrio)

- Produce un potencial proporcional al pH de la solución en el cual está inmerso
- Cuando este potencial se compara al potencial de un electrodo de referencia se puede medir un voltaje
- Los voltímetros especiales para este propósito se denominan pH metros.

Electrodo indicador (vidrio)



Electrodo (vidrio)



En una solución ácida, pH de 0 a 7, se produce un voltaje positivo y en una solución básica, de pH 7 a 14, se produce un voltaje negativo. Siempre que se estandarice con buffer pH=7. Este voltaje es indicado por el pH metro en unidades de pH.

Ventajas

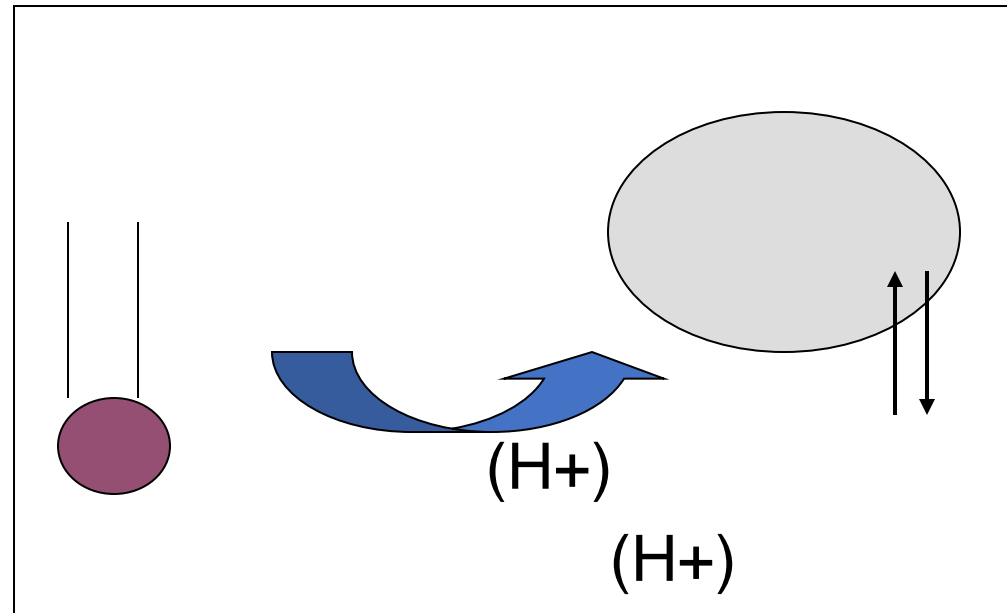
- Preciso, estable y versátil
- Rango de medida de pH de 0 a 14
- No interferencia de agentes oxidantes o reductores
- Temperatura de uso -20°C a 130°C
- Uso con algunas soluciones no acuosas
- Amplia reproducibilidad y fácil de usar

Constitución (1)

- tubo de vidrio o plástico inerte y sellado
- bulbo de vidrio al final del tubo para medir pH
- bulbo lleno con electrolito a pH y fuerza iónica ctes.
- elemento de referencia (Ag/AgCl), inmerso en el electrolito mide el potencial creado por el electrodo
- espacio con aire dentro del tubo, permite expansión térmica del electrolito

Constitución (2)

- membrana de vidrio hidratada



- equilibrio iónico
- se crea un potencial en la fase de unión
- composición del vidrio variable
60% [SiO_2], 30% [M^{+1}O], y 10% [$\text{M}^{+2}, \text{M}^{+3} \text{O}$]

Constitución (2)

$$\text{Potencial}_{\text{electrodo vidrio}} = \sum V1 + V2 + V3$$

- V1 y V2 = potenciales fuera y dentro de la membrana de vidrio (potenciales de unión)

El potencial en el interior membrana de vidrio = f[H⁺] del electrolito, este potencial es conducido al elem. ref. Ag/AgCl a través del electrolito interno.

- V3 = potencial del elem. ref. Ag/AgCl
Está determinado por [Cl⁻] electrolito interno

Propiedades del electrodo

- Error alcalino
 - alta $[\text{Na}^+]$ altera el potencial
 - 1 unidad pH < 0.10 unidades pH
 - vidrios de baja resistencia vidrios especiales
 - solución pH 13 pH>>
 - $[\text{Na}^+] = 1\text{M}$
 - K y Li
- Soluciones ácidas concentradas (>2M) pH mayores
 - 0.1 unidad pH para sln. 2M
 - > 8 unidades pH para ácidos conc.

Electrodo de referencia

- **Objeto.** Completar el circuito de medida y proveer un potencial estable y reproducible contra el cual se compare el electrodo indicador
- **Composición.** Por cuatro partes distintas: un cuerpo externo inerte, un elemento de referencia, un electrolito y un líquido de unión.

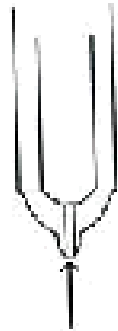
Partes electrodo referencia

- Cuerpo: reservorio del electrolito de referencia
- Elemento de referencia interna Ag/AgCl .
 - $V \approx [Cl^-]$, NaCl, NH₄Cl, etc
- Electrolito: KCl más usado, no genera interferencia con la medida del pH, la movilidad de K⁺ y Cl⁻ son casi iguales
- Unión líquida: tapón poroso (contacto entre celda de referencia y muestra; restringe flujo del electrolito). Materiales: cerámica, Teflón poroso, fibras de poliéster, tipo manga.

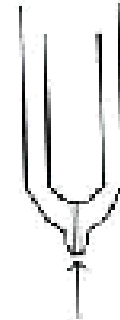
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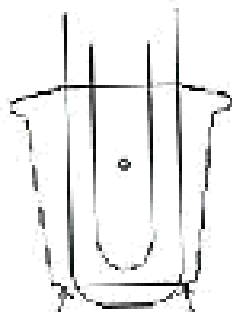
Uniones electrodo referencia



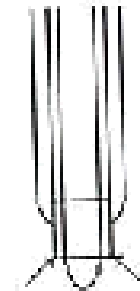
cerámica y vidrio poroso



Cuarzo y asbesto



Tipo manga



Con anillo

Mantenimiento de los electrodos

- Electrodos **sumergidos en agua** destilada o solución buffer (seco colocarlo en agua antes de su uso, hrs.)
- **Llenar** el electrodo de referencia con sln. **KCl** saturada.
- **Limpieza** de la fibra de unión en punta del electrodo de referencia.. Procedimiento: calentamiento de la punta del electrodo en ácido nítrico diluido o sln. KCl.
- Fallas en electrodo de vidrio por formación de recubrimientos de proteína o carbonatos que se eliminan con solución fuerte de detergente en agua o ácido diluido.

Un buen funcionamiento del aparato

- Instrumento conectado todo el tiempo, a menos que éste no se vaya a utilizar por periodos largos. Esto asegurará un funcionamiento estable y preciso, la vida de los componentes se alargará.
- Control de calibración del electrodo

Ecuación de Nernst:

$$E_{\text{obs}} = E^0 - S \text{ pH}$$

E_{obs} = Potencial observado

E^0 = potenciales estables

S = factor de pendiente

Sugerencias para el trabajo de calidad

- Soluciones buffer **frescas**, recipientes cerrados (previene evaporación y contaminación). Nunca regresar buffer.
- **Lavar electrodos** con agua destilada entre medidas.
- Sumergir completamente **bulbo** sensible al pH del electrodo de vidrio en solución medida. Electrodo no toque pared o fondo del recipiente.
- Misma **T°** en muestras y buffer.

Calibración del "pH metro"

Principio. calibración diaria con *solución buffer
*aquella en la que el pH permanece casi constante

- **Utilizar un buffer** en el rango de la muestra a medir.
- Soluciones buffer más usadas:
 - * pH=4 para medimos cerca del rango ácido
 - * pH=7 para medimos cerca del rango neutro
 - * pH=9 para medimos cerca del rango alcalino
- **Temperatura** de las buffer y muestras lo más cercana posible (Δ rango $<10^{\circ}\text{C}$)

Procesamiento de medida

1. Calentamiento aprox. 30 min
Precaución. Posición de reposo cuando no se usa, en algunos instrumentos
2. **Lavar** electrodo con agua des. y remover exceso agua
3. **Calibrar** con las soluciones buffer adecuadas.
4. Colocar los **electrodos en el vaso** con solución a medir.
5. Ajustar la **temperatura**
6. Colocar en **posición de medida** del pH
7. **Terminada** la determinación:
 - * colocar en posición de reposo **STANDBY**
 - * lavar **electrodos con agua destilada** y dejar en reposo