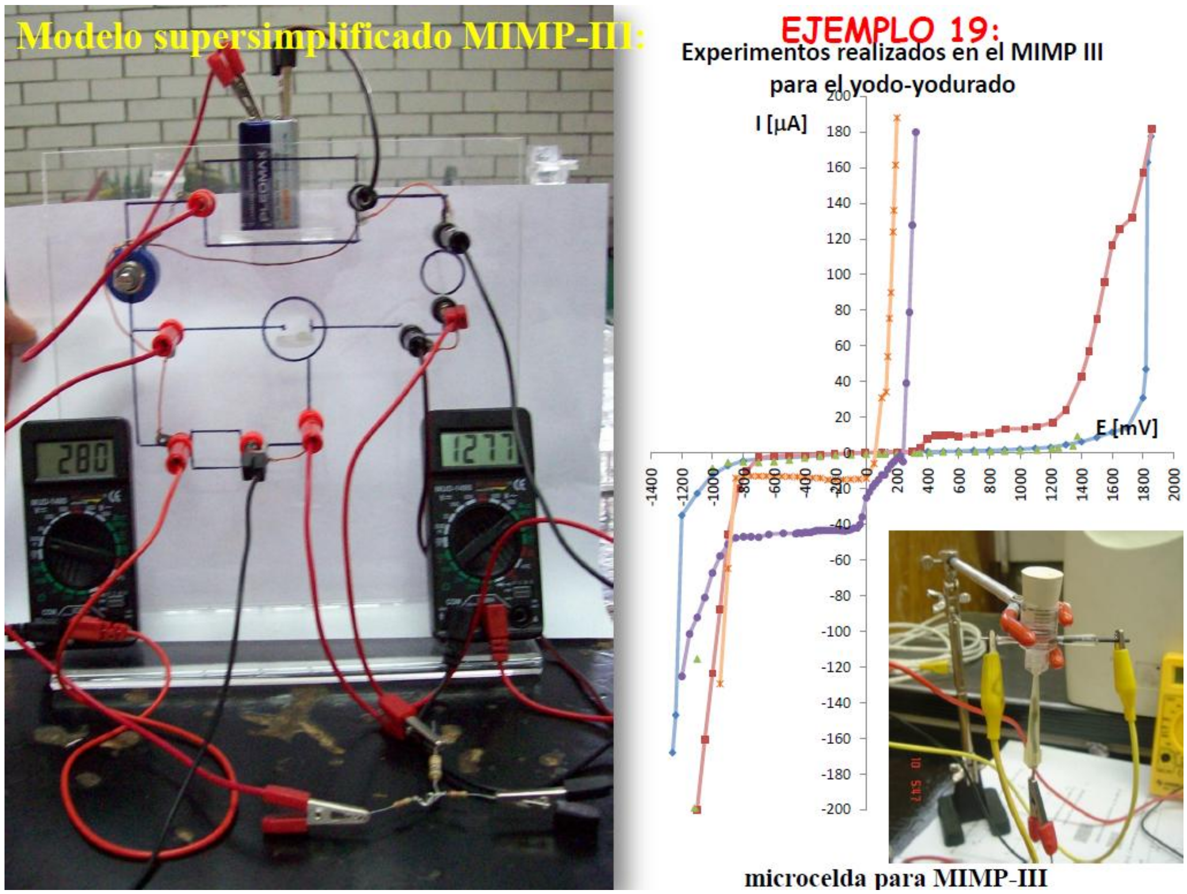
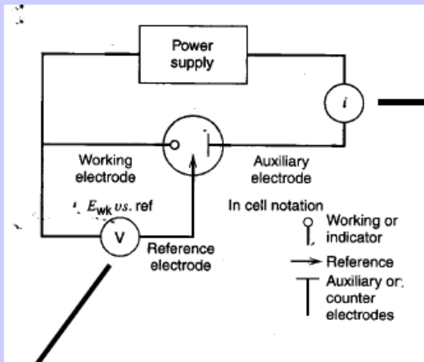
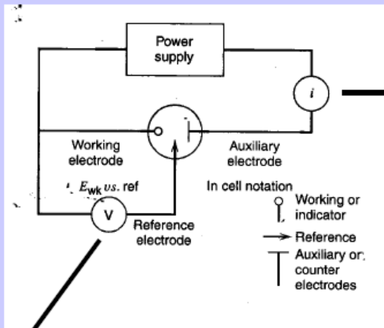

Modelo supersimplificado MIMP-III:
EJEMPLO 19:
Experimentos realizados en el MIMP III
para el yodo-yodurado
I [µA]
E [mV]
microcelda para MIMP-III



$$I_{leía} = I_{capacitiva} + I_{faradaica} = I_{cap} + (I_{migr} + I_{convec} + I_{dif})$$

$$E_{imp.} = E_{ohm} + E_{despol} + \eta$$



microelectrodo

EGD
EGM
Sin agit

$$I_{leida} = I_{capacitiva} + I_{faradaica} = I_{cap} + (I_{migr} + I_{convec} + I_{dif})$$

EBS

$$E_{imp} = E_{ohm} + E_{despol} + \eta$$

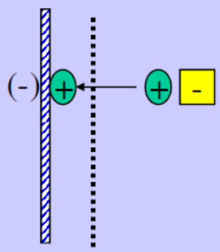
EBS:

"minimiza" la caída óhmica:

KNO_3 0.1 mol/L ⇒ $R_s \downarrow$

$IR_s \downarrow = E_{caida\ óhmica}$

"Minimiza" el número de Transporte del despolarizante: $I_m = t_+I_m + t_-I_m$

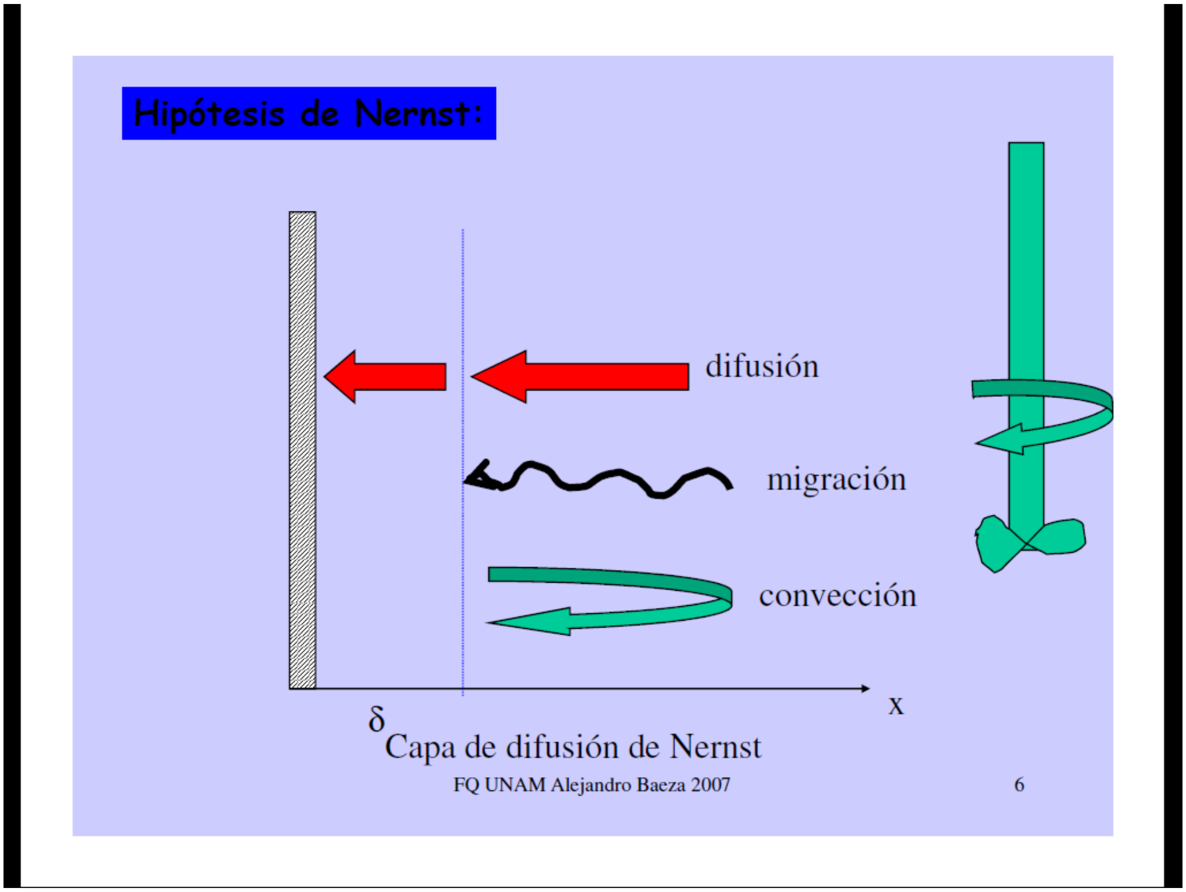


a) Sin KNO_3 :

$$t_+ = \frac{\lambda_+C_+}{\lambda_+C_+ + \lambda_-C_-} \approx 0.5$$

b) Con KNO_3 $100C_+$

$$t_+ = \frac{\lambda_+C_+}{\lambda_+C_+ + \lambda_-C_- + \Lambda_{KNO_3}100C} < 0.001$$


Hipótesis de Nernst:
difusión
migración
convección
x
δ
Capa de difusión de Nernst
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Leyes de Faraday

$Q = nF\,m$ $F = 96500$ C/mole

$(dQ/dt) = i = nF(dm/dt) = nF\,v_{elec}$

Ecuación de Nernst-Planck

$t_+ \rightarrow 0$

Cte. ó cero

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)$$

Velocidad de transferencia de masa

$$(dQ/dt) = i = nF(dm/dt) = nF\, v_{elec}$$

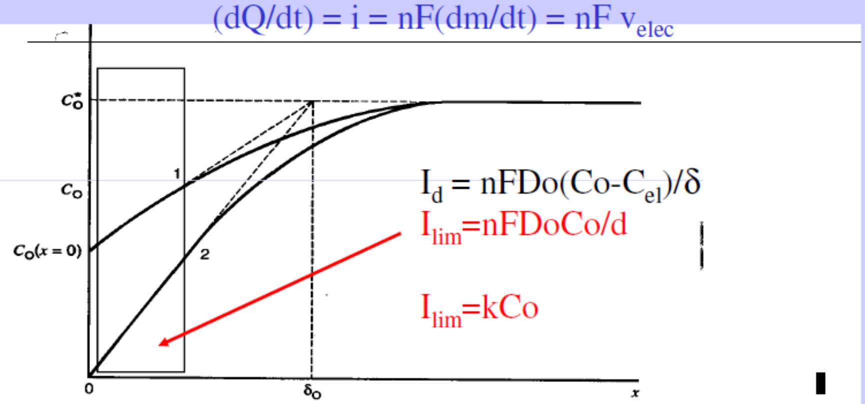

Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (*1*) where $C_O(x = 0)$ is about $C_O^*/2$, (*2*) where $C_O(x = 0) \approx 0$ and $i = i_l$.

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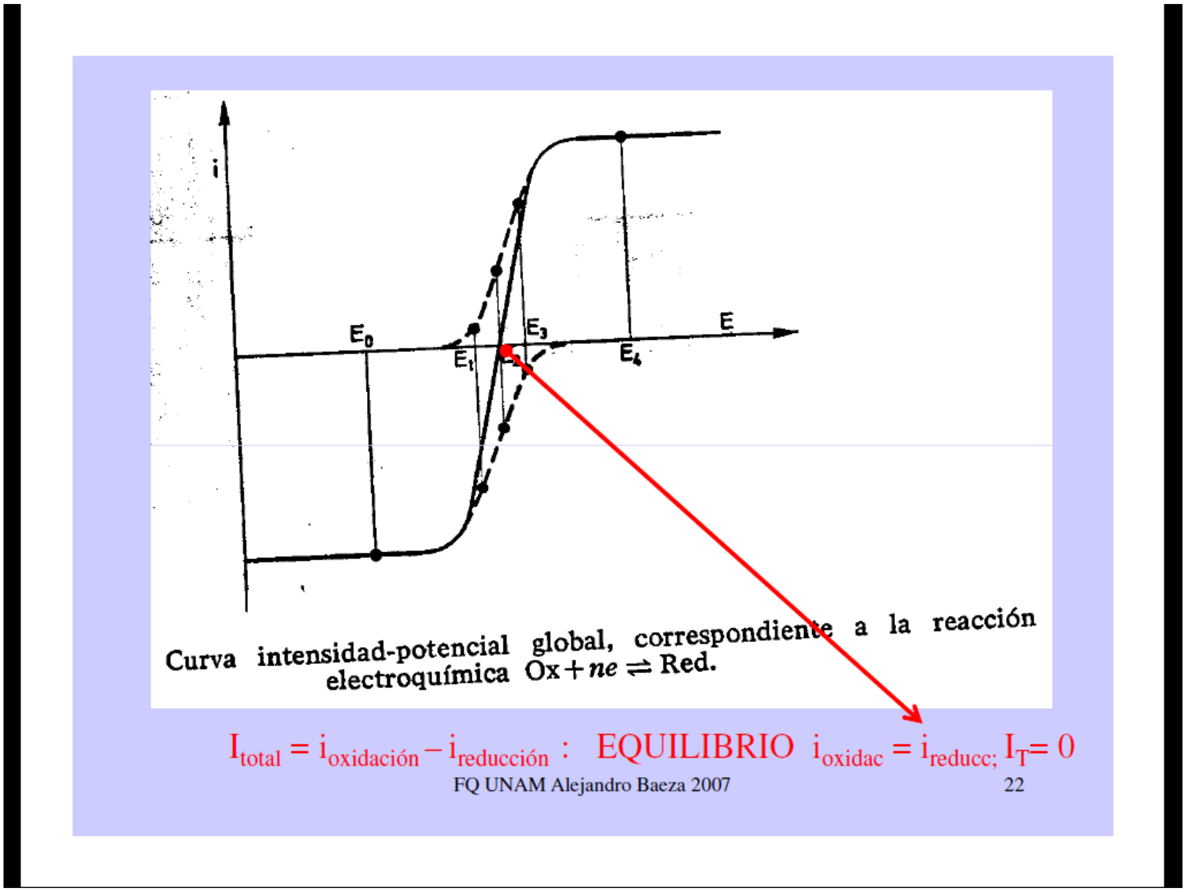
i
E
E0
E1
E3
E4
Curva intensidad-potencial global, correspondiente a la reacción electroquímica Ox + ne ⇌ Red.
$I_{total} = i_{oxidación} - i_{reducción}$: EQUILIBRIO $i_{oxidac} = i_{reducc;}$ $I_T = 0$
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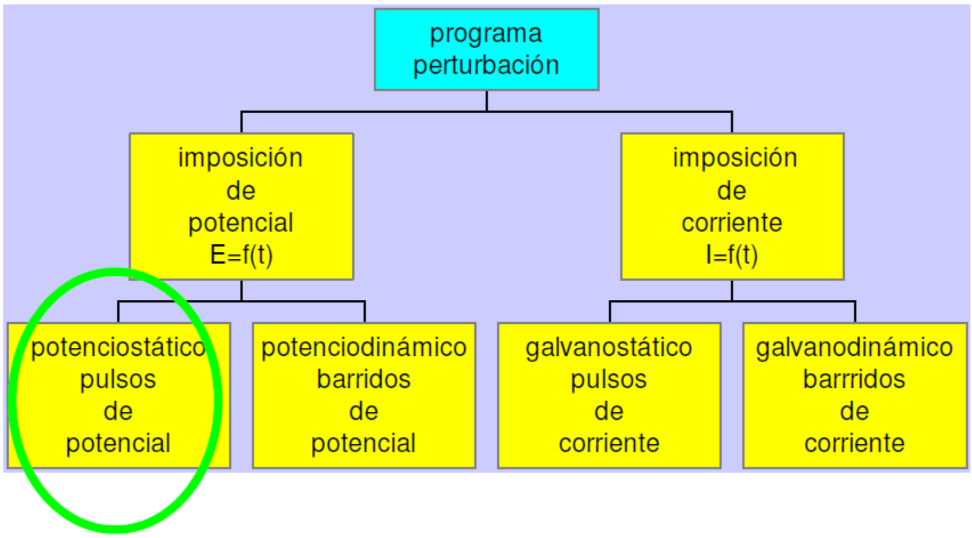
programa perturbación
imposición de potencial E=f(t)
imposición de corriente I=f(t)
potenciostático pulsos de potencial
potenciodinámico barridos de potencial
galvanostático pulsos de corriente
galvanodinámico barrridos de corriente

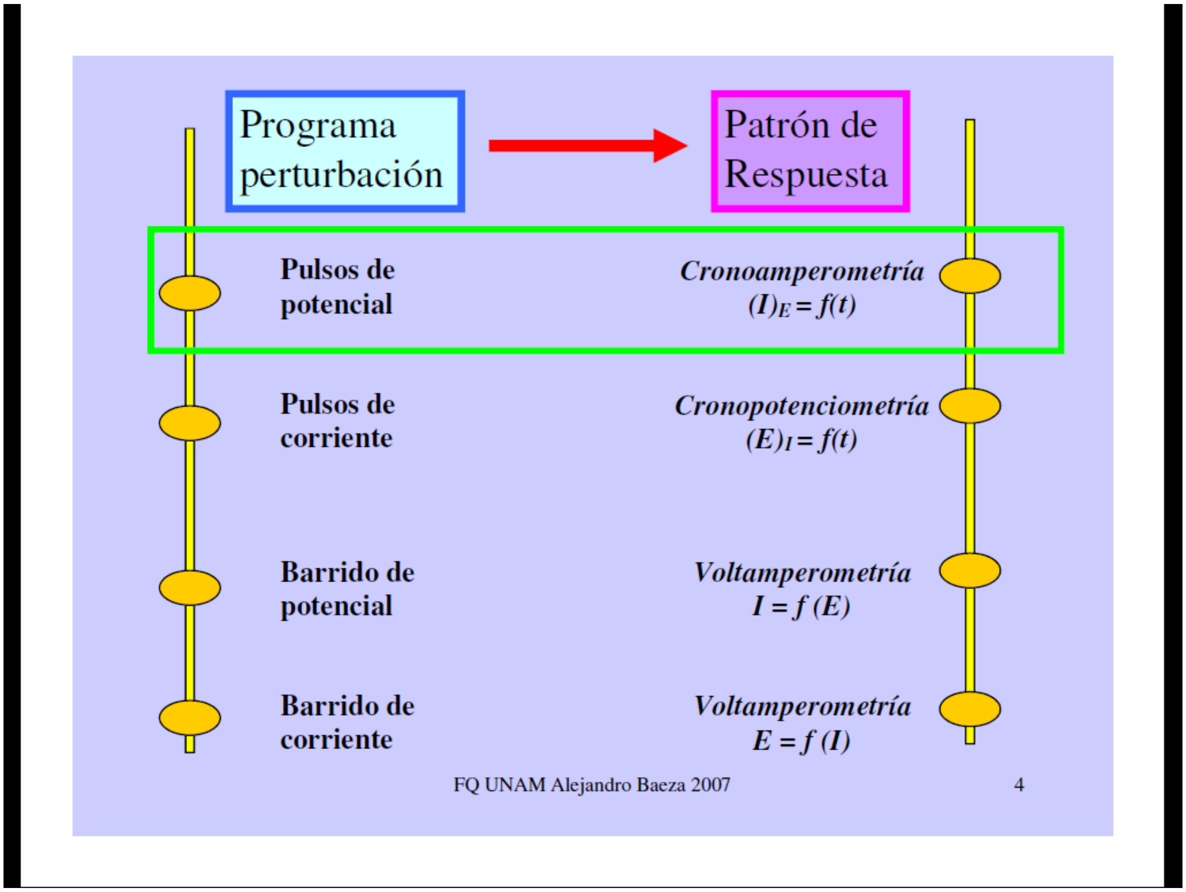
Programa perturbación
Patrón de Respuesta
Pulsos de potencial
Cronoamperometría
$(I)_E = f(t)$
Pulsos de corriente
Cronopotenciometría
$(E)_I = f(t)$
Barrido de potencial
Voltamperometría
$I = f(E)$
Barrido de corriente
Voltamperometría
$E = f(I)$
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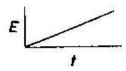
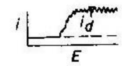
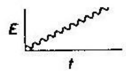
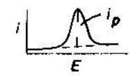
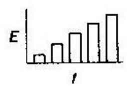
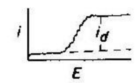
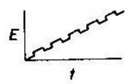
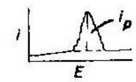
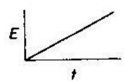
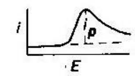
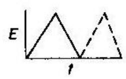
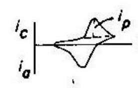
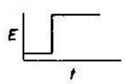
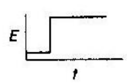
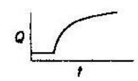
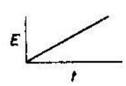
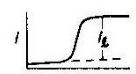
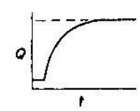
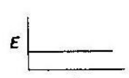
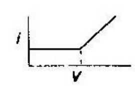
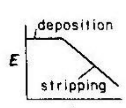
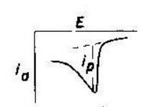
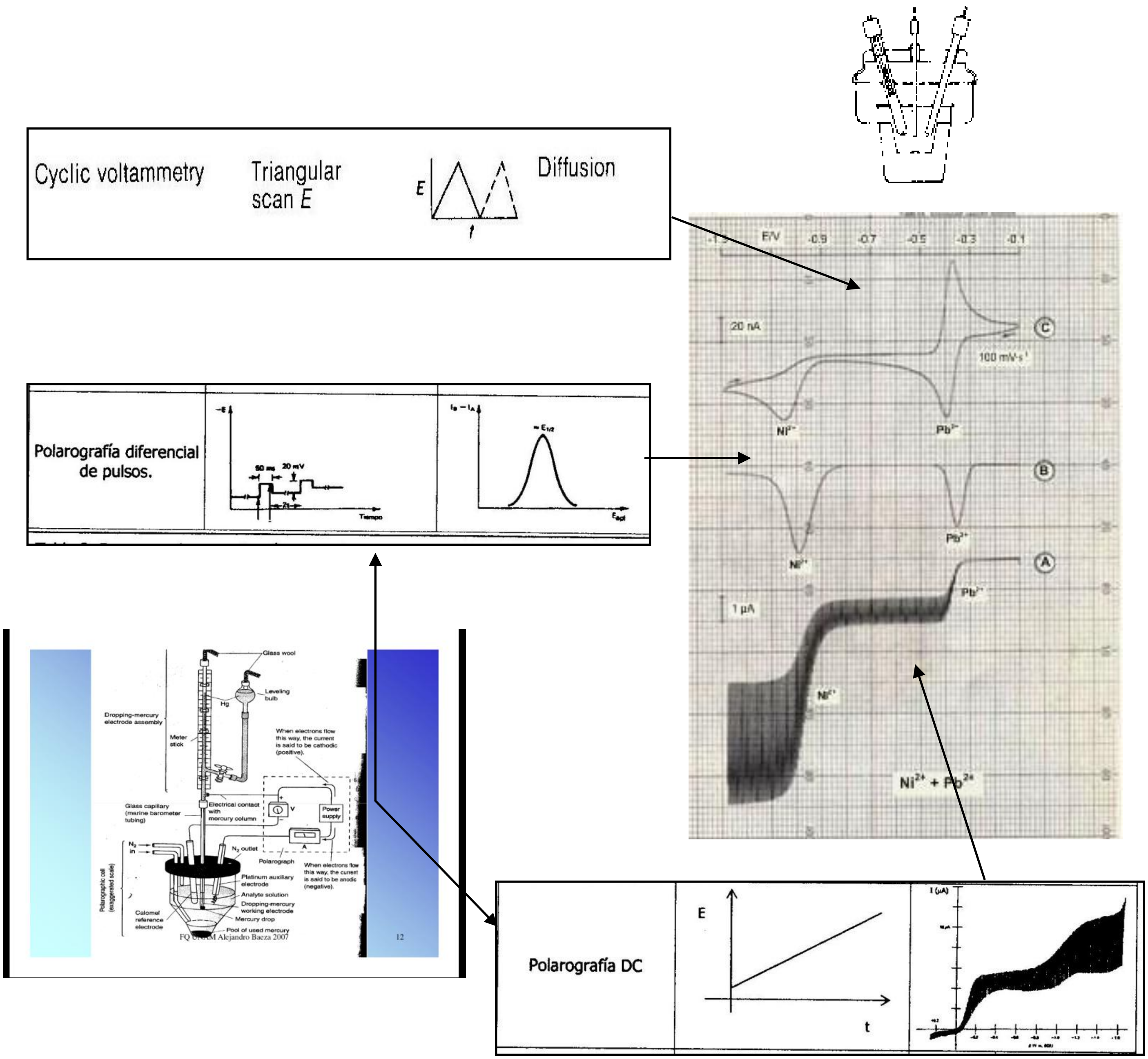
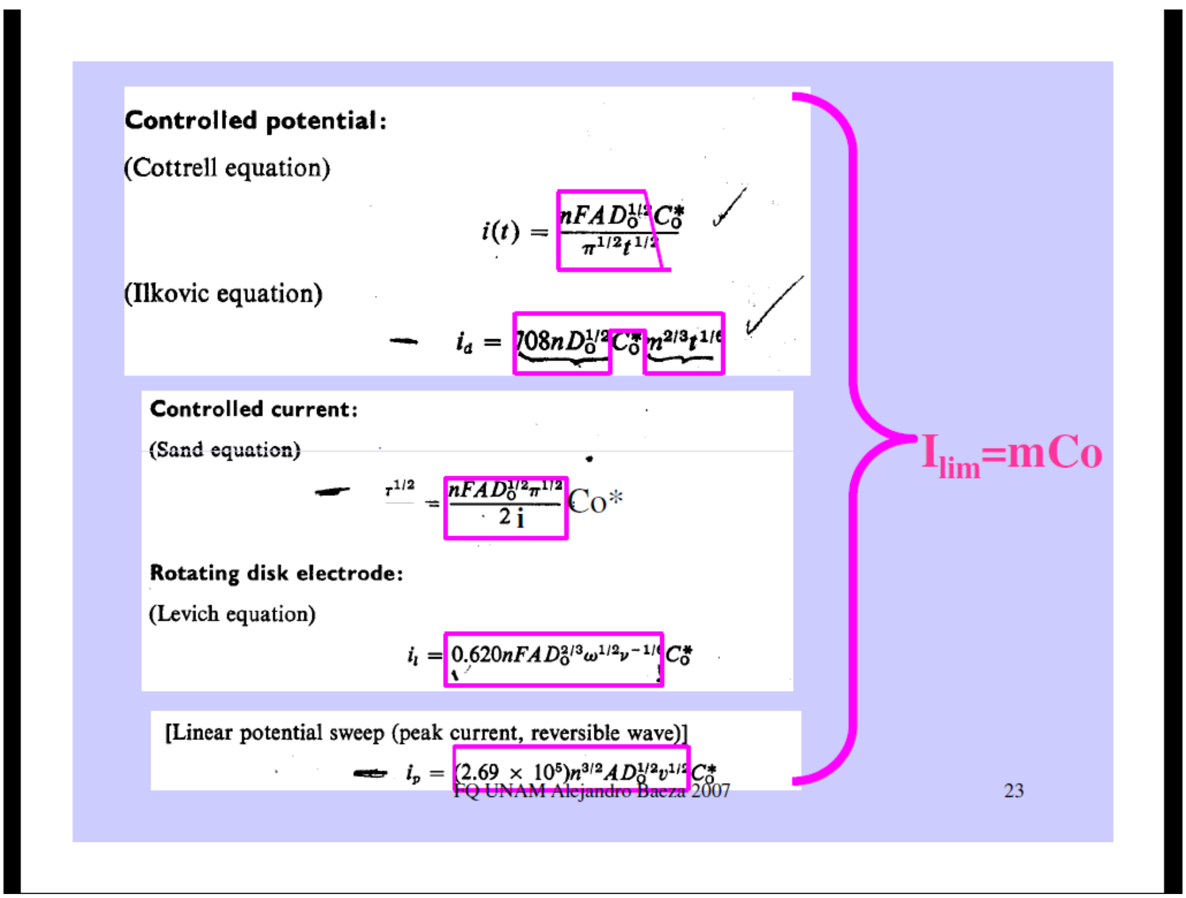
Table 4-1 / Controlled Potential Methods

Name of Technique	Potential Excitation Signal	Mass Transfer	Measurement	Analytical Relation to Bulk Concentration	Typical Display
Polarography (dc or normal)	Slow linear scan (or constant E) 	Diffusion	i vs. E	$i_d \propto C$	
AC polarography	Slow linear scan + low amplitude sine wave 	Diffusion	i_{ac} vs. E	$i_p \propto C$	
Pulse polarography	Square voltage pulses of increasing amplitude 	Diffusion	i vs. E	$i_d \propto C$	
Differential pulse polarography	Square voltage pulses of constant amplitude + linear ramp 	Diffusion	Δi vs. E	$i_p \propto C$	
Single sweep voltammetry	Linear scan E 	Diffusion	i vs. E	$i_p \propto C$	
Cyclic voltammetry	Triangular scan E 	Diffusion	i vs. E	$i_p \propto C$	
Chronoamperometry	Step E 	Diffusion	i vs. t	$i_t \propto C$	
Chronocoulometry	Step E 	Diffusion	Q vs. t	$Q \propto C$	
Hydrodynamic voltammetry	Linear scan E (or constant E) 	Convection/diffusion	i vs. E	$i_\ell \propto C$	
Controlled potential coulometry	Constant E 	Convection/diffusion	Q vs. t	$Q = \int_0^t i\,dt = nFVC$	
Controlled potential electrogravimetry	Constant E 	Convection/diffusion	Weight of deposit	Weight $\propto VC$	None
Amperometric titration (one or two polarized electrodes)	Constant E + titrant addition 	Convection/diffusion	i vs. volume	Volume of titrant $\propto VC$	
Stripping voltammetry	Constant E followed by linear scan or differential pulse scan 	Convection/diffusion	i vs. E	$i_p \propto C$	


Cyclic voltammetry
Triangular scan E
E
t
Diffusion
Polarografía diferencial de pulsos.
50 ms
20 mV
Tiempo
E1/2
E/V
-0.9
-0.7
-0.5
-0.3
-0.1
20 nA
100 mV·s-1
C
B
A
Ni2+
Pb2+
1 µA
Ni2+ + Pb2+
Glass wool
Leveling bulb
Hg
Dropping-mercury electrode assembly
Meter stick
When electrons flow this way, the current is said to be cathodic (positive).
Glass capillary (marine barometer tubing)
Electrical contact with mercury column
V
Power supply
N2 in
N2 outlet
Polarograph
Polarographic cell (exaggerated scale)
Platinum auxiliary electrode
Analyte solution
Dropping-mercury working electrode
Mercury drop
When electrons flow this way, the current is said to be anodic (negative).
Calomel reference electrode
Pool of used mercury
12
Polarografía DC
E
t
I (µA)


Controlled potential:
(Cottrell equation)
$i(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$
(Ilkovic equation)
$i_d = 708nD_O^{1/2}C_O^*m^{2/3}t^{1/6}$
Controlled current:
(Sand equation)
$\tau^{1/2} = \frac{nFAD_O^{1/2}\pi^{1/2}}{2i}Co^*$
Rotating disk electrode:
(Levich equation)
$i_l = 0.620nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}C_O^*$
[Linear potential sweep (peak current, reversible wave)]
$i_p = (2.69 \times 10^5)n^{3/2}AD_O^{1/2}v^{1/2}C_O^*$
I_{lim}=mCo
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