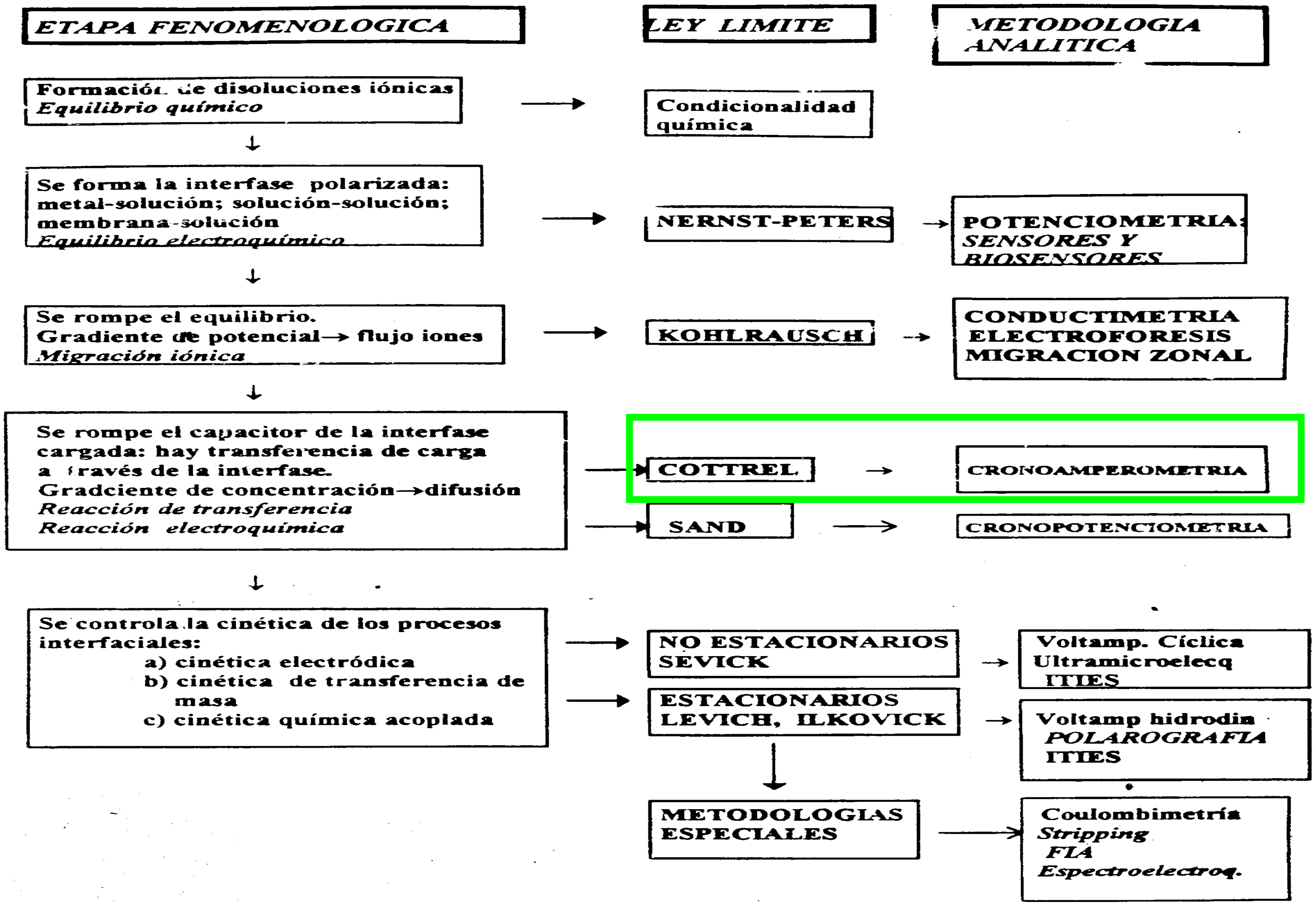
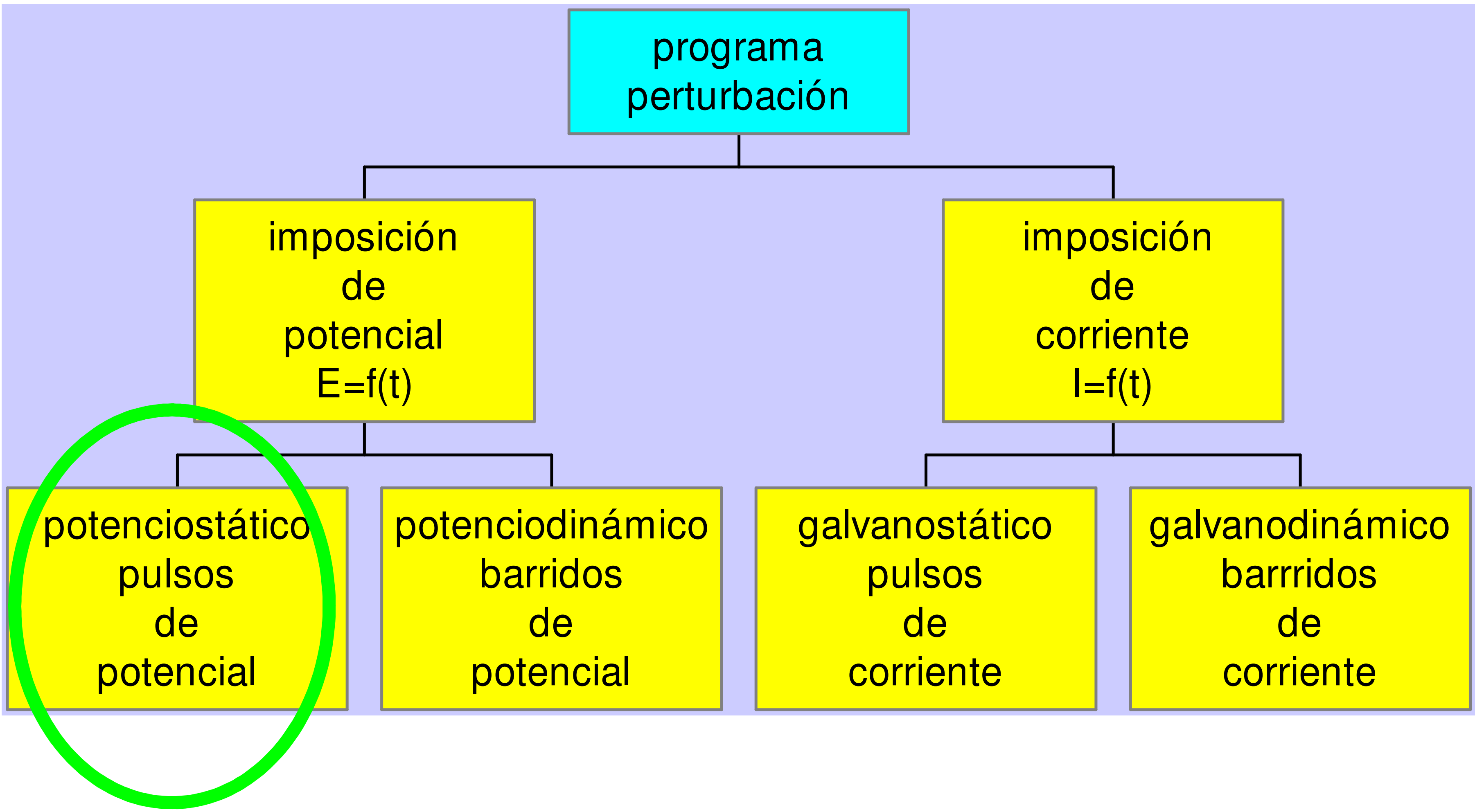
Cronoamperometría: Ecuaciòn de Cottrell

ESQUEMA FENOMENOLOGICO PARA LA ENZEÑANZA DE LA ELECTROQUÍMICA ANALÍTICA
Candidato a Doctor Alejandro Baeza




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*** $E = f(I)$

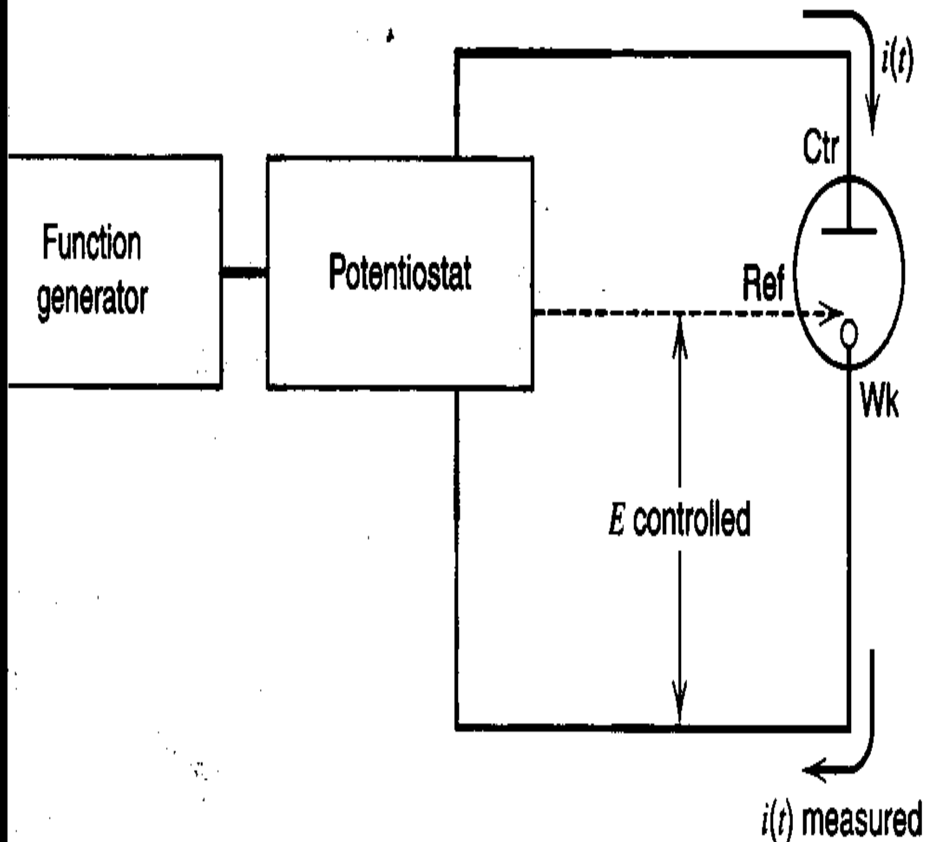


Figure 5.1.1
Experimental arrangement for controlled-potential experiments.

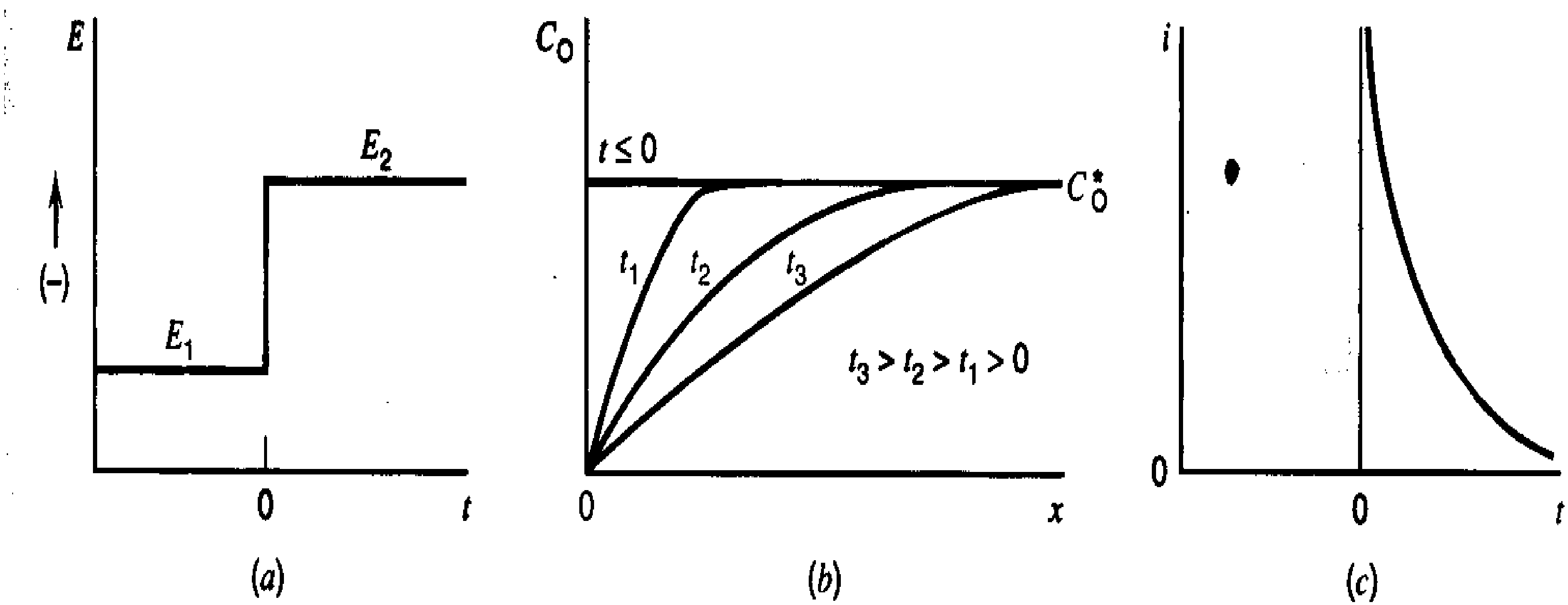


Figure 5.1.2 (*a*) Waveform for a step experiment in which species O is electroinactive at E_1, but is reduced at a diffusion-limited rate at E_2. (*b*) Concentration profiles for various times into the experiment. (*c*) Current flow vs. time.

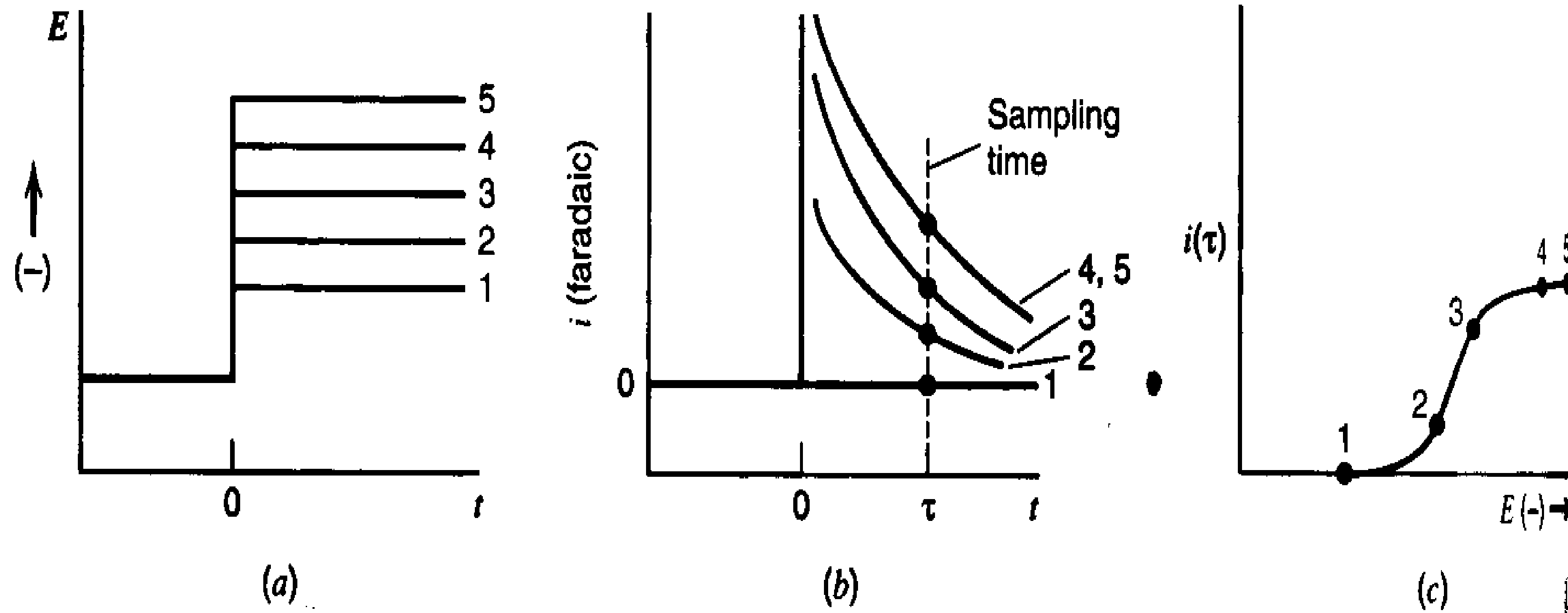


Figure 5.1.3 Sampled-current voltammetry. (*a*) Step waveforms applied in a series of experiments. (*b*) Current-time curves observed in response to the steps. (*c*) Sampled-current voltammogram.

▶ 5.2 POTENTIAL STEP UNDER DIFFUSION CONTROL

5.2.1 A Planar Electrode

(a) Solution of the Diffusion Equation

The calculation of the diffusion-limited current, i_d, and the concentration profile, $C_O(x, t$ involves the solution of the linear diffusion equation:

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} \quad 5.2.1$$

under the boundary conditions:

$$C_O(x,0) = C_O^* \quad 5.2.2$$

$$\lim_{x \to \infty} C_O(x,t) = C_O^* \quad 5.2.3$$

$$C_O(0,t) = 0 \quad (\text{for } t > 0) \quad 5.2.4$$

$$\bar{C}_O(x, s) = \frac{C_O^*}{s} + A(s)\, e^{-\sqrt{s/D_O}\,x} \tag{5.2.5}$$

By applying the third condition, (5.2.4), the function $A(s)$ can be evaluated, and the $\bar{C}_O(x, s)$ can be inverted to obtain the concentration profile for species O. Transformin (5.2.4) gives

$$\bar{C}_O(0, s) = 0 \tag{5.2.6}$$

which implies that

$$\bar{C}_O(x, s) = \frac{C_O^*}{s} - \frac{C_O^*}{s}\, e^{-\sqrt{s/D_O}\,x} \tag{5.2.7}$$

In Chapter 4, we saw that the flux at the electrode surface is proportional to the curren specifically,

$$-J_O(0, t) = \frac{i(t)}{nFA} = D_O\left[\frac{\partial C_O(x, t)}{\partial x}\right]_{x=0} \tag{5.2.8}$$

which is transformed to

$$\frac{\bar{i}(s)}{nFA} = D_O\left[\frac{\partial \bar{C}_O(x, s)}{\partial x}\right]_{x=0} \tag{5.2.9}$$

The derivative in (5.2.9) can be evaluated from (5.2.7). Substitution yields

$$\bar{i}(s) = \frac{nFAD_O^{1/2}C_O^*}{s^{1/2}} \tag{5.2.10}$$

and inversion produces the current-time response

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \tag{5.2.11}$$

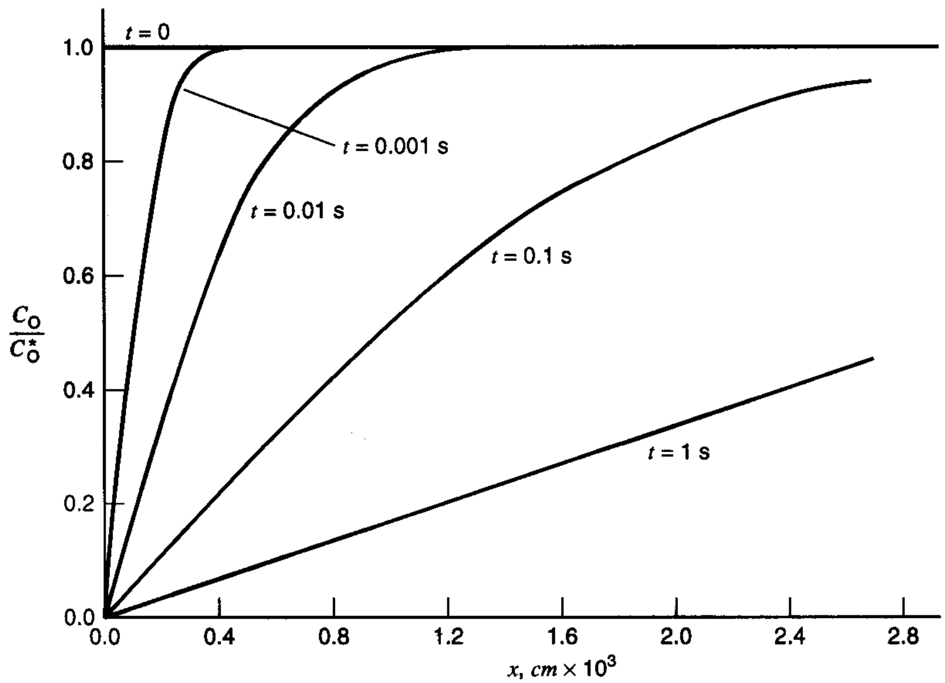
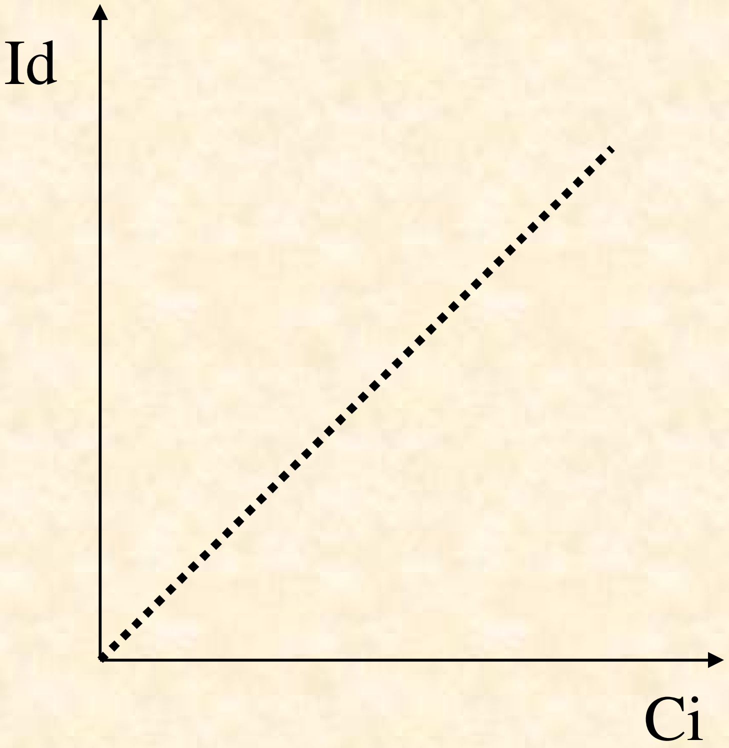
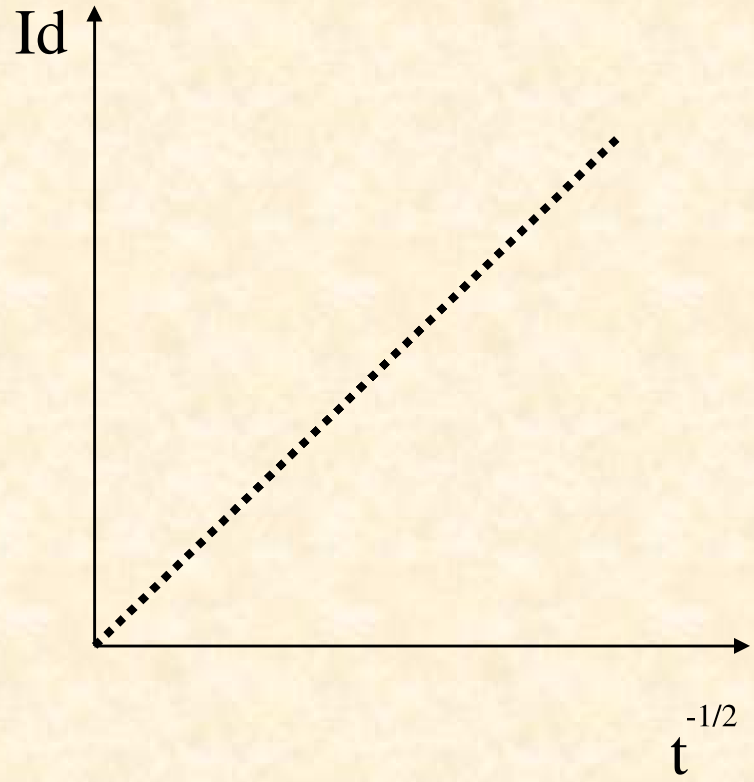


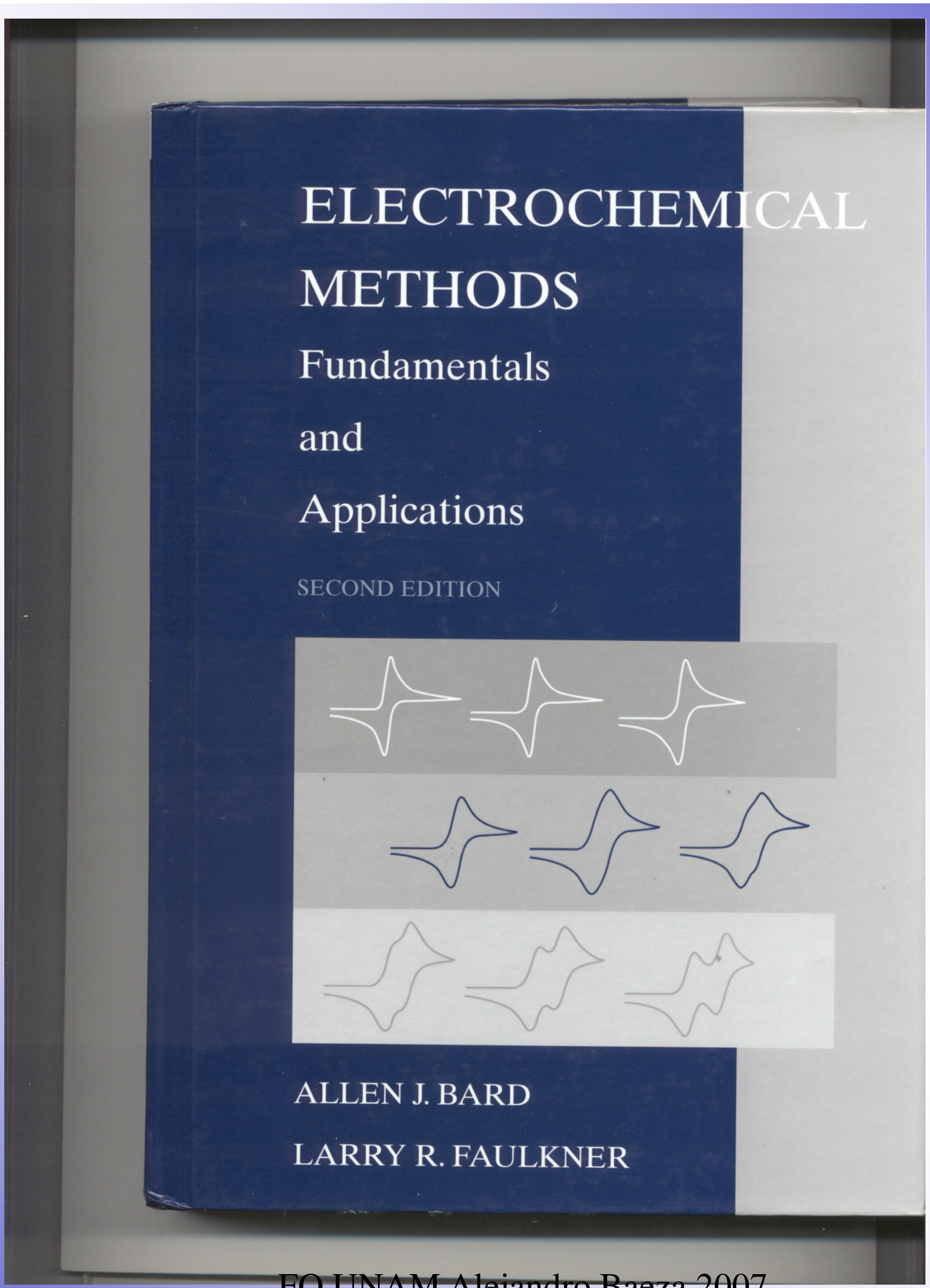
Figure 5.2.1 Concentration profiles for several times after the start of a Cottrell experiment. $D_O = 1 \times 10^{-5}$ cm^2/s

(curva de calibración: Electroanálisis)



Determinación de ne⁻ D_0, A.

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COTTRELL

$$i = \frac{nFAD^{1/2}C}{\sqrt{\pi t}}$$

Frederick Gardner Cottrell (1877-1948) is best known to electrochemists for the "Cottrell equation*". His primary source of fame is as the inventor of electrostatic precipitators for removal of suspended particles from gases. These devices are widely used for abatement of pollution by smoke from power plants and dust from cement kilns and other industrial sources.

Cottrell was born in Oakland, California. He received a B.S. in chemistry from the University of California at Berkeley in 1896 and a Ph.D. from the University of Leipzig in 1902. He was an instructor of chemistry at the University of California, a chief physical chemist of the U.S. Bureau of Mines, chairman of the division of chemistry and chemical technology of the National Research Council, and director of the Fixed Nitrogen Research Laboratory.

In 1912, he founded the Research Corporation. This nonprofit foundation, for the advancement of science, secured and developed over 750 patents.

Cottrell played a part in the development of a process for separation of helium from natural gas. He also had a role in establishing the synthetic ammonia industry in the United States during attempts to perfect a process for formation of nitric oxide at high temperatures.

*F.G. Cottrell, Z. Physik. Chem. (1902) 42, 385

Ejercicio de aplicación.

El ácido ascòrbico se oxida sobre microelectrodos de carbòn de acuerdo a las siguientes condiciones:

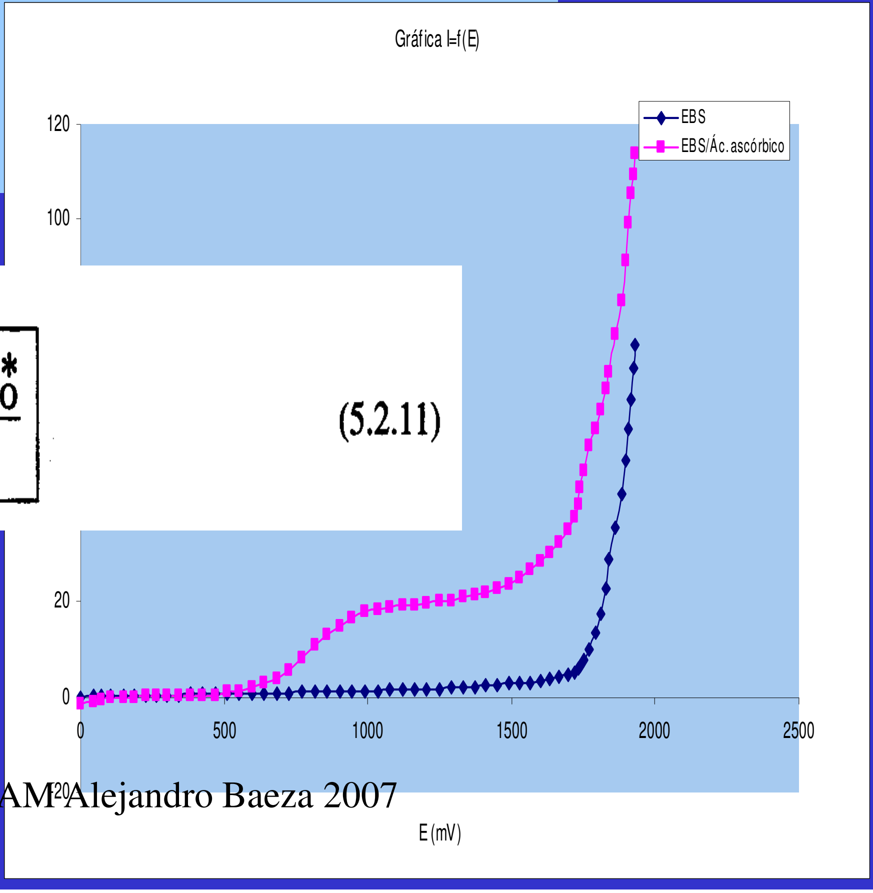
Vo= 3 mL; Co=10 mM; d=0.2cm; I_r=2uA;

I_T=28uA

tiempo de muestreo: 3' segundos, $E_{muestreo}$=1300 mV.

Calcular el coeficiente de difusiòn del ácido ascórbico en el medio de reacción (EBS pH=4).

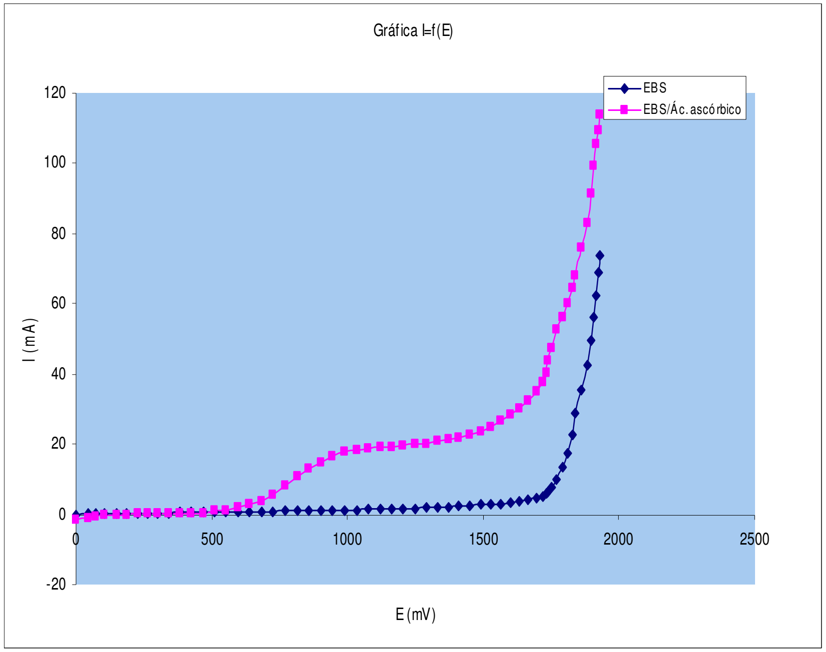
Nota: F = 96,500 C/mol



and inversion produces the current-time response

$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}} \qquad (5.2.11)$$

Resp.



$D_o = 1.79 \times 10^{-5}\ cm^2/s$