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CARACTERIZACIÓN DEL ÁCIDO GAMMA HIDROXIBUTÍRICO SOBRE SUPERFICIES DE PLATINO

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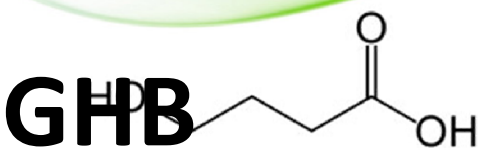
INTRODUCCIÓN



- GHB en el organismo→ 1.46 mg/L - 6.63 mg/L
- GHB como droga de abuso

PROBLEMÁTICA

- *Técnicas disponibles*:

  GC/MS

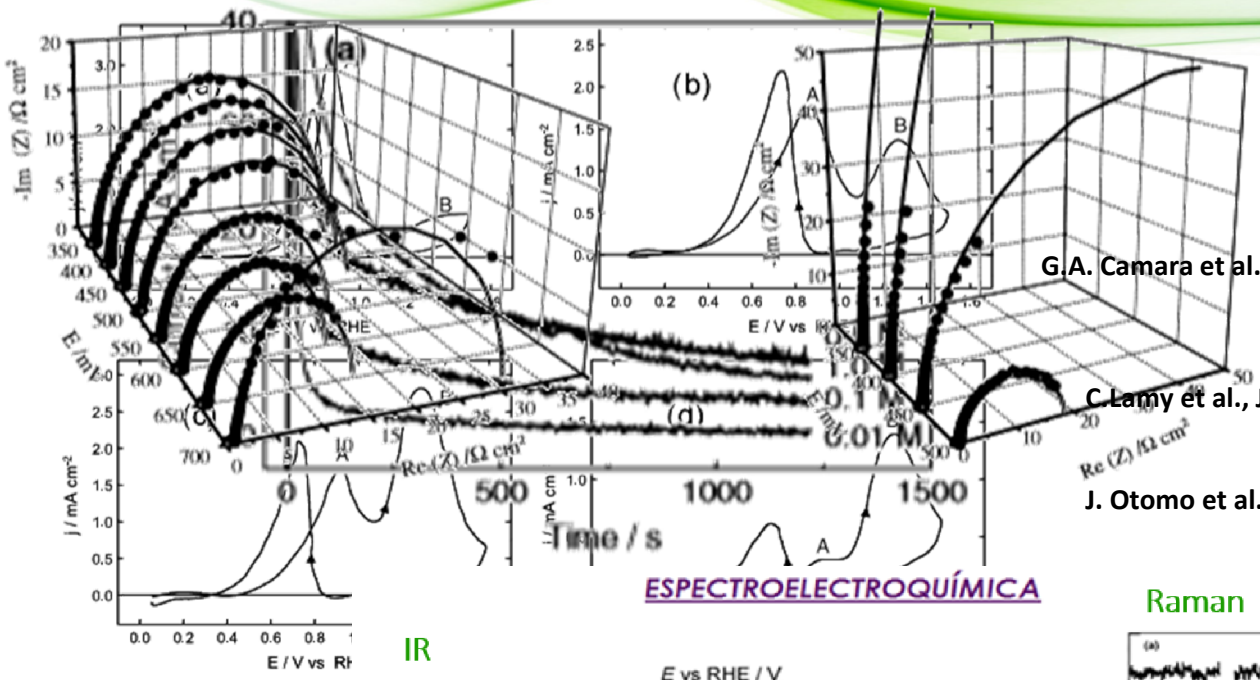
  LC/MS

  Test de identificación de patrones microcristalinos

  Sensores fluorescentes

➡ $t_{1/2}$ → Consumo GHB / 3-9 h / < 0.1% en organismo

ANTECEDENTES



Voltammograms showing the oxidation
sweep rate 50 mV s^{-1}): (a) methanol, (b) etha

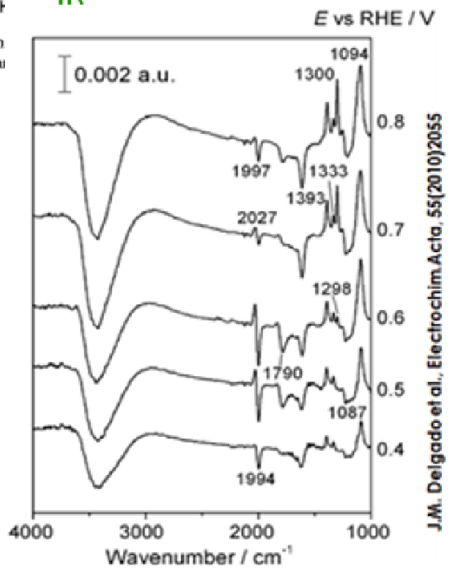
G.A. Camara et al., J. Electroanal. Chem., 578(2005)315

C.Lamy et al., J. Appl.Electrochem,, 31(2001)799

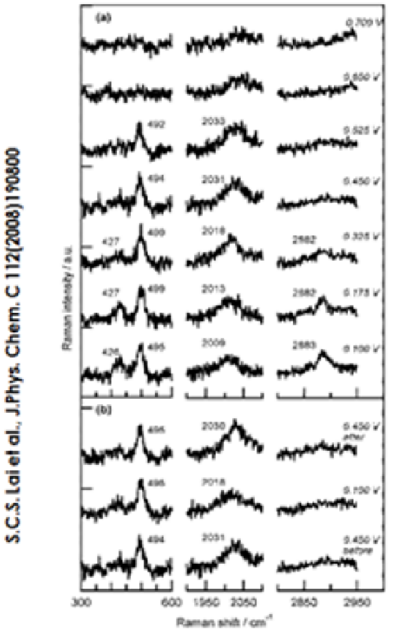
J. Otomo et al., J.Electroanal.Chem., 573(2004)99

ESPECTROELECTROQUÍMICA

IR

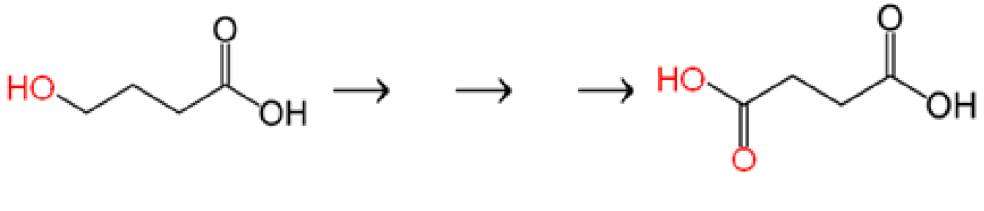


Raman



PLANTEAMIENTO

Bloque I

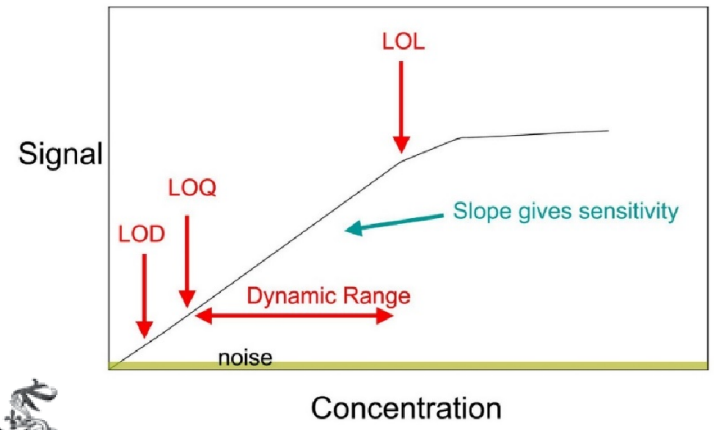


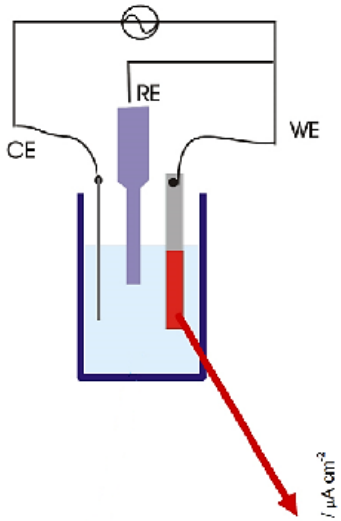
Electroquímica

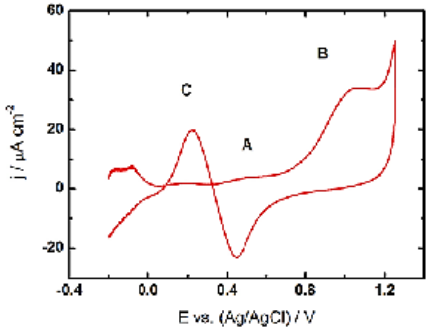
Bloque II

Espectroelectroquímica

Bloque III



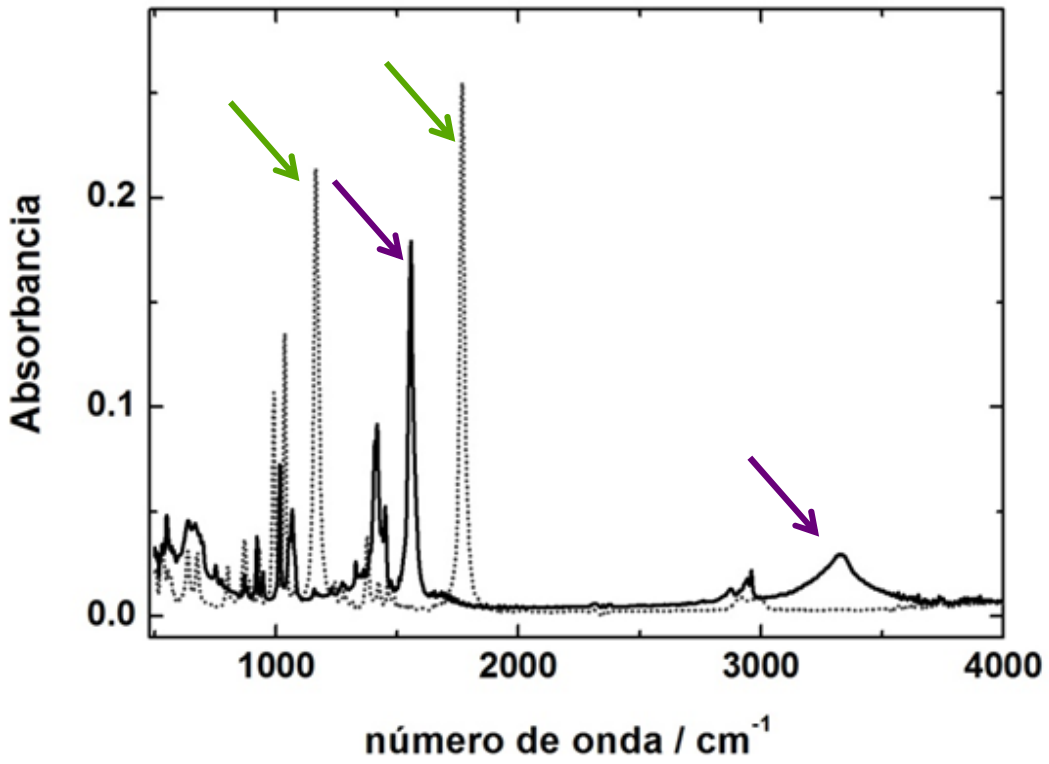




TÉCNICAS

IR

Síntesis



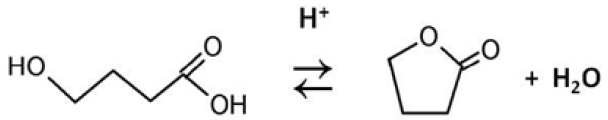
Espectros de absorción de (—)GHB (de la síntesis) y (- -) GBL

- 1770 cm^{-1} (tension sim. carboxilato en lactonas de 4 C)
- 1170 cm^{-1} (tensión C-O en γ- y δ- lactonas)

- 3345 cm^{-1} (tensión OH)
- 1560 cm^{-1}(tensión del grupo carboxilato)

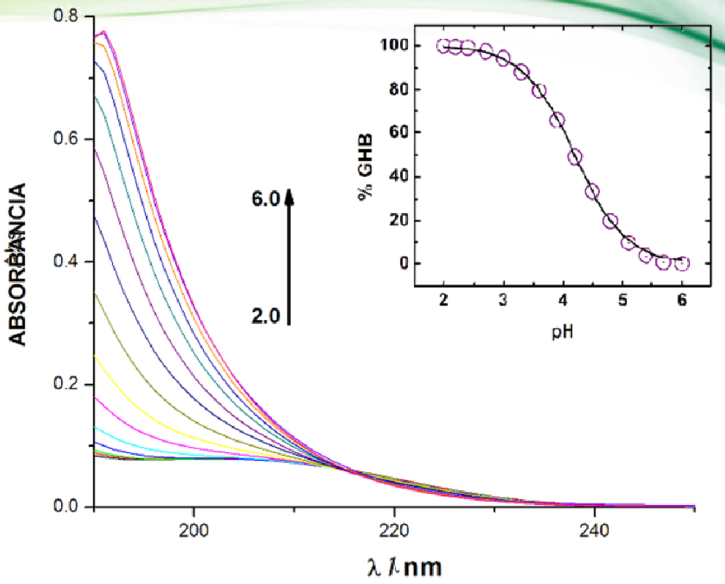
UV-VIS

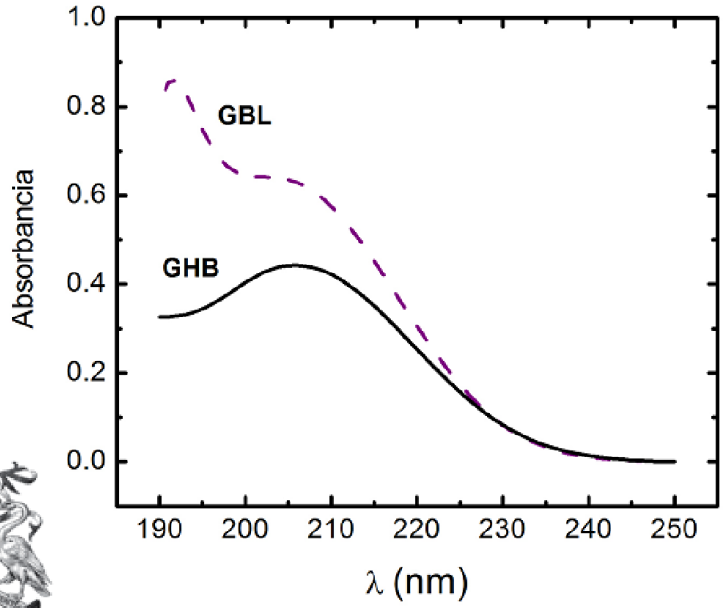
Doble equilibrio de la GHB

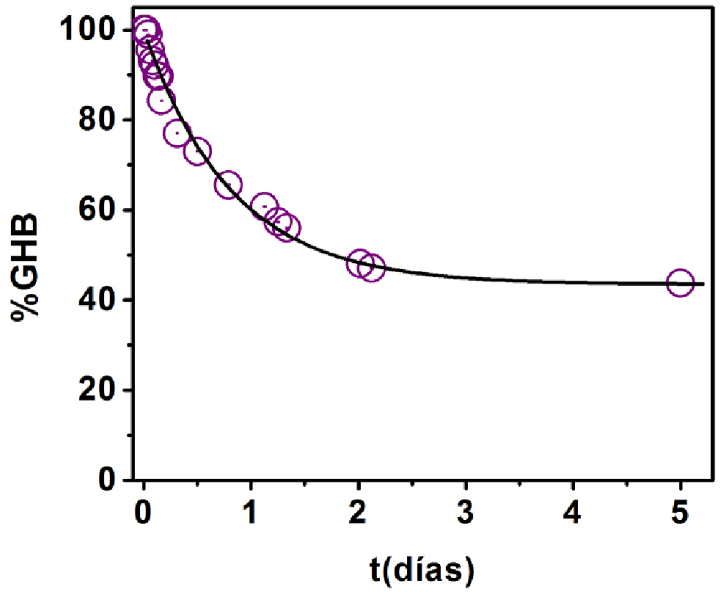
[1] 

[2] $HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH \rightleftarrows HO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COO^- + H^+$

pKa= 4.2 ± 0.1

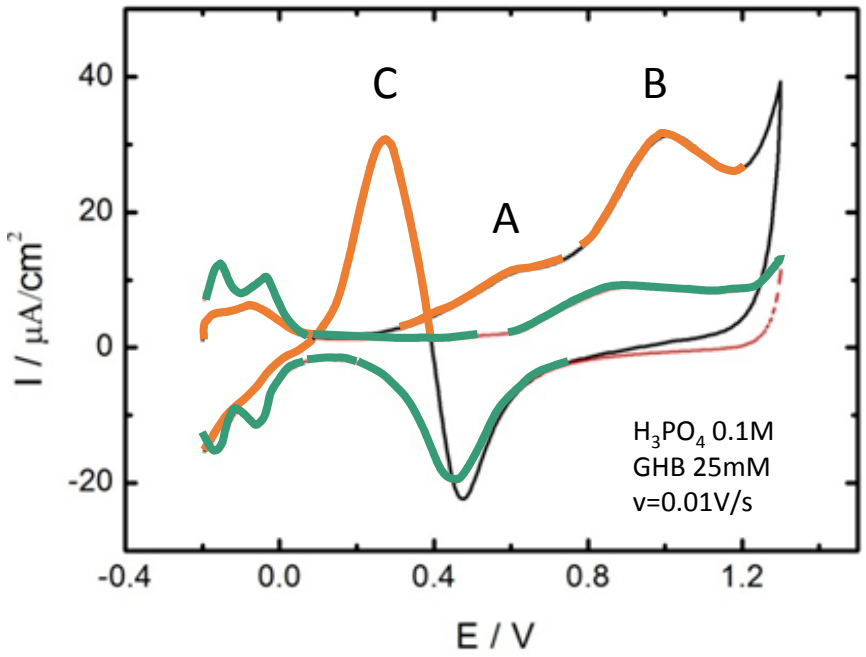




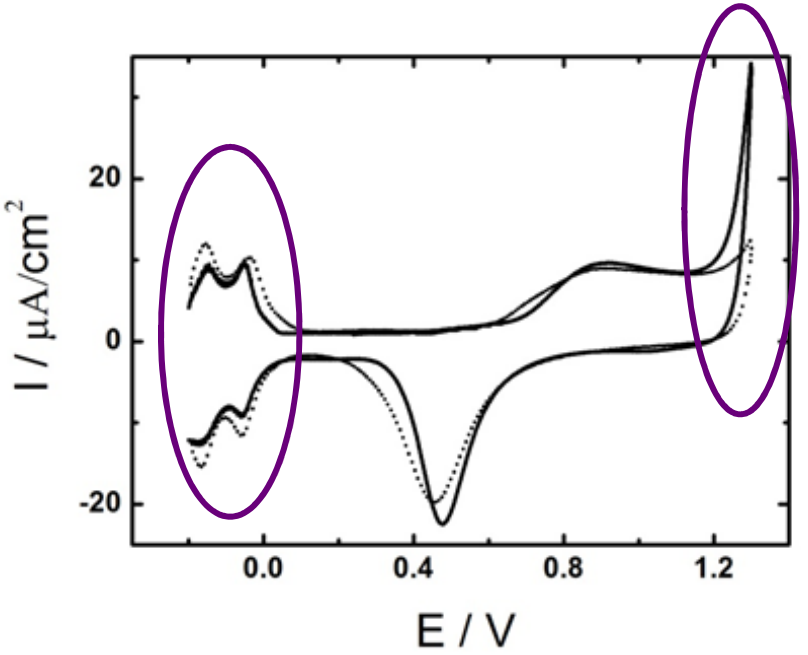


ELECTROQUÍMICA

Voltametría cíclica

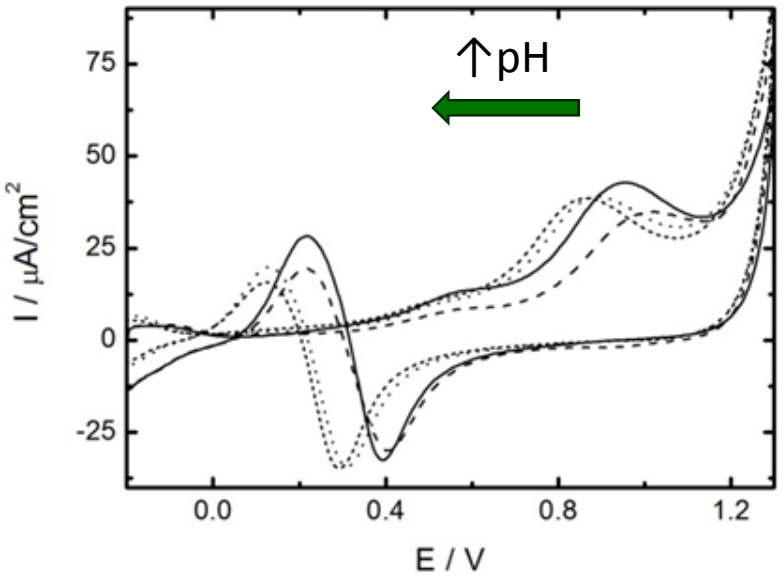


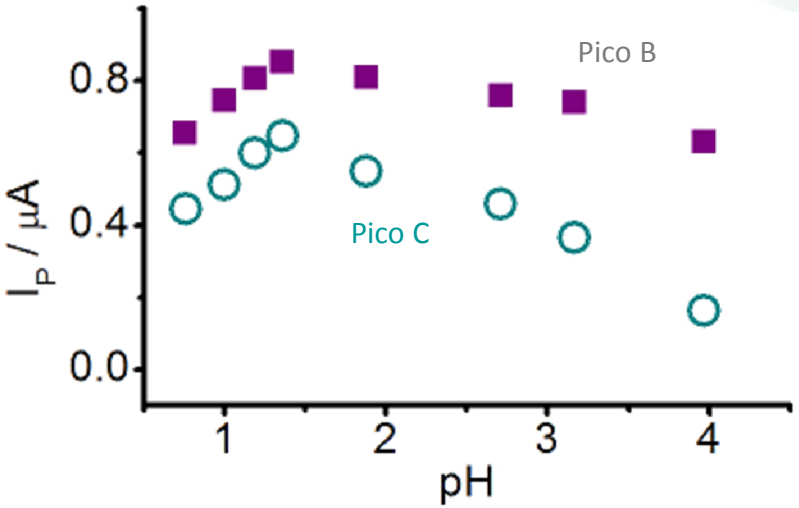
GBL

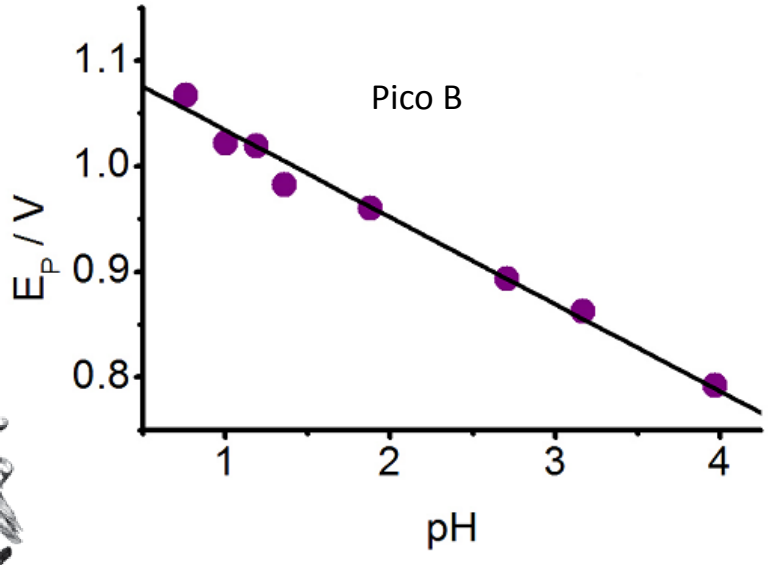


1) Influencia del pH
2) Efecto de la velocidad de barrido
3) Efecto de la concentración

Influencia del pH



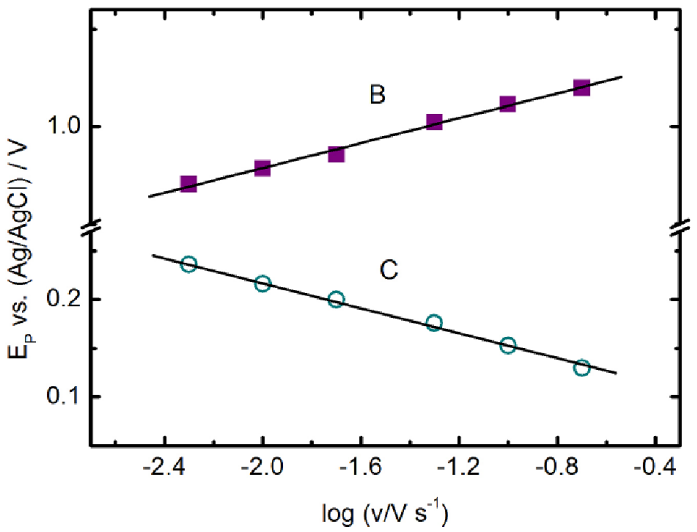




$$E_P = 1.090 - 0.073pH$$

$$R\text{-}CH_2OH + H_2O \rightarrow R\text{-}COOH + 4H^+ + 4e^-$$

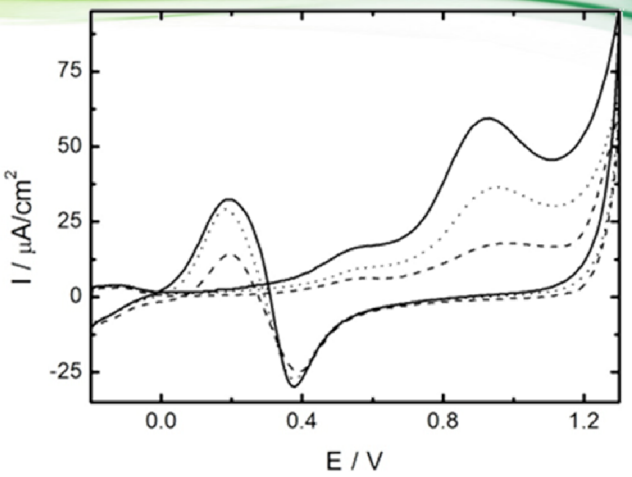
Efecto de la velocidad de barrido



log i_p vs. log v:

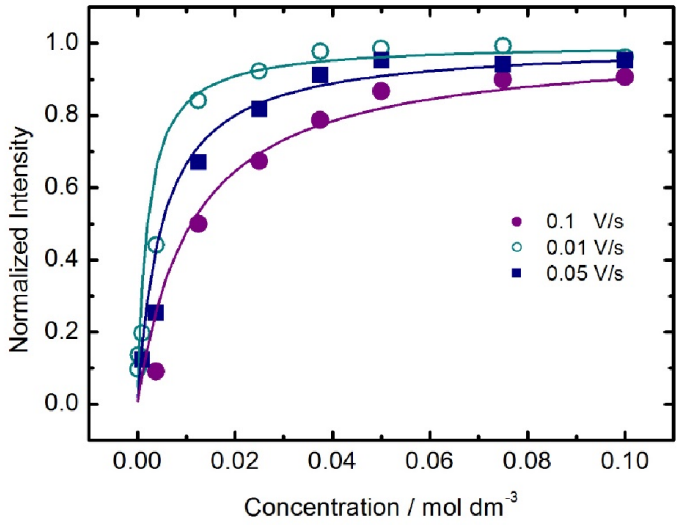
- Pico B
  - ↑c → m= 0.56
  - ↓c → m=0.63
  - Control mixto Adsorción/difusión
- Pico C
  - i_p ↓→v↑
  - Adsorción de la molécula/controlada por difusión

Efecto de la concentración



log i_p vs. log c

- Pico B→ Variación lineal m= 0.94→ Orden 1
- Pico C

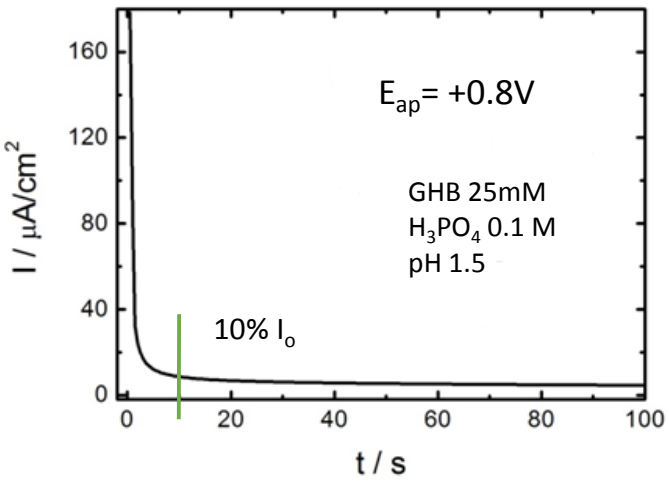


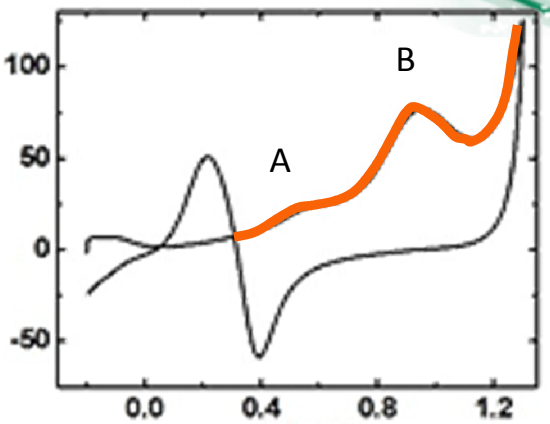
Relación tipo-Langmuir

$$\frac{I_p}{I_p^L} = \frac{Bc}{1+Bc}$$

Cronoamperometría

A altos potenciales (>0.3V)

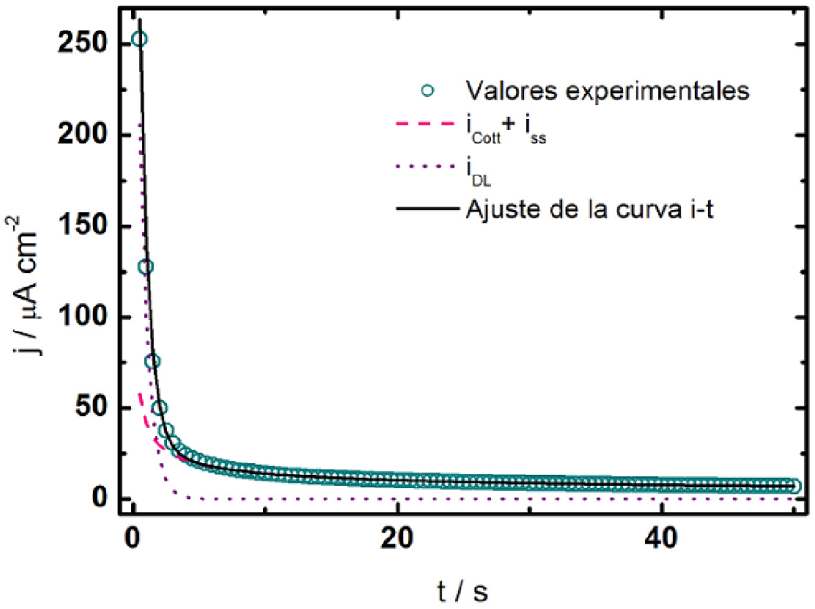




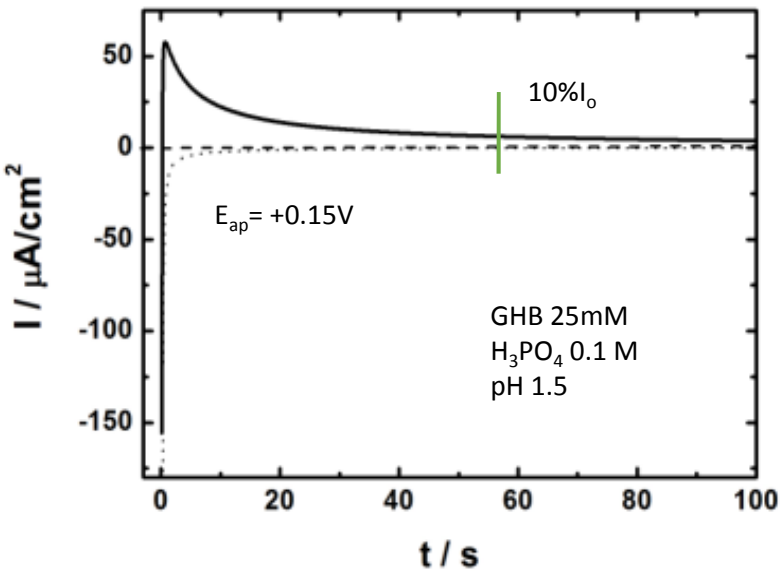
Ajustes teóricos:

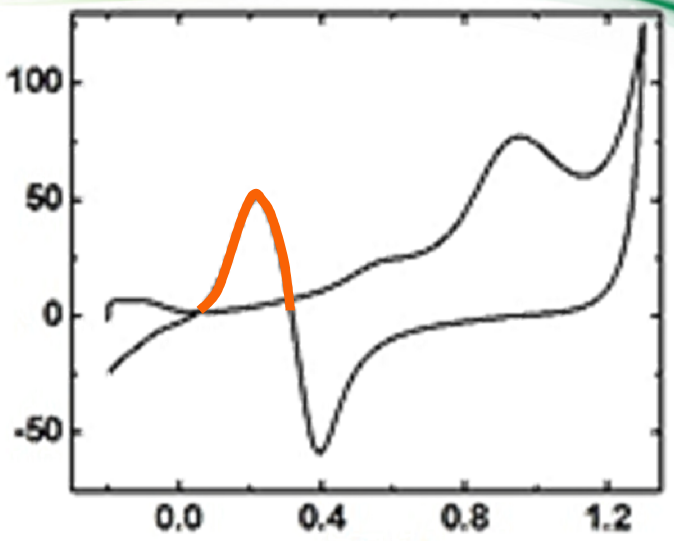
- Contribución Langmuir DL (a ↓ t)
- Transporte por difusión→ Cottrell
- Corriente estacionaria

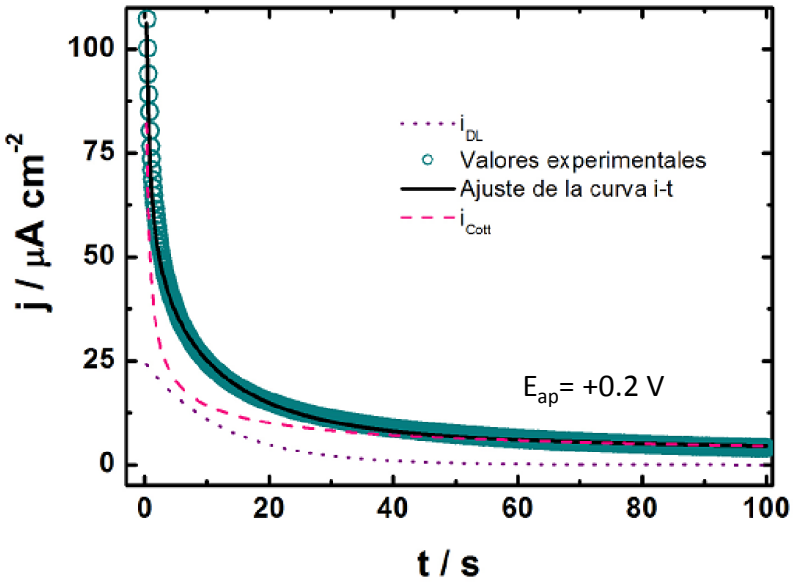
$$i(t) = i_{DL} + i_{Cott} + i_{SS} = a \cdot e^{-bt} + \frac{c}{t^{1/2}} + d$$



A bajos potenciales (<0.3V)



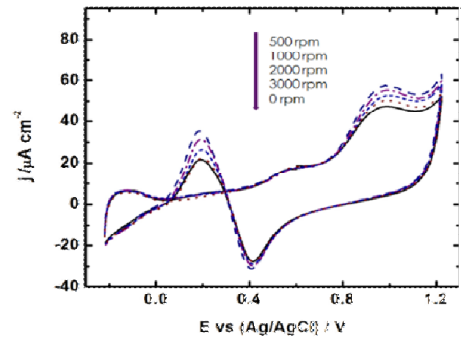




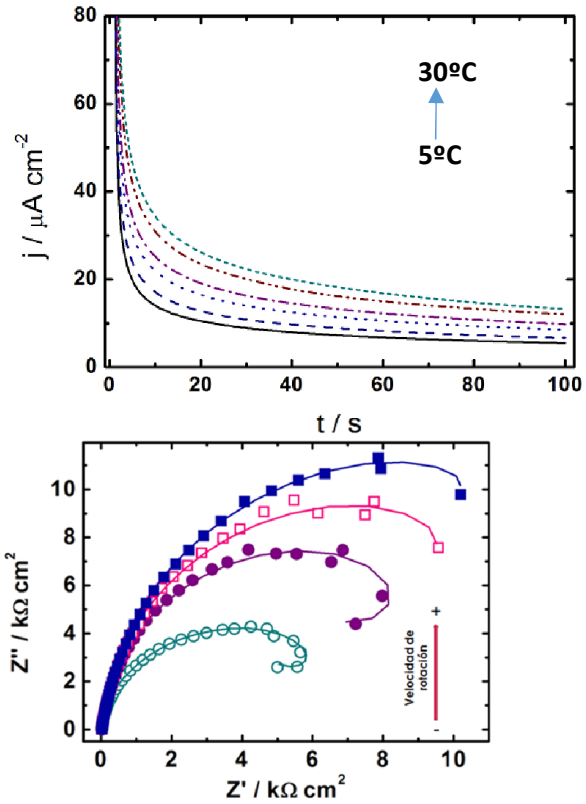
$$i(t) = i_{DL} + i_{Cott} = a' \cdot e^{-b't} + \frac{c'}{t^{1/2}}$$

ESTUDIO CON LA TEMPERATURA

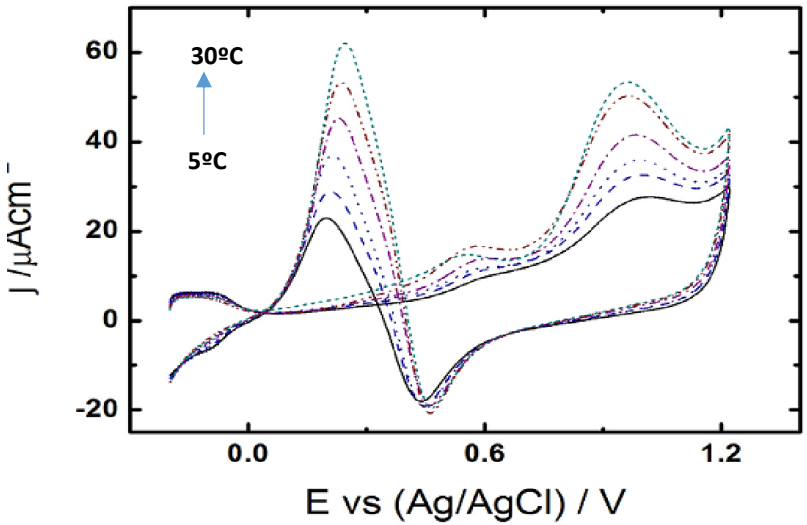
RDE



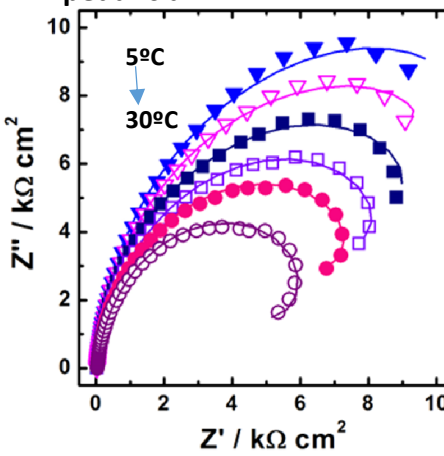
Cronoamperometría



Voltametría cíclica



Impedancia

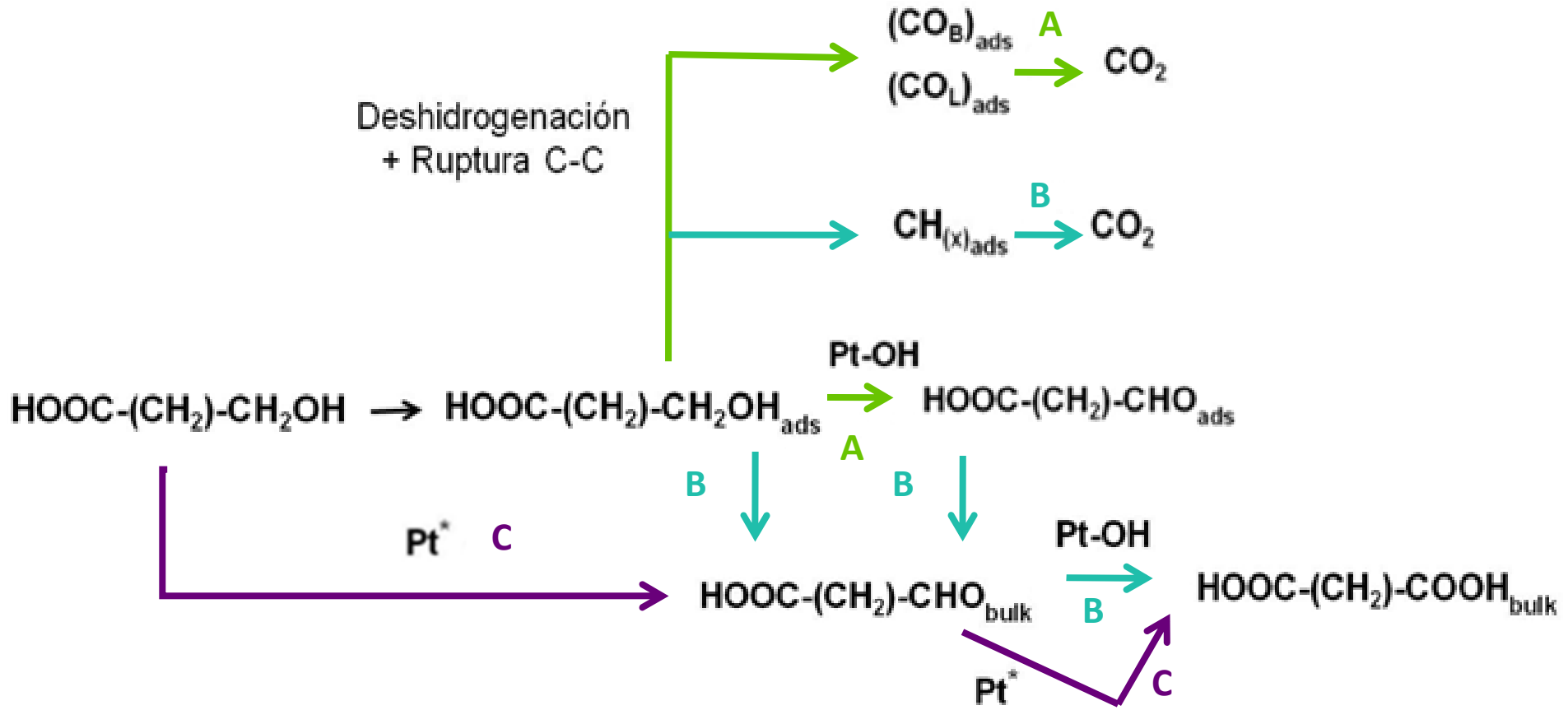


E (V) / Ea (KJ/mol)	0.7	0.8	0.9	0.2
Voltametría cíclica	17.4	24.3	19.5	22.5
Crono-amperometría	27.7	24.1	26.1	
Impedancia (50mM)	17.5	17.8	14.5	
Impedancia (100mM)	23.2	17.8	13.5	

DEPENDENCIA CON LA TEMPERATURA DE LA ELECTROOXIDACIÓN DEL ÁCIDO GAMMA HIDROXIBUTÍRICO SOBRE ELECTRODO DE PLATINO

ESQUEMA GENERAL

Oxidación de GHB



Técnicas Espectroelectroquímicas ➡ IR y Raman

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