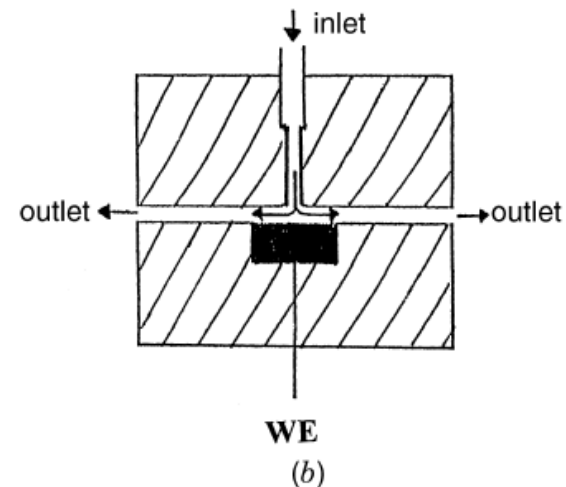
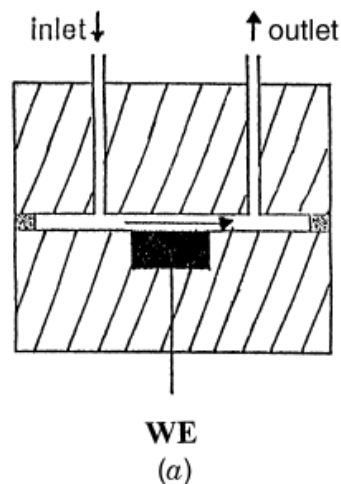


Průtočné detektory – FIA, ECLC

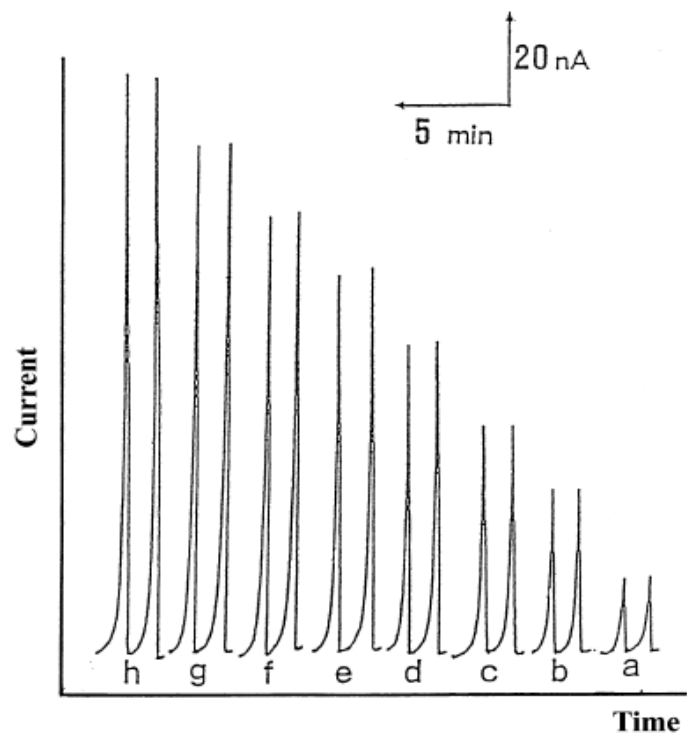
- Amperometrický mód
- Pulsní mód



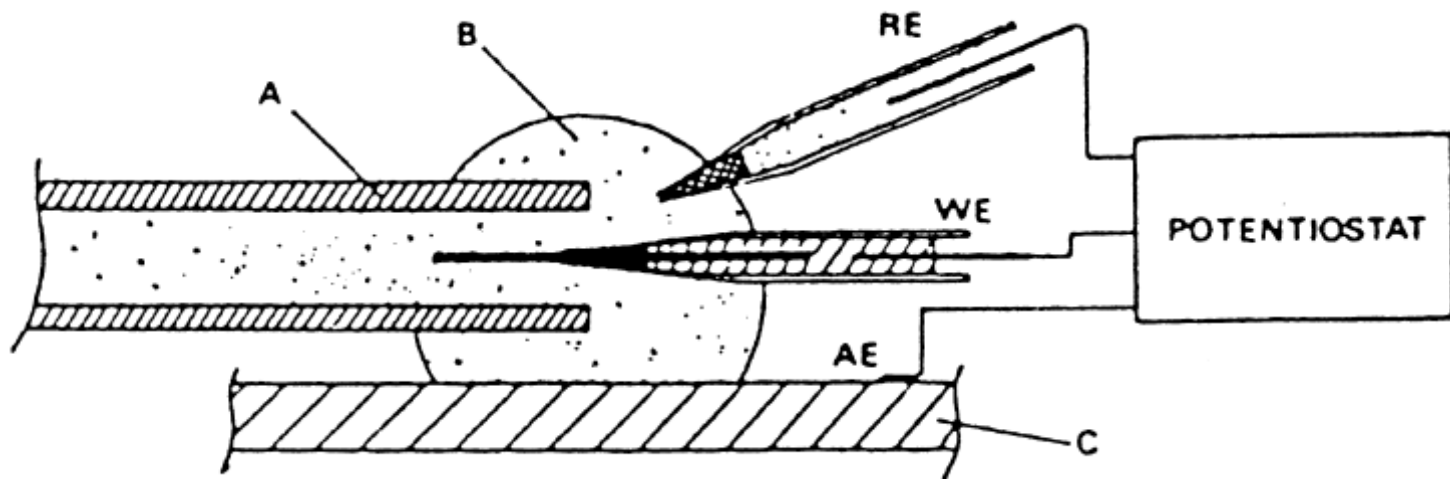
The Limiting-Current Response of Various Flow-Through Electrodes

Electrode Geometry	Limiting Current Equation
Tubular	$i = 1.61 nFC(DA/r)^{2/3} U^{1/3}$
Planar (parallel flow)	$i = 0.68 nFC D^{2/3} \nu^{-1/6} (A/b)^{1/2} U^{1/2}$
Thin-layer cell	$i = 1.47 nFC(DA/b)^{2/3} U^{1/3}$
Planar (perpendicular)	$i = 0.903 nFC D^{2/3} \nu^{-1/6} A^{3/4} u^{1/2}$
Wall-jet detector	$i = 0.898 nFC D^{2/3} \nu^{-5/12} a^{-1/2} A^{3/8} U^{3/4}$

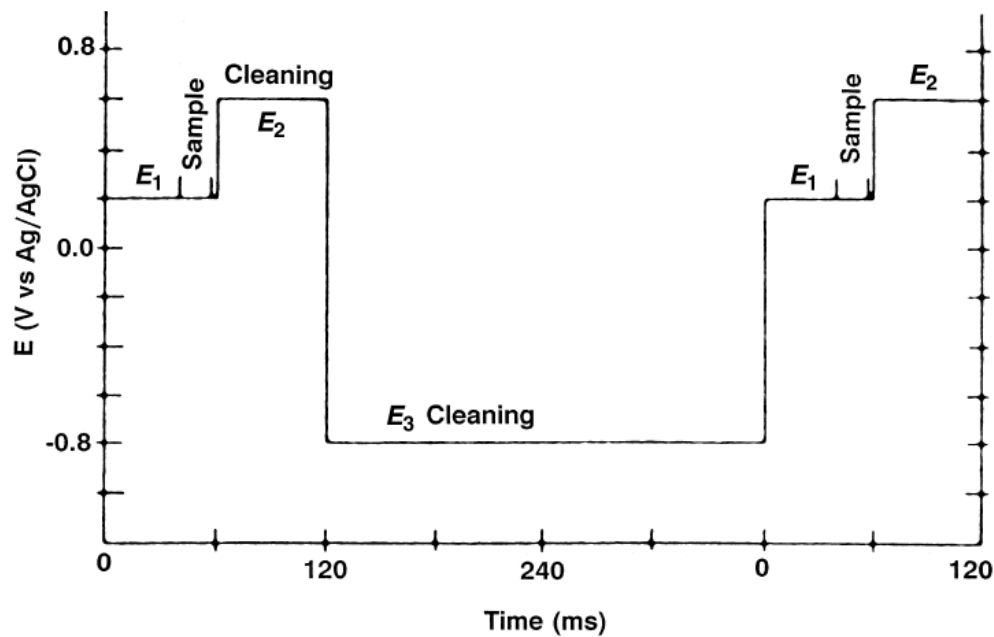
a = diameter of inlet; A = electrode area; b = channel height; C = concentration (mM); F = Faraday constant; D = diffusion coefficient; ν = kinematic viscosity; r = radius of tubular electrode; U = average volume flow rate; u = velocity (cm s^{-1}); n = number of electrons.



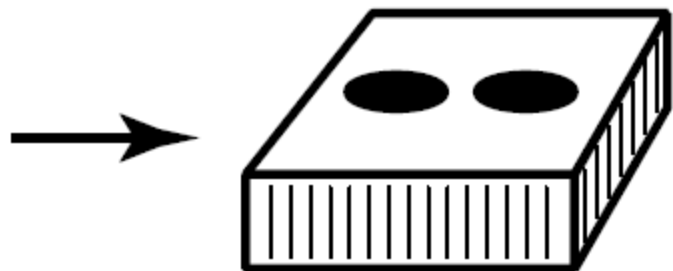
Detektor pro kapilární elektroforézu



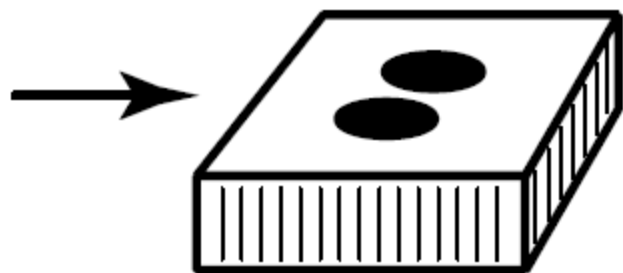
Čištění detektoru -
elektrochemické



Multielektrodové techniky



Series
(a)



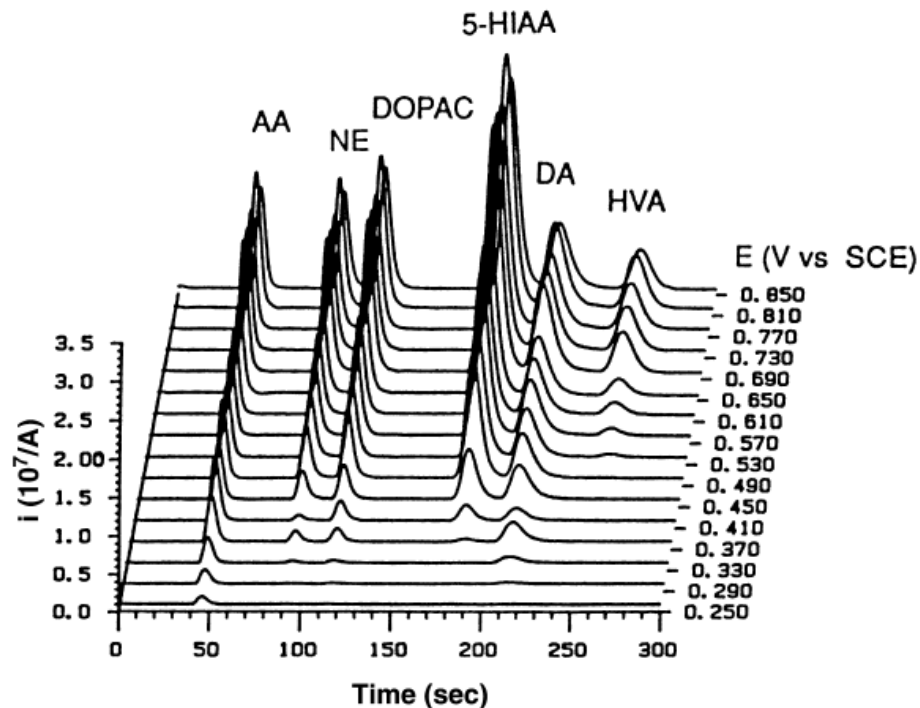
Parallel adjacent
(b)

Sériové uspořádání:

- měření recovery
- rozlišení látek se stejným retenčním časem, ale jinou elektrochemií
- generace aktivní formy látky pro detekci
- Rozlišení látek s reverzibilní elektrochemií

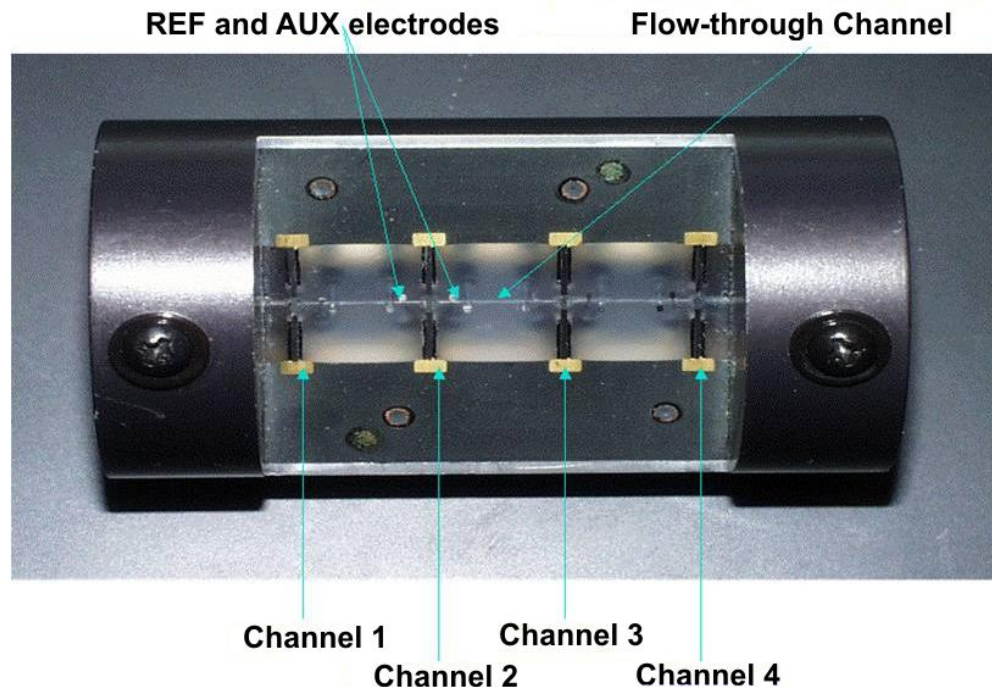
Paralelní uspořádání:

- Měření při více potenciálech - fingerprints
- 3D chromatogram

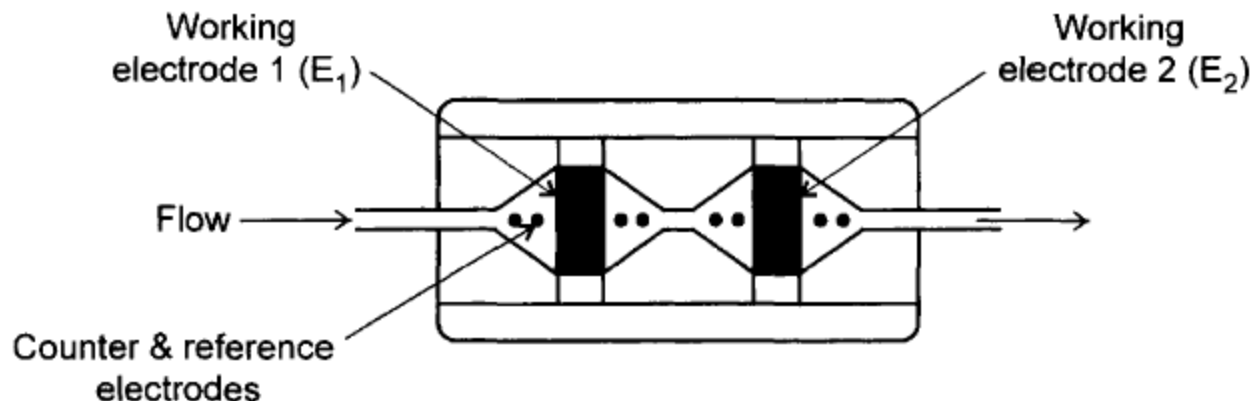


Coulometrický detektor (ESA Coulochem)

- Elektrolýza probíhá kompletně
- Iontová síla nosného elektrolytu nemusí být příliš vysoká
- Pórovité elektrody (uhlík)



- Screen mode
- Difference mode
- Redox mode



Spektroelektrochemie

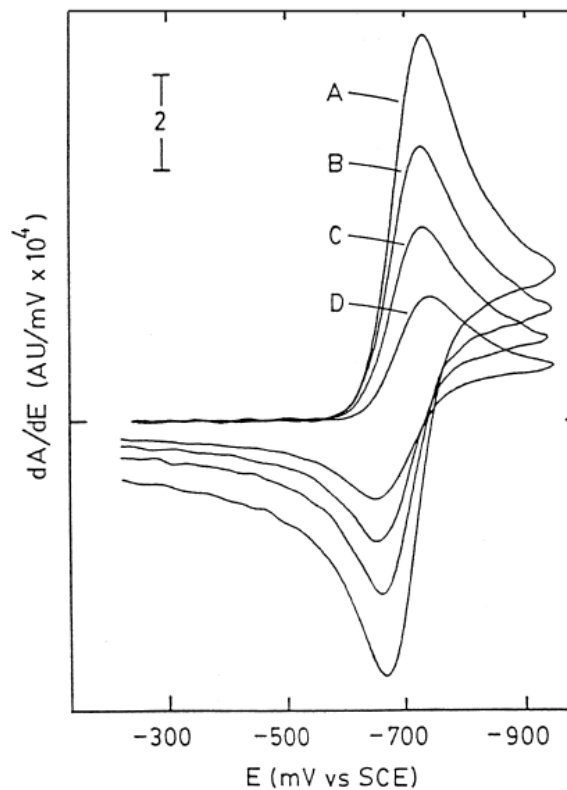
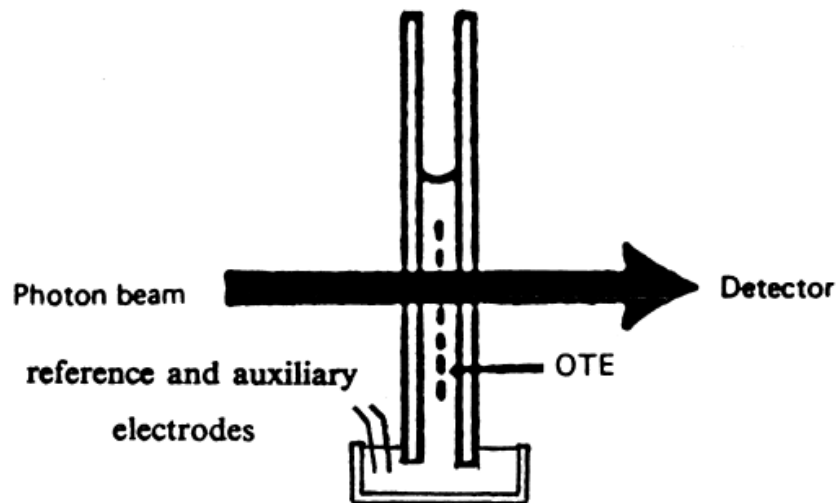
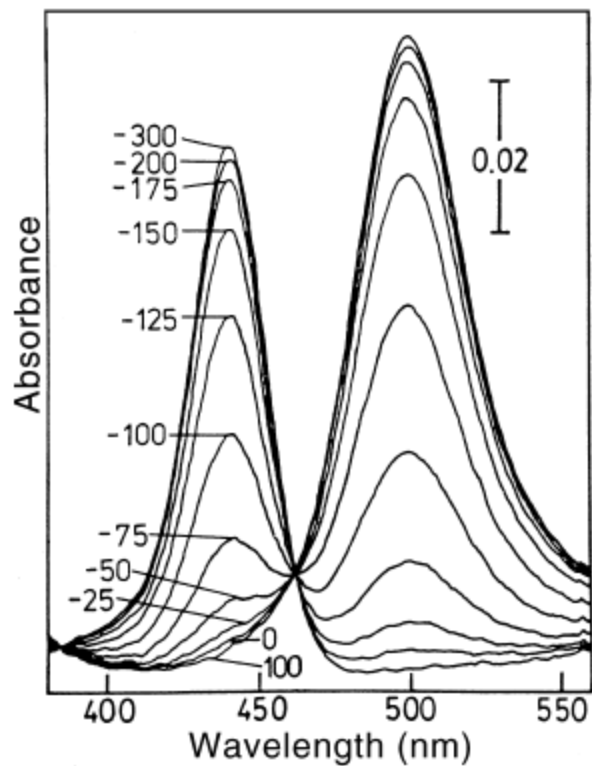
Thin layer cell, OTE (Pt mesh, ITO, SnO₂)

Chronoabsorptometry

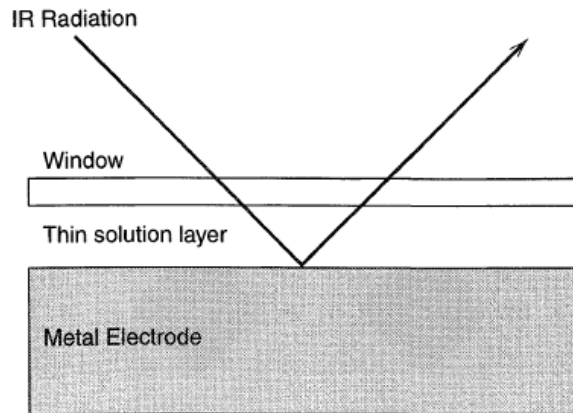
$$A = \frac{2C_O \varepsilon_R D_O^{1/2} t^{1/2}}{\pi^{1/2}}$$

Steady state

Měření std. (formálního) potenciálu



IR spektroelektrochemie (IR-SEC)



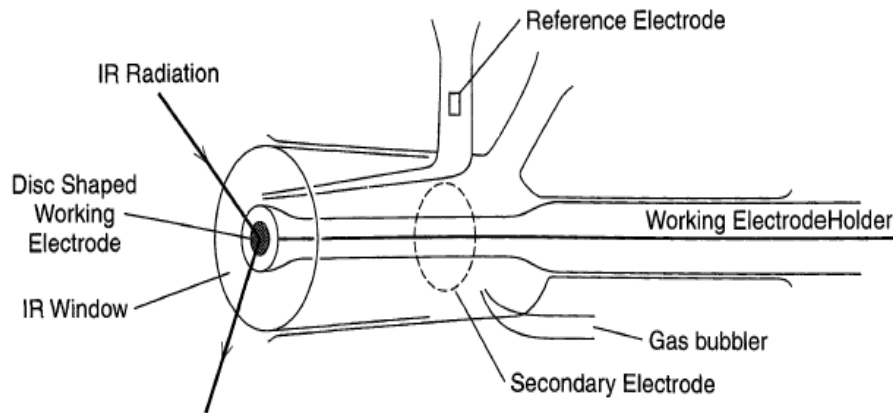
External reflectance mode

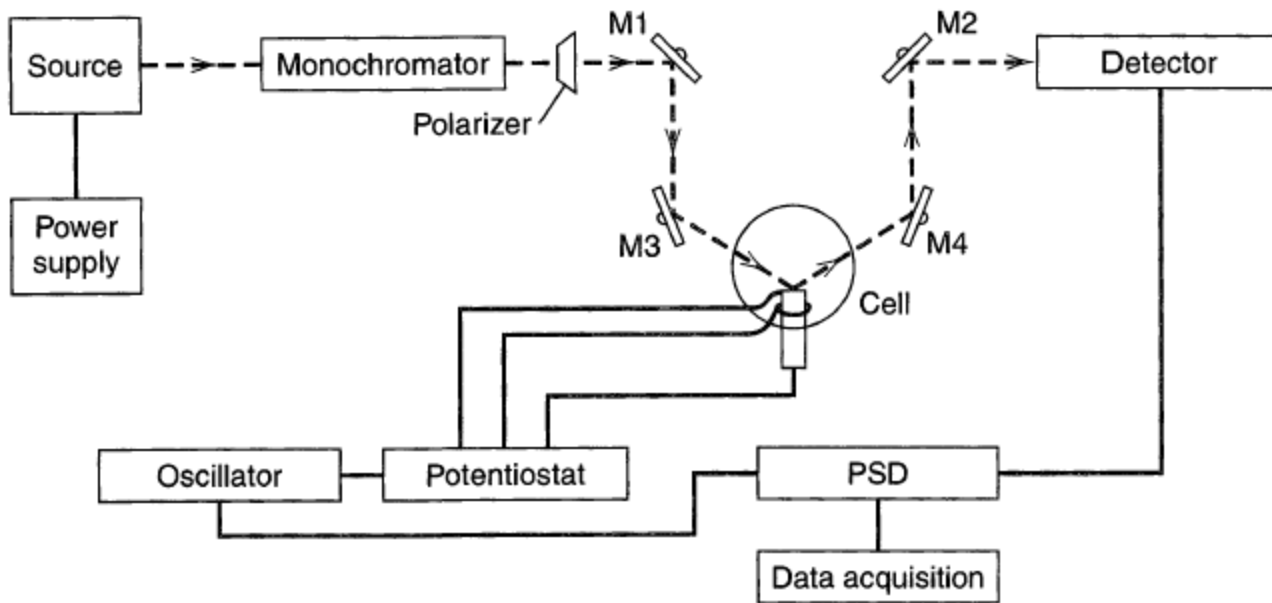
Malé signály – modulace a subtraktivní metody

EMIRS = electrochemically modulated infrared reflectance spectroscopy

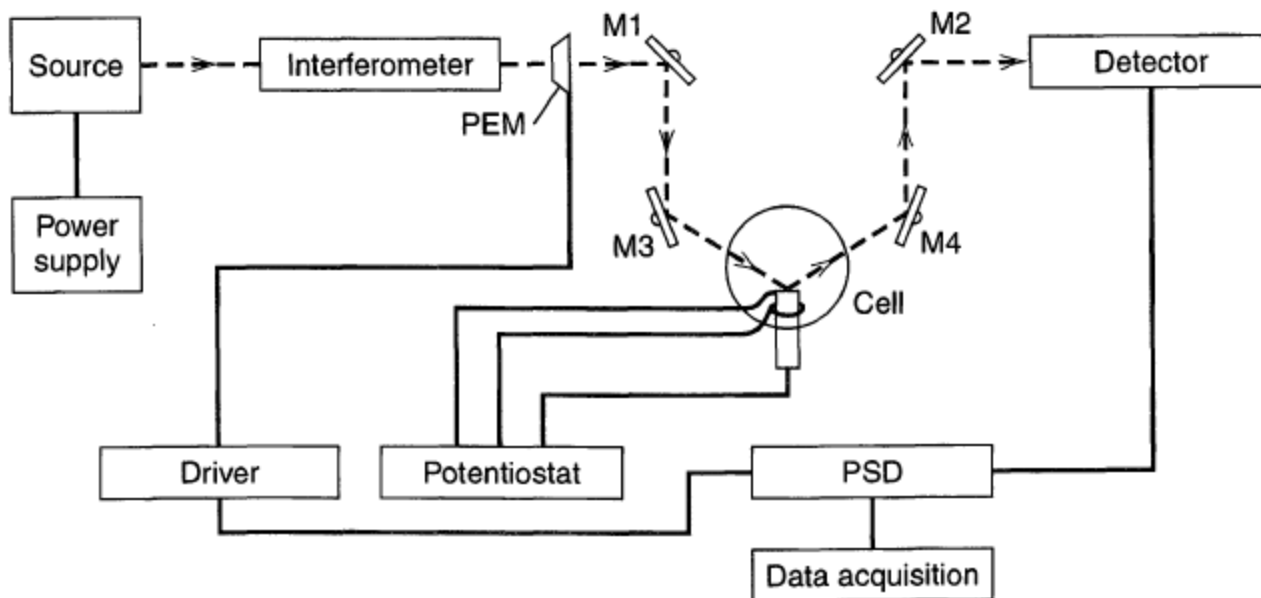
SNIFTIRS – subtractively normalized fourier transform infrared spectroscopy

SEIRA – surface enhanced infrared absorption

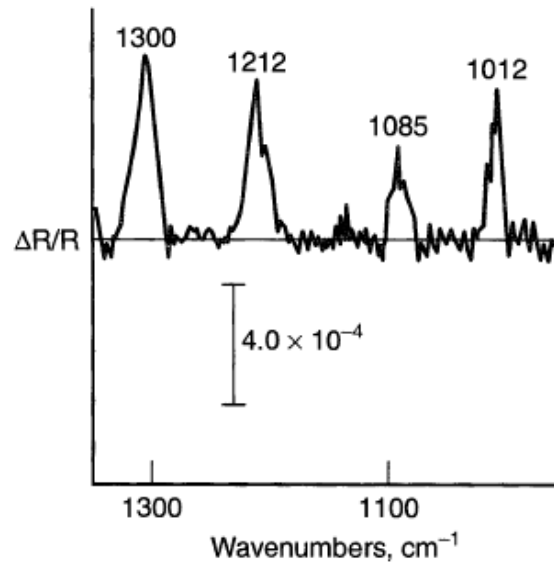
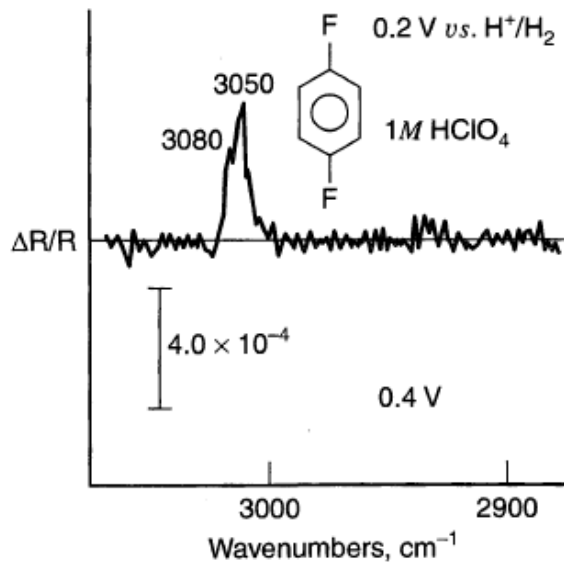




EMIRS

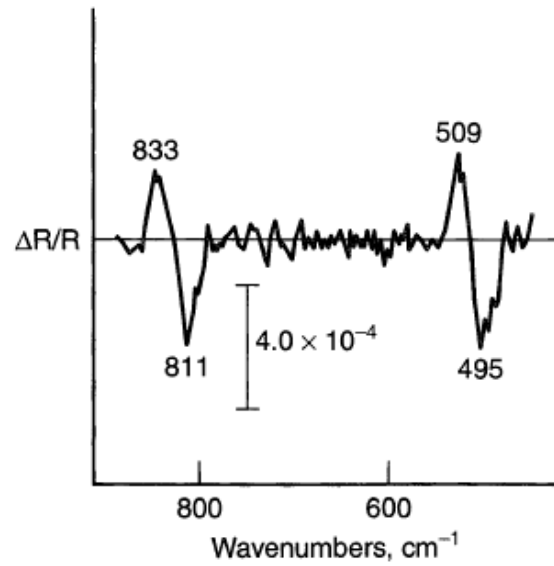
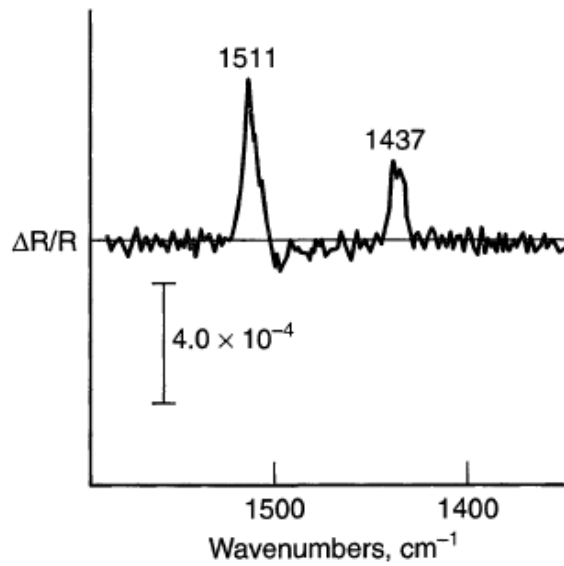


SNIFTIRS



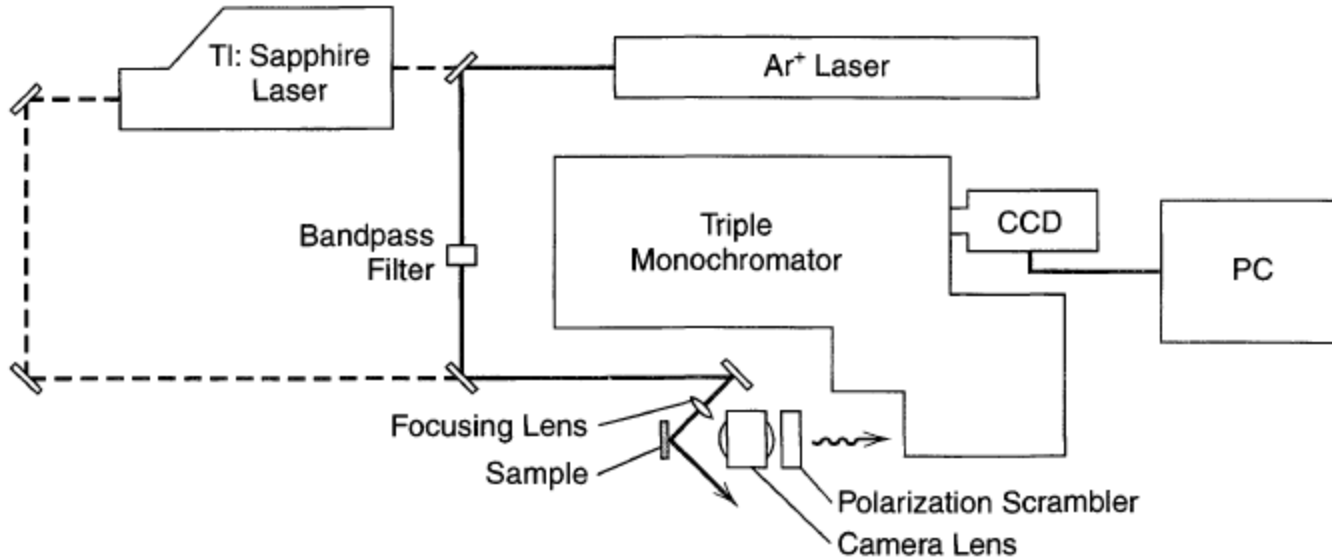
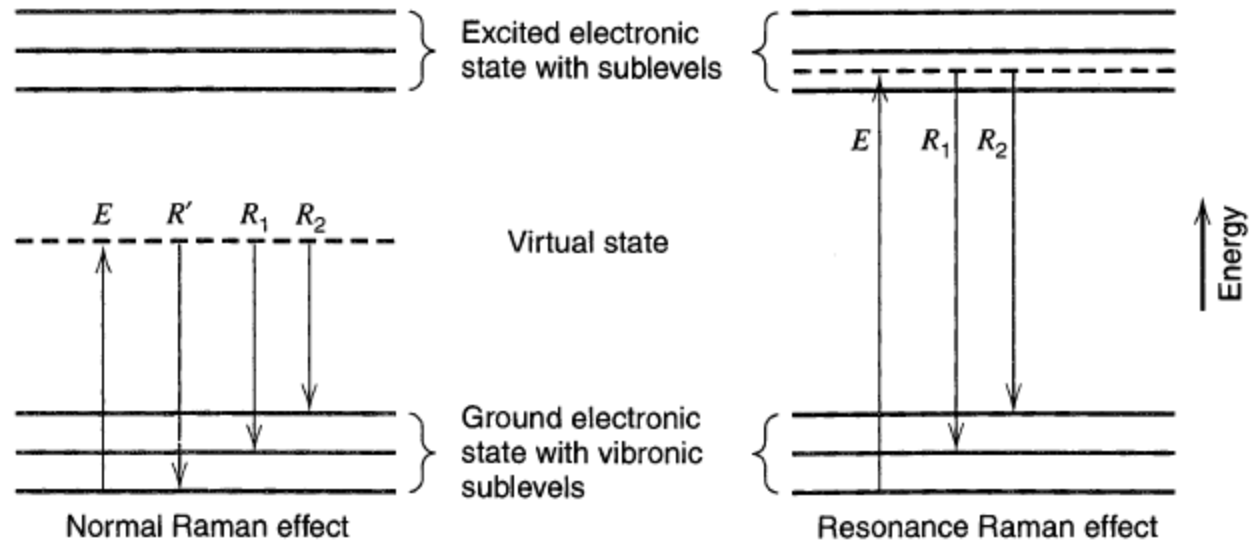
Elektroadsorpce
difluorbenzenu

0,4 a 0,2 V



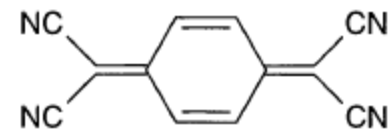
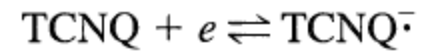
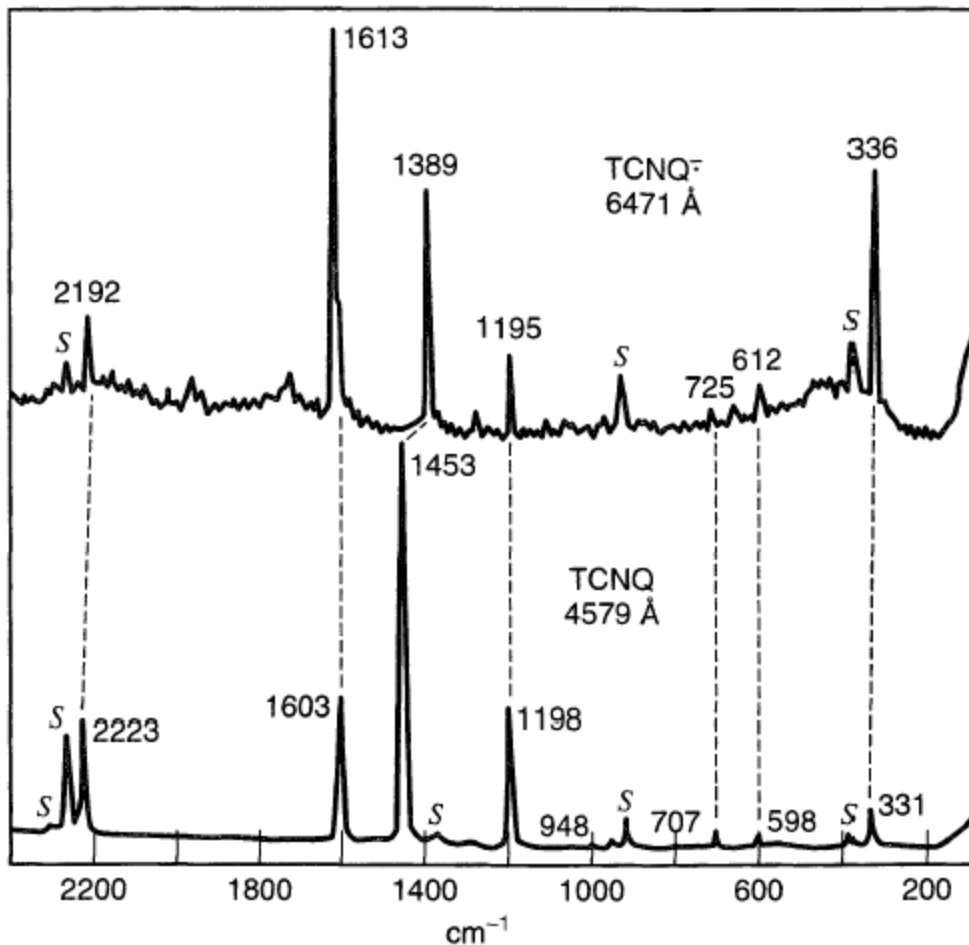
RAMAN

Neelastický rozptyl



SERS
SERRS

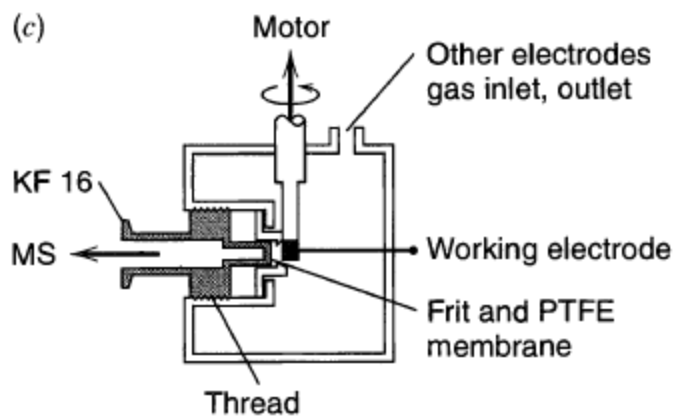
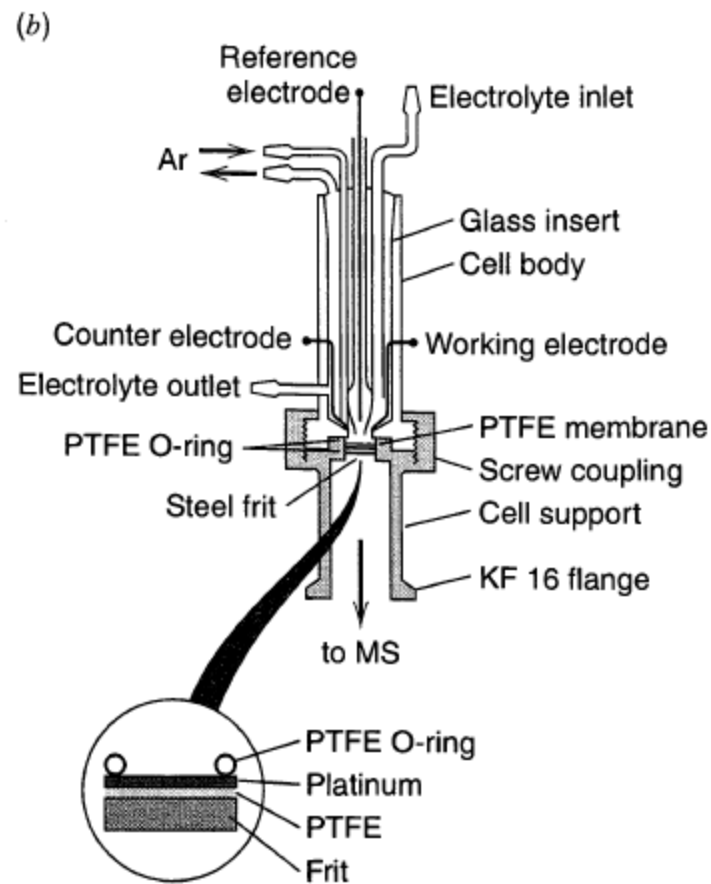
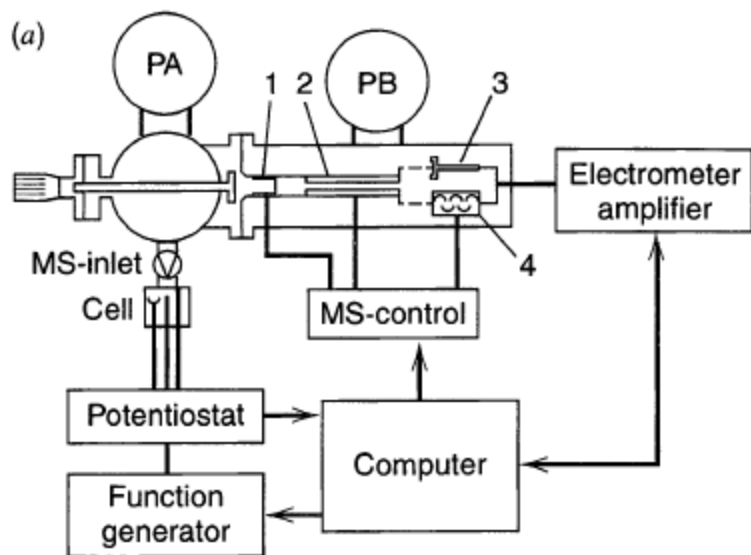
(Ag, Au,
Cu)



Identifikace
(mezi)produktů

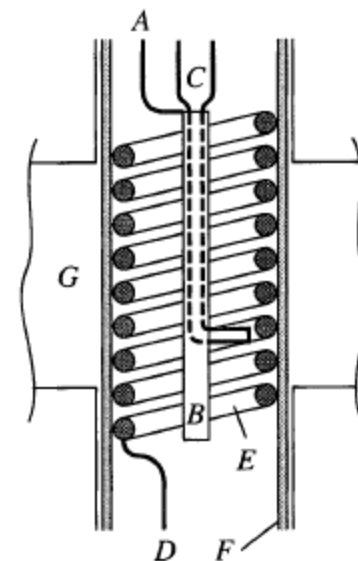
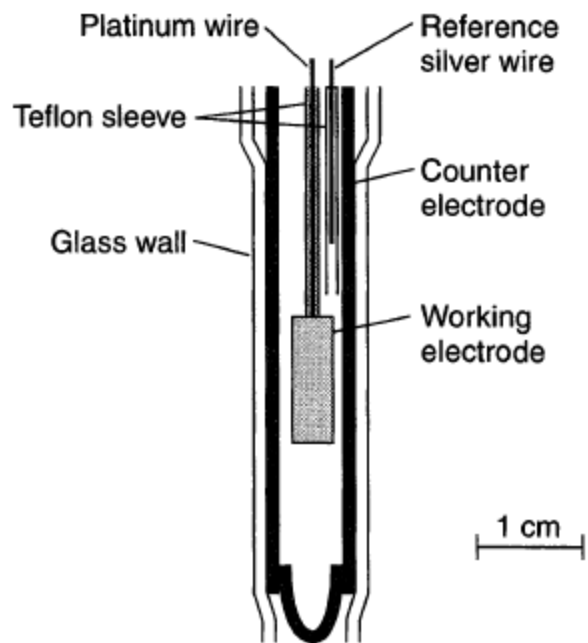
Transienty – pozorujeme
zvolenou čáru

Elektrochemie a MS spektroskopie



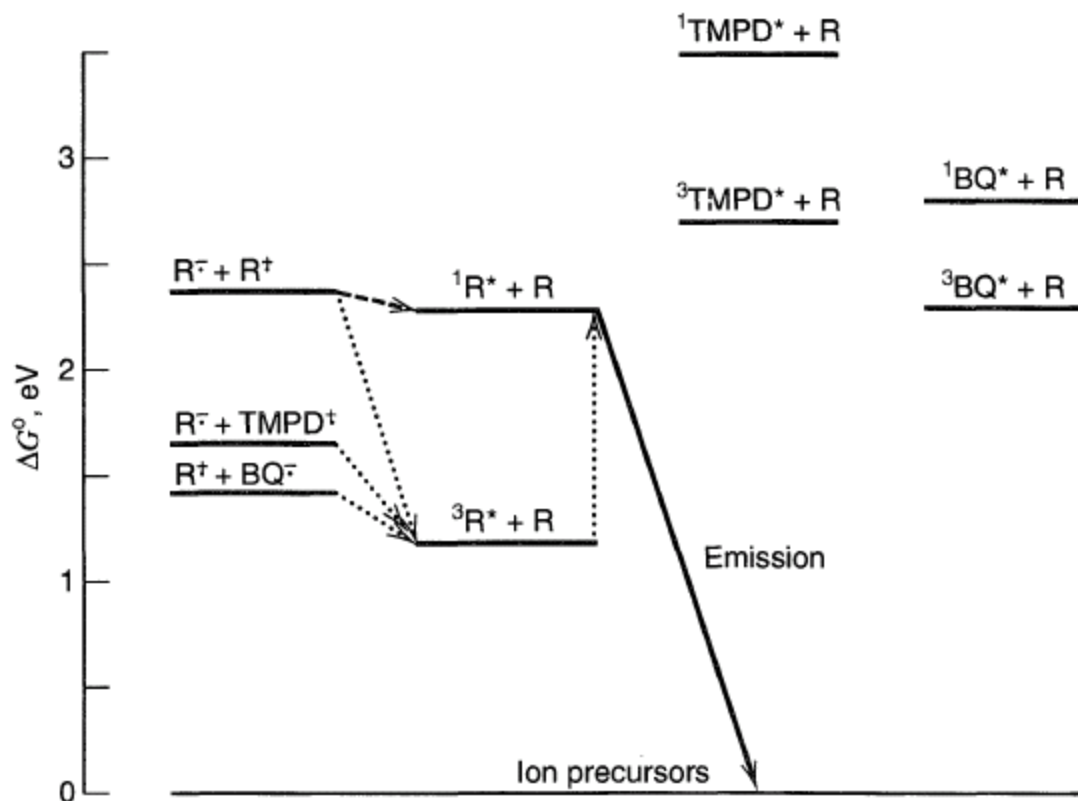
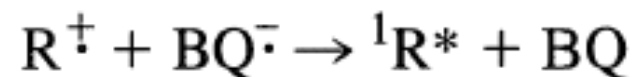
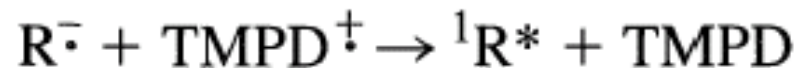
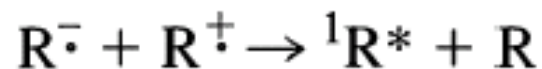
Elektrochemie a EPR

Radikálové ionty Spin trapping

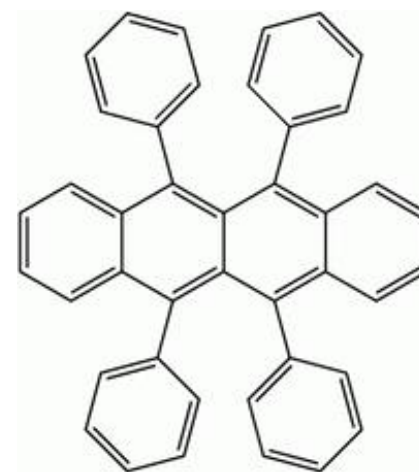


Elektrogenerovaná chemiluminiscence

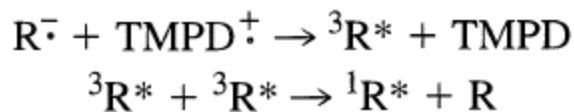
anihilace radikálů



rubrene (R), N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), and p-benzoquinone (BQ)

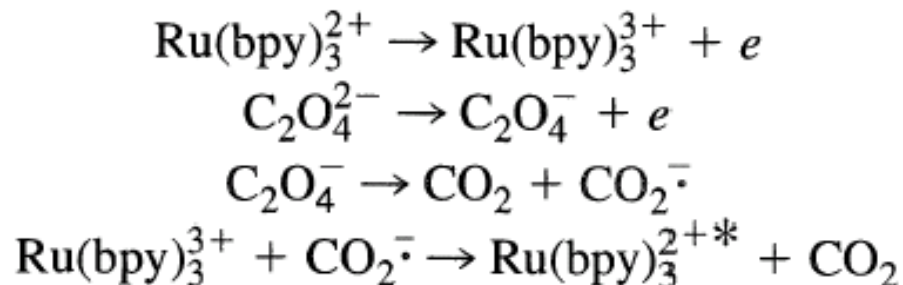
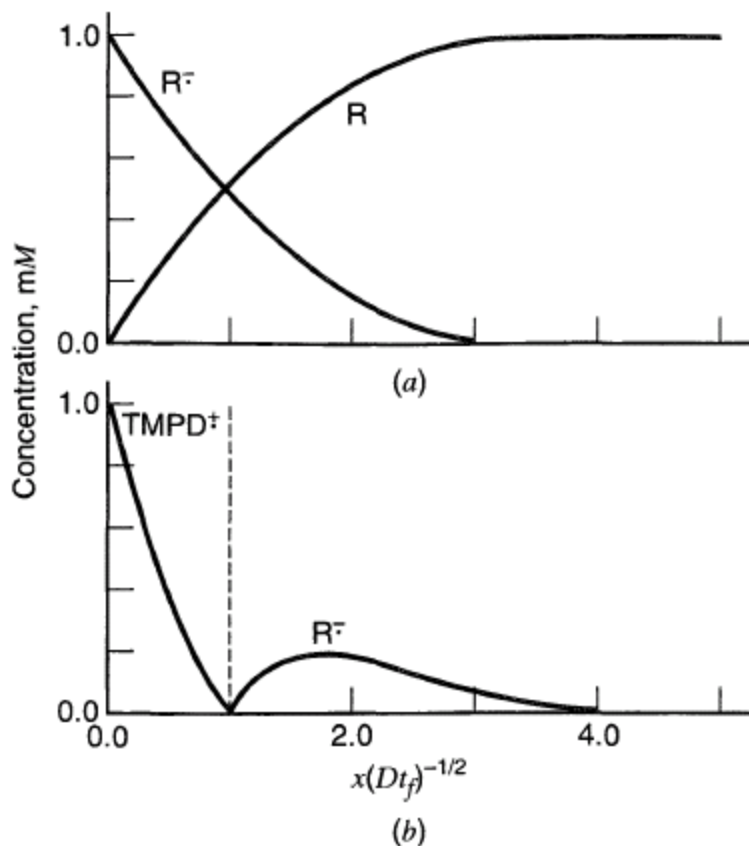


S a T cesta



ECL step, RRDE

použití „koreaktantu“

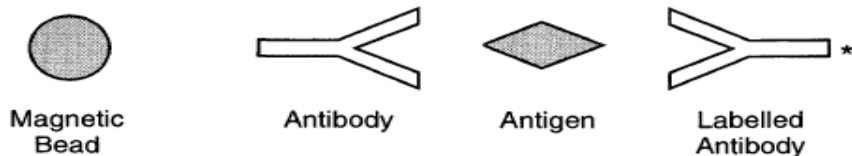


ECL jako detekční metoda pro HPLC

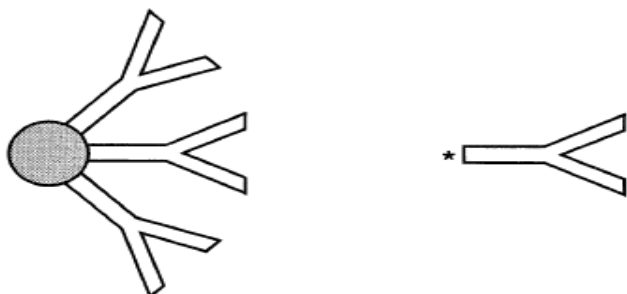
- využívá $\text{Ru}(\text{bpy})_3$ – imobilizovaný na elektrodě v Nafionu
- detekce NADH, aminů a aminokyselin (koreaktanty)

Elektrogenerovaná chemiluminiscence klasických CL indikátorů

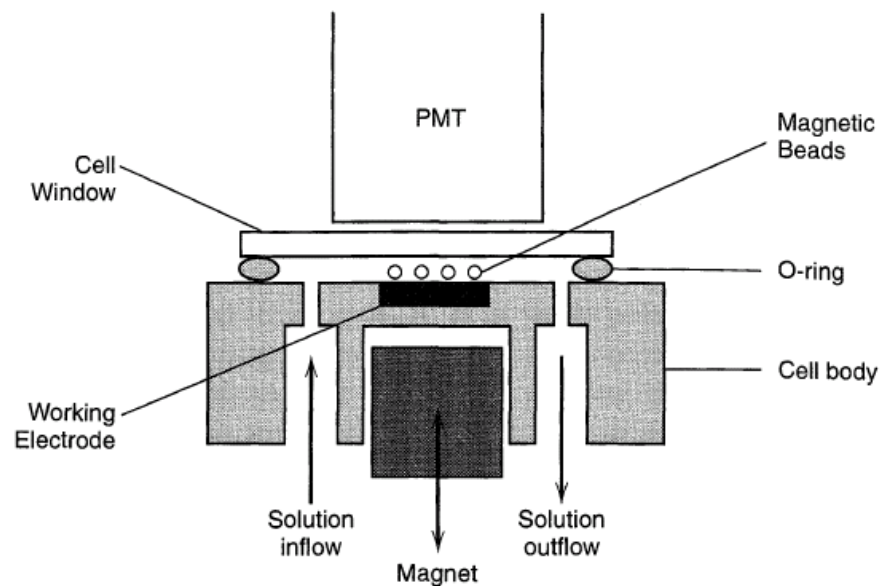
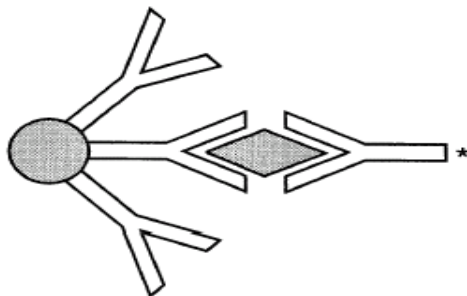
(luminol, lucigenin) – stopy peroxidu vodíku, vizualizace „horkých míst“ na elektrodách



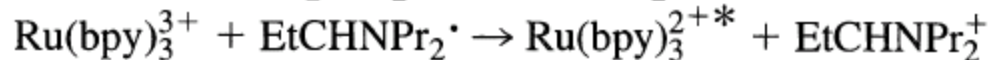
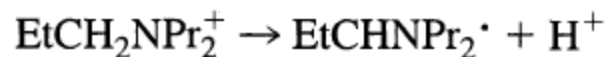
(a) Sample with no antigen (labelled antibody not attached to bead)



(b) Sample with antigen (labelled antibody attaches to bead)

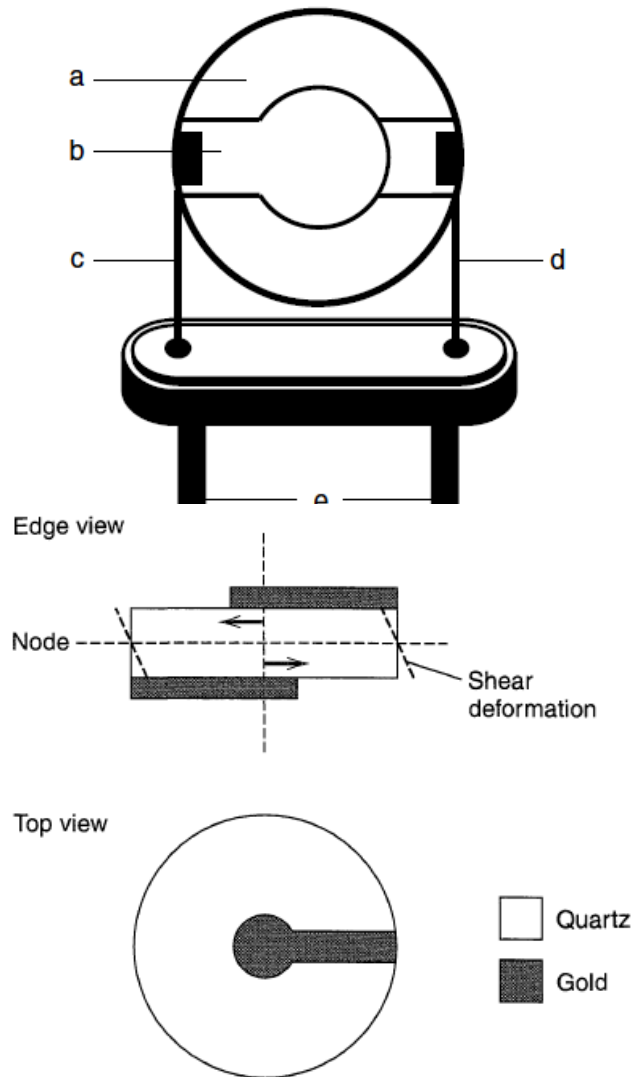


PSA – prostate specific antigen



tri-*n*-propylamine, TPrA

EQCM = electrochemical quartz crystal microbalance



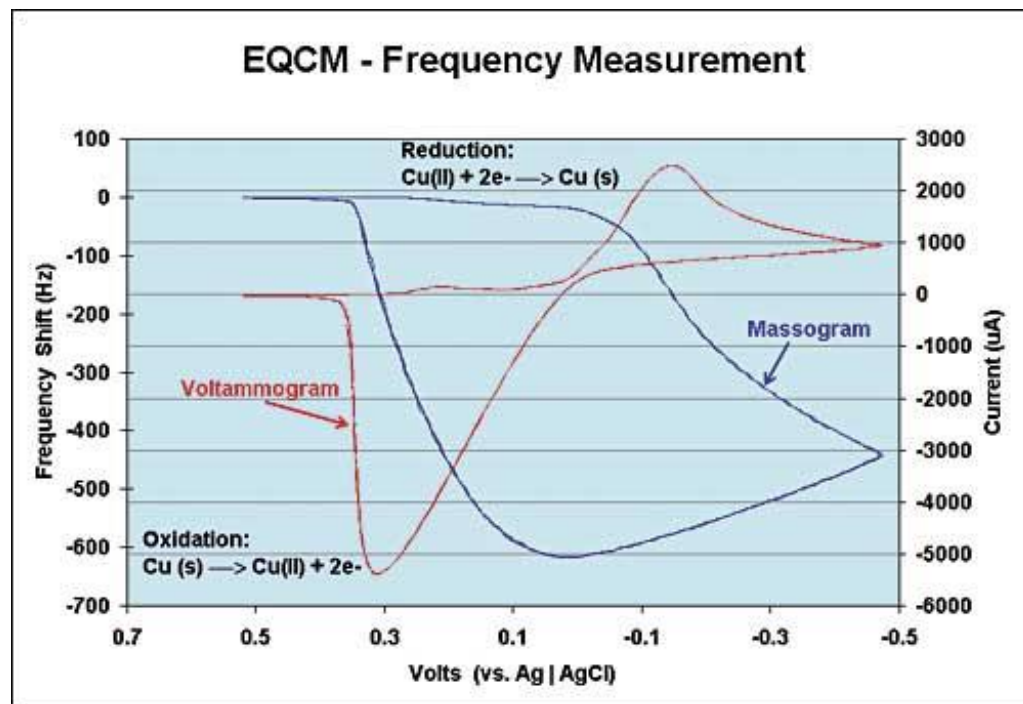
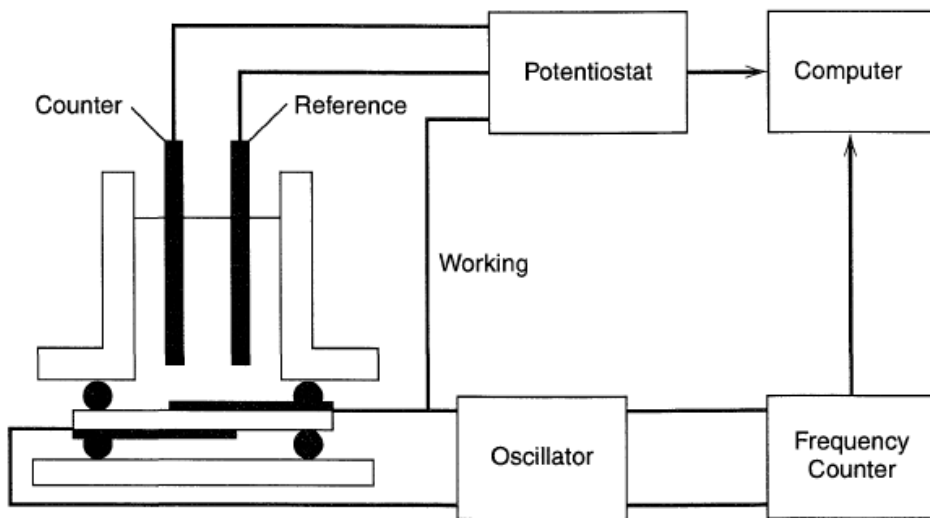
$$\Delta f = \frac{-2\Delta m n f_0^2}{A\sqrt{\mu\rho}}$$

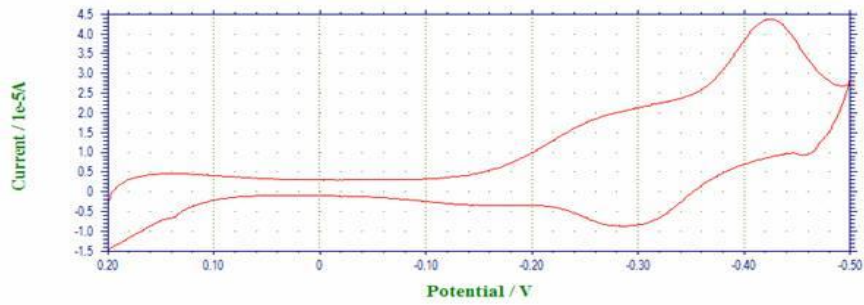
Sauerbrey equation

Δm změna hmotnosti
 n harmonická frekvence
 f_0 základní frekvence

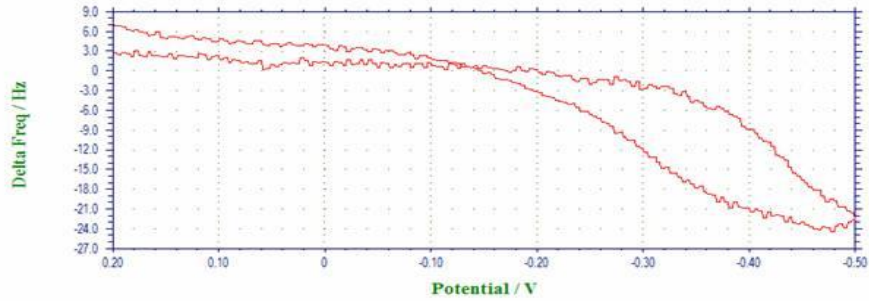
A plocha elektrody

μ modul pružnosti ve smyku pro SiO_2
 ρ hustota SiO_2

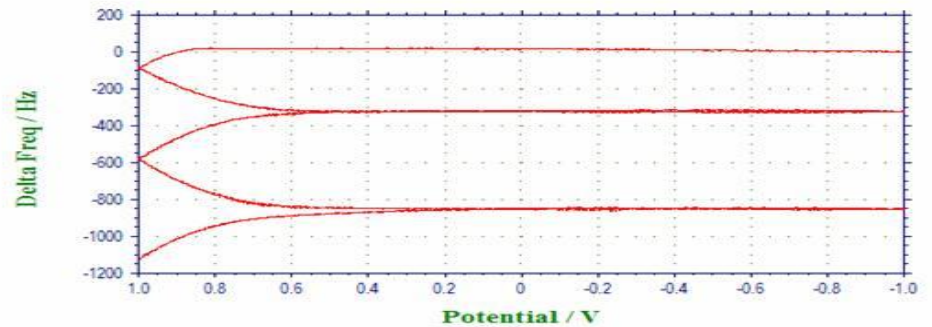
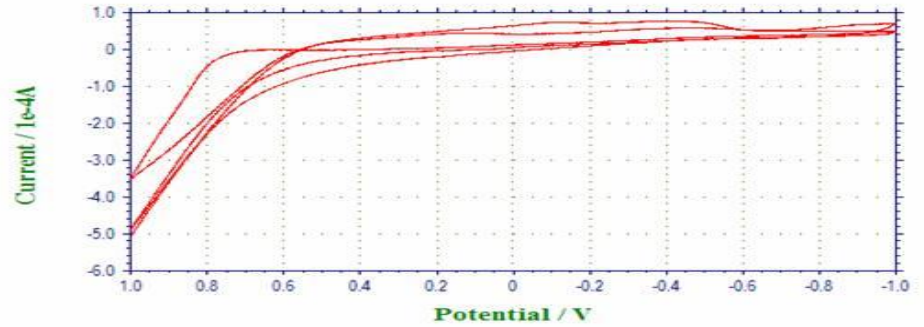


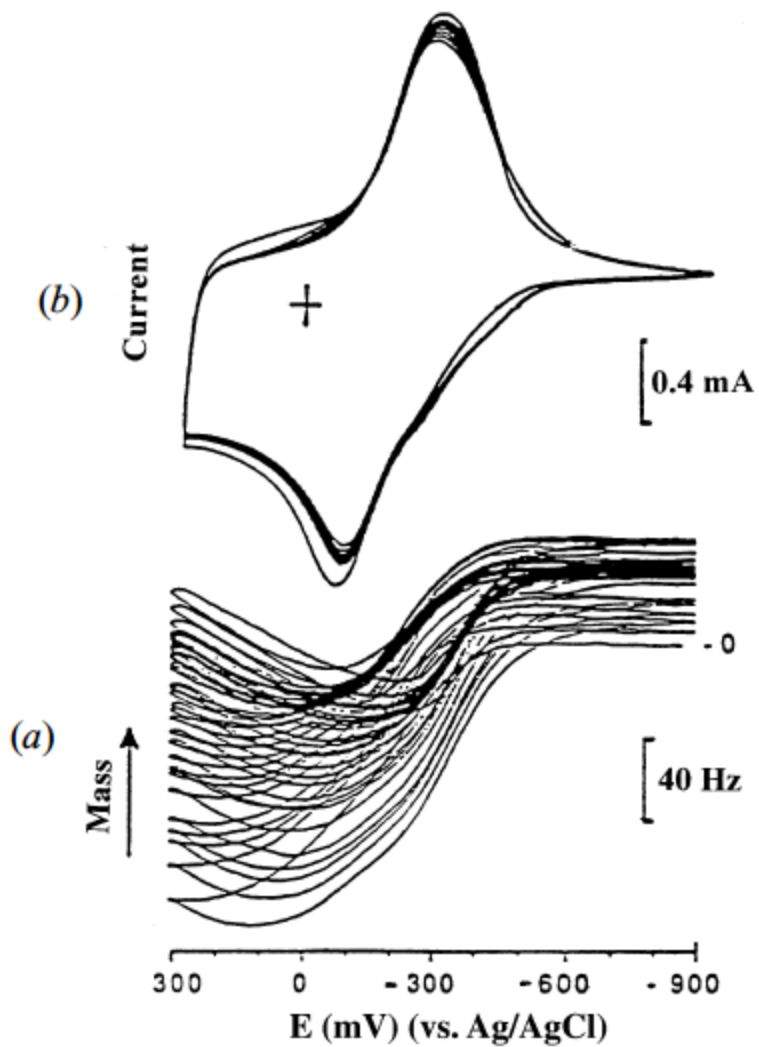


UPD olova

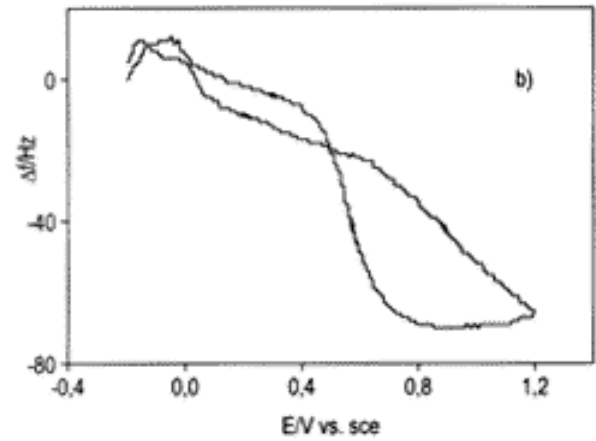
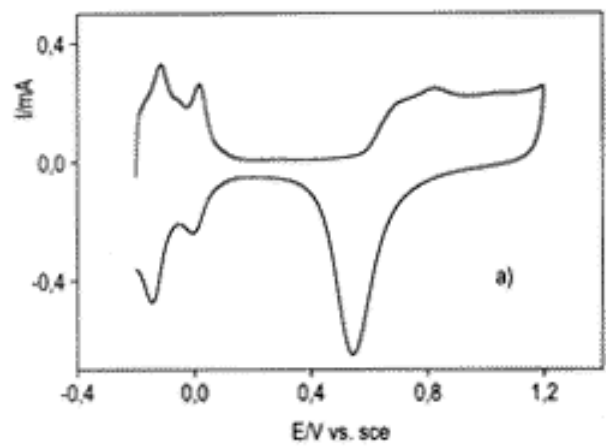


Růst polypyrrolového filmu



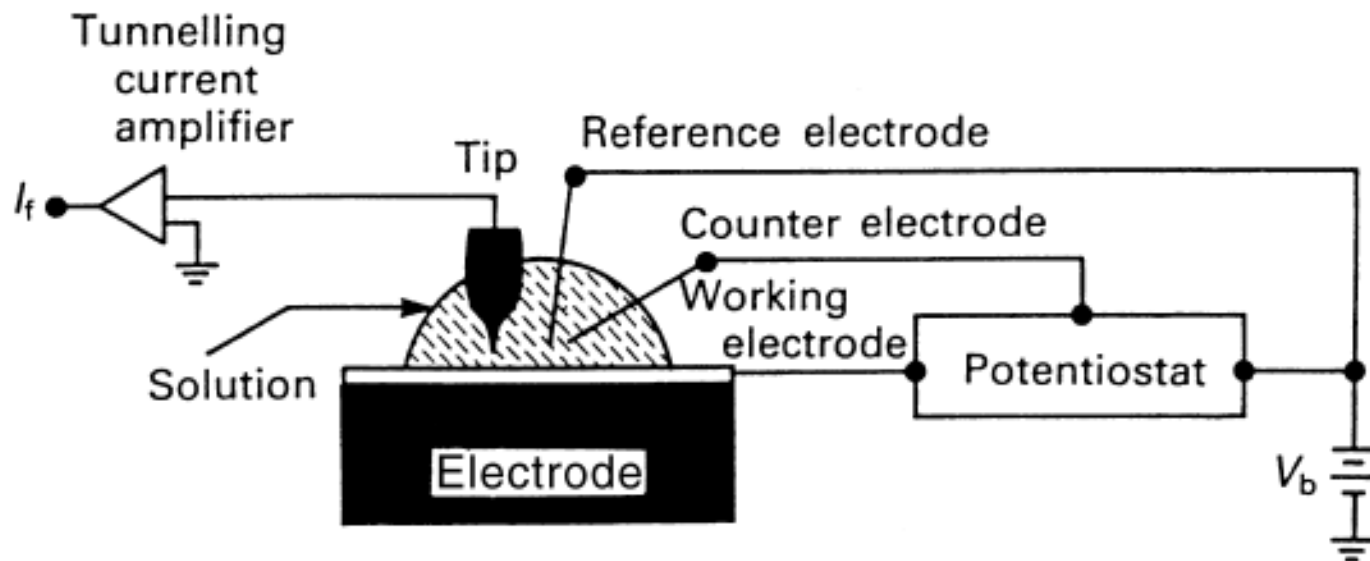


Iontoměnič



Pt povrch

Elektrochemická STM (SECM)

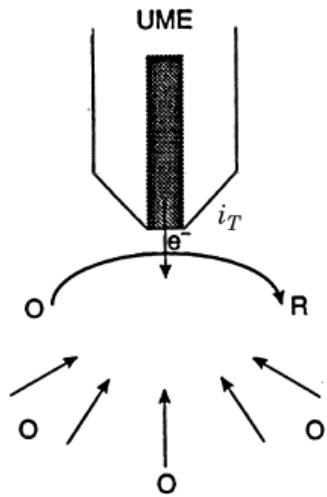


Mikroelektrodové tipy

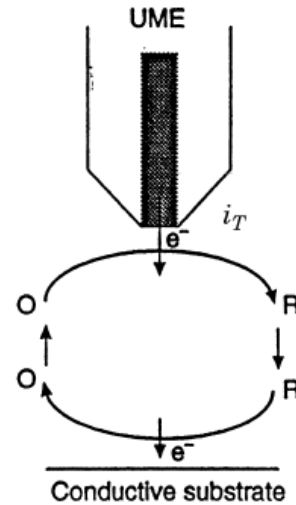
Potenciometrické tipy (pH)

Sledování distribuce Aktivních míst elektrodových povrchů

Elektrochemická fabrikace povrchů

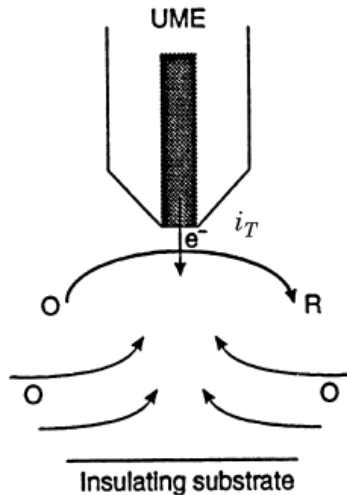


(a) $i_{T,\infty} = 4nFDca$



(b) $i_T > i_{T,\infty}$

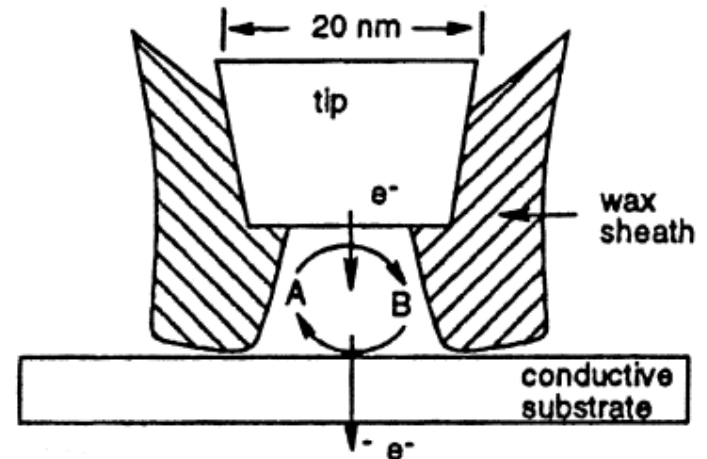
A: elektroda
vzdálená od
povrchu – steady
state current i_T



(c) $i_T < i_{T,\infty}$

„positive feedback mode“

Rozlišení nedosahuje atomárních
rozměrů,
Single molecule techniky



Bipolar electrochemistry

