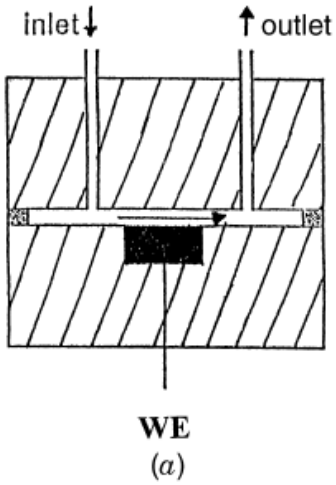
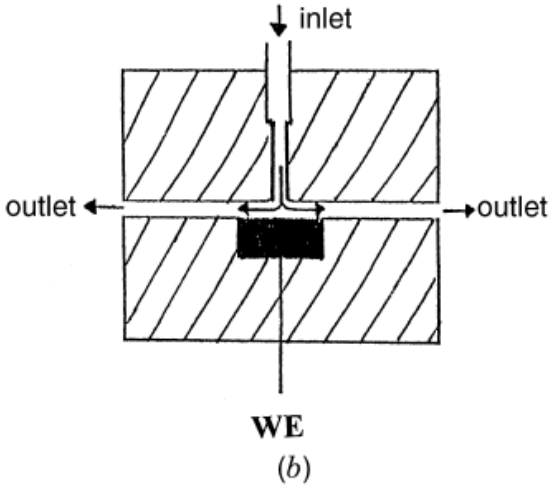
Průtočné detektory – FIA, ECLC

- Amperometrický mód
- Pulsní mód

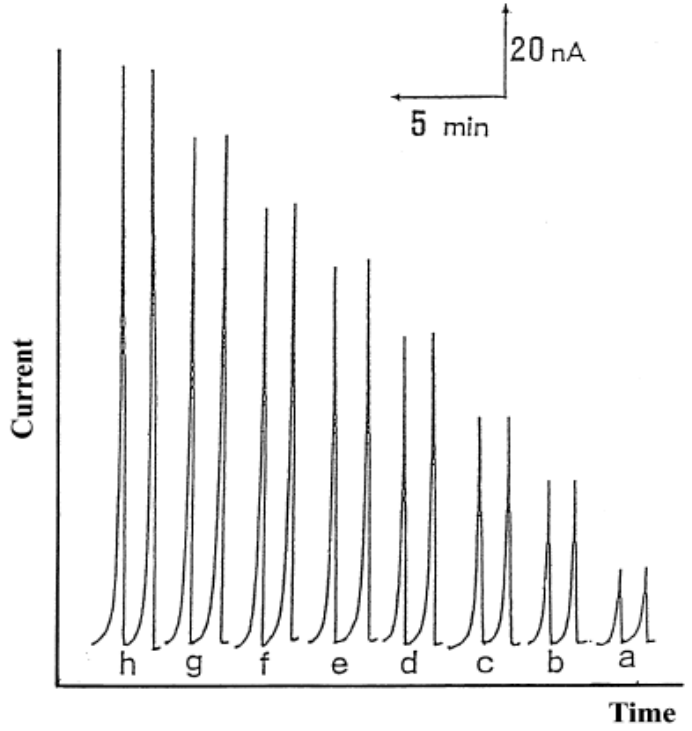




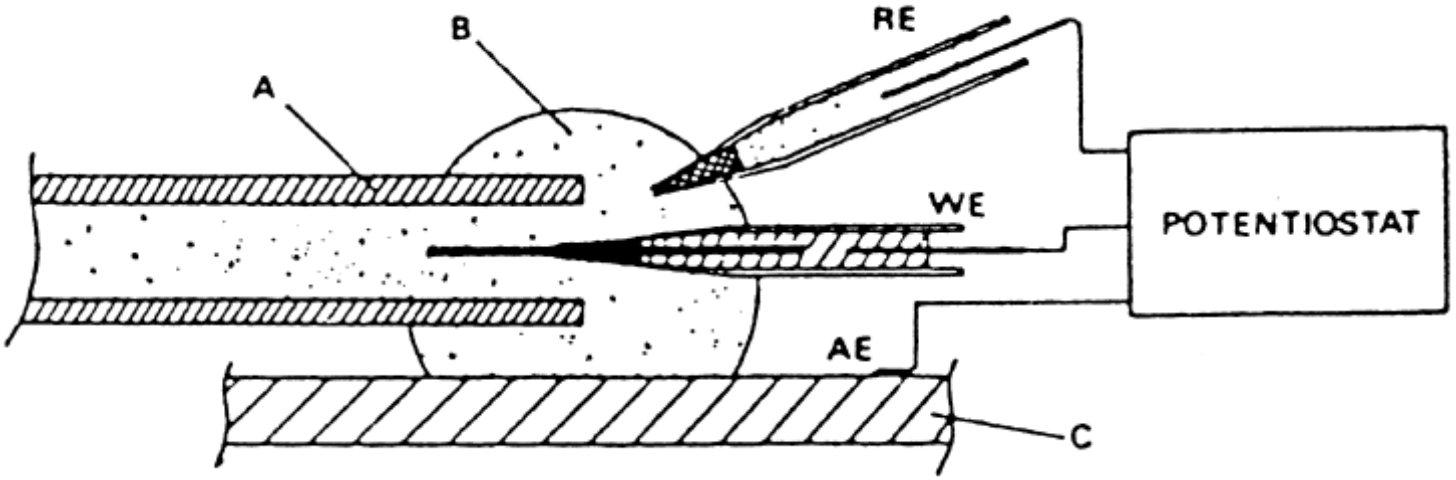
The Limiting-Current Response of Various Flow-Through Electrodes

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

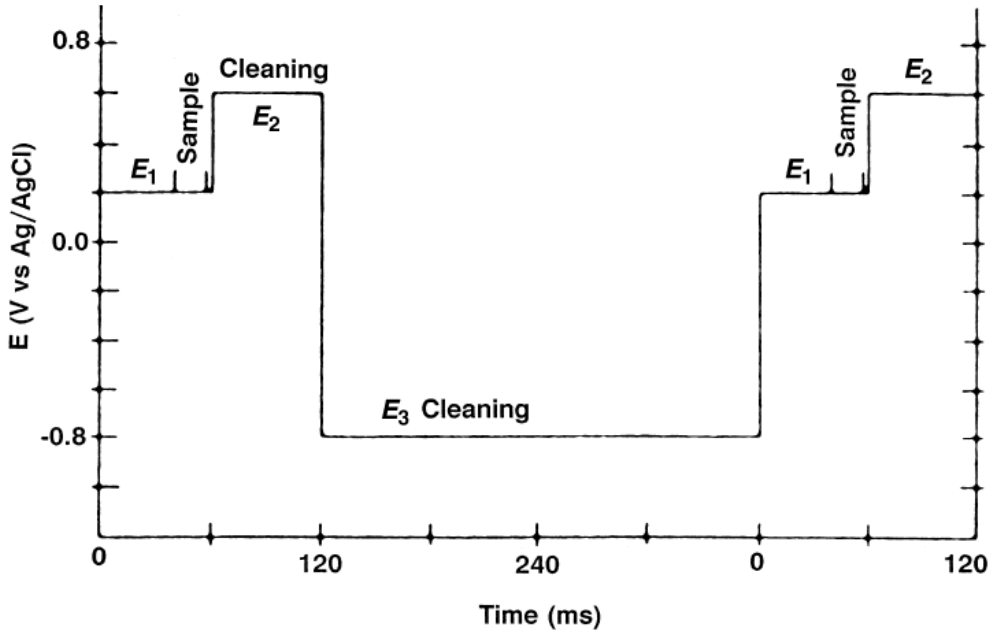
a = diameter of inlet; A = electrode area; b = channel height; C = concentration (mM); F = Faraday constant; D = diffusion coefficient; v = kinematic viscosity; r = radius of tubular electrode; U = average volume flow rate; u = velocity (cm s^{-1}); n = number of electrons.



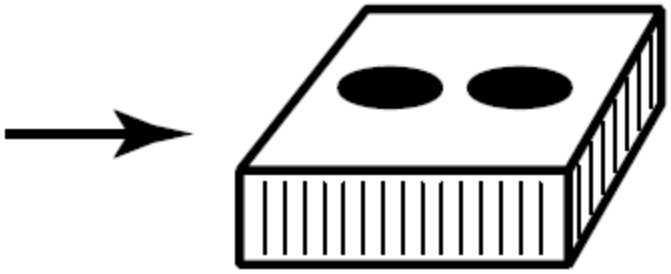
Detektor pro kapilární elektroforézu



Čištění detektoru - elektrochemické

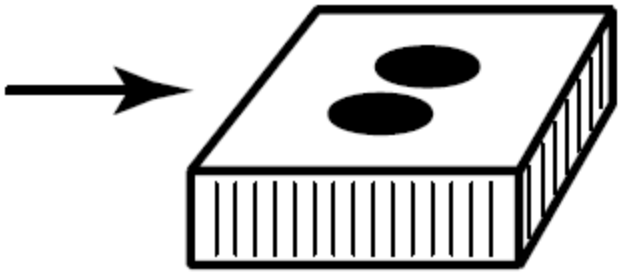


Multielektrodové techniky



Series

(*a*)



Parallel adjacent

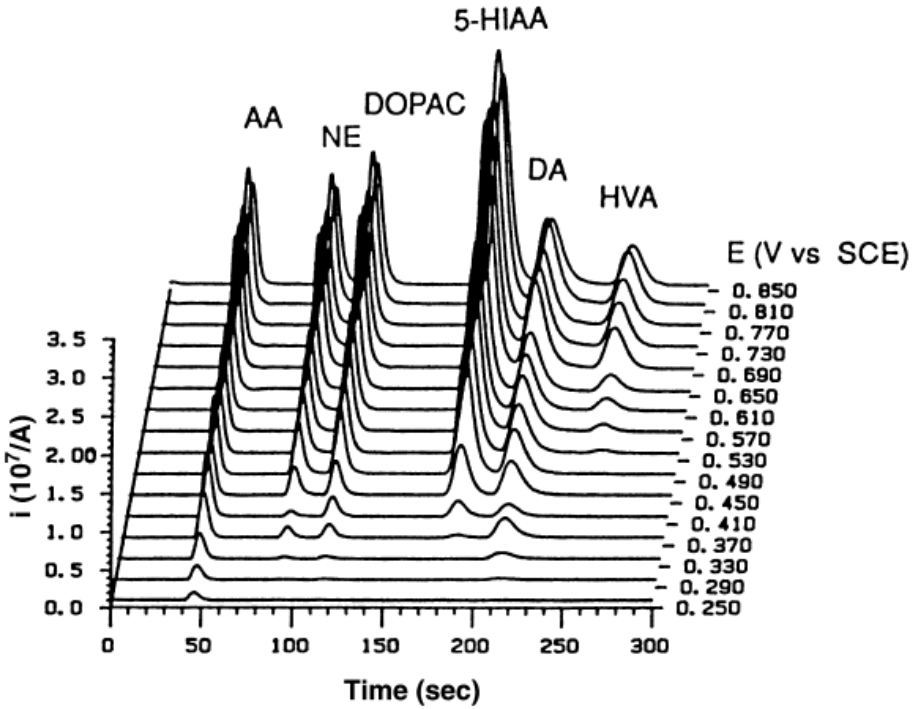
(*b*)

Sériové uspořádání:

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

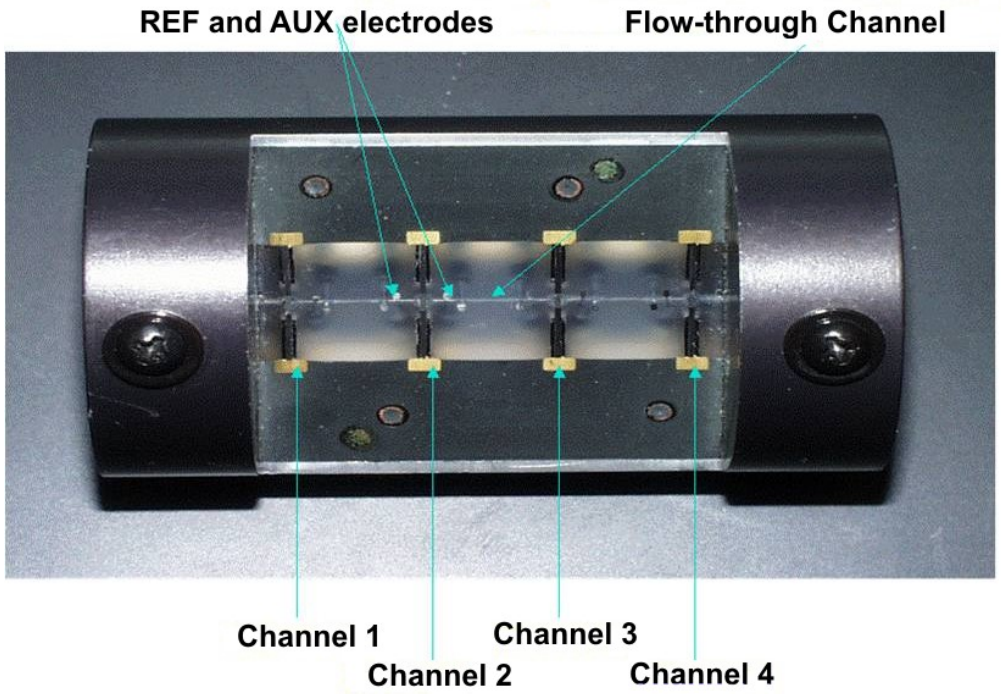
Paralelní uspořádání:

- Měření při více potenciálech - fingerprints
- 3D chromatogram

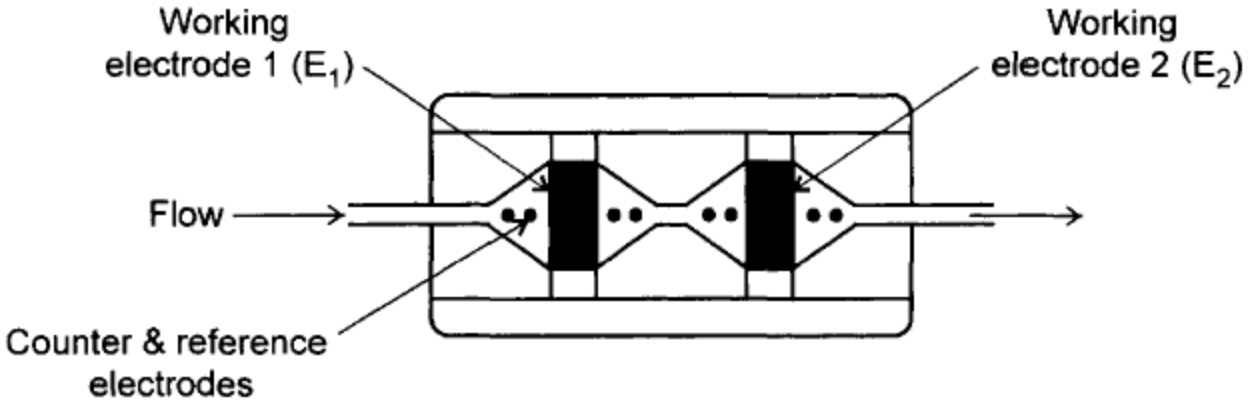


Coulometrický detektor (ESA Coulochem)

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



- Screen mode
- Difference mode
- Redox mode

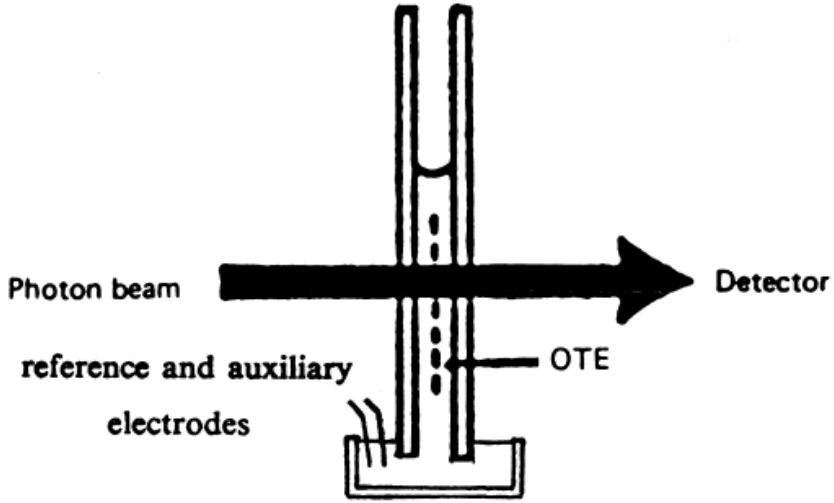


Spektroelektrochemie

Thin layer cell, OTE (Pt mesh, ITO, SnO_2)

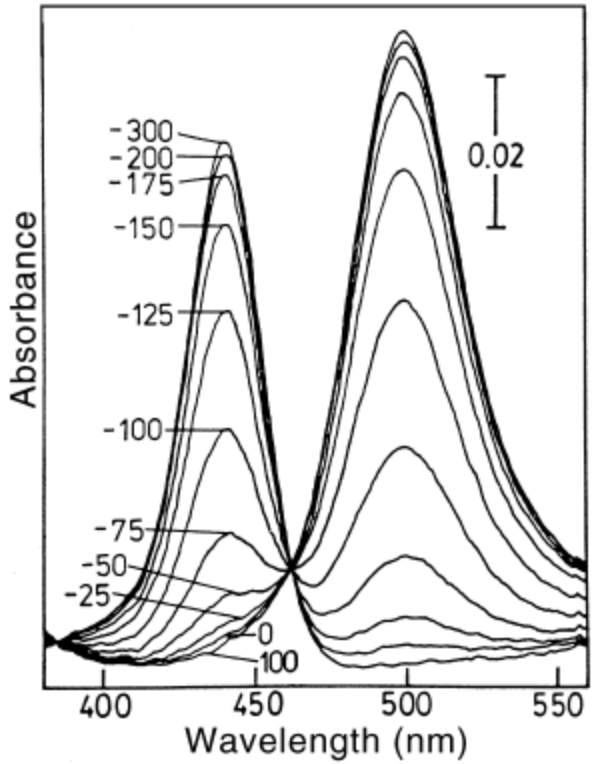
Chronoabsorptometry

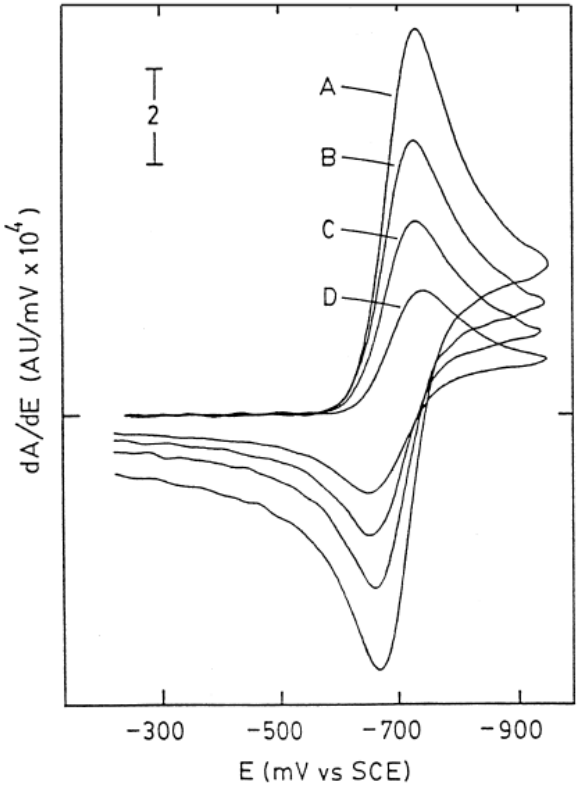
$$A = \frac{2C_O\varepsilon_R D_O^{1/2} t^{1/2}}{\pi^{1/2}}$$



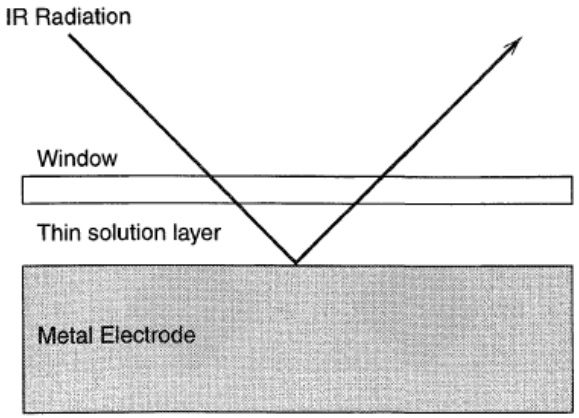
Steady state

Měření std. (formálního) potenciálu

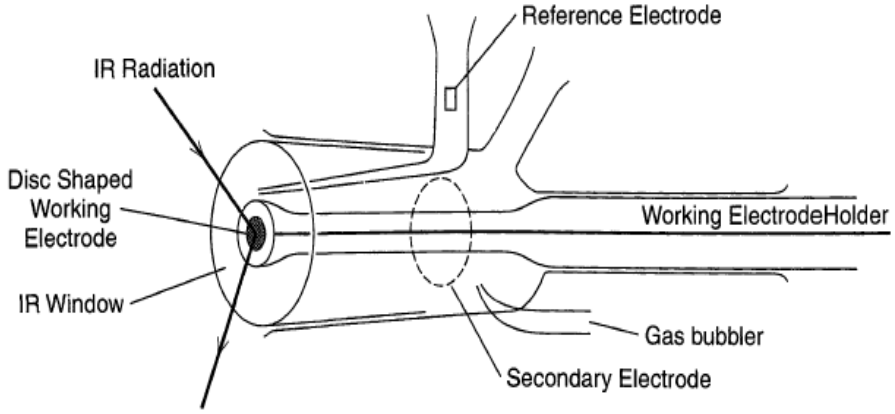




IR spektroelektrochemie (IR-SEC)



External reflectance mode

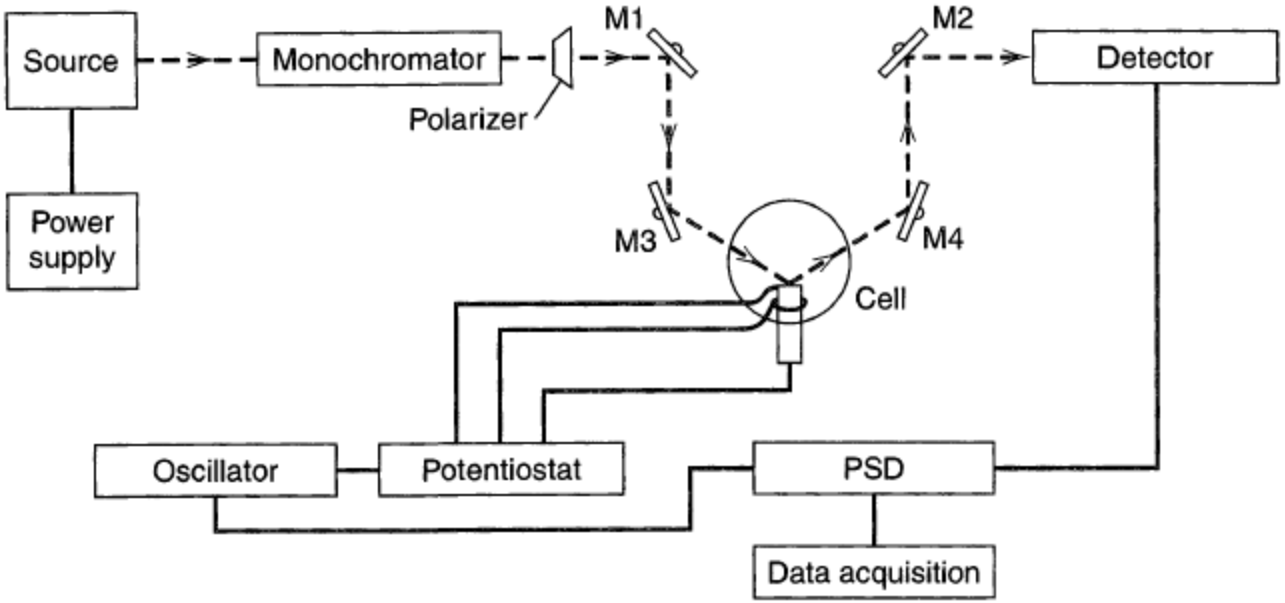


Malé signály – modulace a subtraktivní metody

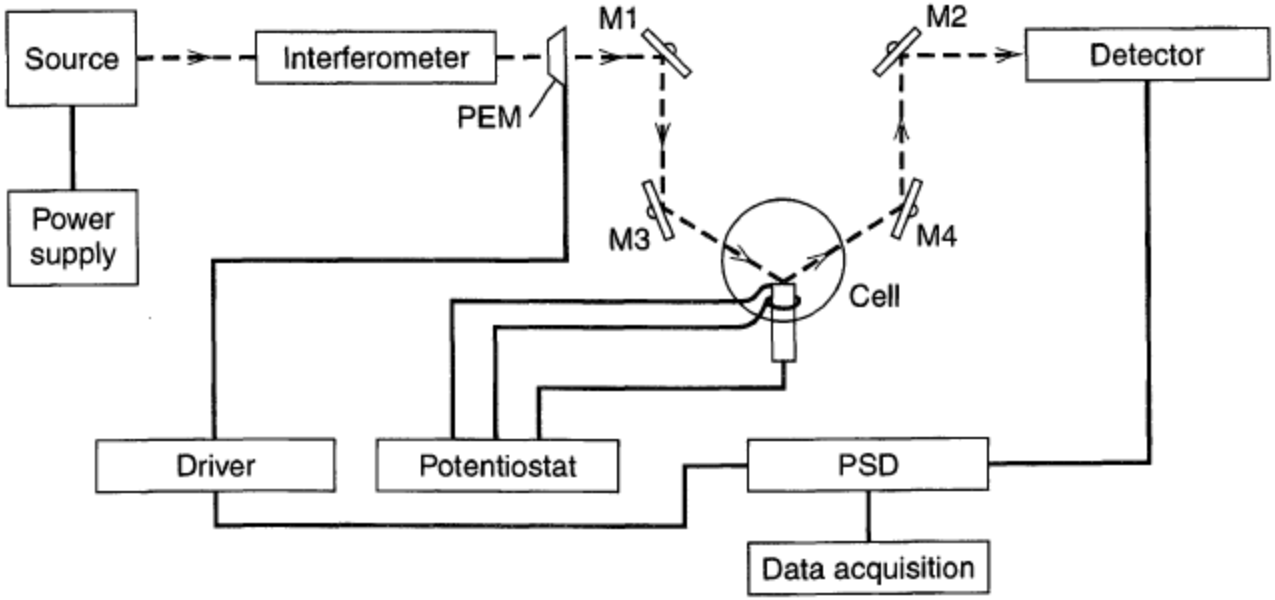
EMIRS = electrochemically modulated infrared reflectance spectroscopy

SNIFTIRS – subtractively normalized fourier transform infrared spectroscopy

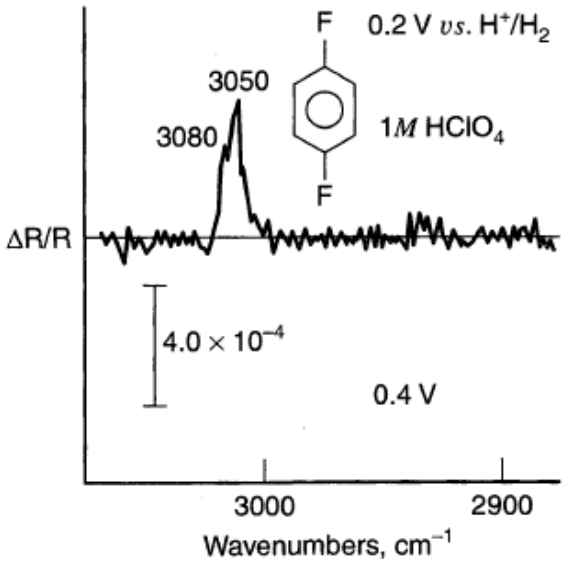
SEIRA – surface enhanced infrared absorption

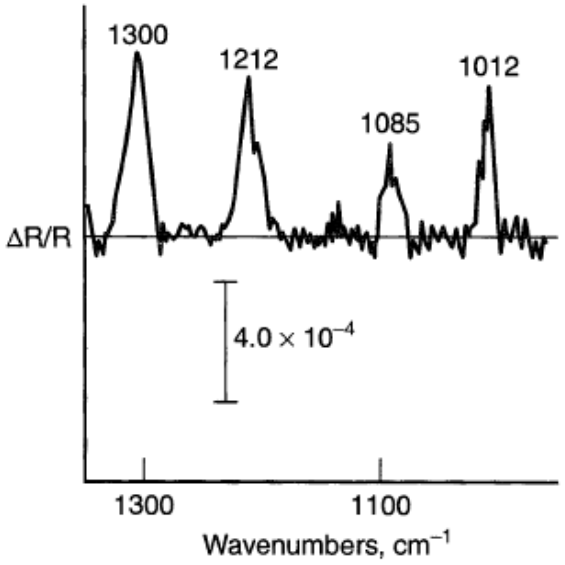


EMIRS



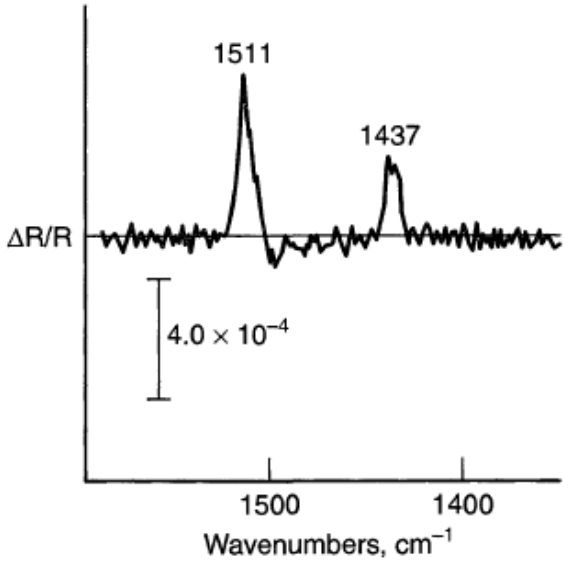
SNIFTIRS

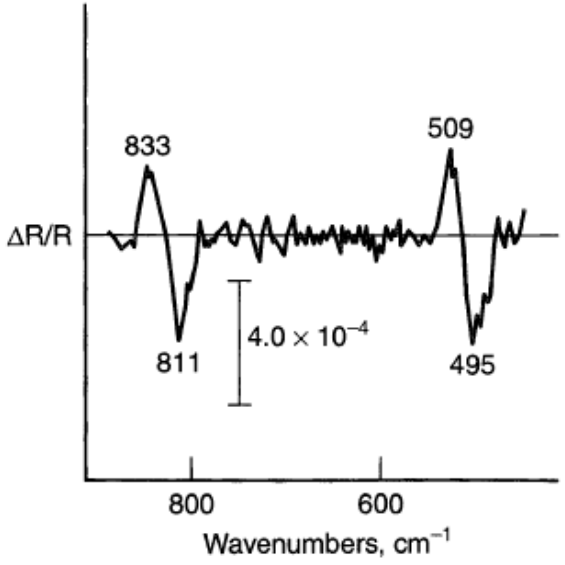




Elektroadsorpce difluorbenzenu

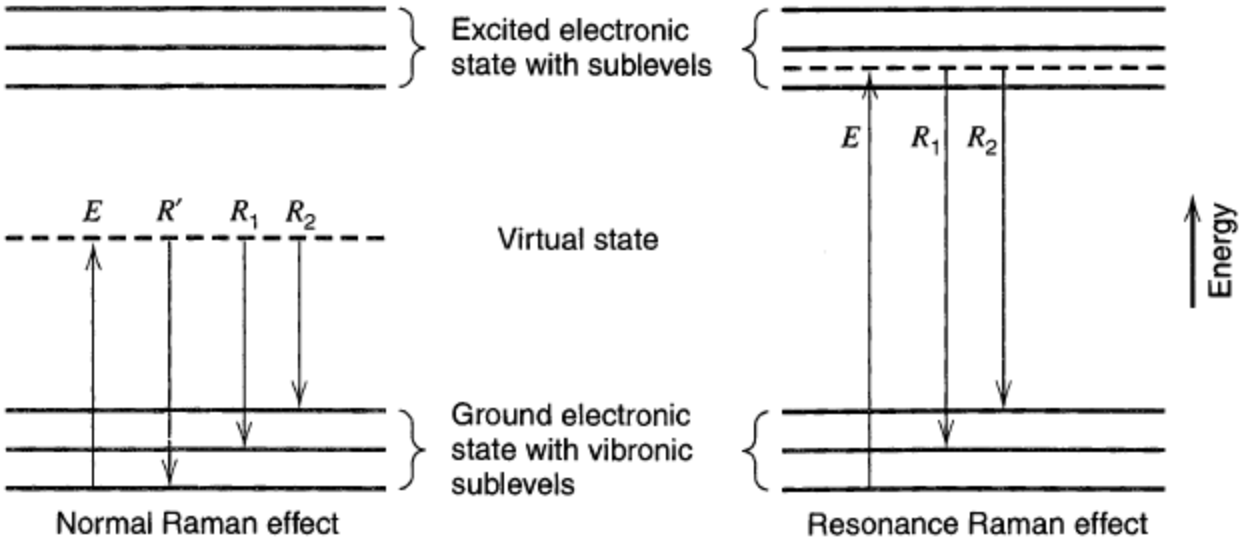
0,4 a 0,2 V





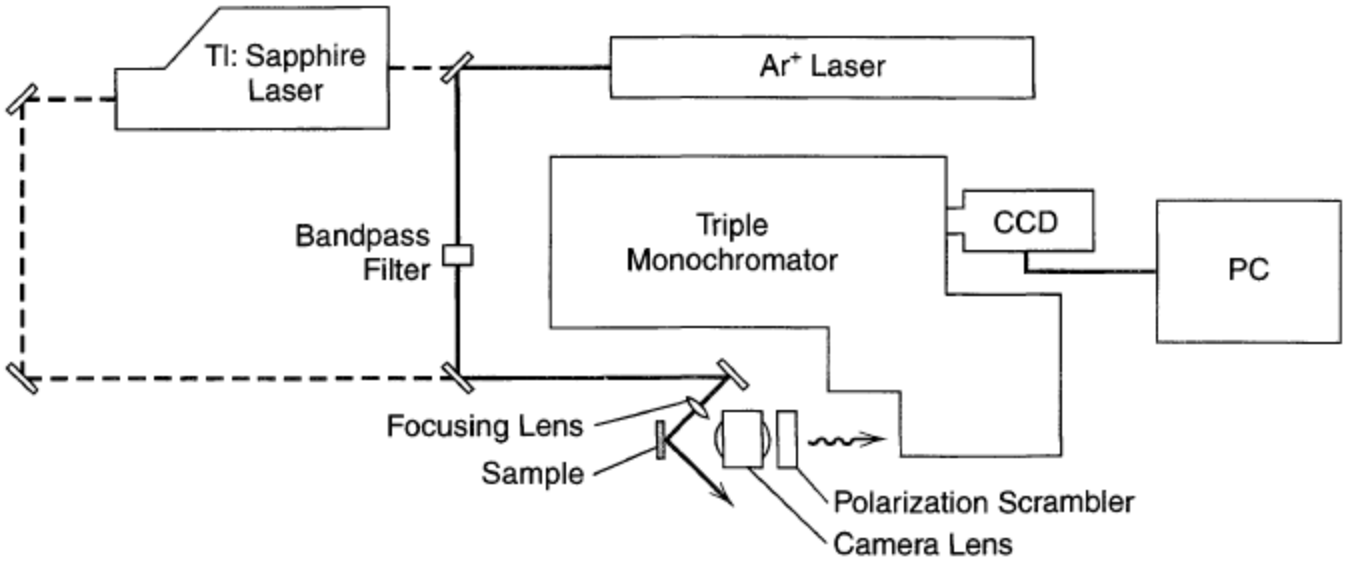
RAMAN

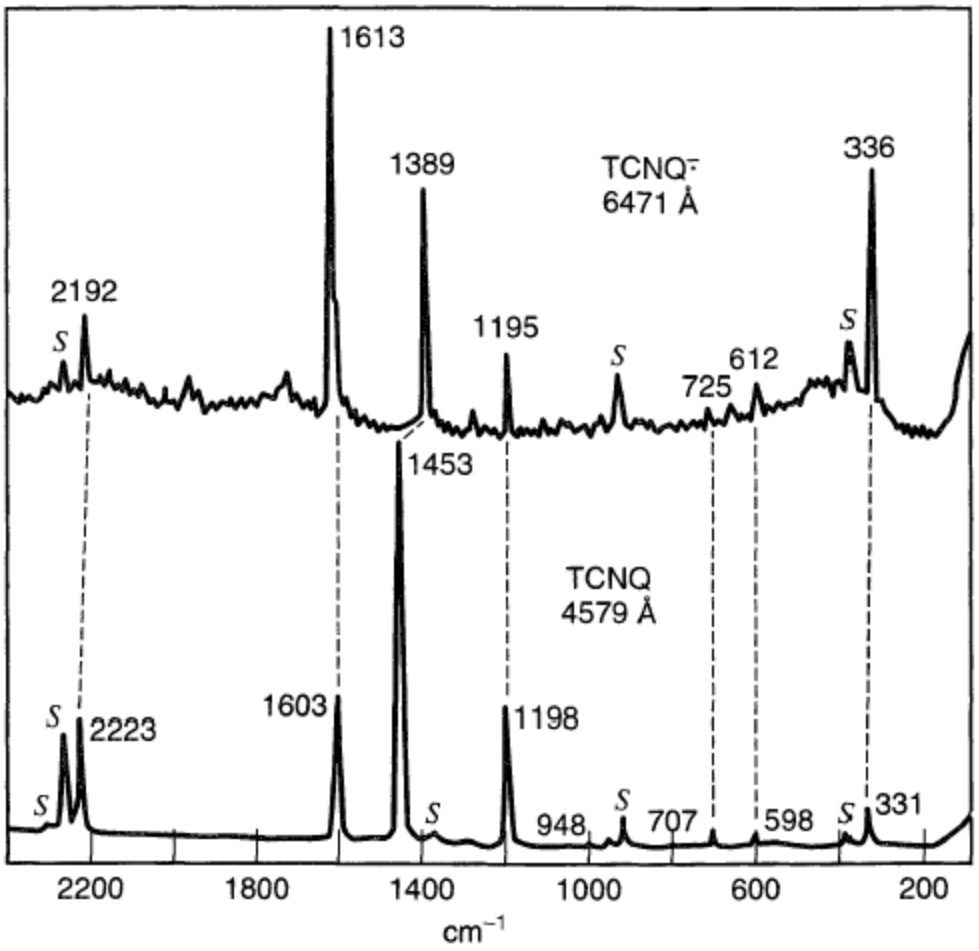
Neelastický rozptyl



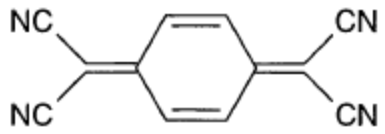
SERS
SERRS

(Ag, Au, Cu)





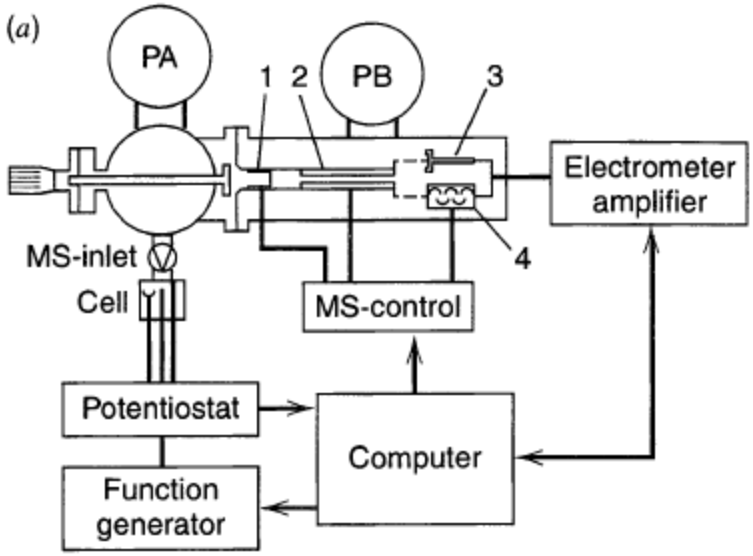
$$TCNQ + e \rightleftharpoons TCNQ^{\cdot -}$$

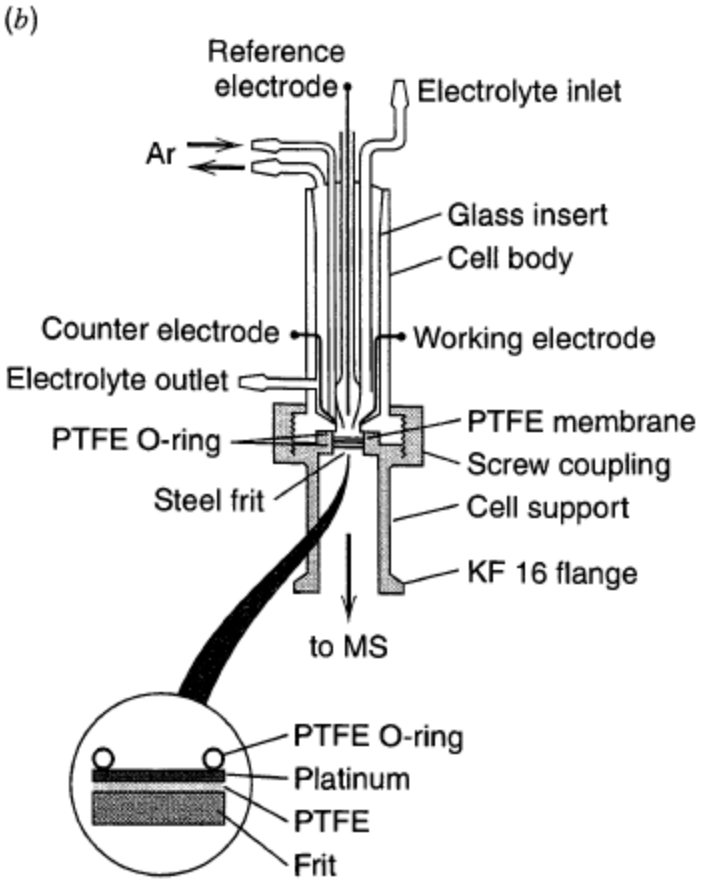


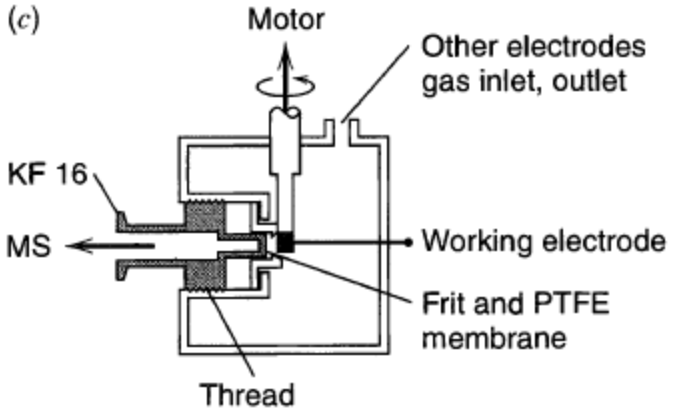
Identifikace (mezi)produktů

Transienty – pozorujeme zvolenou čáru

Elektrochemie a MS spektroskopie

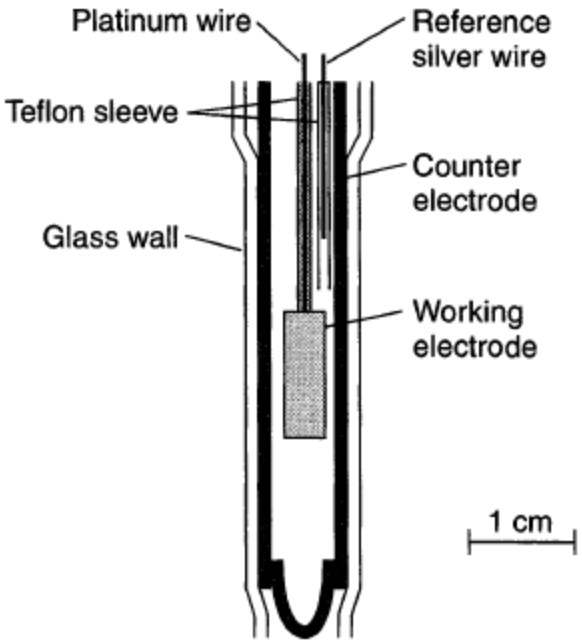


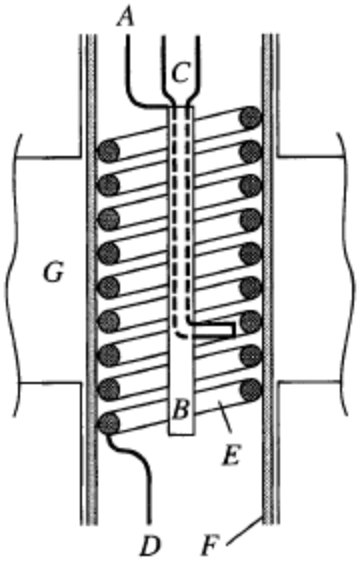




Elektrochemie a EPR

Radikálové ionty
Spin trapping

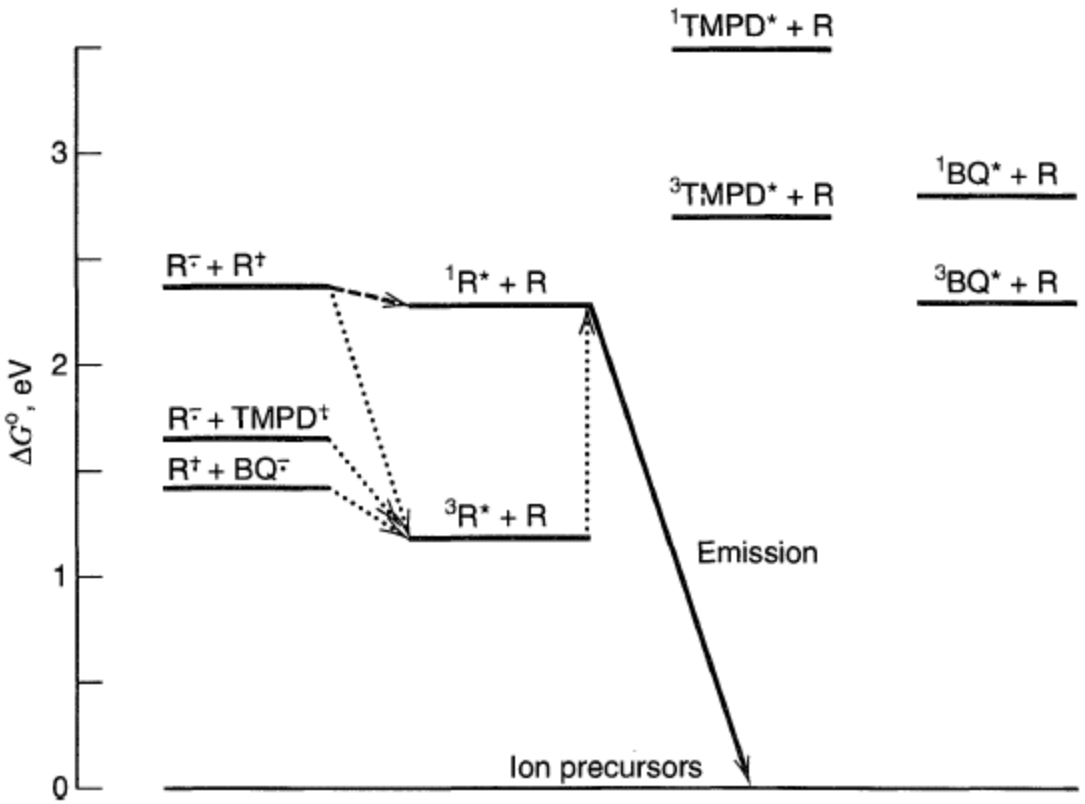




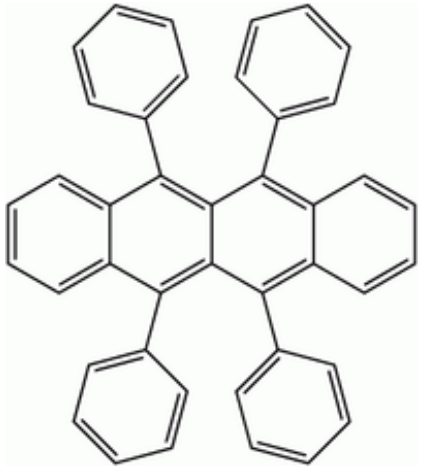
Elektrogenerovaná chemiluminiscence

anihilace radikálů

$$R^{-\cdot} + R^{+\cdot} \rightarrow {}^1R^* + R$$
$$R^{-\cdot} + TMPD^{+\cdot} \rightarrow {}^1R^* + TMPD$$
$$R^{+\cdot} + BQ^{-\cdot} \rightarrow {}^1R^* + BQ$$



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

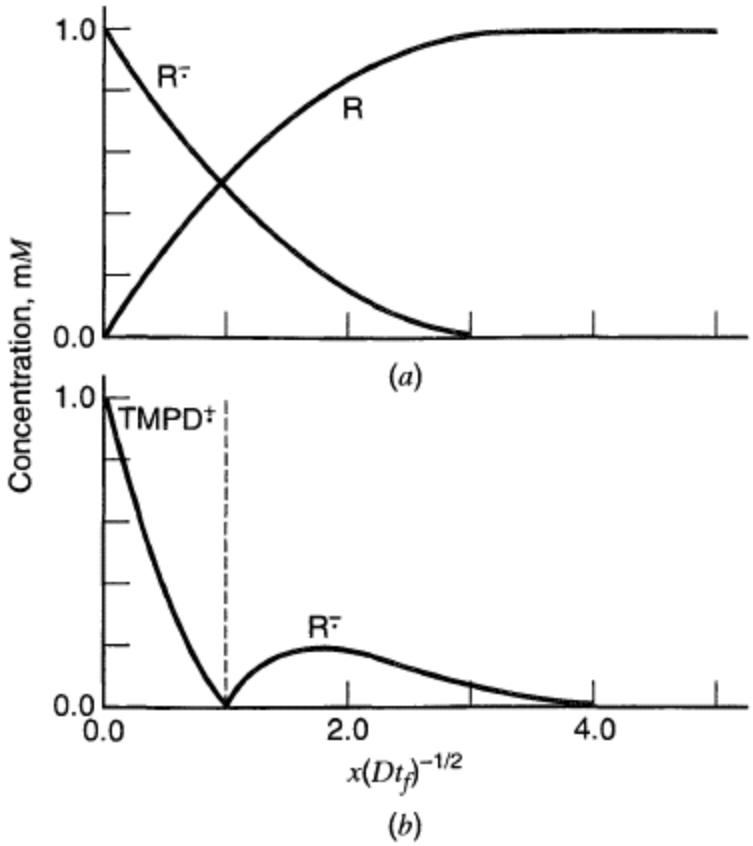


S a T cesta

ECL step, RRDE

$$R^{\bullet-} + TMPD^{\bullet+} \rightarrow {}^3R^* + TMPD$$
$$^3R^* + {}^3R^* \rightarrow {}^1R^* + R$$

použití „koreaktantu“



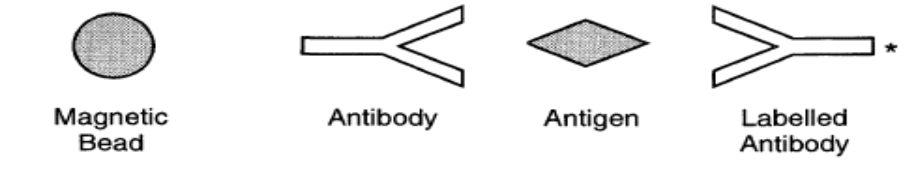
$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e$$
$$C_2O_4^{2-} \rightarrow C_2O_4^{-} + e$$
$$C_2O_4^{-} \rightarrow CO_2 + CO_2^{\bullet-}$$
$$Ru(bpy)_3^{3+} + CO_2^{\bullet-} \rightarrow Ru(bpy)_3^{2+*} + CO_2$$

ECL jako detekční metoda pro HPLC

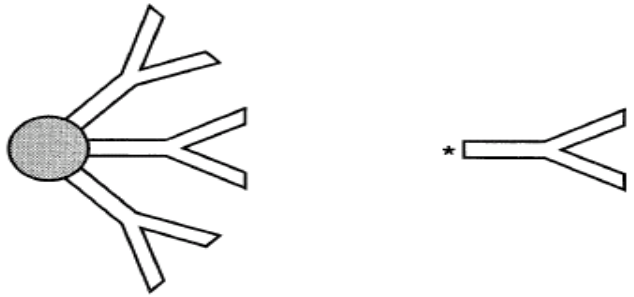
•využívá $Ru(bpy)_3$ – imobilizovaný na elektrodě v Nafionu

• detekce NADH, aminů a aminokyselin (koreaktanty)

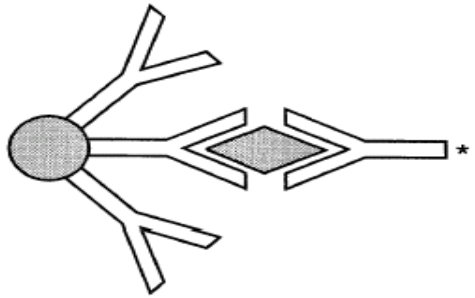
Elektrogenerovaná chemiluminiscence klasických CL indikátorů
(luminol, lucigenin) – stopy peroxidu vodíku, vizualizace „horkých míst“ na elektrodách

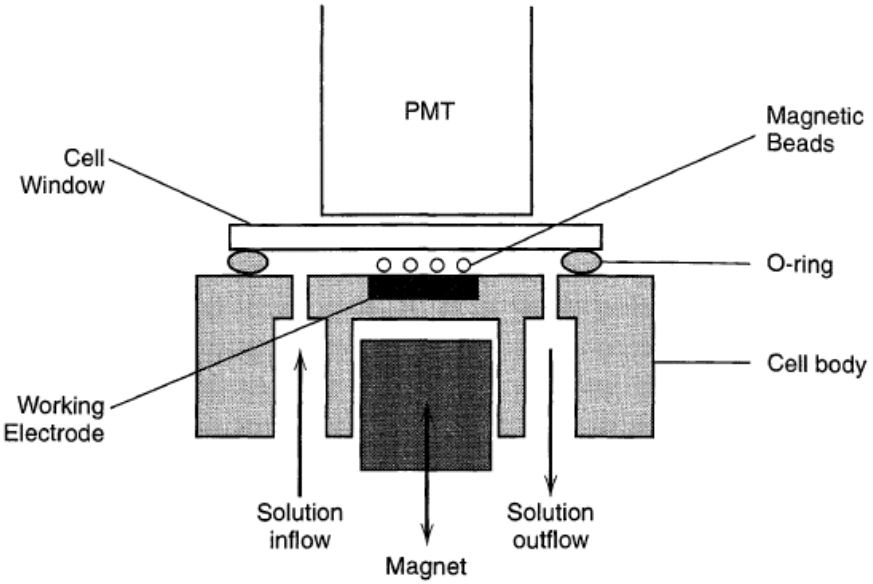


(*a*) Sample with no antigen (labelled antibody not attached to bead)



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





PSA – prostate specific antigen

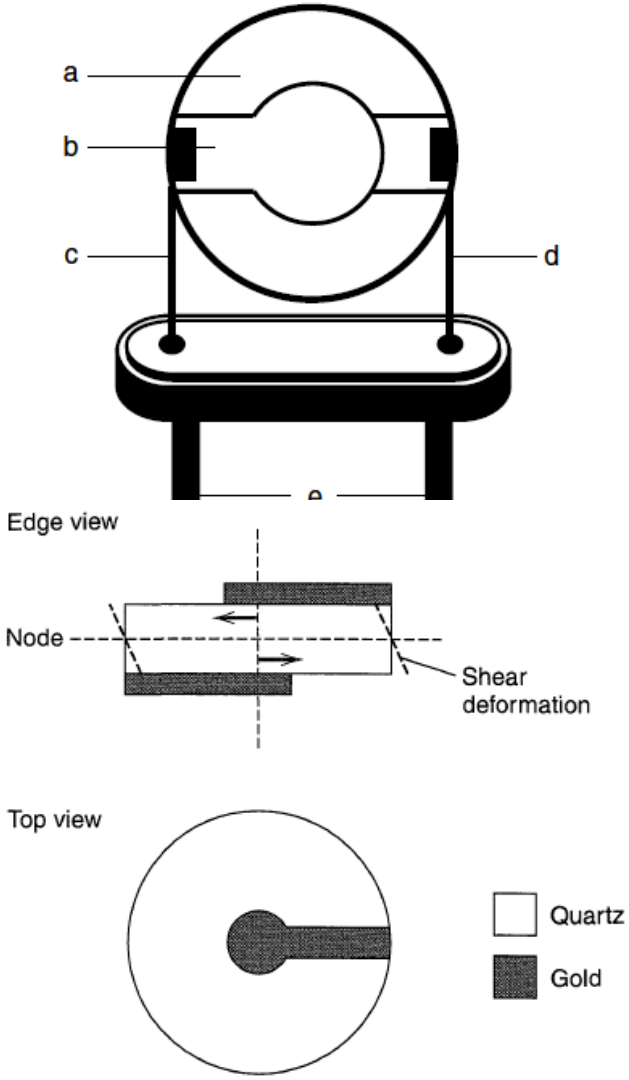
$$EtCH_2NPr_2 \rightarrow EtCH_2NPr_2^+ + e$$

tri-*n*-propylamine, TPrA

$$EtCH_2NPr_2^+ \rightarrow EtCHNPr_2^{\cdot} + H^+$$

$$Ru(bpy)_3^{3+} + EtCHNPr_2^{\cdot} \rightarrow Ru(bpy)_3^{2+*} + EtCHNPr_2^+$$

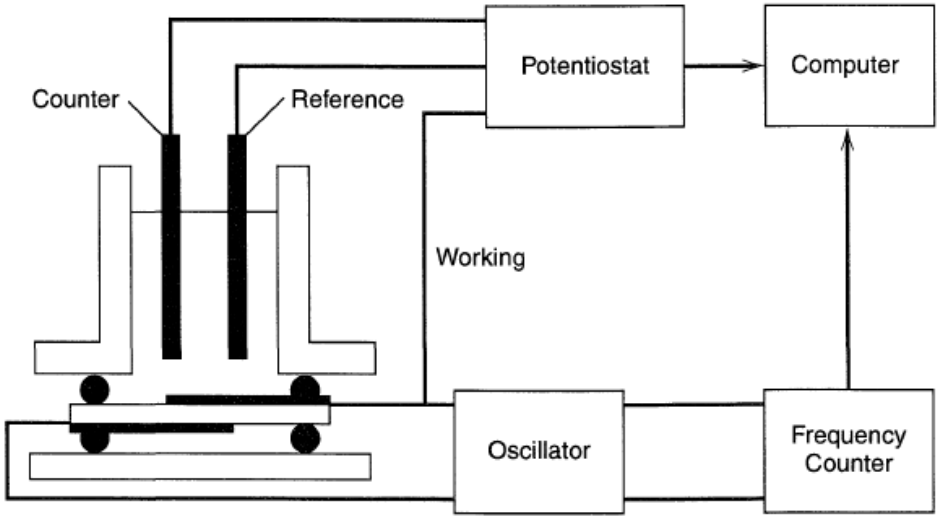
EQCM = electrochemical quartz crystal microbalance

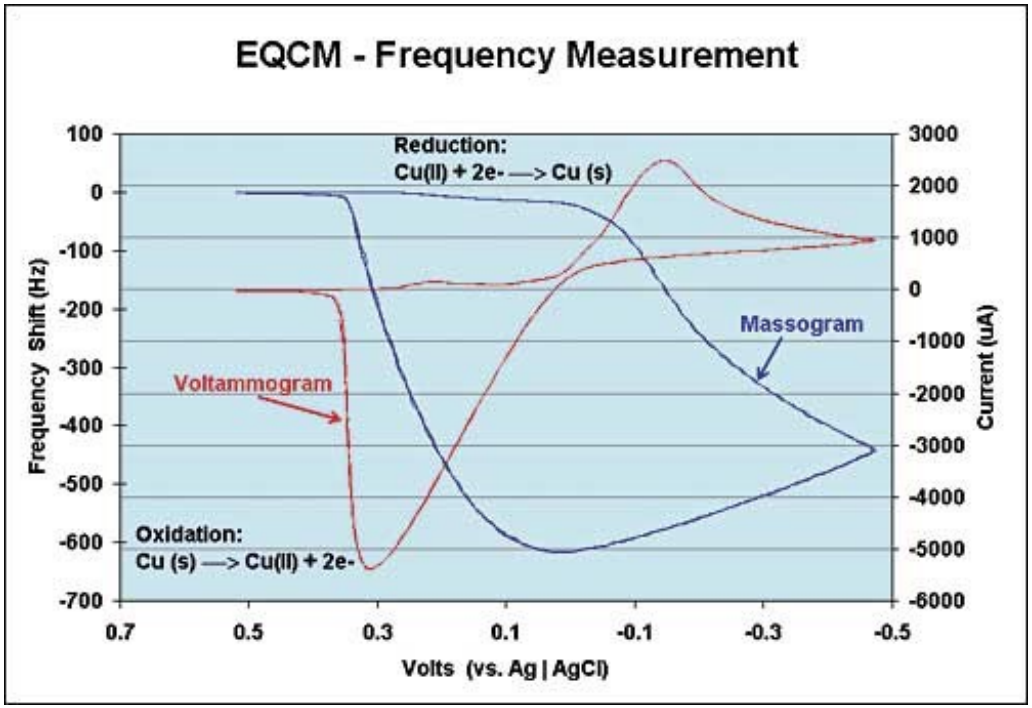


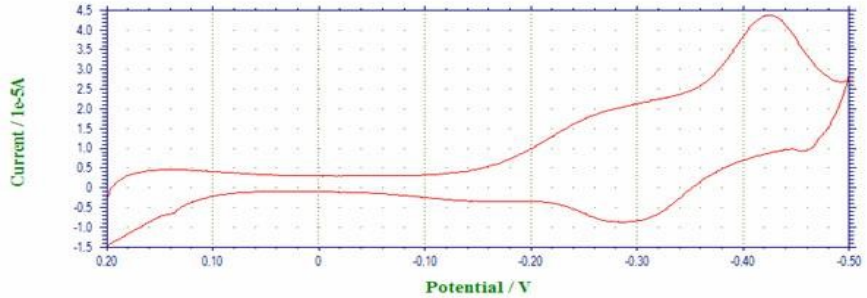
$$\Delta f = \frac{-2\Delta m n f_0^2}{A\sqrt{\mu\rho}}$$

Sauerbrey equation

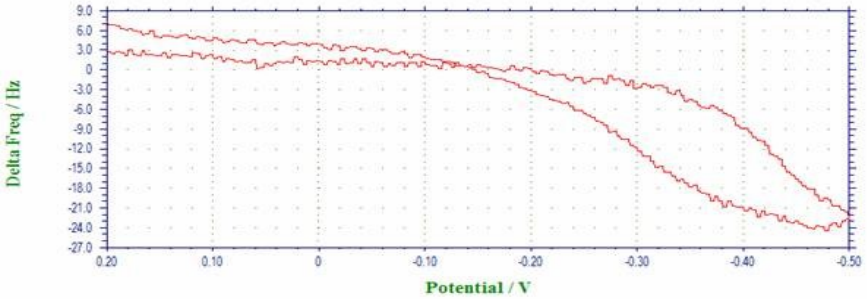
Δm změna hmotnosti
n harmonická frekvence
f_0 základní frekvence
A plocha elektrody
μ modul pružnosti ve smyku pro SiO_2
ρ hustota SiO_2

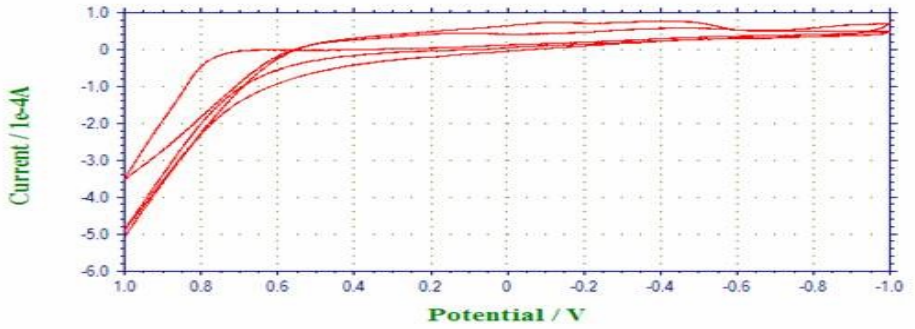

Potentiostat
Computer
Counter
Reference
Working
Oscillator
Frequency Counter


EQCM - Frequency Measurement
Reduction:
Cu(II) + 2e- —> Cu (s)
Massogram
Voltammogram
Oxidation:
Cu (s) —> Cu(II) + 2e-
Frequency Shift (Hz)
Current (uA)
Volts (vs. Ag | AgCl)
100
0
-100
-200
-300
-400
-500
-600
-700
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
0.7
0.5
0.3
0.1
-0.1
-0.3
-0.5

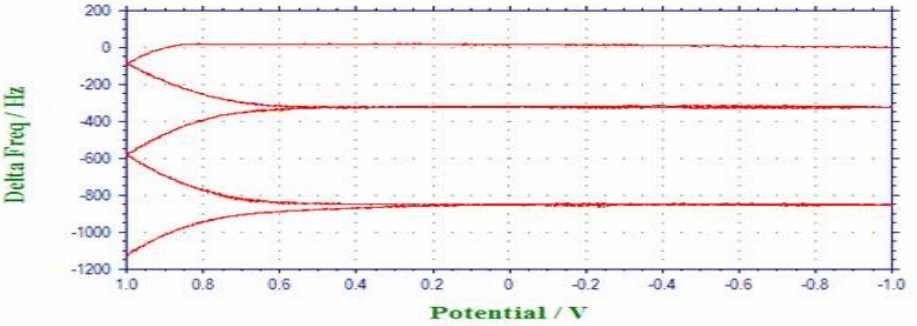


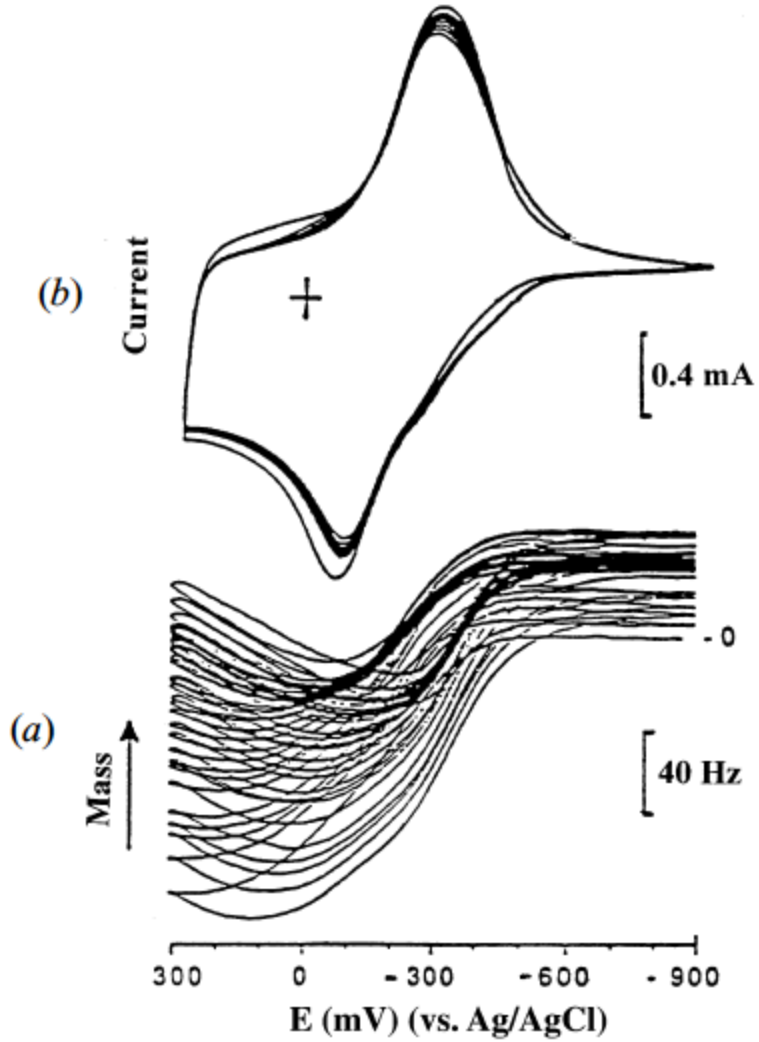
UPD olova



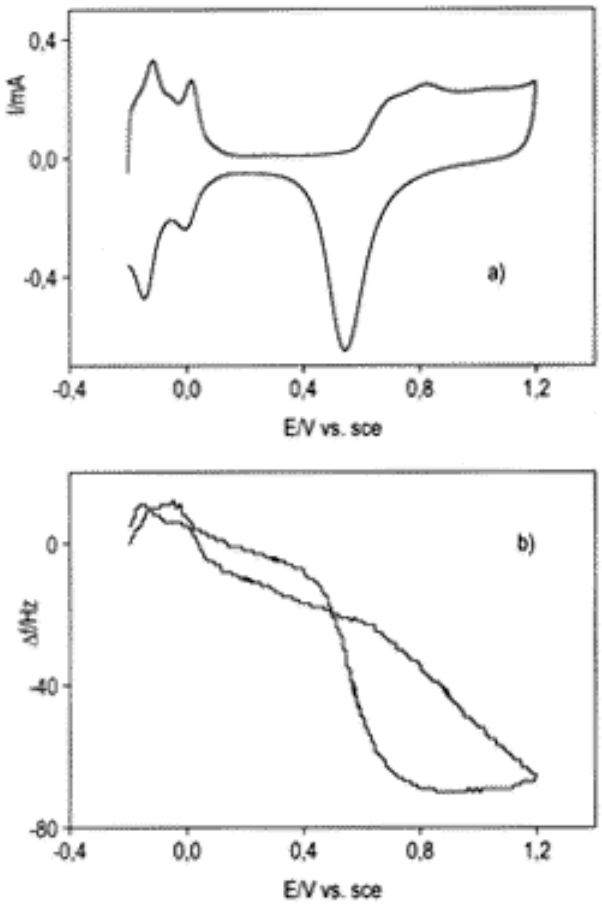


Růst polypyrrolového filmu



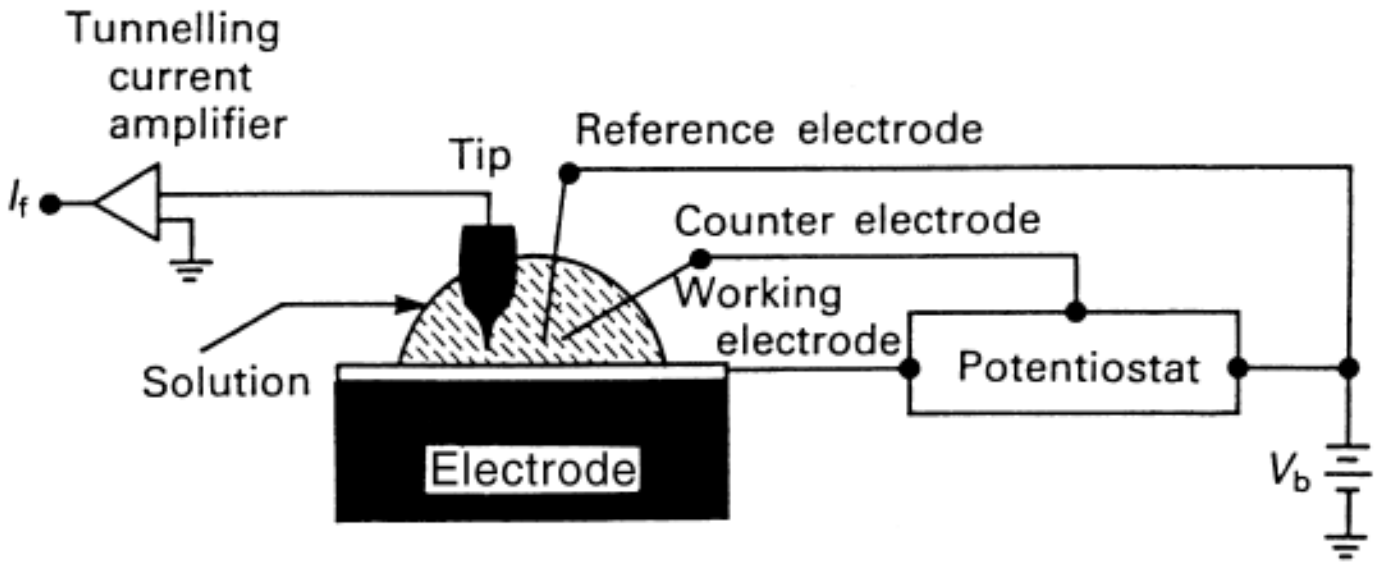


Iontoměnič



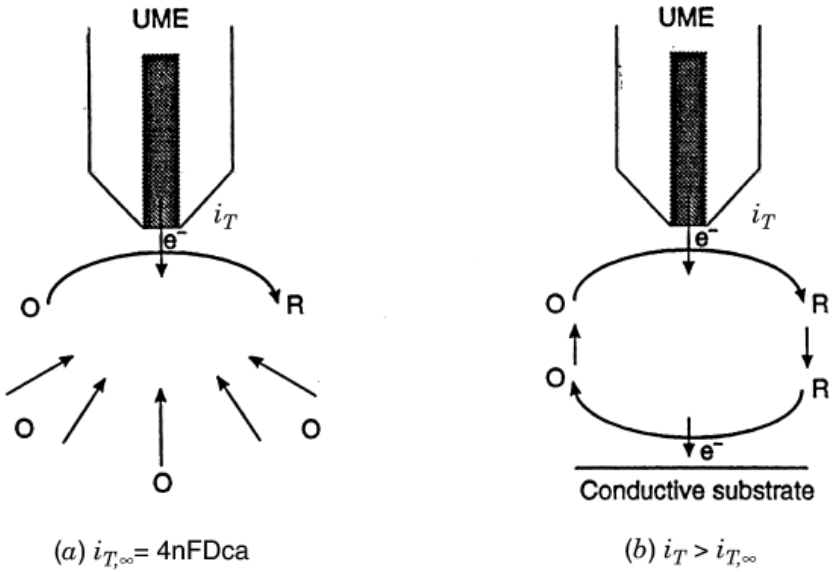
Pt povrch

Elektrochemická STM (SECM)



Mikroelektrodové tipy

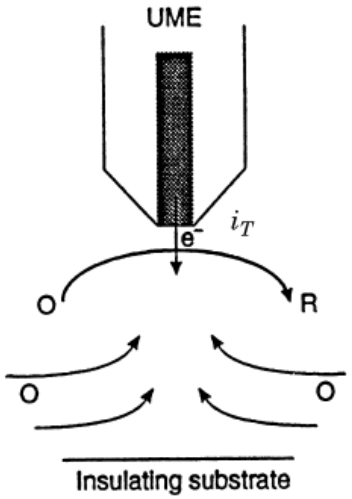
Potenciometrické tipy (pH)



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

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

A: elektroda vzdálená od povrchu – steady state current i_T



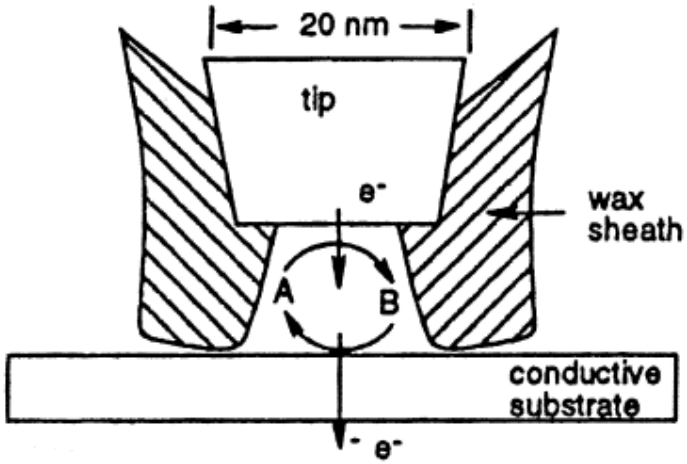
(c) $i_T < i_{T,\infty}$

„positive feedback mode“

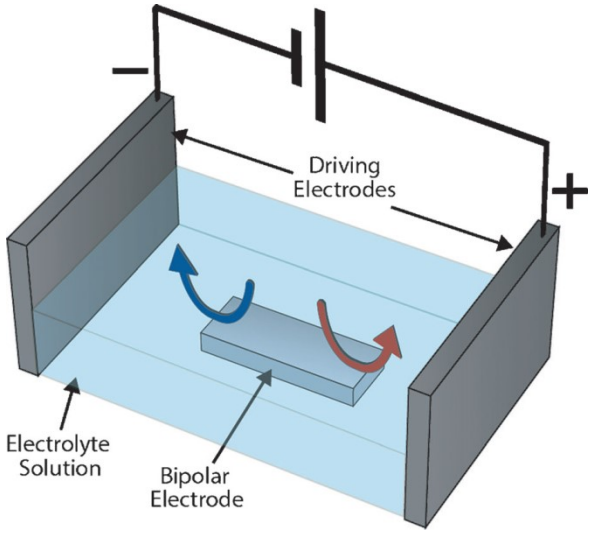
Sledování distribuce Aktivních míst elektrodových povrchů

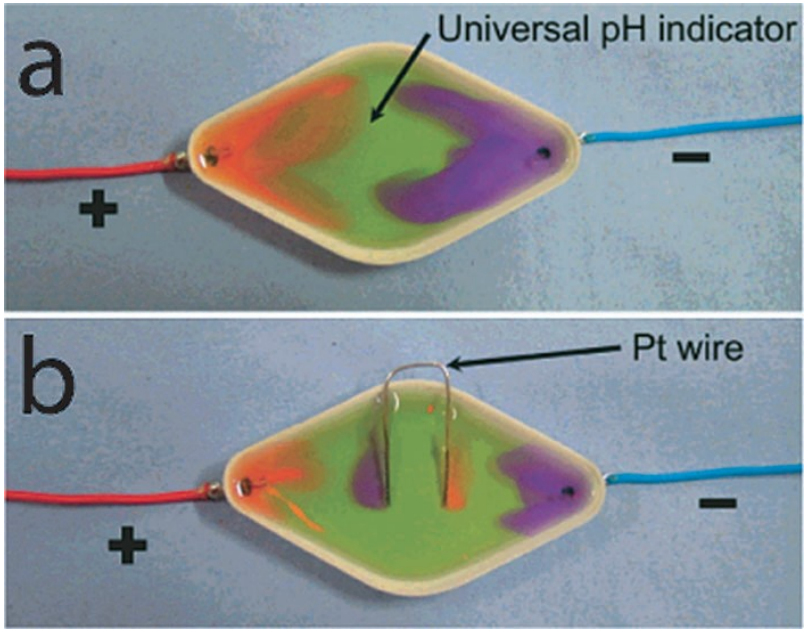
Elektrochemická fabrikace povrchů

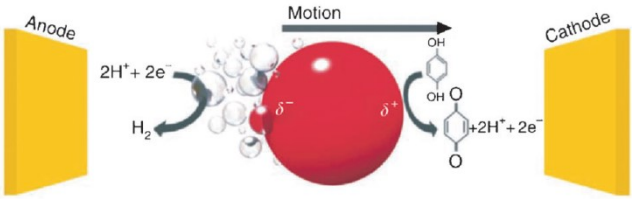
Rozlišení nedosahuje atomárních rozměrů,
Single molecule techniky

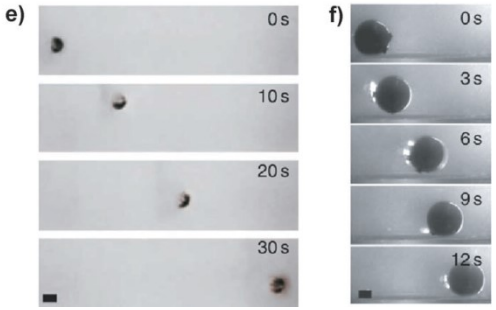


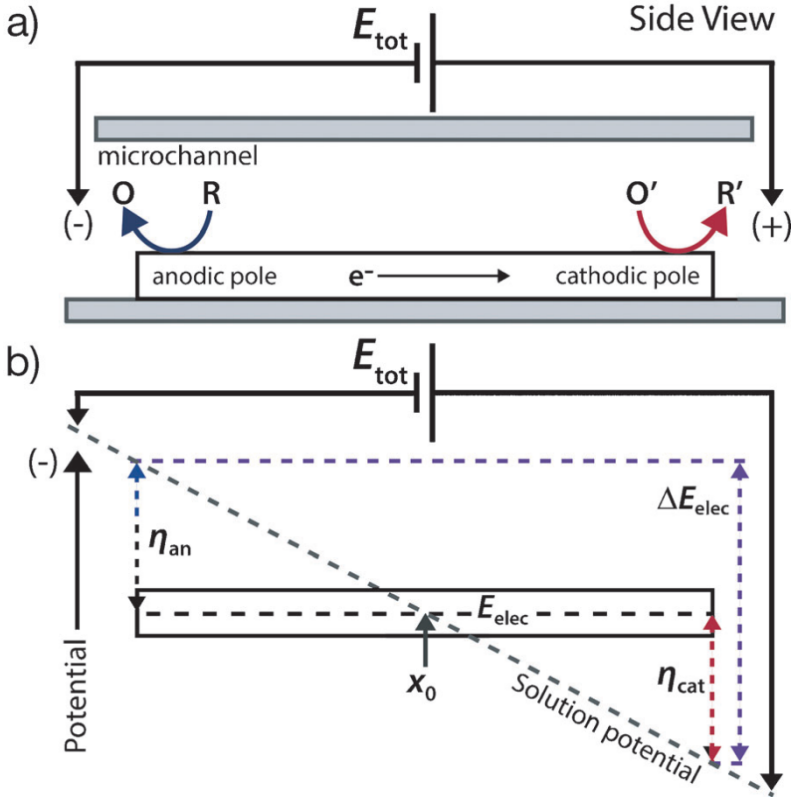
Bipolar electrochemistry

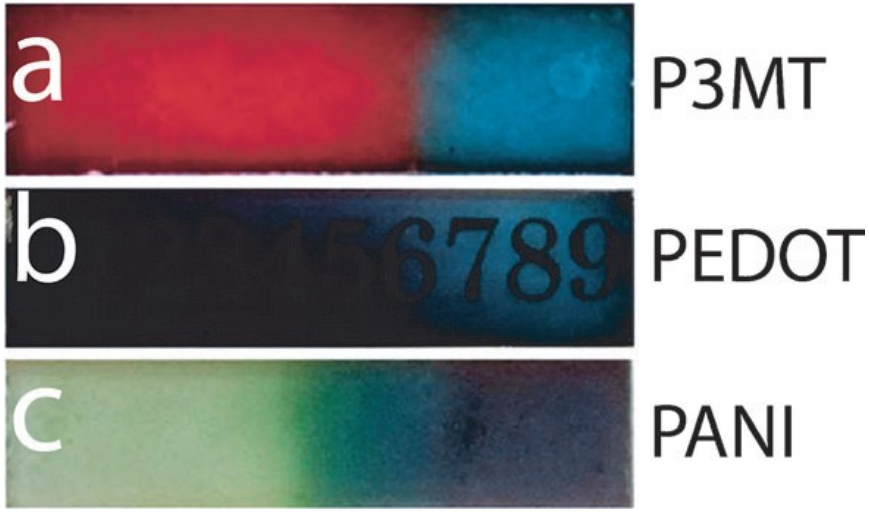


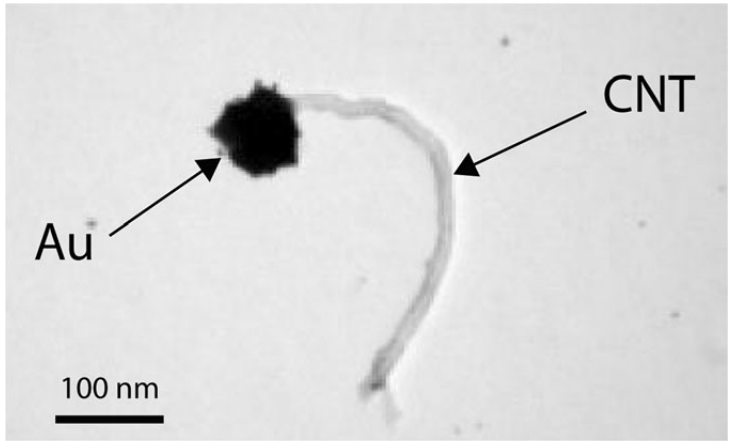







a)
E_{tot}
Side View
microchannel
O
R
O′
R′
(-)
(+)
anodic pole
e⁻
cathodic pole
b)
E_{tot}
(-)
ΔE_{elec}
η_{an}
E_{elec}
x_0
η_{cat}
Solution potential
Potential


a
P3MT
b
PEDOT
c
PANI


CNT
Au
100 nm