



SENSORY PLYNNÝCH LÁTEK

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katedra analytické chemie

ELEKTROCHEMICKÉ SENSORY

s kapalným elytem
s tuhým elytem

SENSORY ZALOŽENÉ NA MĚŘENÍ EL. VODIVOSTI

metaloxidové sens.
chemirezistory

SENSORY HMOTNOSTNÍ

BAW, SAW

SENSORY ZALOŽENÉ NA MĚŘENÍ TEPLoty

pelistory, pyroel.
sensory, TCD

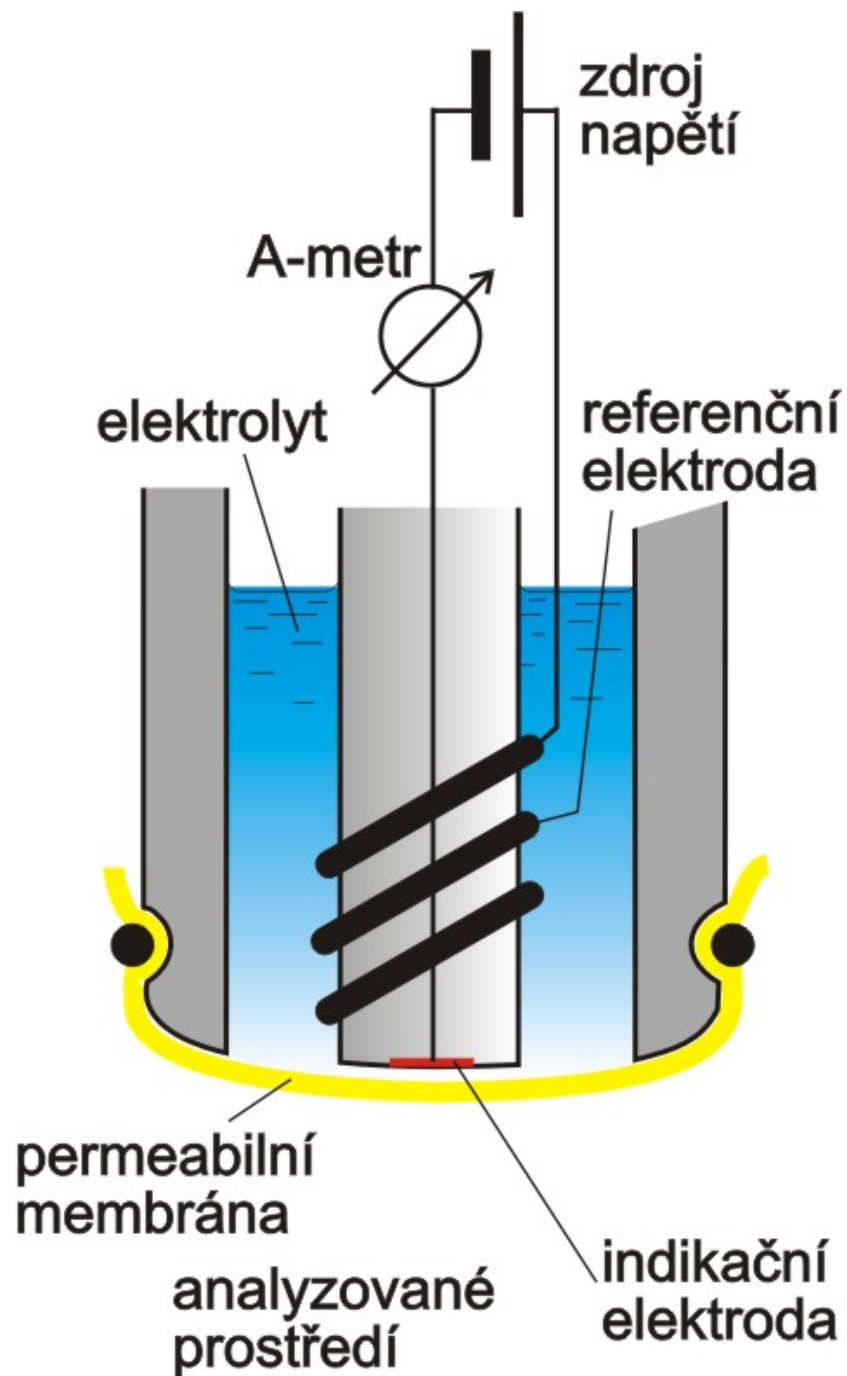
SENSORY OPTICKÉ

optrody (optody)

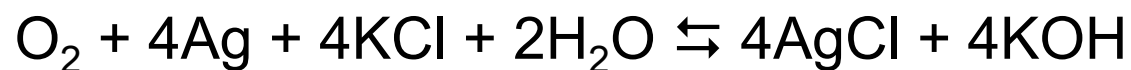
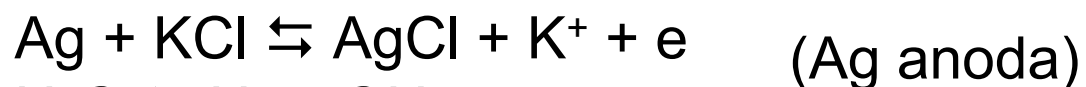
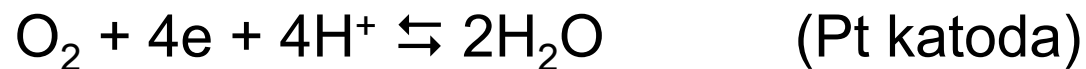
SENSORY S MIKROELEKTRO- NICKOU STRUKTUROU

ISFET, CSFET
work-function sens.

1.1 AMPÉROMETRICKÉ MEMBRÁNOVÉ SENSORY S KAPALNÝM ELEKTROLYTEM

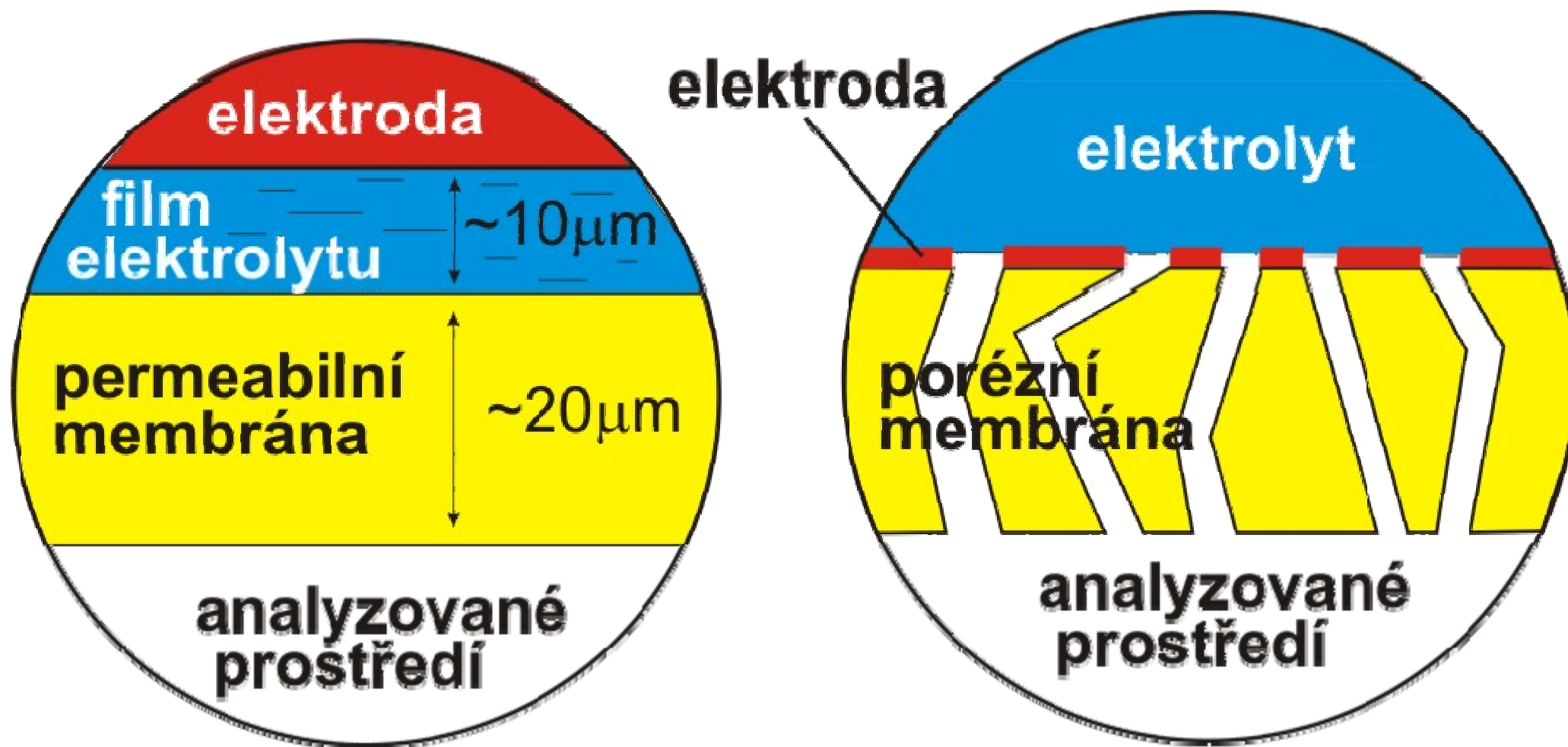


Leland C. Clark

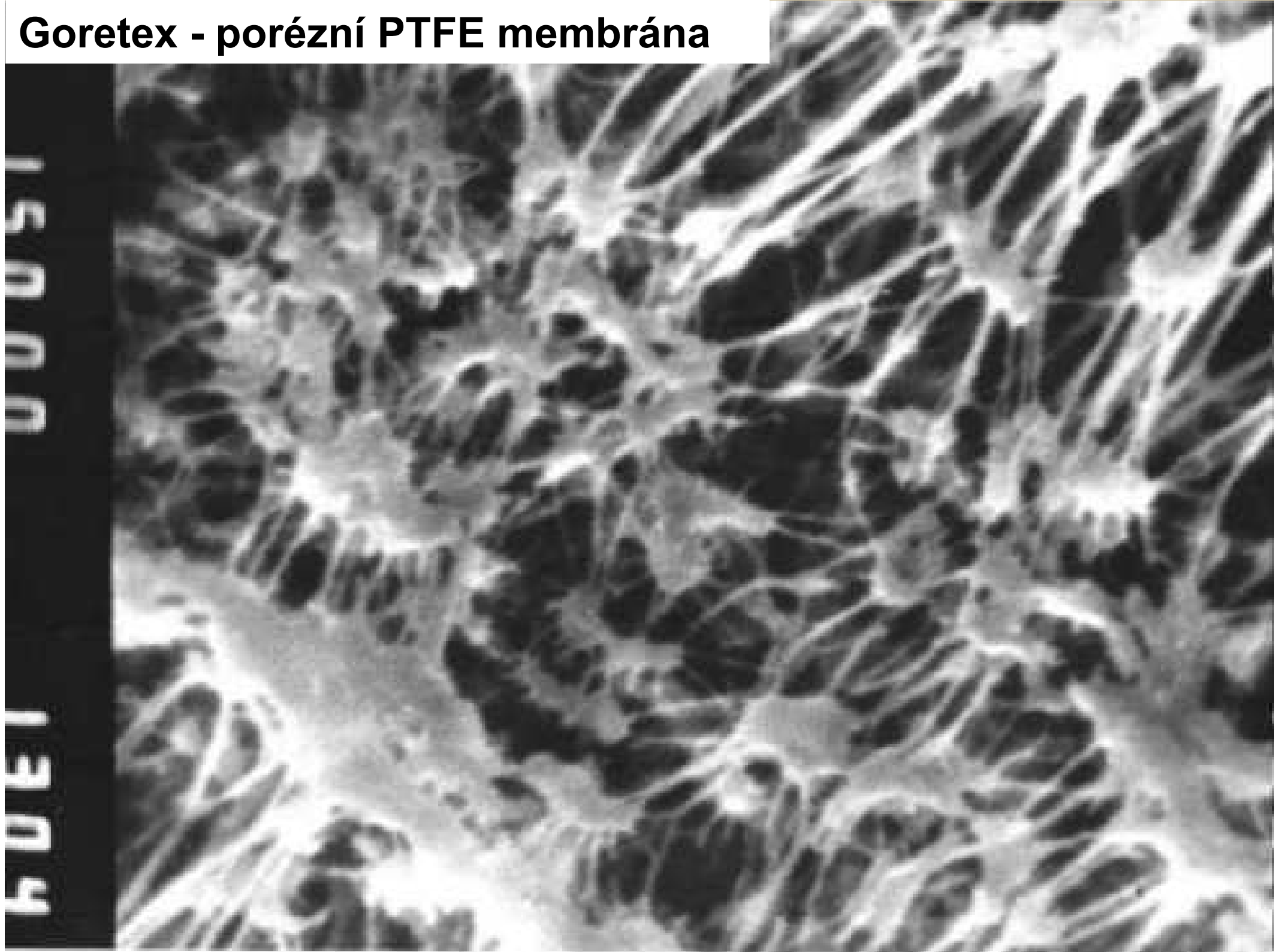




Sensory s filmem elektrolytu a pokovenou membránou



Goretex - porézní PTFE membrána



Soubor individuálně adresovatelných sensorů Clarkova typu

čip 1x1 cm

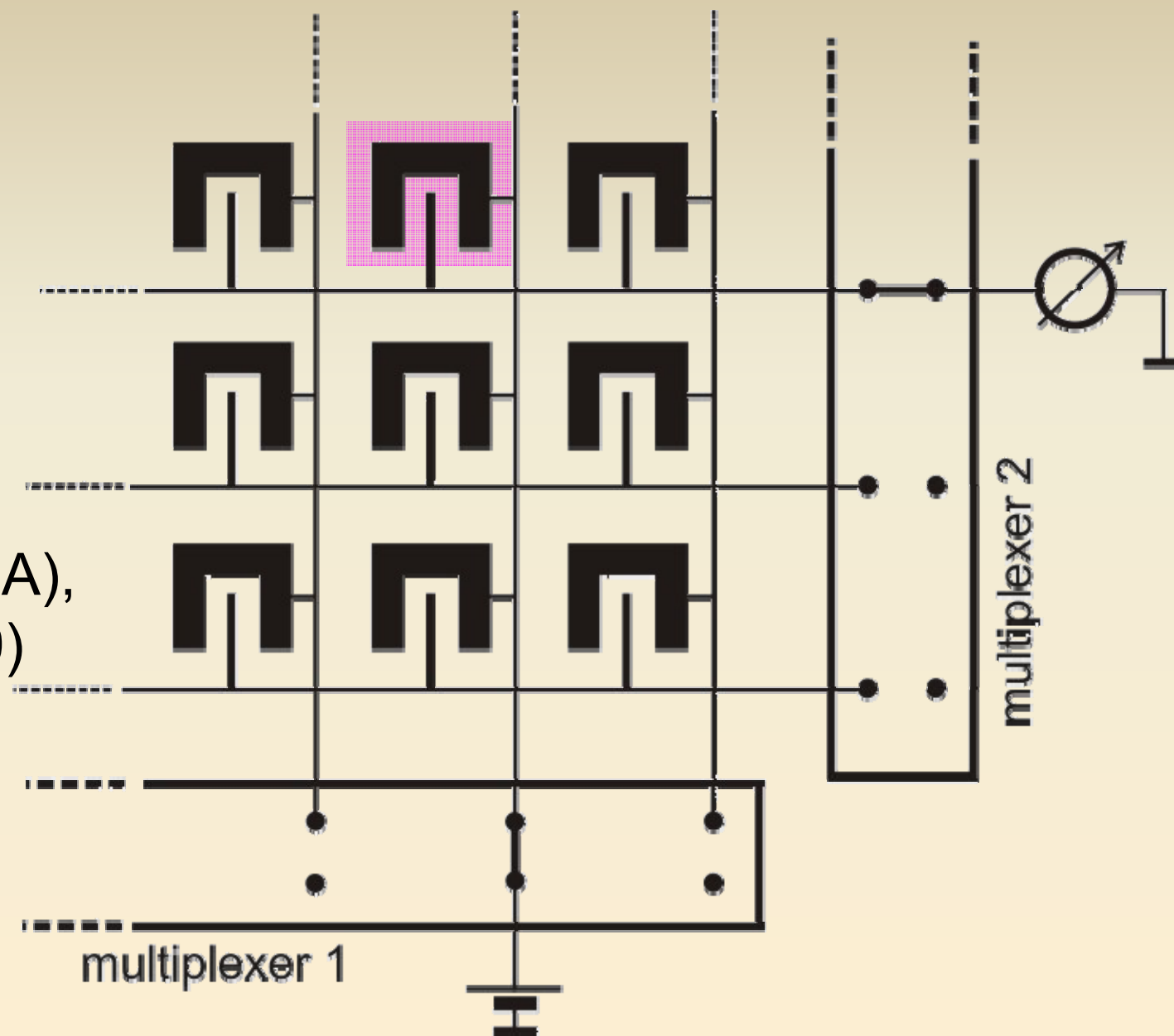
1024 sensorů

Pt katody

AgCl anody

hydrogel (HEMA),

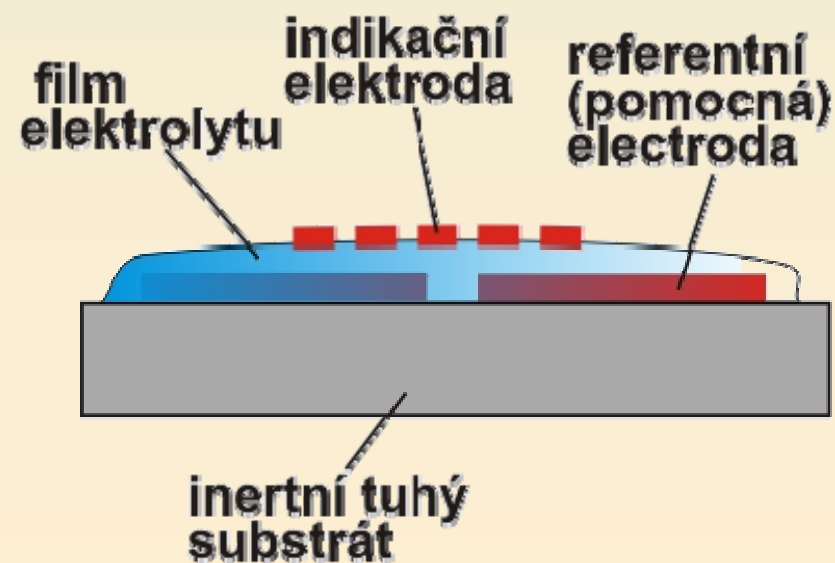
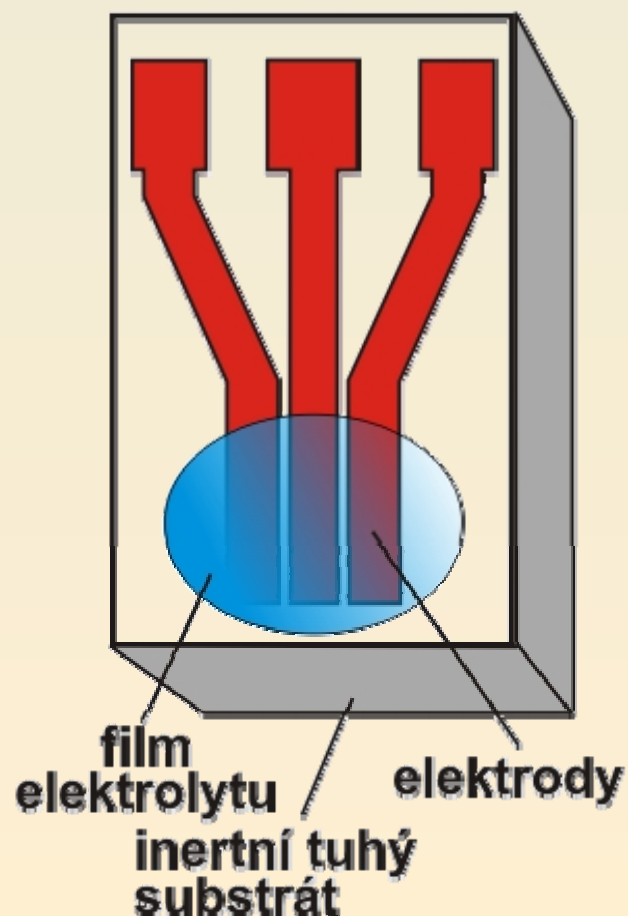
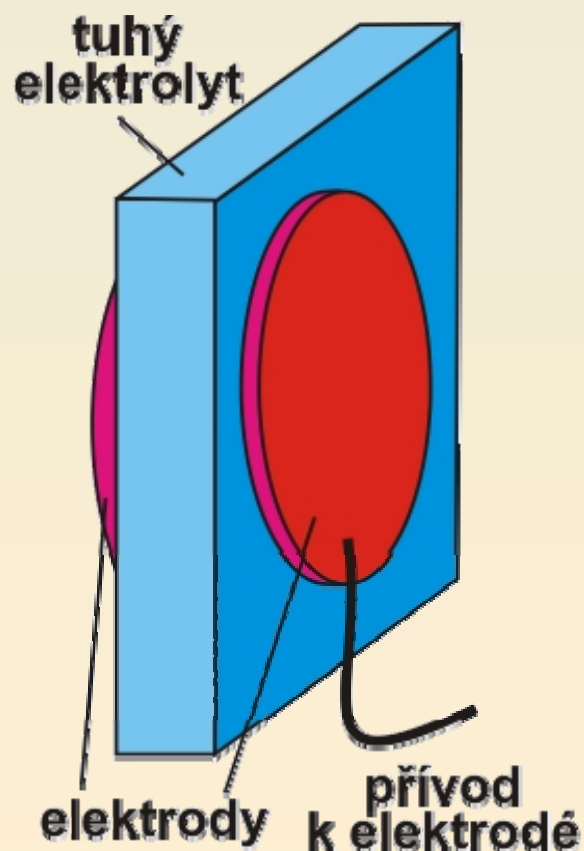
elyt KCl (pH 10)

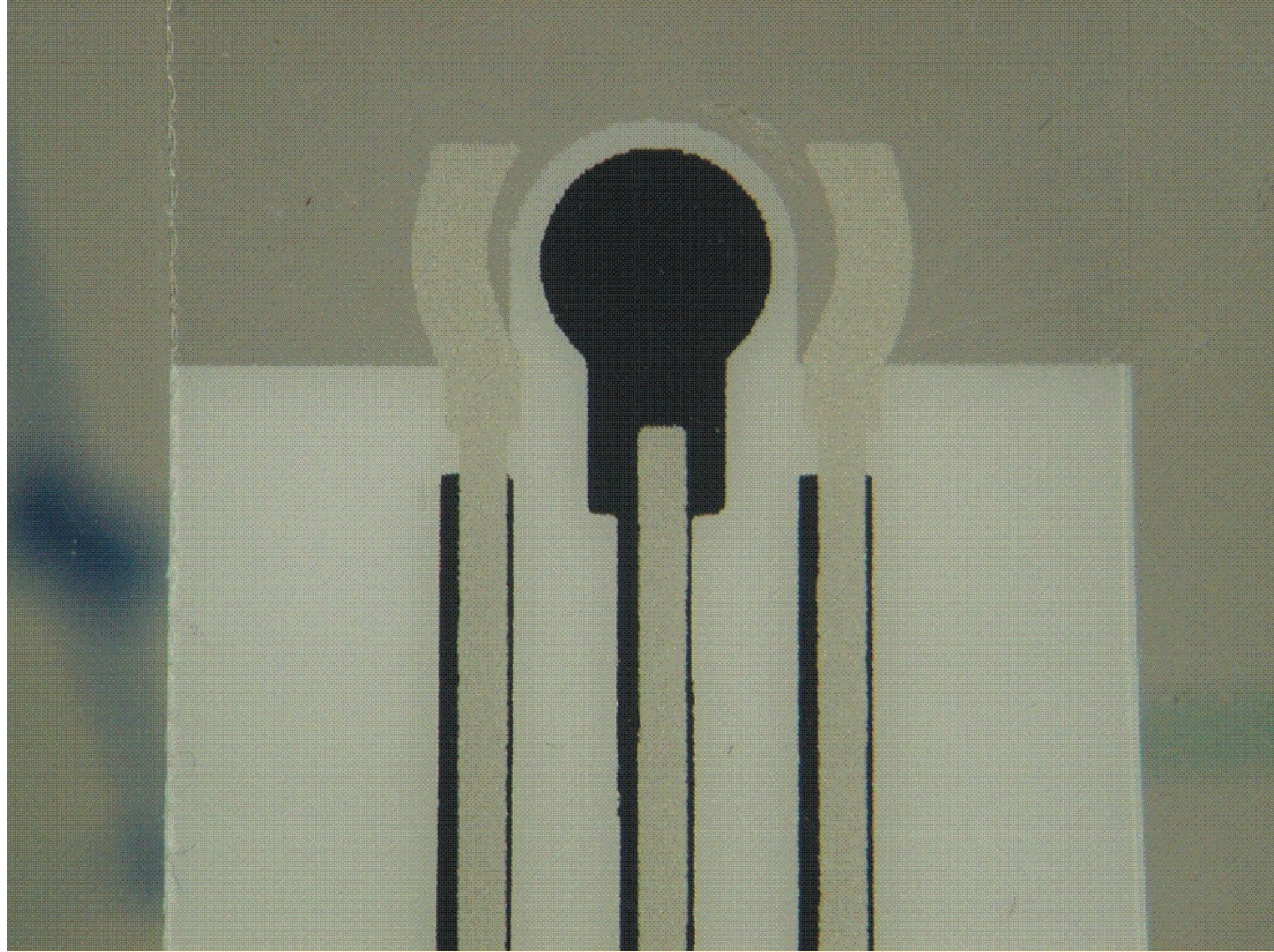


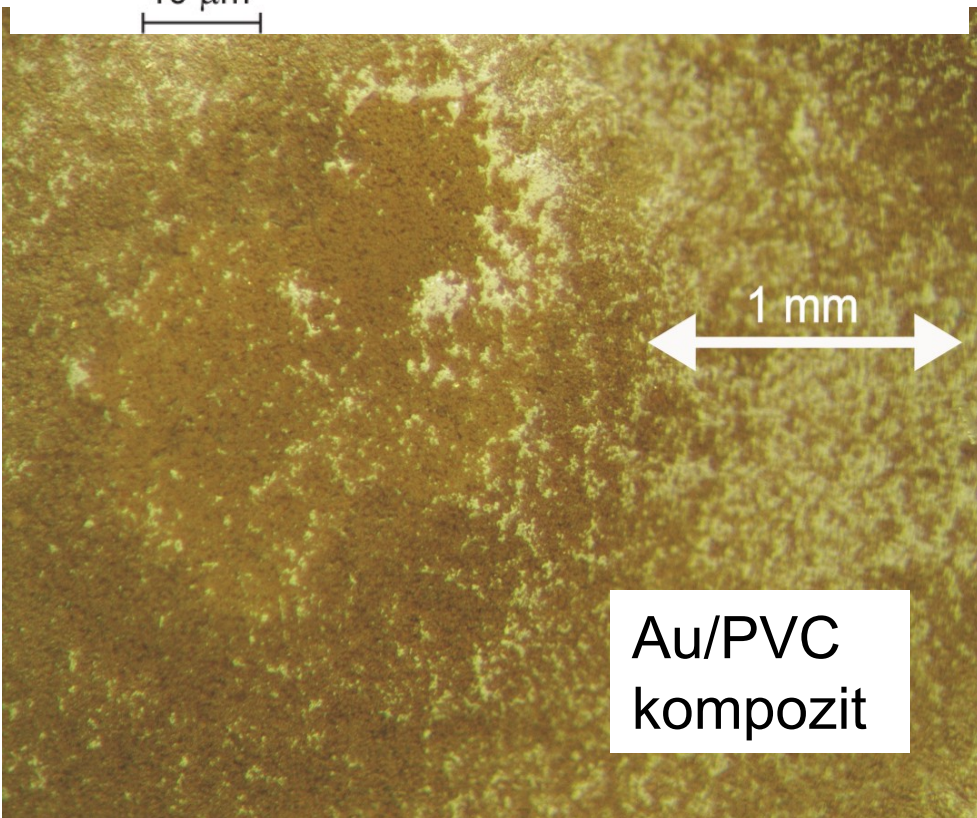
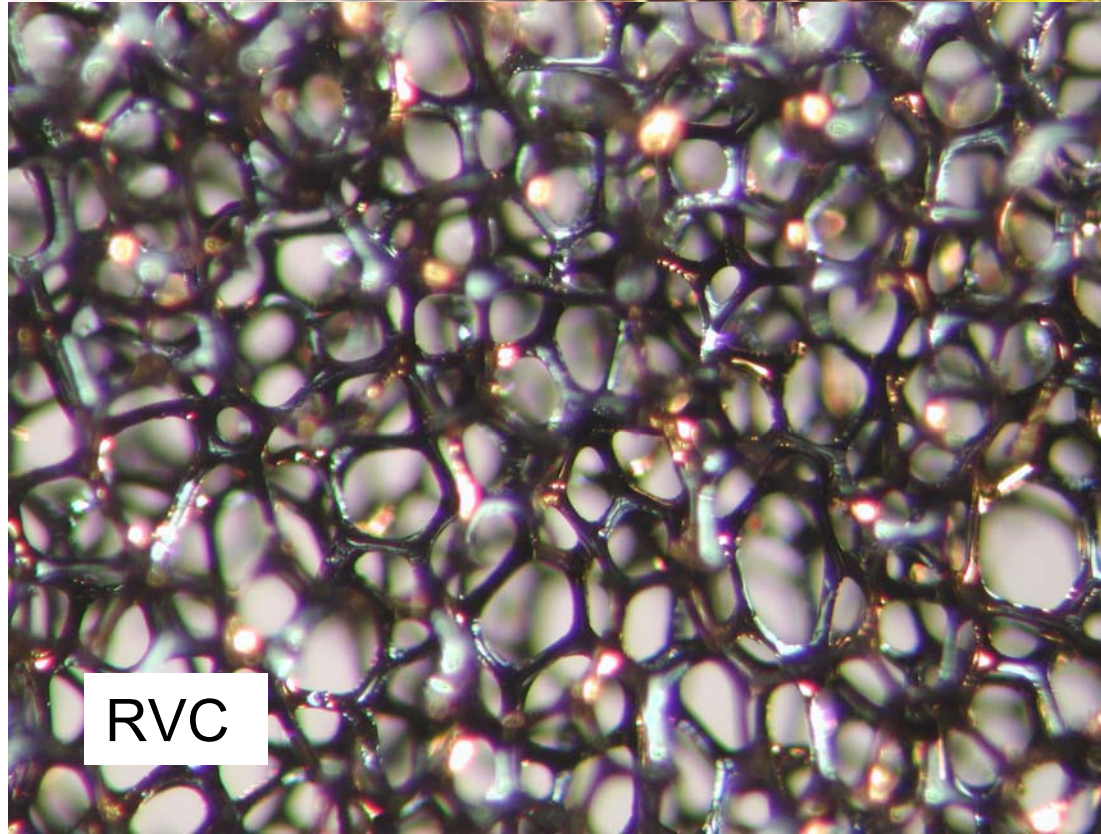
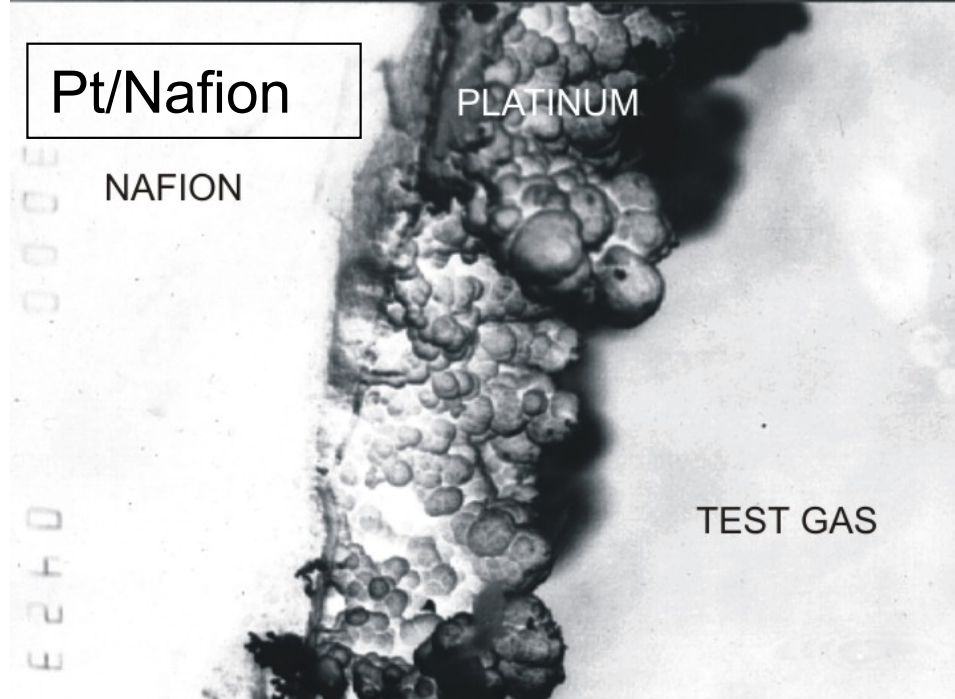
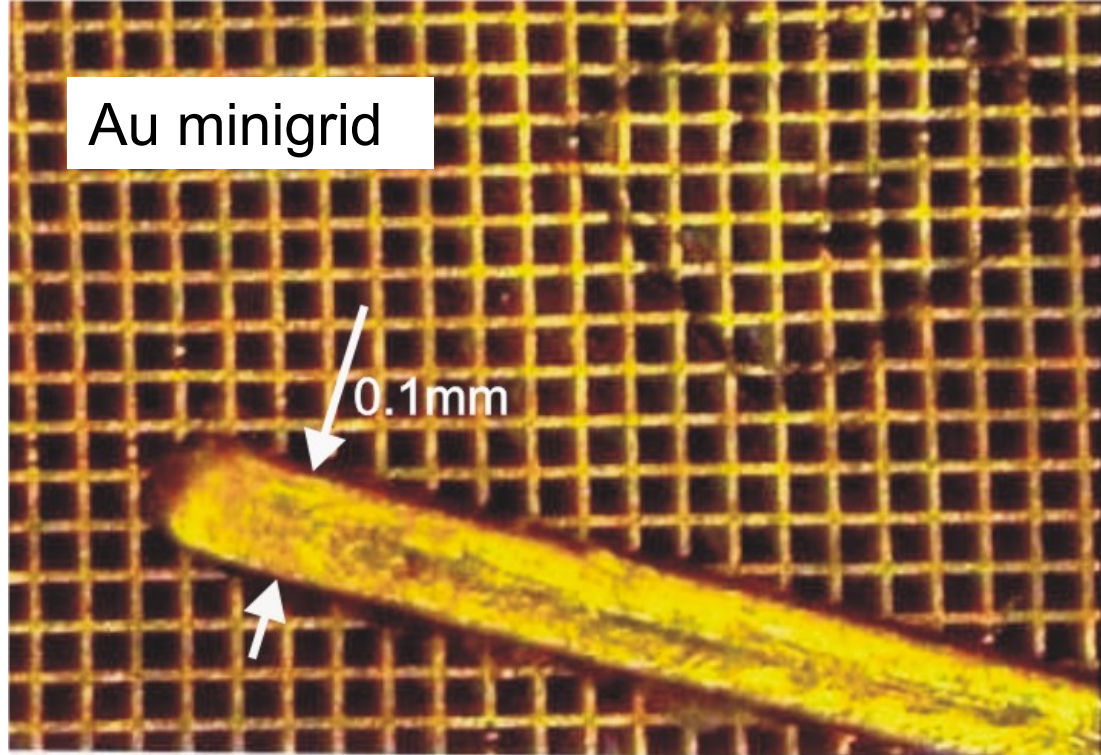
1.2 AMPÉROMETRICKÉ SOLID-STATE SENSORY

H ₂	H ₂ → 2H ⁺ + 2e
CO	CO + H ₂ O → CO ₂ + 2H ⁺ + 2e
O ₂	O ₂ + 4e → 2O ²⁻

$$I = nFAj$$

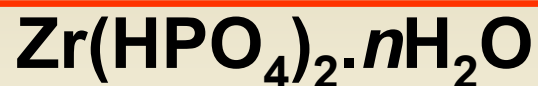
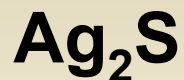




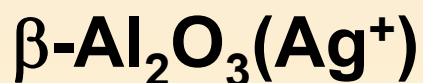
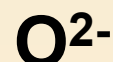
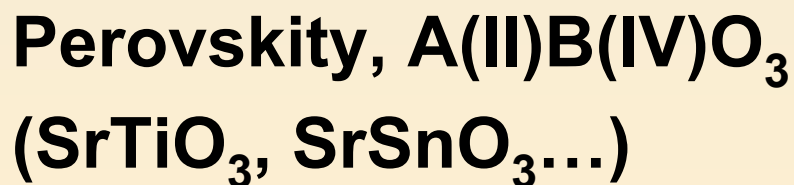
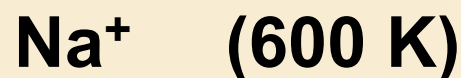
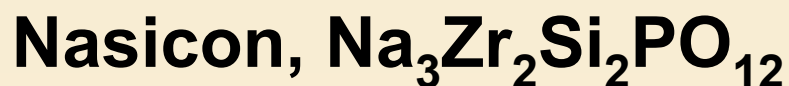
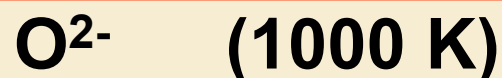
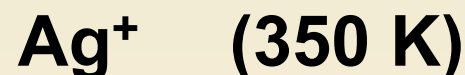


Anorganické tuhé elektrolyty

dostatečná iontová vodivost už za normální teploty:



iontová vodivost až za zvýšené teploty:

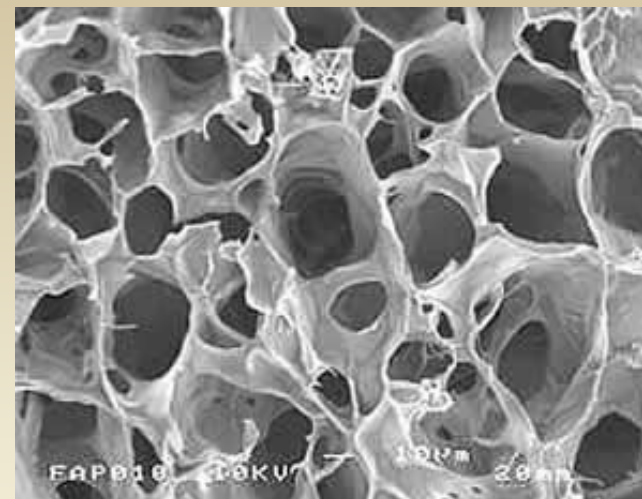


Organické tuhé elektrolyty

gely:

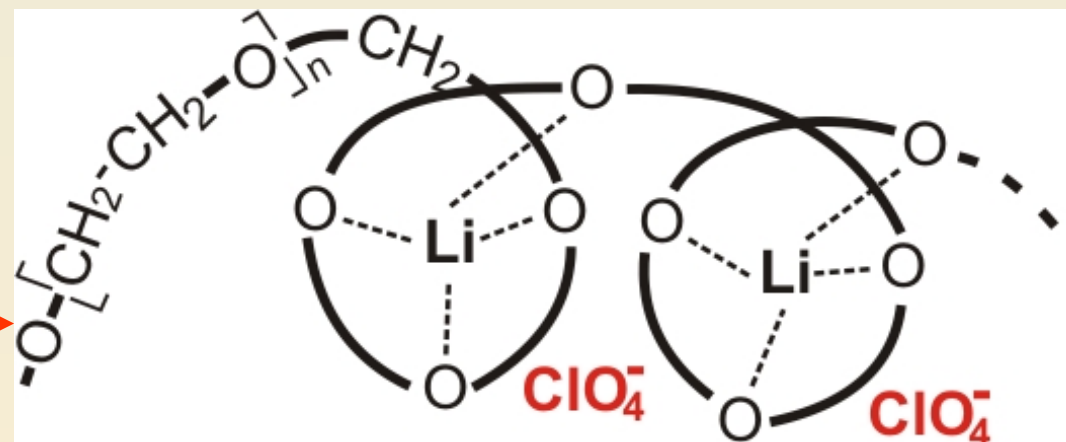
PMMA, změkč. PVC,

hydrogely (na bázi $\text{Si}(\text{OCH}_3)_4$)...;



elektrolyty „rozpuštěné“ v polymeru:

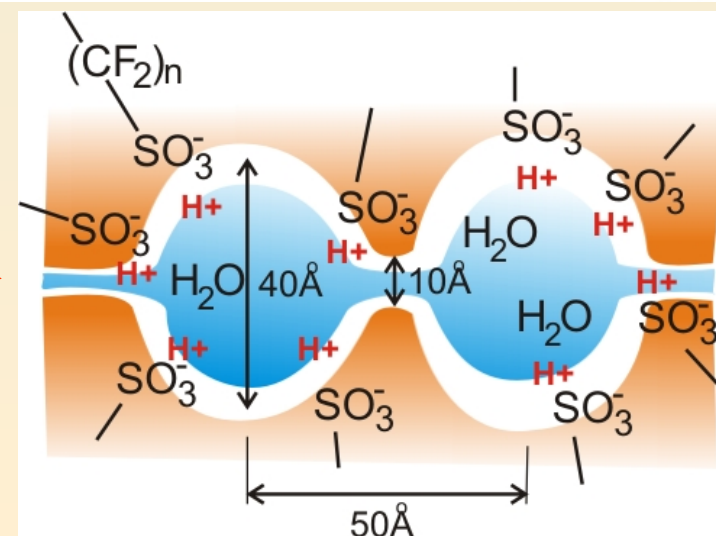
$(\text{PEO})_4\text{LiClO}_4$



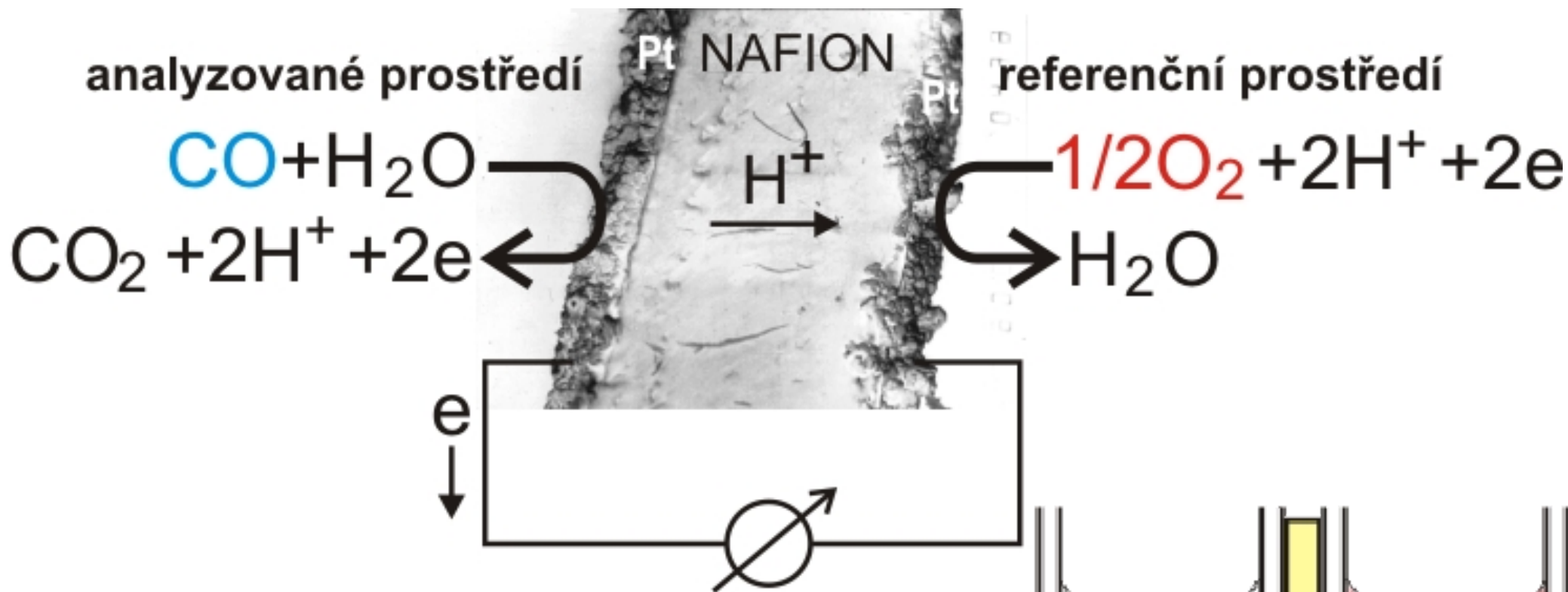
polymerní „sol“:

iontoměniče, NAFION

kopolymer polytetrafluoroethylenu
s polysulfonylfluor-vinyletherem

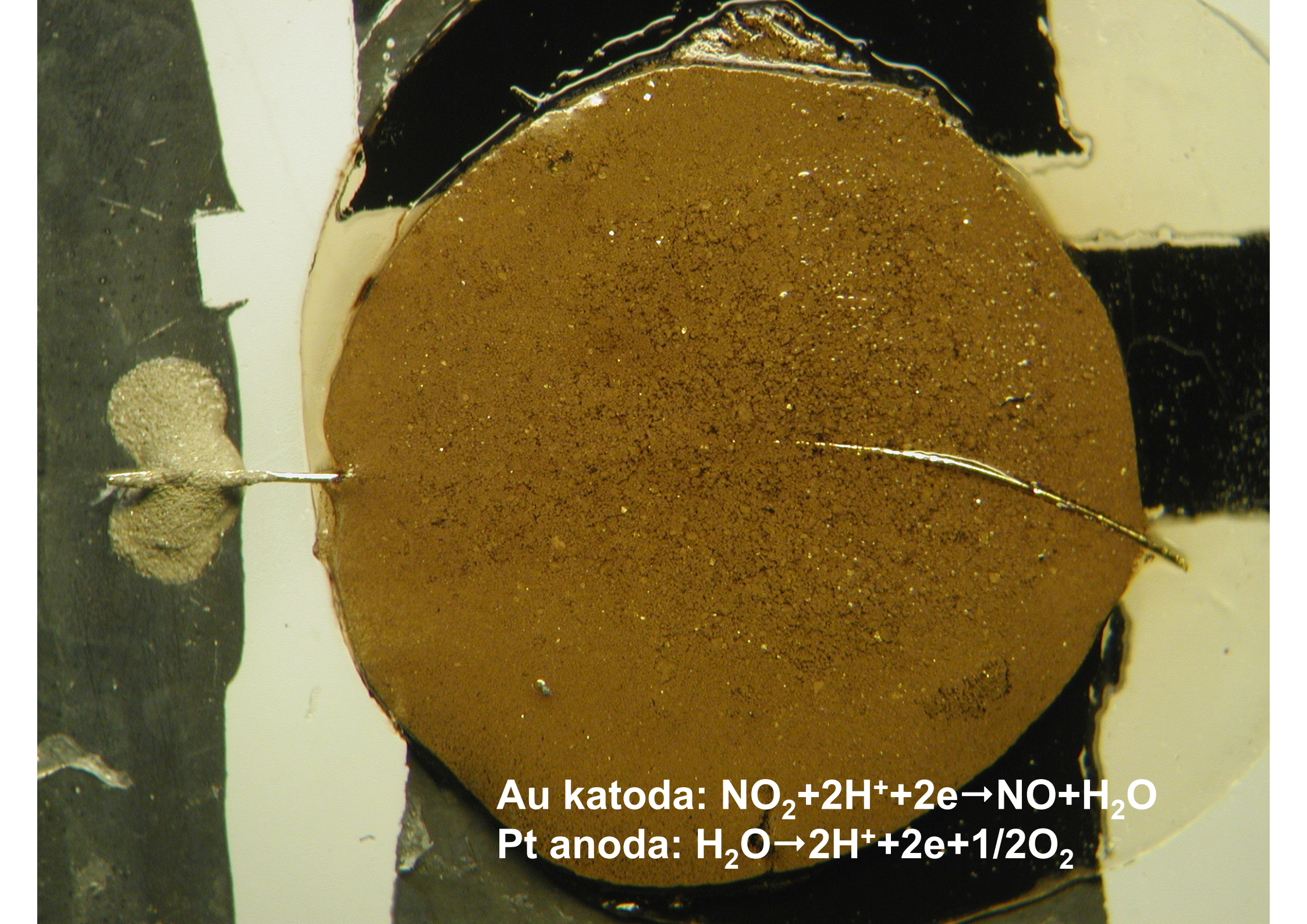


Sensory s protonovým vodičem



$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	$2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$
$\text{NO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O}$	$\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{e}^- + \frac{1}{2}\text{O}_2$
$\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^-$	$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$

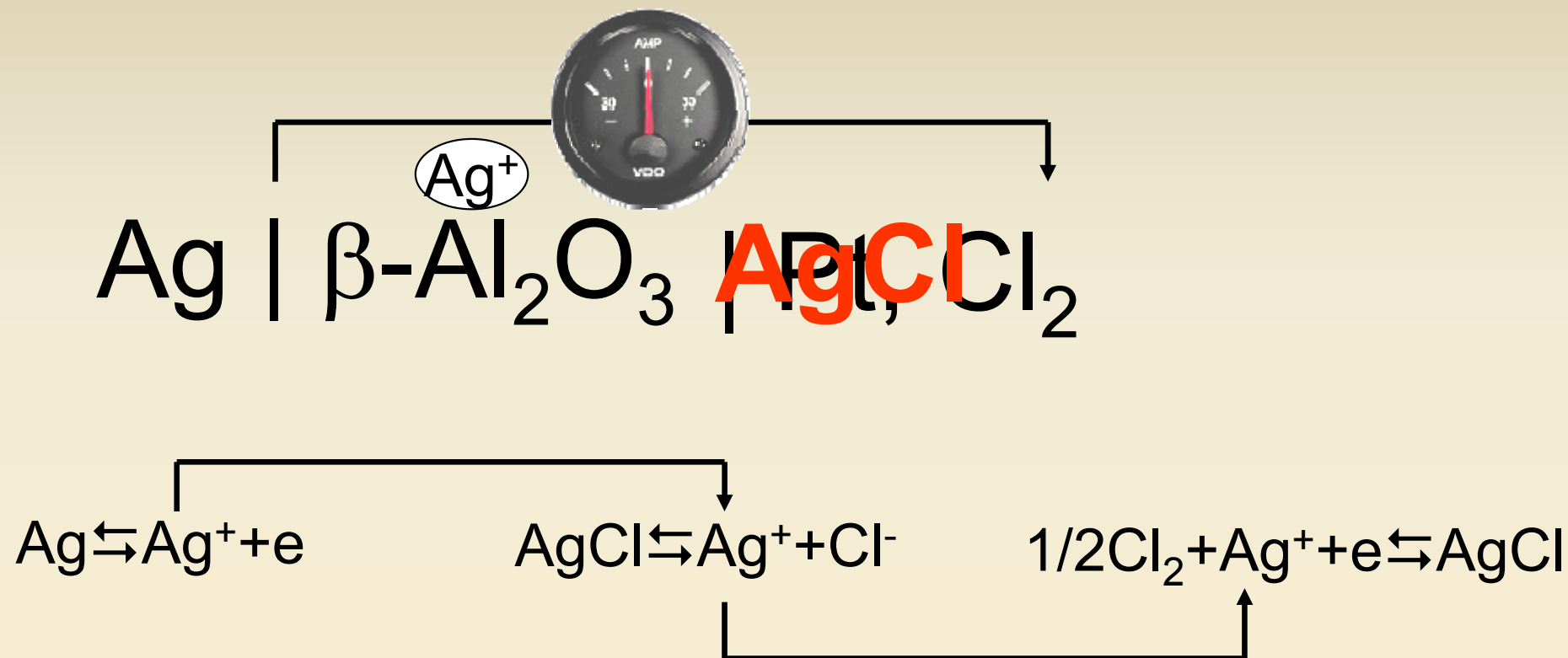
Nafion



Au katoda: $\text{NO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NO} + \text{H}_2\text{O}$
Pt anoda: $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{e}^- + 1/2\text{O}_2$

Ampérometrické solid-state sensory s pomocnou fází

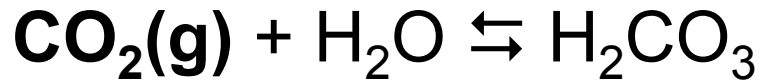
příklad: stanovení chloru:



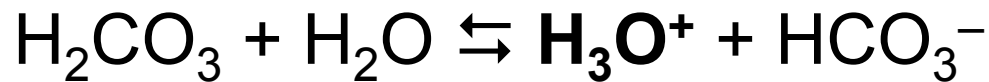
bez pom. vrstvy: $\frac{1}{2}\text{Cl}_2 + \text{e}^- \rightarrow \text{Cl}^-$

s pomoc. vrstvou: $\frac{1}{2}\text{Cl}_2 + \text{Ag} \rightarrow \text{AgCl}$

2.1 POTENCIOMETRICKÉ MEMBRÁNOVÉ SENSORY S KAPALNÝM ELEKTROLYTEM



$$K_s = \frac{[\text{H}_2\text{CO}_3]}{p\text{CO}_2}$$



$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$[\text{H}_3\text{O}^+] = \frac{K_s K_1}{[\text{HCO}_3^-]} p\text{CO}_2$$

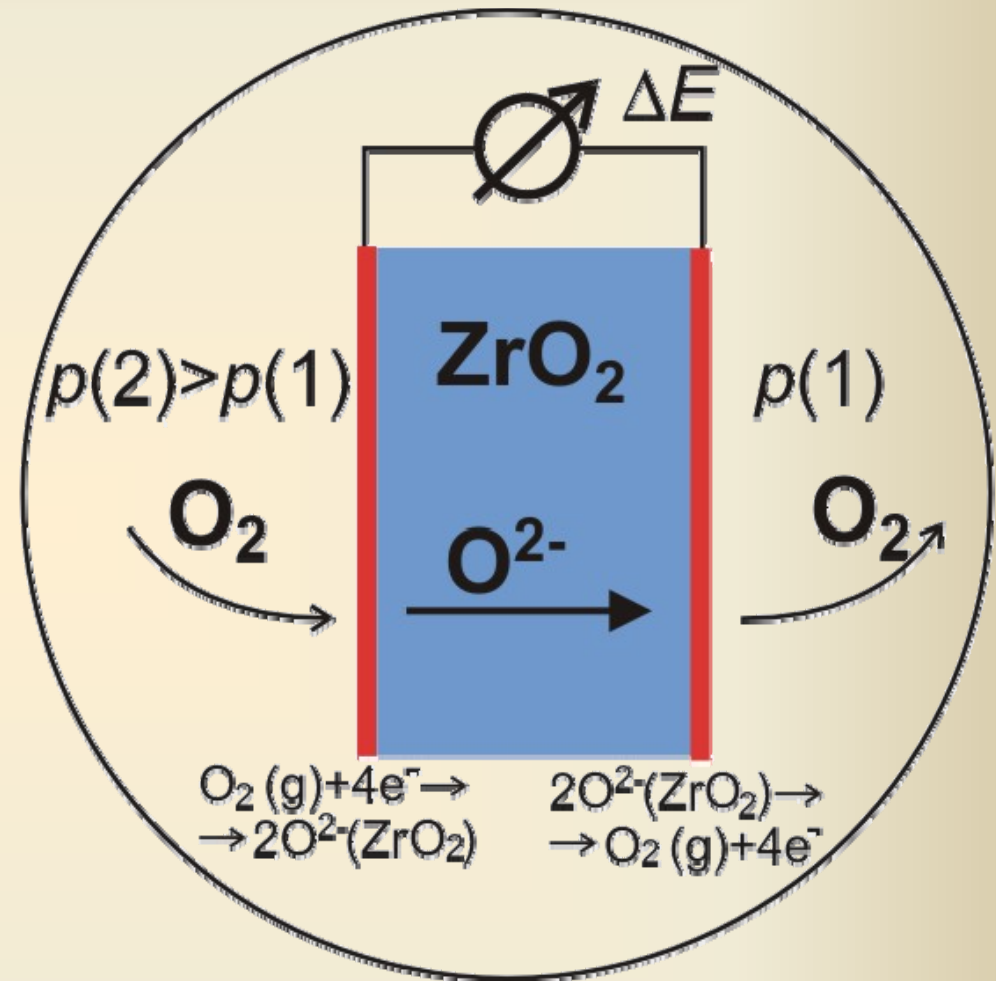
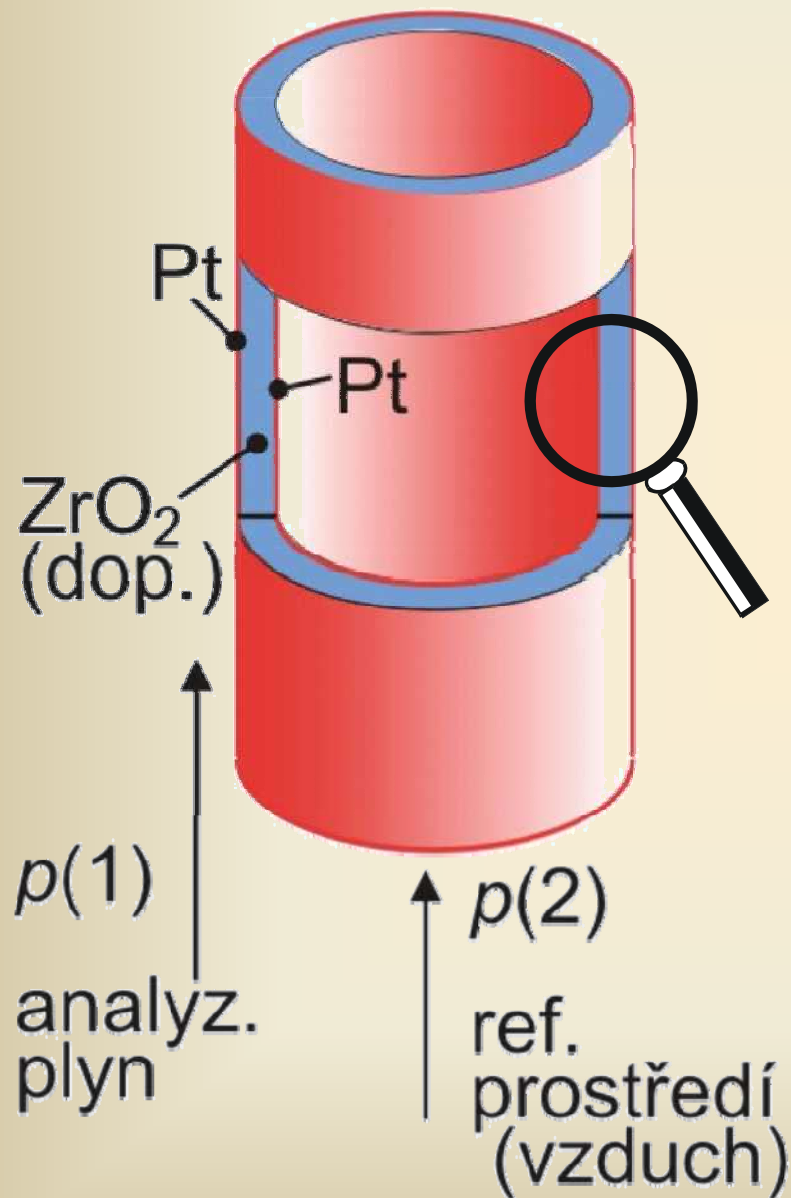


John W. Severinghaus



2.2 POTENCIOMETRICKÉ SOLID-STATE SENSORY

Sensory kyslíku na bázi dopovaného ZrO_2



a) potenciometrický článek

$$\Delta E = K + \frac{0,059}{4} \log \frac{p(1)}{p(2)}$$

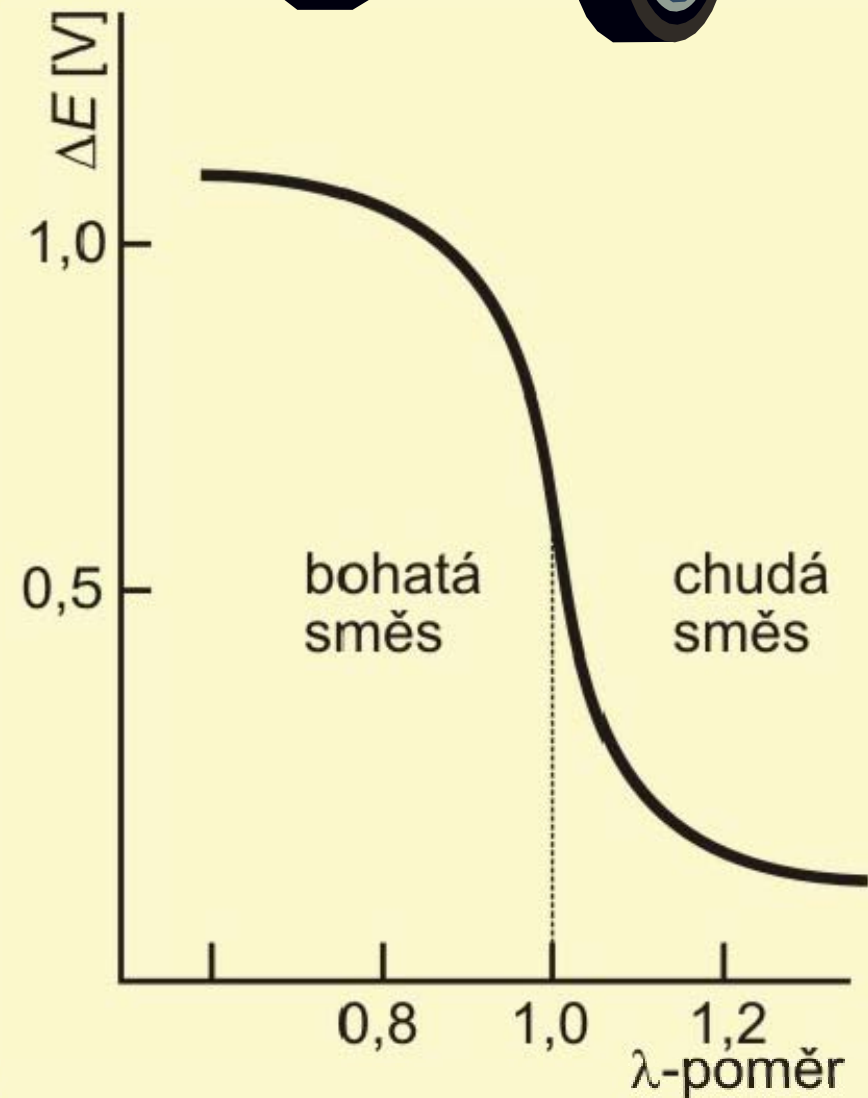
Potenciometrický lambda-sensor

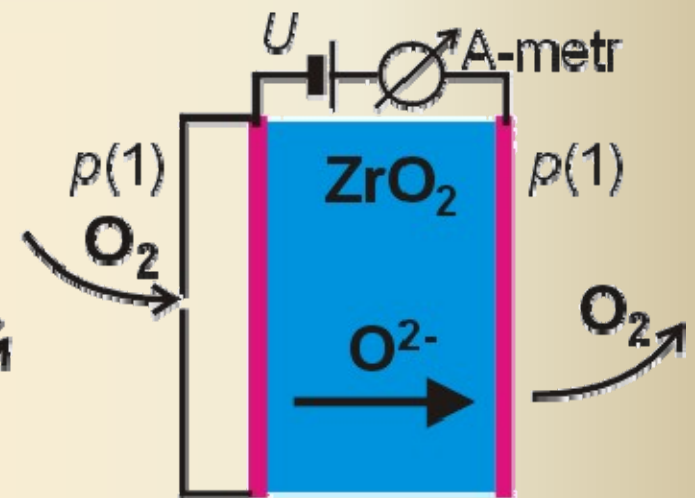
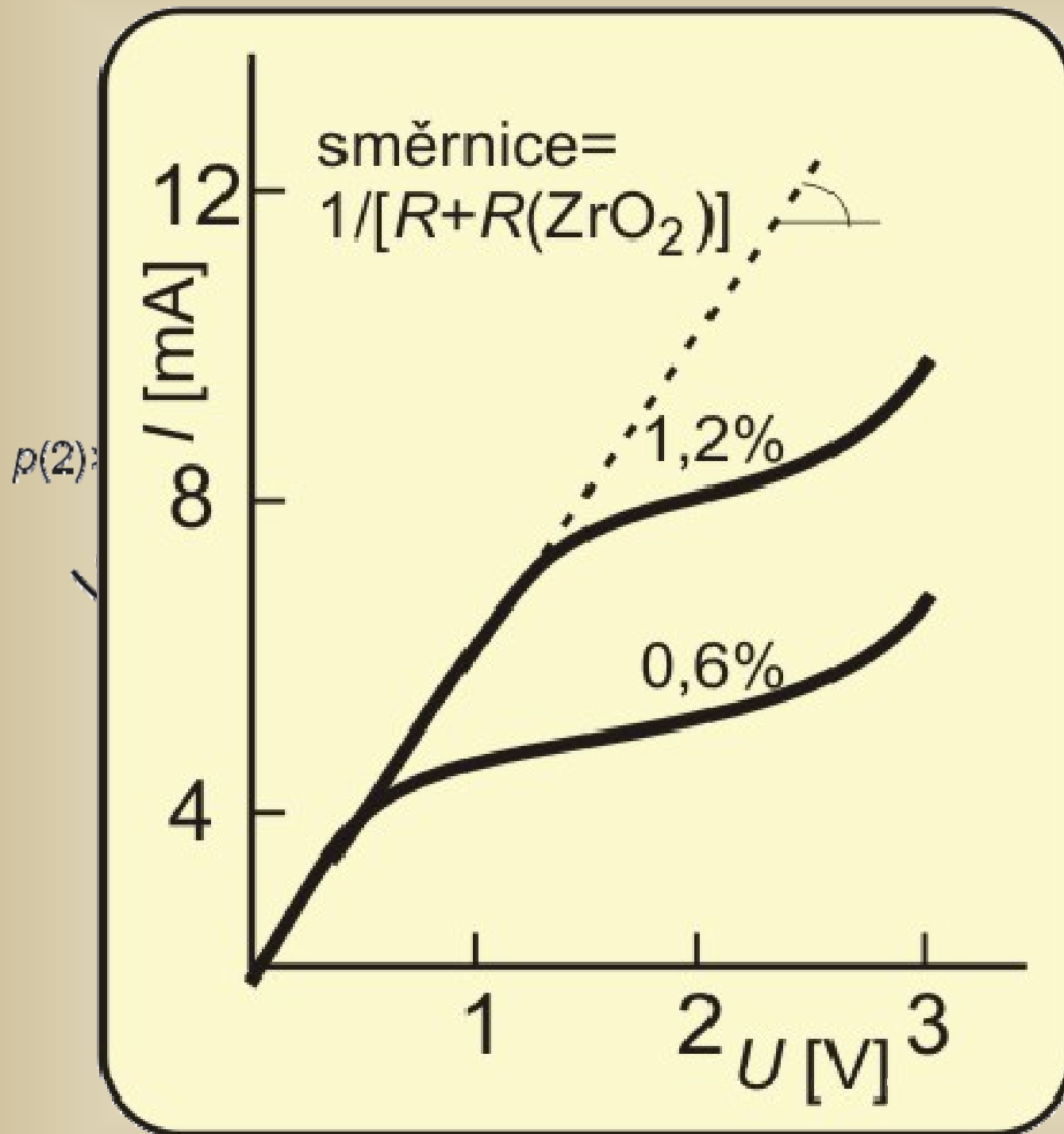
$$\lambda = \frac{\text{aktuální poměr vzduch/palivo}}{\text{stechiometrický poměr vzduch/palivo}}$$

$\lambda > 1$ chudá směs

$\lambda = 1$ stechiom. směs

$\lambda < 1$ bohatá směs

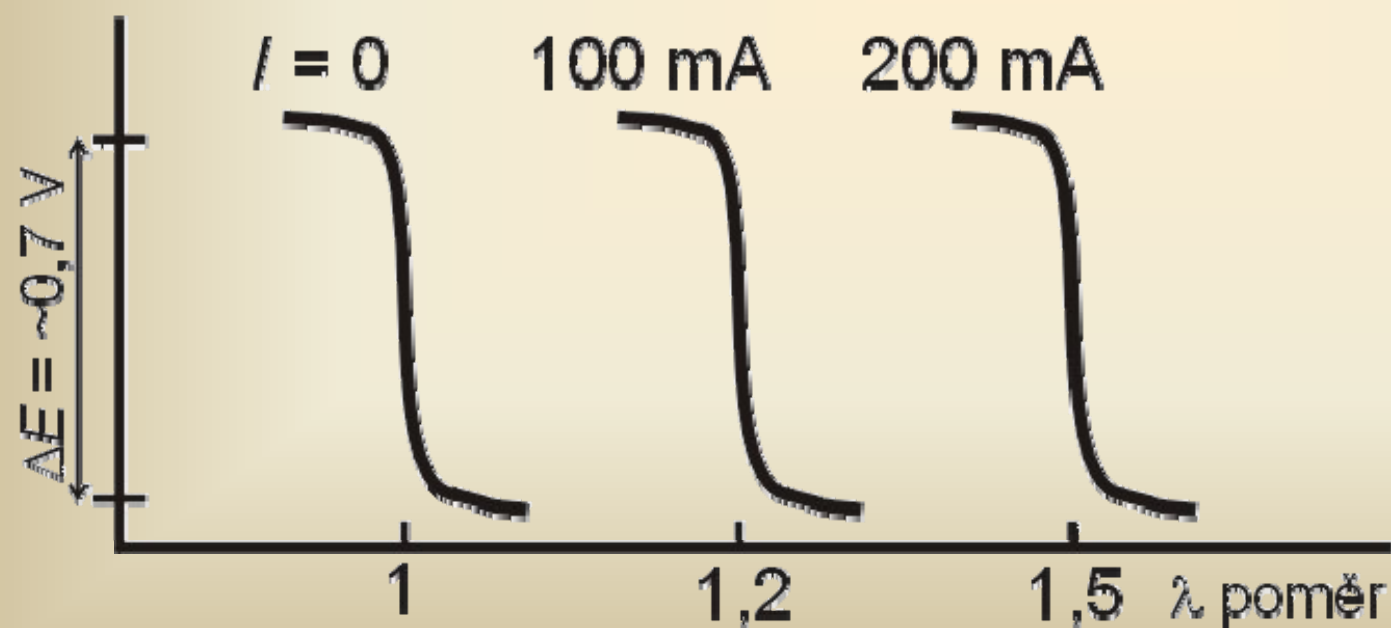
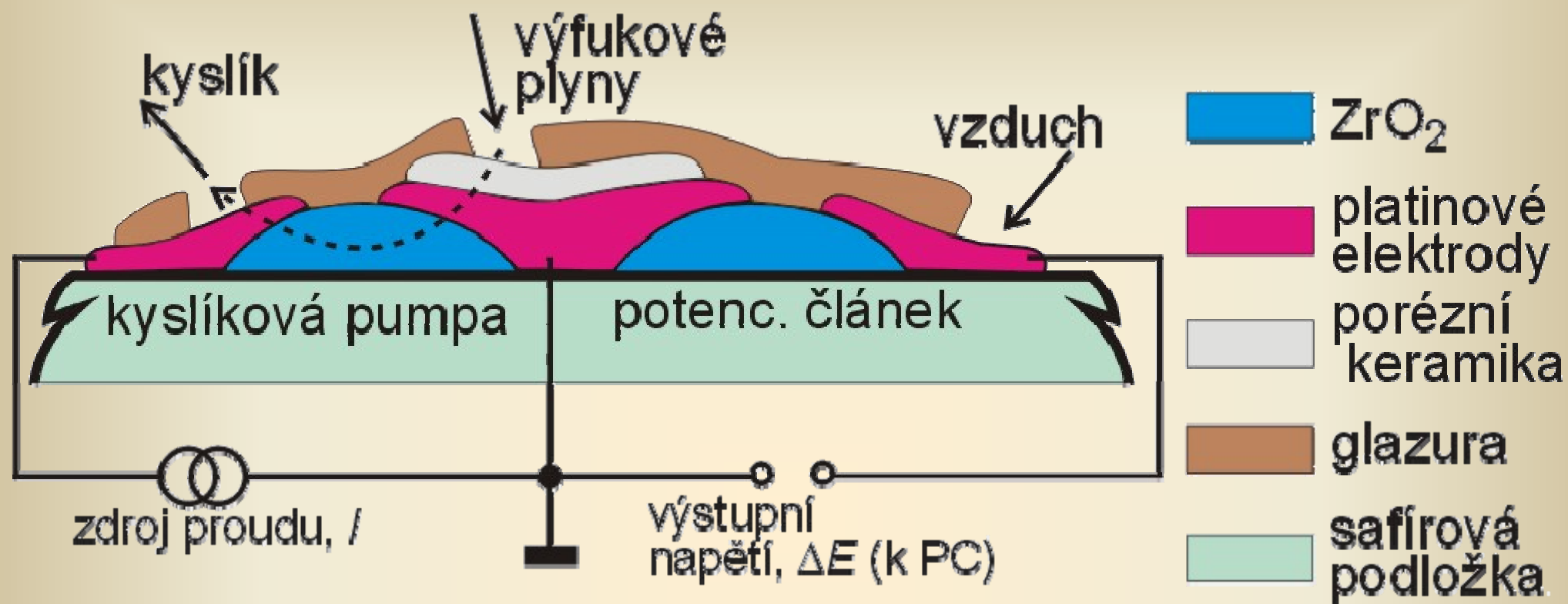




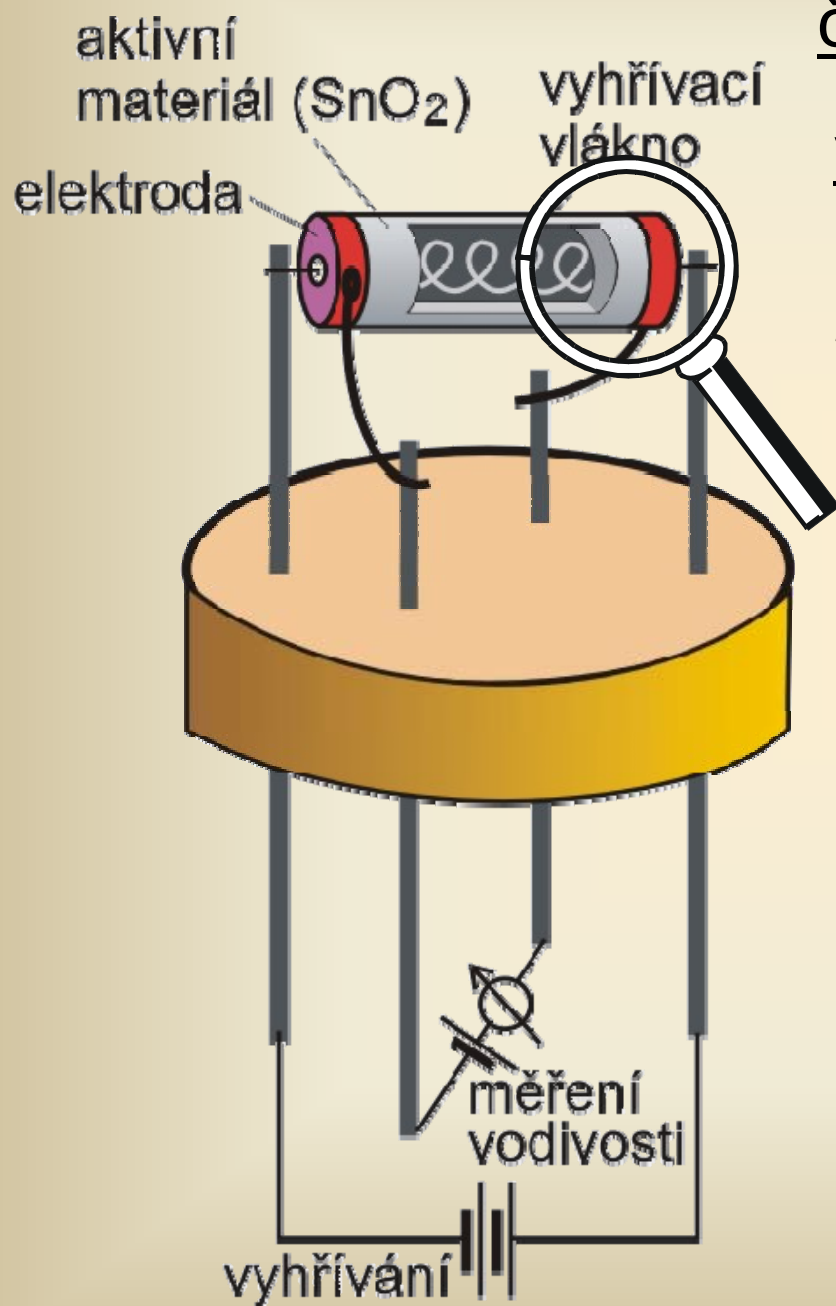
d) ampérom.
sensor

$$I = kp(1)$$

LAMBDA SENSOR S KYSLÍKOVOU PUMPOU

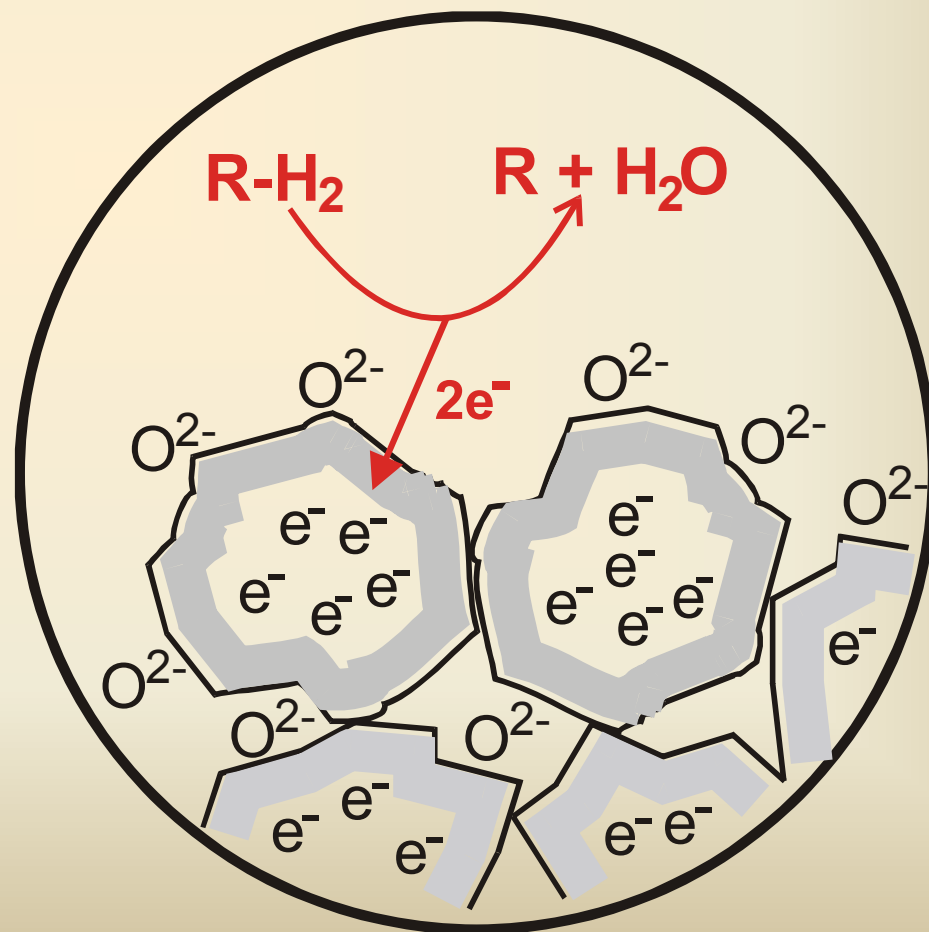
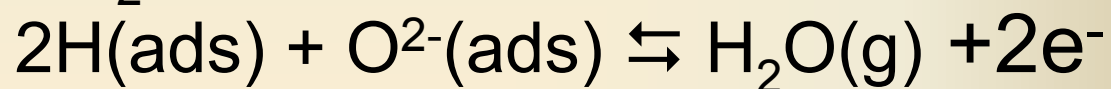
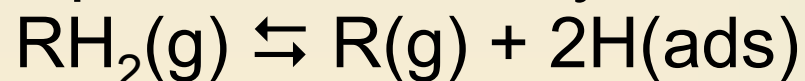


3.1 SENSORY ZALOŽENÉ NA MĚŘENÍ ELEKTRONOVÉ VODIVOSTI – METALOXIDOVÉ SENSORY

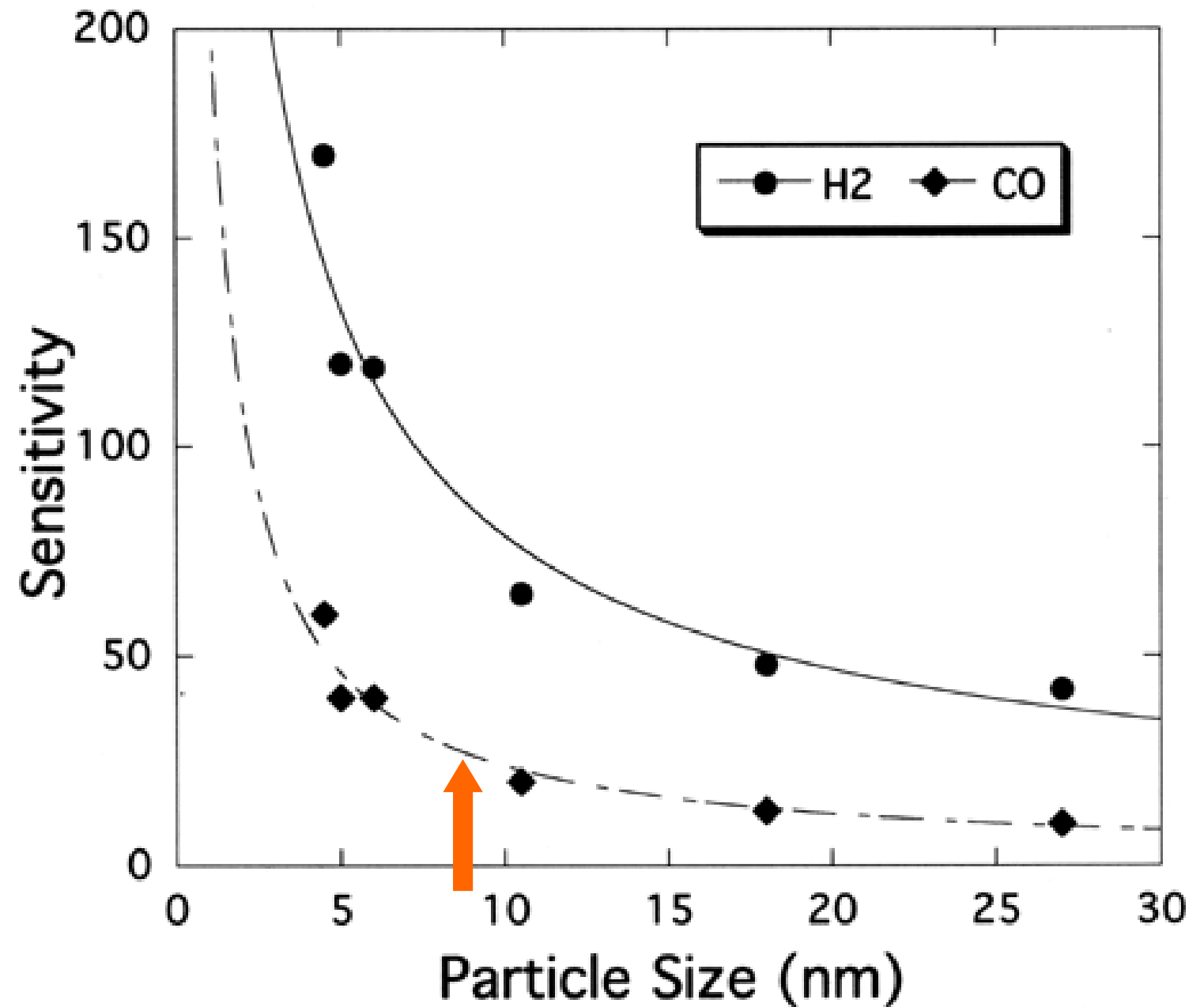


čistý vzduch: $\frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^- \rightleftharpoons \text{O}^{2-}(\text{ads})$

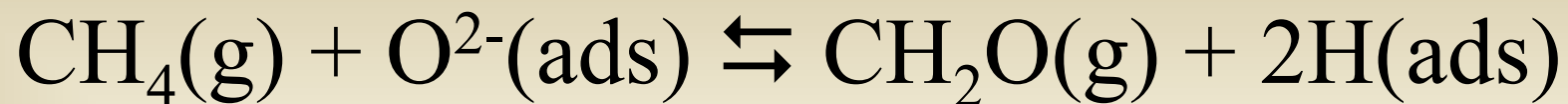
v přítomnosti analytu:



Citlivost metaloxidových (SnO_2) sensorů v závislosti na velikosti zrn oxidu.



příklady použití:



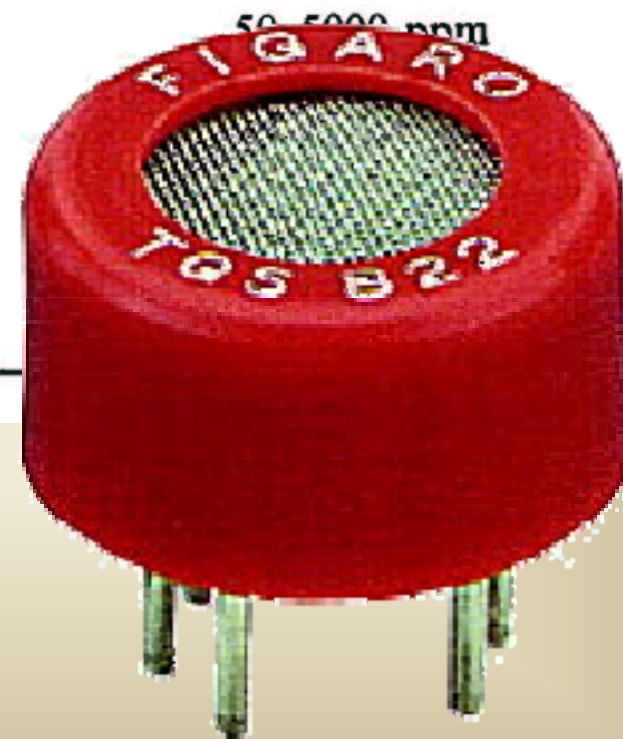
ovlivnění se

- * přím
- * prac
- * chem
- mem
- * použ



Table 9-4. The different types of Tagushi sensors and their specifications [1].

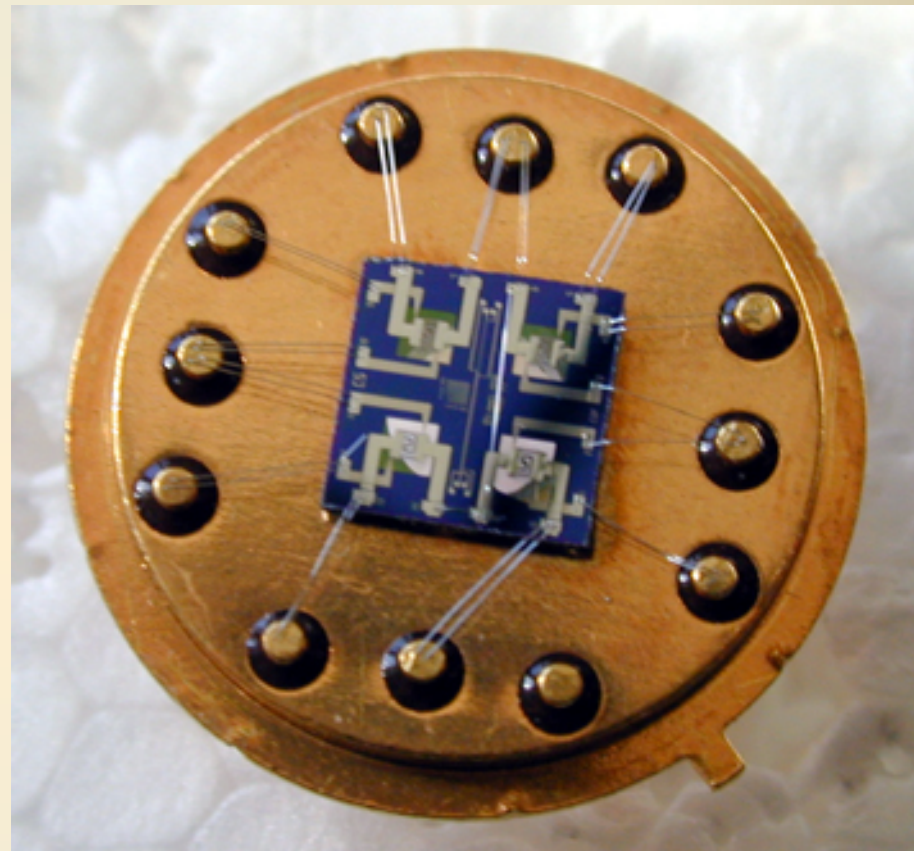
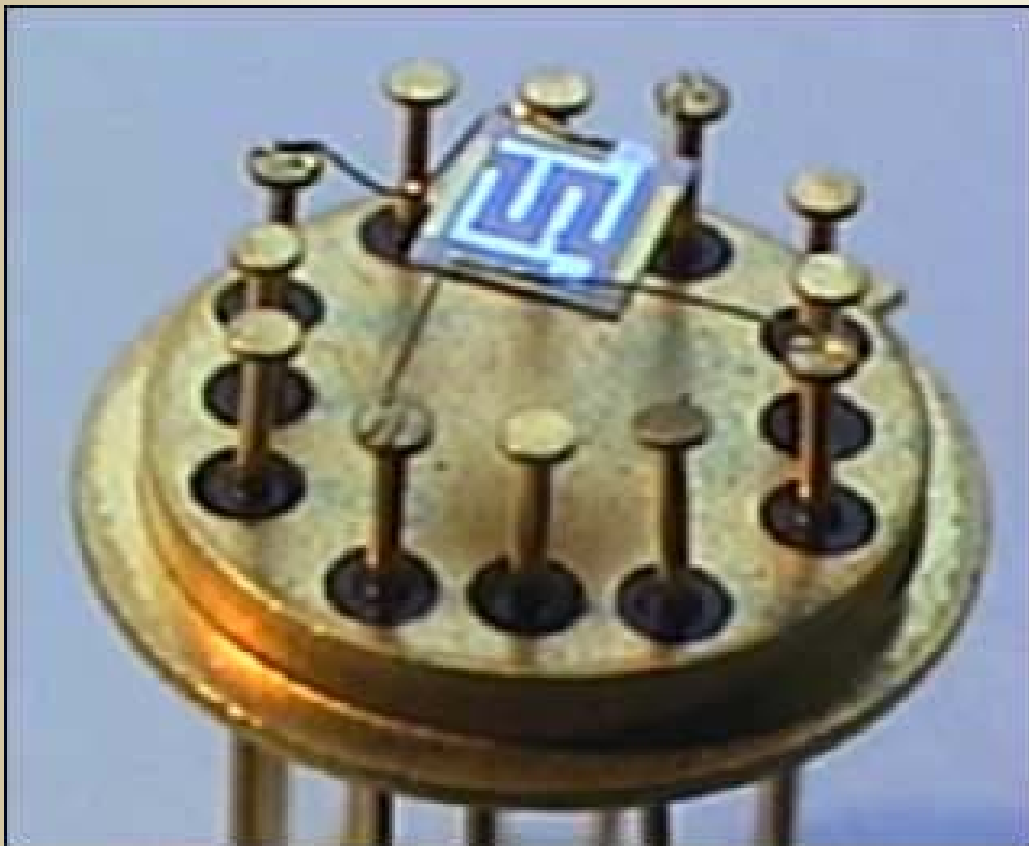
Type of sensor <i>former types</i>	Compound (decreasing sensitivity for identical partial pressures)	Detection range
TGS 109, TGS 109M	Iso - C ₄ H ₁₀ > C ₃ H ₈ > CH ₄ > CH ₃ > OH > H ₂ > CO	500-10000 ppm
TGS 813, <i>TGS 813 C</i>		
TGS 816, <i>TGS 911</i>	H ₂ > iso - C ₄ H ₁₀ > CH ₄ > C ₂ H ₅ OH > CO	500-10000 ppm
<i>TGS 812, TGS 817</i>	C ₂ H ₅ OH > H ₂ > iso - C ₄ H ₈ > CO	500-5000 ppm
<i>TGS 711</i>	C ₂ H ₅ OH > H ₂ > CO	50-500 ppm
<i>TGS 712D</i>	C ₂ H ₅ OH > H ₂ > CO	20-200 ppm
TGS 100, TGS 800	C ₂ H ₅ OH > H ₂ > iso - C ₄ H ₈ > CO	1-300 ppm
TGS 203	CO > H ₂ > C ₂ H ₅ OH	50-1000 ppm
TGS 822, TGS 823	CH ₃ COCH ₃ ≈ C ₂ H ₅ OH ≈ C ₆ H ₆ ≈ n - C ₆ H ₁₄ > iso - C ₄ H ₈ > CO > CH ₄	50-5000 ppm
<i>TGS 814D, TGS 824</i>	NH ₃	
TGS 825	H ₂ S > H ₂	
TGS 880, TGS881	<u>Volatile compounds during cooking of foods</u>	
TGS 830	Freon 113	
TGS 831	Freon 21, freon 22	



Soubor metaloxidových sensorů pro elektronický nos



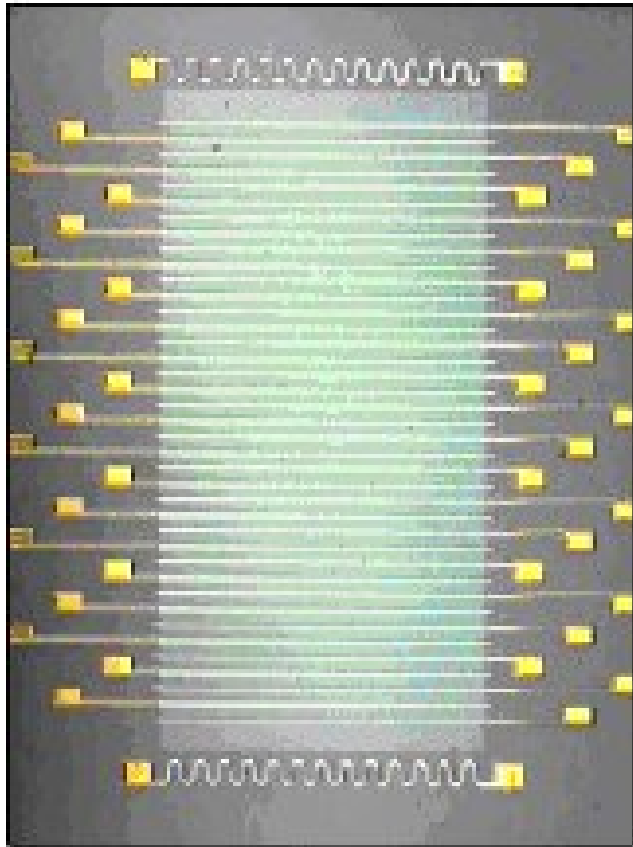
Tenkovrstvé metaloxidové sensory



sensor ethylenu, det limit $< 0,1$ ppm

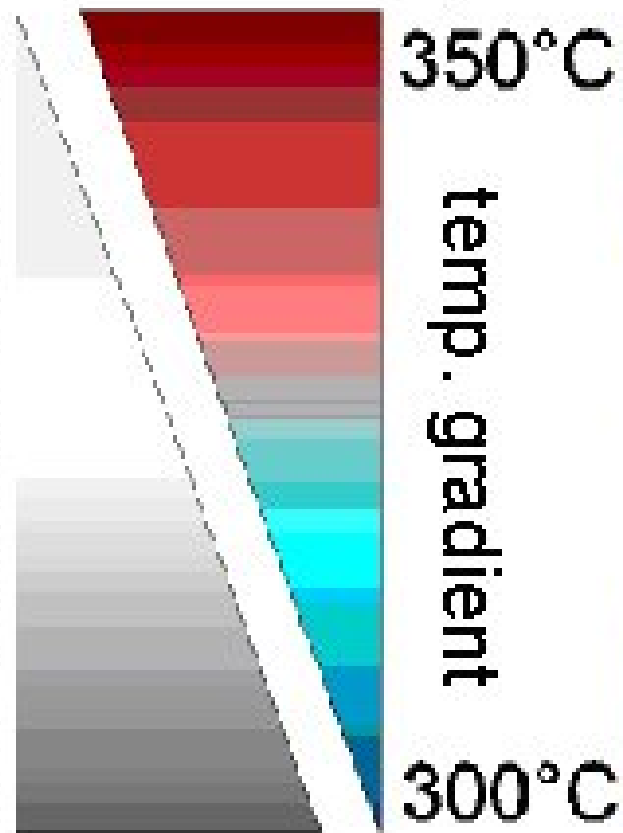
Soubor metaloxidových μ -sensorů s teplotním gradientem

front side

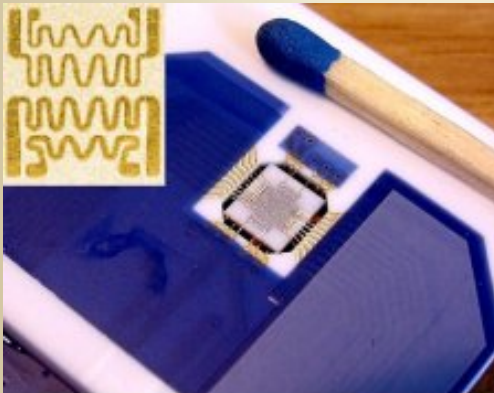
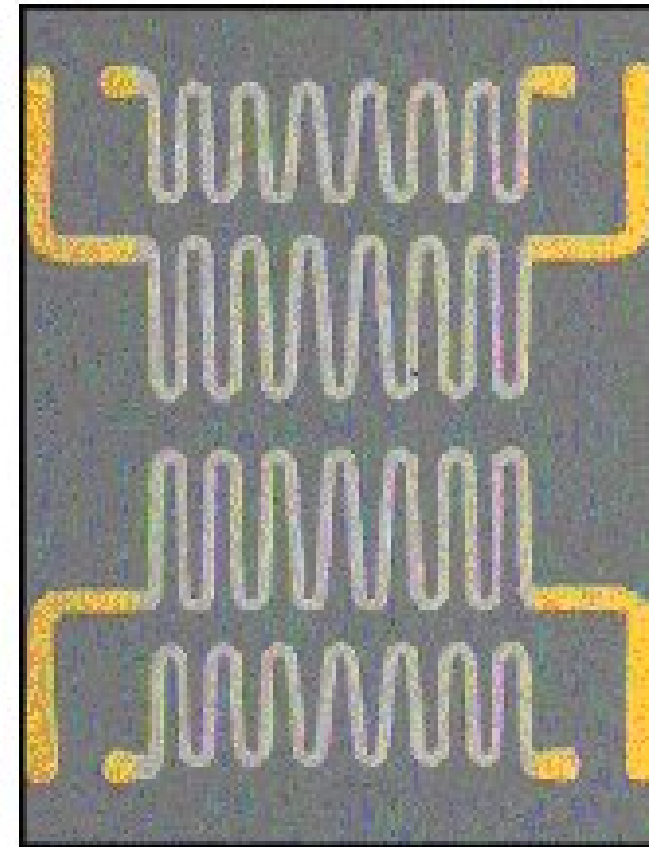


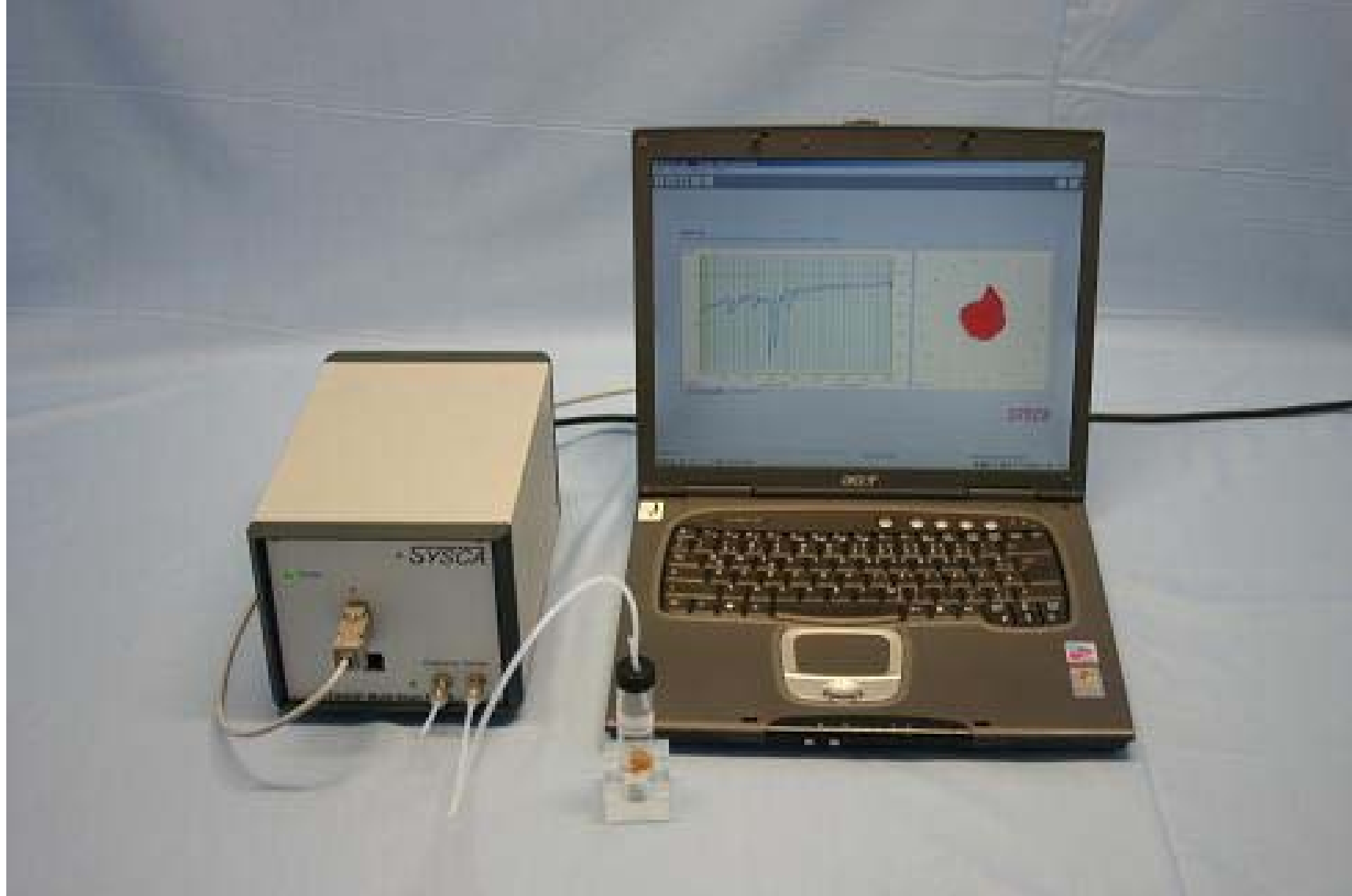
gradient technique

∞ thickness gradient
of SiO_2 membrane



rear side

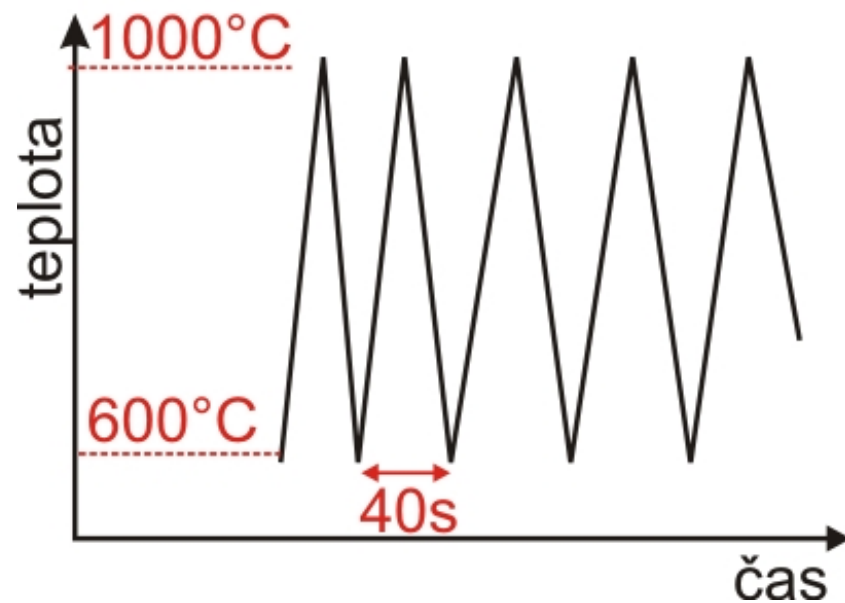
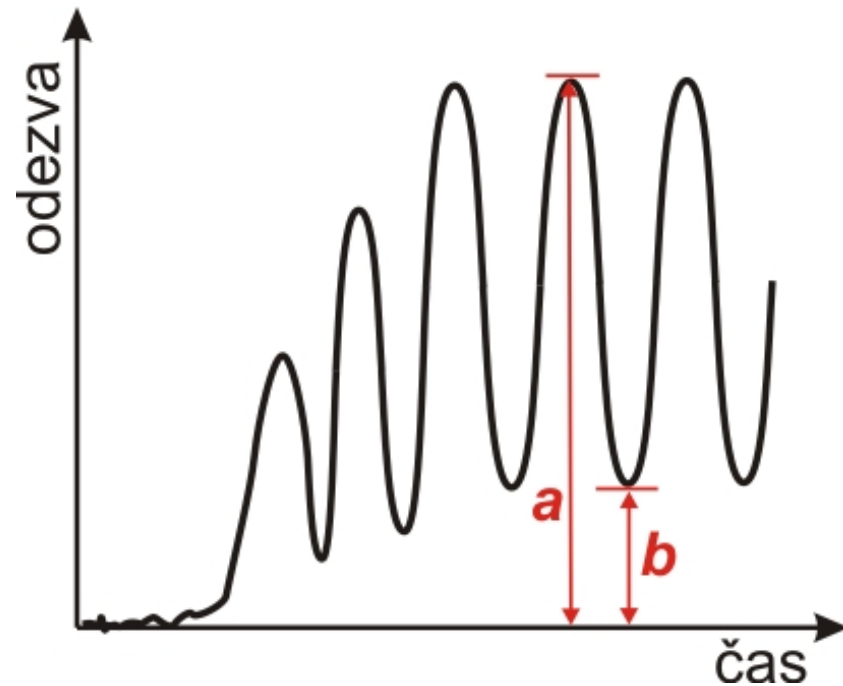
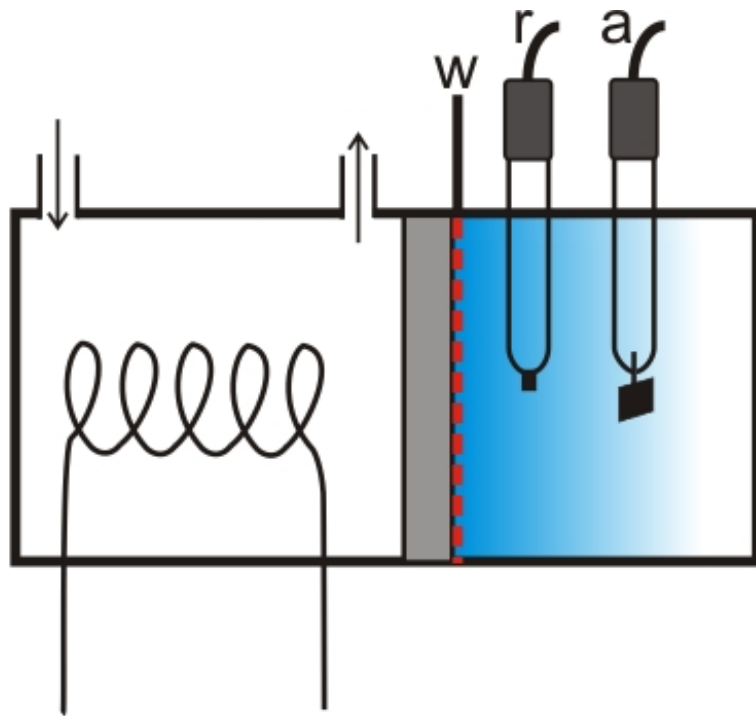




- ◆ NH_3 , H_2S , xylen, akrolein < 10 vppb
- ◆ Ethanol, methanol, aceton, ethylacetát, toluen, DMF, NO_2 , SO_2 < 100 vppb
- ◆ Methan, propan, benzen, CO < 1 vppm
- ◆ CCl_4 , CHCl_3 , C_2HCl_3 < 100 vppm

Apérimetrický sensor s tepelně modulovaným vláknem

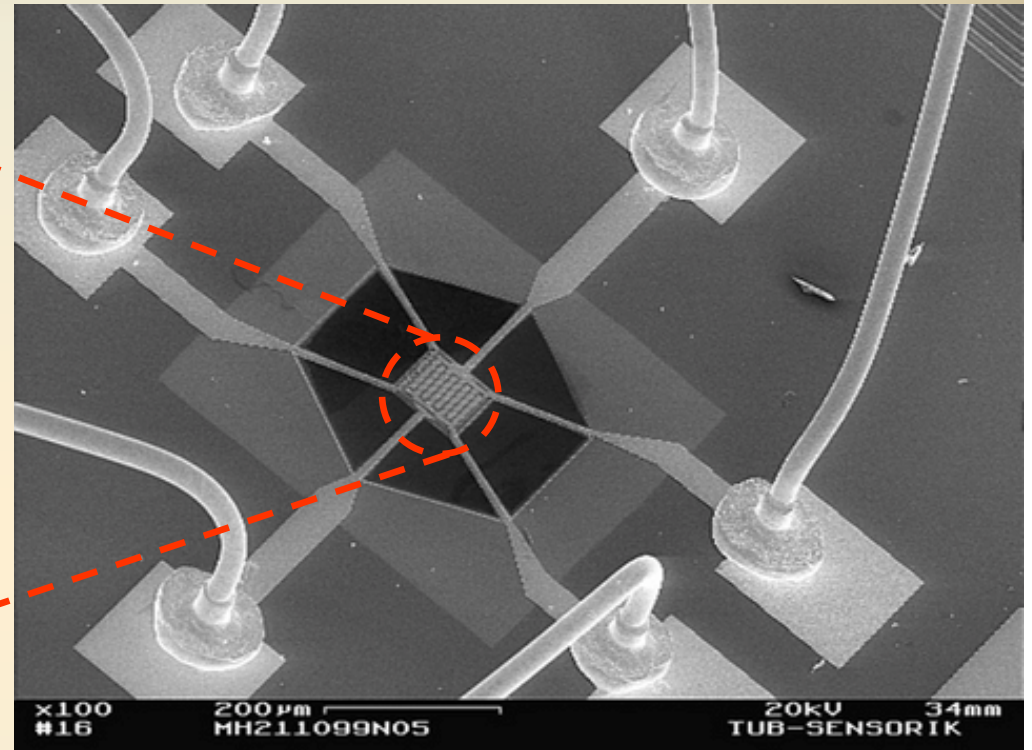
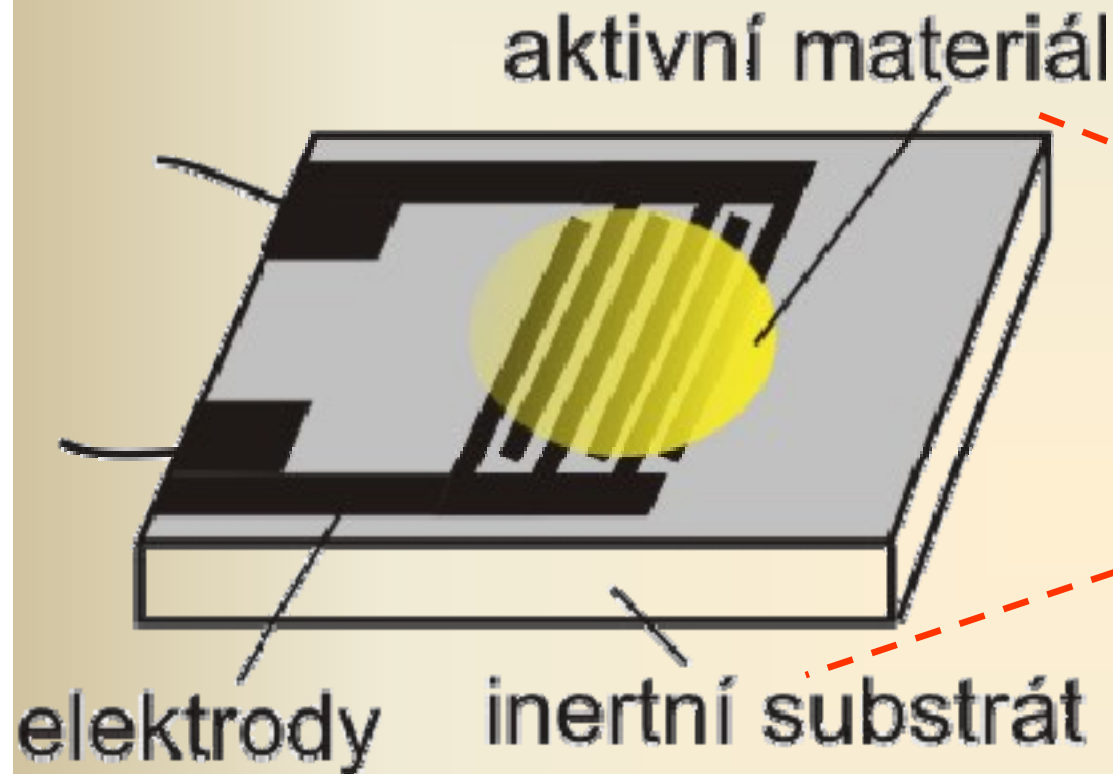
T. Otagawa, J. Stetter, Sensors and Actuators 11 (1987) 251



		b/a
aromat.	benzen	0,05
	toluen	0,075
alifat.	methan	0,211
	cyklohexan	0,3
obs. N	amoniak	0,701
	akrylonitril	0,742

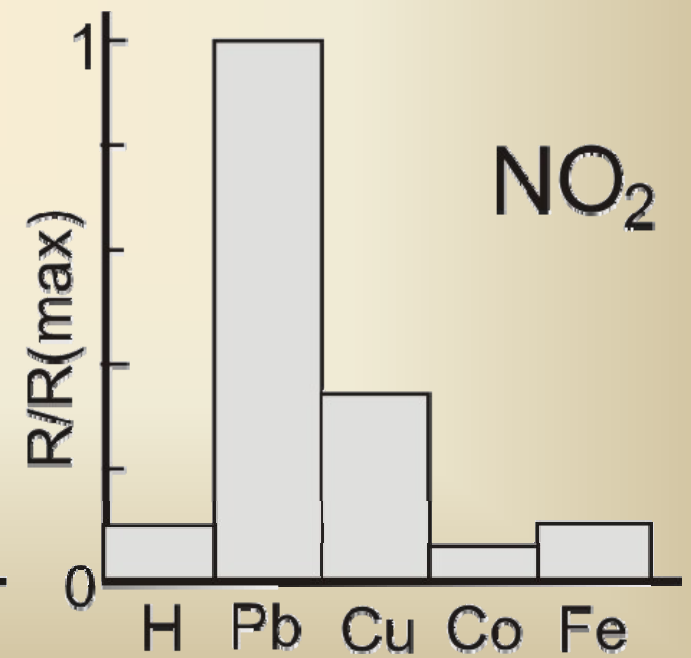
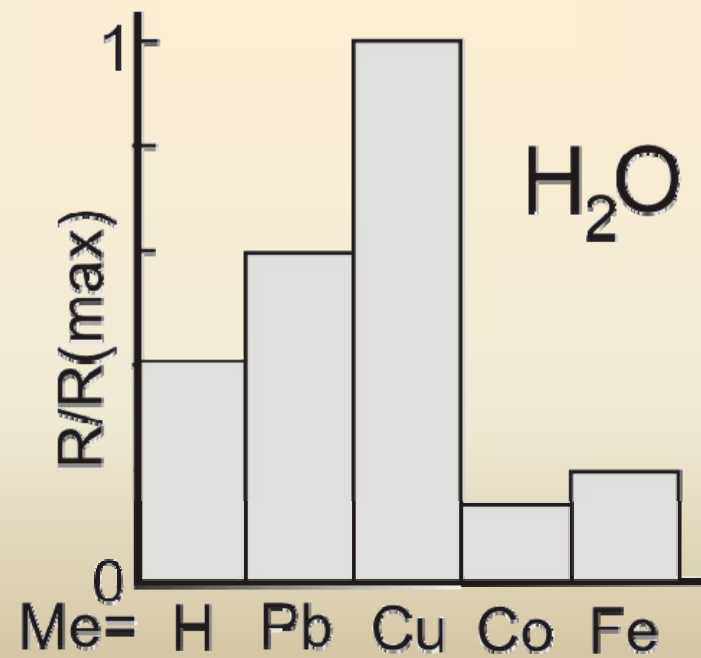
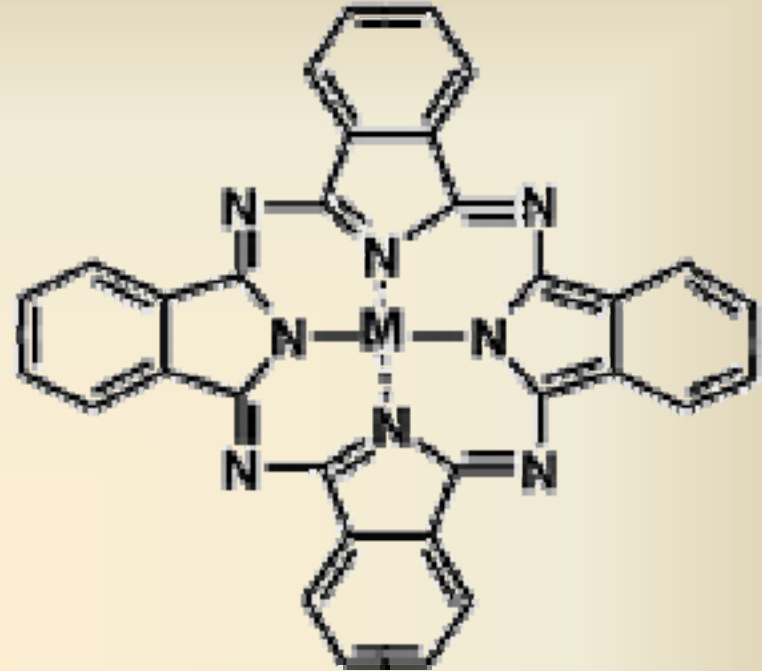
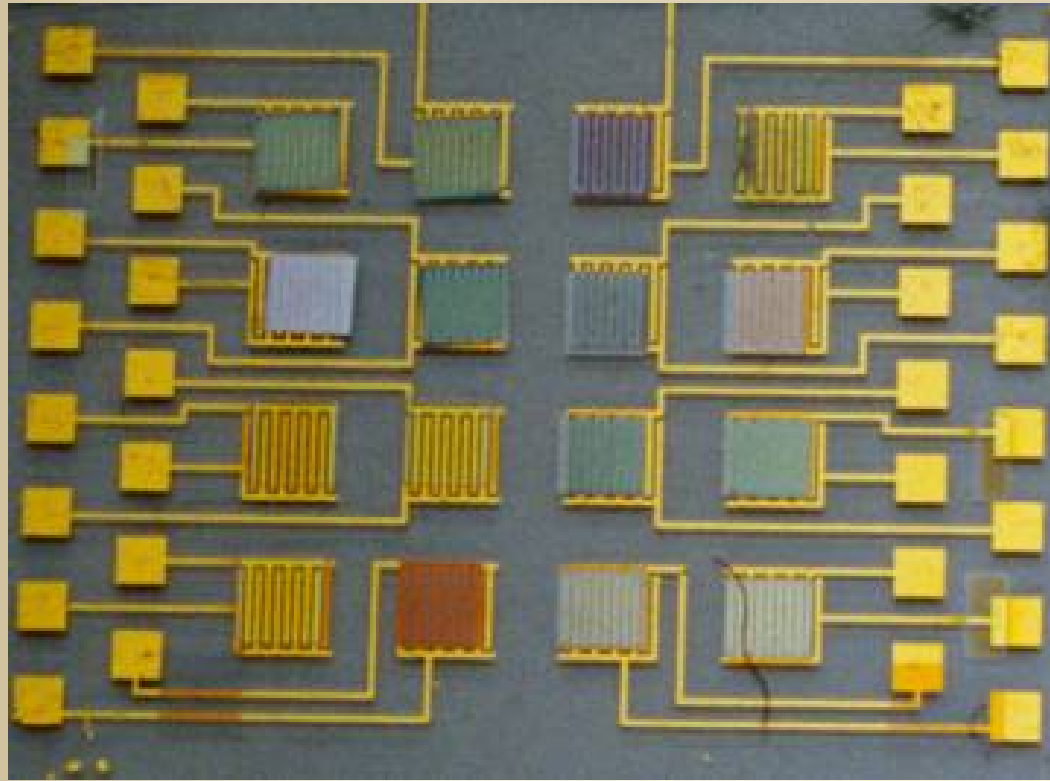
3.2 CHEMIREZISTORY

Chemrezistory s filmem chemické látky

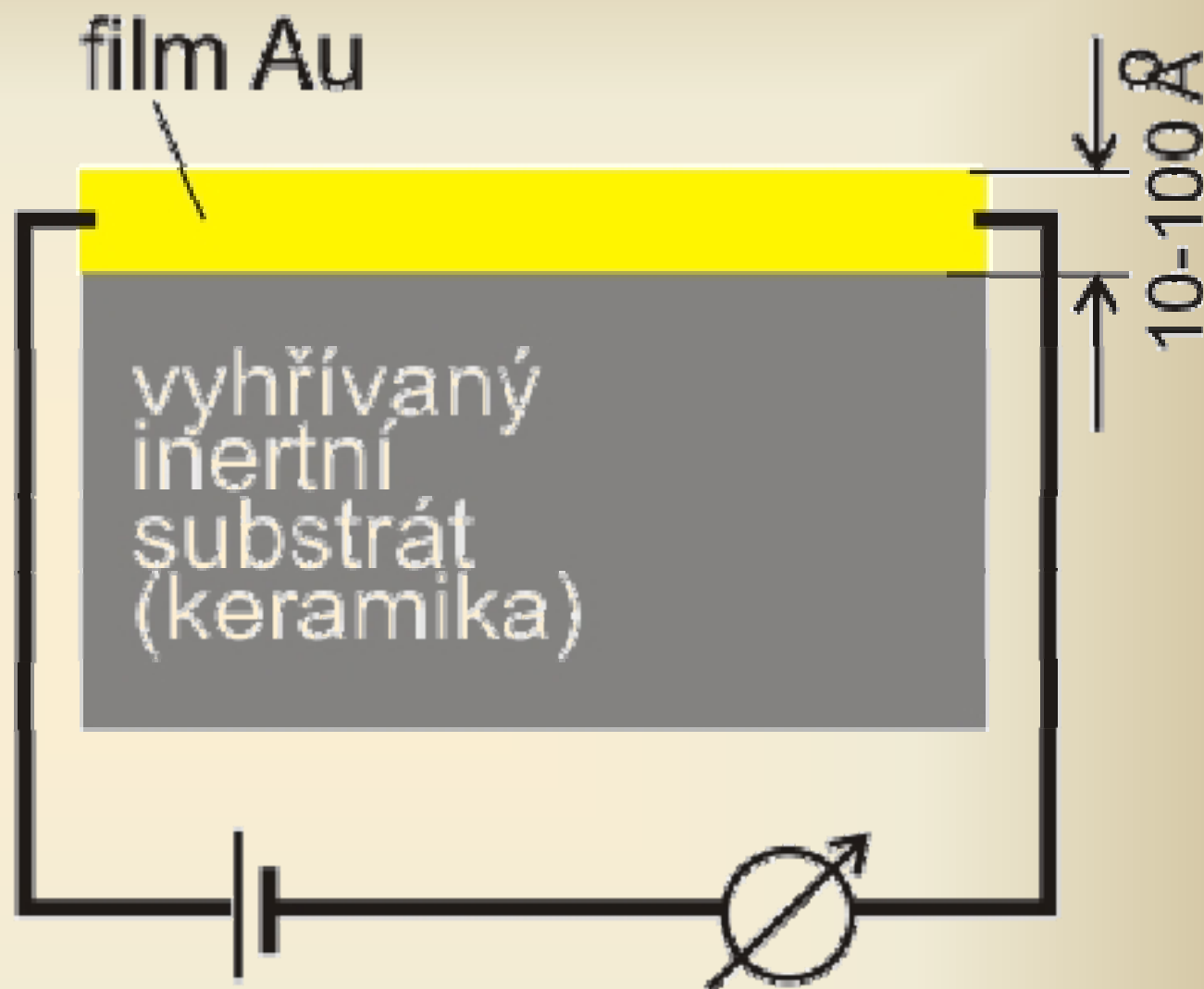
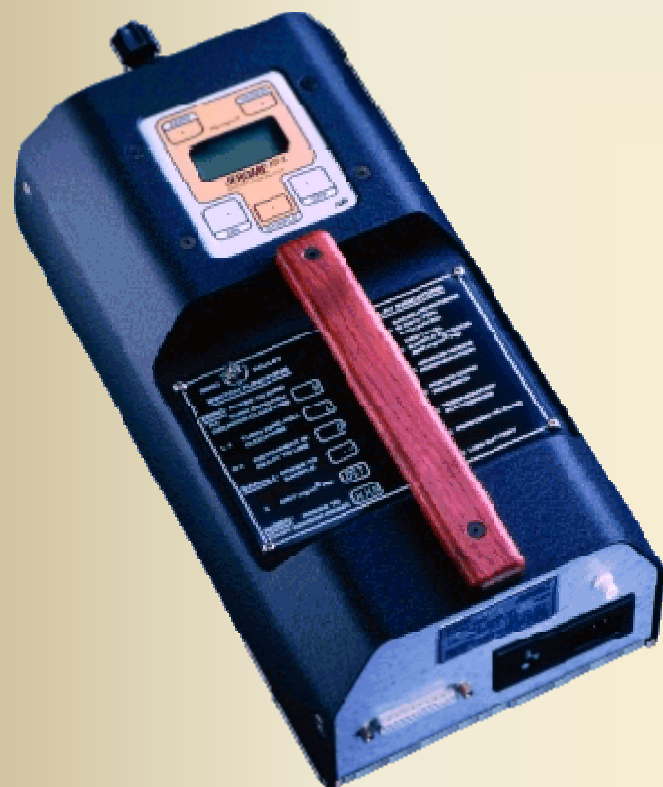


Aktivní materiály: oxidy kovů (SnO_2 , Fe_2O_3 ...);
 metaloftalocyaniny;
 org. vodivé a polovodivé polymery;
 filmy kovů....

Soubor chemirezistorů



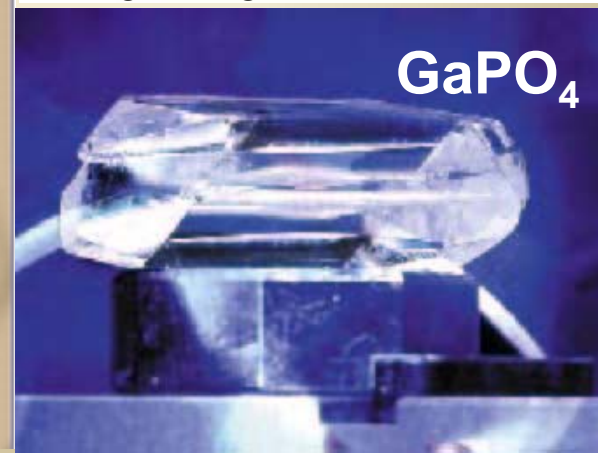
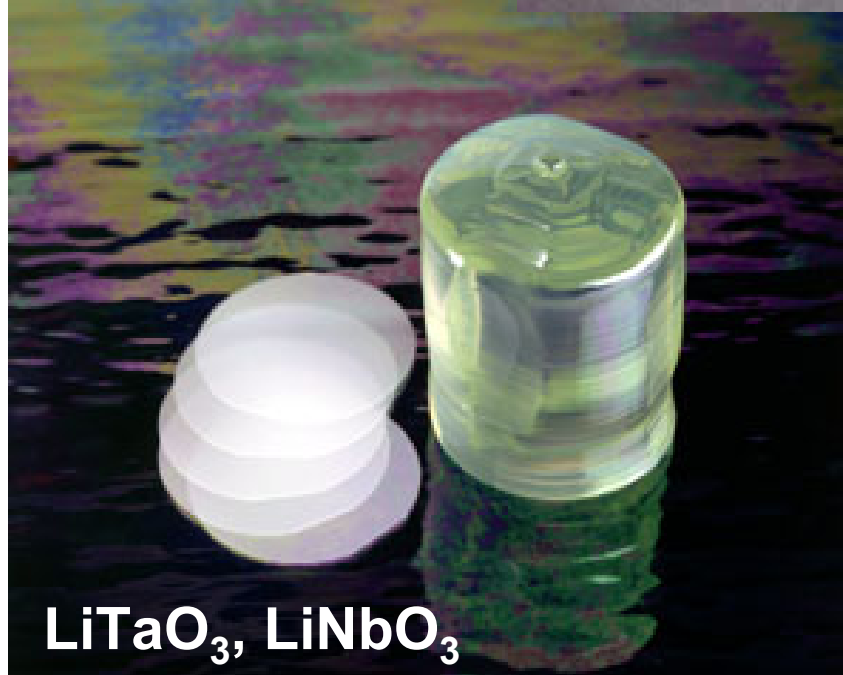
Chemirezistor s filmem kovu



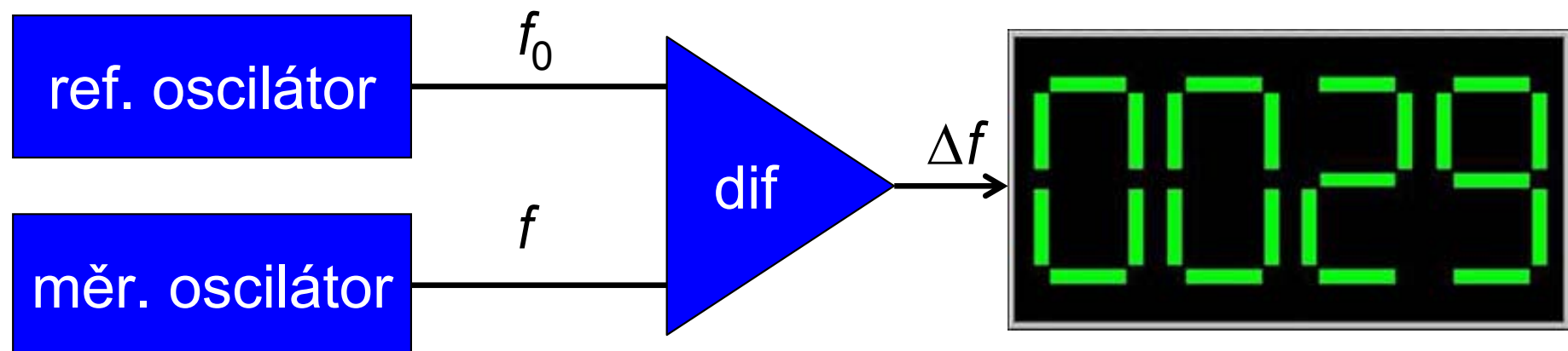
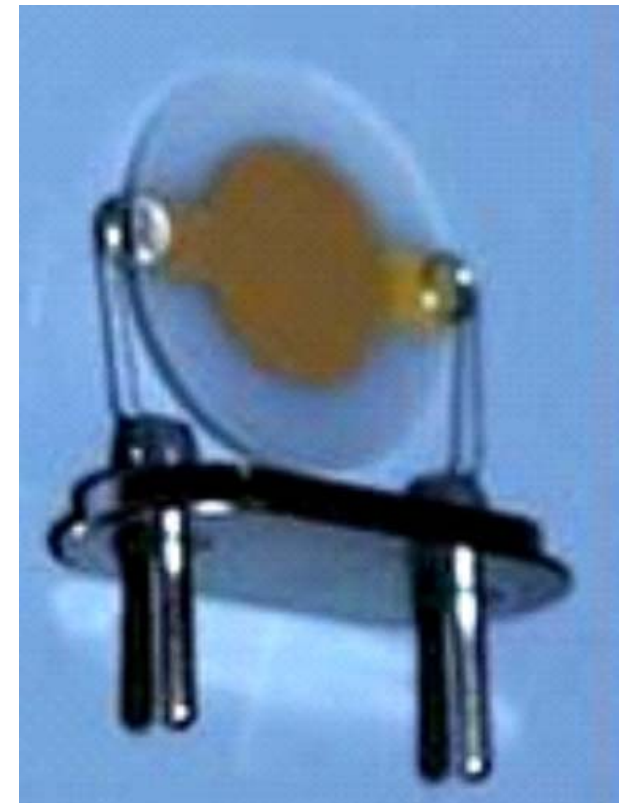
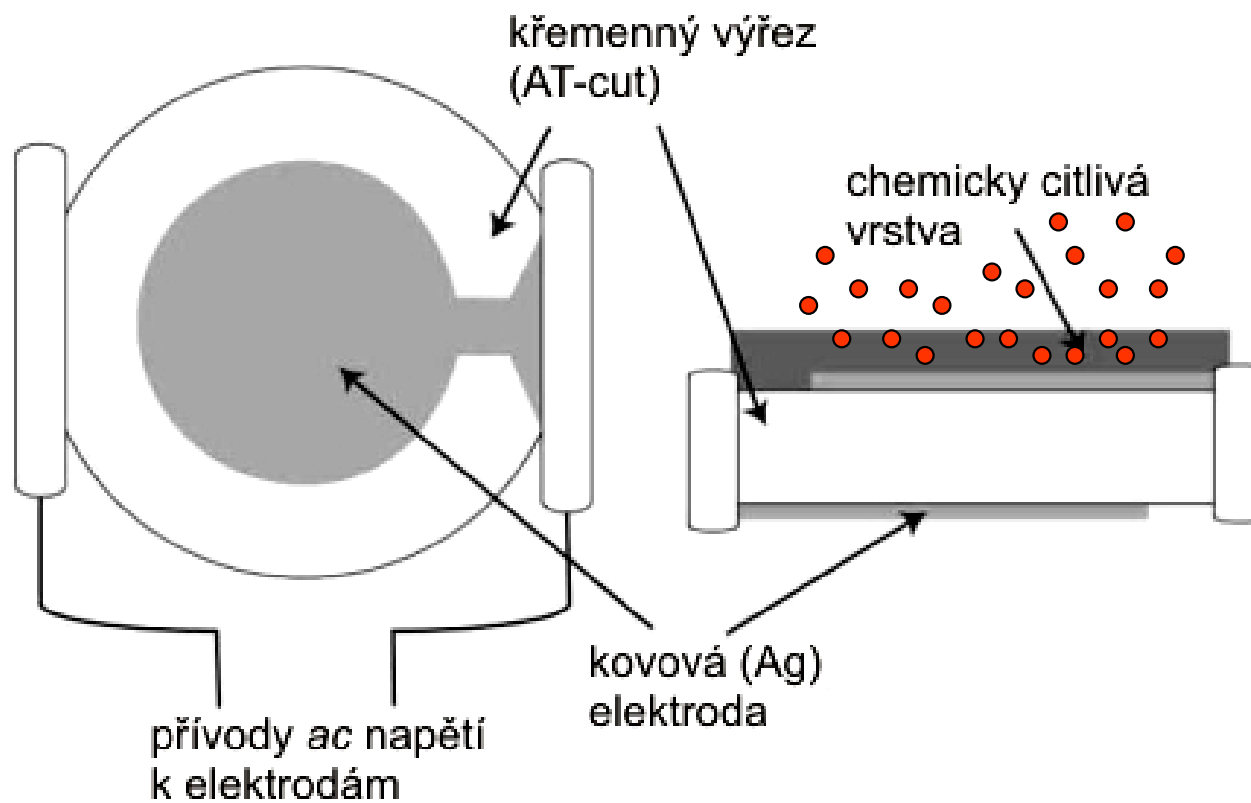
$\text{Au} + \text{H}_2\text{S} \rightarrow \text{AuS} + \text{H}_2$
 $\text{AuS} + \text{O}_2 \rightarrow \text{Au} + \text{SO}_2 \text{ (250}^\circ\text{C)}$
0,003 - 50 ppm H_2S (5% RSD)

$\text{Au} + \text{Hg} \rightarrow \text{AuHg}$
 $\text{AuHg} \rightarrow \text{Au} + \text{Hg} \text{ (250}^\circ\text{C)}$
0,003 – 0,999 mg Hg/m^3 (5% RSD)

4. HMOTNOSTNÍ SENSORY



4.1 QCMB – KŘEMENNÉ MIKROVÁHY



pro AT výbrus platí:

$$\Delta f = - \text{konst. } f_0^2 \Delta m / A$$

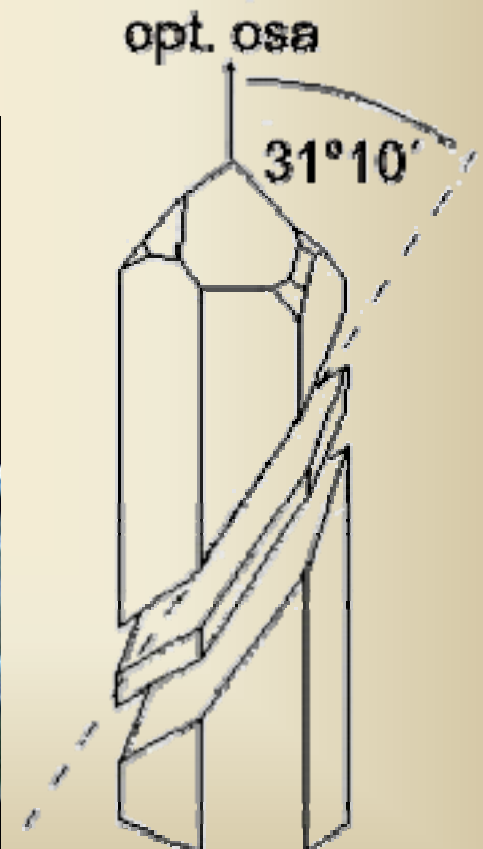
Δf = změna frekvence [Hz], konst. = 2.3×10^6 ,

f_0 = rezonanční frekvence [MHz],

A = plocha krystalu [cm^2],

Δm = změna hmotnosti [g];

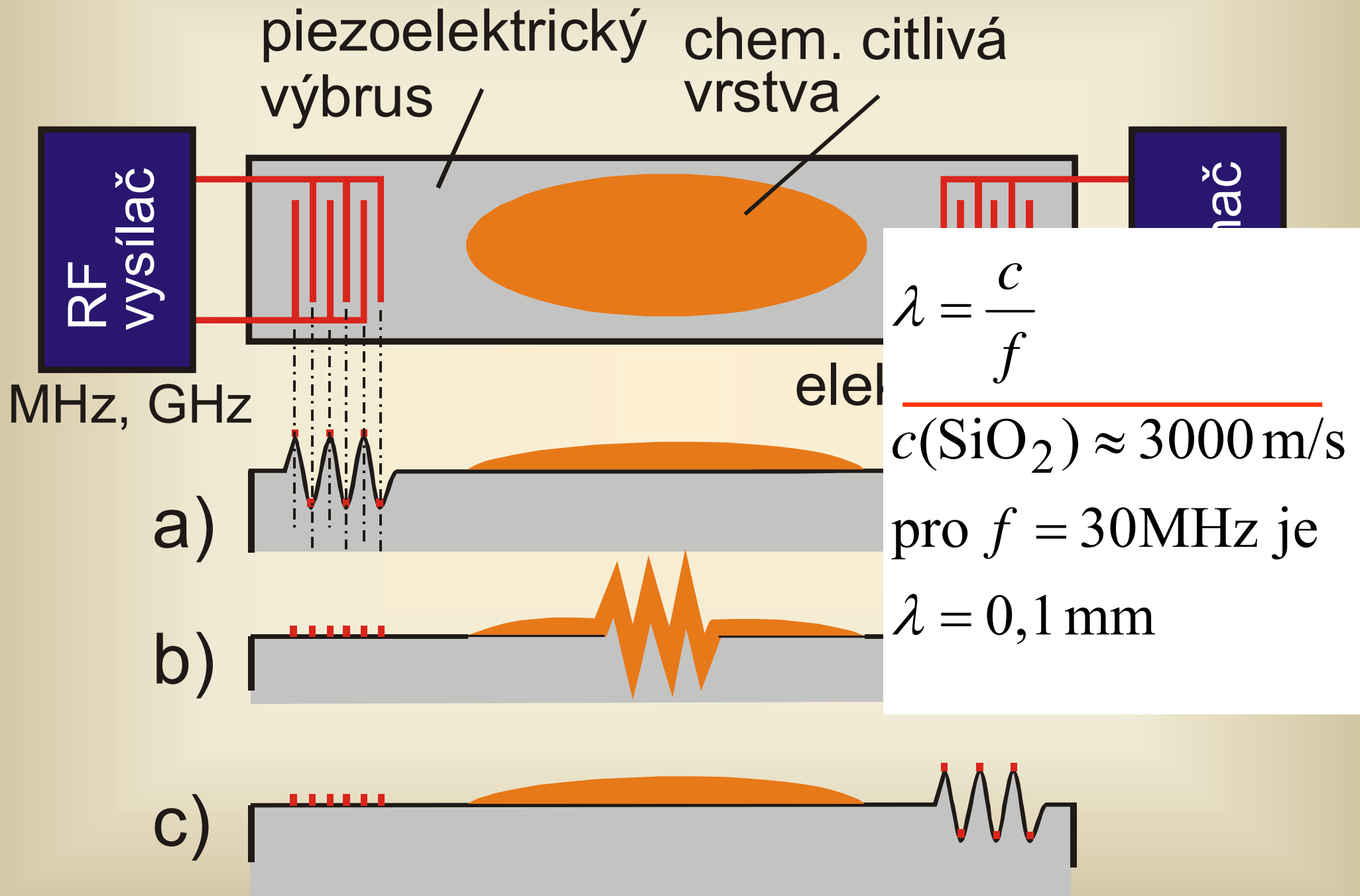
$$f_0 = 10 \text{ MHz}, \Delta f = 0,1 \text{ Hz} \Rightarrow \Delta m \approx 10^{-10} \text{ g/cm}^2$$

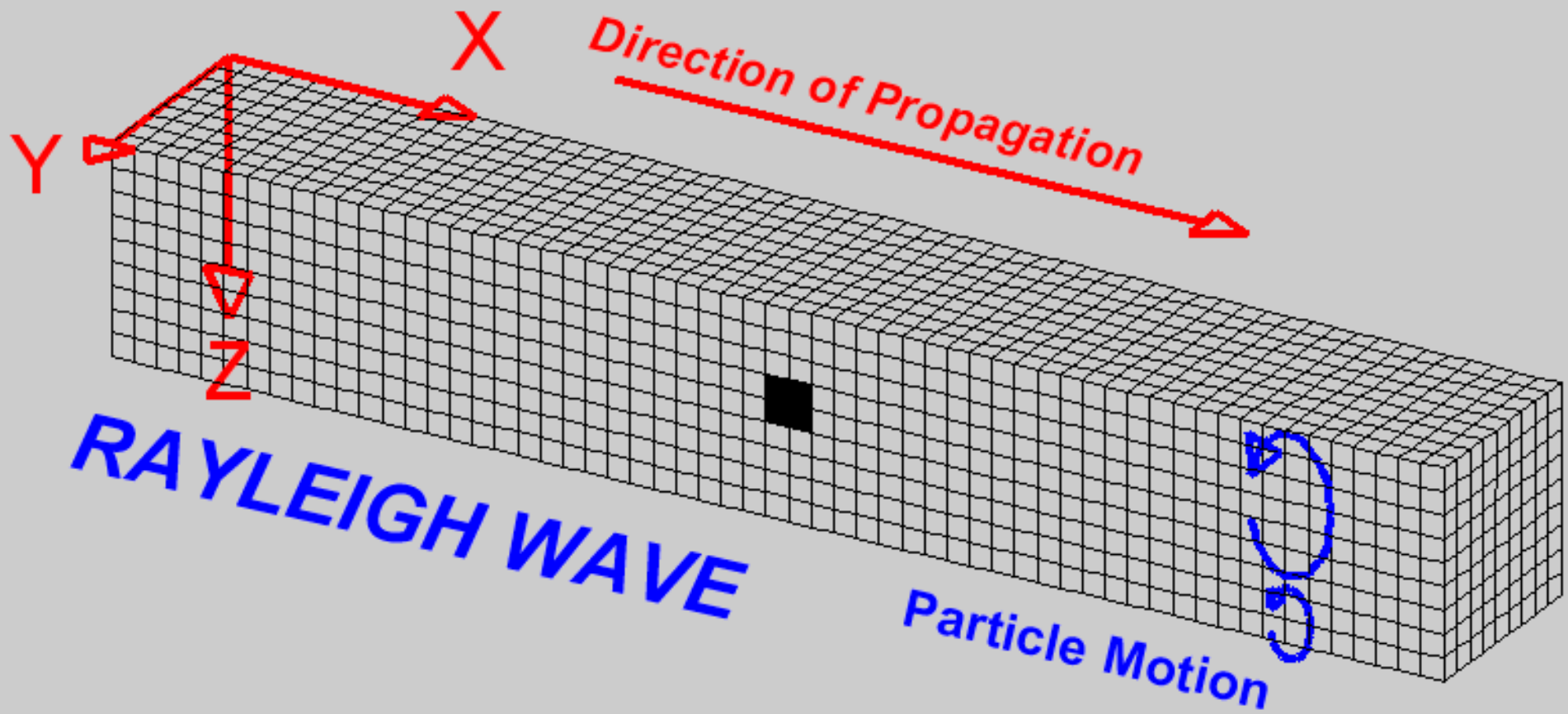


Příklady použití QCMB (det. limity 1 – 10 ppm):

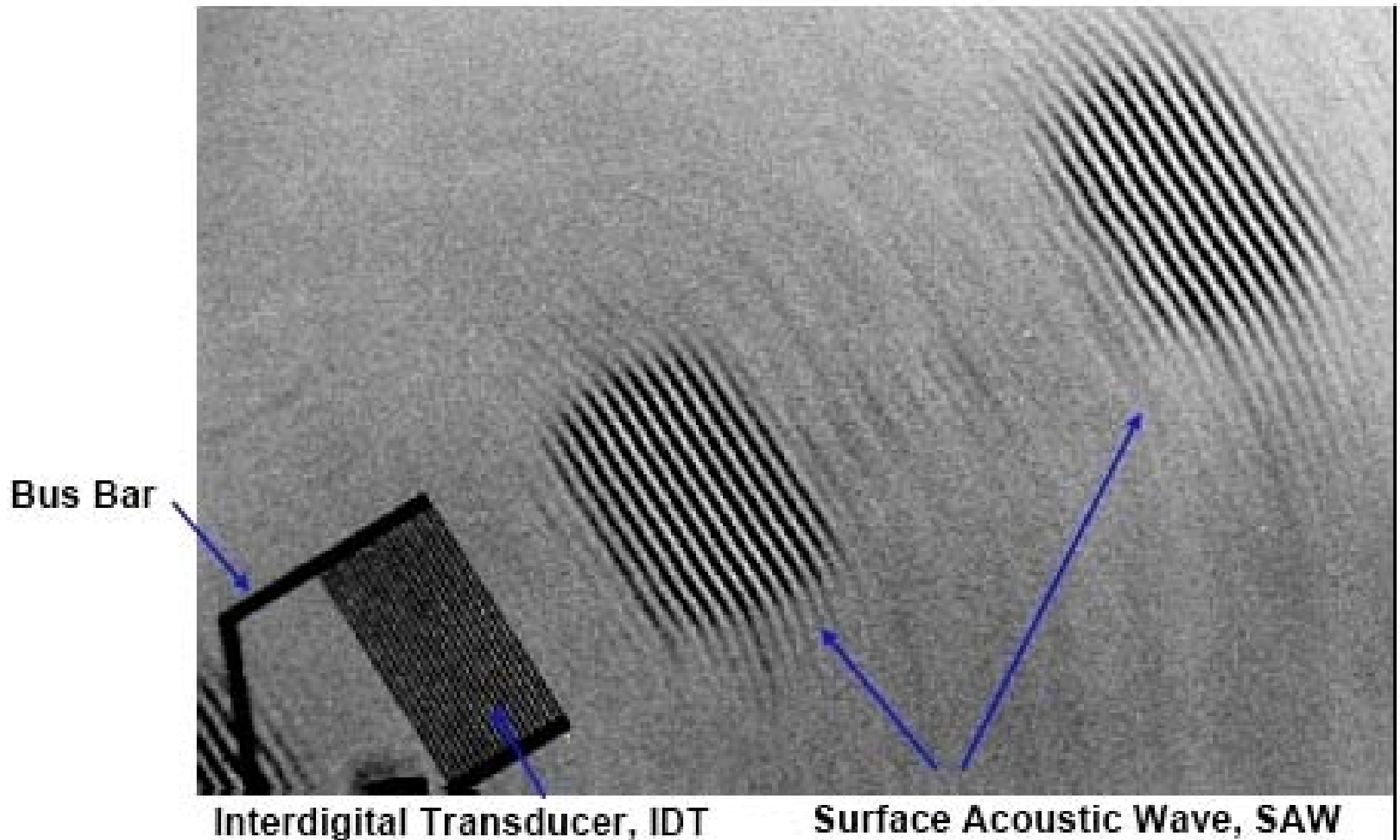
Analyt	Aktivní vrstva
H ₂	Pd
Hg	Au (regenerace 400°C)
SO ₂	triethanolamin
NH ₃	kys. sorbová, polyvinylpyrolidon
H ₂ O	LiCl immobiliz. v hydrogelu
O ₂	Mn-thiokyanato-tributylfosfin-tetrahydrofuran-polyvinylalkohol
CO ₂	7,10-dioxa-3,4-diaza-1,5,12,16-hexadekatetrol
uhlovodíky	chromatografické stacionární fáze

4.2 HMOTNOSTNÍ SENSORY: SAW – SENSORY S POVRCHOVOU AKUSTICKOU VLNOU

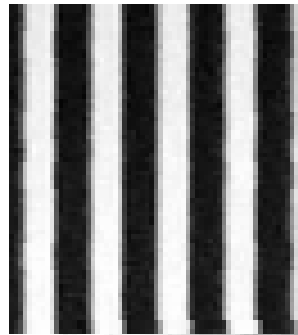




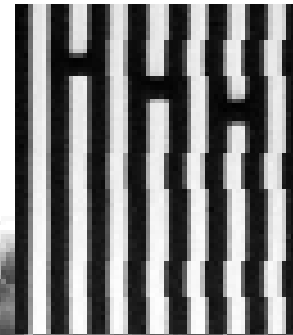
SEM mikrofotografie Rayleighovy povrchové vlny



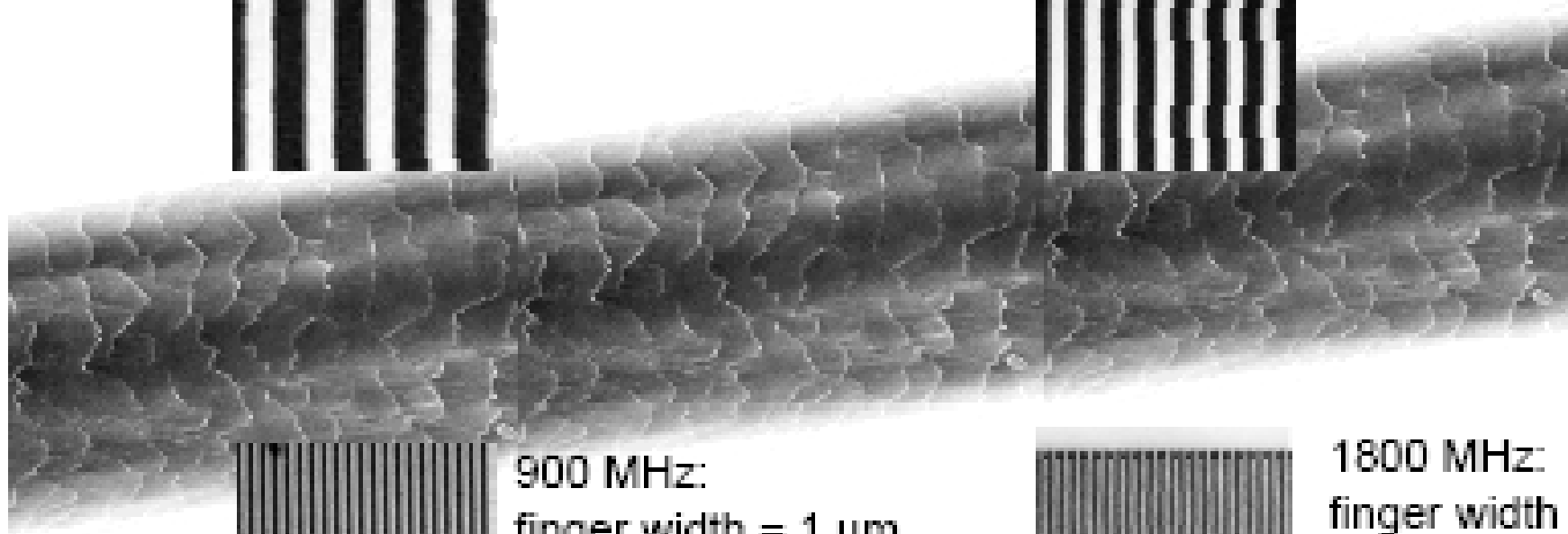
Rozměry interdigitálních elektrod SAW sensoru



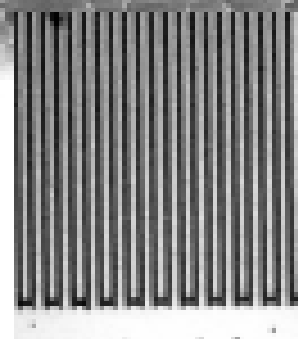
100 MHz:
finger width = 8 μm



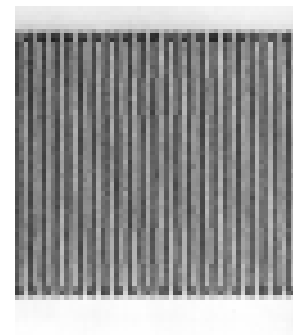
250 MHz:
finger width = 3 μm



human hair:
60 μm thick



900 MHz:
finger width = 1 μm

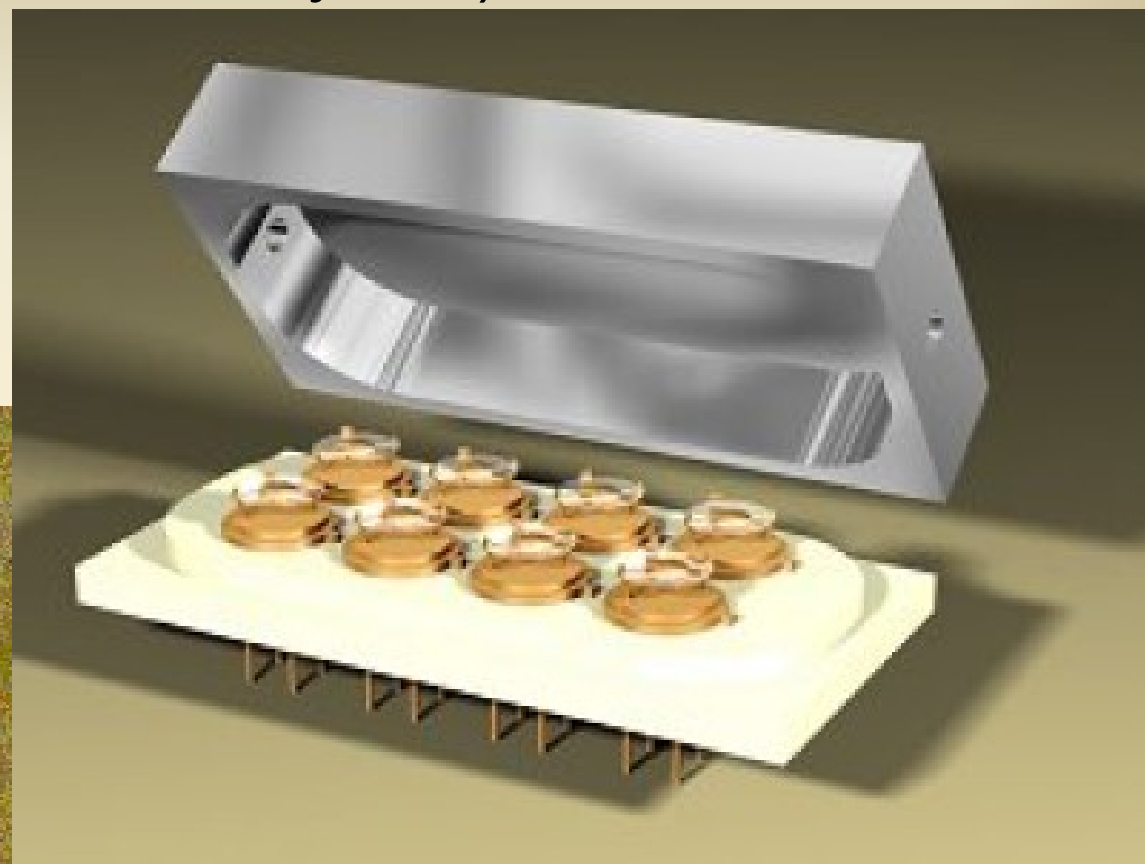
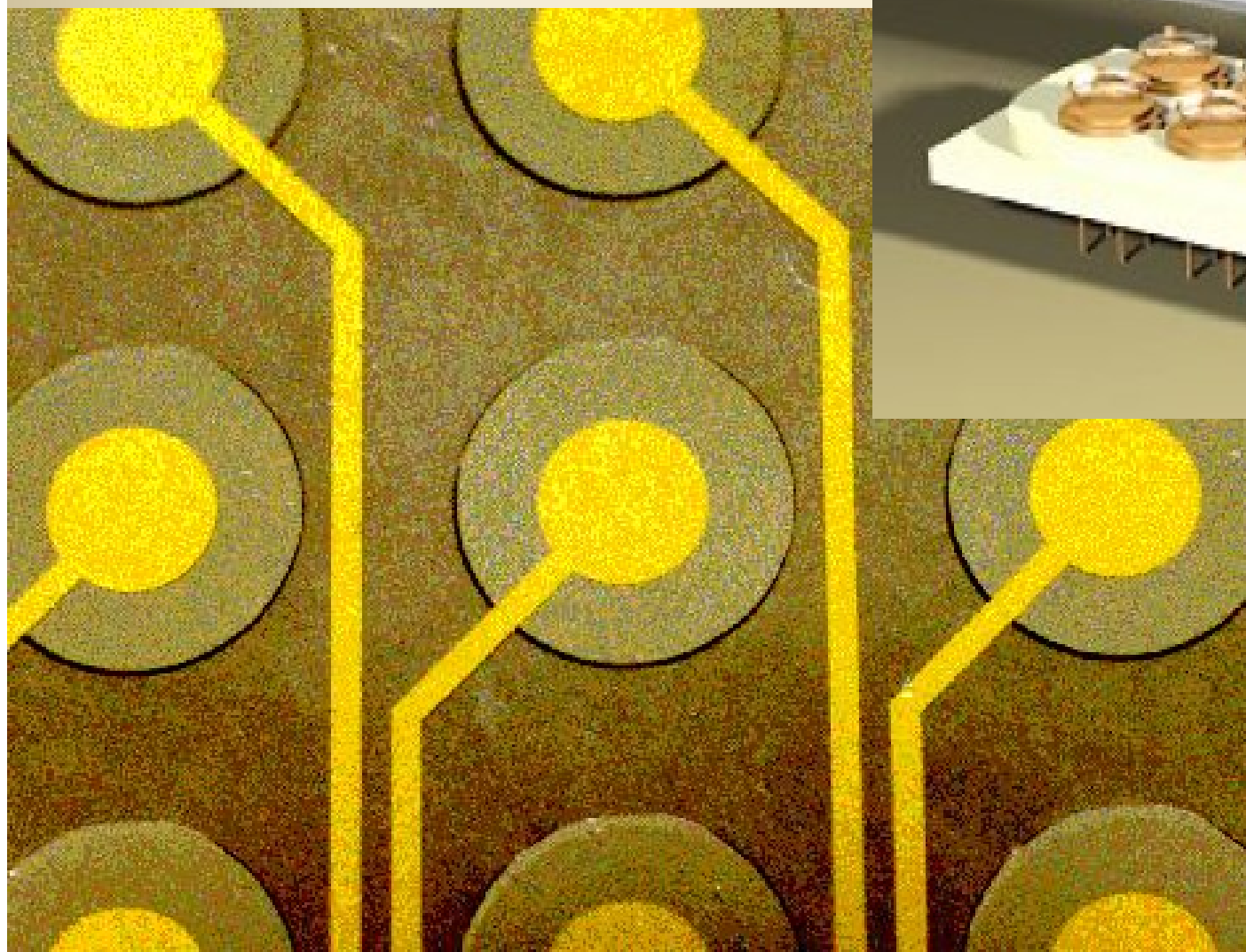


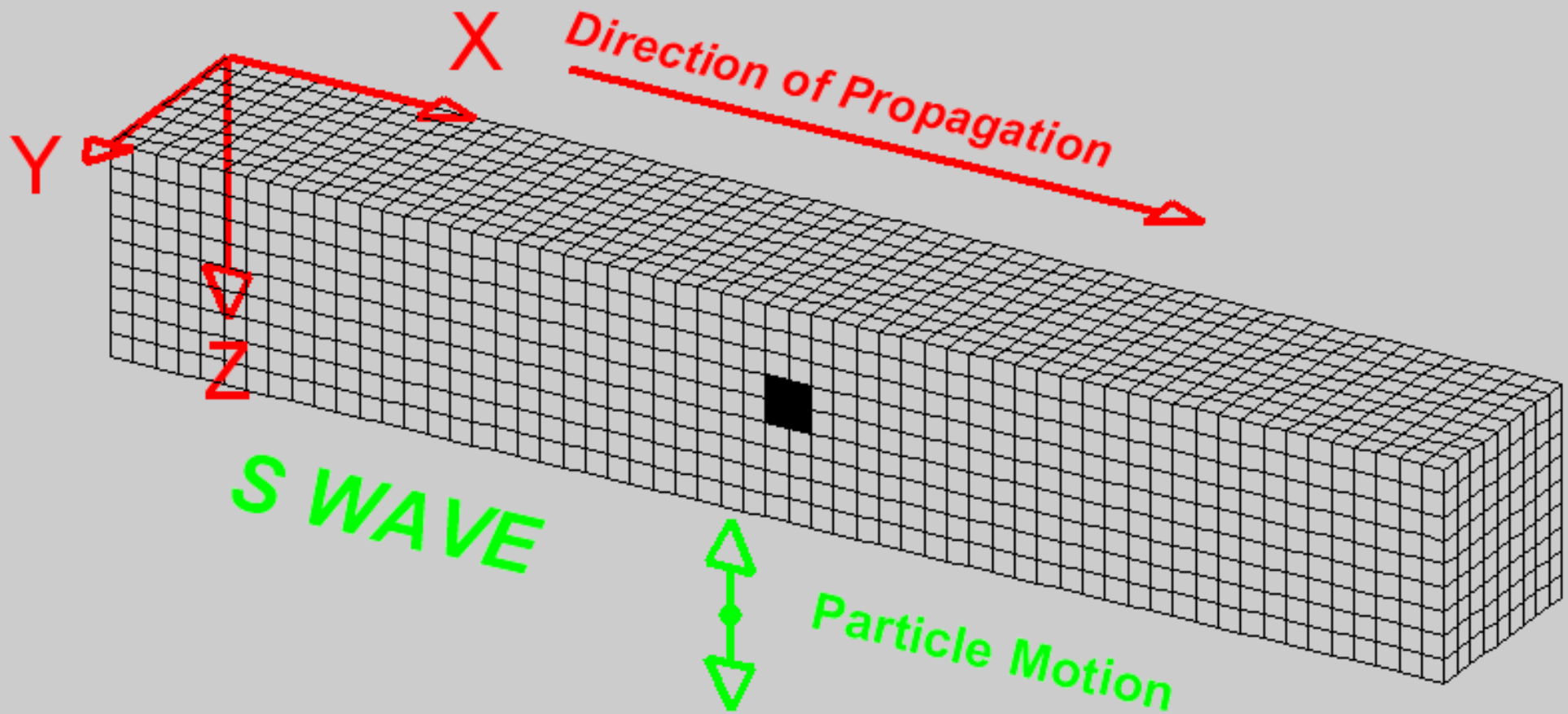
1800 MHz:
finger width = 0.5 μm

Příklady použití SAW (det. limity 10 – 100 ppb):

Analyt	Aktivní vrstva
H ₂	Pd
NO ₂	Pb-ftalocyanin
SO ₂	triethanolamin
H ₂ S	WO ₃
H ₂ O	polyimid
styren	[Pt(ethylen)(pyridin)]Cl ₂
uhlovodíky	chromatografické stacionární fáze

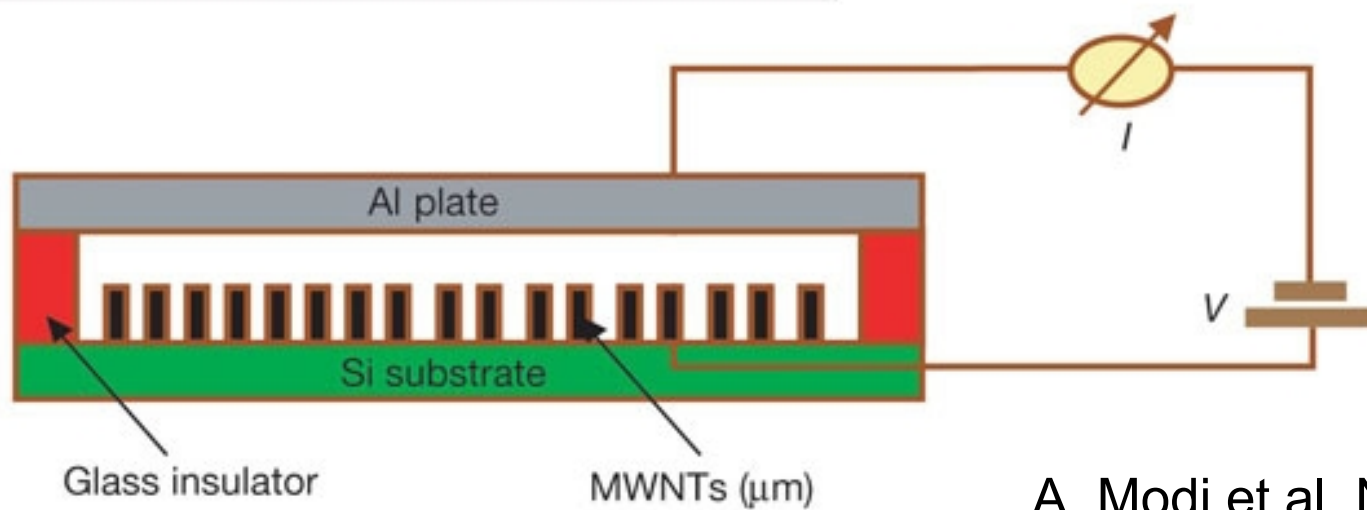
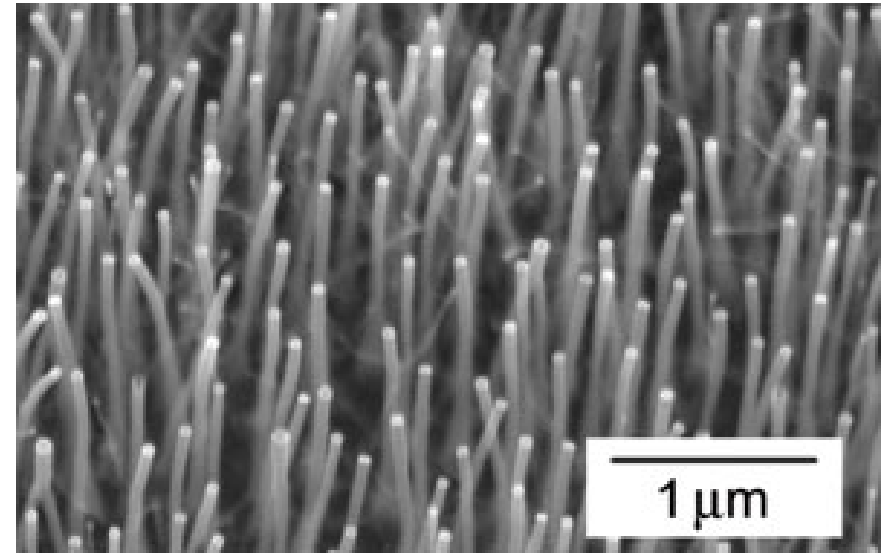
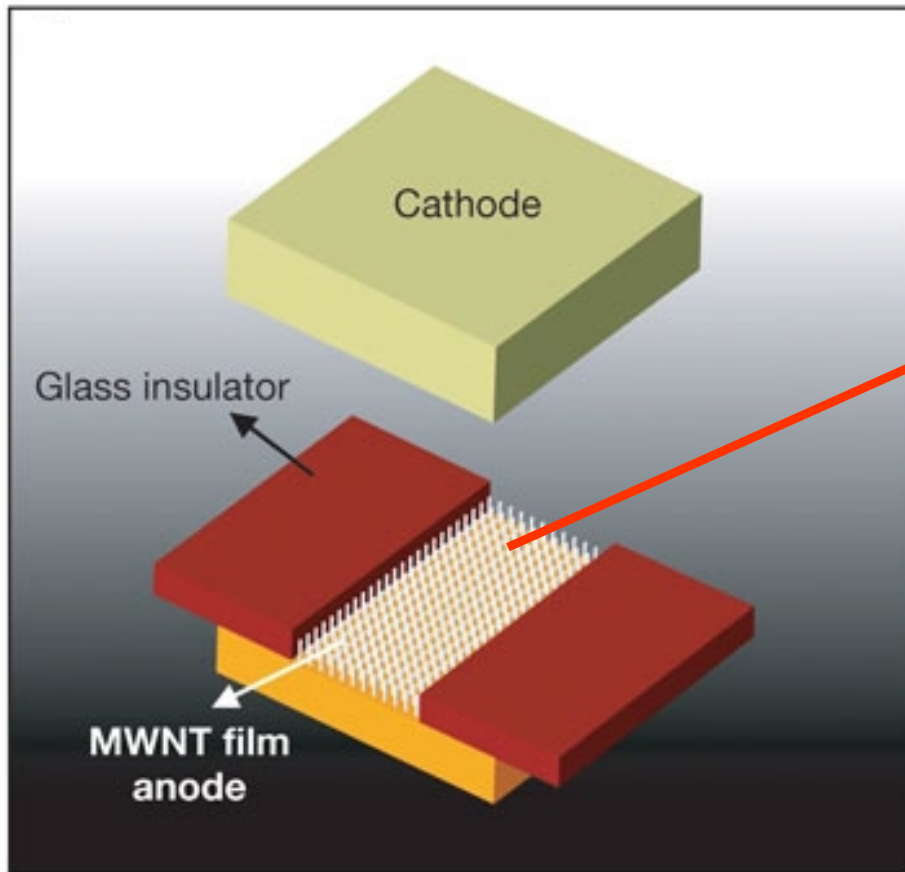
Soubory sensorů (pro elektronický nos)





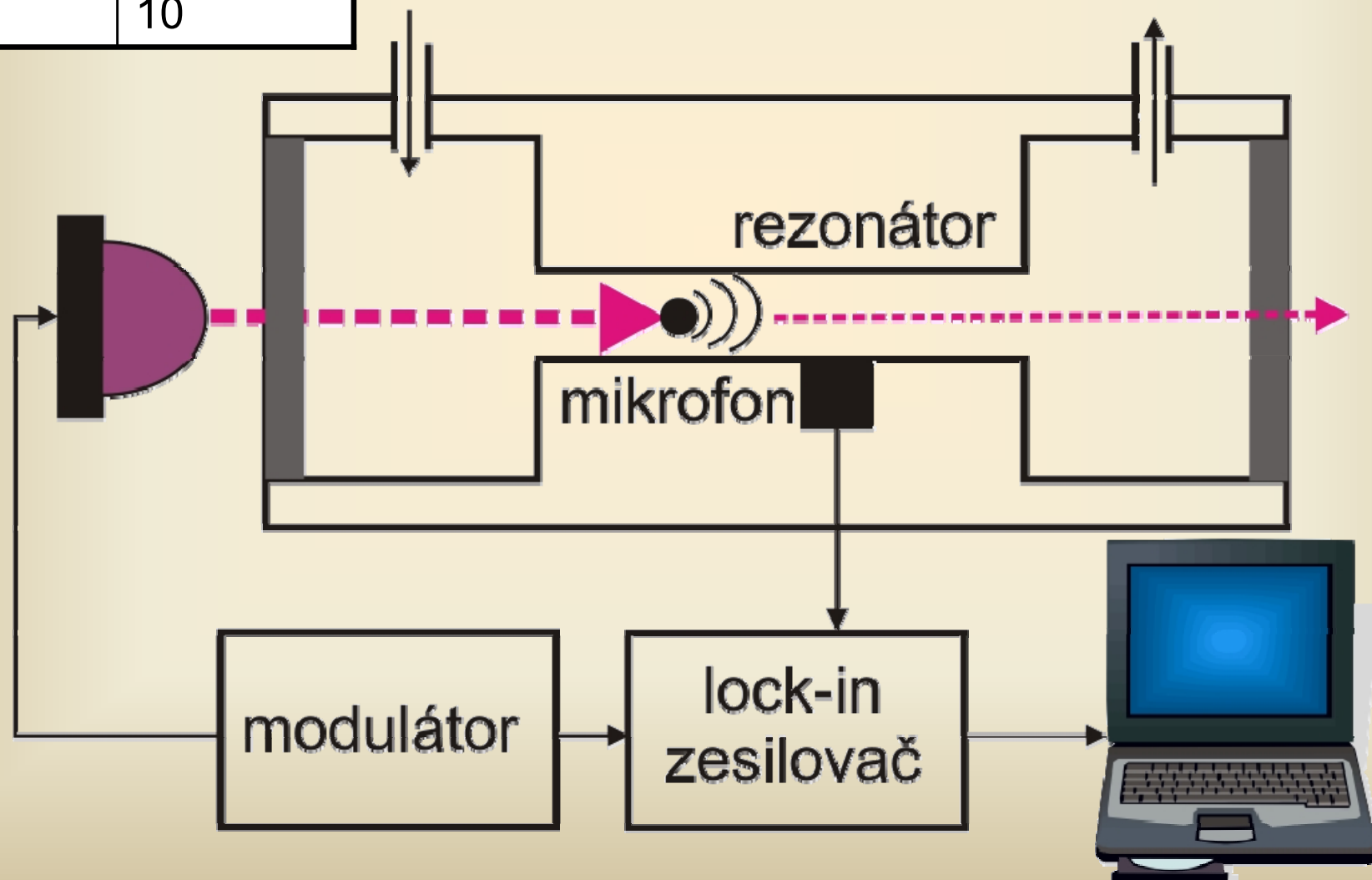


Ionizační mikrosensory

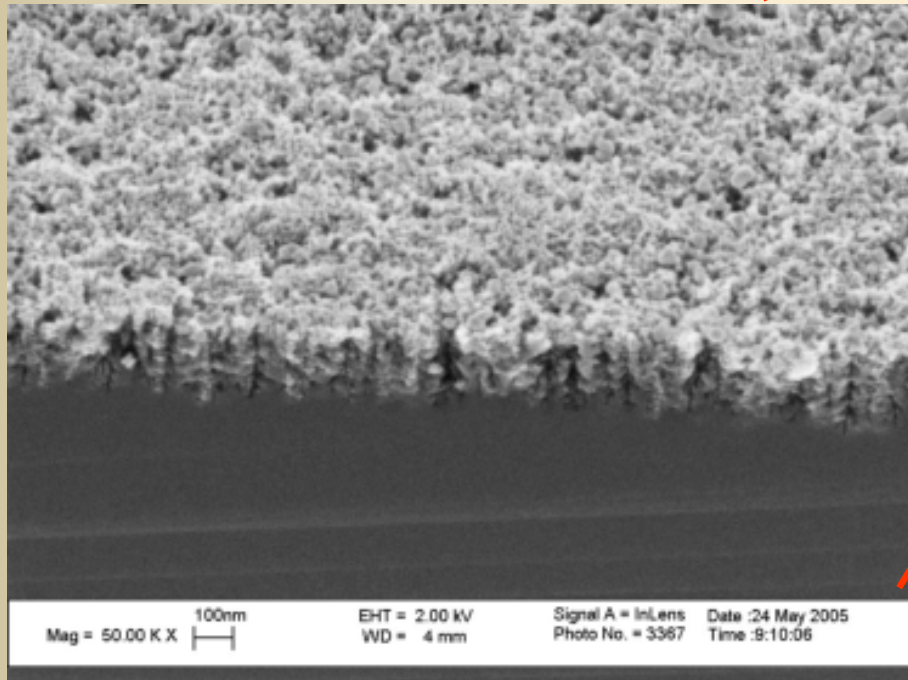
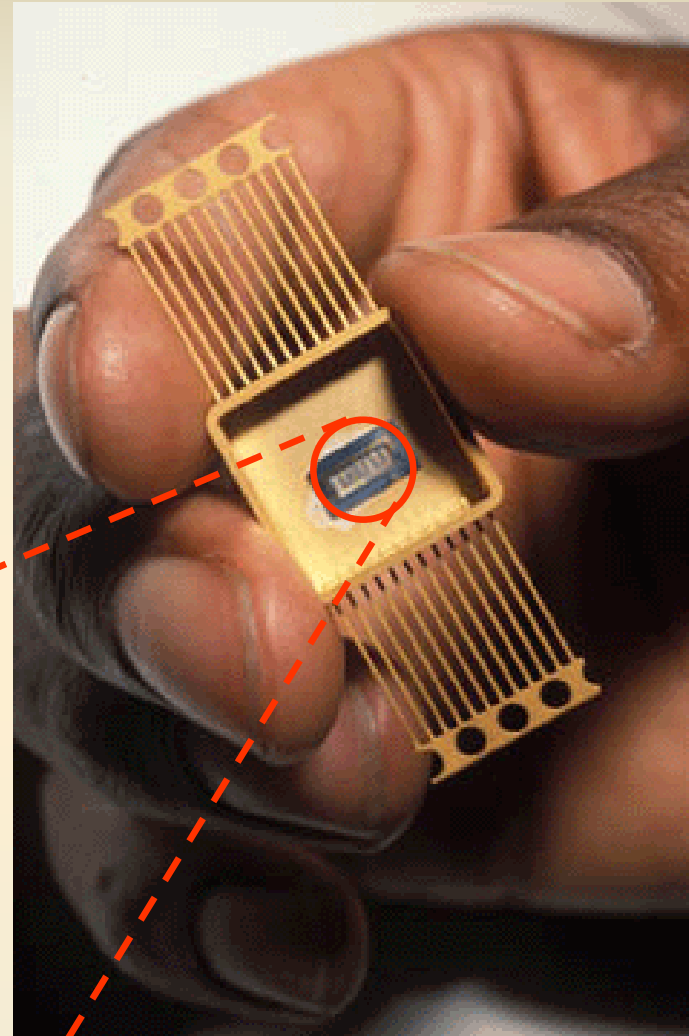
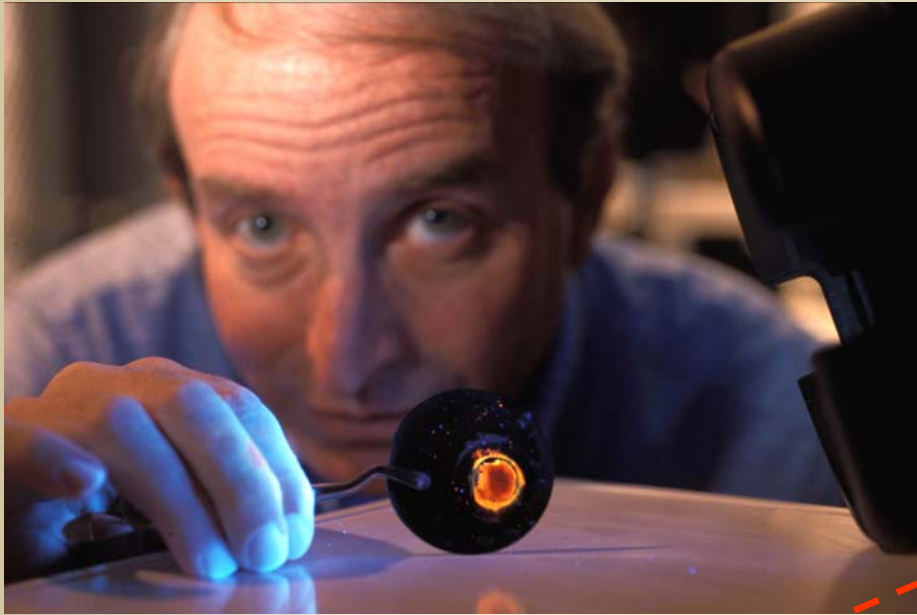


Fotoakustické sensory

Plyn	LOD, ppb
N ₂ O	30
Halothan	20
CO ₂	1500
SF ₆	6
Freon	10



Vodivostní sensory s porézním křemíkem



NH_3 , HCl , NO_x , $\sim 10 - 100$ ppm

L.Seals et al, J. Appl. Phys. **91** (2002) 2519

