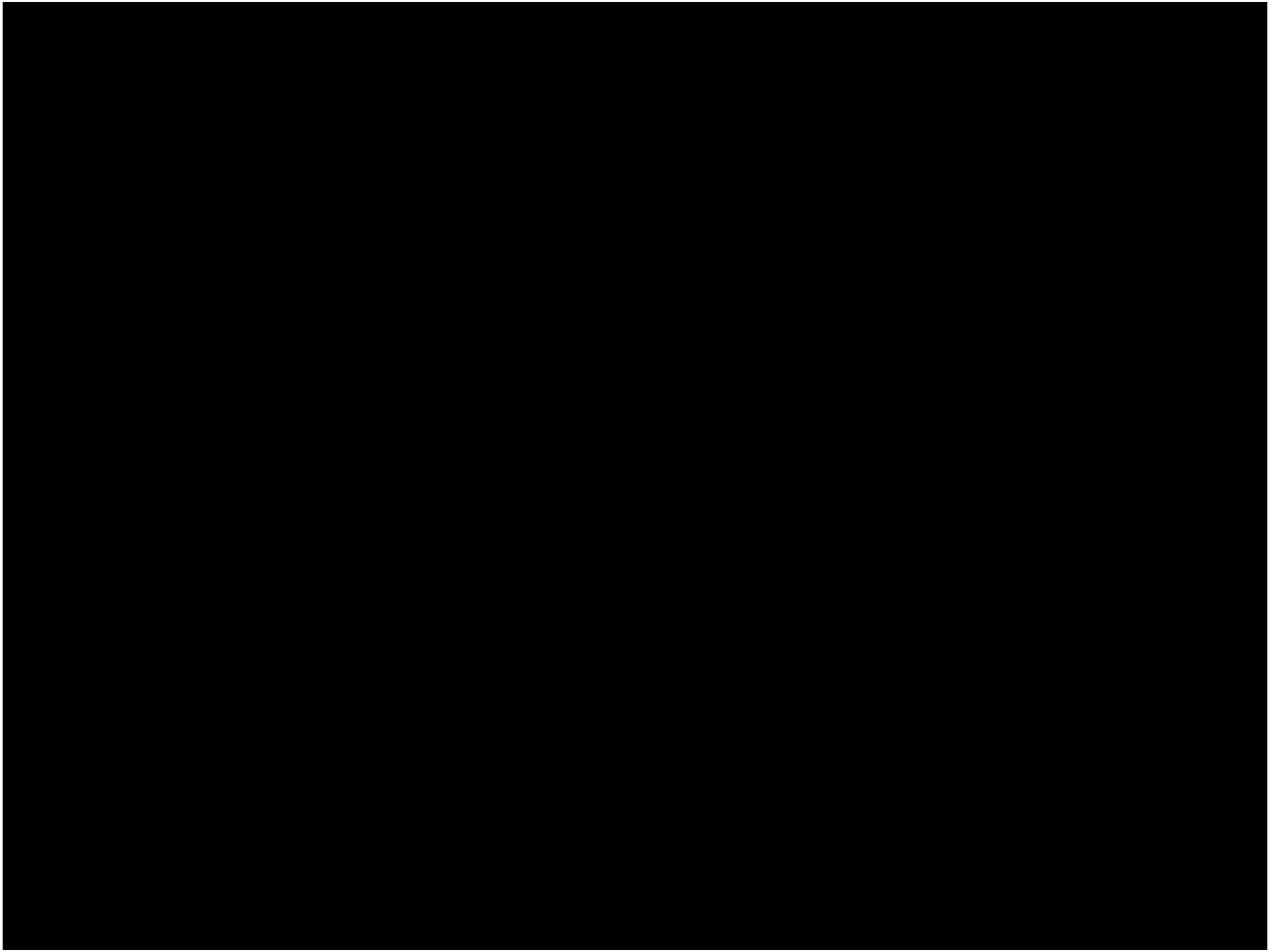


- ❖ Direktni tehniki – sledljivi do SI enot (masa, naboj).
- ❖ Visoka točnost ($u < 0{,}5$ %).
- ❖ Primerni za določanje glavnih sestavin (0,01-100 %).

- ➢ V posebni izvedbi omogočata določanja mikrosestavin:
- Kvarčna mikrotehnica (QCMB)-ugotavljanje nanogramskih sprememb mase med elektrolizo;
- Mikrokulometrija: merjenje debeline monoplasti, ugotavljanje valence, določanje difuzijskih koeficientov, ..

- Med elektrolizo se potencial posamezne elektrode spreminja: $E = f(C, \eta_a, \eta_c, iR)$.

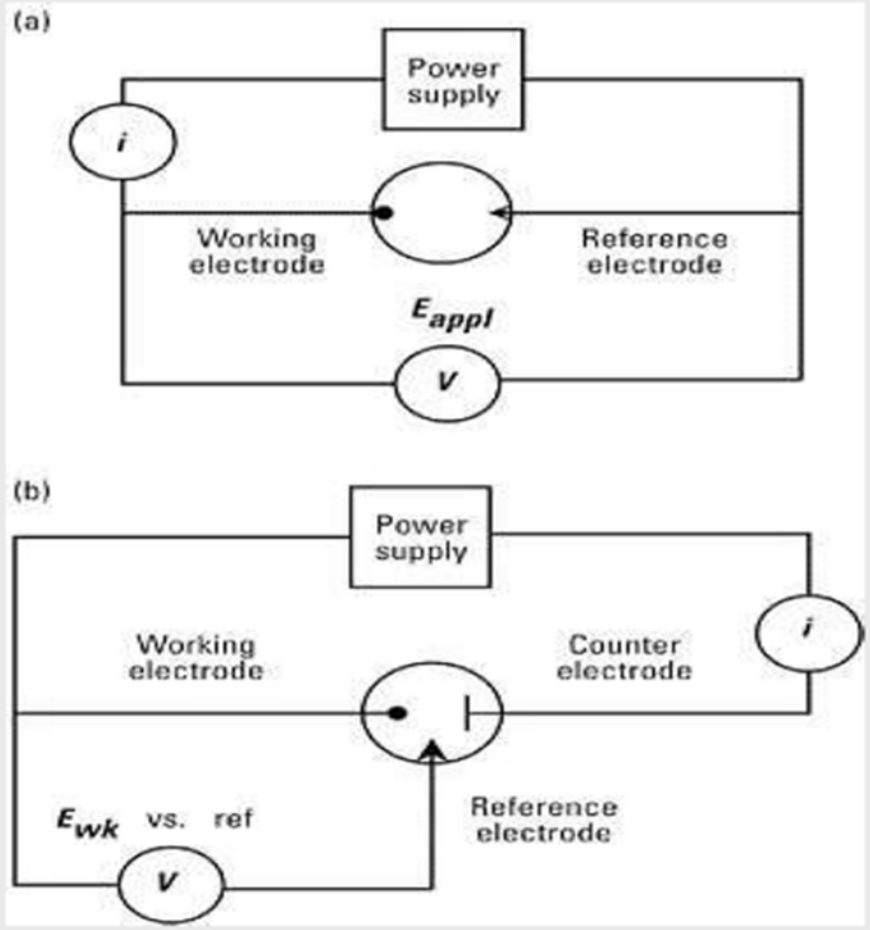
$$E_{čl} = (E_r + \eta_a + \eta_c)_k - (E_r + \eta_a + \eta_c)_a - iR$$

E_r: ravnotežni potencial (Nernst)

η_a : aktivacijska prenapetost

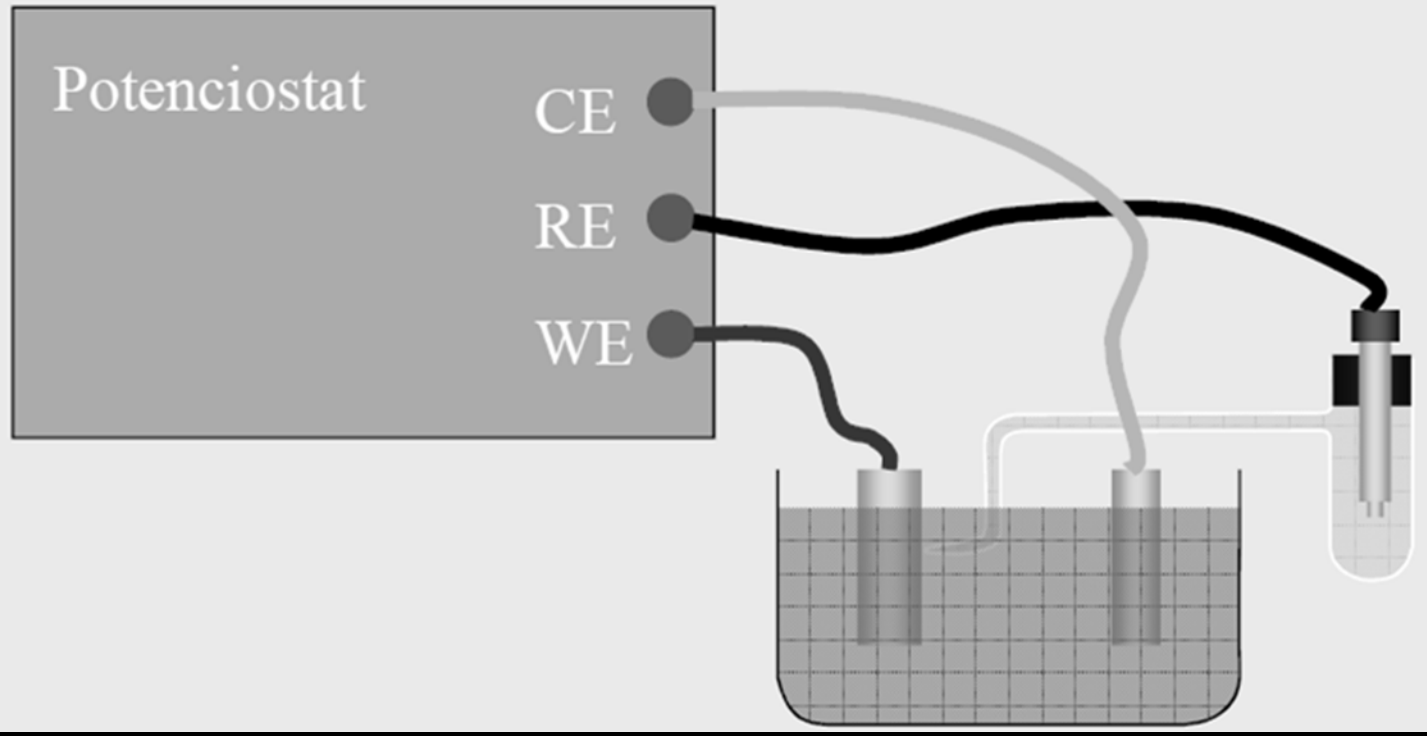
η_c: koncentracijska prenapetost

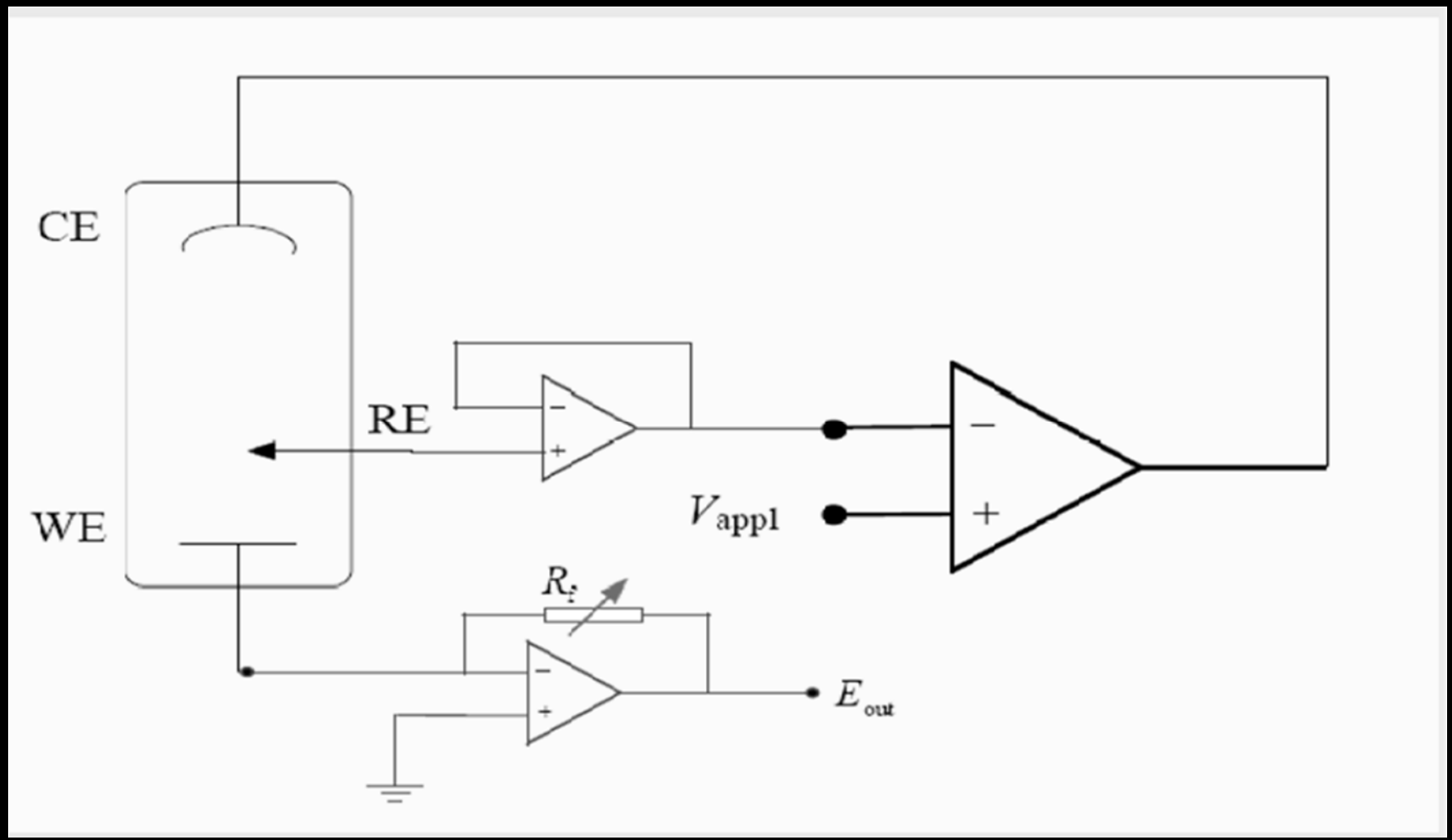
iR: ohmski padec napetosti

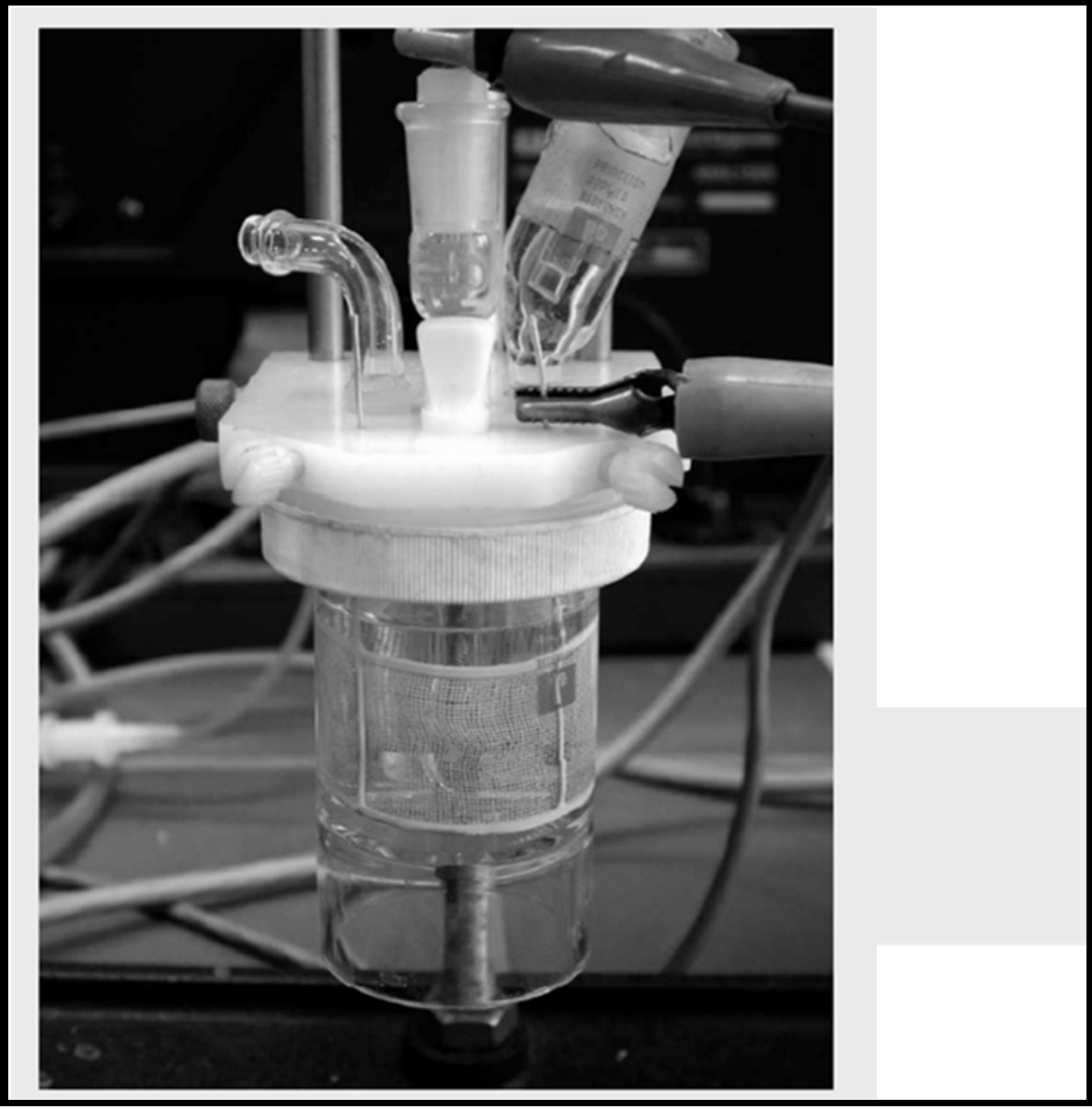


A.J. Bard, C.G. Zoski, Voltammetry Retrospective, *Anal. Chem.*, **72** (2000)346 A.

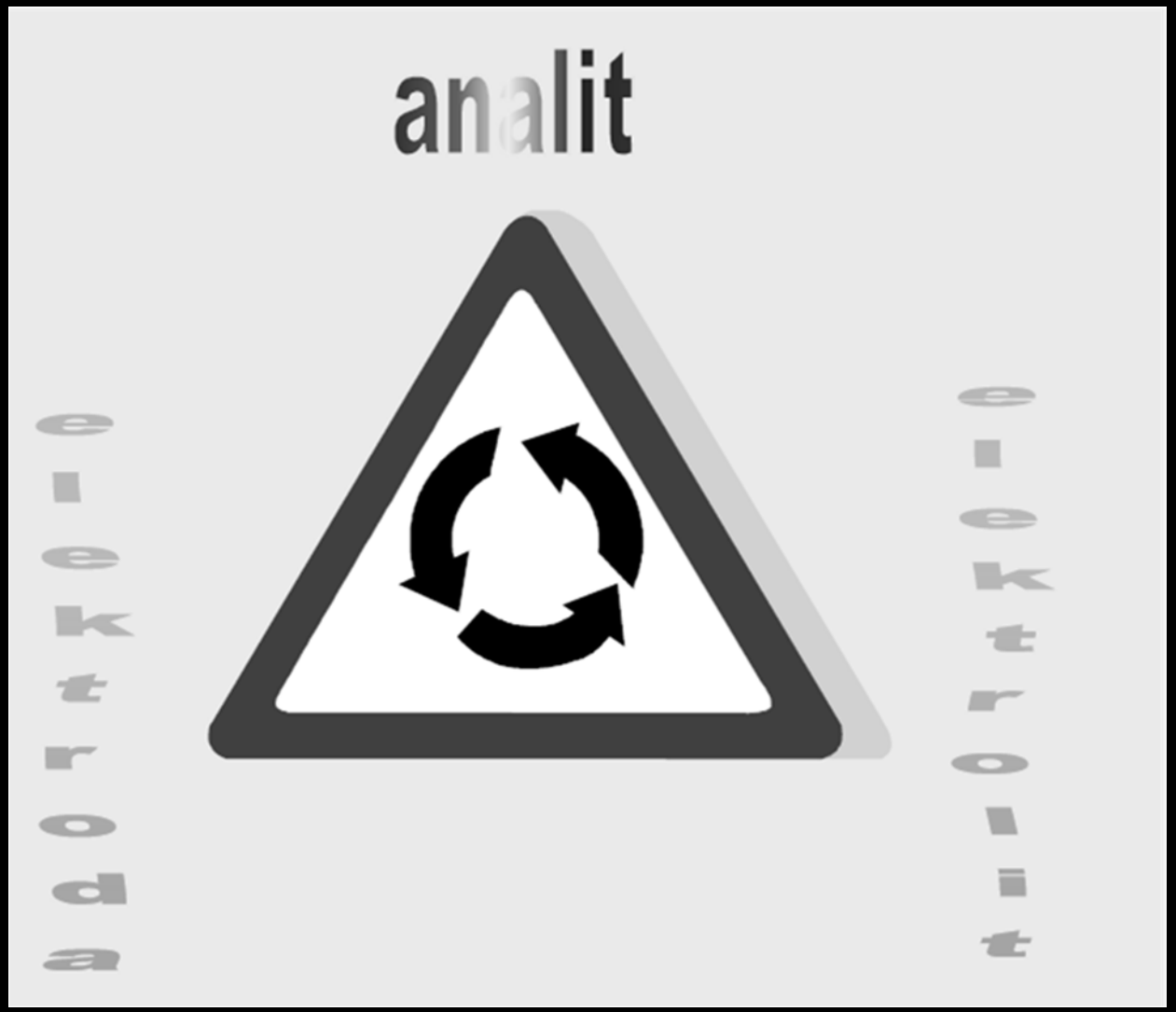
- Kontrola napetosti: E_w - E_r = konst.

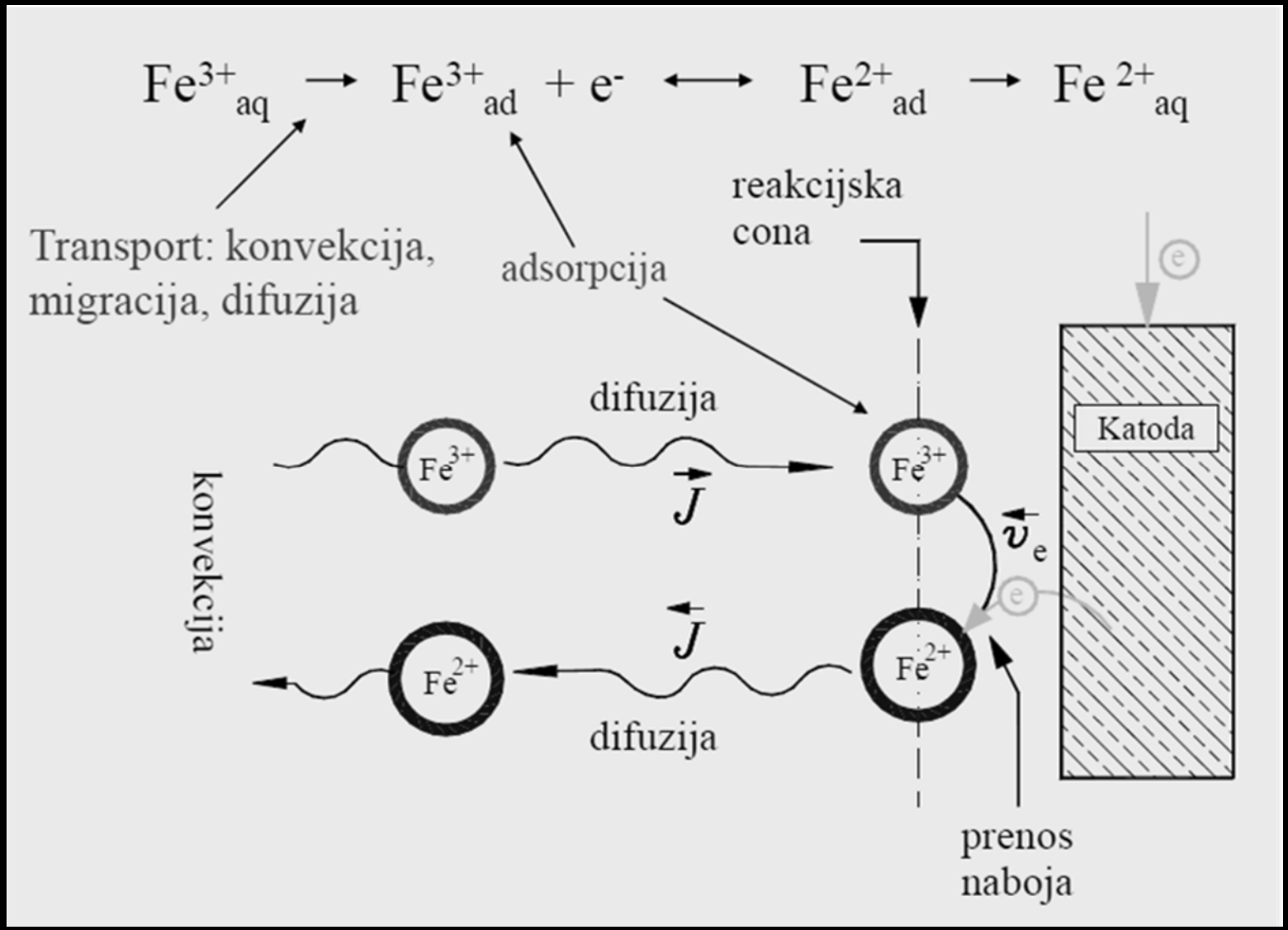


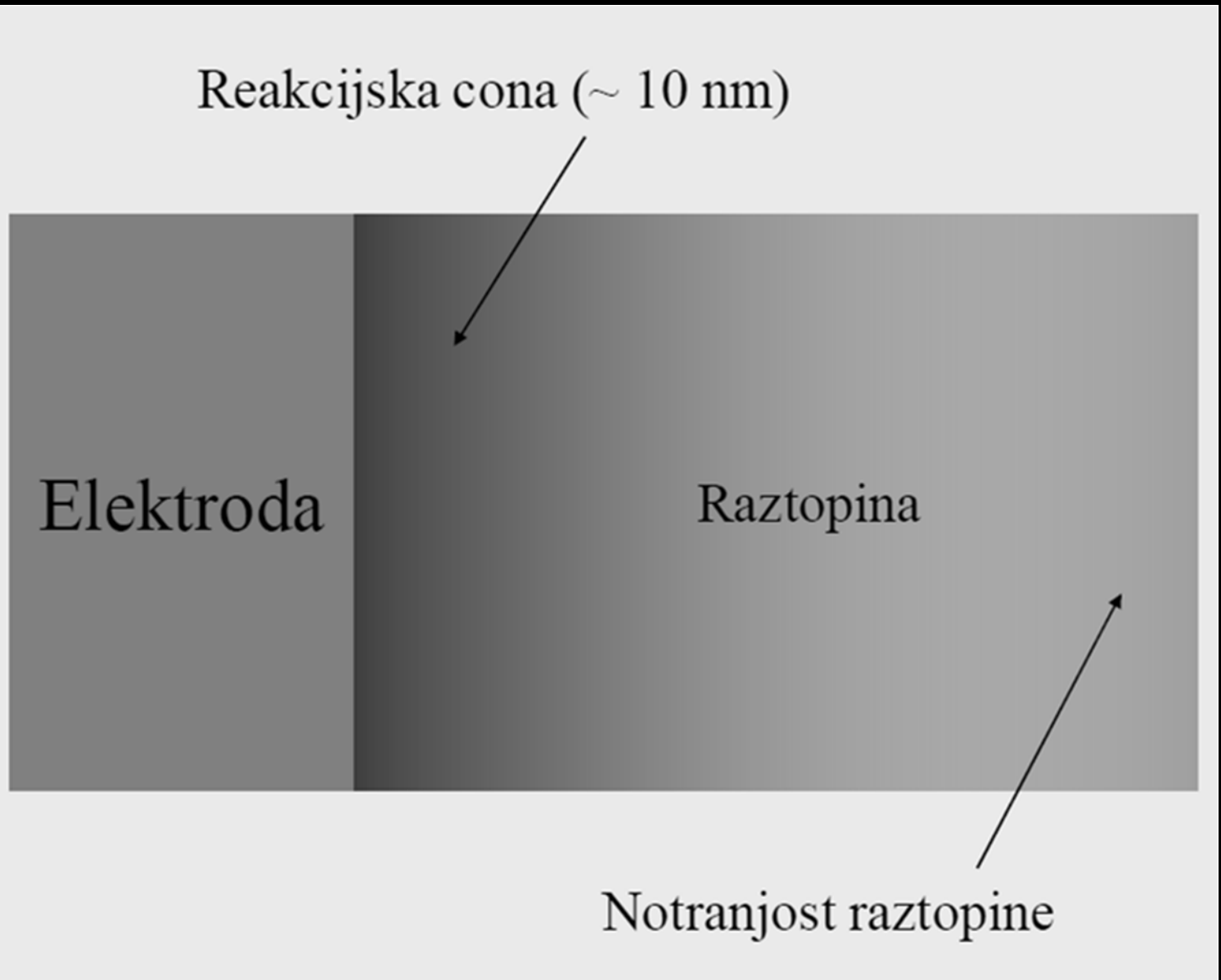

CE
RE
WE
V_{appl}
R_f
E_{out}

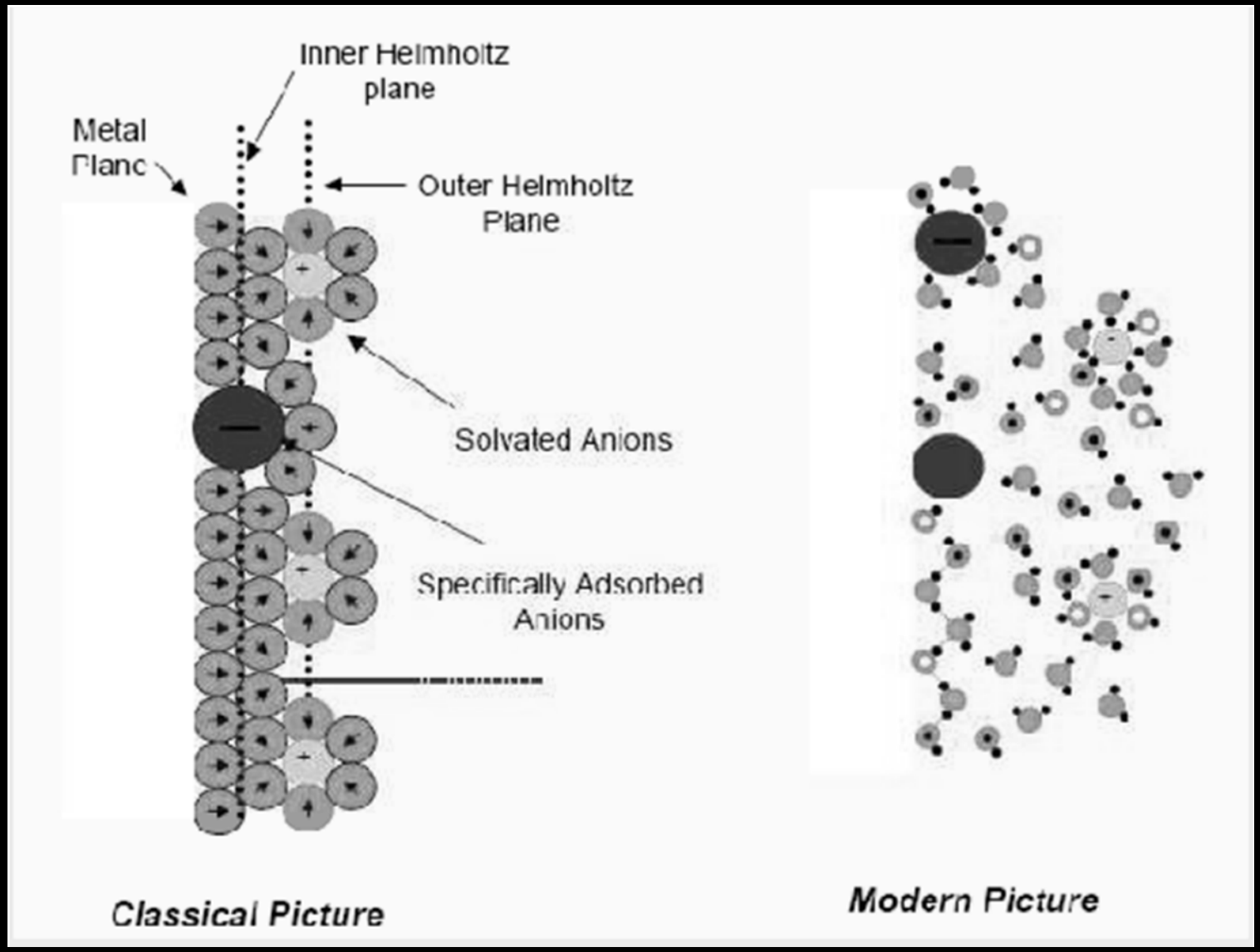


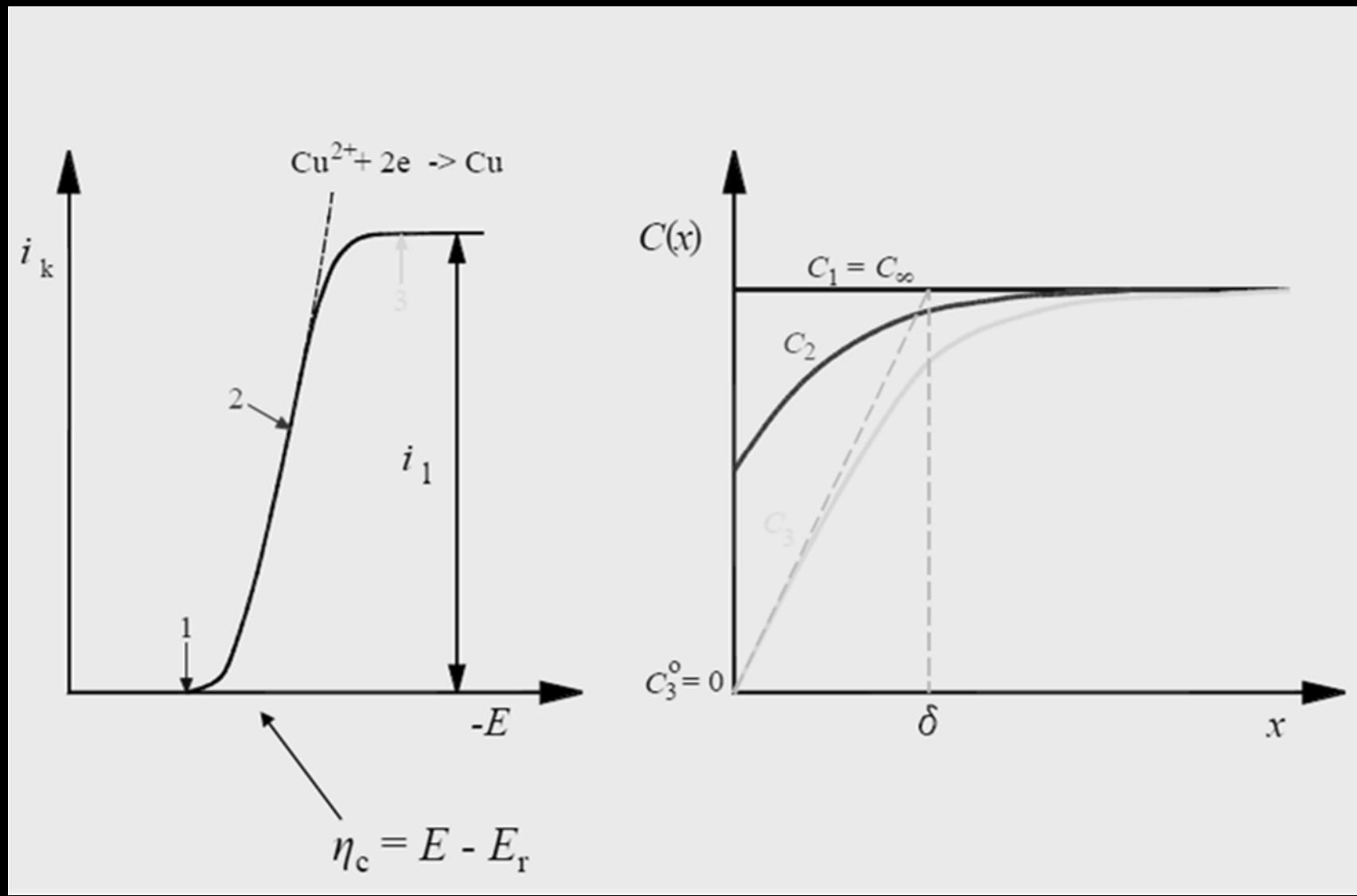

MODEL 377
SYNCHRONOUS
STIRRING MOTOR
ON
OFF
MODEL 173
POTENTIOSTAT/
GALVANOSTAT


analit
elektroda
elektrolit


Fe^{3+}_{aq} → Fe^{3+}_{ad} + e^- ⟷ Fe^{2+}_{ad} → Fe^{2+}_{aq}
Transport: konvekcija, migracija, difuzija
adsorpcija
reakcijska cona
e
Katoda
difuzija
Fe^{3+}
$\vec{J}$
Fe^{3+}
$\vec{v}_e$
konvekcija
e
$\vec{J}$
Fe^{2+}
Fe^{2+}
difuzija
prenos naboja


Reakcijska cona (~ 10 nm)
Elektroda
Raztopina
Notranjost raztopine


Inner Helmholtz plane
Metal Plane
Outer Helmholtz Plane
Solvated Anions
Specifically Adsorbed Anions
Classical Picture
Modern Picture


Cu2+ + 2e -> Cu
ik
1
2
3
i1
-E
ηc = E - Er
C(x)
C1 = C∞
C2
C3
C3° = 0
δ
x

$$(Cu^{2+})_{razt.} \longrightarrow (Cu^{2+})_{el.} + 2e^{-} = Cu$$

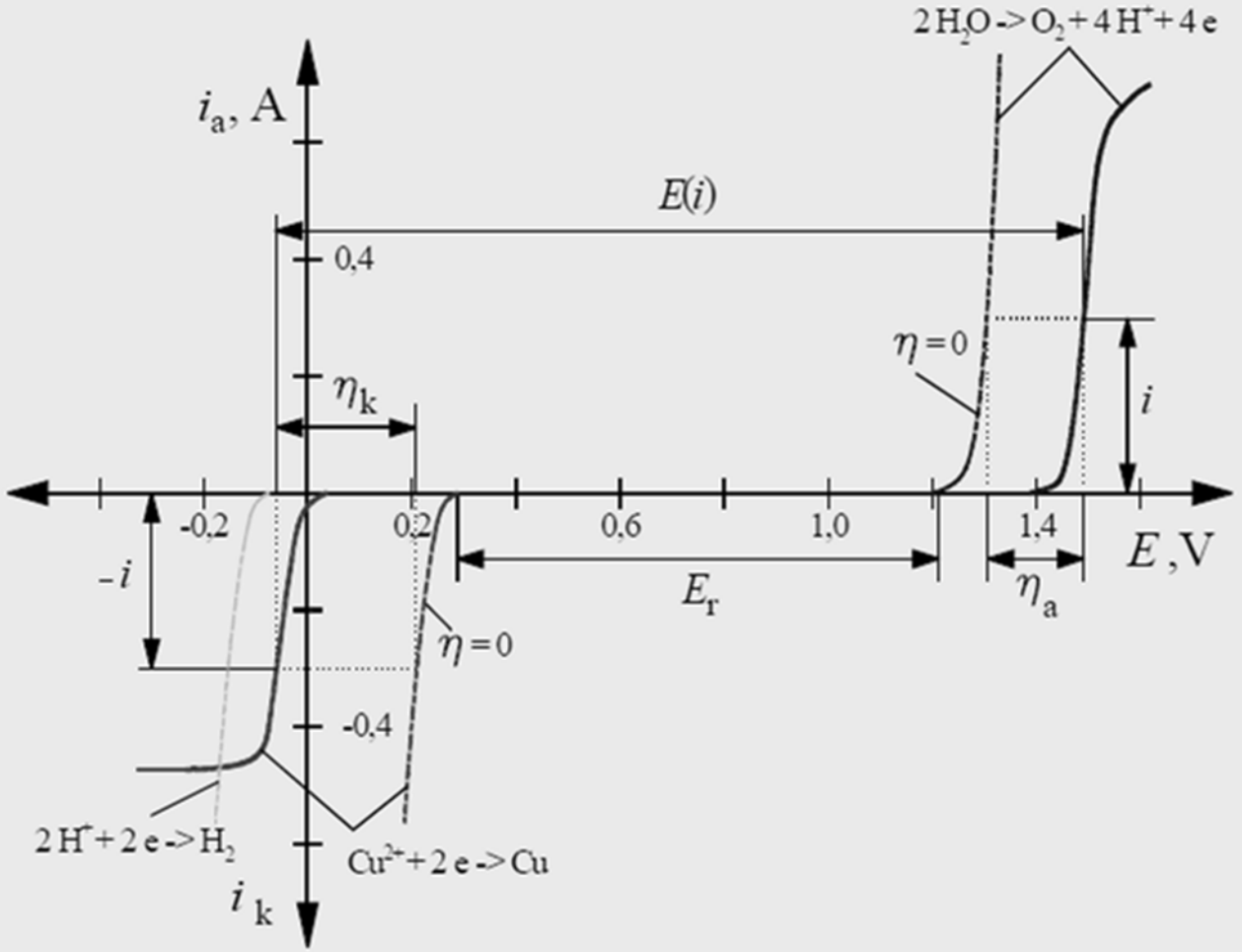
$$E_{r(i=0)} = E^{0}{}_{Cu^{2+}/Cu} + \frac{0{,}0591}{2} \log\left[Cu^{2+}\right]^{x=\infty}$$

$$E_{(i\neq 0)} = E^{0}{}_{Cu^{2+}/Cu} + \frac{0{,}0591}{2} \log\left[Cu^{2+}\right]^{x=0}$$

$$\eta_c = E_{(i\neq 0)} - E_{r(i=0)} = \frac{0{,}0591}{2} \log \frac{\left[Cu^{2+}\right]^{x=0}}{\left[Cu^{2+}\right]^{x=\infty}}$$

$$0 \leq \eta_c \leq \pm \infty$$

Elektroliza $CuSO_4$ – kaj se dogaja na elektrodah?



- **Faradayev zakon**: $Q = zFn$; $m = QM/(zF)$
- Kulometrija s konstantnim tokom (kulometrična titracija):

$$Q = i\,t$$

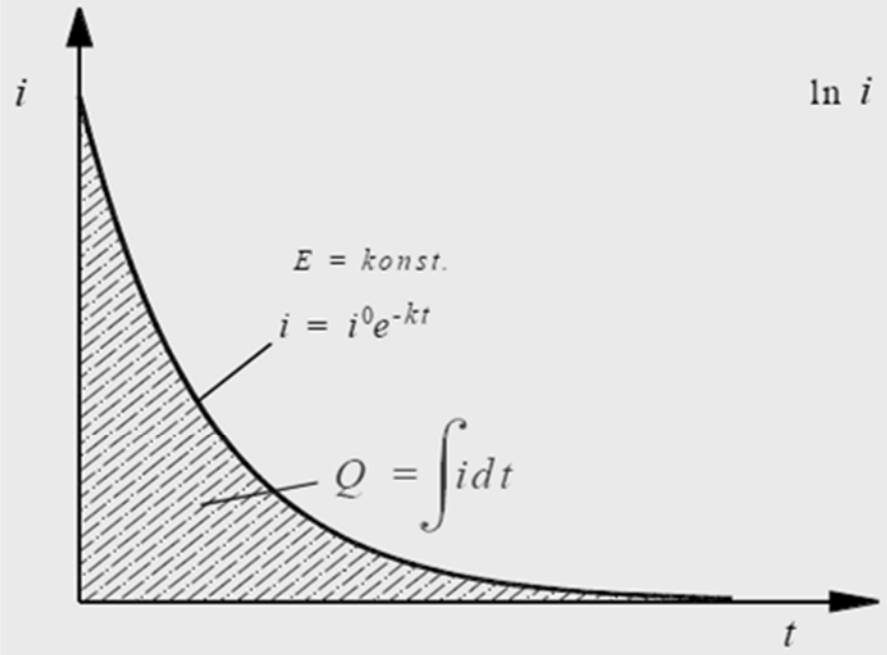
- Kulometrija pri kontrolirani napetosti (CPC):

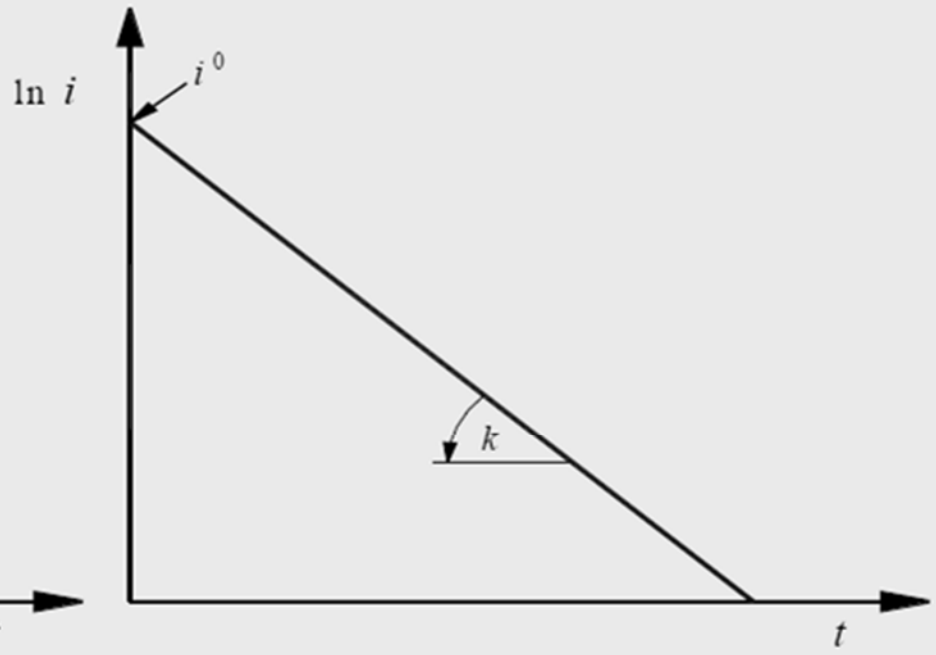
$$Q = \int_0^t i(t)dt$$

Pt-katoda: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$; $\eta = 100{,}0000\ \%$

Pt-anoda: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; $\eta = 102 - 104\ \%$

$N_2H_5^+ \rightarrow N_2 + 5H^+ + 4e^-$; $\eta = 100{,}0000\ \%$





Konstanta hitrosti: $k = \frac{AD}{V\delta}$

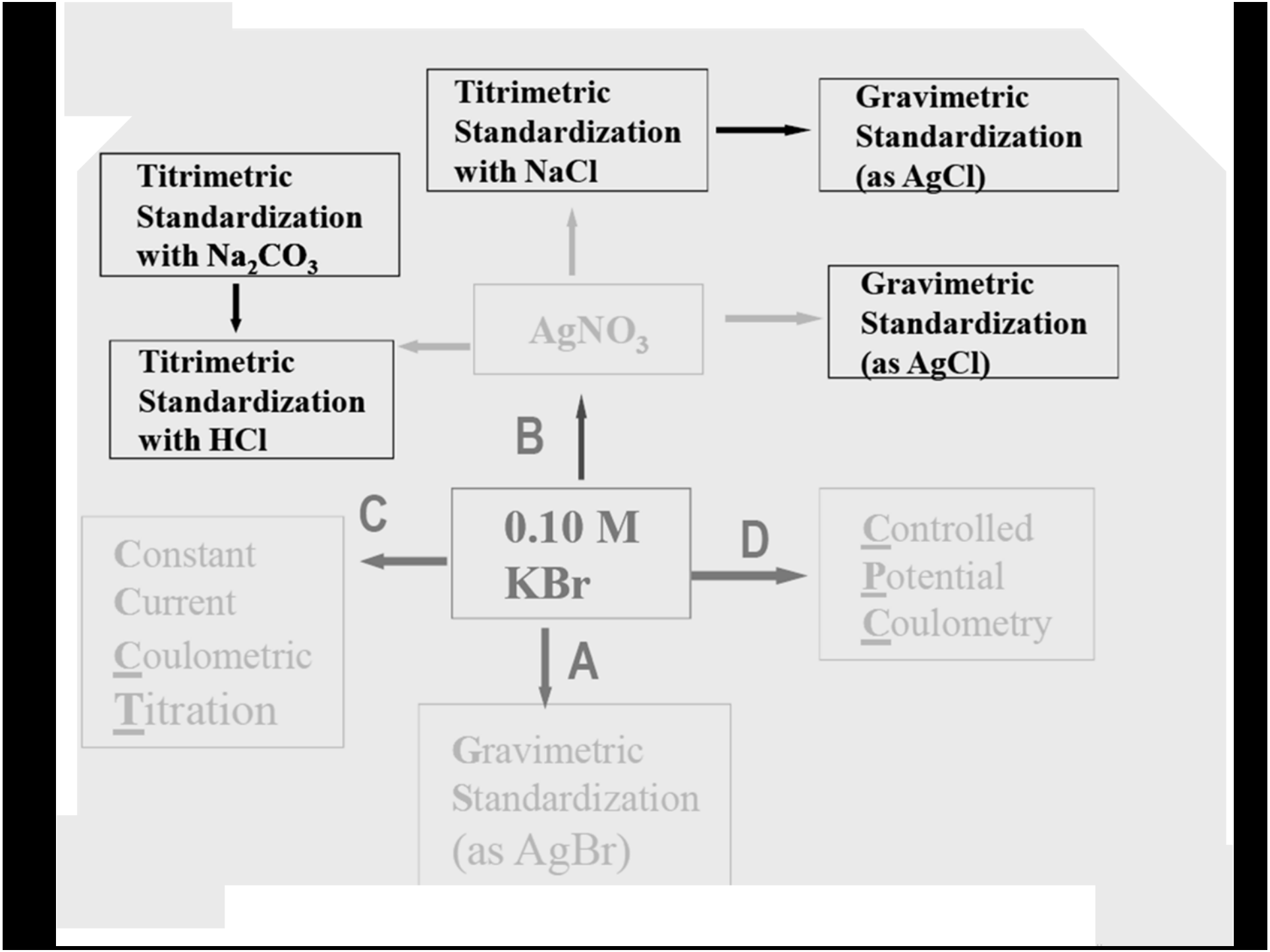
Določanje $K_3Fe(CN)_6$ s CPC

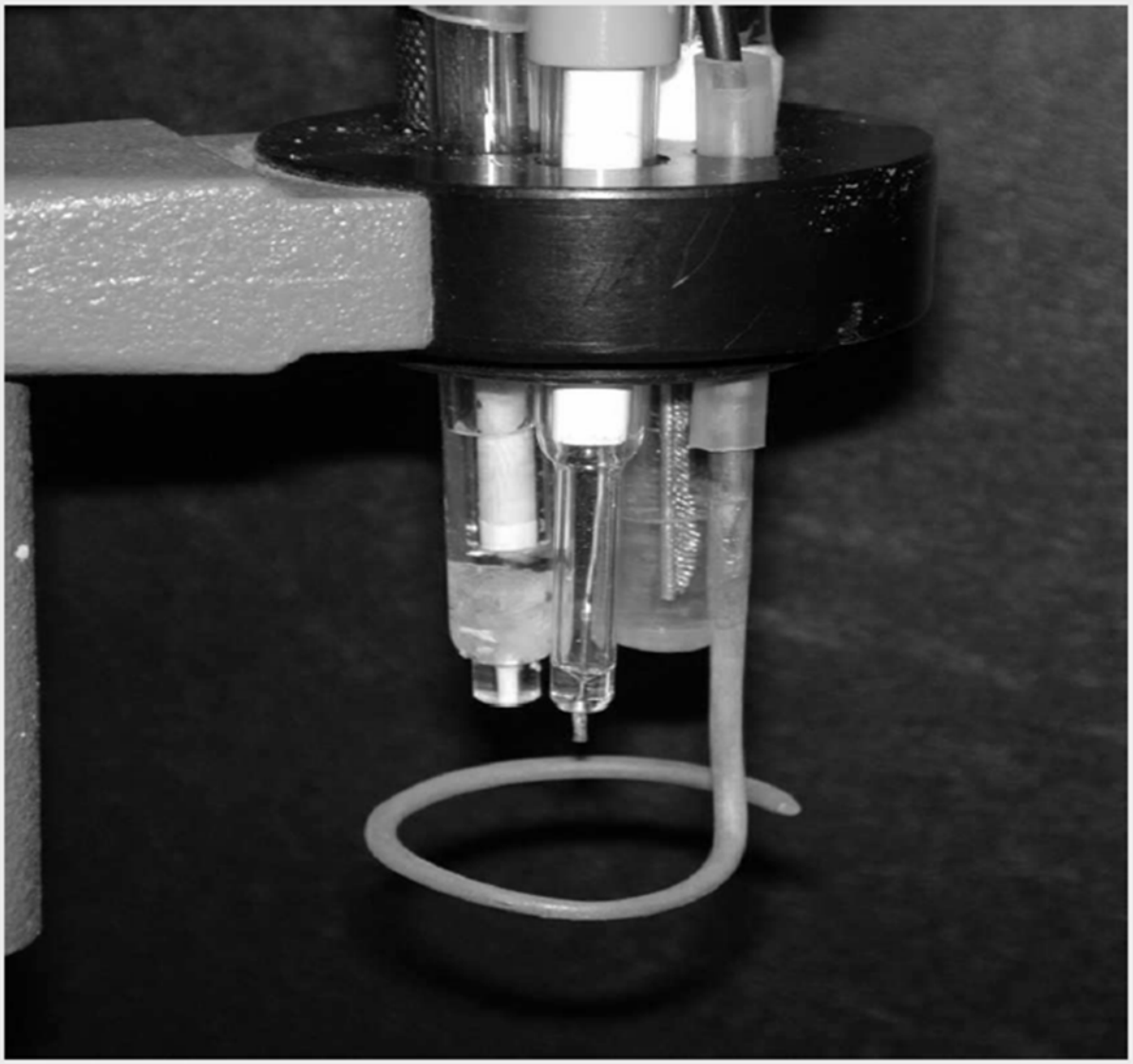
(0,25 M H_2SO_4, Pt elektroda, 0,23 V vs. SCE)

$K_3Fe(CN)_6$ dodan (mg)	**$K_3Fe(CN)_6$ izm. (mg)**	**Rel napaka, %**
24,76	24,74	0,08
35,79	35,76	0,08
39,11	39,07	0,1
32,75	32,71	0,12
31,36	31,36	0
4,930	4,920	0,20
3,346	3,348	0,05
3,346	3,347	0,01
3,346	3,347	0,01
	Povpr. napaka:	0,07

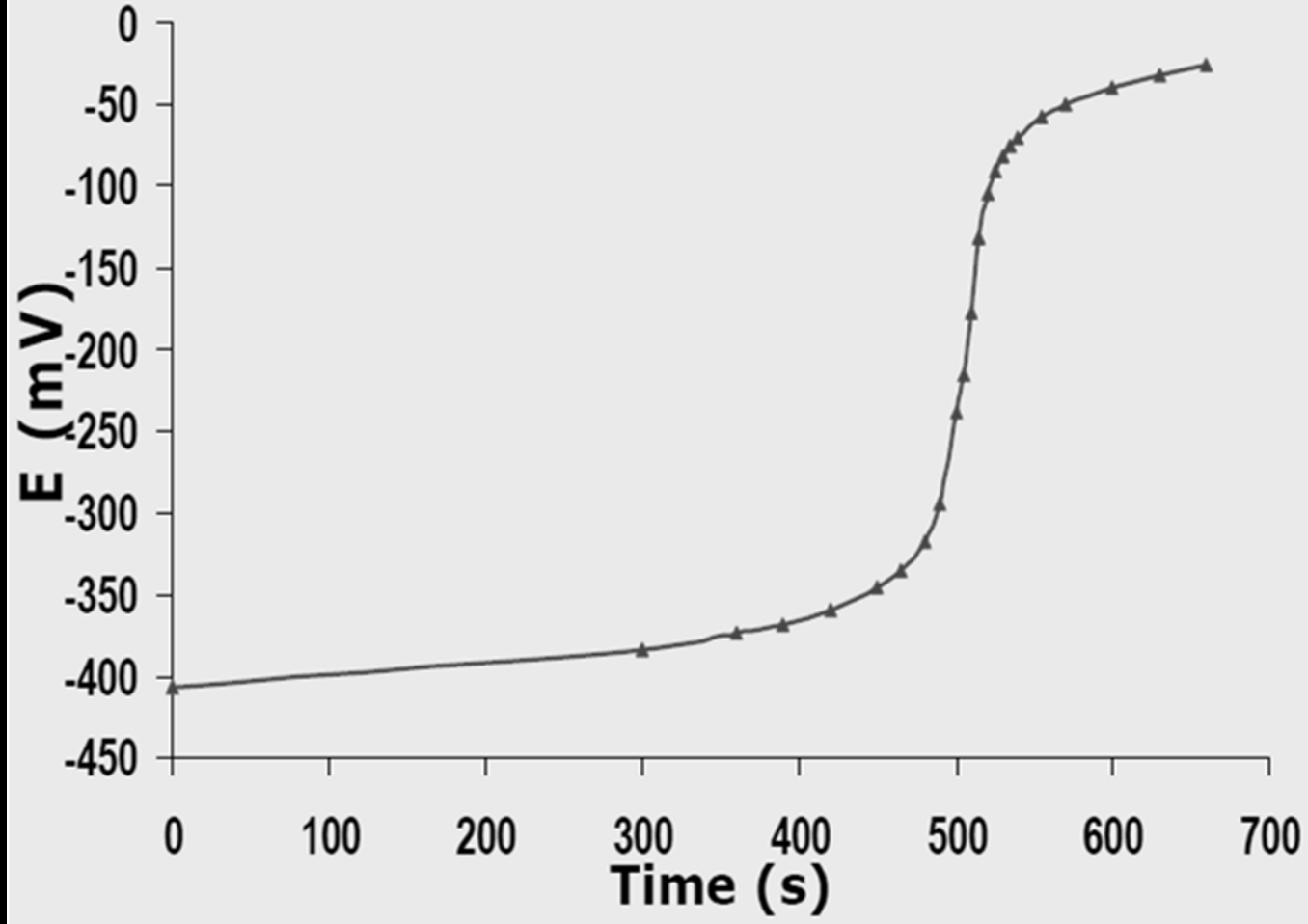
Reakcija	**Elektrolit**	**Delovna elektroda**
$AuCl_4^- \leftrightarrow Au$	HCl + sulfam. kislina	Pt
$Ag^+ \leftrightarrow Ag$	H_2SO_4	Pt
$Ir^{4+} \leftrightarrow Ir^{3+}$	HCl	Pt
$Pd^{4+} \leftrightarrow Pd^{2+}$	$NaN_3/Na_2HPO_4/HCl$	Pt
$Rh^{3+} \leftrightarrow Rh(Hg)$	HCl	Hg
$Pt^{4+} \leftrightarrow Pt^{2+}$	HCl-etilendiamin	Pt
$Ru^{4+} \leftrightarrow Ru^{3+}$	HCl	Pt
$(CrO_4^{2-}+Cr^{3+})\ Cr^{2+} \leftrightarrow Cr^{3+}$	HCl	Hg
$Sn^{4+} \leftrightarrow Sn(Hg)$	HBr	Hg

Reagent	Reakcija proizvajanja	Analit
H^+	$N_2H_5^+ = N_2 + 5H^+ + 4e^-$	baze
OH^-	$2H_2O + 2e^- = 2OH^- + H_2$	kisline
Ag^+	$Ag = Ag^+ + e^-$	Cl^-, Br^-, I^-, RS^-
Ag^{2+}	$Ag = Ag^{2+} + 2e^-$	Ce(III), As(III), V(IV), ..
Ti^{3+}	$TiO^{2+} + 2H^+ + e^- = Ti^{3+} + H_2O$	Fe(III), Ce(IV), U(VI), ..
I_2	$2I^- = I_2 + 2e^-$	SO_2, $S_2O_3^{2-}$, As(III), Sb(III),
Br_2	$2Br^- = Br_2 + 2e^-$	As(III), Sb(III), Tl(I), I^-, N_2H_4, fenol, anilin, ...


Titrimetric Standardization with NaCl
Gravimetric Standardization (as AgCl)
Titrimetric Standardization with Na_2CO_3
$AgNO_3$
Gravimetric Standardization (as AgCl)
Titrimetric Standardization with HCl
B
C
0.10 M KBr
D
Constant Current Coulometric Titration
Controlled Potential Coulometry
A
Gravimetric Standardization (as AgBr)



C) Constant Current Coulometric Titration of KBr

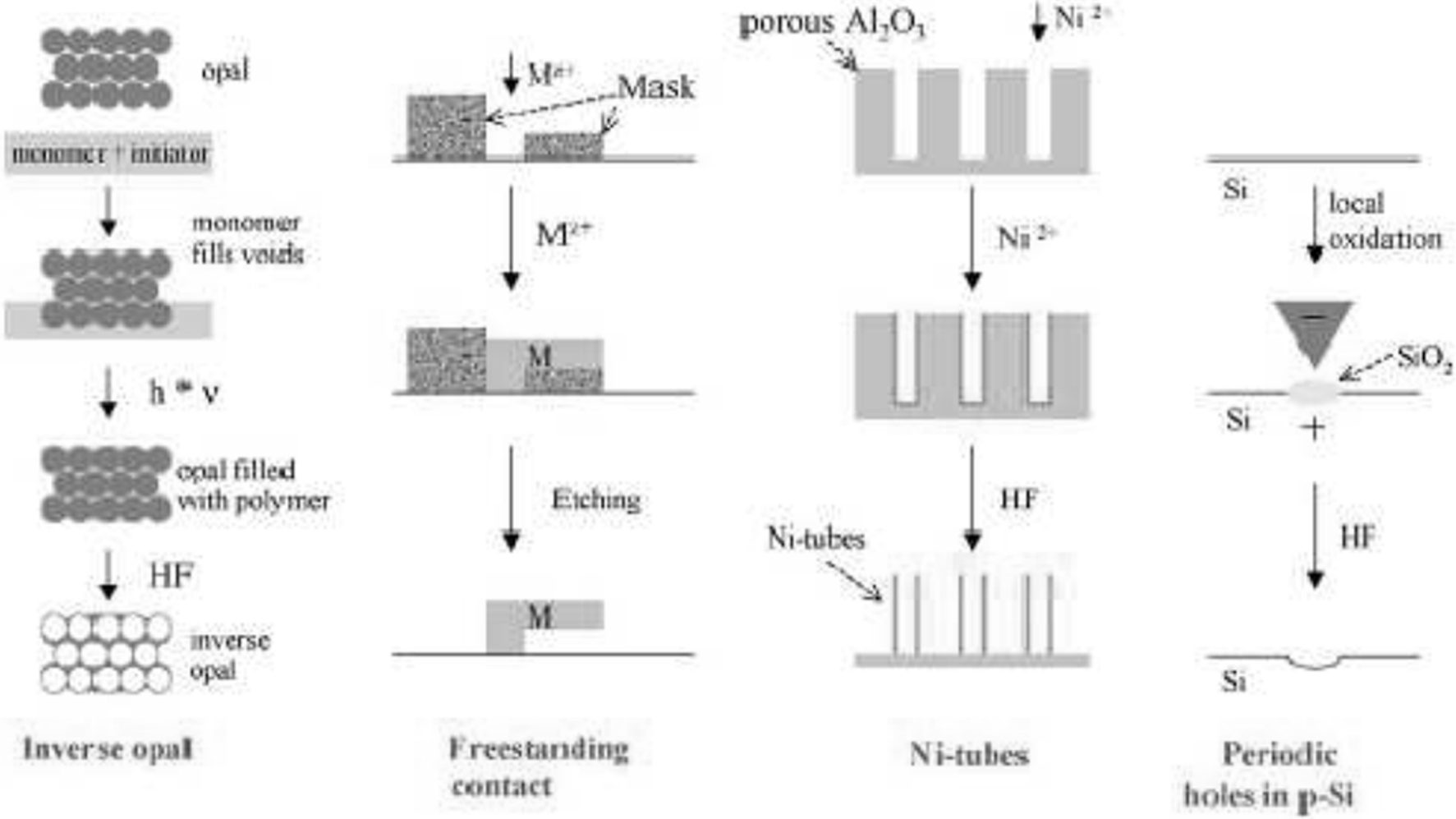


Standardization of 0,10 M KBr Solution by Different Methods

Method	C(KBr) found (M)	s	RSD %
Titrim. with $AgNO_3$	0.1003	0.0003	0.3
Gravimetric as AgBr	0.1001	0.0001	0.1
Coulometric titration	0.1020	0.00042	0.4
CPC	0.1005	0.0005	0.5

Elektrokemijska nanotehnologija – ENT

J.W. Shultze et al., *Electrochim Acta*, **51**(2005)775-786.



- B. Pihlar: *Osnove analizne kemije, Zapiski predavanj II. del*, FKKT, Ljubljana, 2007.
- D.A. Skoog, F.J. Holler, S.R. Crouch: *Principles of Instrumental Analysis*, 6th Edition, Section IV, Chapters 22, 24, Thomson Brooks/Cole, Belmont, CA, 2007.