



Tehnika	Merjena veličina	Zveza s koncentracijo
Potenciometrija	E (V)	$E = f(\log a_i)$
Elektrogravimetrija in kulometrija	m (g) Q (C)	$m \propto n$ $Q \propto n$
Voltometrija - Polarografija (DC, pulzna, ..), - Ciklična, - Inverzna (anodna, katodna, ..) -	$i, \Delta i$ (A) i_v (A)	$i, i_v \propto C$

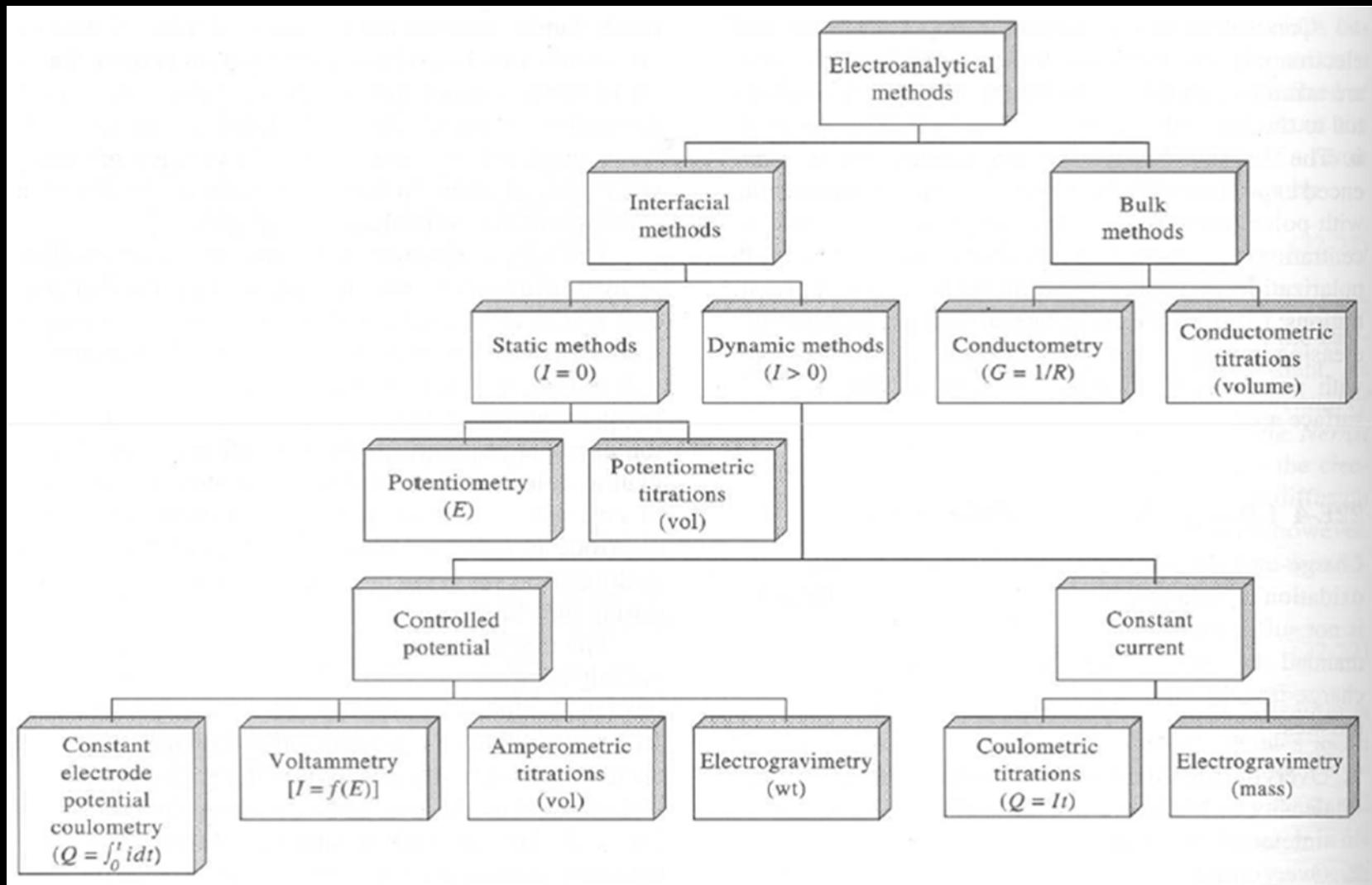
- Elektroanalizne tehnike temeljijo na dveh procesih:

- oksidacijsko redukcijski procesi:



- transport snovi v električnem polju (migracija)





➤ Koncentracijo analita ugotavljamo na osnovi napetosti člena:

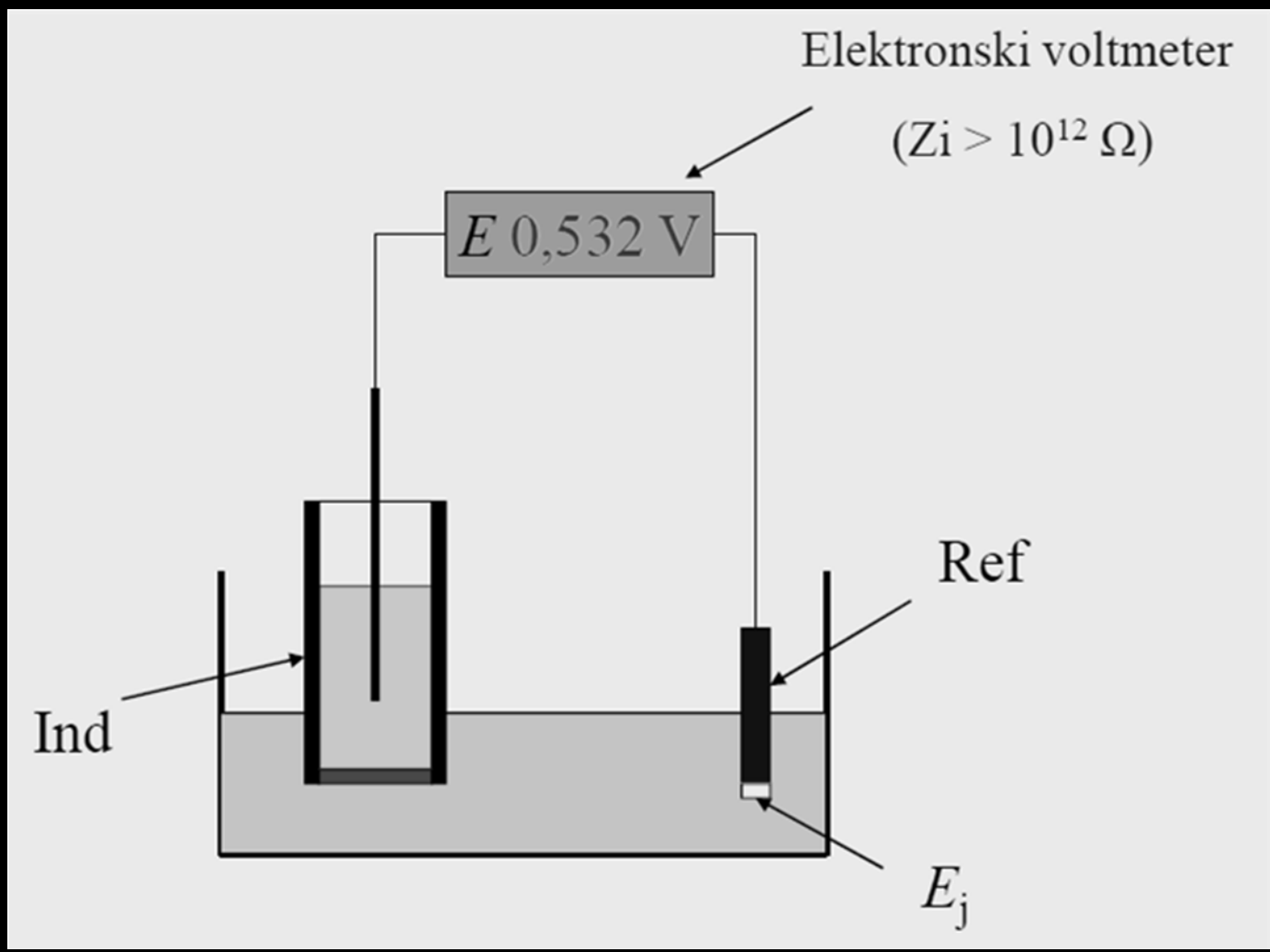
referenčna elektroda | | vzorec ($C = ?$) | indikatorska elektroda

- Z merjenjem napetostne razlike med indikatorsko in referenčno elektrodo ugotavljamo aktivnost analita:

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_j$$



$$E_{\text{ind}} = E' \pm \frac{RT}{zF} \ln a_x$$





(1864-1941)

WALTHER NERNST

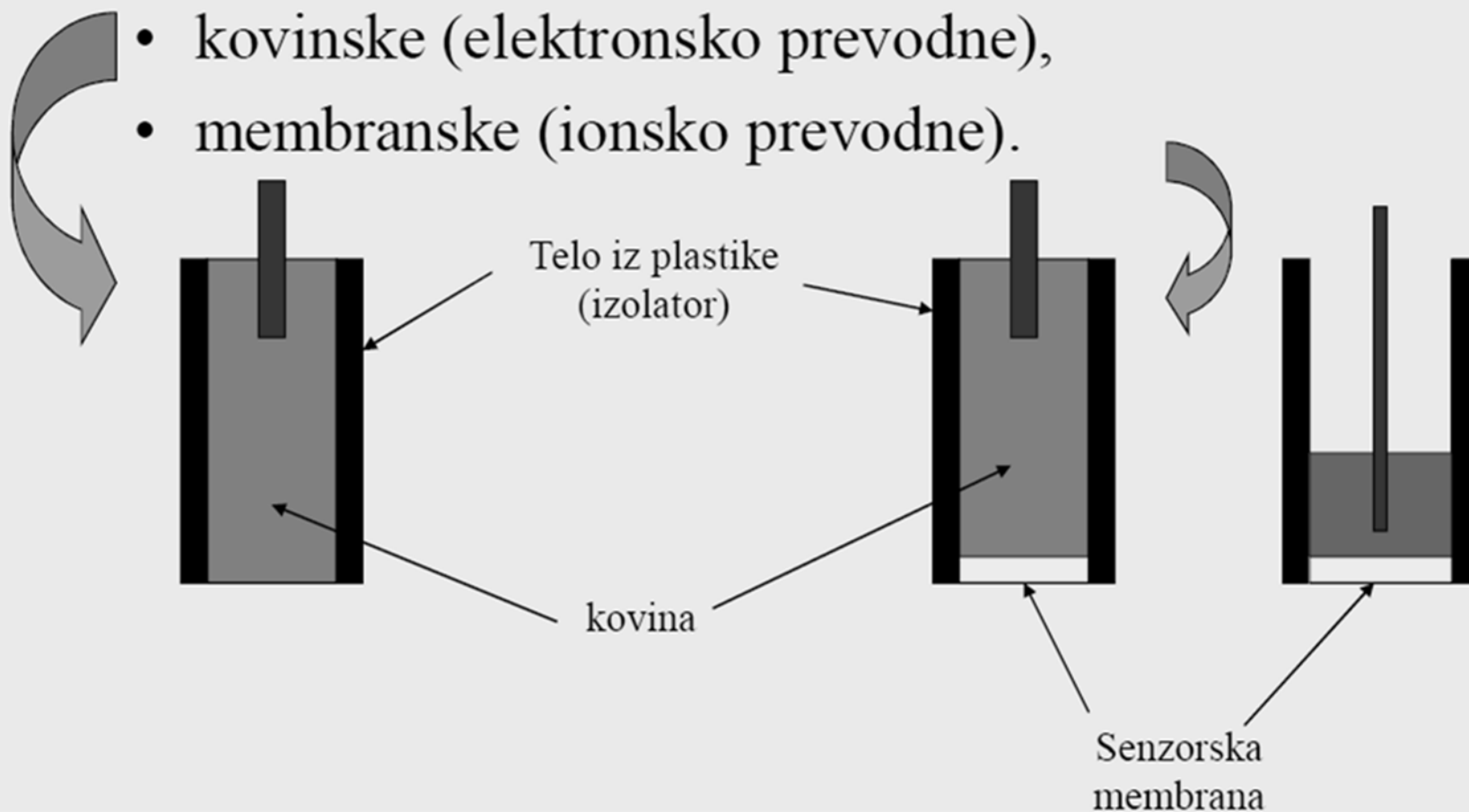
Studies in chemical thermodynamics

Nobel Lecture, December 12, 1921

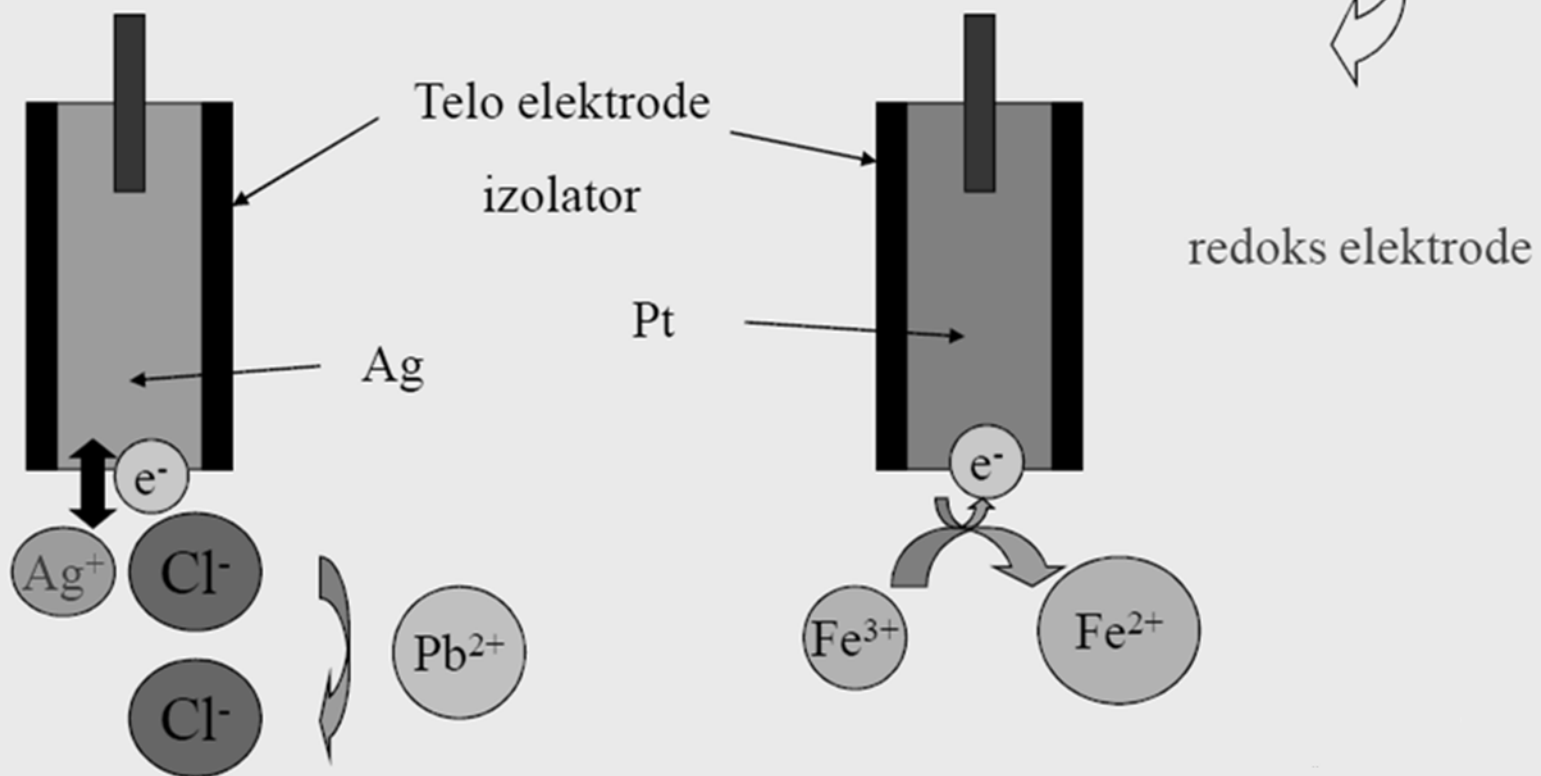
I should best fulfil my obligation to give a lecture relating to my prizewinning publications, if I discussed my heat theorem, which supplements the older thermodynamics, with special reference to its chemical applications, and described the experimental tests which it has undergone in numerous investigations in my laboratory. But this has already been done, especially in recent years, by a number of different authors in textbooks and monographs. On this important occasion, a keen desire to avoid simply repeating what has been said earlier, prompts me to discuss the subject from the viewpoint of electrochemistry.

Potenciometrija uporablja dve vrsti elektrod:

- kovinske (elektronsko prevodne),
- membranske (ionsko prevodne).

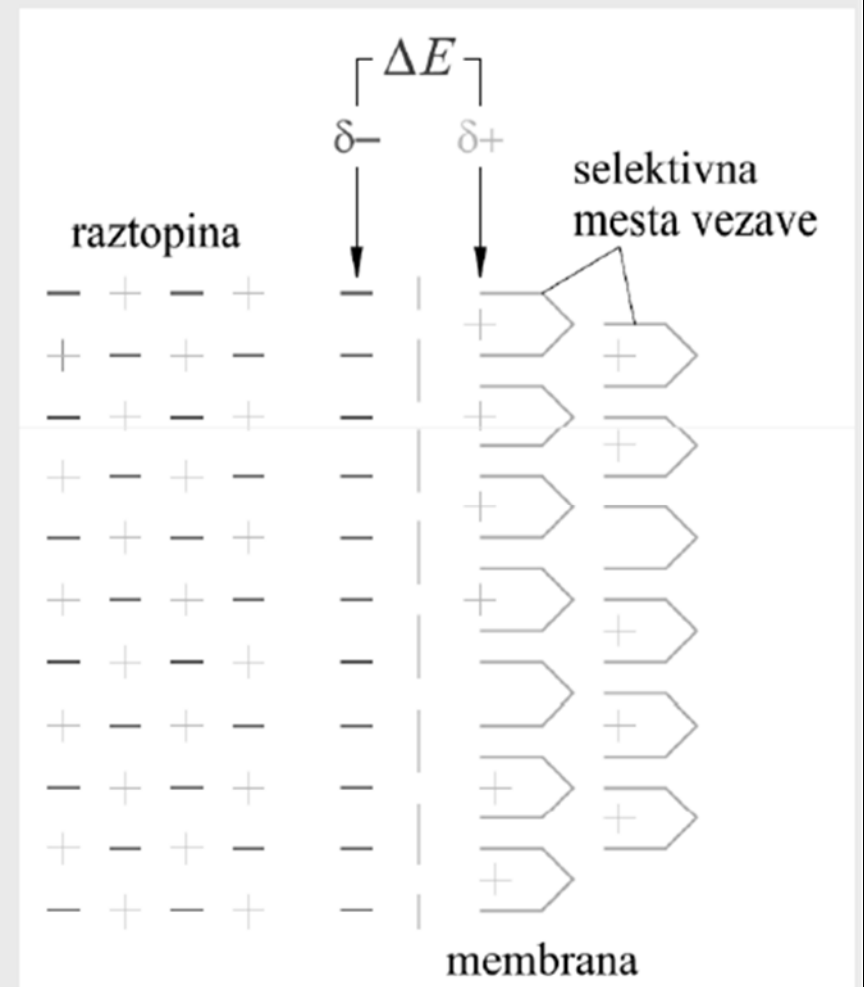


- Aktivne kovine (sodelujejo v redoks procesu),
- Inertne elektrode (elektronsko prevodne)



□ Razlika potencialov ΔE , nastane zaradi selektivne vezave (neprepustnosti, izmenjave, ..) delcev.

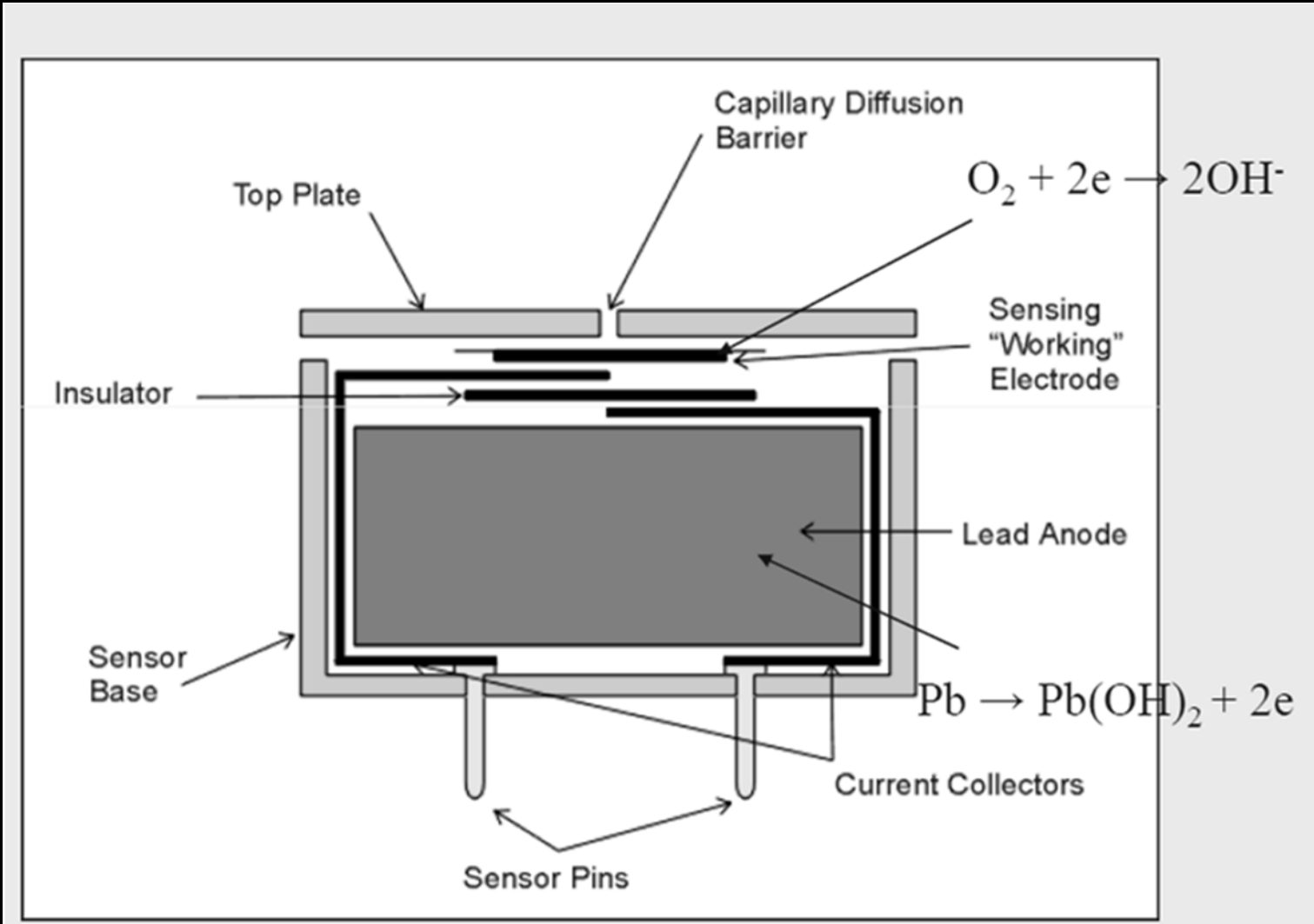
❖ Membranski potencial je osnova za potenciometrično merjenje koncentracije.





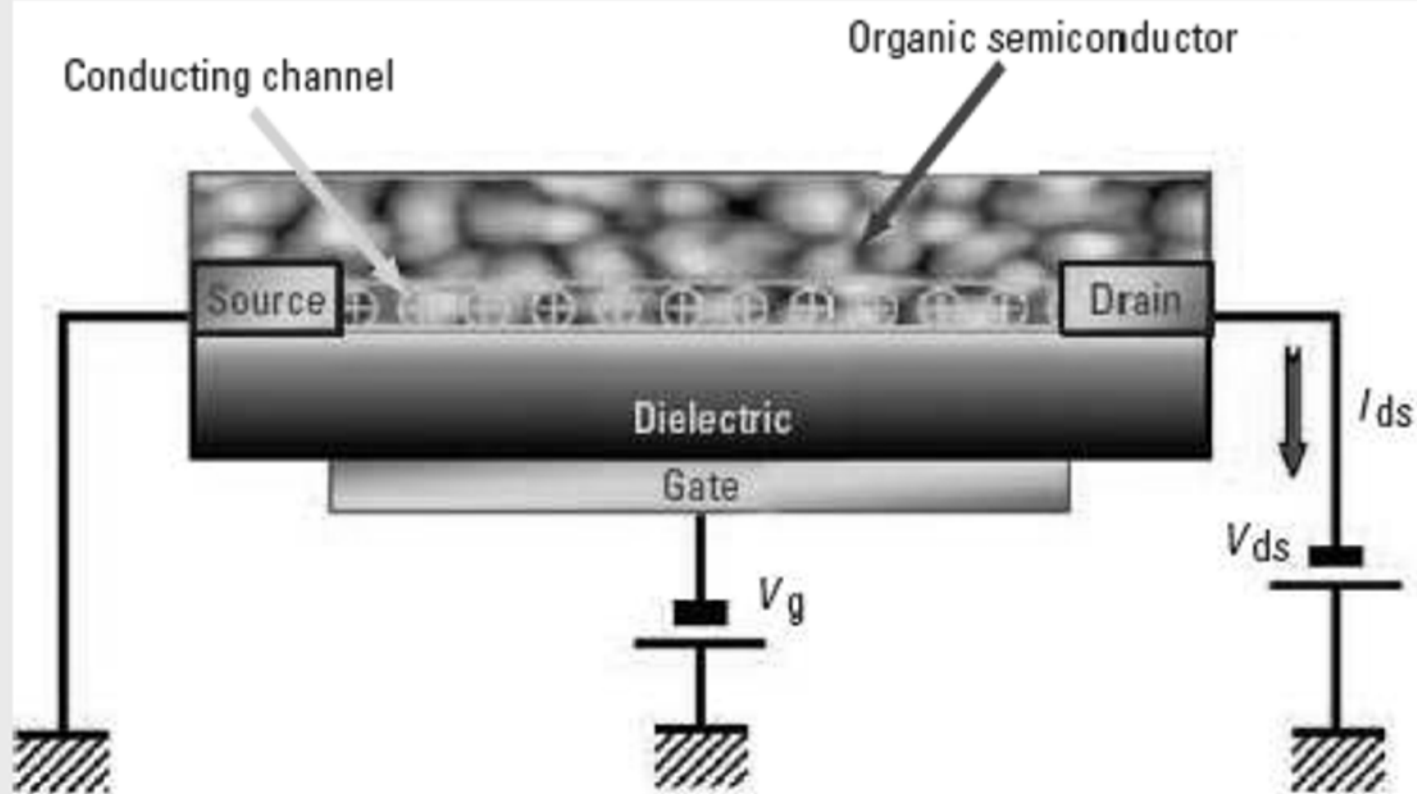
Alcotest 7410 (Dräger)
(elektrokemijski senzor)





Organski tankoplastni tranzistorji – OTFTs

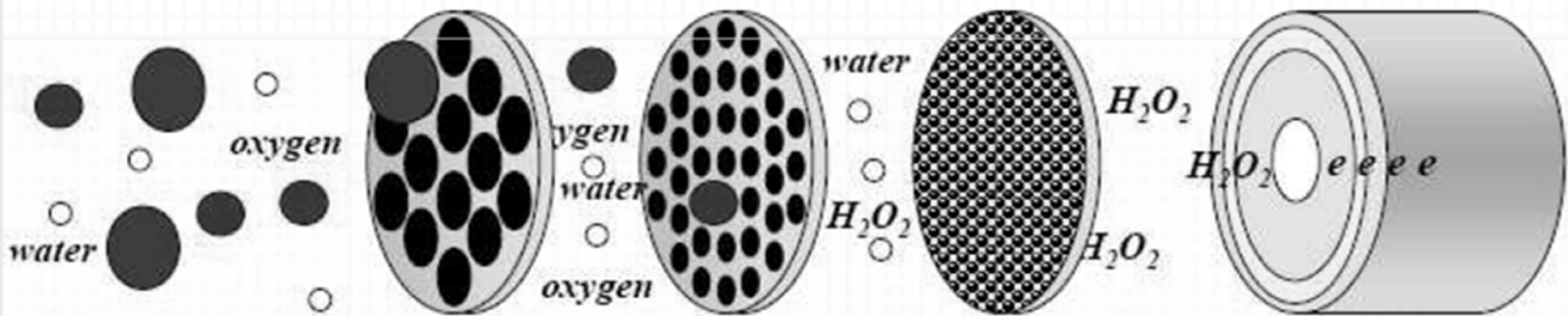
L. Torsi, A. Dodabalapur, *Anal. Chem.*, (2005)381 A.



Analyte solution

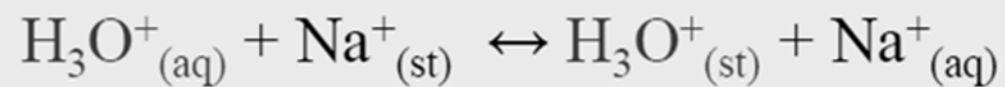
Bio-active layer

Electrochemical Transducer

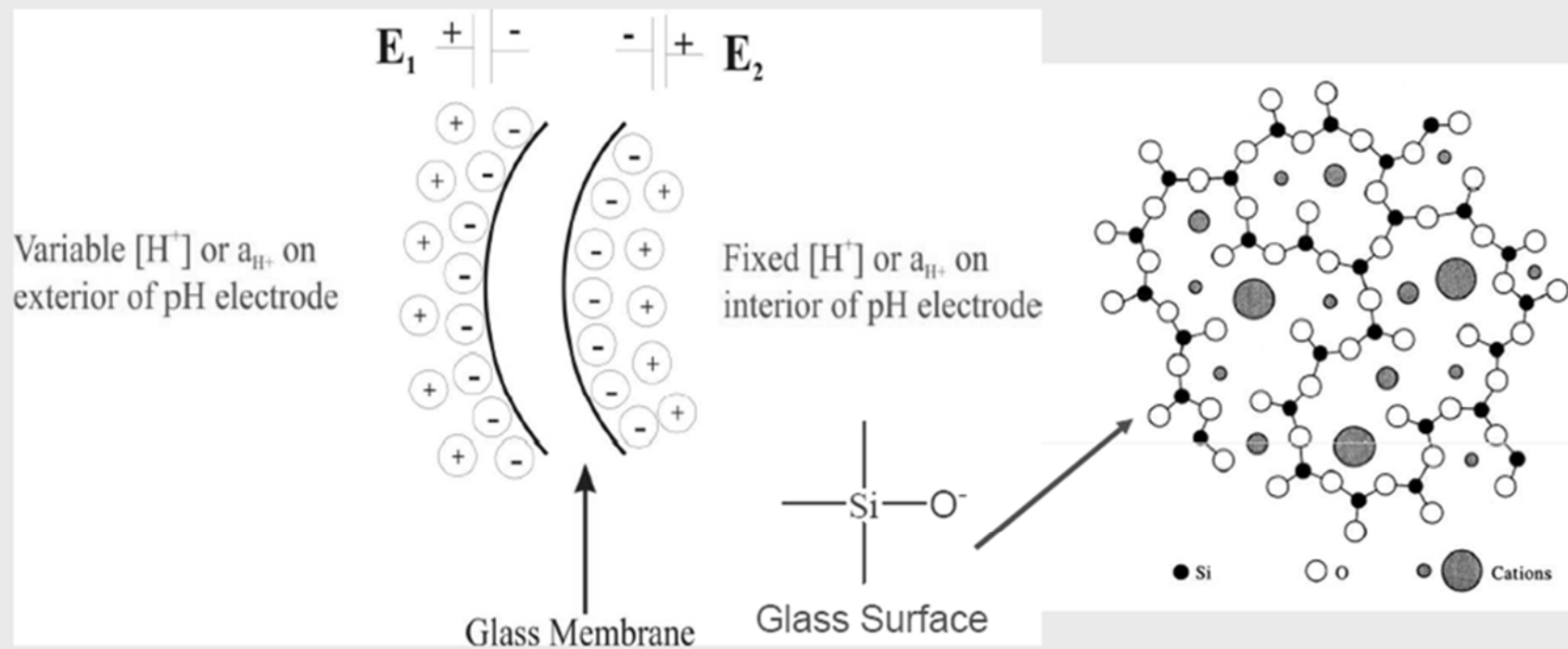


Steklena elektroda je specifični senzor H_3O^+ ionov.

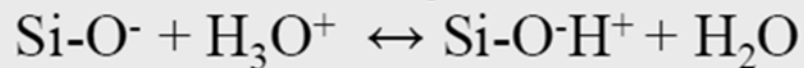
- Potencialna razlika na membrani nastane zaradi izmenjave H_3O^+ ionov, z Na^+ ioni v hidratiziranem sloju membrane:



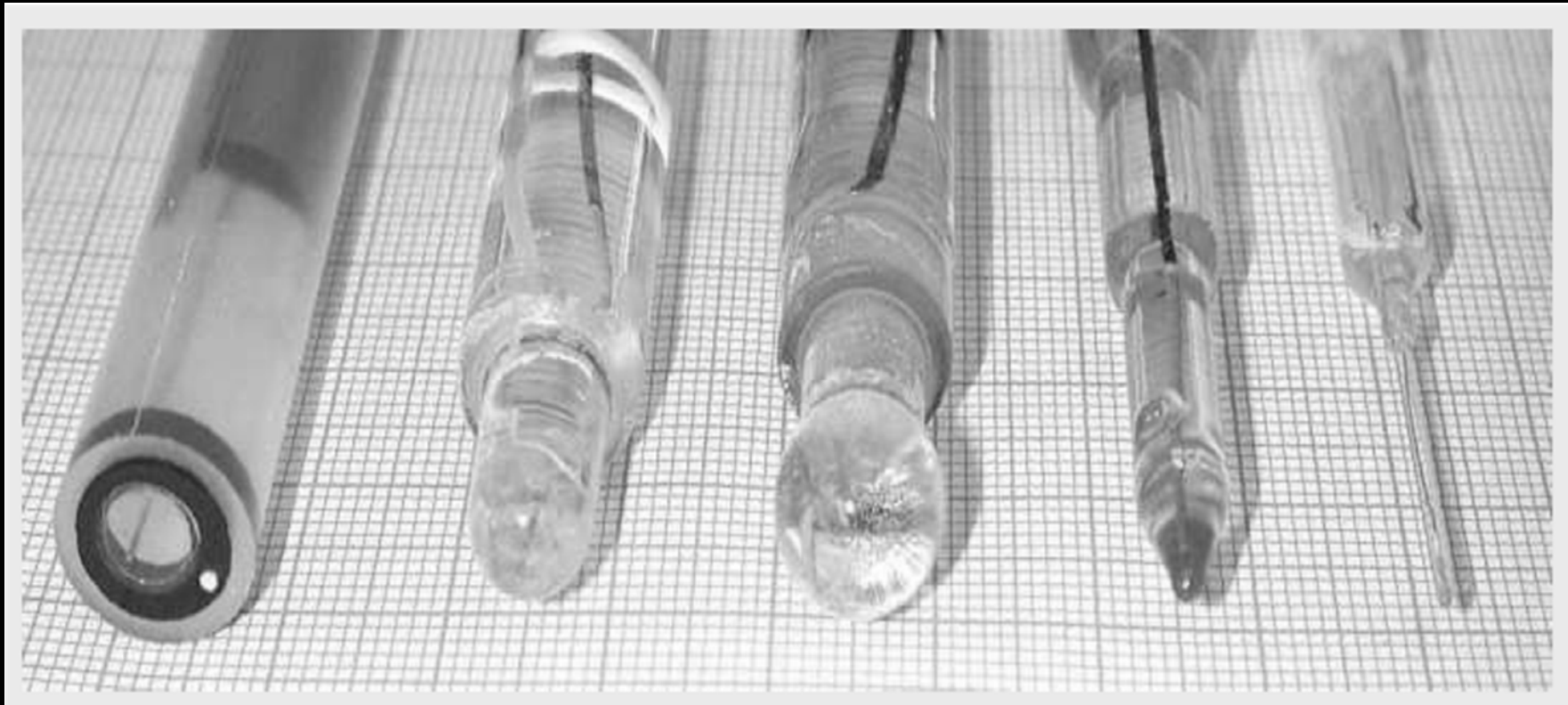
$$K_i = \frac{a(\text{H}_3\text{O}^+)_{\text{st}} a(\text{Na}^+)_{\text{aq}}}{a(\text{H}_3\text{O}^+)_{\text{aq}} a(\text{Na}^+)_{\text{st}}}$$

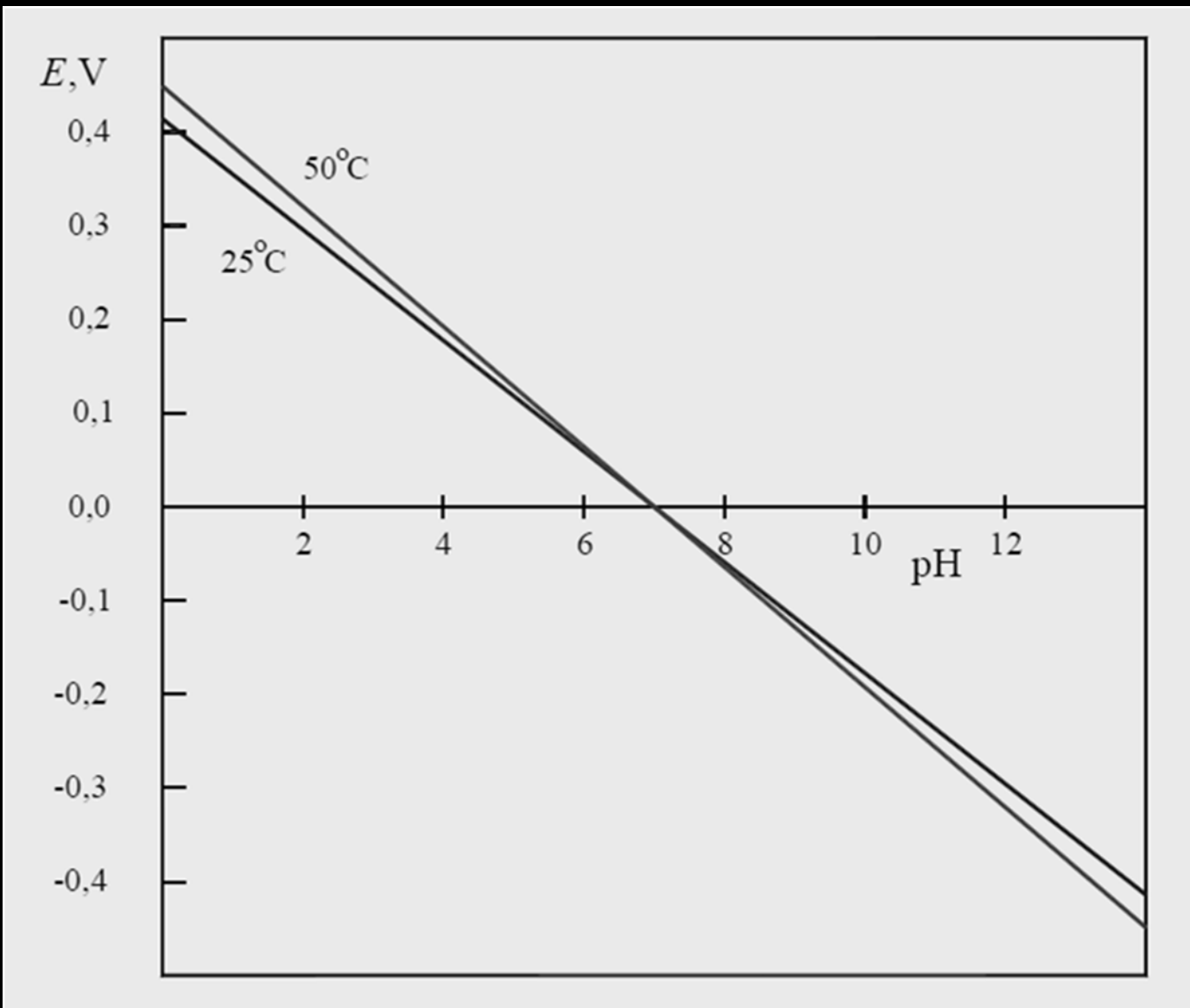


Na fazni meji membrana-topilo nastane razlika potencialov zaradi preferenčne adsorpcije H_3O^+ ionov na steklo:



$$\Delta E = E_1 - E_2, \rightarrow E_m = K - 0.0591pH$$





- Logaritemska odvisnost (Nerstova enačba) prispeva skozi vse merilno območje relativno veliko napako: negotovost potenciala $s(E) \pm 1$ mV rezultira v ± 4 z % negotovosti koncentracije (RSD):

$$\Delta E = \frac{RT}{z_i F} \left(\frac{da_i}{a_i} \right)$$

- Tekočinski potencial E_j , zavisi od temperature in sestava raztopine:

$$E_j = E_2 - E_1 = -\frac{RT}{F} \int_1^2 \sum_{i=0}^n \frac{t_i}{z_i} d \ln a_i$$

- Imunost na interference
- odziv indikatorske elektrode na druge interferenčne ione (neselektivnost):

$$R = S_m c_m + S_i c_i = S_m (c_m + k_{i,m} c_i)$$

Koeficient selektivnosti: $k_{i,m} = \frac{S_i}{S_m}$

$$E_m = E' \pm \frac{RT}{z_m F} \ln \left(a_m + \sum k_{i,m} a_i^{z_m/z_i} \right)$$

- odziv indikatorske elektrode na druge interferenčne ione (neselektivnost):

$$E_i = E' \pm \frac{RT}{z_i F} \ln \left(a_i + K_{ij} a_j^{z_i/z_j} \right)$$

Vpliv temperature

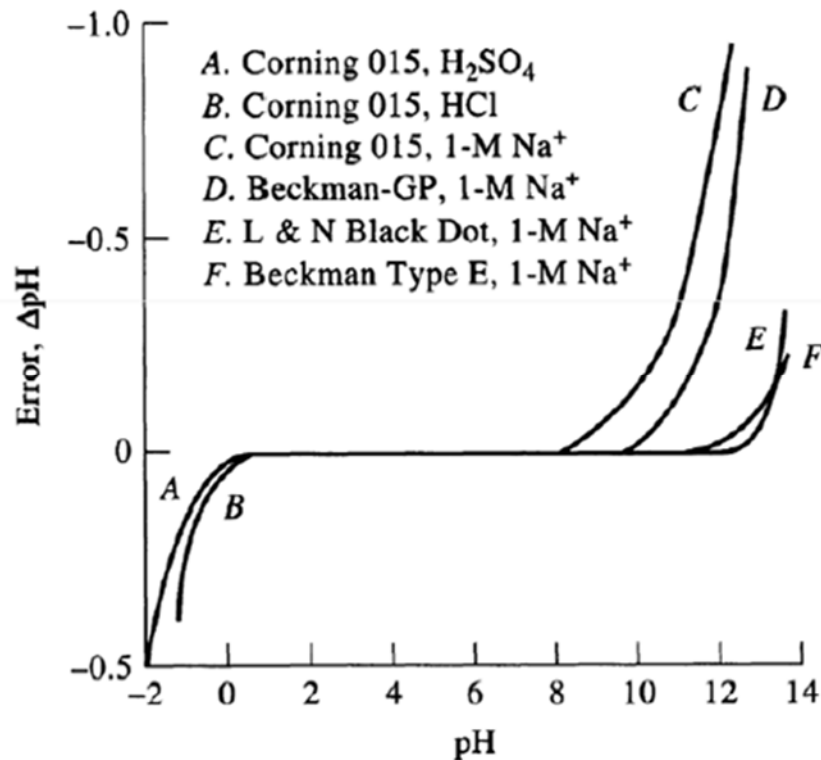
Temperatura vpliva na indikatorsko in referenčno elektrodo:

$$\frac{\partial E}{\partial T} = \frac{\partial E'}{\partial T} + \frac{R}{zF} \ln a_i + \frac{RT}{zF} \frac{d \ln a_i}{dT}$$

T vzorca in standarda naj
bosta čimbolj enaki

$$\Delta \text{pH} = \frac{T_x - T_s}{T_x} \text{pH}_i$$

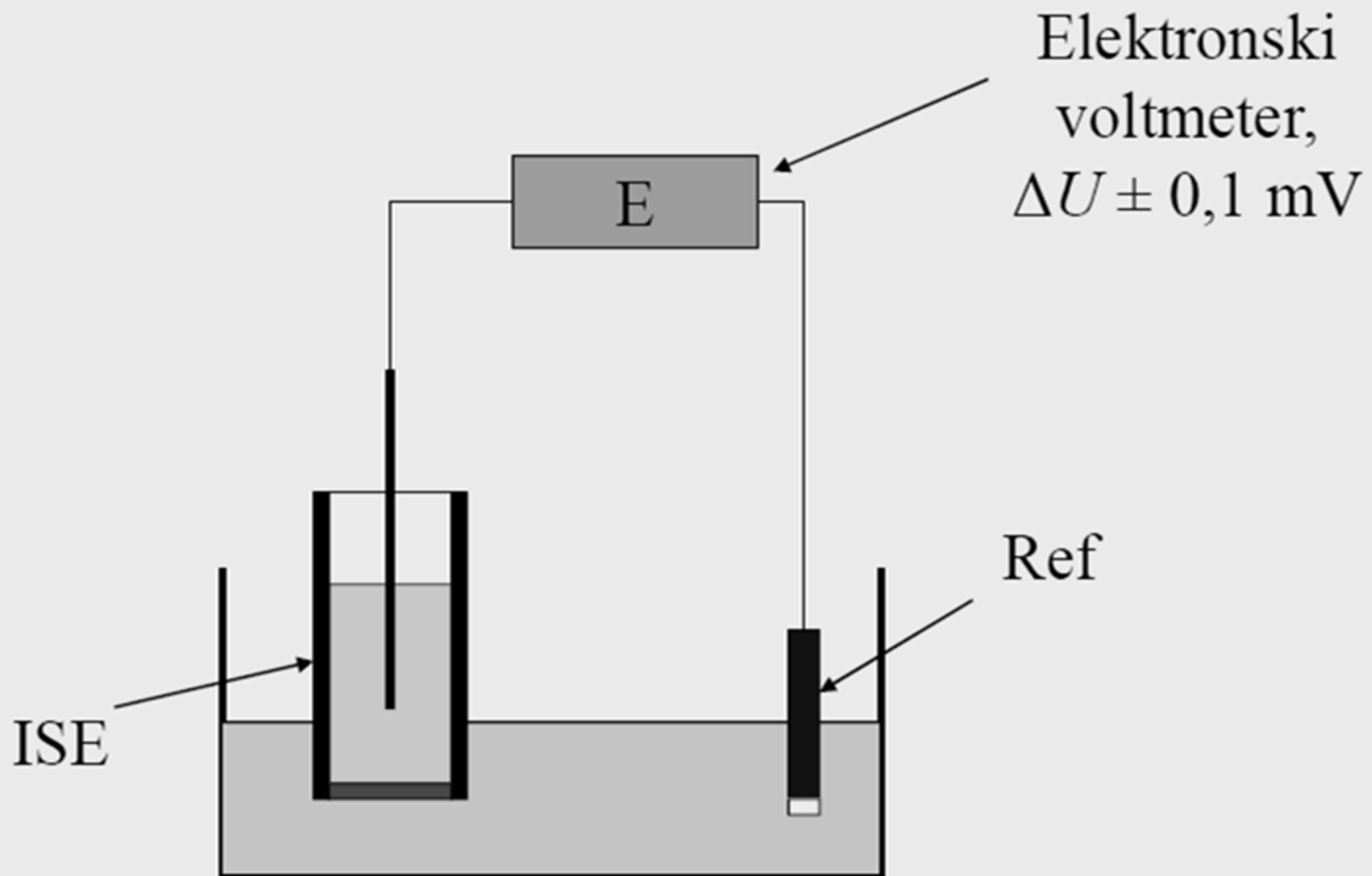
- Na izmenjavo vpivajo drugi ioni (alkalije)
- pojavi se pri nizki koncentraciji H^+ ionov ($pH > 10$)



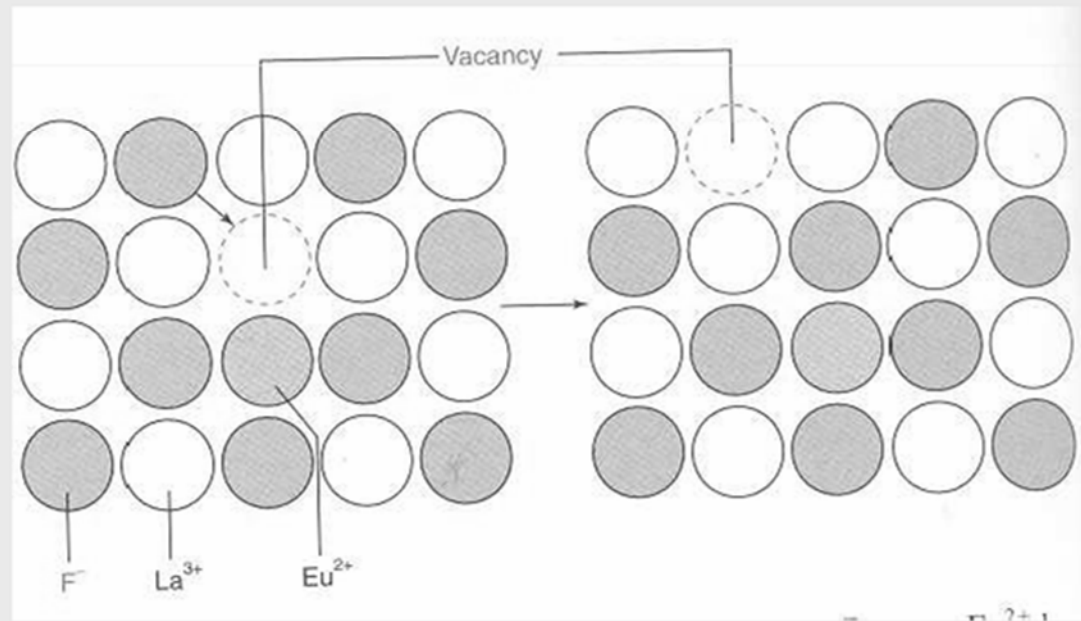
Pri visokem pH se poveča delež vezave Na^+ ali K^+ ionov, kar navidezno poveča koncentracijo H^+ ionov.

R.G. Bates, *Determination of pH, Theory and Practice*,
 John Wiley, New York 1973





- LaF_3 je dopiran z EuF_2 .
- Eu^{2+} ima nižji naboj od La^{3+} kar povzroča anionske praznine, zato sosednji F^- zapolni praznino.
- Plaz teh procesov povzroči gibanje F^- skozi kristalo strukturo.



$$E = E' - S \log a_{\text{F}^-} - E_{\text{ref}} = k - S \log [\text{F}^-]$$

Kaj izmerimo z ISE? Kako določamo zvrsti?
Kako izmerimo celokupni fluorid?

$$C_{\text{F}} = [\text{F}^-] + [\text{HF}] + 2[\text{HF}_2^-] + i \sum [\text{M}_a \text{F}_i] + j \sum [\text{M}_b \text{F}_j] + \dots$$

E.Bakker, E. Pretsch, Anal. Chem., (2002)420 A.

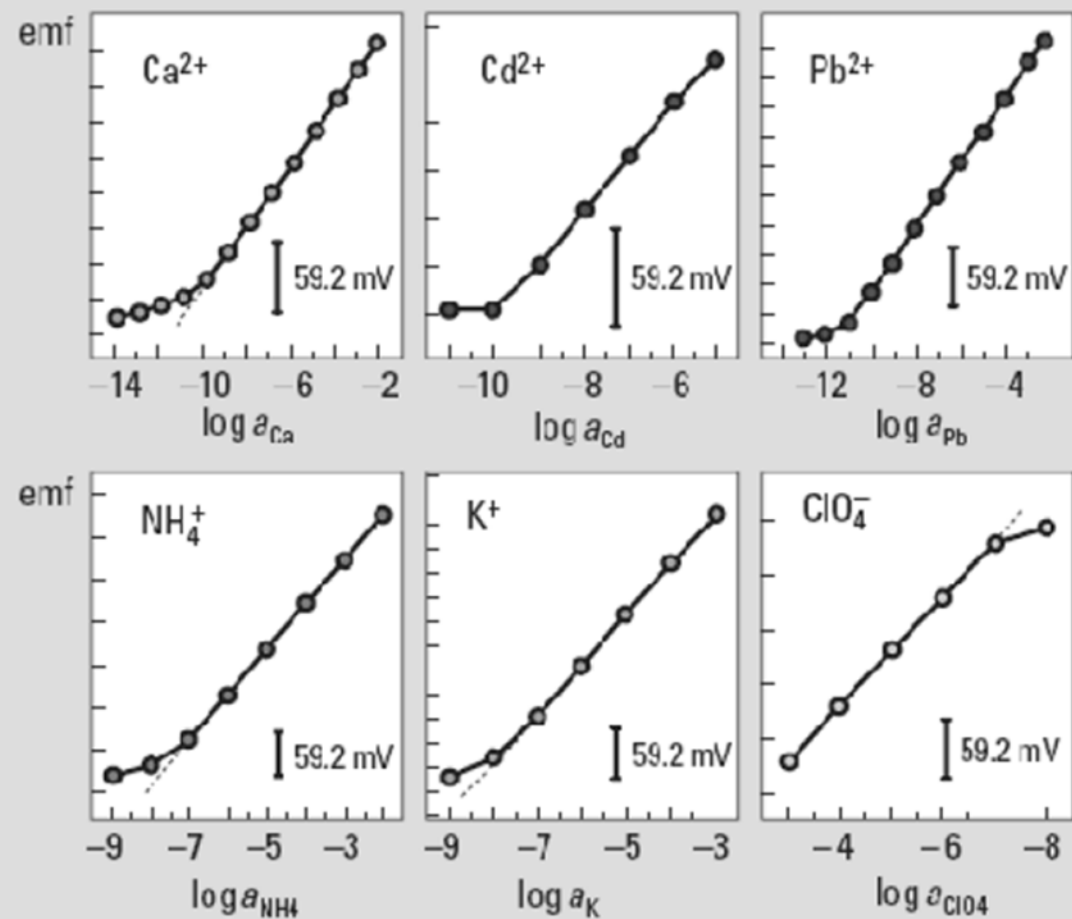


FIGURE 3. Response functions of some ISEs with recently improved lower detection limits.

A. Malon, T. Vigassy, E. Bakker, E. Pretsch, Potentiometry at Trace Levels in Confined Samples: Ion Selective Electrodes with Subfemtomole Detection Limits, *J. Amer. Chem. Soc.*, **128**(2006)8154-8155.

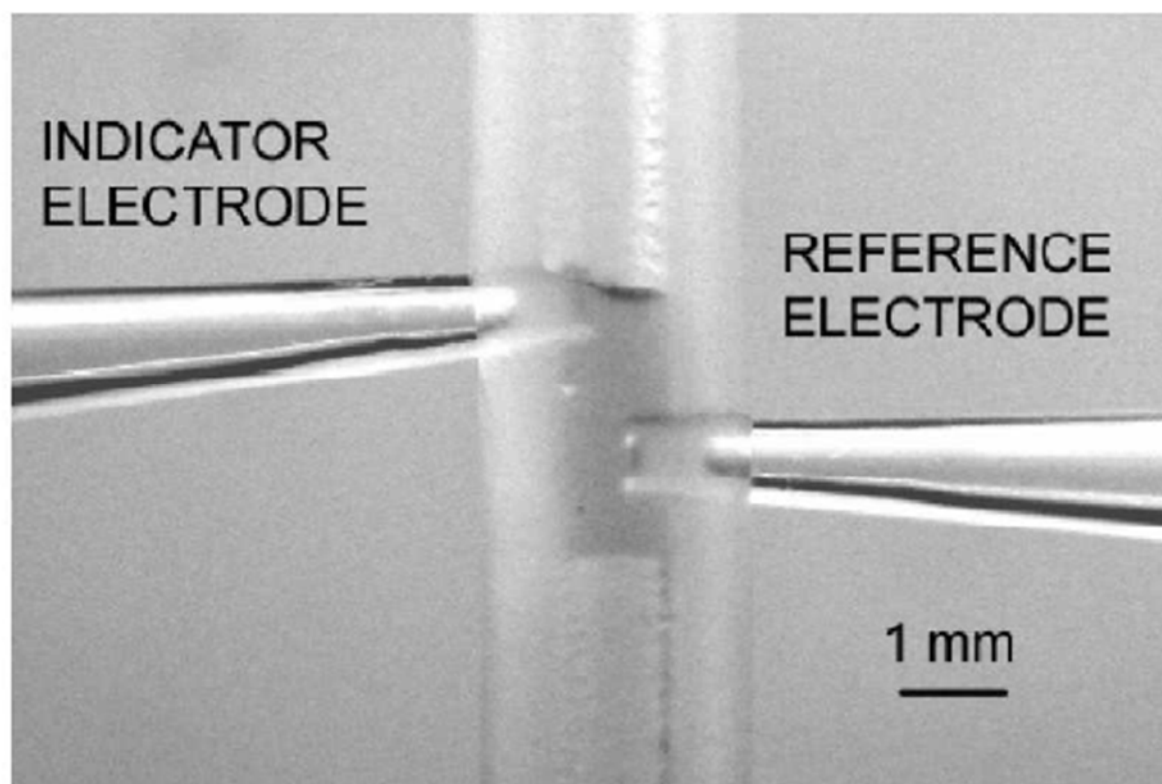


Figure 2. Detail of the 3- μ L measuring cell. The indicator electrode (left) and sodium-selective pseudoreference electrode (right) are inserted into a 1-mm i.d. silicone tube and placed in contact with the aqueous sample plug.

E. Bakker, E. Pretsch, *Anal. Chem.*, (2002)420 A.

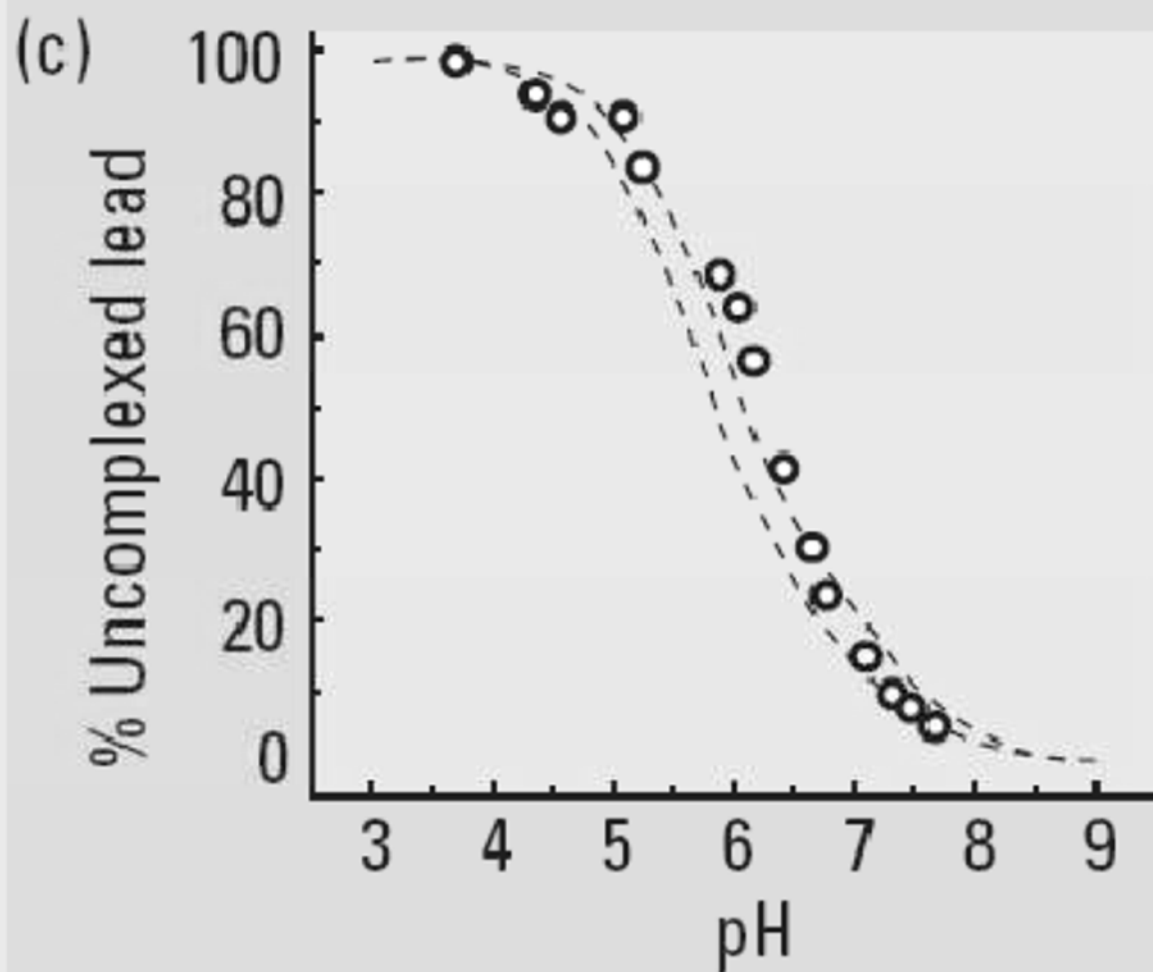
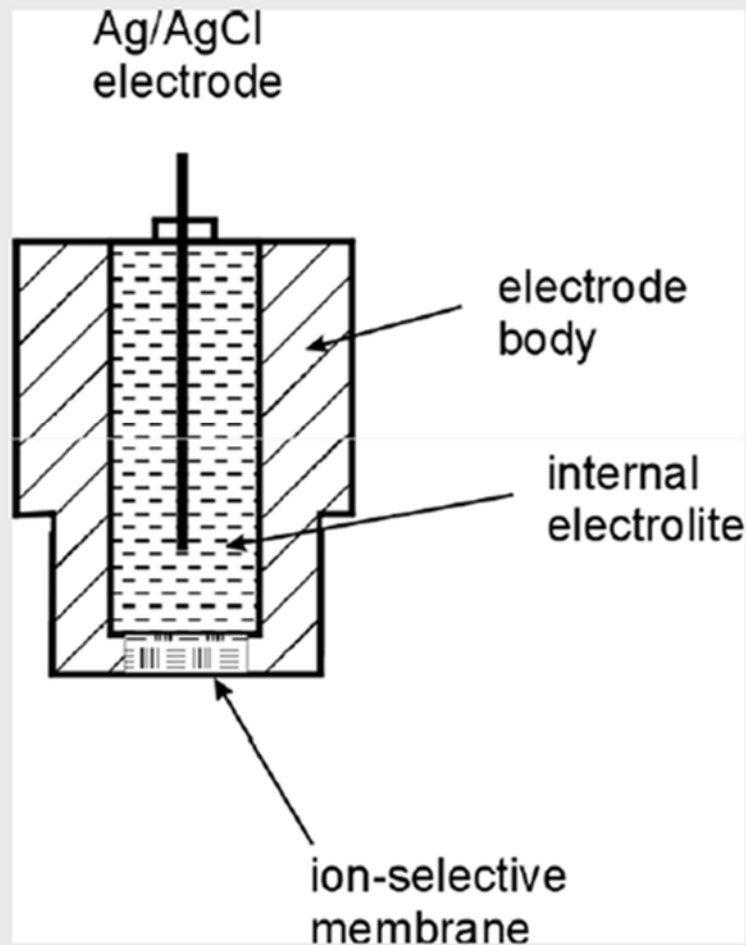


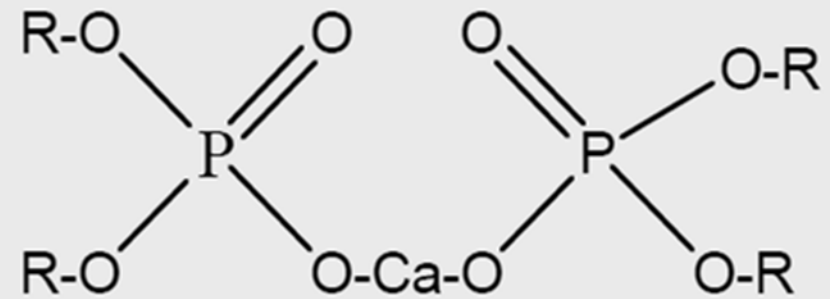
Table 7-1. Analytical Methods for Determining Fluoride in Biological Materials

Sample matrix	Preparation method	Analytical method	Sample detection limit	Percent recovery	Reference
Urine	Extract with TMCS; inject organic phase (microwave induced plasma emission detector)	GC	4 µg/L	93%	Chiba et al. 1982
	Add equal volume TISAB solution	ISE, NIOSH 8308	0.1 mg/L	95%	NIOSH 1994
	Add TMCS toluene solution; centrifuge; inject toluene layer	GC	>5 ng/mL	No data	Ikenishi et al. 1988
Biological fluids and tissue extracts (ionic and ionizable fluoride)	Absorb with calcium phosphate; centrifuge; analyze	ISE	10 µg/L	92–102%	Venkateswarlu et al. 1971
Saliva	Resuspend in TISAB buffer; analyze	ISE	No data	99.8%	Petersson et al. 1987; Schamschula et al. 1985
Biological fluids	Add TMCS toluene solution; centrifuge; inject toluene layer and analyze by measuring TMFS peak height	GC	5 ng/L	88.1–97.2%	Ikenishi et al. 1988
Biological tissues and fluids	Extraction from acidified sample as fluorosilane; reverse extraction as fluoride ion into alkaline solution	ISE with hanging drop assembly	>0.04 ng/sample	No data	Venkateswarlu 1974
Biological tissues	Sample pulverized to fine powder; irradiate with energetic beam of protons; detect gamma rays emitted	PAA	<10 ng/sample	No data	Rudolph et al. 1973
	Decomposition of sample at 700–1,000 °C (pyrohydrolytic technique)	Colorimetry	1 µg/sample	No data	Kakabadse et al. 1971
Tooth enamel	Soak teeth; decalcify in HClO ₄ ; add TISAB; analyze	ISE	No data	No data	Schamschula et al. 1982; Shida et al. 1986
Plaque	Dried; microdiffusion; analyze	ISE	No data	97%	Schamschula et al. 1985
Bone	Ash sample; dissolve in perchloric acid; add 1,2-cyclohexylenedinitrotetraacetic acid	ISE	No data	No data	Boivin et al. 1988
Hair/fingernail	Wash in diethylether; dry; decompose in NaOH	ISE	No data	94–96%	Schamschula et al. 1985
Fingernail	HMDS-facilitated diffusion overnight	ISE	No data	No data	Whitford et al. 1999a

GC = gas chromatography; HClO₄ = perchloric acid; HMDS = hexamethyldisiloxane; ISE = ion selective electrode; NaOH = sodium hydroxide; NIOSH = National Institute for Occupational Safety and Health; PAA = proton activation analysis; TISAB = total ionic strength adjustment buffer; TMCS = trimethylchlorosilane; TMFS = trimethylfluorosilane



Membrana je selektivna na analit
Ca - dialkil fosfat membranska elektroda

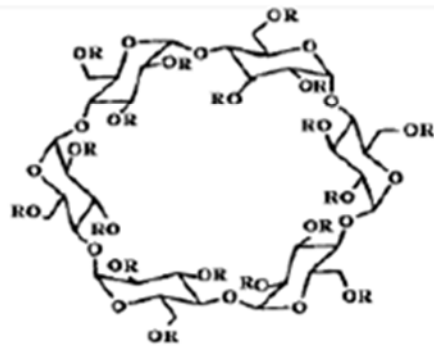


Ravnotežje raztopina - membrana:

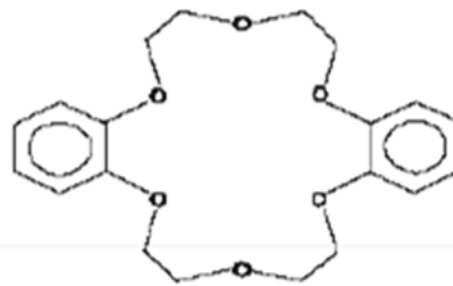


$$E_{\text{ind}} = k - 0.0592/2 \text{ pCa}$$

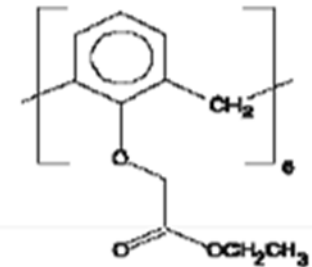
cation complexing substances



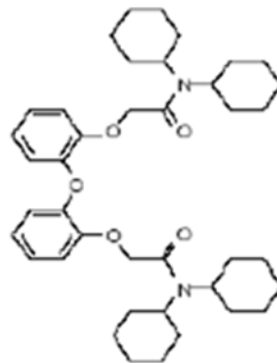
cyclodextrin



crown ether



calixarene



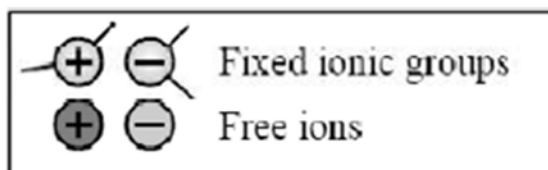
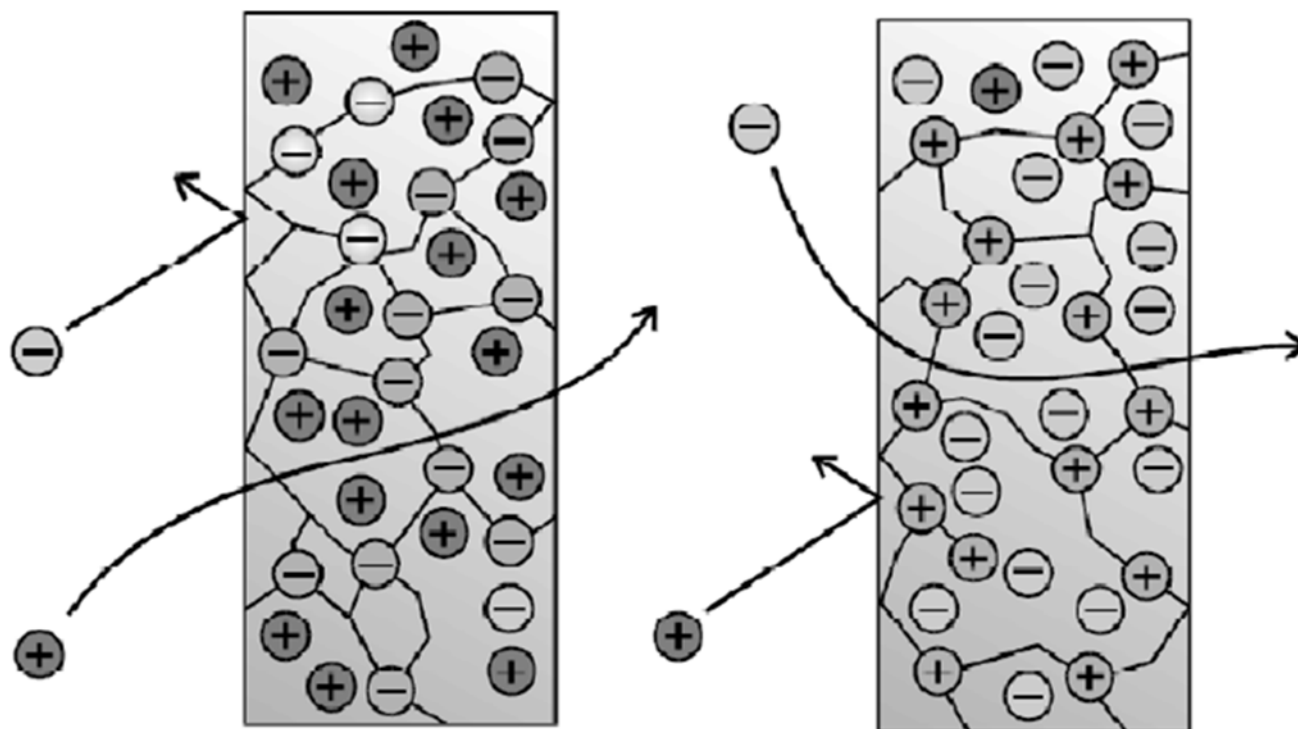
TOPA

kationska

anionska

CEM

AEM



- kationi → kationska izmenjalna membrana
- anioni → anionska izmenjalna membrana

Analyte Ion	Concentration Range, M	Interferences ^c
Ca ²⁺	10 ⁰ to 5 × 10 ⁻⁷	10 ⁻⁵ Pb ²⁺ ; 4 × 10 ⁻³ Hg ²⁺ , H ⁺ , 6 × 10 ⁻³ Sr ²⁺ ; 2 × 10 ⁻² Fe ²⁺ ; 4 × 10 ⁻² Cu ²⁺ ; 5 × 10 ⁻² Ni ²⁺ ; 0.2 NH ₃ ; 0.2 Na ⁺ ; 0.3 Tris ⁺ ; 0.3 Li ⁺ ; 0.4 K ⁺ ; 0.7 Ba ²⁺ ; 1.0 Zn ²⁺ ; 1.0 Mg ²⁺
BF ₄ ⁻	10 ⁰ to 7 × 10 ⁻⁶	5 × 10 ⁻⁷ ClO ₄ ⁻ ; 5 × 10 ⁻⁶ I ⁻ ; 5 × 10 ⁻⁵ ClO ₃ ⁻ ; 5 × 10 ⁻⁴ CN ⁻ ; 10 ⁻³ Br ⁻ ; 10 ⁻³ NO ₂ ⁻ ; 5 × 10 ⁻³ NO ₃ ⁻ ; 3 × 10 ⁻³ HCO ₃ ⁻ ; 5 × 10 ⁻² Cl ⁻ ; 8 × 10 ⁻² H ₂ PO ₄ ⁻ , HPO ₄ ²⁻ , PO ₄ ³⁻ ; 0.2 OAc ⁻ ; 0.6 F ⁻ ; 1.0 SO ₄ ²⁻
NO ₃ ⁻	10 ⁰ to 7 × 10 ⁻⁶	10 ⁻⁷ ClO ₄ ⁻ ; 5 × 10 ⁻⁶ I ⁻ ; 5 × 10 ⁻⁵ ClO ₃ ⁻ ; 10 ⁻⁴ CN ⁻ ; 7 × 10 ⁻⁴ Br ⁻ ; 10 ⁻³ HS ⁻ ; 10 ⁻² HCO ₃ ⁻ ; 2 × 10 ⁻² CO ₃ ²⁻ ; 3 × 10 ⁻² Cl ⁻ ; 5 × 10 ⁻² H ₂ PO ₄ ⁻ , HPO ₄ ²⁻ , PO ₄ ³⁻ ; 0.2 OAc ⁻ ; 0.6 F ⁻ ; 1.0 SO ₄ ²⁻
ClO ₄ ⁻	10 ⁰ to 7 × 10 ⁻⁶	2 × 10 ⁻³ I ⁻ ; 2 × 10 ⁻² ClO ₃ ⁻ ; 4 × 10 ⁻² CN ⁻ , Br ⁻ ; 5 × 10 ⁻² NO ₂ ⁻ , NO ₃ ⁻ ; 2 HCO ₃ ⁻ , CO ₃ ²⁻ , Cl ⁻ , H ₂ PO ₄ ⁻ , HPO ₄ ²⁻ , PO ₄ ³⁻ , OAc ⁻ , F ⁻ , SO ₄ ²⁻
K ⁺	10 ⁰ to 10 ⁻⁶	3 × 10 ⁻⁴ Cs ⁺ ; 6 × 10 ⁻³ NH ₄ ⁺ , Tl ⁺ ; 10 ⁻² H ⁺ ; 1.0 Ag ⁺ , Tris ⁺ ; 2.0 Li ⁺ , Na ⁺
Water Hardness (Ca ²⁺ + Mg ²⁺)	10 ⁻³ to 6 × 10 ⁻⁶	3 × 10 ⁻⁵ Cu ²⁺ , Zn ²⁺ ; 10 ⁻⁴ Ni ²⁺ ; 4 × 10 ⁻⁴ Sr ²⁺ ; 6 × 10 ⁻⁵ Fe ²⁺ ; 6 × 10 ⁻⁴ Ba ²⁺ ; 3 × 10 ⁻² Na ⁺ ; 0.1 K ⁺

Namen	Način	Metoda	Primer
Analiza	Direktna potenciometrija	Umerjanje s standardi, standardni dodatek, klasični in pretočni načini.	Merjenje pH, aktivnosti ionov (pI), redoks potenciala
	Titracije	Množino analita določimo s spremljanjem potenciala pri kontroliranem dodajanju titranta.	Titracije kislin-baz, redoks titracije, obarjalne in kompleksometrične titracije
Bazične raziskave	Ravnotežje	Pridobivanje termodinamskih podatkov iz direktnih meritev ali iz titracijskih krivulj.	Merjenje E^0 , γ , K_a , K_{sp} , K_f , ΔG^0 , ΔH^0 , ΔS^0
	Kinetika	Študij hitrosti reakcij (kinetike).	Merjenje konstant hitrosti (do 10^8 L/mol)

- D.A. Skoog, F.J. Holler, S.R. Crouch: *Principles of Instrumental Analysis*, 6th Edition, Section IV, Chapters 22-23, Thomson Brooks/Cole, Belmont, CA, 2007.
- R.G. Bates, *Determination of pH, Theory and Practice*, John Wiley, New York 1973.
- H. B. Kristensen, A. Salomon, and G. Kokholm: 'International pH Scales and Certification of pH', *Anal. Chem.*, **63**(1991)885 A.