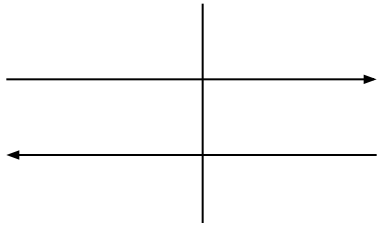
Ионометрия

Потенциометрия

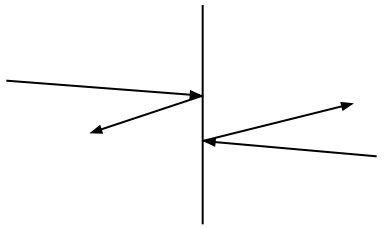
$$E = f(t)$$

Граница раздела фаз

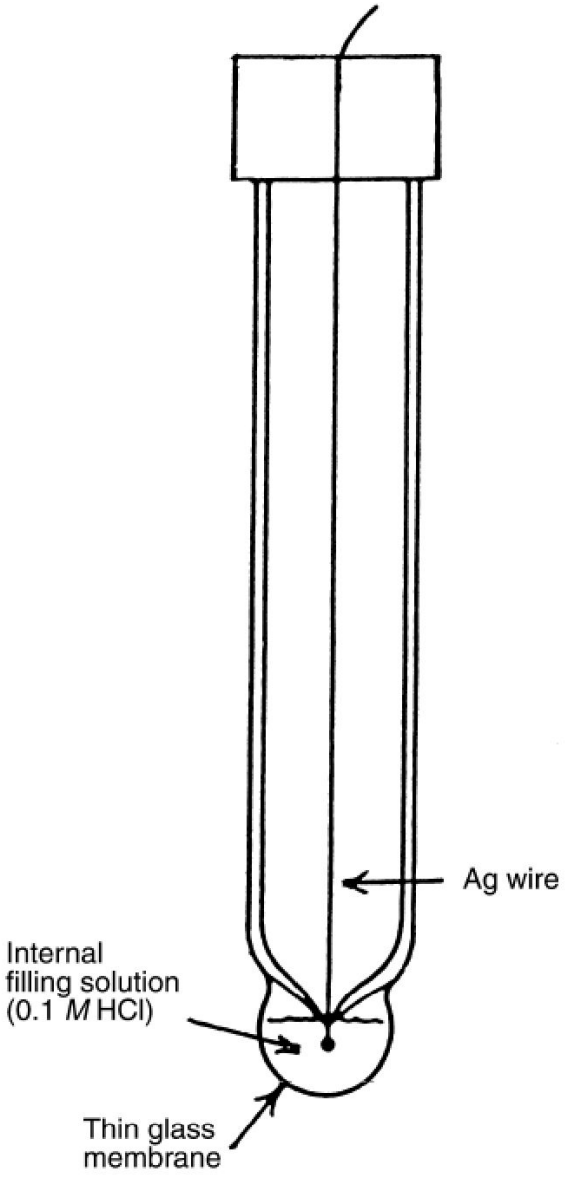
Неполяризуемая



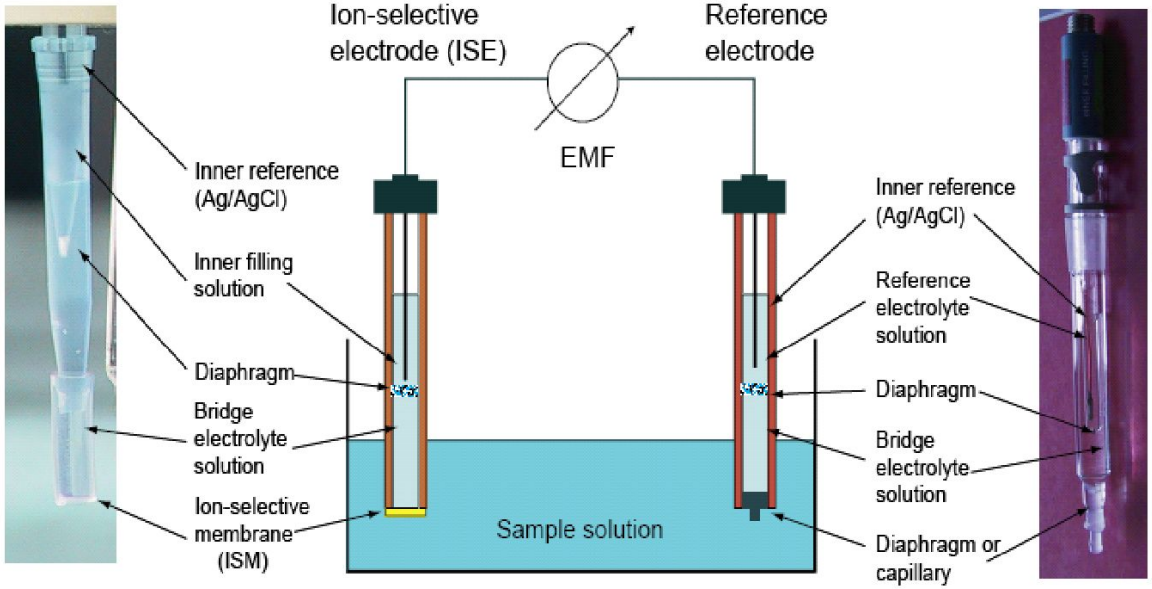
Поляризуемая

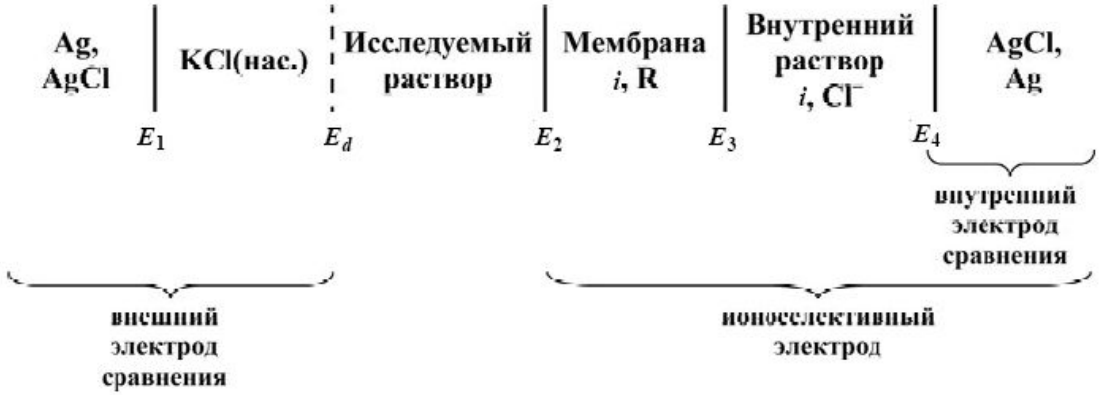


Стеклянный pH электрод



Измерительная ячейка





Условия измерения:

1. I=0 A
2. Входное сопротивление ~ 10^{12}-10^{14} Ом
3. Стабильность работы электрода сравнения

Мембранные электроды

Жидкие мембраны→ пластифицированные мембраны:

- Полимер (ПВХ)

…матрица, основа

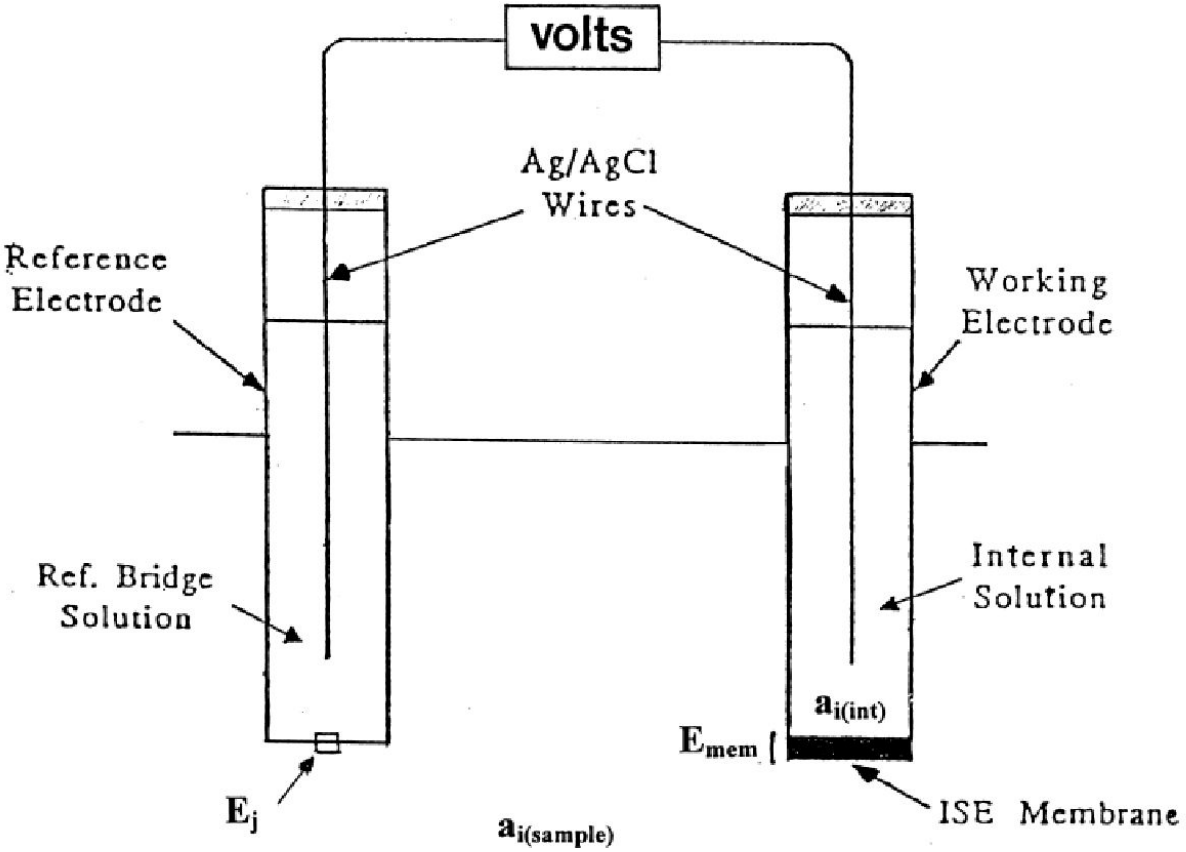
- Пластификатор (о-НФОЭ)

…барьер для ионов

- Переносчик

…транспорт - селективность

Мембранный электрод



$$E = -\frac{\Delta G}{nF} = \frac{RT}{nF}\ln\left(\frac{a_{i,sample}}{a_{i,\text{int}.so\ln}}\right)$$

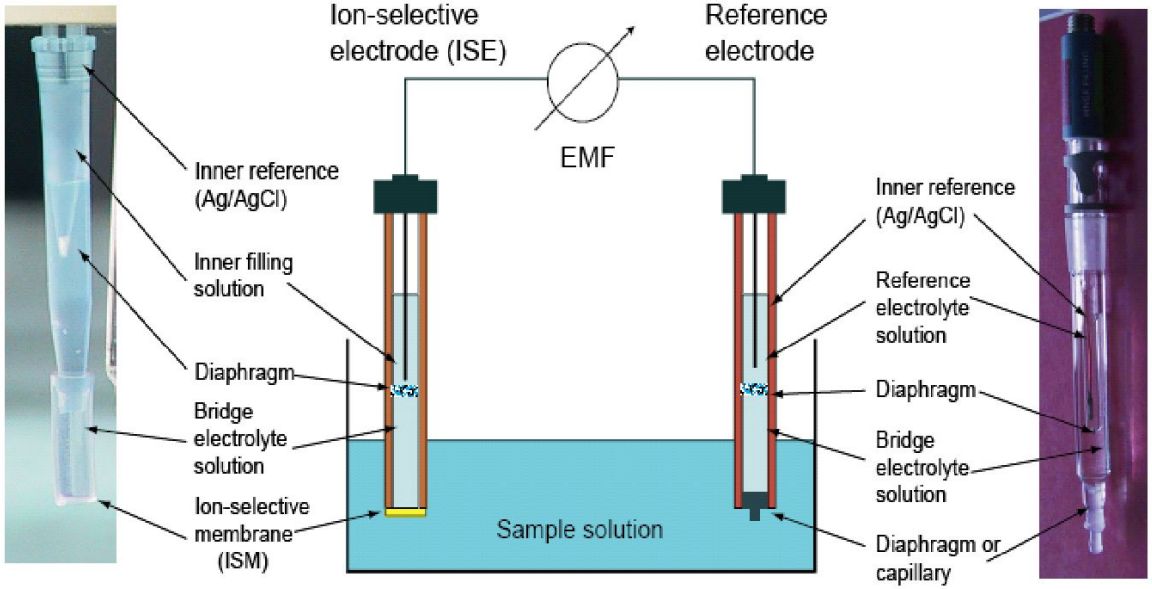
Межфазный потенциал

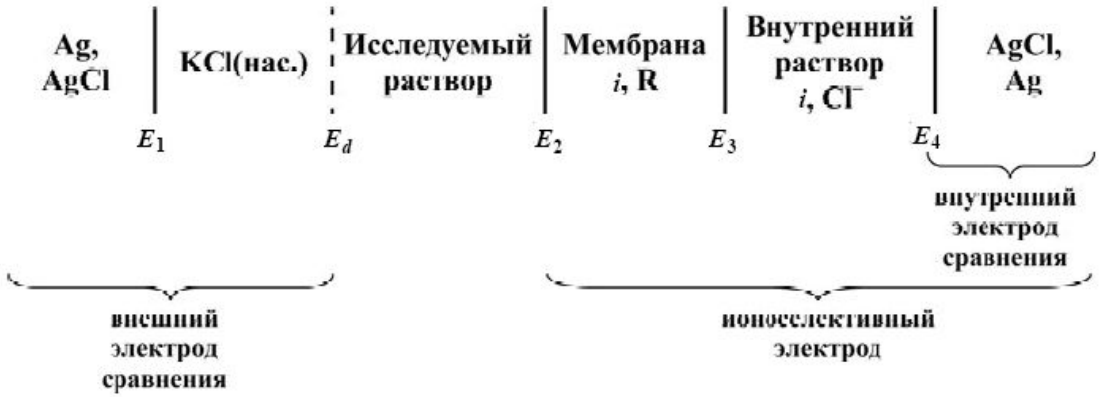
$$\overline{\mu}_i^{\alpha} = \mu_i^{\alpha} + z_i F \phi^{\alpha}$$

$$E = E_0 + \frac{RT}{zF} \ln\left(a_i + \sum_j k_{ij} a_j^{z_i / z_j} \right)$$

Nikolsky-Eisenman

Ионселективный электрод (ИСЭ)

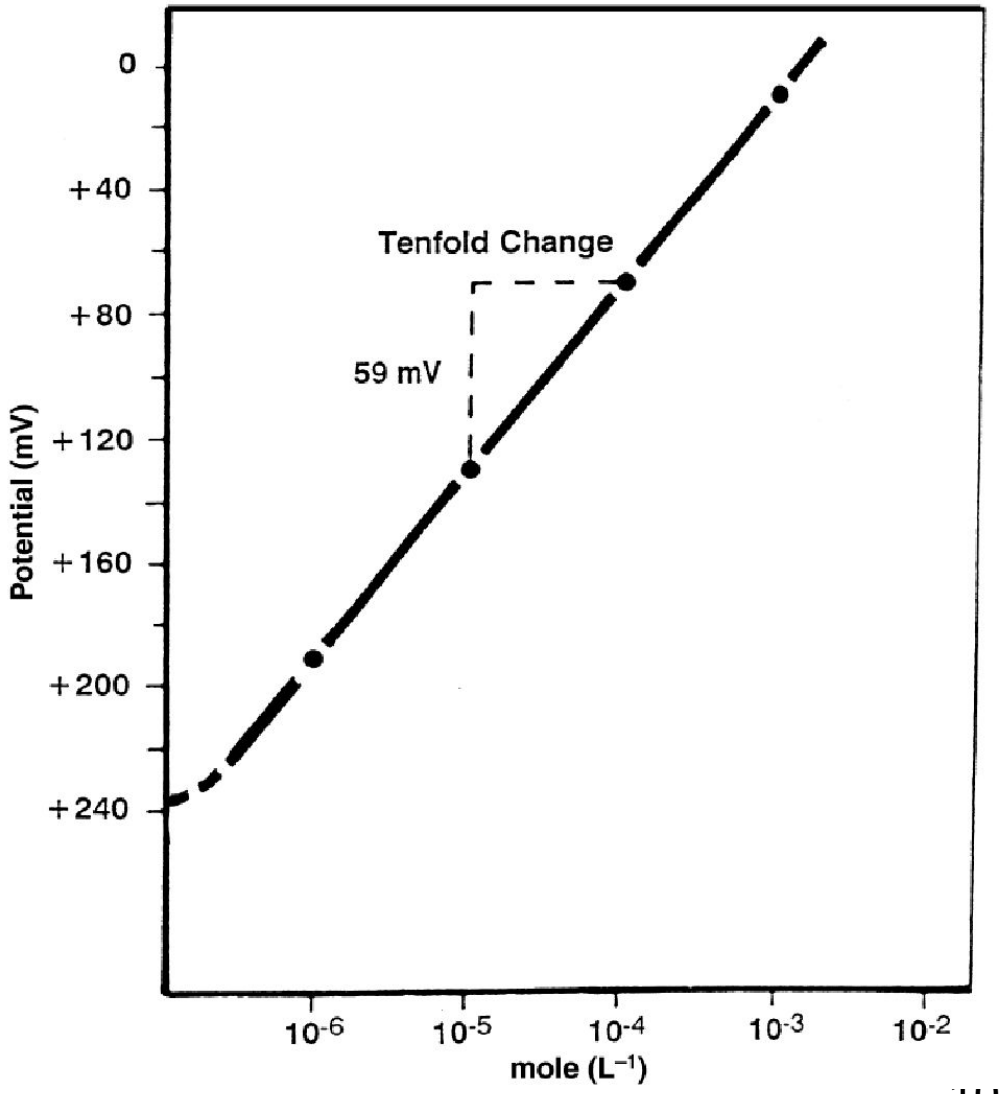




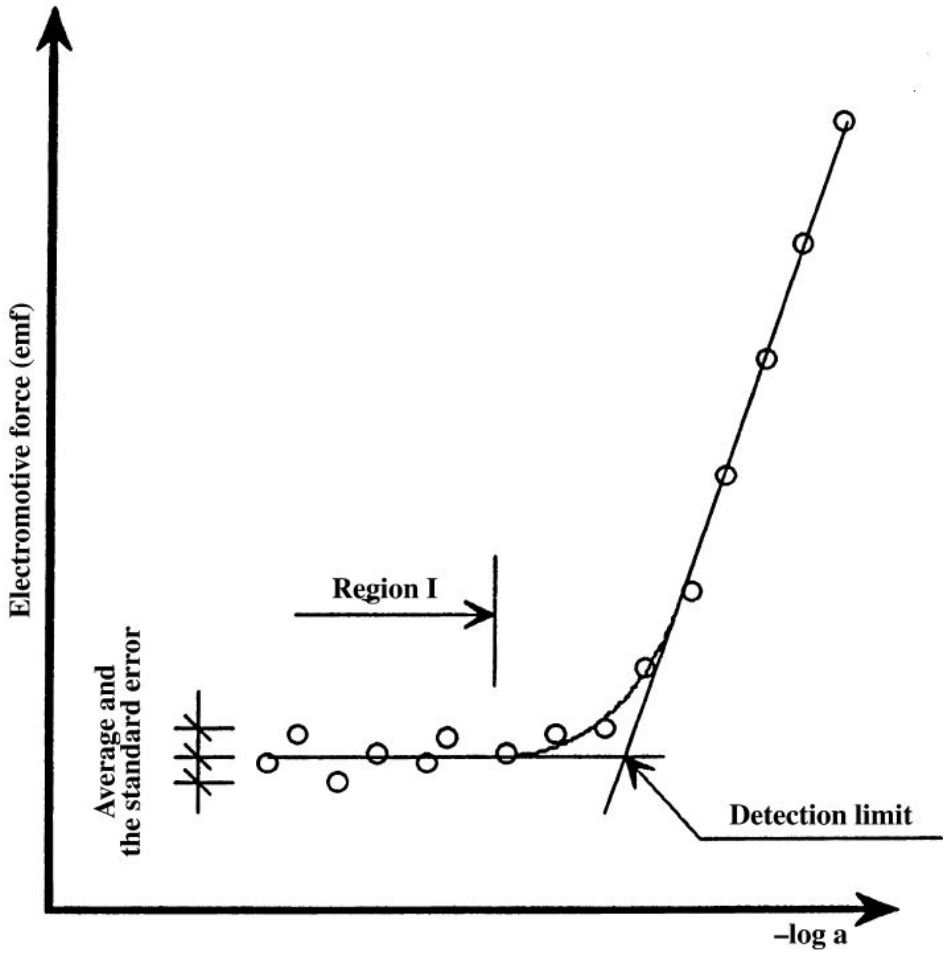
Условия измерения:

1. I=0 A
2. Входное сопротивление ~ 10^{12}-10^{14} Ом
3. Стабильность работы электрода сравнения

Калибровочный график ИСЭ



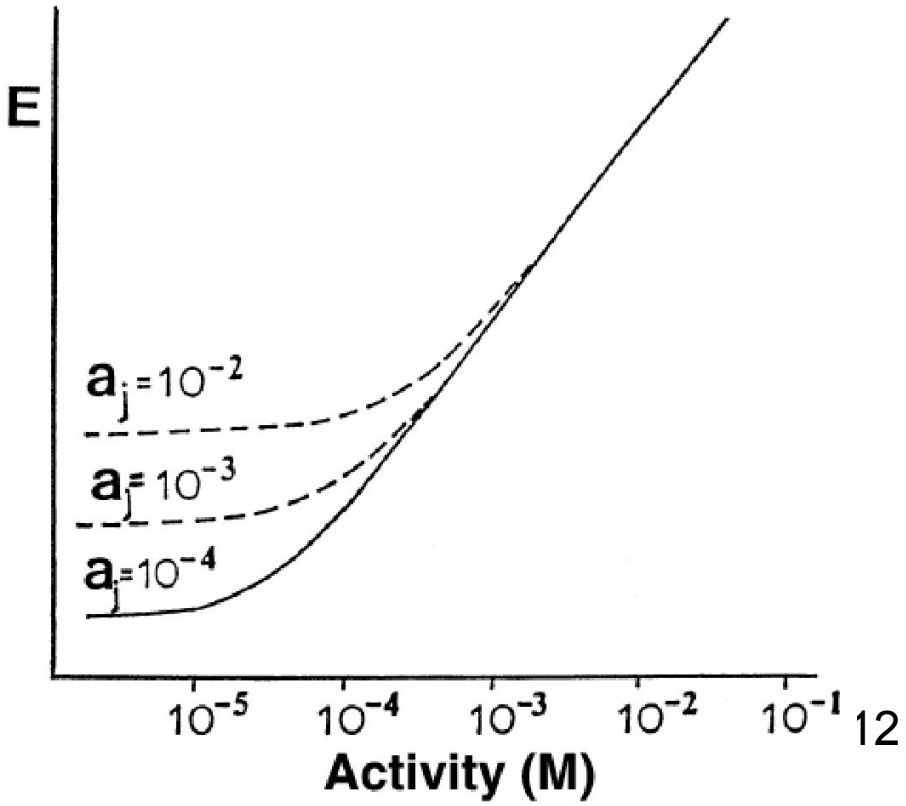
Предел обнаружения ИСЭ



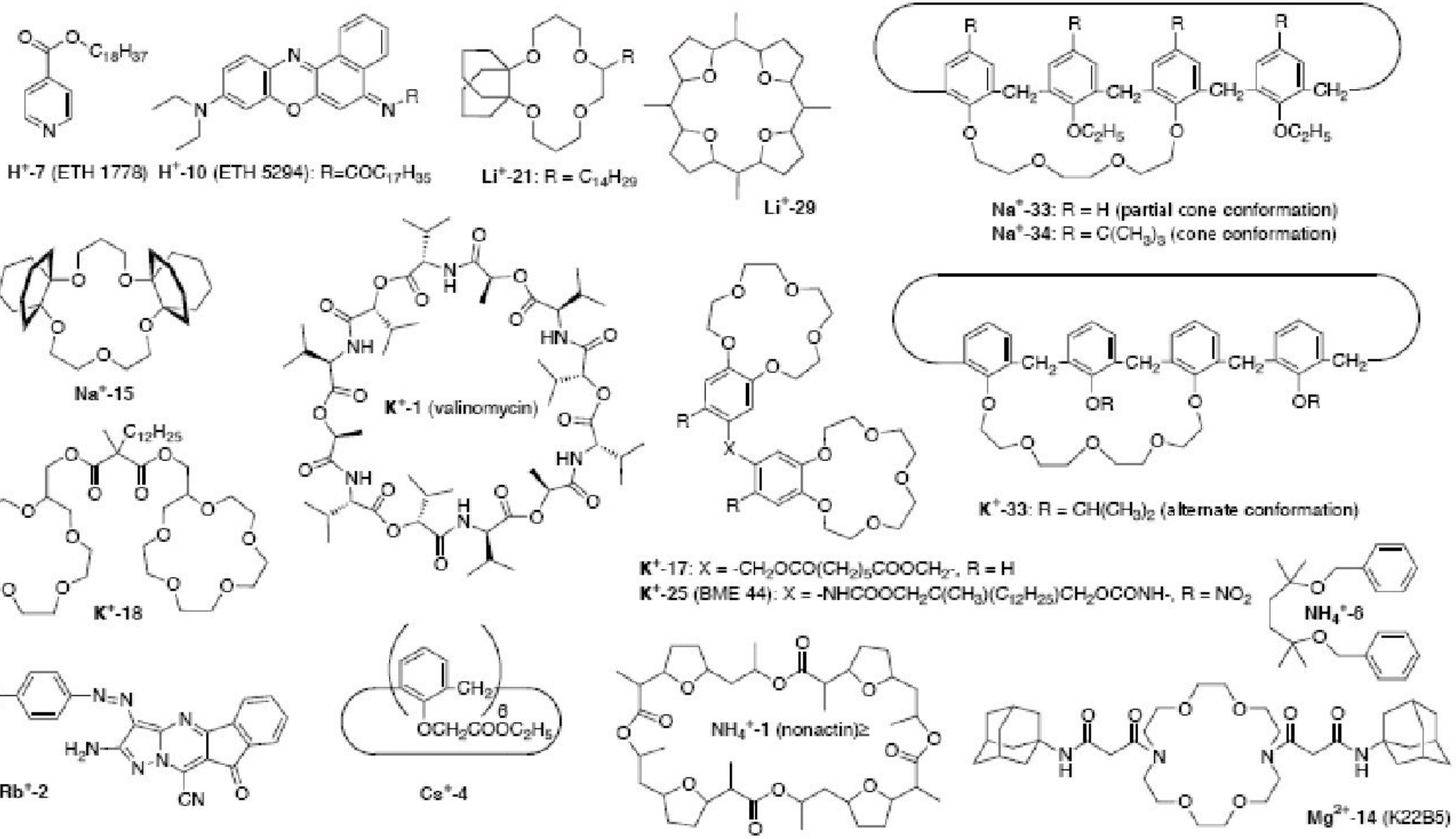
Предел обнаружения ИСЭ

в присутствии мешающих ионов

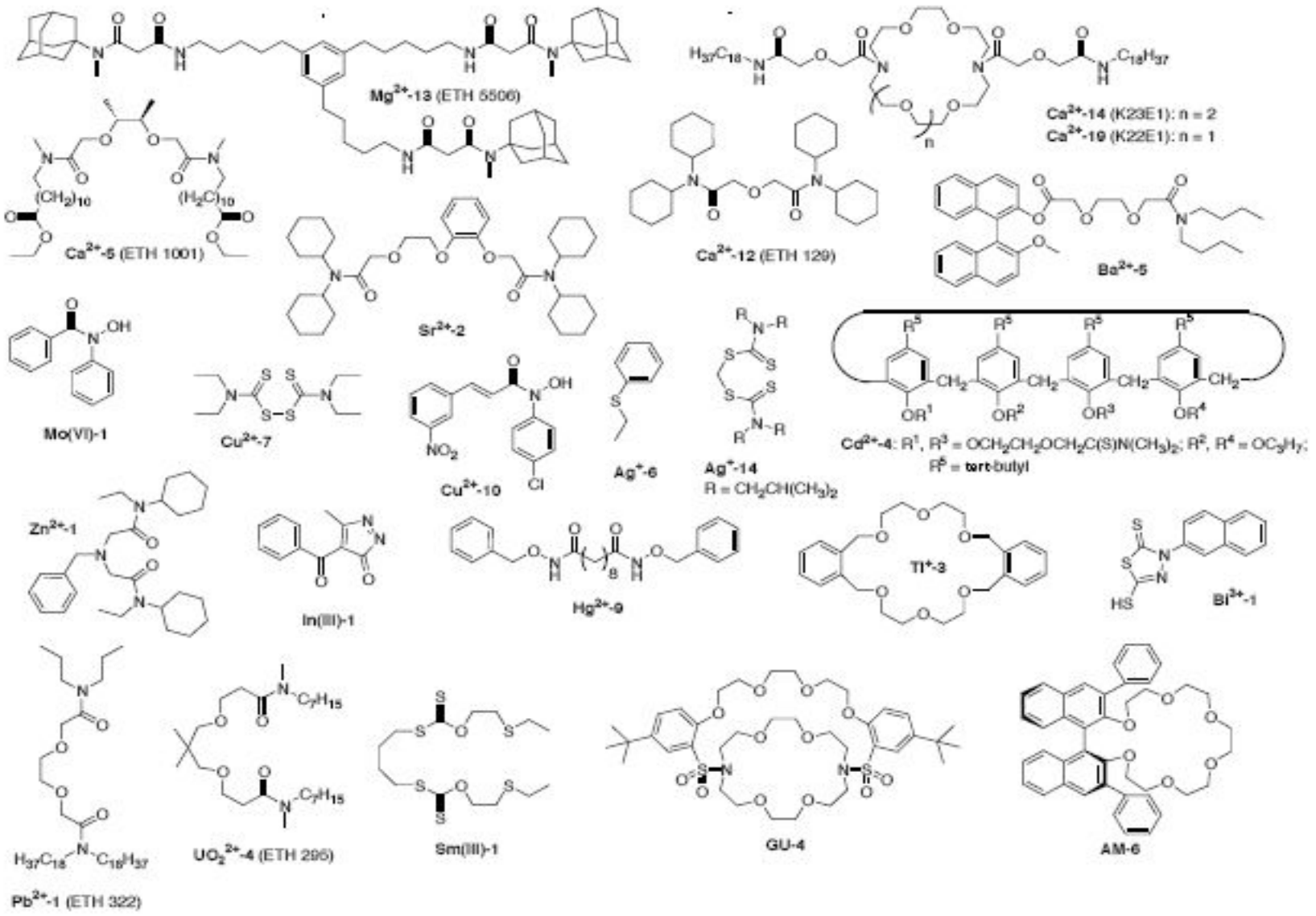
$$a_{i,\min} = k_{ij} a_j^{z_i / z_j}$$



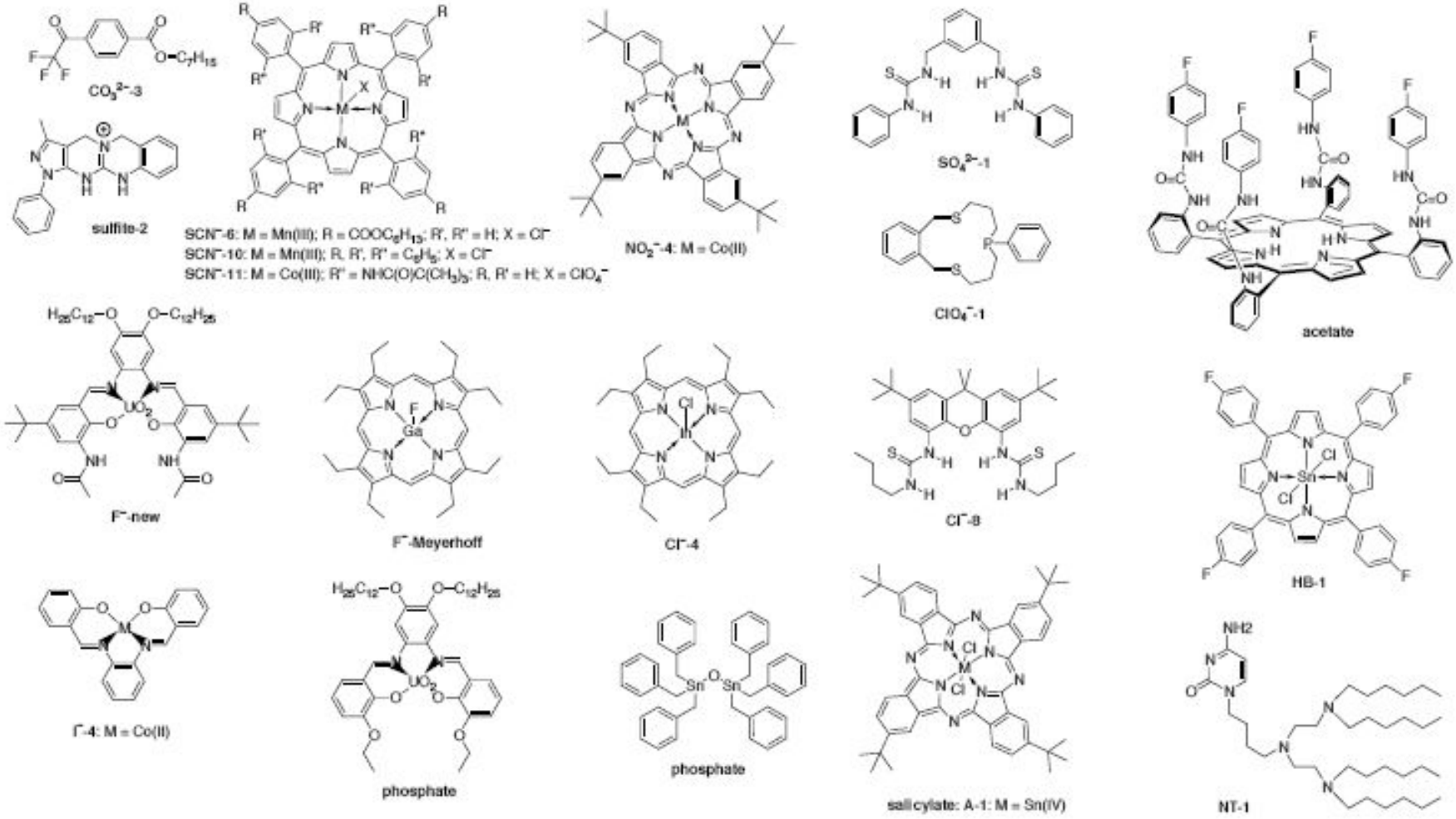
Ионофоры на катионы



Ионофоры на катионы (продолжение)



Ионофоры на анионы



Характеристики ИСЭ

- **Тангенс углового коэффициента электродной функции**

«Slope» ≡ S = 2,303RT/ zF = 59.2 мВ/ра (для однозарядных ионов; z=1)

- **Диапазон линейности**

…обычно 10^{-1}-10^{-5} М

- **Предел обнаружения**

…обычно 10^{-6} -10^{-7} М

- **Время отклика**

…несколько секунд – минут

- **Обратимость отклика**

…возможен т.н. эффект «памяти»

- **Селективность**

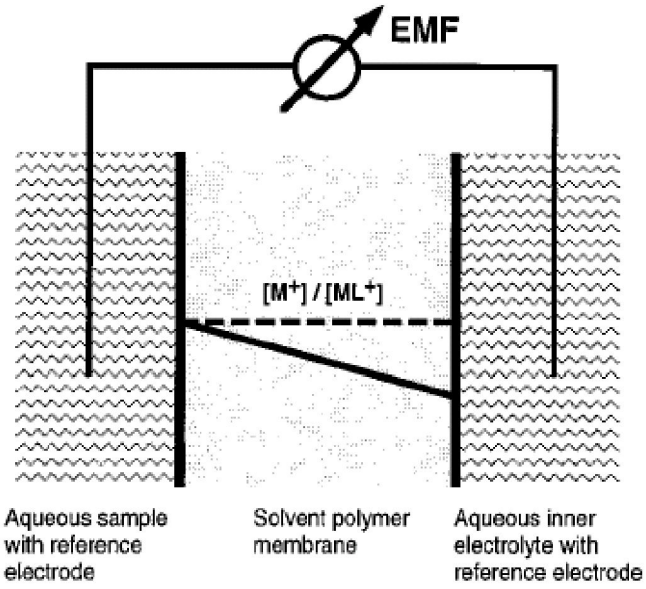
…хорошо, если не мешают 10^{2}-10^{4} количества посторонних ионов

- **Рабочий диапазон pH**

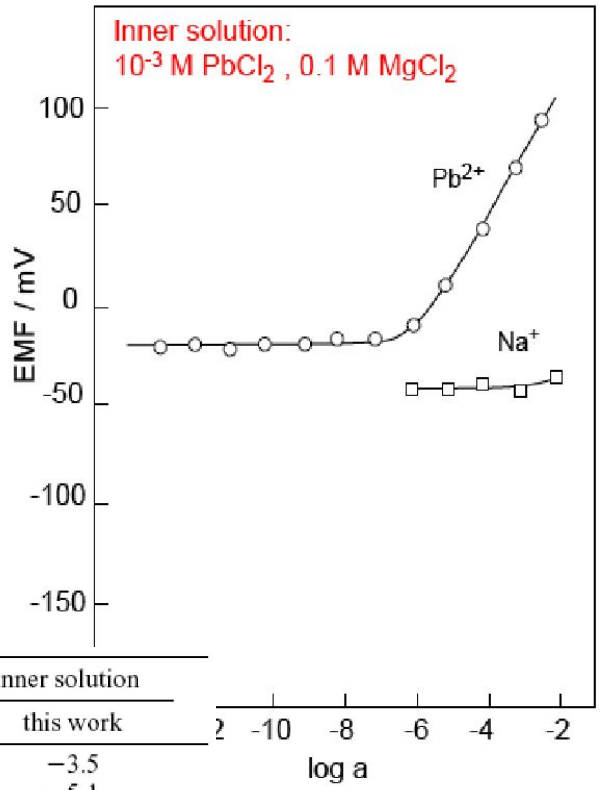
…определяется природой мембранных компонентов и/или определяемых соединений

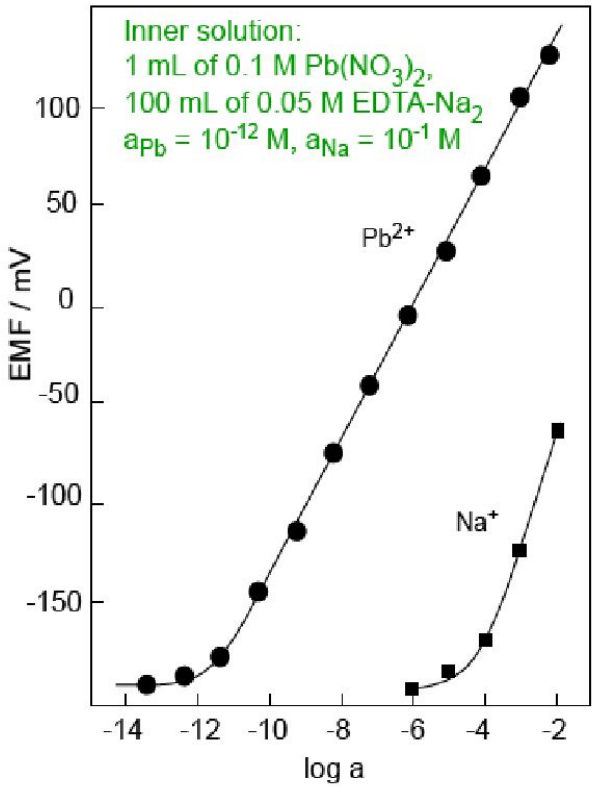
Понижение предела обнаружения ИСЭ

- понижение активности иона во внутреннем растворе
- создание трансмембранного градиента потенциала (иммобилизация ионофора)



Изменение состава внутреннего раствора:





T. Sokalski, A. Ceresa, T. Zwickl, E. Pretsch, J. Am. Chem. Soc. **1997**, 46, 11347.

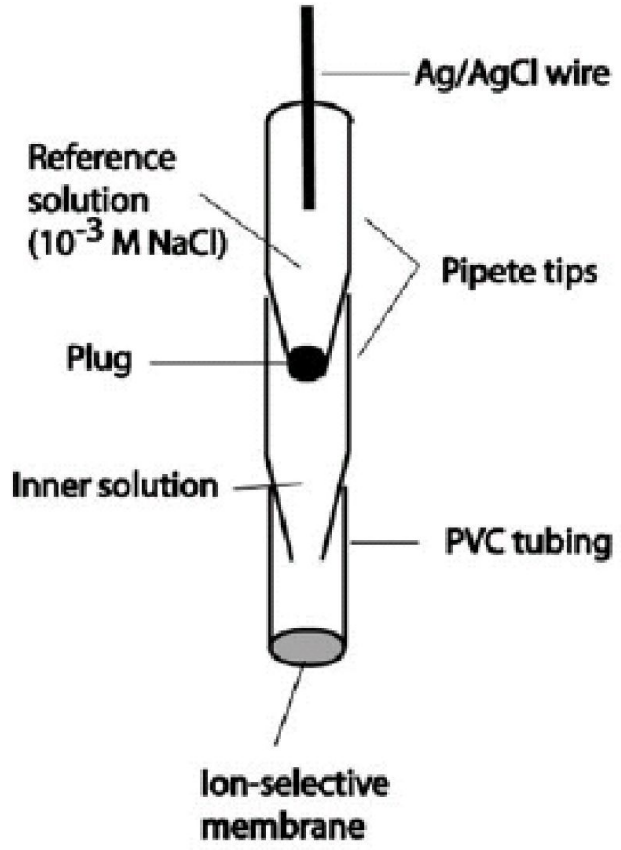
	log K^{pot}_{PbM} for Pb^{2+} ISE with inner solution	
ion M	conventional	this work
H^+	−2.2	−3.5
Li^+	−2.7	−5.1
Na^+	−2.2	−4.7
K^+	−2.2	−4.1
NH_4^+	−2.5	−4.1
Mg^{2+}	−3.6	−9.4
Ca^{2+}	−4.0	−8.6
Cd^{2+}	0.9	0.4
Sr^{2+}	−4.2	−6.7
Ba^{2+}	−4.1	−6.0
Mn^{2+}	−4.1	−5.8
Co^{2+}	−4.3	−6.3
Ni^{2+}	−4.2	−5.9
Cu^{2+}	−0.5	−0.4
Zn^{2+}	−3.7	−5.0

Примеры разработанных ИСЭ

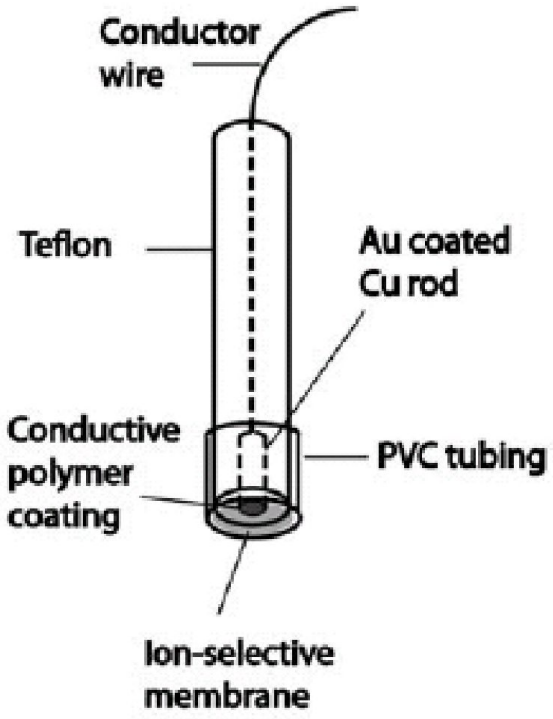
Analyte ion	Det. limit [M]	Selected selectivity coefficients log K_{ij}^{pot}					
Na^+	3×10^{-8}	H^+	-4.8	K^+	-2.7	Ca^{2+}	-6.0
K^+	5×10^{-9}	Na^+	-4.2	Mg^{2+}	-7.6	Ca^{2+}	-6.9
Cs^+	8×10^{-9}	Na^+	-4.7	K^+	-2.9	Mg^{2+}	-8.7 Ca^{2+} -8.5
NH_4^+	2×10^{-8}						
Ca^{2+}	3×10^{-9}–10^{-11}	H^+	-4.9	Na^+	-4.8	Mg^{2+}	-5.3
Ag^+	$1–2 \times 10^{-9}$	H^+	-10.2	Na^+	-10.3	Ca^{2+}	-11.3
Pb^{2+}	10^{-9}– 6×10^{-11}	H^+	-5.6	Na^+	-5.6	Mg^{2+}	-13.8
Cd^{2+}	10^{-10}	H^+	-6.7	Na^+	-8.4	Mg^{2+}	-13.4
Cu^{2+}	10^{-8}–10^{-9}	H^+	-0.7	Na^+	<-5.7	Mg^{2+}	-6.9
Vitamin B1	10^{-8}						
ClO_4^-	2×10^{-8}	OH^-	-5.0	Cl^-	-4.9	NO_3^-	-3.1
I^-	2×10^{-9}	OH^-	-1.7				

cf. E. Bakker, E. Pretsch, TrAC, Trends Anal. Chem. **2005**, *24*, 199.

Внутреннее заполнение и твердый контакт



Liquid-contact electrode



Solid-contact electrode

Твердоконтактные ИСЭ (solid-contact ISE)

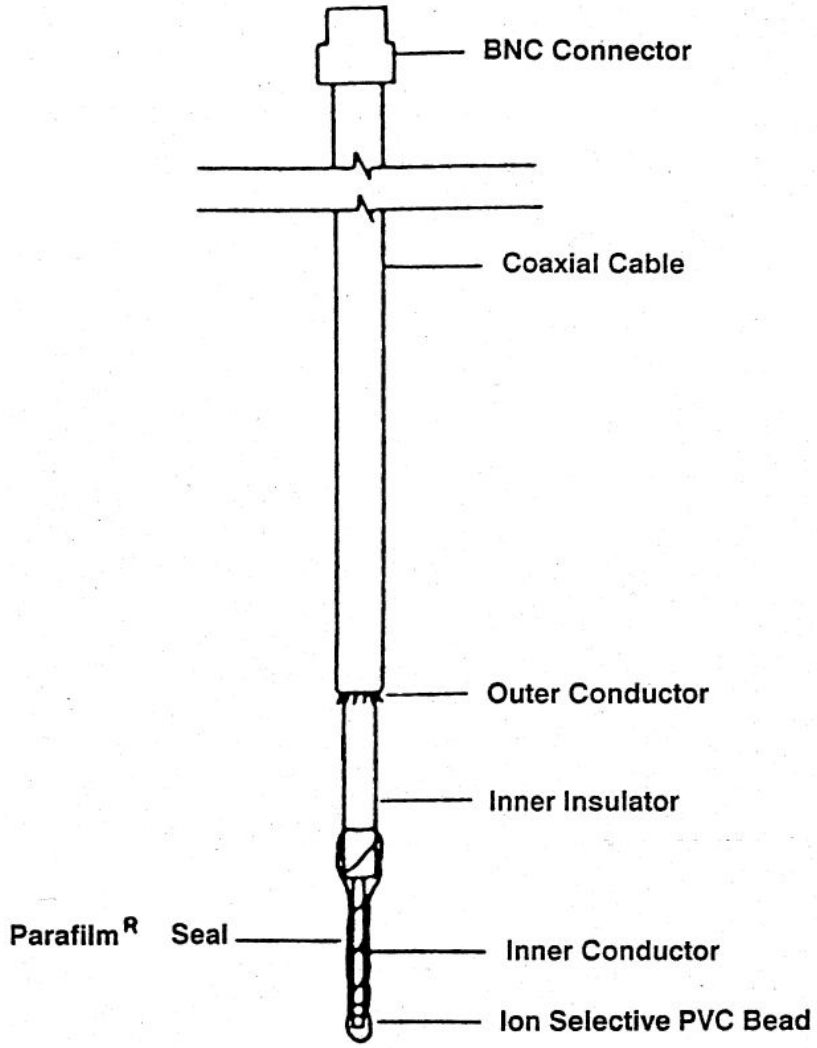
Твердотельные ИСЭ (all solid state ISE)

TABLE 5-1 Characteristics of Solid-State Crystalline Electrodes[a]

Analyte Ion	Concentration Range (M)	Major Interferences
Br^-	10^0 to 5×10^{-6}	CN^-, I^-, S^{2-}
Cd^{2+}	10^{-1} to 1×10^{-7}	Fe^{2+}, Pb^{2+}, Hg^{2+}, Ag^+, Cu^{2+}
Cl^-	10^0 to 5×10^{-5}	CN^-, I^-, Br^-, S^{2-}
Cu^{2+}	10^{-1} to 1×10^{-8}	Hg^{2+}, Ag^+, Cd^{2+}
CN^-	10^{-2} to 1×10^{-6}	S^{2-}
F^-	Saturated to 1×10^{-6}	OH^-
I^-	10^0 to 5×10^{-8}	
Pb^{2+}	10^{-1} to 1×10^{-6}	Hg^{2+}, Ag^+, Cu^{2+}
Ag^+/S^{2-}	Ag^+: 10^0 to 1×10^{-7} S^{2-}: -10^0 to 1×10^{-7}	Hg^{2+}
SCN^-	10^0 to 1×10^{-6}	I^-, Br^-, CN^-, S^{2-}

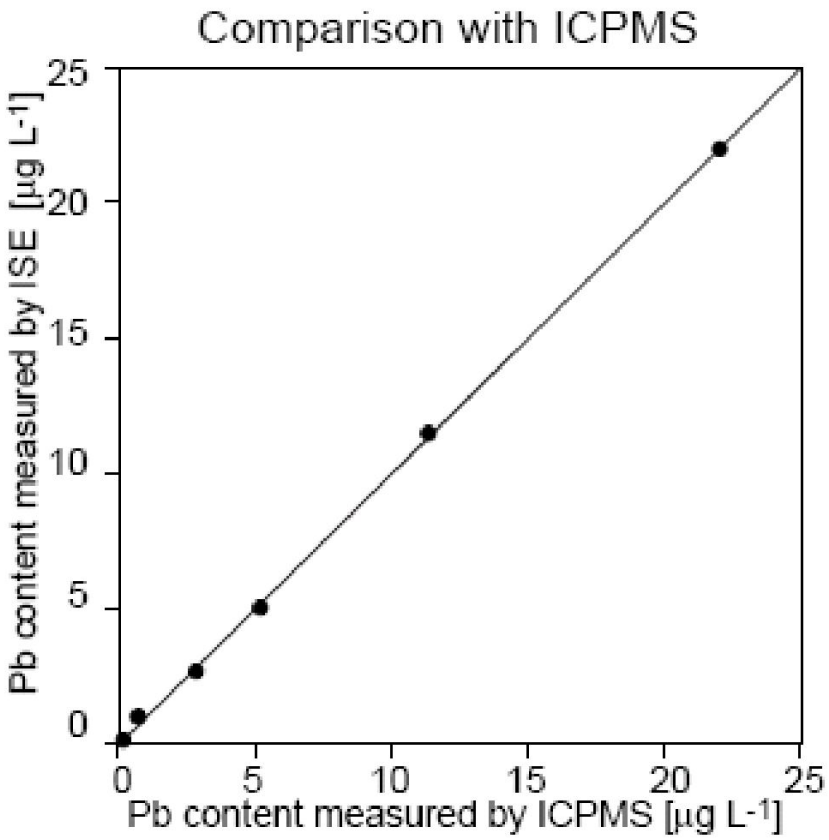
ИСЭ типа «покрытая проволока» (coated wire ISE)

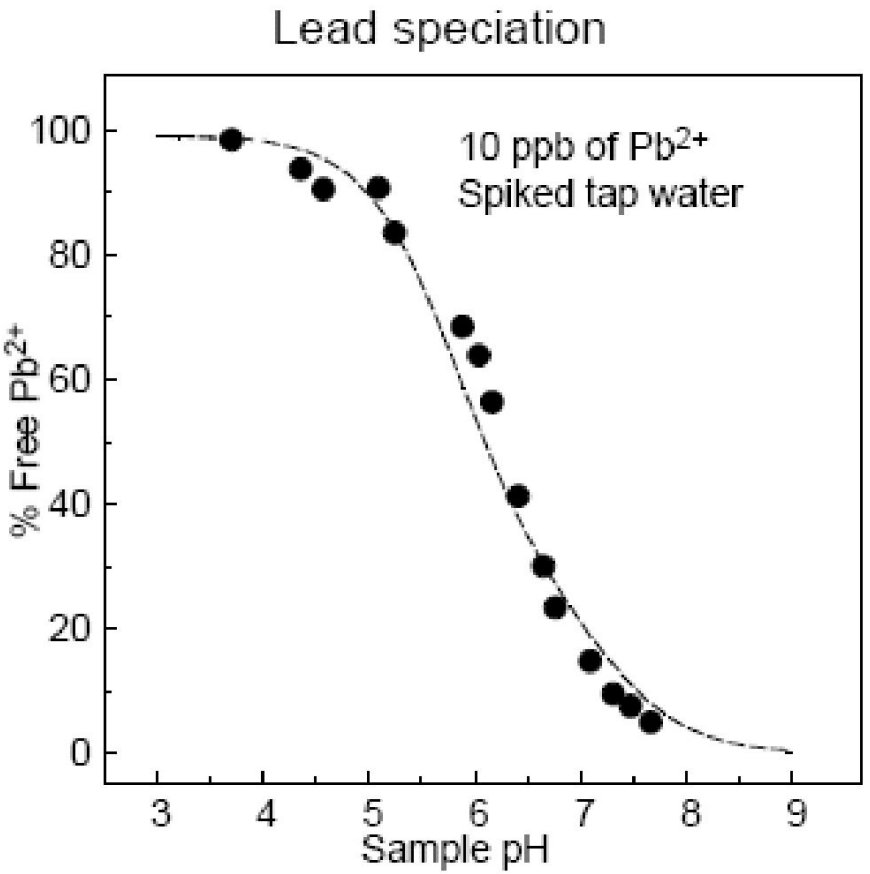
$10^{-1} \div 10^{-5}$ M



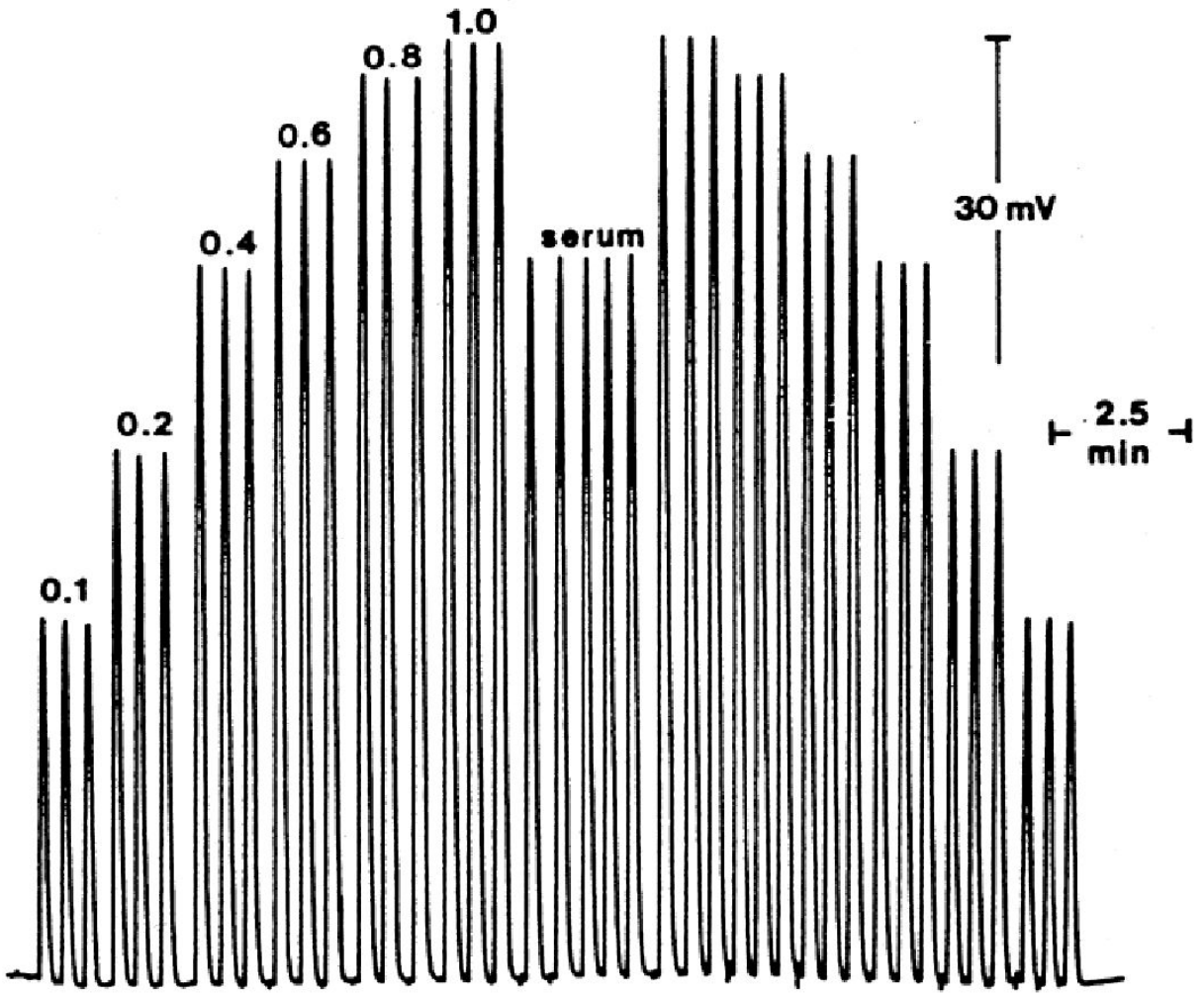
Примеры использования

Определение свинца в питьевой воде – сравнение с ИСП-МС

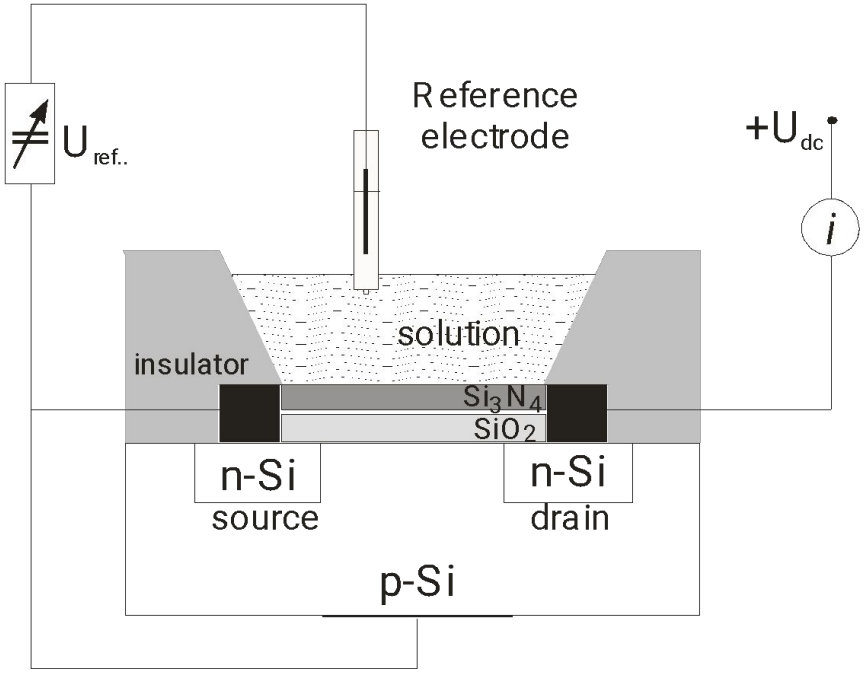




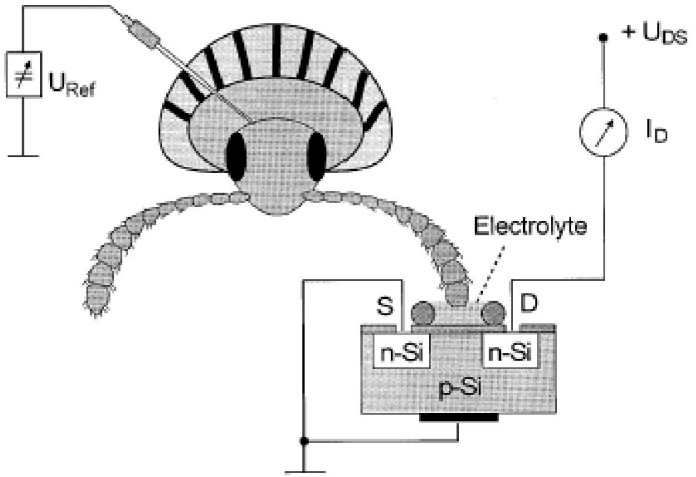
Калий в сыворотке крови (ПИА)



Field-effect transistor

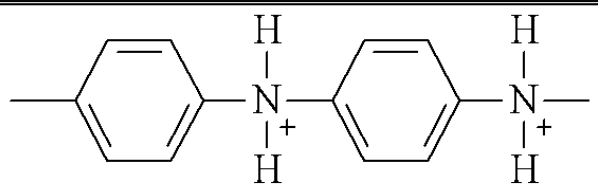
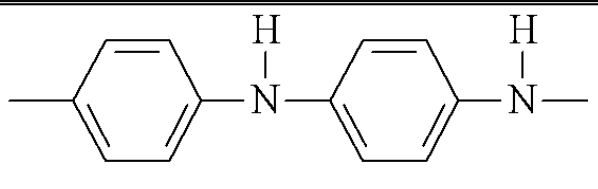
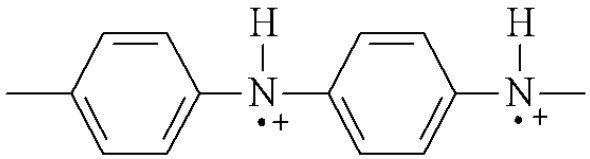
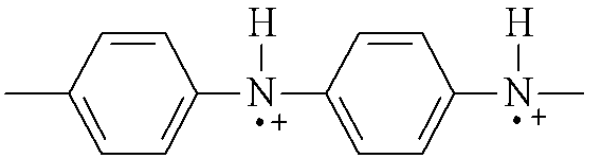
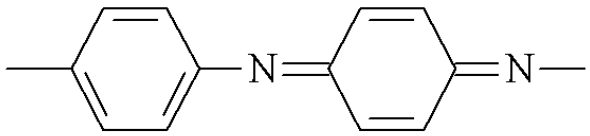
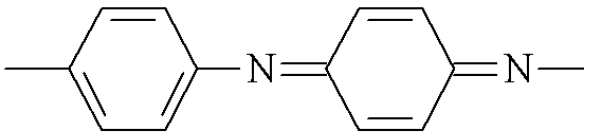


Field-effect transistor



Polyaniline

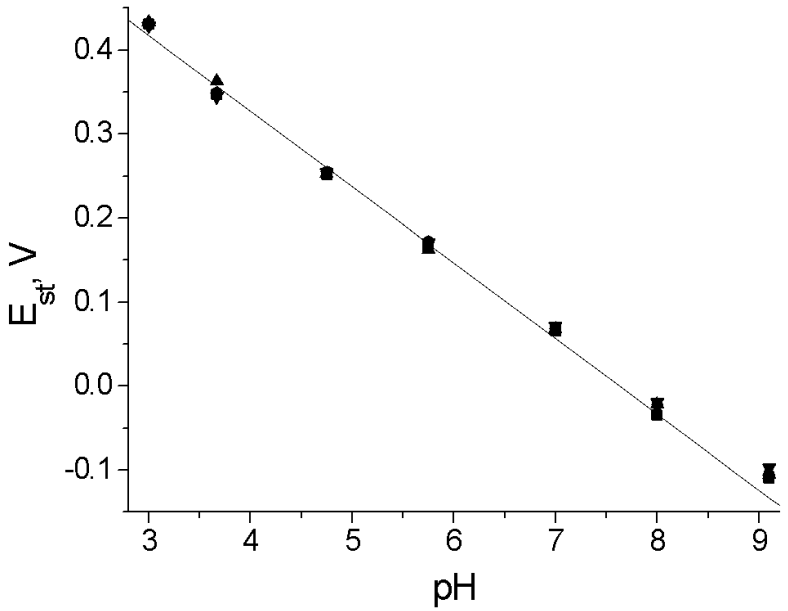
$\frac{[H]^+}{e}$

	pH < 1	pH > 1	pH<1	pH>1
leucoemeraldine			1	0
emeraldine				
pernigraniline			2	2

Polyaniline: *an advanced pH transducer*

7 different electrodes:

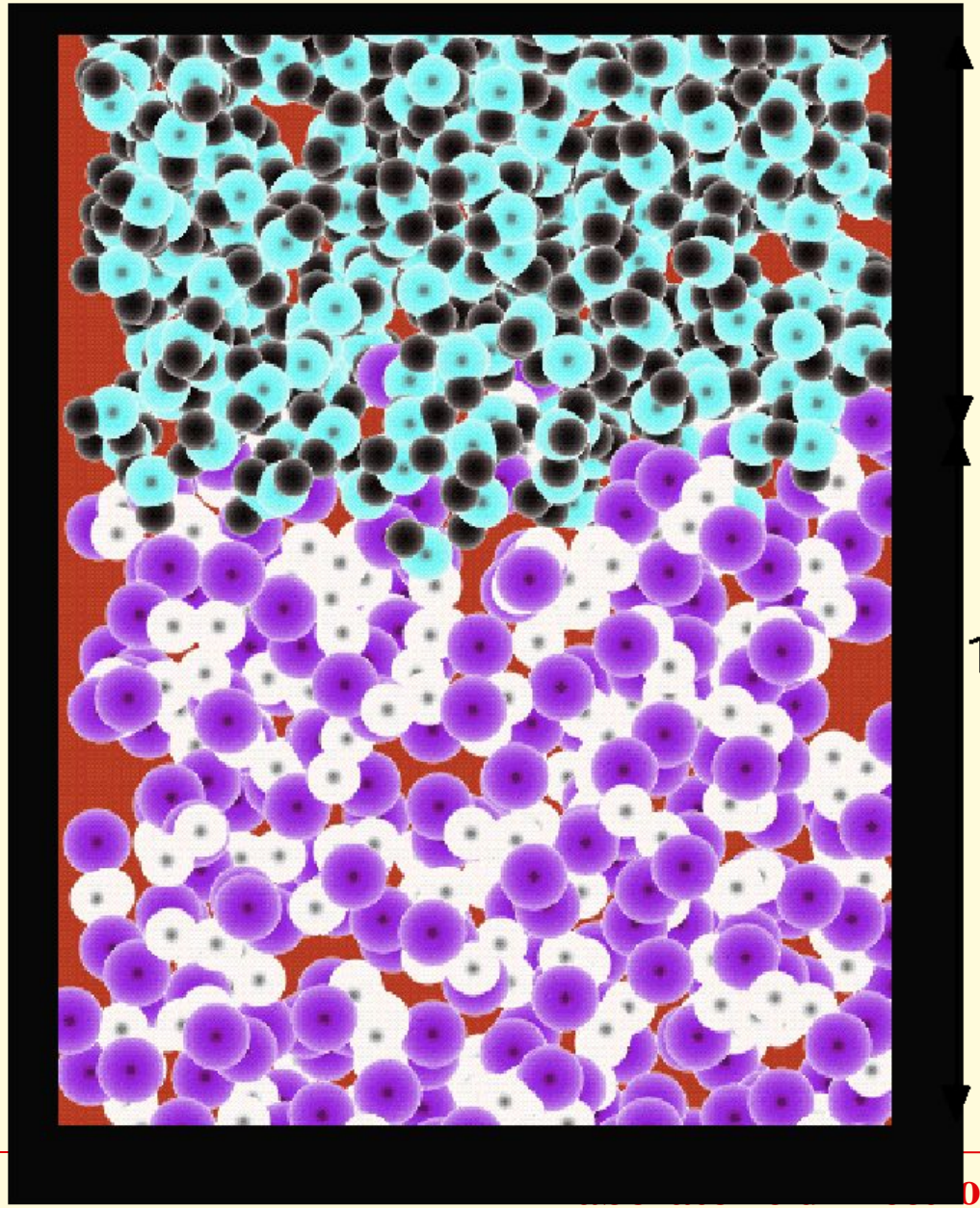
Tan(ϕ) ≅ 90 mV/pH



A.A. Karyakin, M. Vuki, L.V. Lukachova, E.E. Karyakina, A.V. Orlov, G.P. Karpacheva, J. Wang. *Analytical Chemistry* **71** (1999) 2534-40

Граница раздела несмешивающихся жидкостей (liquid|liquid interface)

Water|1,2-DCE



H_2O

1,2-dichlororethane

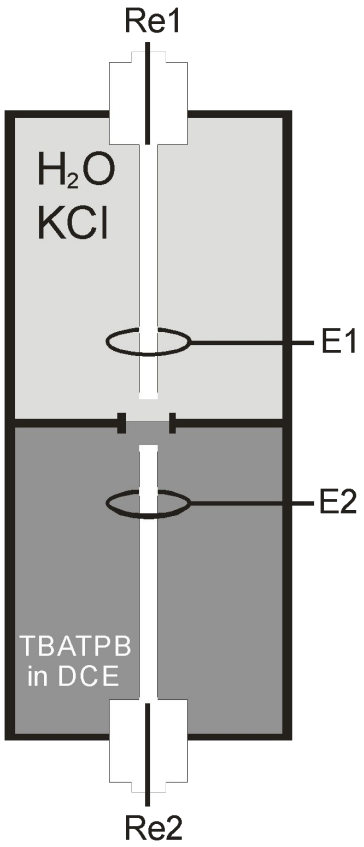
Private communication:
Prof. I. Benjamin

The lower the miscibility the larger the interfacial tension and the thinner the interfacial thickness

Solvent	Solubility In water/M	Water Solubility/M	Interfacial Tension/ $mN \cdot m^{-1}$
Nitrobenzene	$8.5 \cdot 10^{-2}$	0.11	25
1,2 dichloroethane	$1.5 \cdot 10^{-2}$	0.2	27.5
Nitrophenyl-octyl ether	$2.0 \cdot 10^{-6}$	$4.6 \cdot 10^{-2}$	

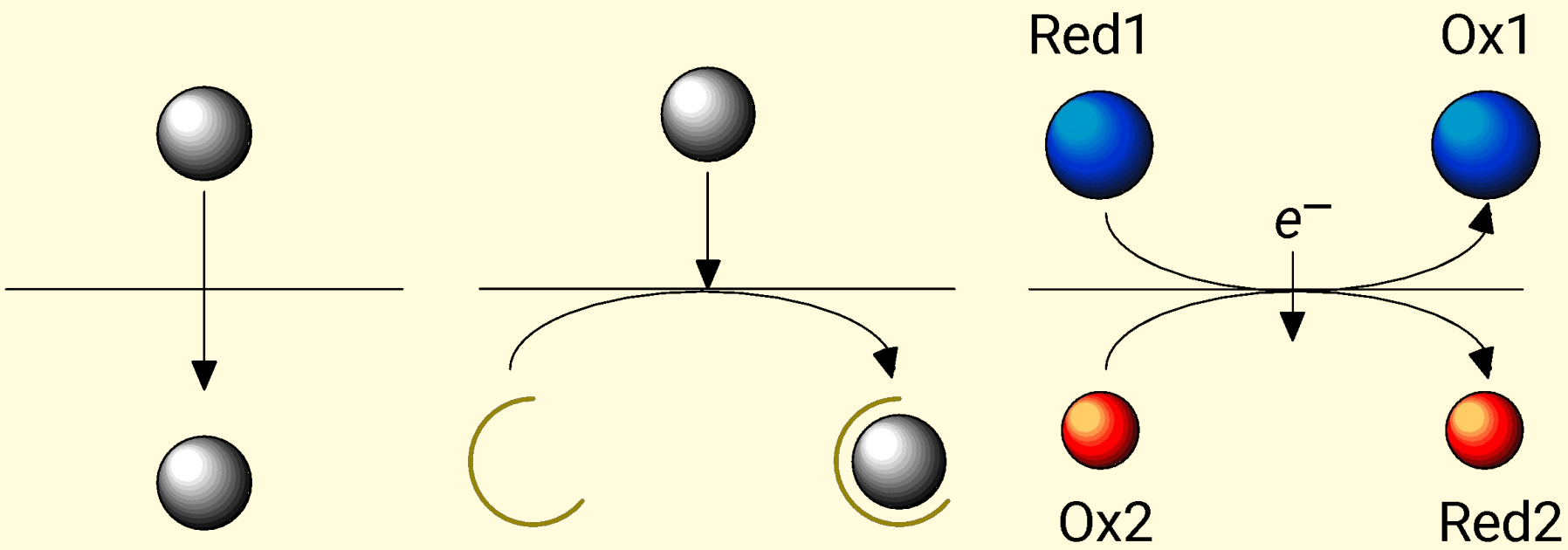
Voltammetry of electro-inactive ions

Polarizable liquid|liquid interface



Koryta, J.; Vanysek, P.; Brezina, M. *J.Electroanal.Chem.* **1976**, *67*, 263

Charge transfer reactions at ITIES



Ion transfer

Assisted ion transfer

(Acid-Base reaction)

Electron transfer

Ion transfer

$$I^{w} \rightleftharpoons I^{o}$$

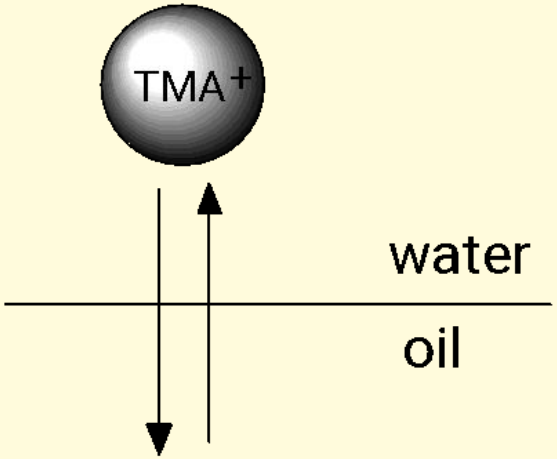
Equality of electrochemical potentials $\tilde{\mu}_i^{w} = \tilde{\mu}_i^{o}$

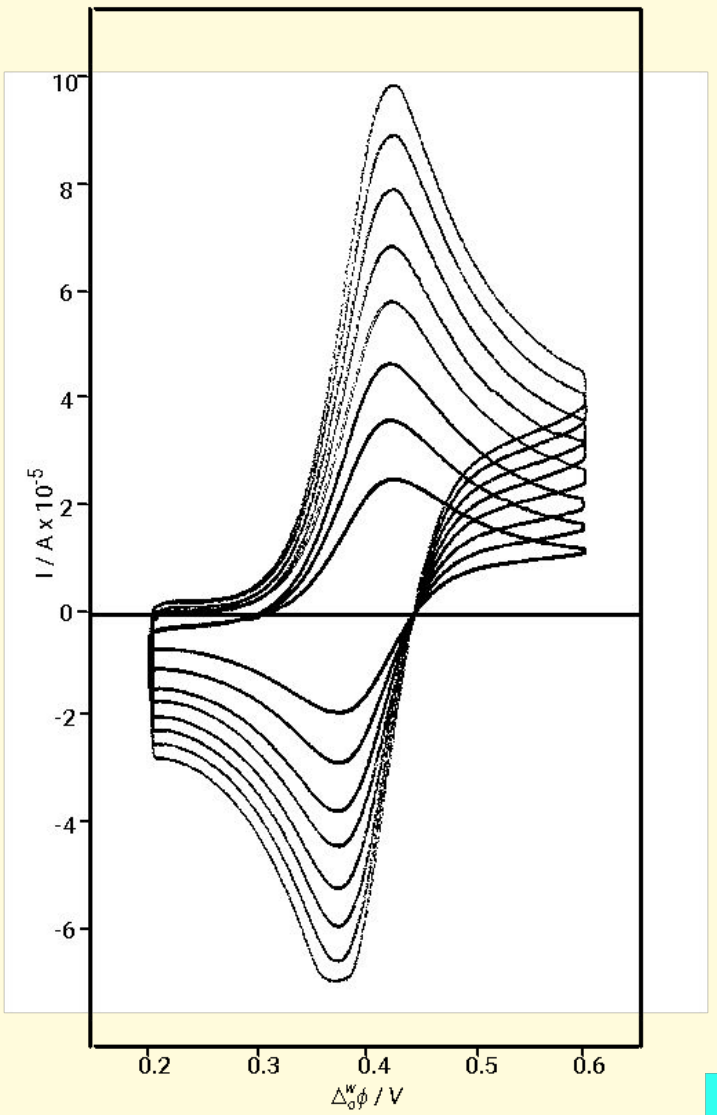
$$\tilde{\mu} = \mu^{o} + RT \ln a + zF\phi$$

Nernst equation for ion transfer

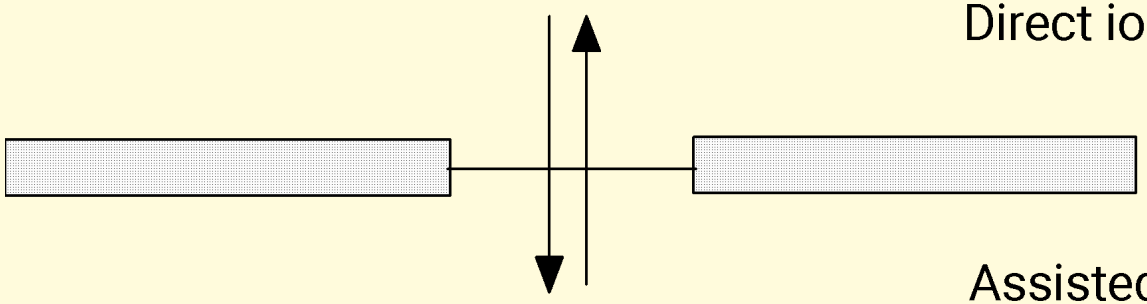
$$\Delta_o^w \phi = \Delta_o^w \phi_i^{o\prime} + \frac{RT}{z_i F} \ln\left(\frac{c_i^o}{c_i^w}\right)$$

Transfer of tetramethylammonium



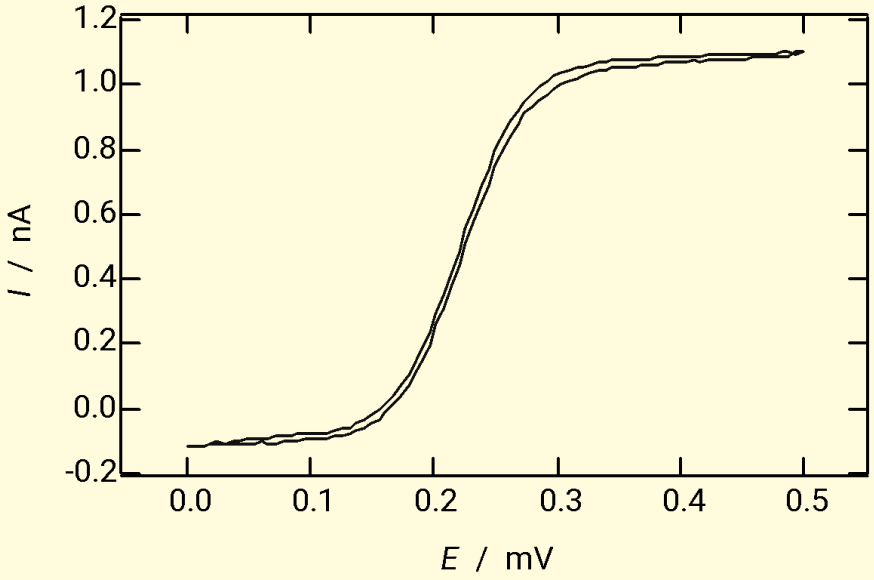


Microholes

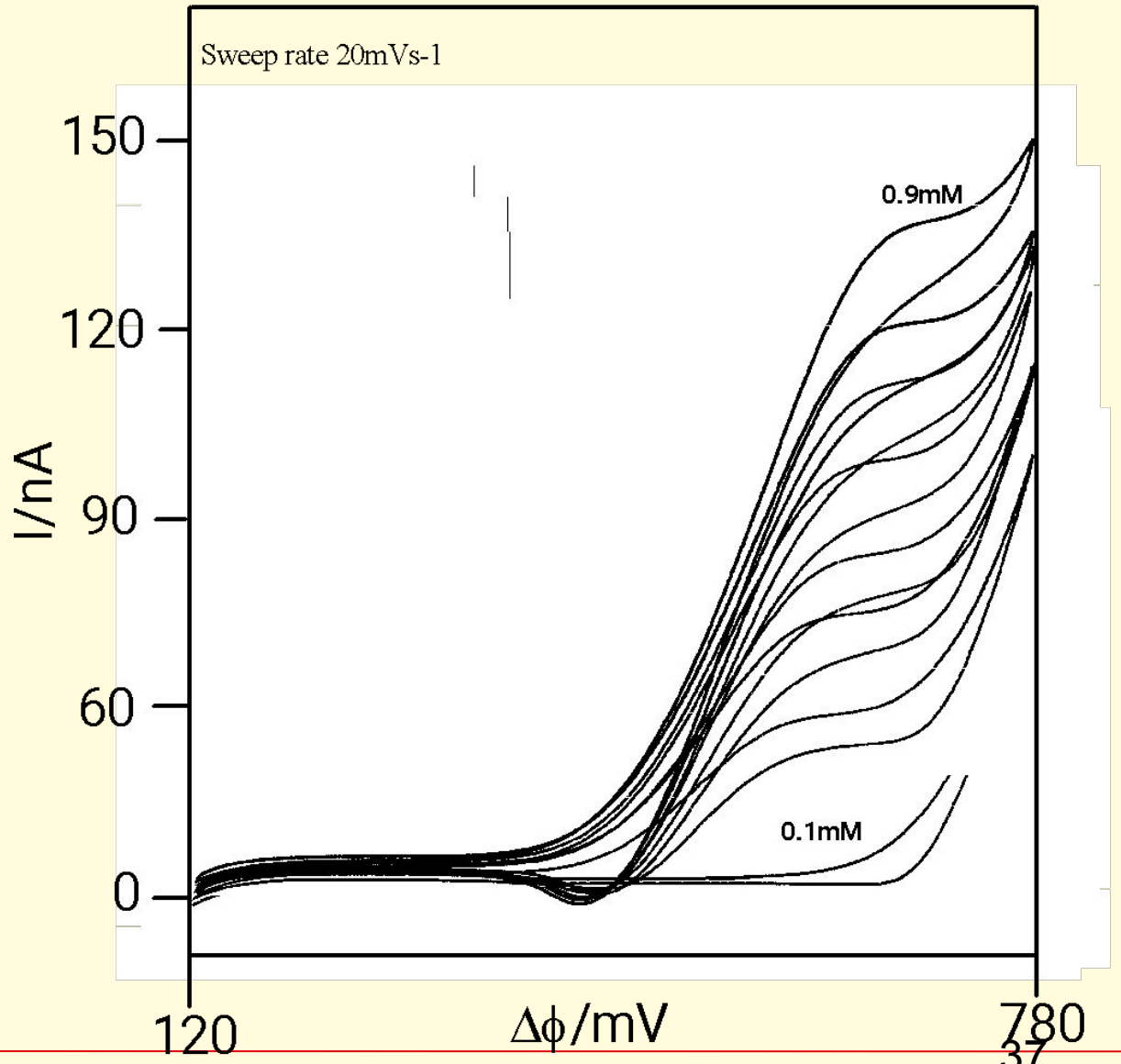


Direct ion transfer

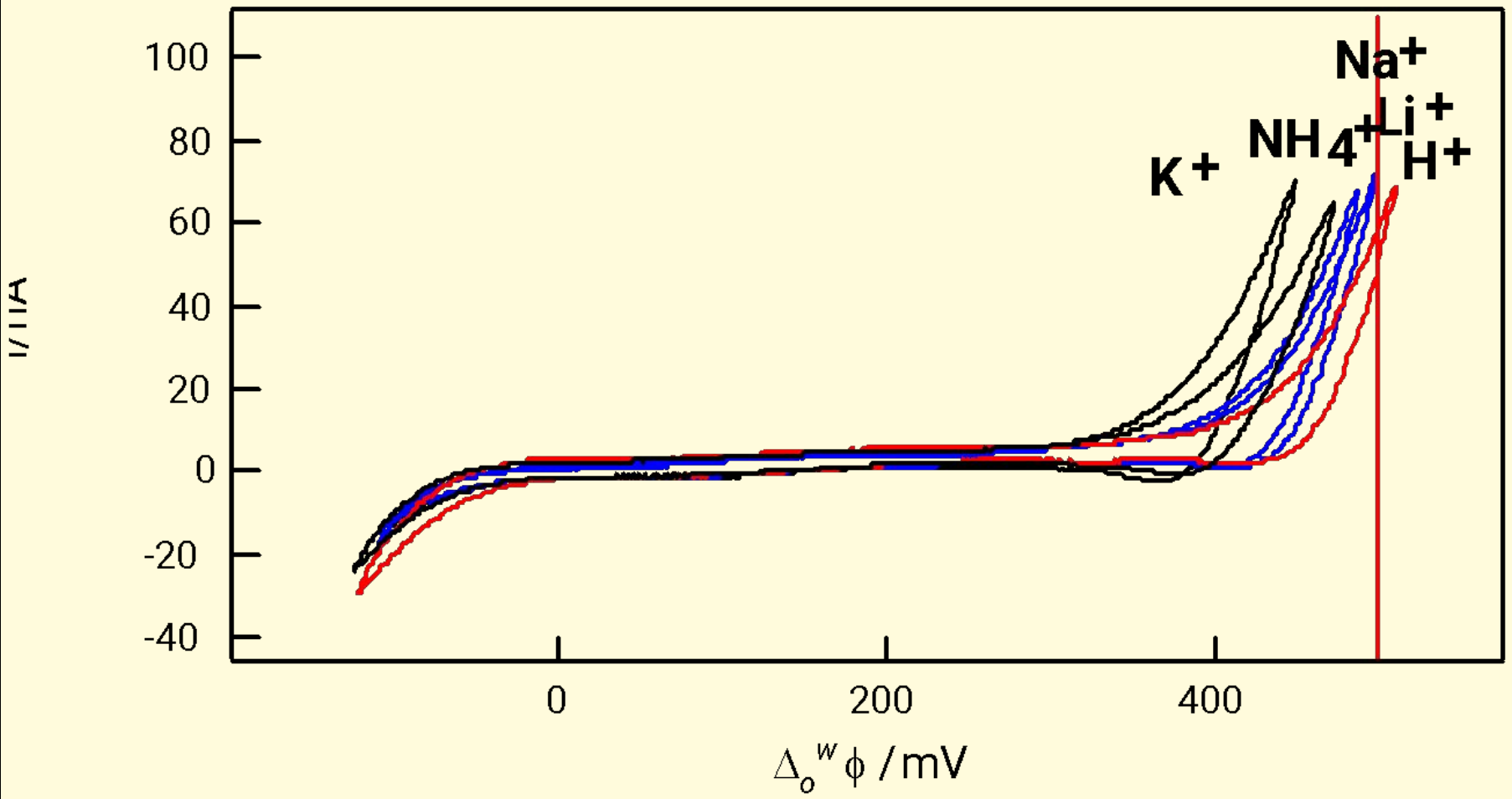
Assisted ion transfe



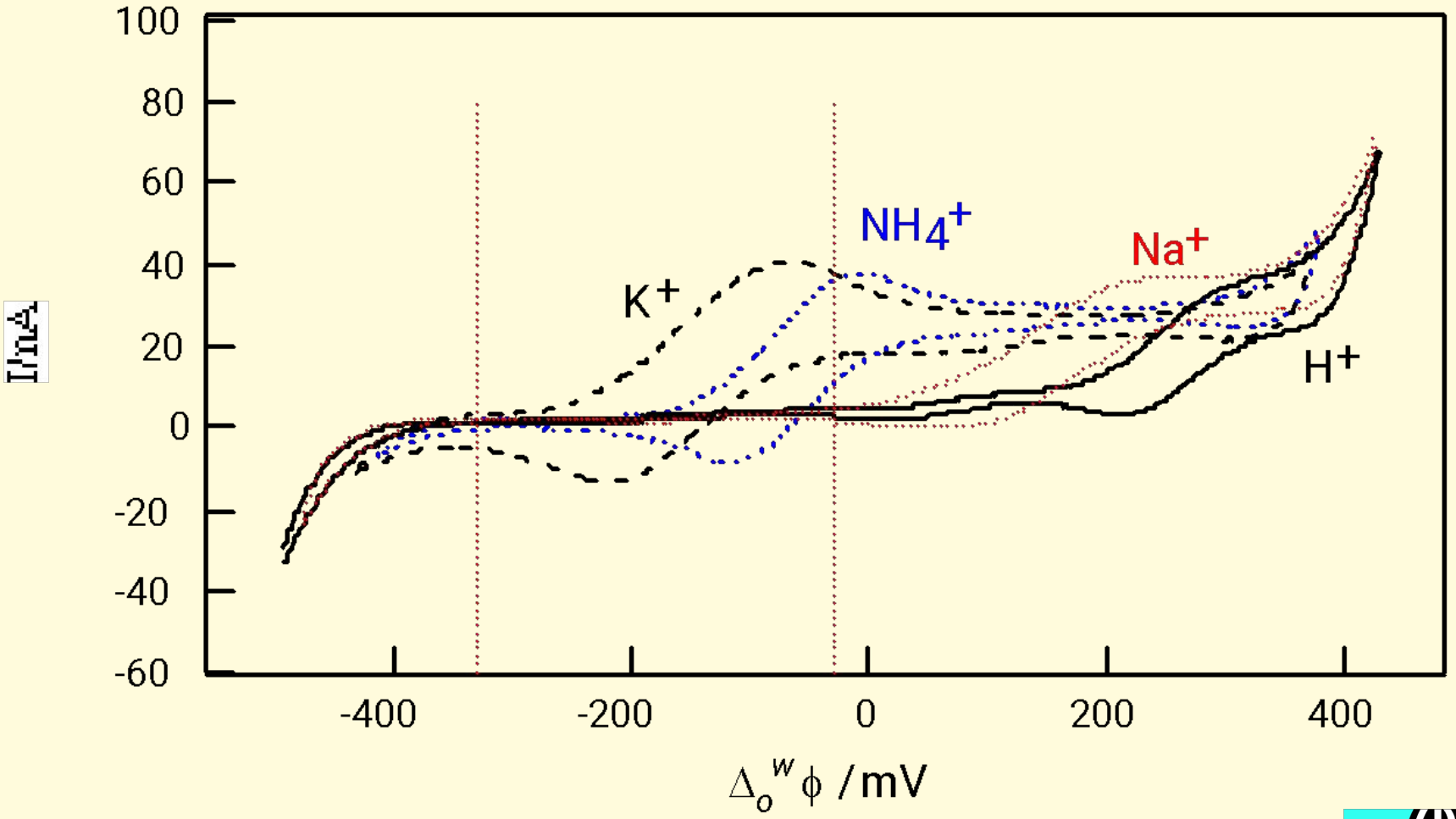
Choline transfer



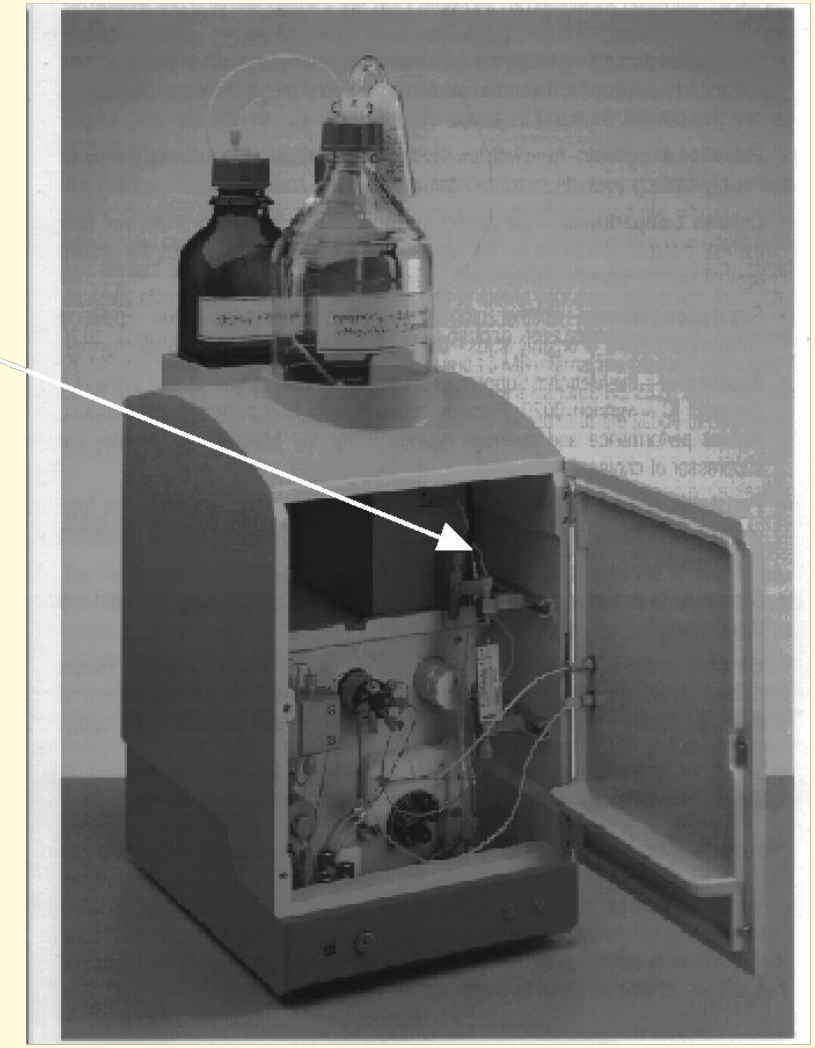
Alkali transfer at an ionode



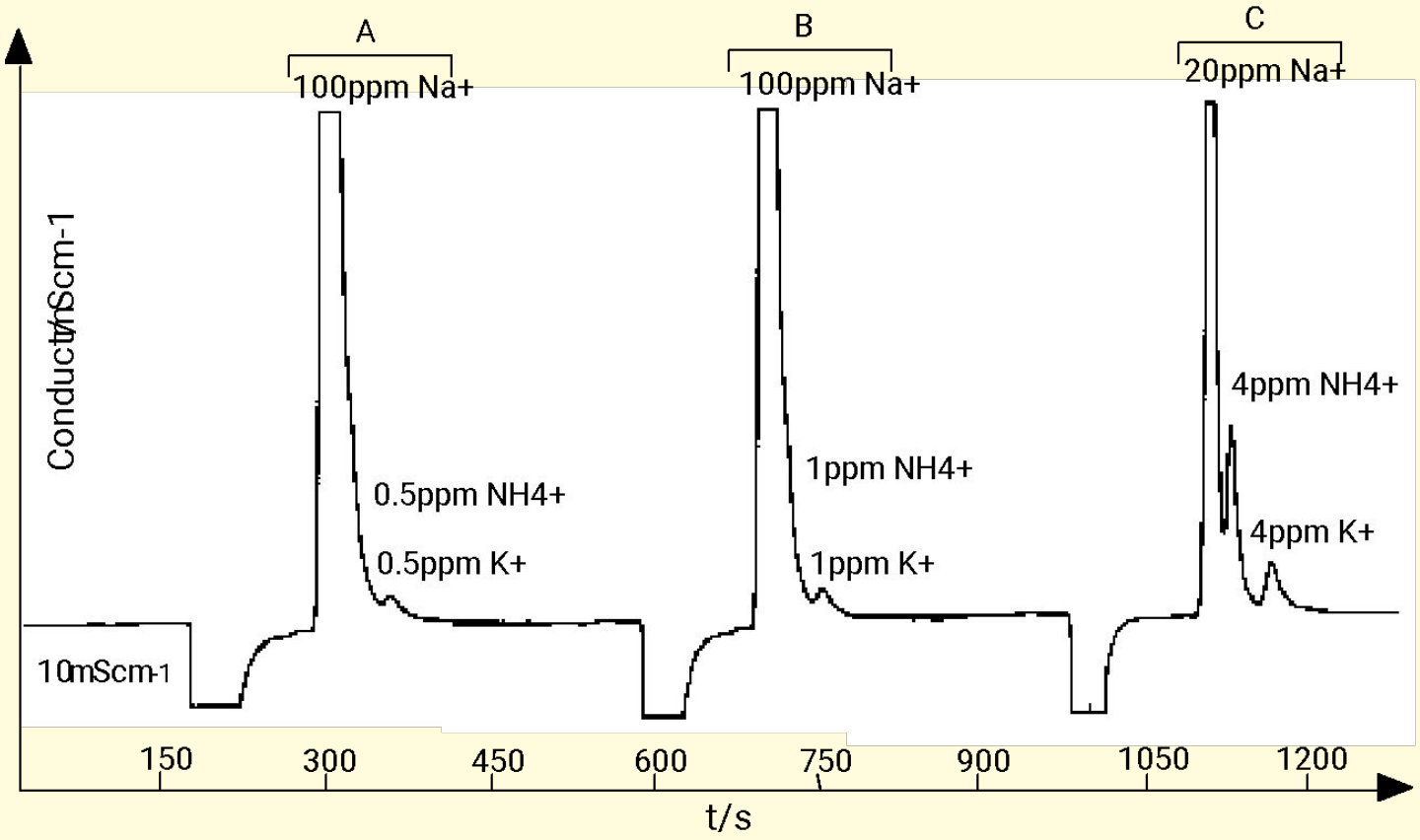
Assisted ion transfer



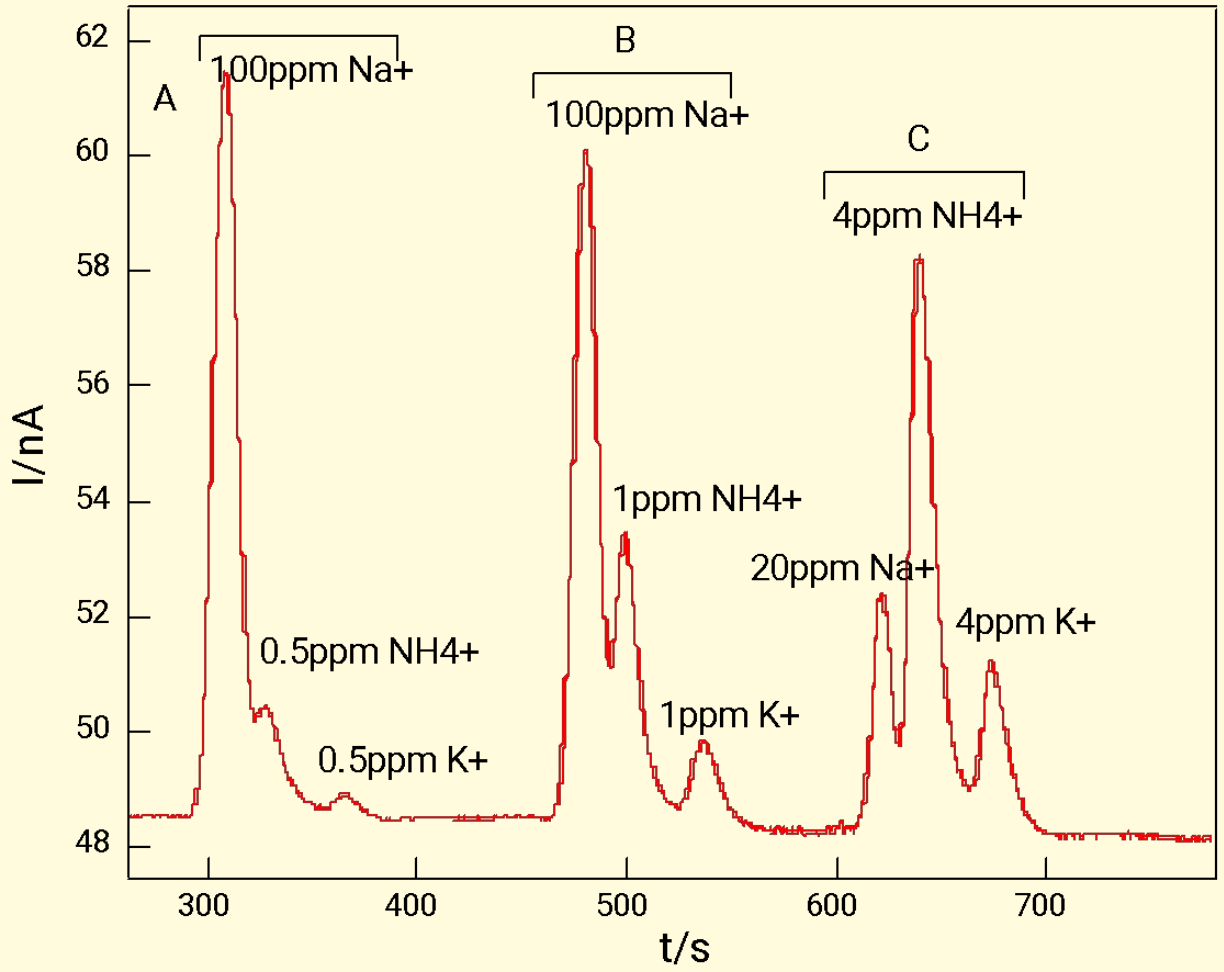
Ion chromatography



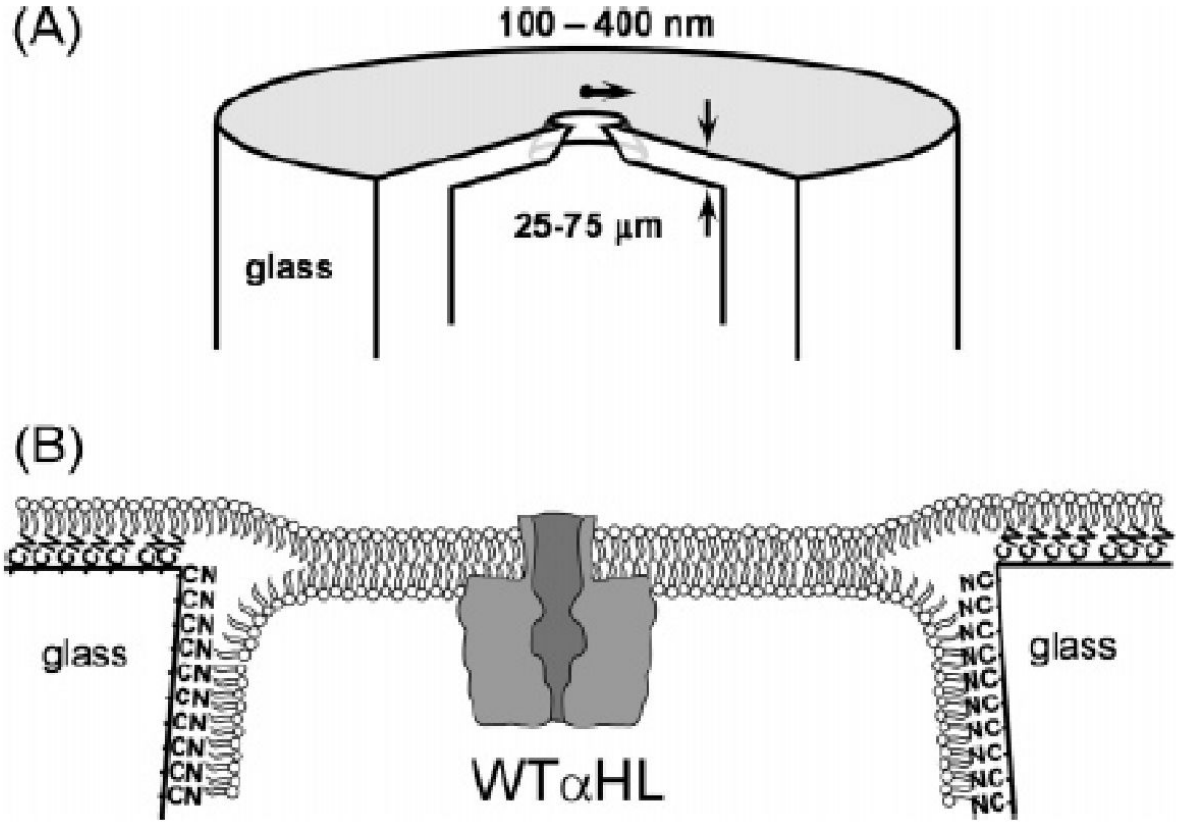
Conductometric ammonium detection



Amperometric Ammonium detection



Детекция единичной молекулы



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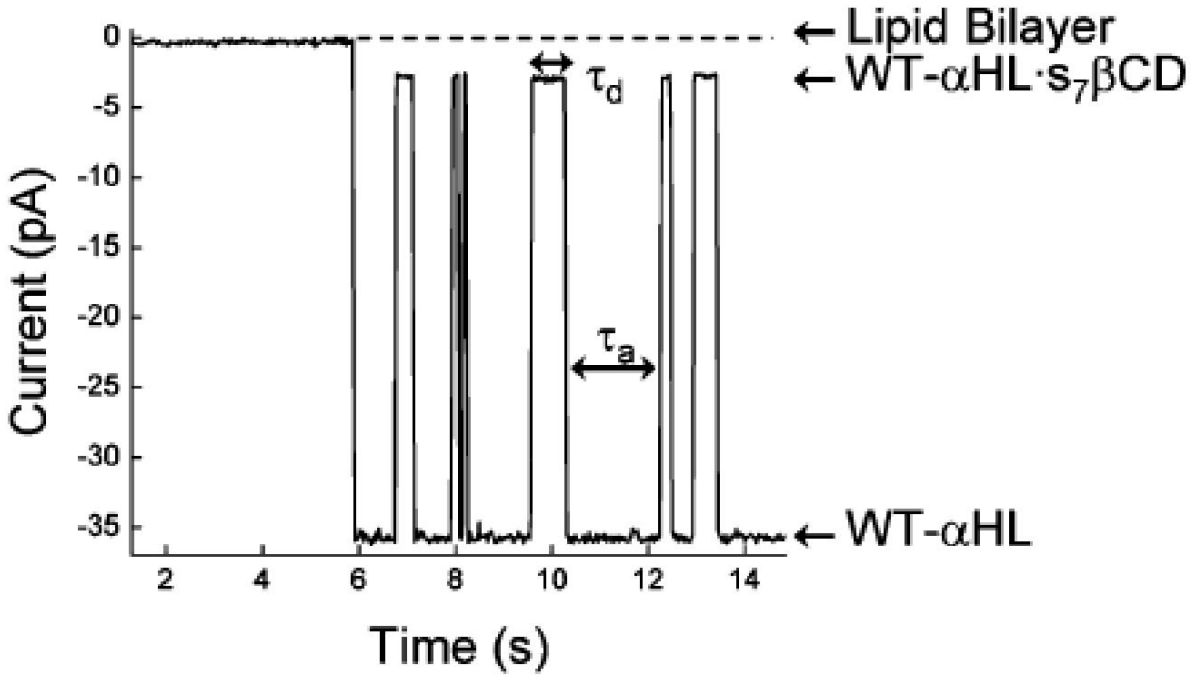
Детекция единичной молекулы



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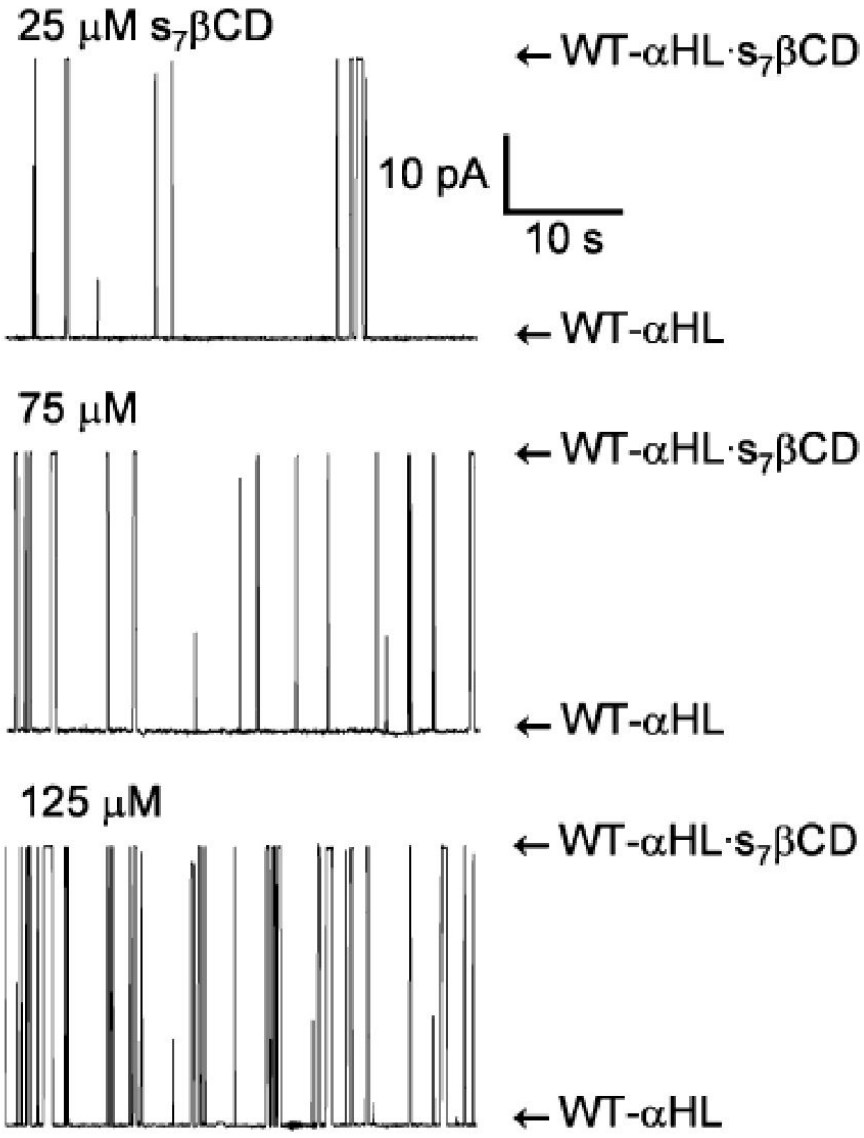
Детекция единичной молекулы



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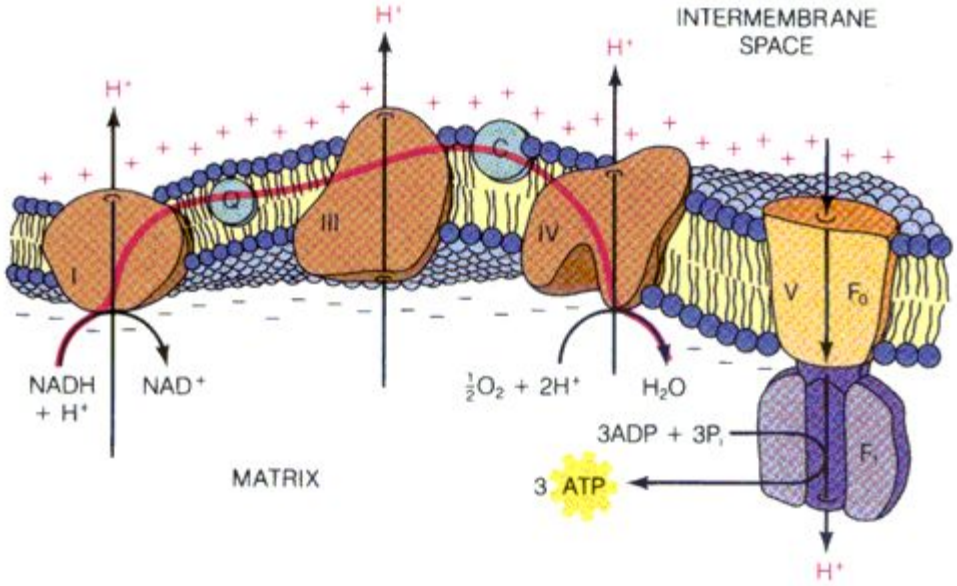
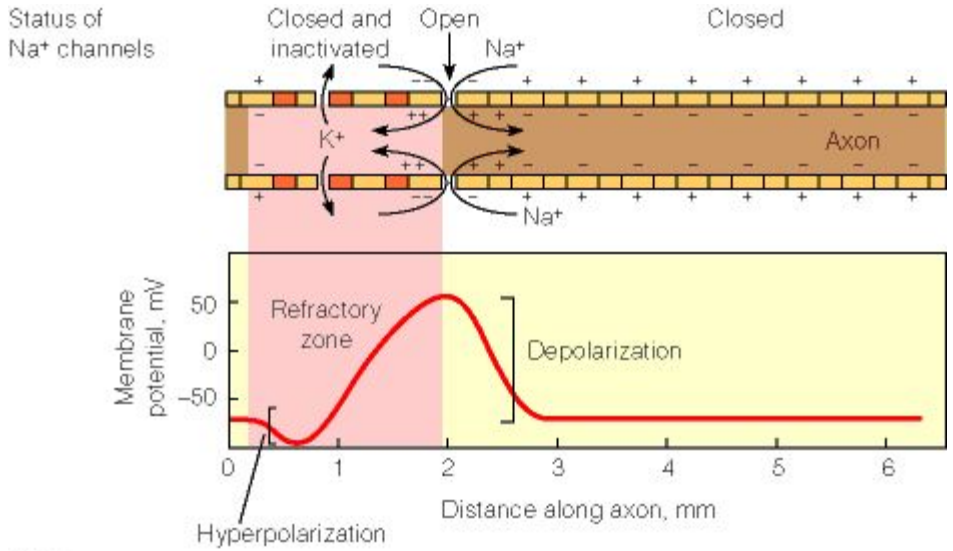
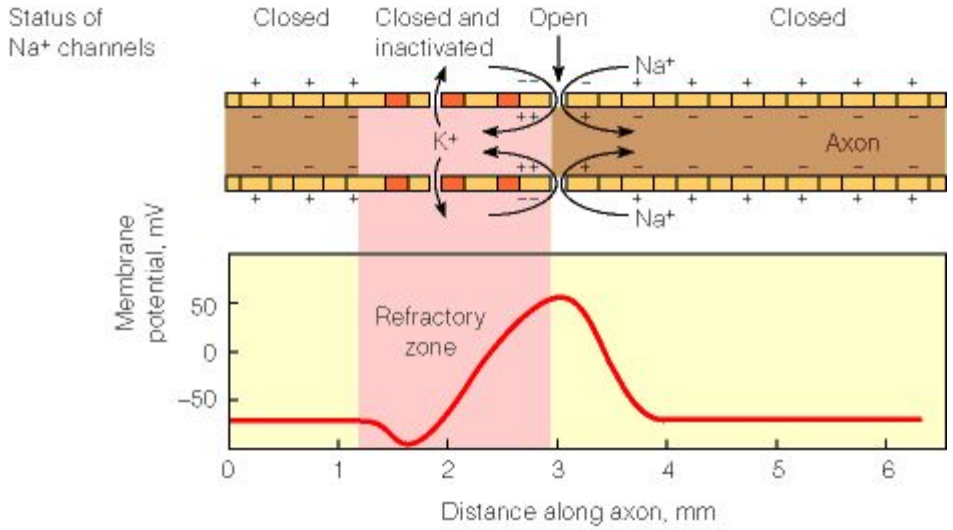
Хемиосмотическая теория



Передача нервного импульса



(a) Time = 0



(b) Time = 1 ms