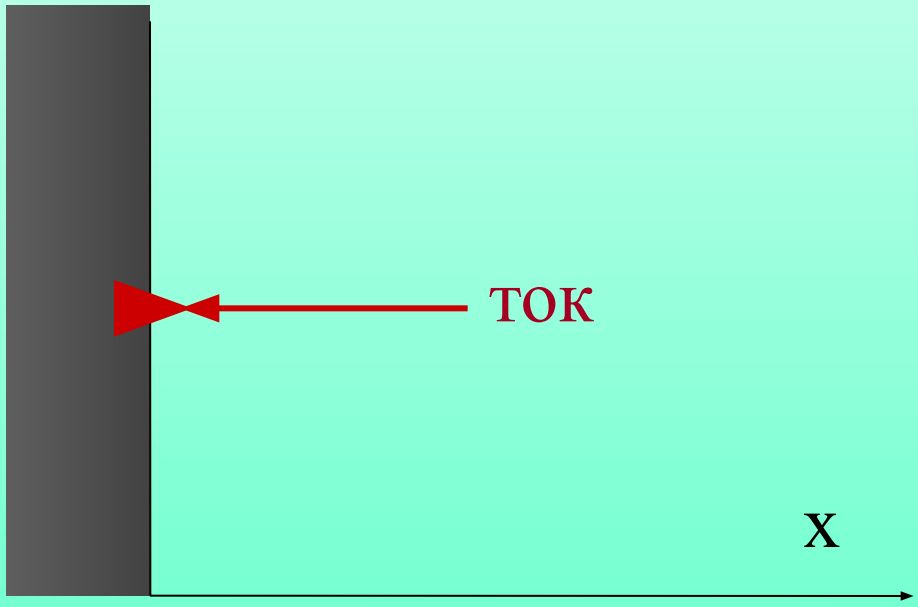
Массоперенос в аналитической химии

Ток:

$$i = nFAJ$$

$$[J] = \frac{mol}{s \cdot cm^2}$$



Диффузионные законы (1885)

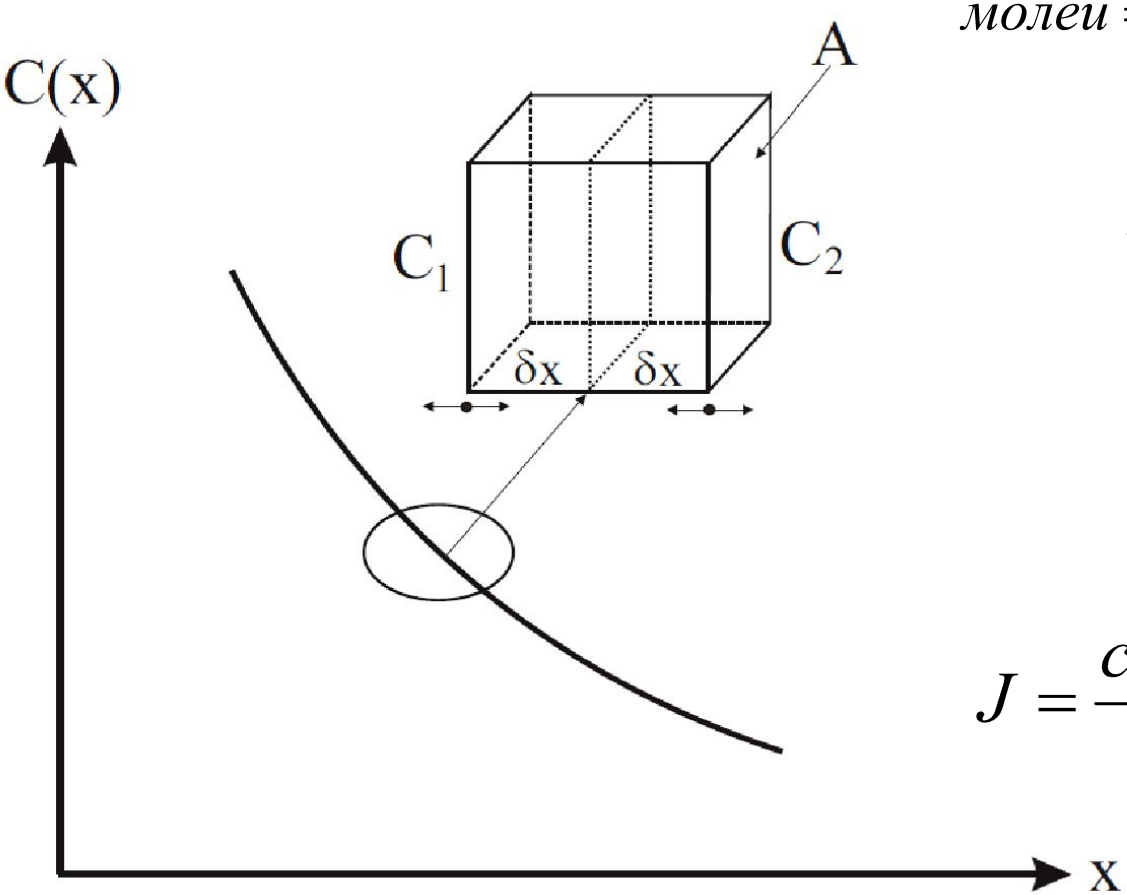
Adolf Fick

(1829-1901)

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x}$$

$$[D] = \frac{cm^2}{s}$$

Einstein – Van Smoluckowskii approach



$$\overleftarrow{\text{молей}} = \frac{C_2 A \delta x}{2} \qquad \overrightarrow{\text{молей}} = \frac{C_1 A \delta x}{2}$$

$$\text{скорость} = \frac{(C_1 - C_2) A \delta x}{2 \delta t}$$

$$(C_1 - C_2) \approx -\delta x \left(\frac{\partial C}{\partial x} \right)$$

$$J = \frac{\text{скорость}}{A} \approx -\frac{(\delta x)^2}{2 \delta t} \left(\frac{\partial C}{\partial x} \right)$$

Einstein – Van Smoluckowskii approach

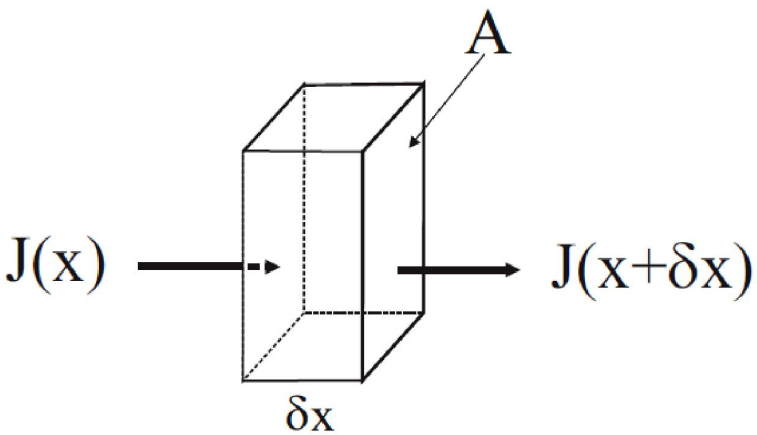
$$J = \frac{\text{скорость}}{A} \approx -\frac{(\delta x)^2}{2\delta t}\left(\frac{\partial C}{\partial x}\right)$$

$$\boxed{J = -D\left(\frac{\partial C}{\partial x}\right)}$$

$$D = \frac{(\delta x)^2}{2\delta t}$$

$$\boxed{\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}}$$

II диффузионный закон



$$\text{молей} = \delta n = \left[J(x) - J(x+\delta x)\right] A\,\delta t$$

Тейлор:

$$J(x+\delta x) \approx J(x) + \delta x\left(\frac{\partial J}{\partial x}\right)$$

$$\delta n \approx -\delta x\left(\frac{\partial J}{\partial x}\right) A\,\delta t \qquad \delta C = \frac{\delta n}{A\,\delta x}$$

$$\frac{\delta C}{\delta t} \approx \boxed{\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} = D\frac{\partial^2 C}{\partial x^2}}$$

II диффузионный закон

$$\boxed{\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}}$$

Одномерный вариант

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right)$$

$$\frac{\partial C}{\partial t} = D\nabla^2 C$$

Общие уравнения массопереноса

Конвекция:

$$J_i^c = C_i \vec{\upsilon}$$

Массоперенос без конвекции:

$$J_i = -\left(\frac{D_i C_i}{RT}\right) \overrightarrow{grad}\, \mu_i^e$$

Общие уравнения массопереноса

Электрохимический потенциал:

$$\mu_i^e = \mu_i^o + RT \ln a_i + z_i F \phi$$

Безконвекционный массоперенос:

$$J_i = -D_i C_i \overrightarrow{grad}(\ln a_i) - \frac{z_i F D_i C_i}{RT} \overrightarrow{grad}\phi$$

для разбавленных растворов:

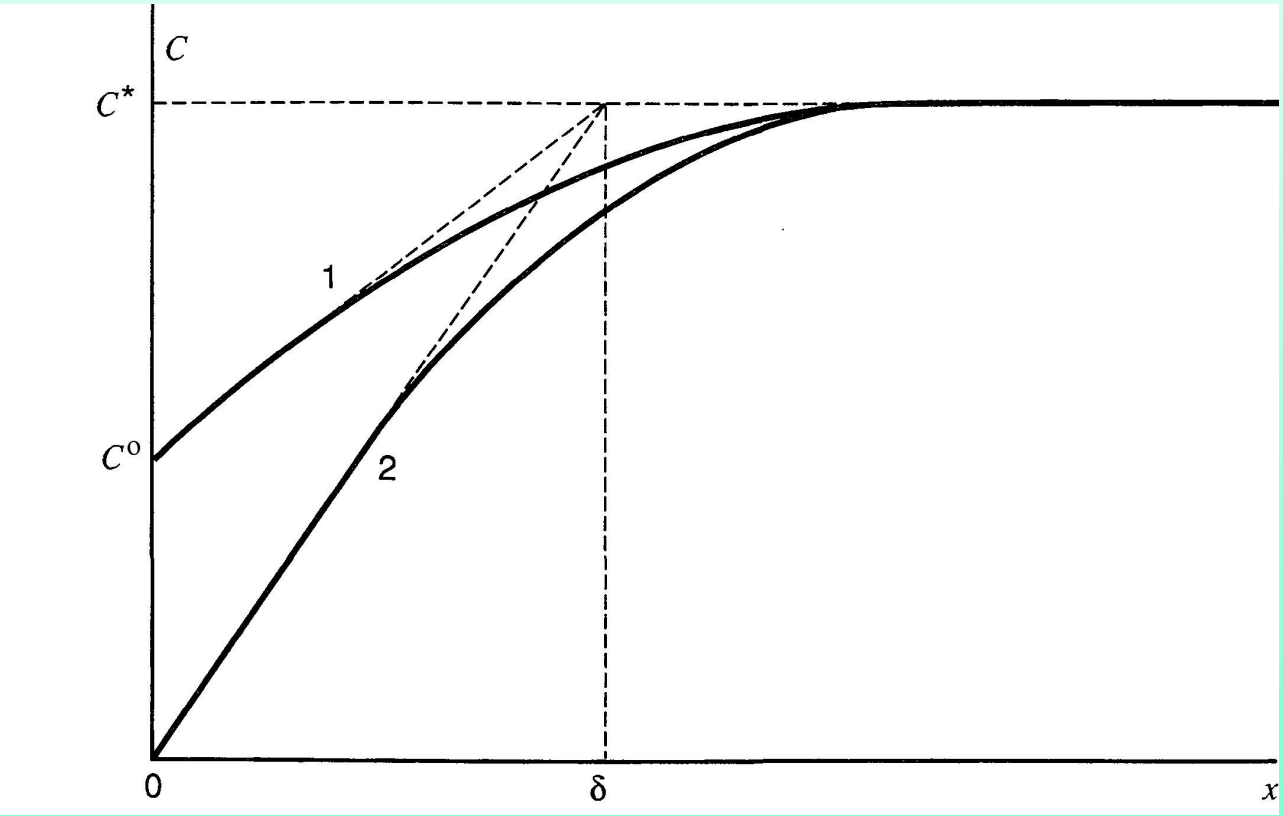
$$J_i = -D_i \overrightarrow{grad} C_i - \frac{z_i F D_i C_i}{RT} \overrightarrow{grad}\phi$$

Общие уравнения массопереноса

Уравнение Нернста-Планка:

$$J_i^{\Sigma} = \underbrace{C_i\vec{\upsilon}}_{\text{конвекция}} - \underbrace{D_i\overrightarrow{grad}C_i}_{\text{диффузия}} - \underbrace{\cancel{\frac{z_i F D_i C_i}{RT}\overrightarrow{grad}\phi}}_{\text{миграция}}$$

Профиль концентрации и диффузионный слой

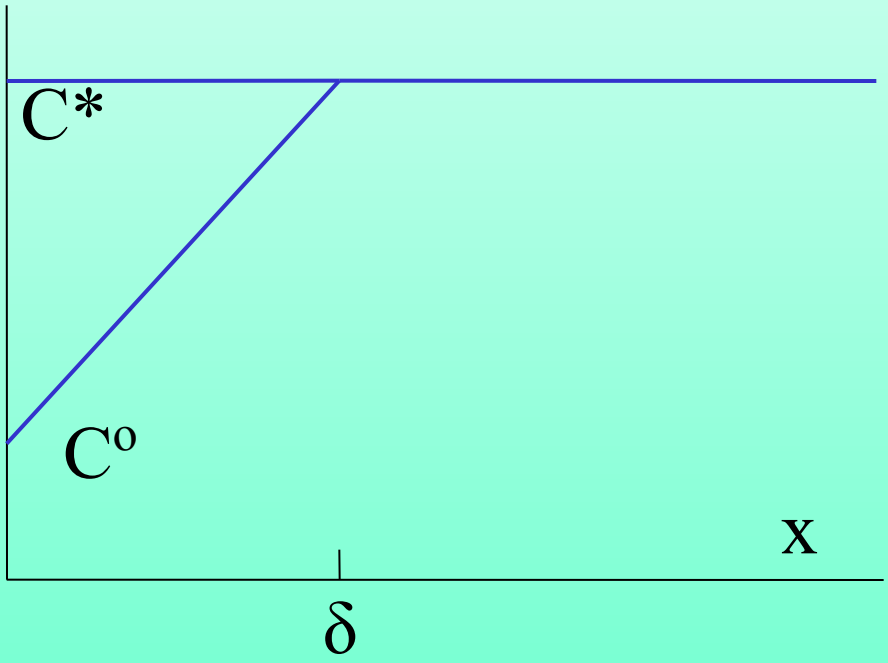


Полуэмпирическое решение нестационарной реакции

$$-J(x=0)=D\left(\frac{\partial C(x)}{\partial x}\right)_{x=0}=\frac{i}{nFA}$$

$$\left(\frac{\partial C(x)}{\partial x}\right)_{0\le x\le\delta}=\frac{C^*-C^o}{\delta}$$

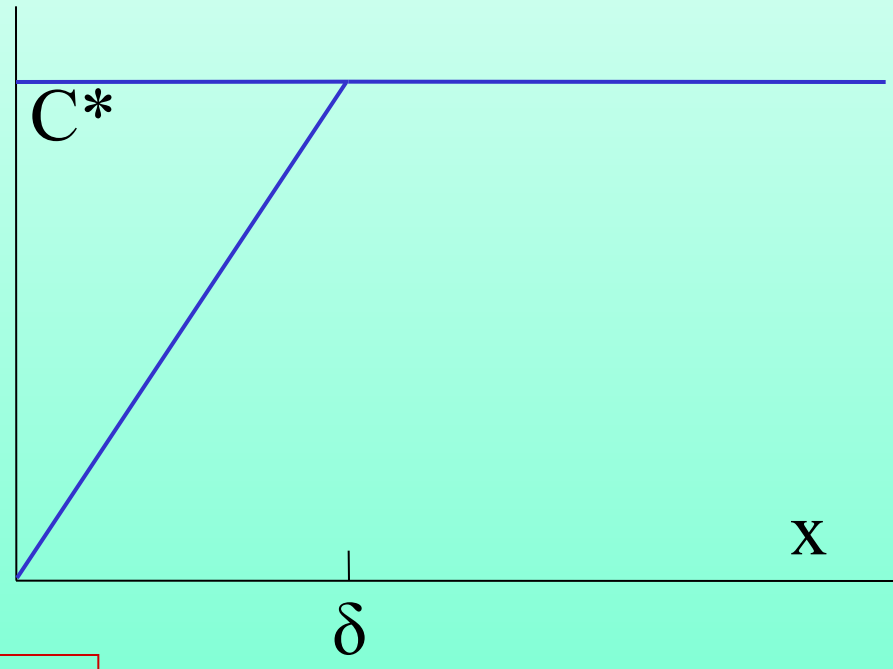
$$\boxed{\frac{i}{nFA}=\frac{D}{\delta}[C^*-C^o]}$$



Предельный диффузионный ток

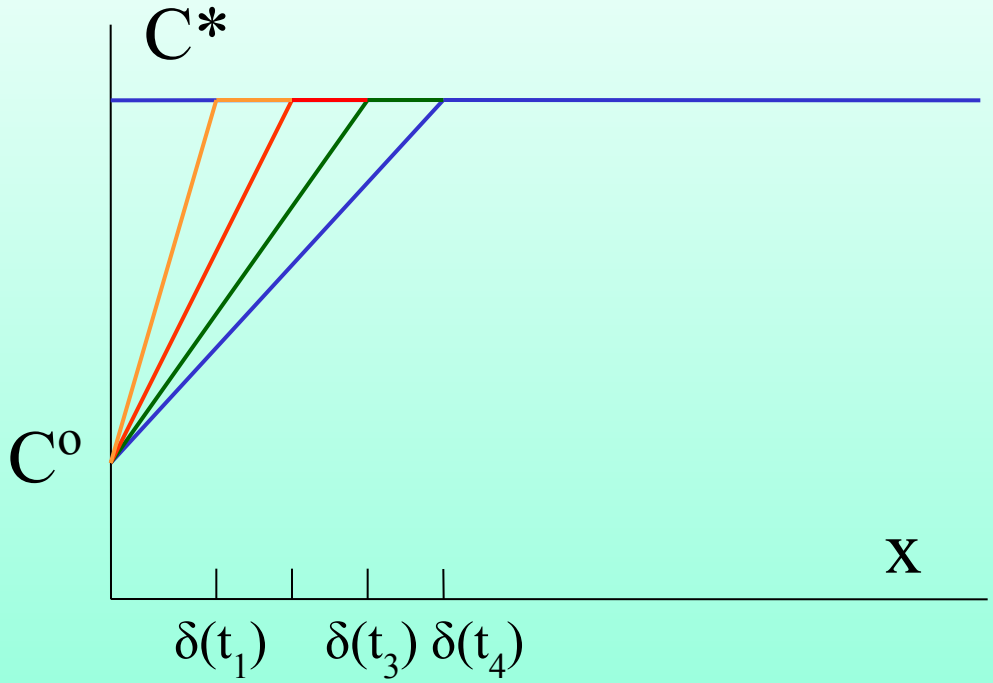
$$m = \frac{D}{\delta}$$

$$C^o = 0$$



$$\boxed{i_l = nFA \cdot m \cdot C^*}$$

Полуэмпирическое решение нестационарной реакции



число молей $\cong [C^* - C^o]\dfrac{A\delta(t)}{2} = \displaystyle\int_0^t \frac{i \cdot dt}{nF}$

Полуэмпирическое решение нестационарной реакции

$$[C^* - C^o]\frac{A\delta(t)}{2} = \int_0^t \frac{i \cdot dt}{nF}$$

$$\frac{i}{nFA} = \frac{D}{\delta}[C^* - C^o]$$

$$\frac{[C^* - C^o]}{2}\frac{A \cdot d\delta(t)}{dt} = \frac{i}{nF} = \frac{DA}{\delta(t)}[C^* - C^o]$$

$$\frac{d\delta(t)}{dt} = \frac{2D}{\delta(t)}$$

$$\boxed{\delta(t) = 2\sqrt{Dt}}$$

Полуэмпирическое решение нестационарной реакции

$$\frac{i}{nFA} = \frac{D^{1/2}}{2t^{1/2}}[C^* - C^o]$$

Диффузионно-контролируемый процесс: $C(0,t) = 0$

$$\boxed{\frac{i}{nFA} = \frac{D^{1/2}}{2t^{1/2}}C}$$

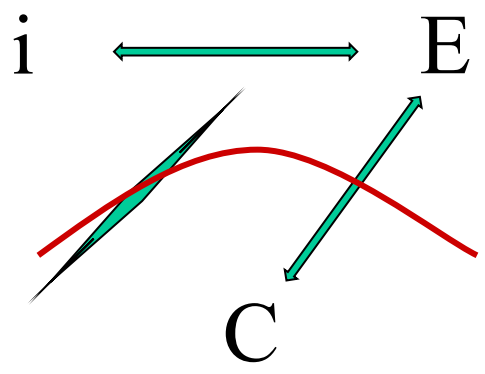
Уравнение Котрелла:

$$\frac{i(t)}{nFA} = \frac{D^{1/2}}{\pi^{1/2}t^{1/2}}C$$

Электрохимические методы:

$$i = f(E, t) \longleftrightarrow E = f(i, t)$$

$$i = f(E, C^*, t) \longleftrightarrow E = f(i, C^*, t)$$



Диффузионные законы

$$J(x,t) = -D\frac{\partial C(x,t)}{\partial x}$$

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

Скачок потенциала – Cottrell equation (1902)

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

t = 0: C(x) = C*

t > 0: C(0) = 0

C(x→∞) = C*

подстановка

$$\Gamma = \frac{x}{2\sqrt{Dt}} \quad \Longrightarrow \quad \frac{d^2C}{d\Gamma^2} + 2\Gamma\frac{dC}{d\Gamma} = 0$$

$$\frac{dC}{d\Gamma} = a \cdot \exp\left\{-\Gamma^2\right\}$$

Уравнение Котрелла:

$$\frac{dC}{d\Gamma} = a \cdot \exp\left\{-\Gamma^2\right\}$$

С учетом граничных условий:

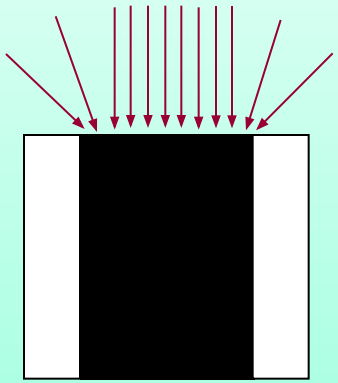
$$C = C^* erf\left\{\frac{x}{2\sqrt{Dt}}\right\}$$

$$i = nFAJ\Big|_{x=0}$$

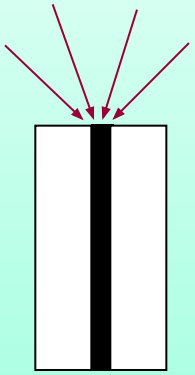
$$J\Big|_{x=0} = D\frac{\partial C}{\partial x}\Big|_{x=0}$$

$$\boxed{i = \frac{nFA\sqrt{D}C^*}{\sqrt{\pi t}}}$$

Миниатюризация



диффузия



Cottrell equation:

$$\frac{it^{1/2}}{\pi r^2 C} = \frac{nFD^{1/2}}{\pi^{1/2}} \left[1 + 2.12 \left(\frac{Dt}{r^2} \right)^{1/2} \right]$$

P.J. Lingane. *Anal. Chem.* **36** (1964) 1723

Ultramicroelectrode:

$$i \approx \lim(i)_{r \to 0} = 4nFDCr$$

K. Aoki. *Electroanalysis* **5** (1993) 627-39

Стационарный ток микроэлектродов

Сферический:

$$I_{ss} = 4\pi nFDCr$$

Полусферический:

$$I_{ss} = 2\pi nFDCr$$

Дисковый:

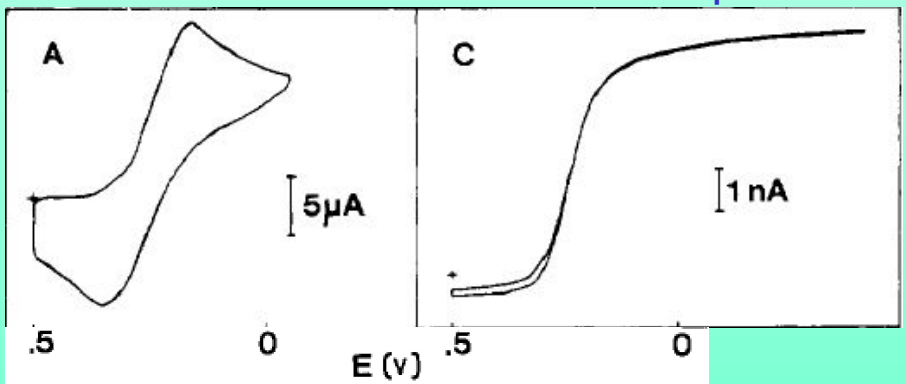
$$I_{ss} = 4nFDCr$$

Преимущества микро-электродов

1. $i_F \sim r$, тогда как $i_c \sim r^2$ → сигнал:шум ~ $1/r$

2. Быстрая релаксация профилей диффузии:

ø = 1.5 mm ø = 10 μm

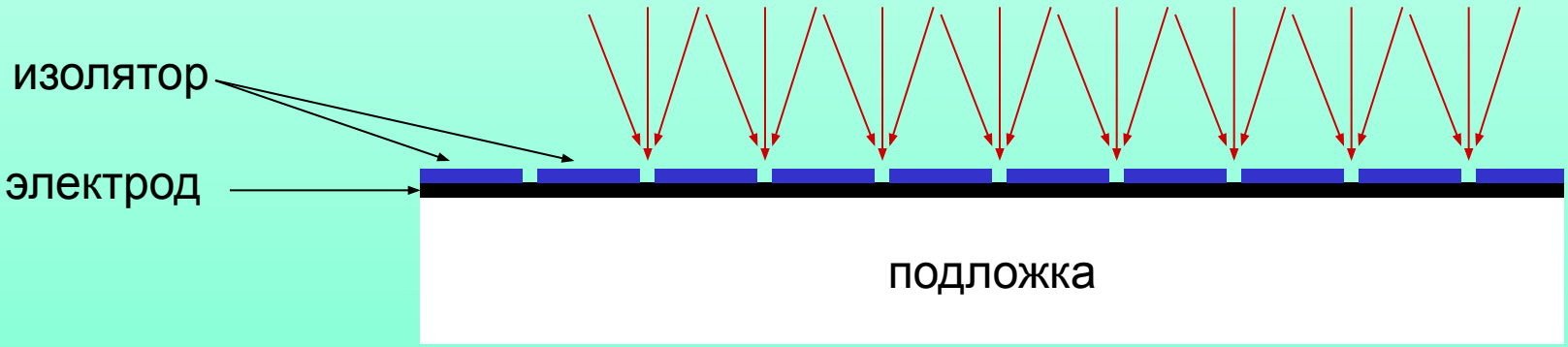


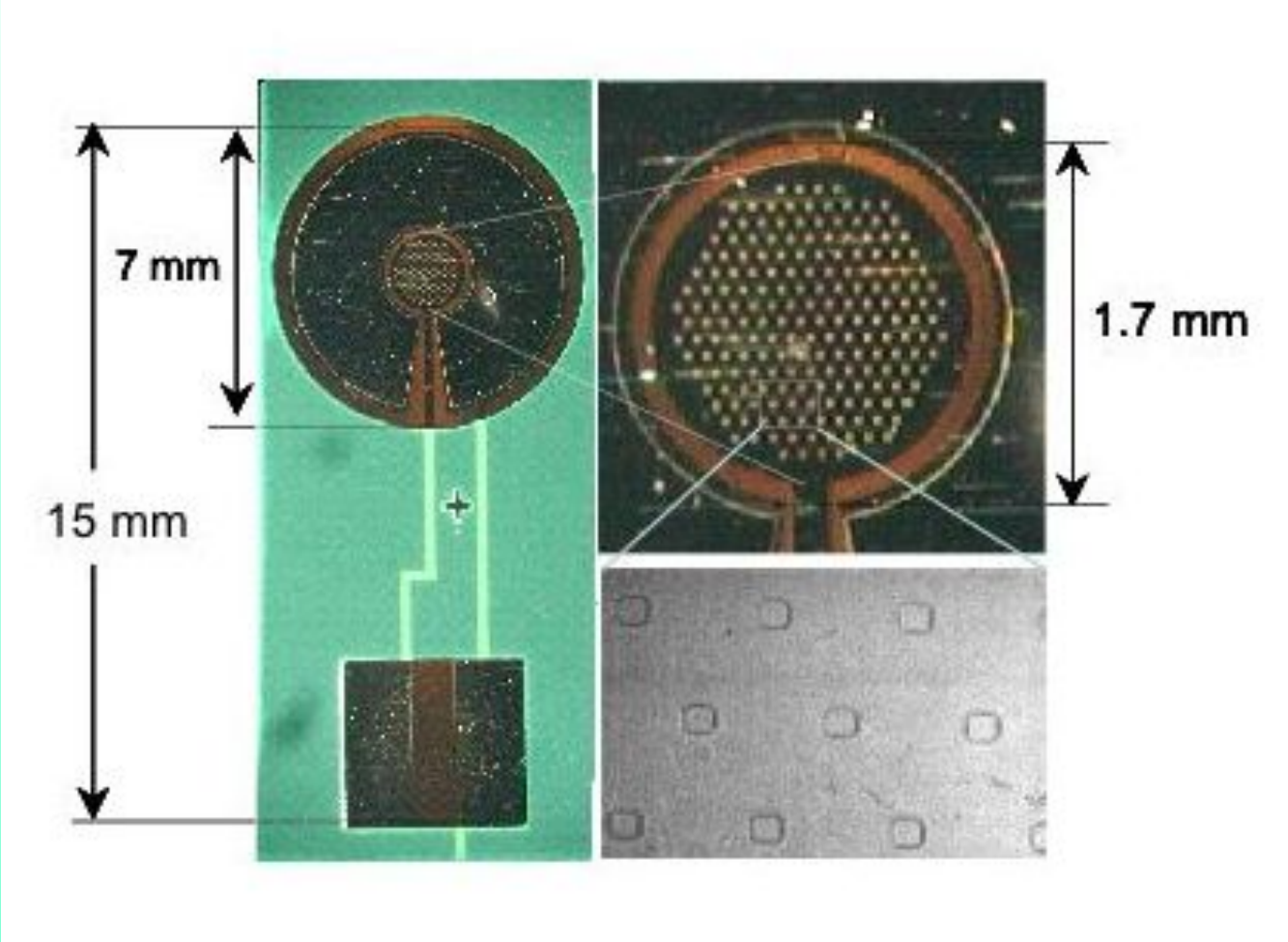
4 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl
100 mV/s

M.A.Dayton, J.C.Brown, K.J.Stutts, R.M.Wightman *Anal. Chem.* **52** (1980) 946-50

низкие величины тока → системы микроэлектродов

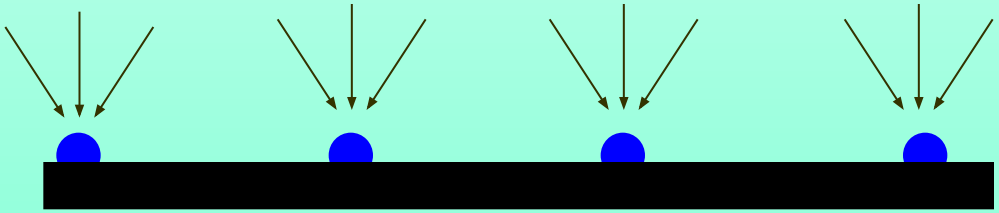
диффузия аналита




7 mm
15 mm
1.7 mm

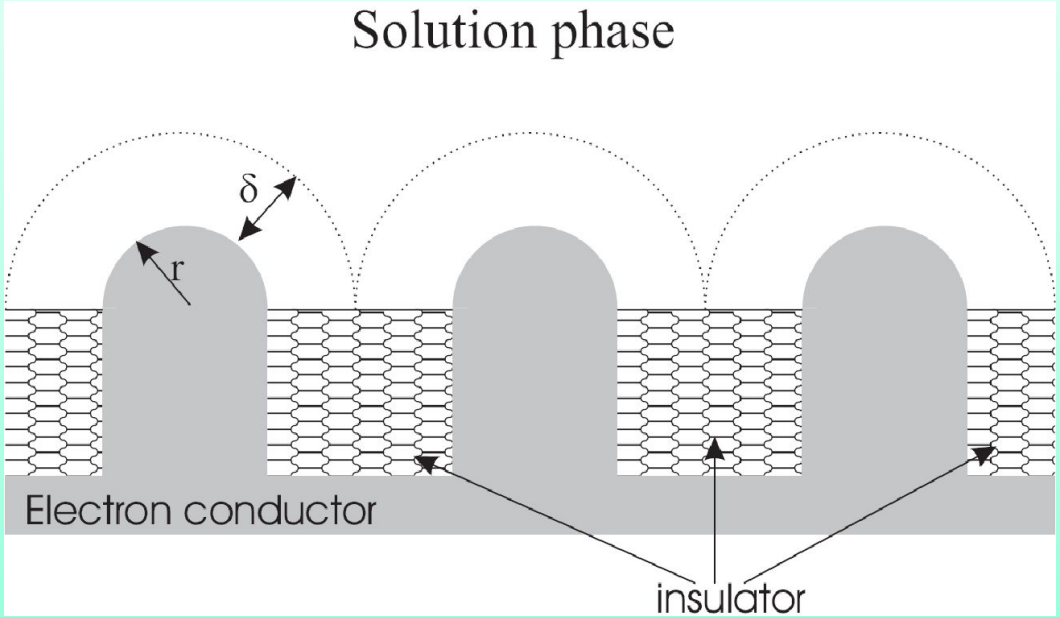
Системы *нано*-электродов

Нано-структурирование электро-катализатора на инертной подложке



A.A. Karyakin, E.A. Puganova et.al. *Analytical Chemistry*, 2004, *76*, 474-8

Оптимальная конфигурация полу-сферических microelectrode arrays

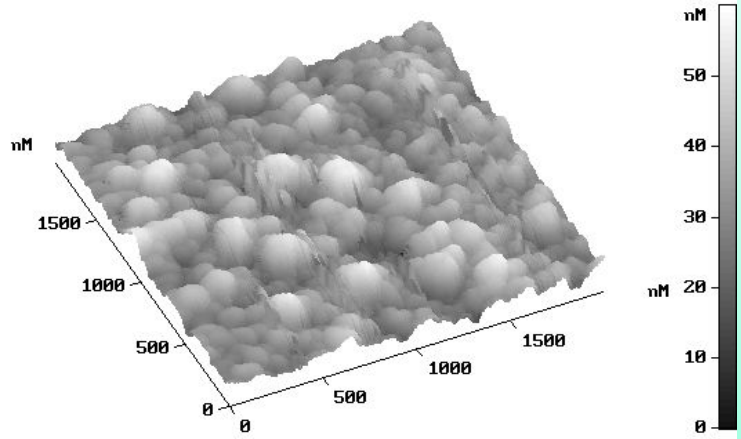


$$2\pi nFDCr = I_{ss} = \frac{nFADC}{\delta}$$

$$\boxed{r = \delta}$$

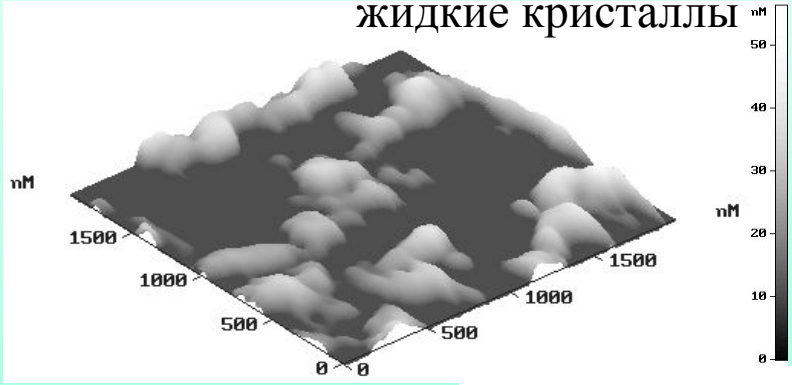
АСМ-изображения Берлинской лазури

обычная

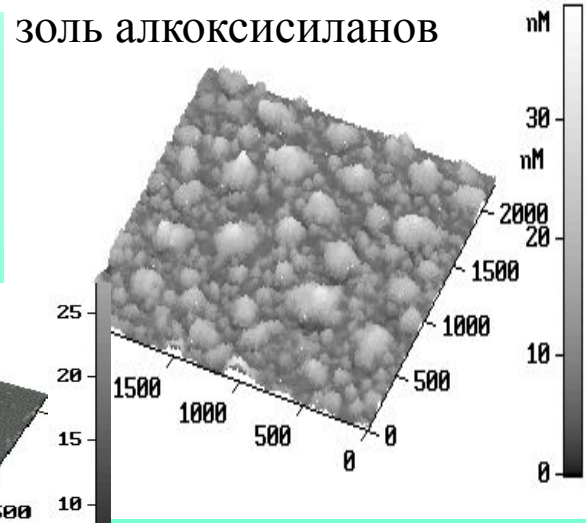


нано-структурированная

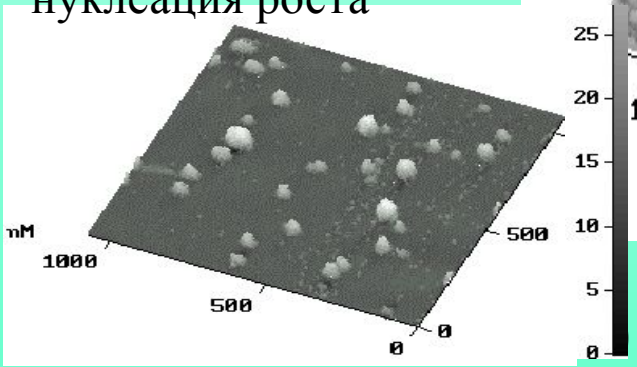
жидкие кристаллы



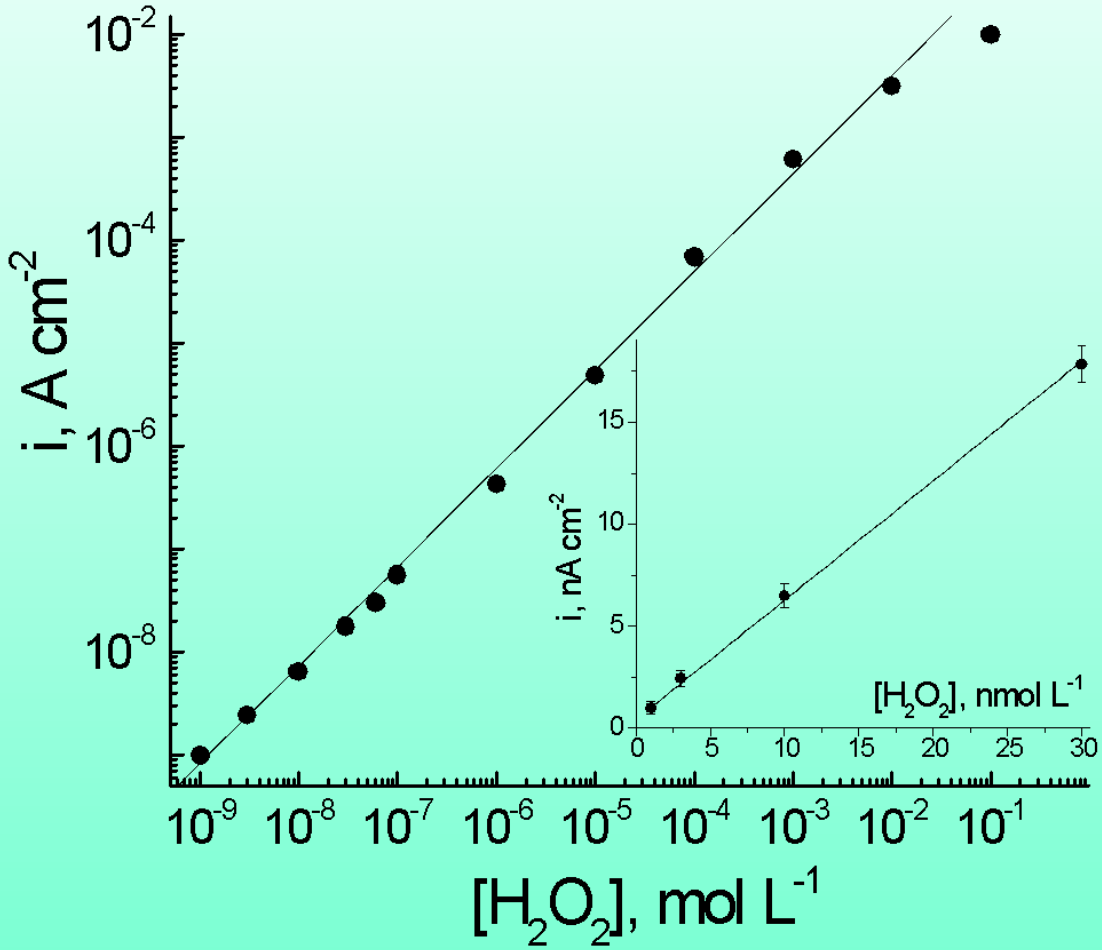
золь алкоксисиланов



нуклеация роста



Рекордный сенсор на основе системы *нано*-электродов



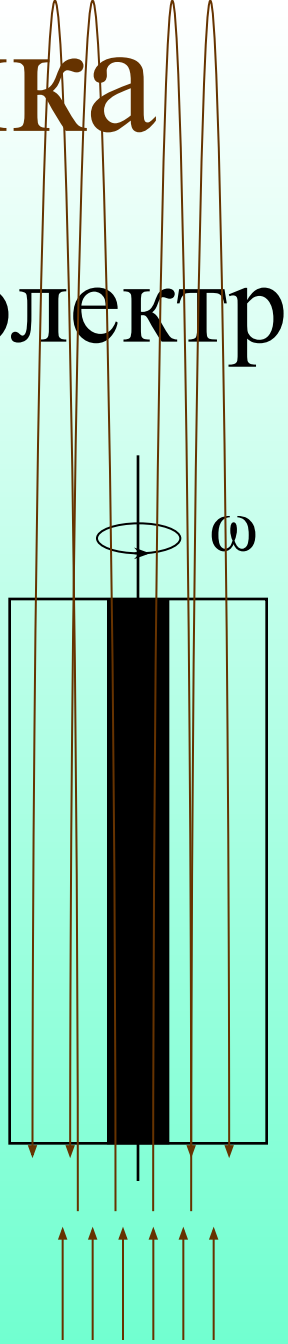
A.A. Karyakin, E.A. Puganova, I.A. Bolshakov, E.E. Karyakina
Angewandte Chemie **46** (2007) 7678-80

Гидродинамика

Вращающийся дисковый электрод

Уравнение Левича:

$$i_l = 0.620 nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C$$



Гидродинамика

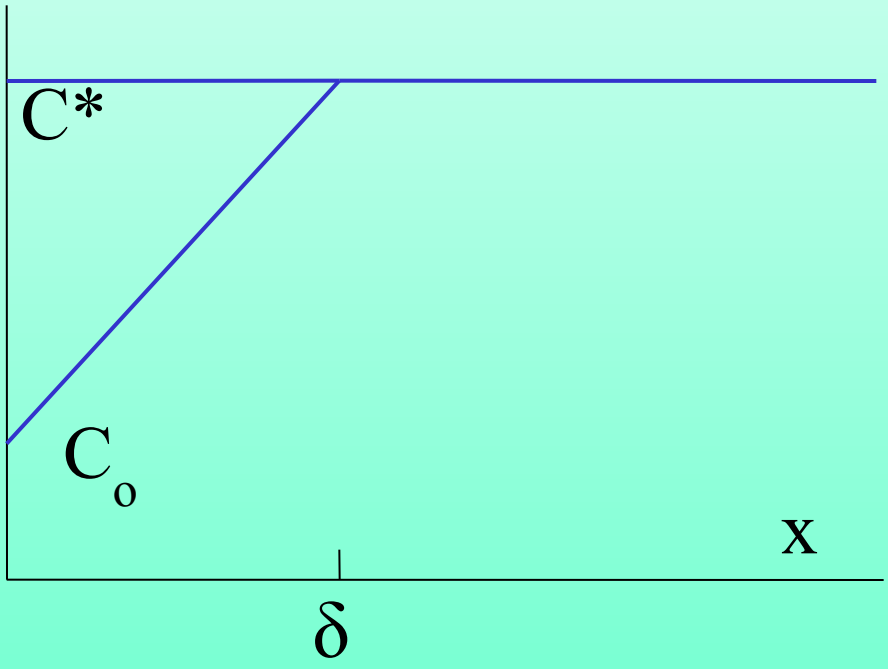
Вращающийся дисковый электрод

Уравнение Левича:

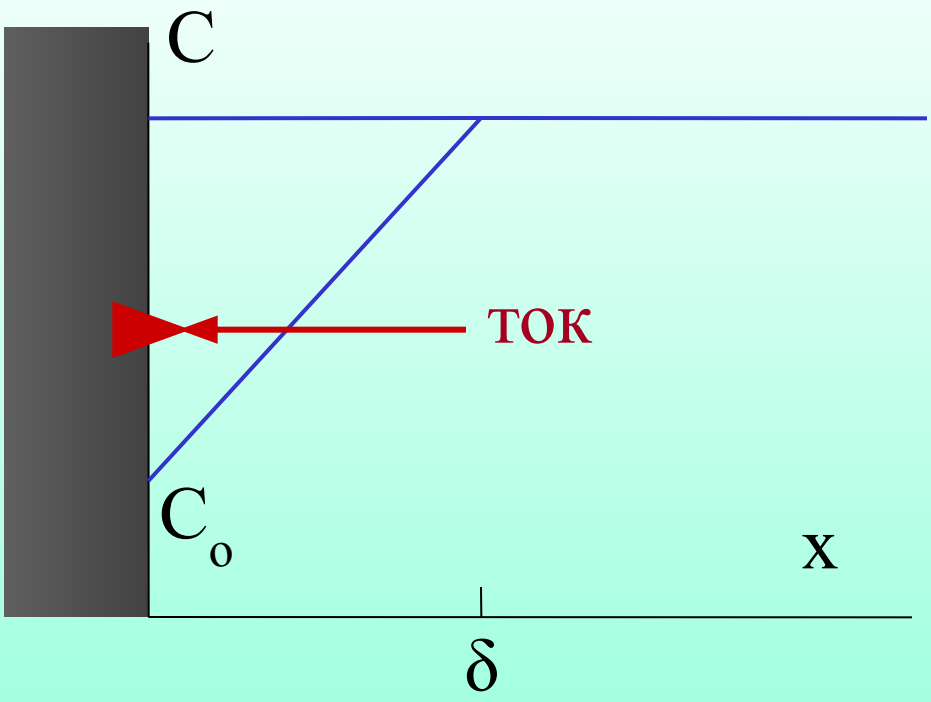
$$i = 0.620nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C$$

$$i = nFA\left(\frac{D}{\delta}\right)C$$

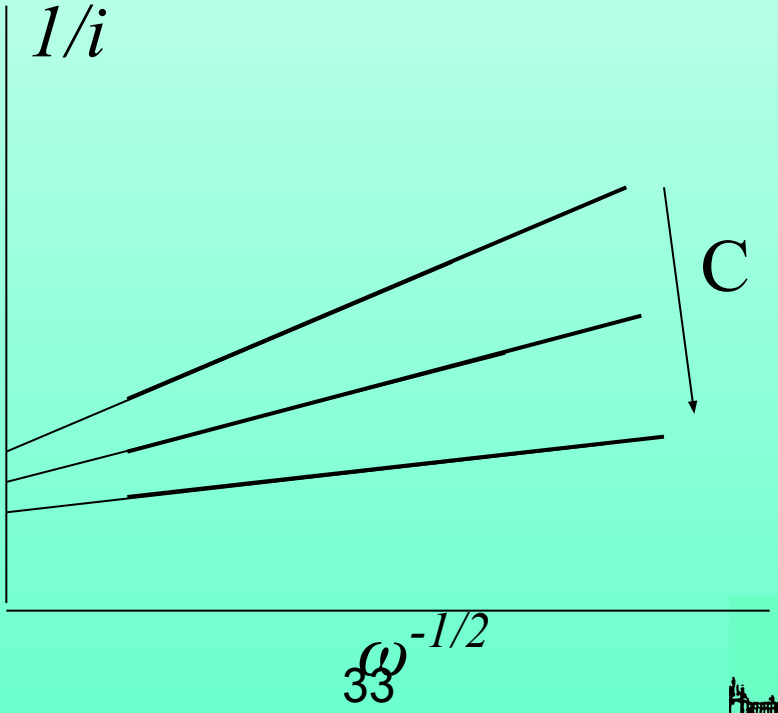
$$\delta = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2}$$



Уравнение Коутецкого-Левича



$$\frac{1}{i} = \frac{1}{i_{диф}} + \frac{1}{i_{кин}}$$



Детекторы

Жидкостная хроматография

Проточно-инжекционный анализ

- тонкослойные;
- wall-jet.

Тонкослойные проточные электроды

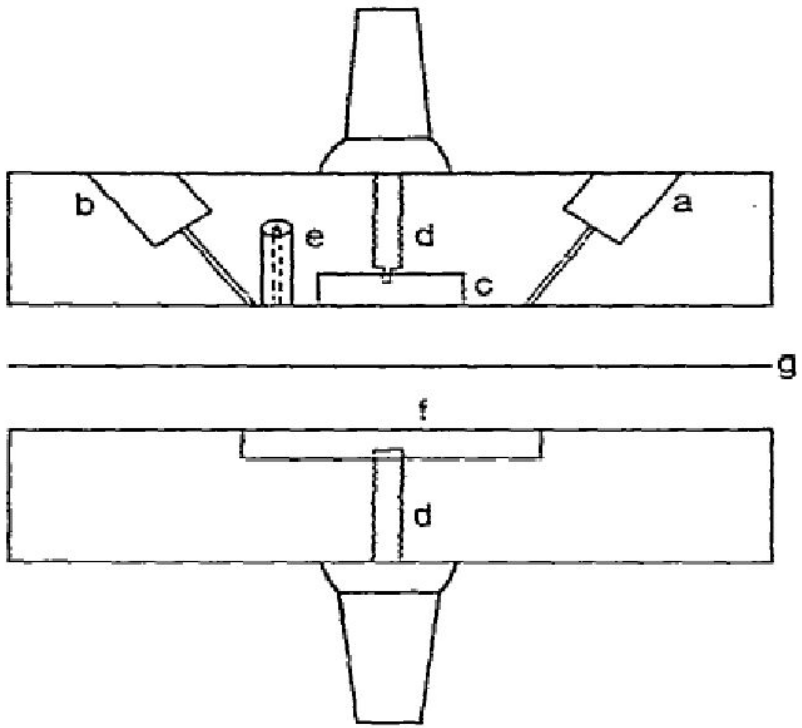
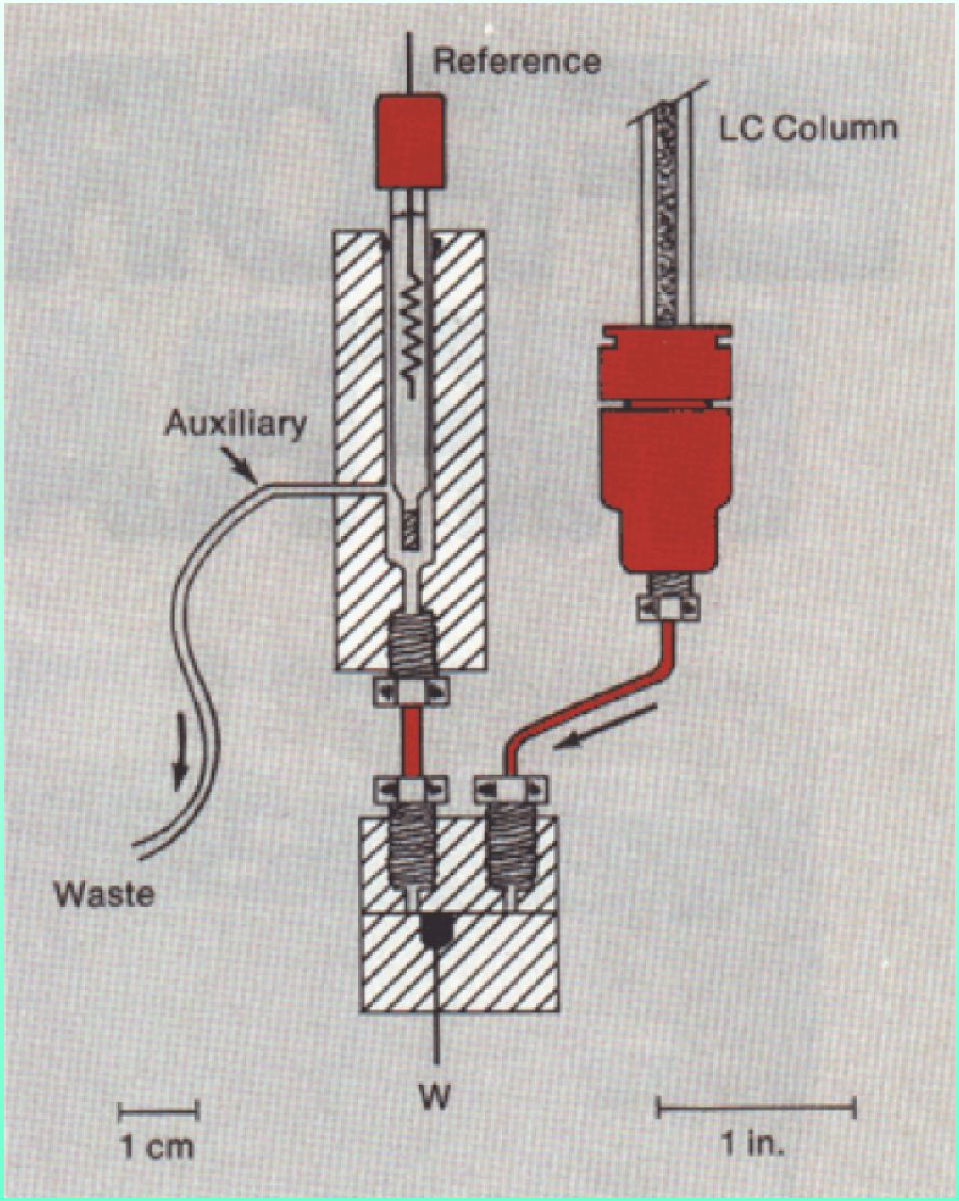
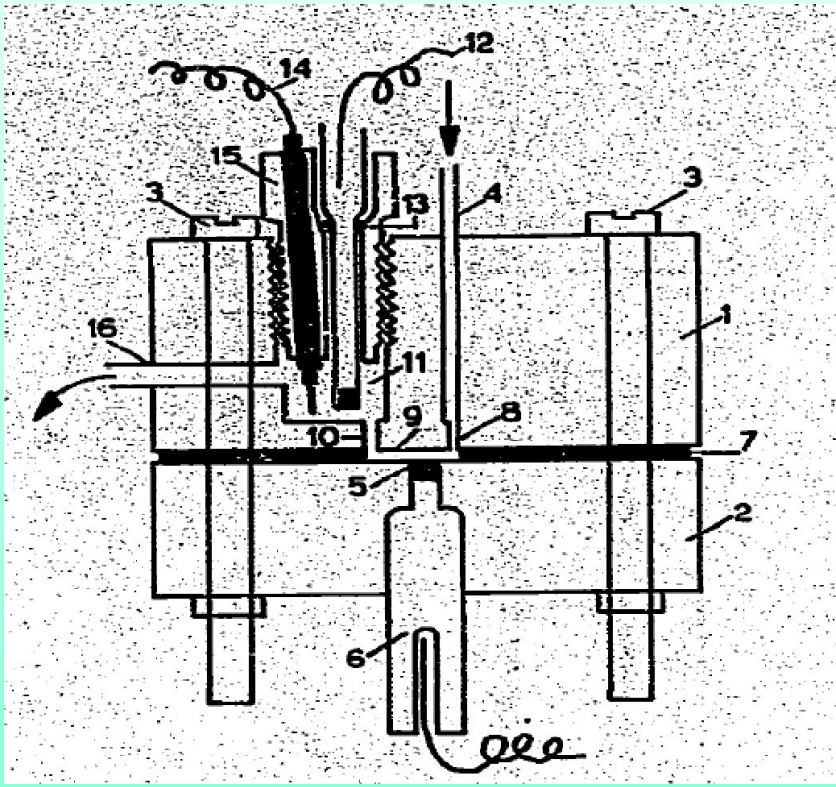


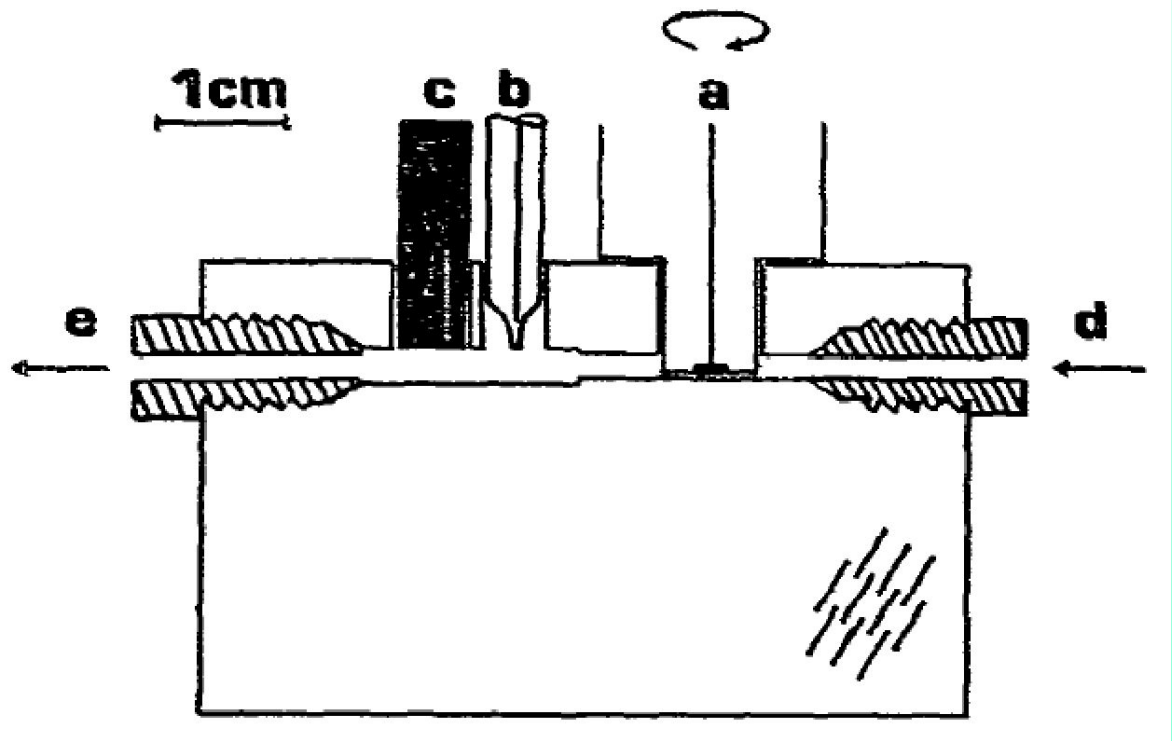
Fig. 3. The cell used. (a) Entry port; (b) exit port; (c) trough for carbon paste; (d) electrical connection to the carbon paste; (e) Ag wire holder; (f) stainless steel counter electrode; (g) PTFE spacer. The cell is assembled with 6 bolts, one at each corner and one on each of the long sides.

Тонкослойные проточные электроды

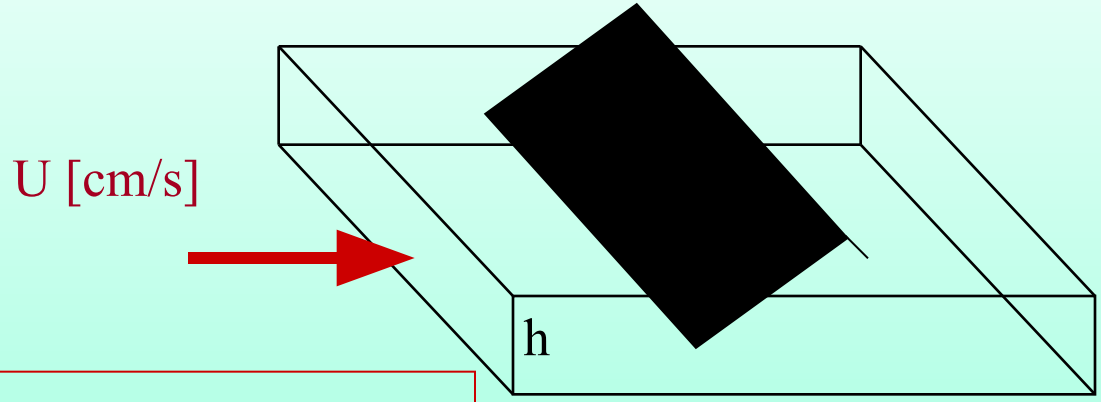




Тонкослойные проточные электроды



Гидродинамика тонкослойных проточных электродов



$$I = K \cdot nF \frac{A}{L^{1/3}} D^{2/3} C \left(\frac{U}{h} \right)^{1/3}$$

$$i = nFA \left(\frac{D}{\delta} \right) C$$

$$\delta = \frac{D^{1/3} L^{1/3} h^{1/3}}{K \cdot U^{1/3}}$$

Гидродинамика тонкослойных проточных электродов

$$i \propto U^{1/2}$$

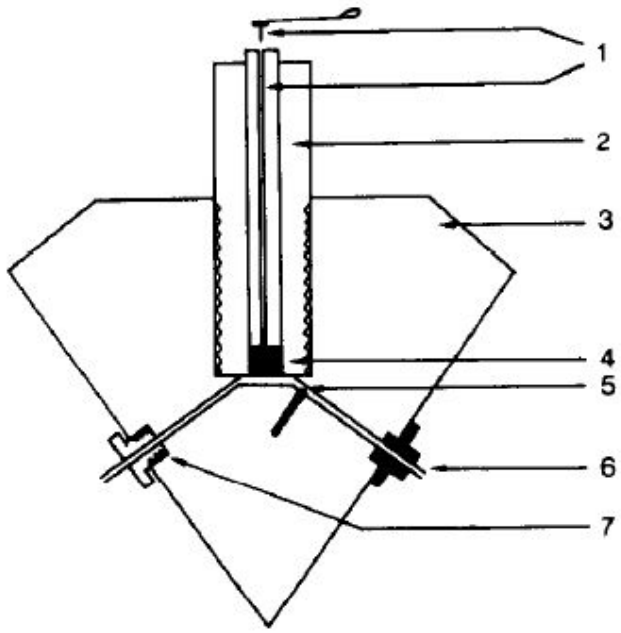
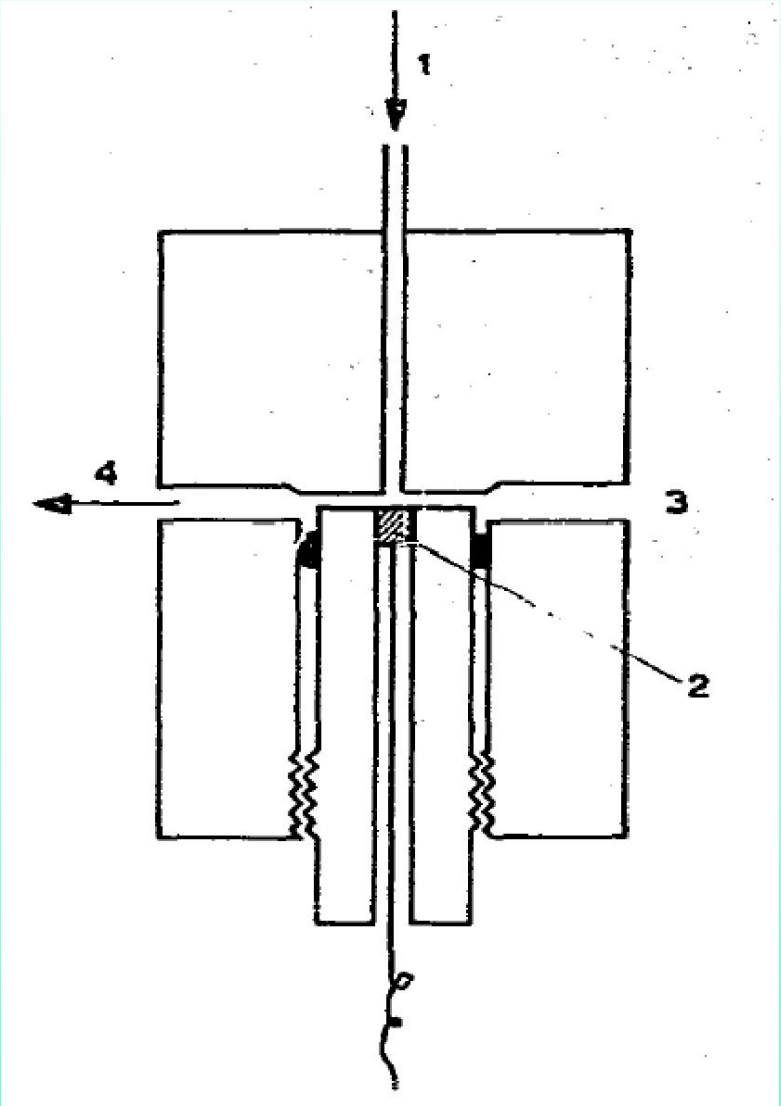


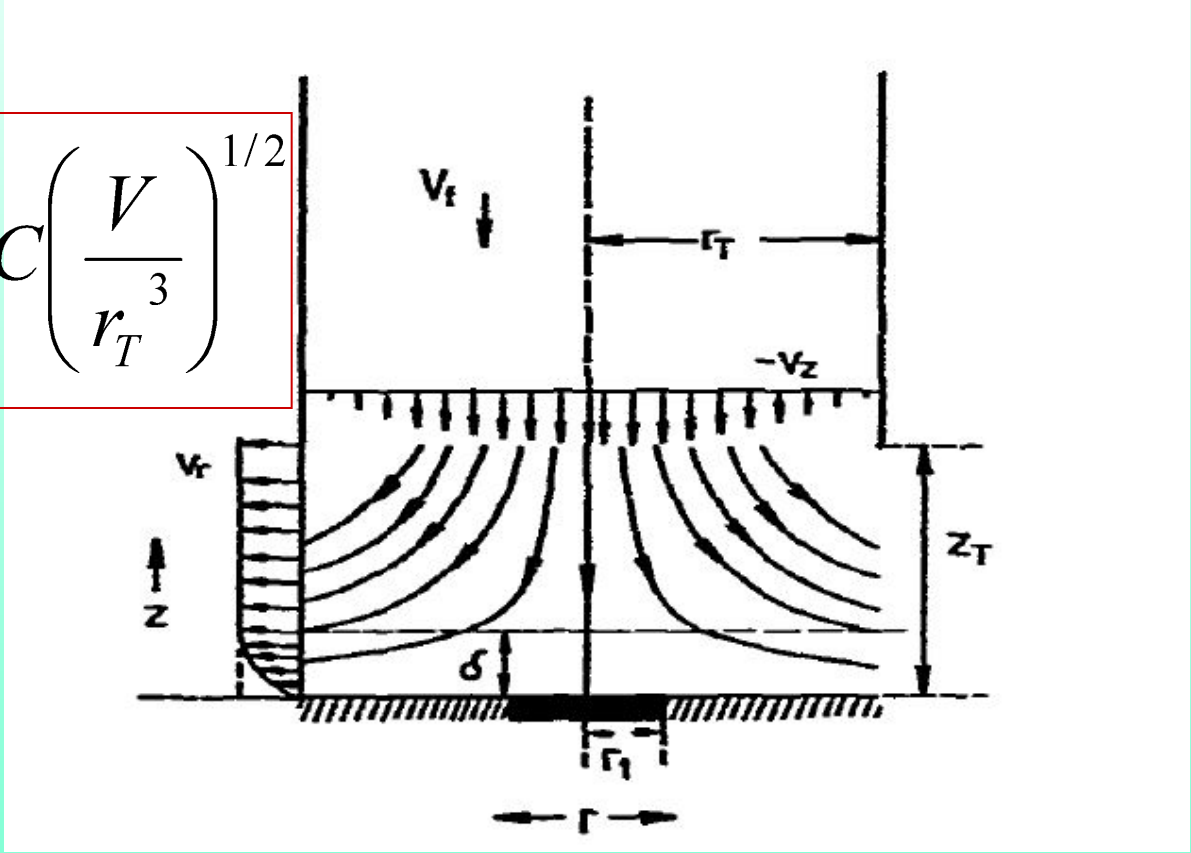
Fig. 1. Electrochemical flow-through cell. 1, Brass screws; 2, "Teflon" holder; 3, "Perspex" box; 4, glassy carbon electrode; 5, reference electrode (Ag/AgCl); 6, outlet with Swagelok connector (auxiliary electrode); 7, inlet.

Wall-jet электроды



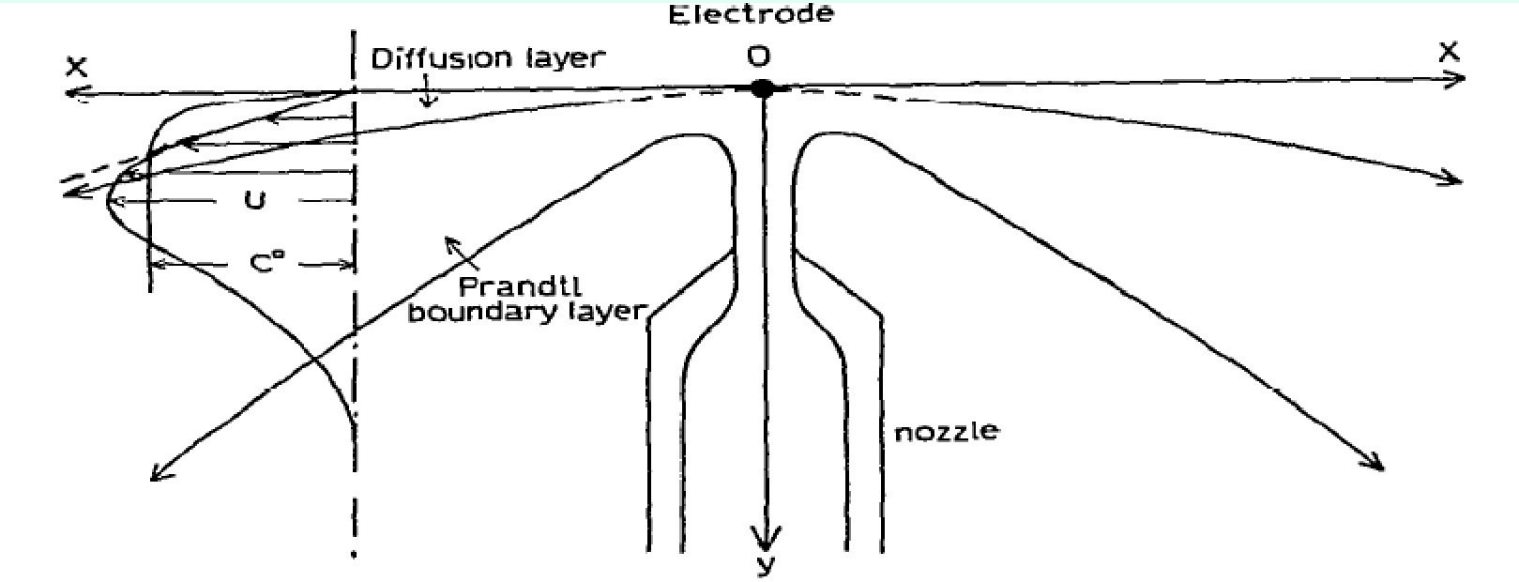
Гидродинамика wall-tube электродов

$$i = 0.61 nFAD^{2/3} \nu^{-1/6} C \left(\frac{V}{r_T^{\,3}} \right)^{1/2}$$



W.J. Albery, S. Bruckenstein *J.Electroanal. Chem.* **144** (1983) 105-12

Гидродинамика wall-jet электродов



$$i = 1.38nFR^{3/4}D^{2/3}\nu^{-5/12}CV^{3/4}a^{-1/2}$$

J. Yamada, H. Matsuda. *J. Electroanal. Chem.* **44** (1973) 189-98

Гидродинамика wall-jet электродов

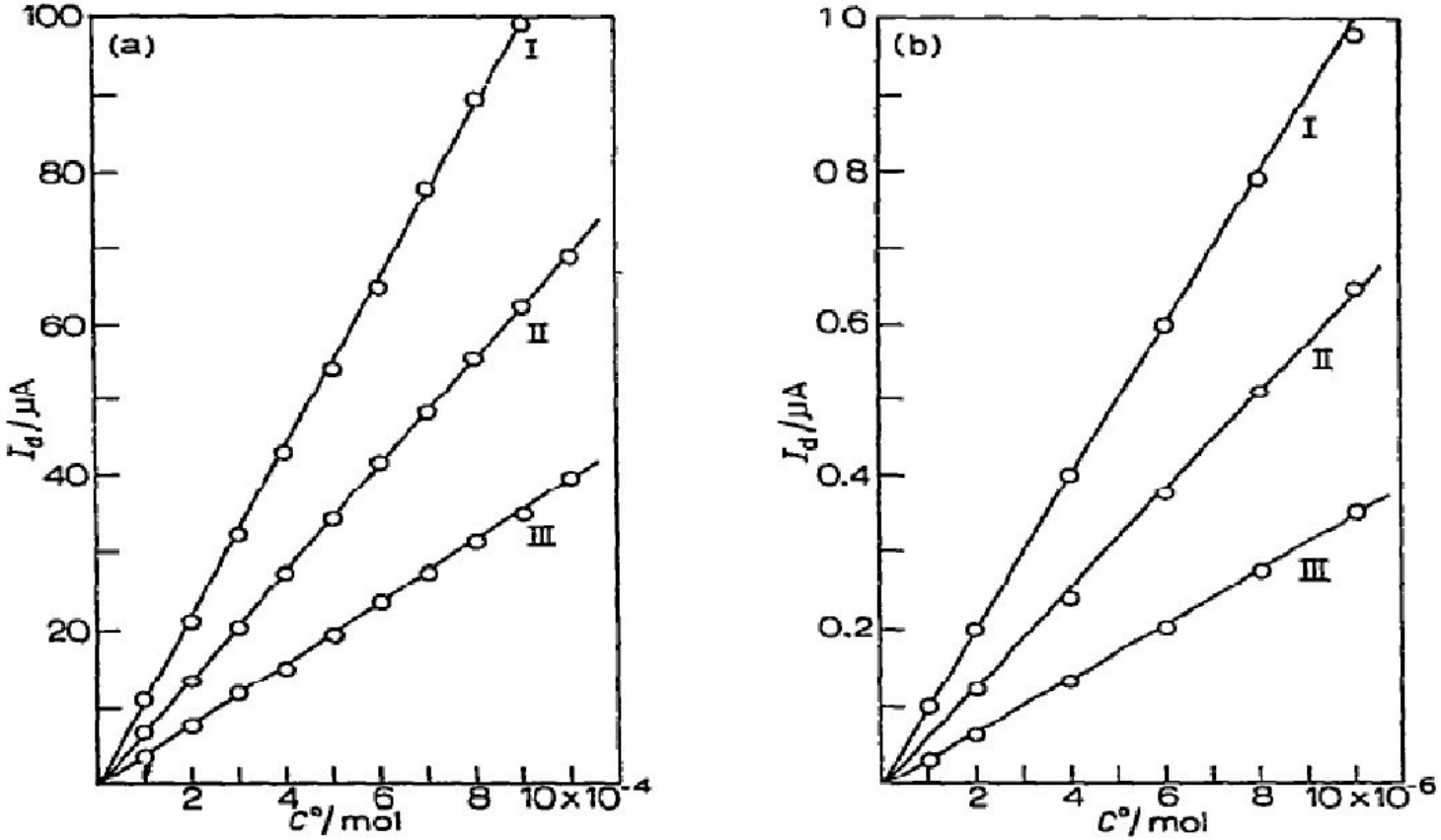
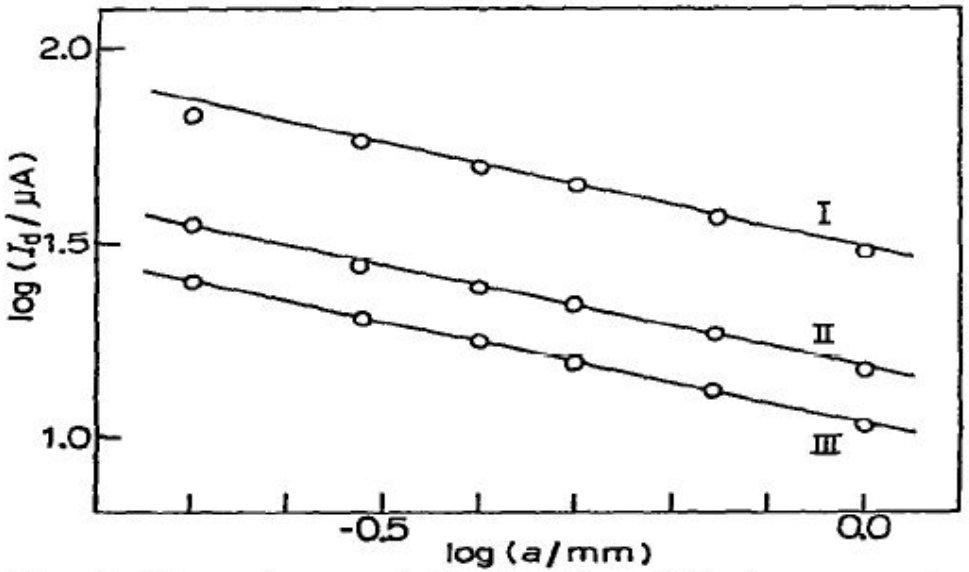


Fig 5. Dependence of the limiting diffusion current on the bulk concentration, C^0. $R=2.0$ mm. (I) $V=0.109$ ml s^{-1}, $a=0.3$ mm; (II) $V=0.0545$ ml s^{-1}, $a=0.3$ mm; (III) $V=0.0327$ ml s^{-1}, $a=0.5$ mm.

$$i = 1.38 nFR^{3/4} D^{2/3} \nu^{-5/12} C V^{3/4} a^{-1/2}$$

Гидродинамика wall-jet электродов



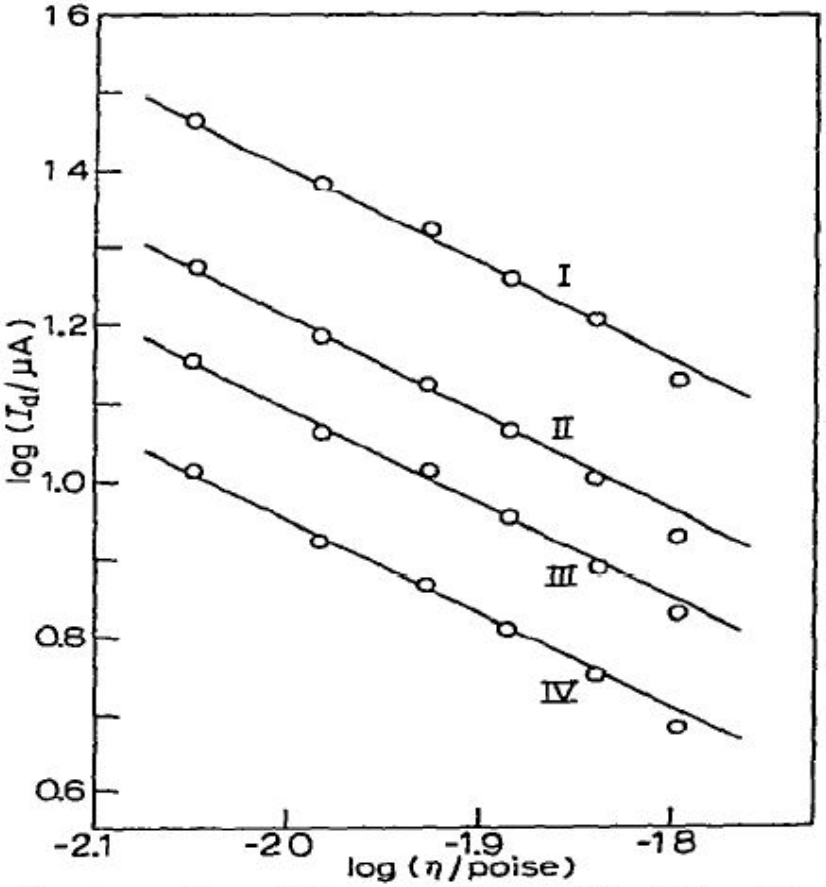
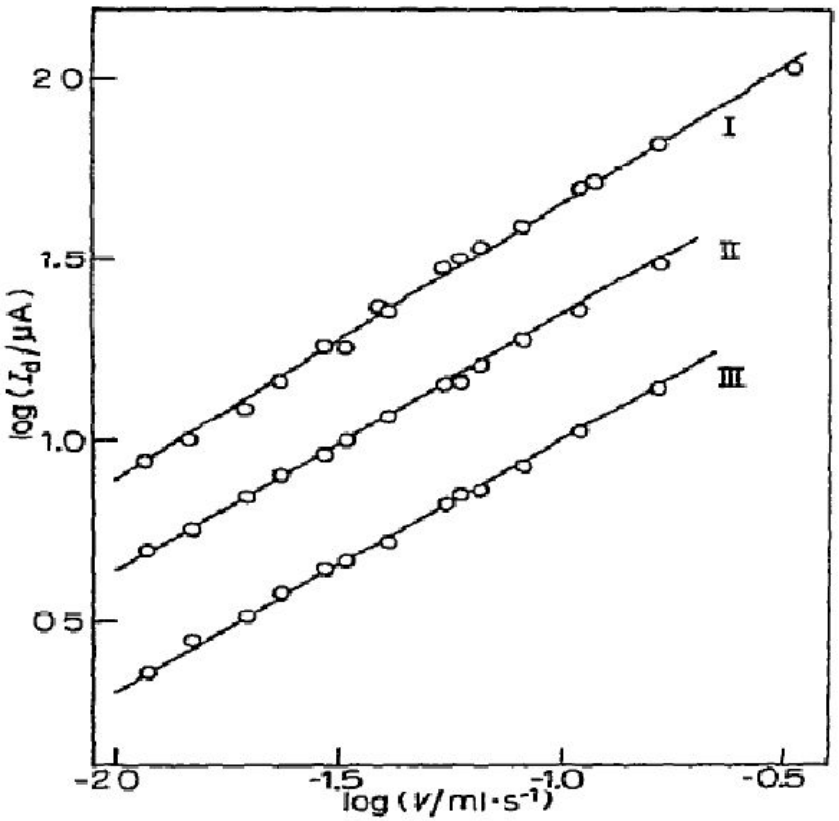


Fig. 8. Dependence of the limiting diffusion current on the diameter of the nozzle, a. $C^0=0.4$ mM; $R=2.0$ mm. (I) $V=0.164$ ml s^{-1}; (II) $V=0.0545$ ml s^{-1}; (III) $V=0.0327$ ml s^{-1}.

Fig. 9 Dependence of the limiting diffusion current on the viscosity of the solution, η. $C^0=0.2$ mM; $R=2.0$ mm; $a=0.3$ mm. (I) $V=0.164$ ml s^{-1}; (II) $V=0.0818$ ml s^{-1}; (III) $V=0.0545$ ml s^{-1}; (IV) $V=0.0327$ ml s^{-1}.

$$i = 1.38 nFR^{3/4} D^{2/3} \nu^{-5/12} C V^{3/4} a^{-1/2}$$

Гидродинамика wall-jet электродов



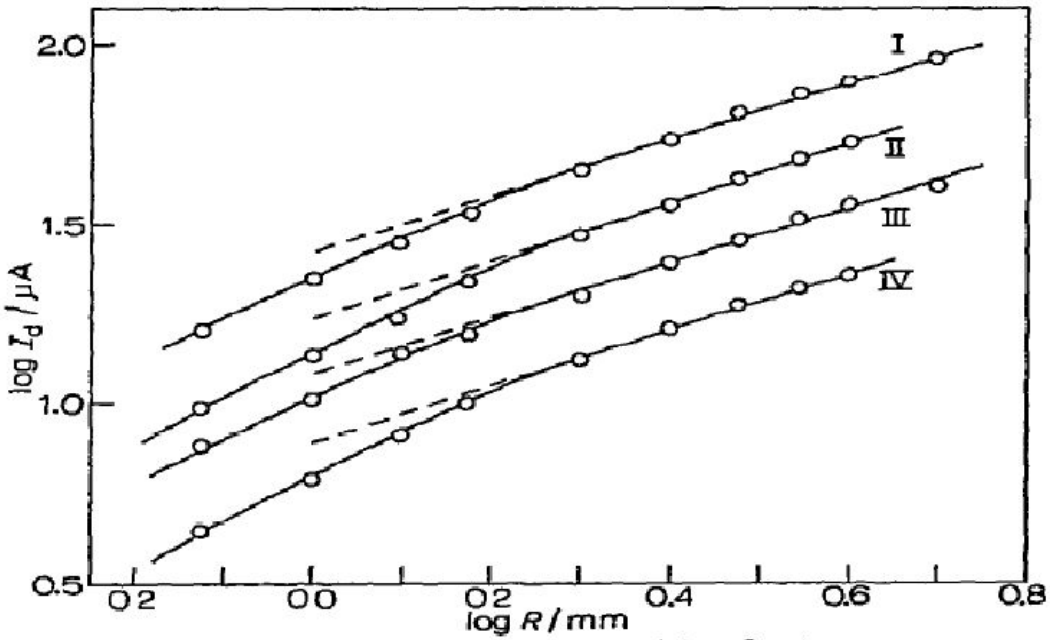


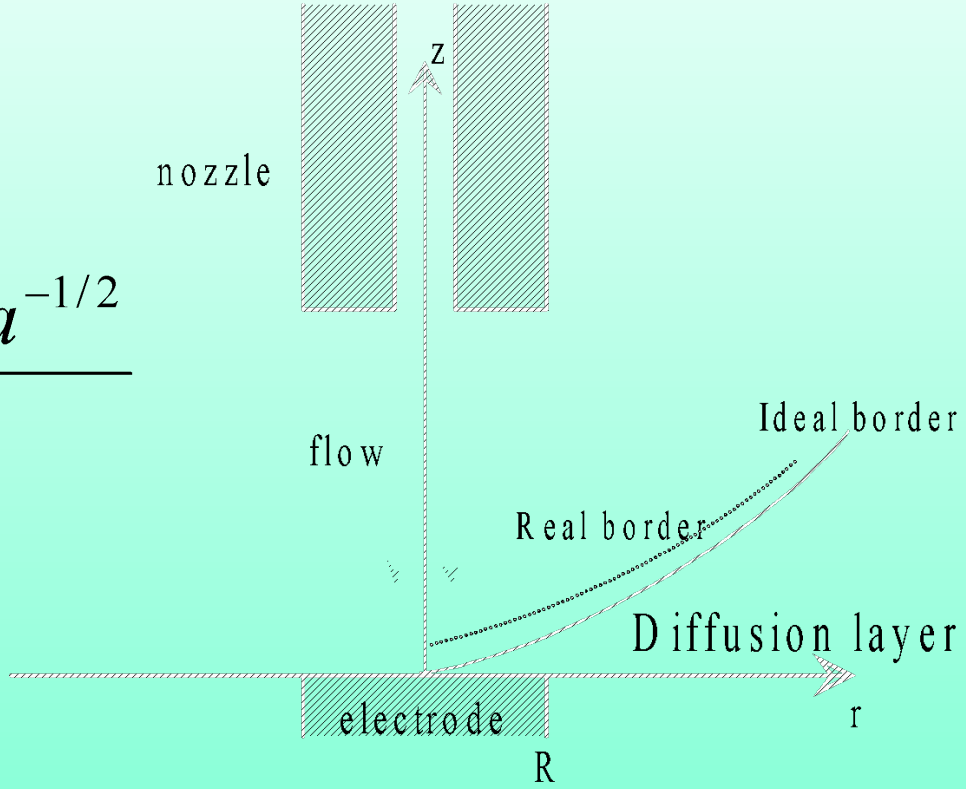
Fig 6 Dependence of the limiting diffusion current on the volume flow rate, V (I) C^0=0.2 mM, R=5.0 mm, a=0.3 mm, (II) C^0=0.2 mM, R=2.0 mm, a=0.3 mm; (III) C^0=0.1 mM, R=2.5 mm, a=0.5 mm .

Fig 7. Dependence of the limiting diffusion current on the radius of the disk electrode, R. C^0=0.4 mM (I) V=0.109 ml s^{-1}, a=0.3 mm, (II) V=0.109 ml s^{-1}, a=0.7 mm, (III) V=0.0327 ml s^{-1}, a=0.3 mm; (IV) V=0.0327 ml s^{-1}, a=0.7 mm

$$i = 1.38 nFR^{3/4} D^{2/3} \nu^{-5/12} C V^{3/4} a^{-1/2}$$

Гидродинамика реальных wall-jet электродов

$$i = 1.38nF\frac{R^2 D^{2/3}\nu^{-5/12}CV^{3/4}a^{-1/2}}{(\underbrace{\bar{\theta}V^{1/4}}_{\theta} + R^{5/4})}$$

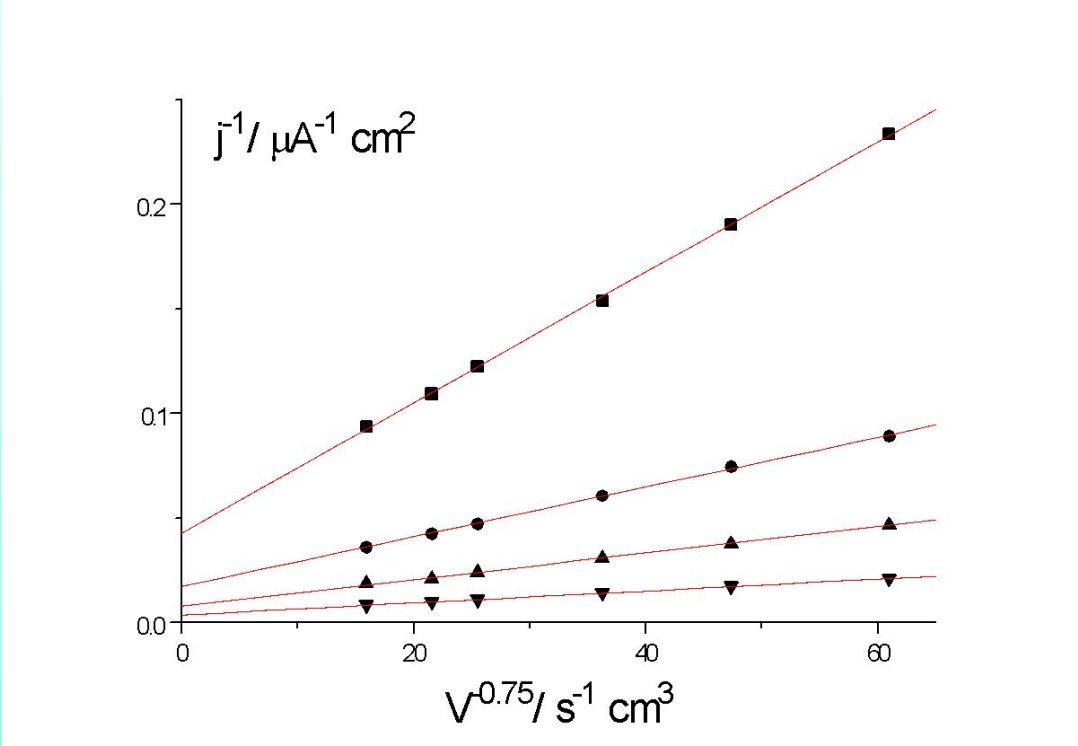


θ/ mm$^{5/4}$

V/ml s^{-1} \ a/mm	0.3	0.7
0.0327	0.25	0.36
0.109	0.30	0.46

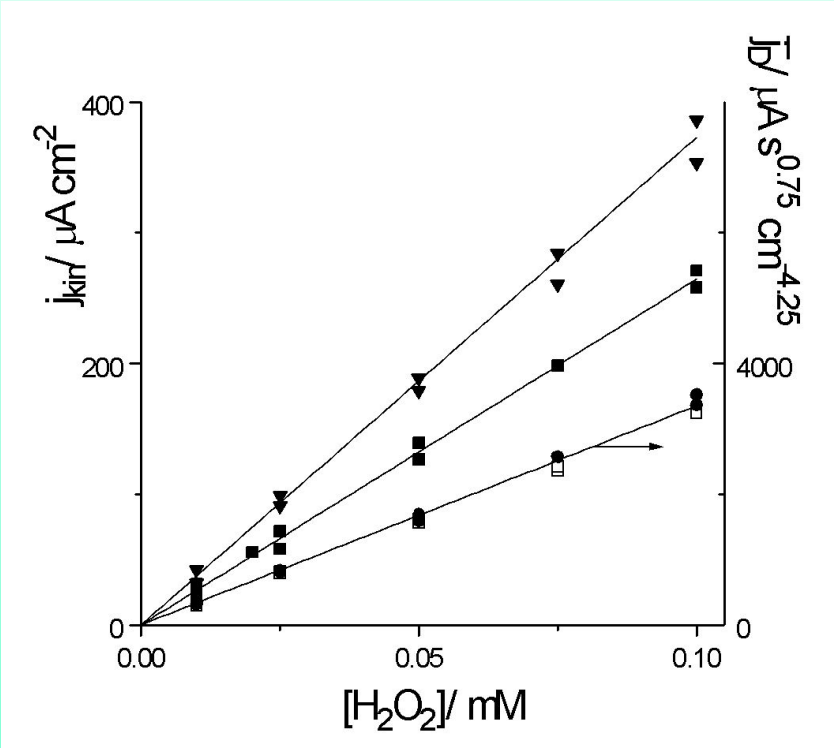
Определение кинетических параметров на wall-jet электродах

$$\frac{1}{j} = \frac{1}{nFc_o} \cdot \left(\frac{1}{k_D} + \frac{1}{k} \right)$$

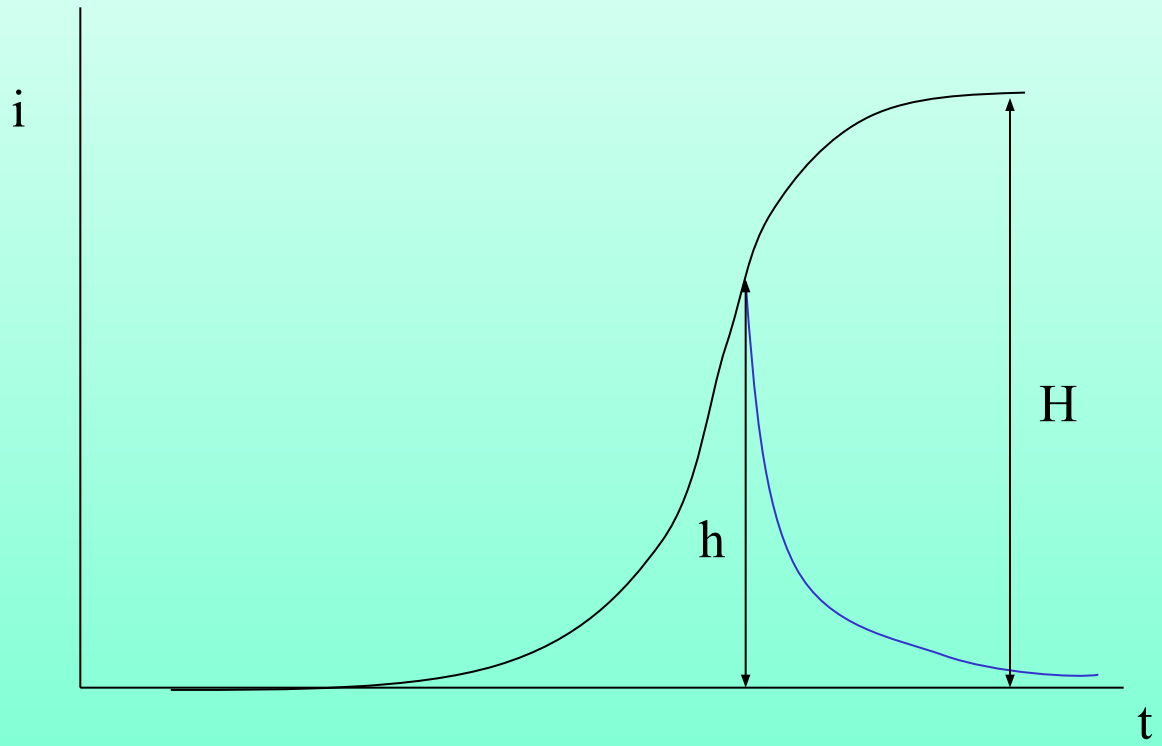


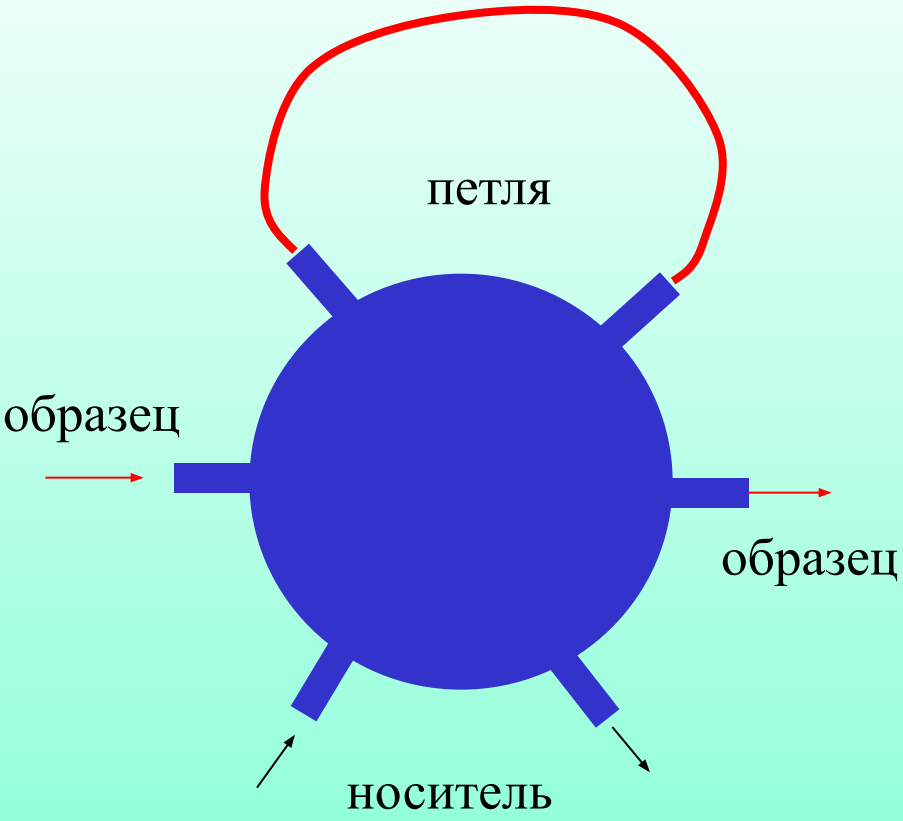
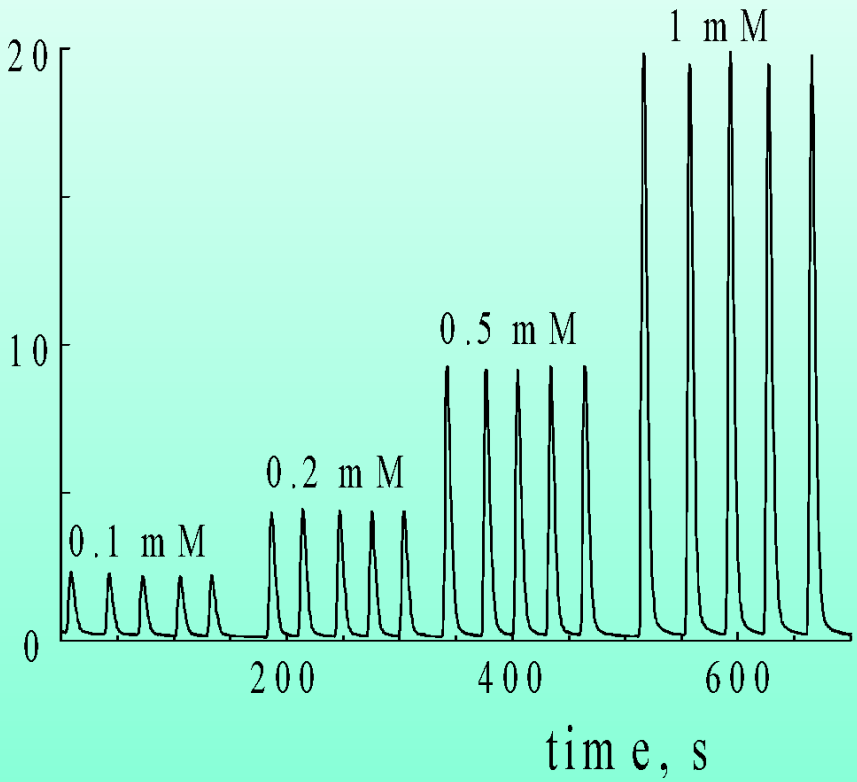
Определение кинетических параметров на wall-jet электродах

$$\frac{1}{j} = \frac{1}{nFc_o} \cdot \left(\frac{1}{\overline{k_D}} + \frac{1}{k} \right)$$



Проточно-инжекционный анализ



Коэффициент дисперсии: D=H/h

Проточно-инжекционный анализ