Electroanalytical flow systems in process analysis

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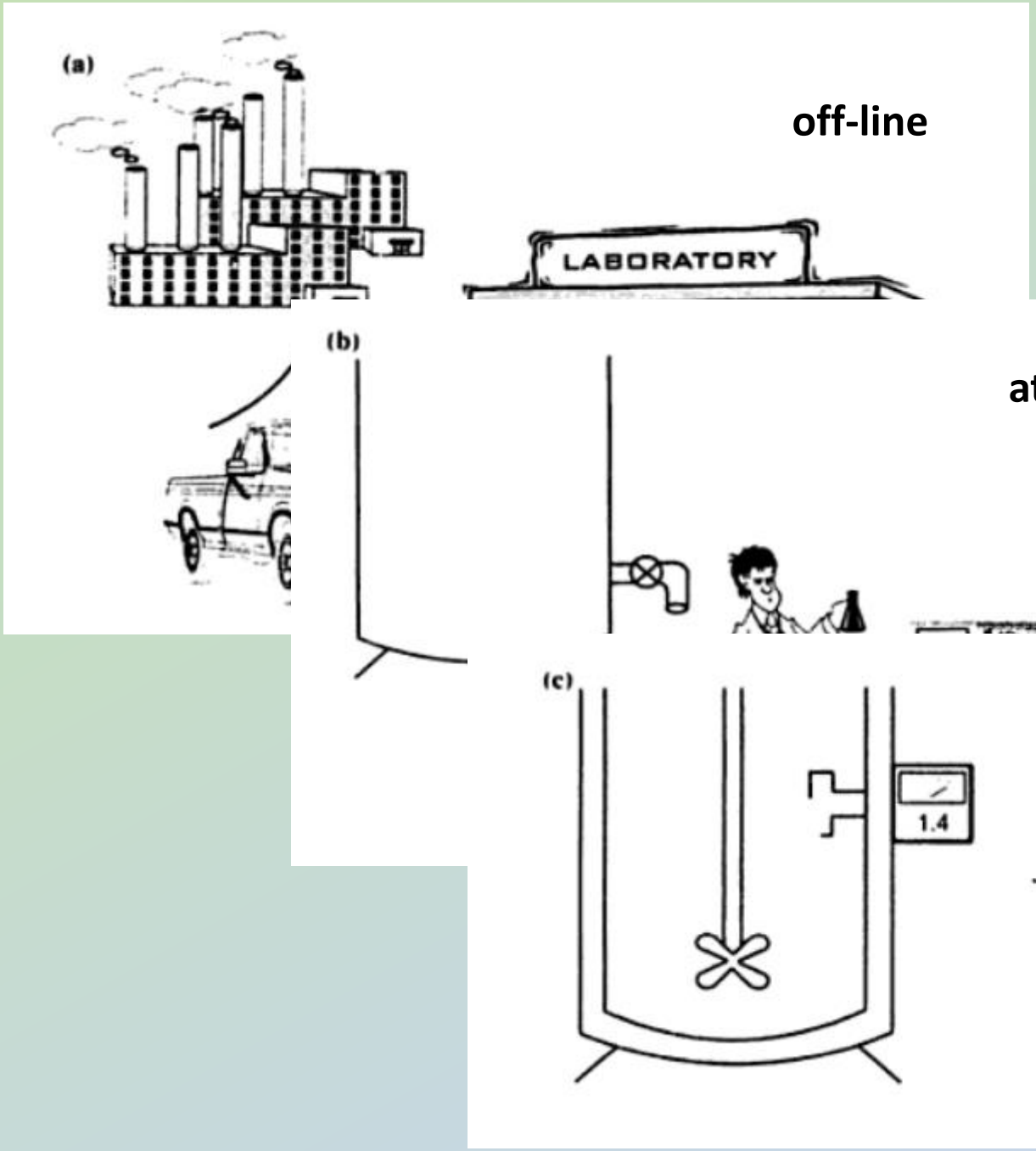
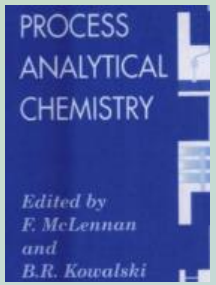
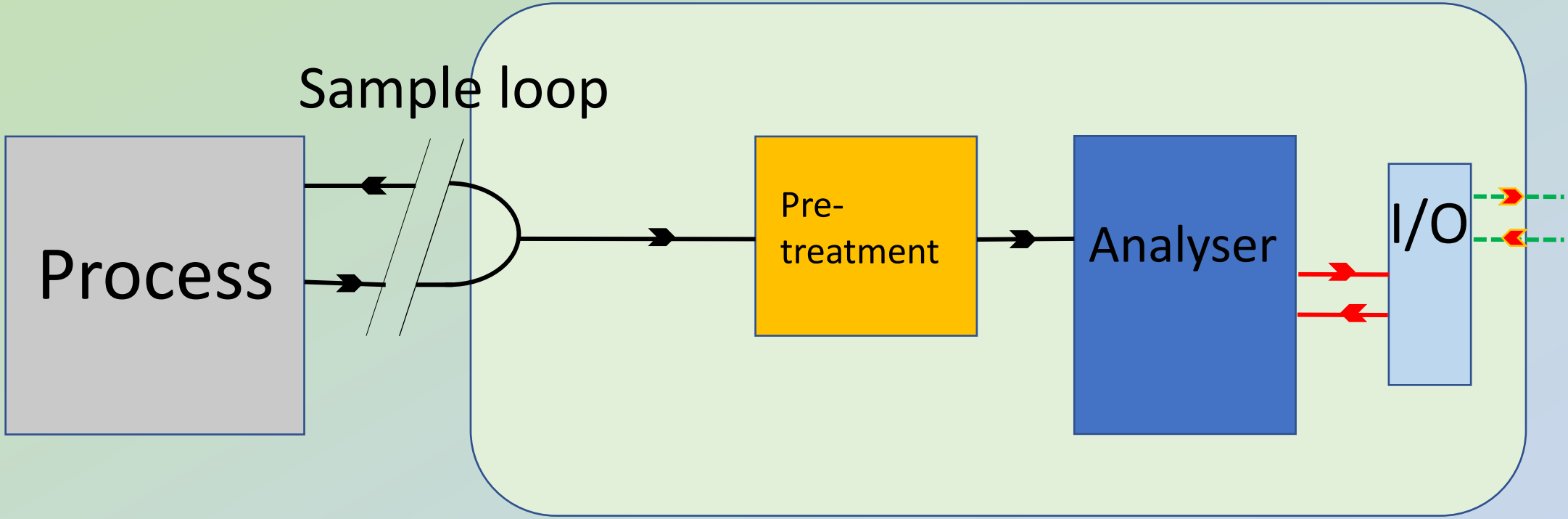

(a)
off-line
LABORATORY
(b)
at-line
(c)
in-line
on-line
1.4


PROCESS
ANALYTICAL
CHEMISTRY
Edited by
F. McLennan
and
B.R. Kowalski

on-line

On-line monitoring system



Monitored parameters

Physical (temperature, pressure, viscosity, flow rate ...)

Chemical (elements, compounds, pH, COD, TOC ...)

Biochemical and biological (BOC, toxicity, chlorophyl ...)

Analytical methods in process analysis

- Titrimetry
- UV-VIS spectrophotometry
- Fluorimetry
- IR spectrometry
- Mass spectrometry
- **Electroanalysis**

Electrochemical methods

Species-sensitive method

Direct contact of the sensor with sample

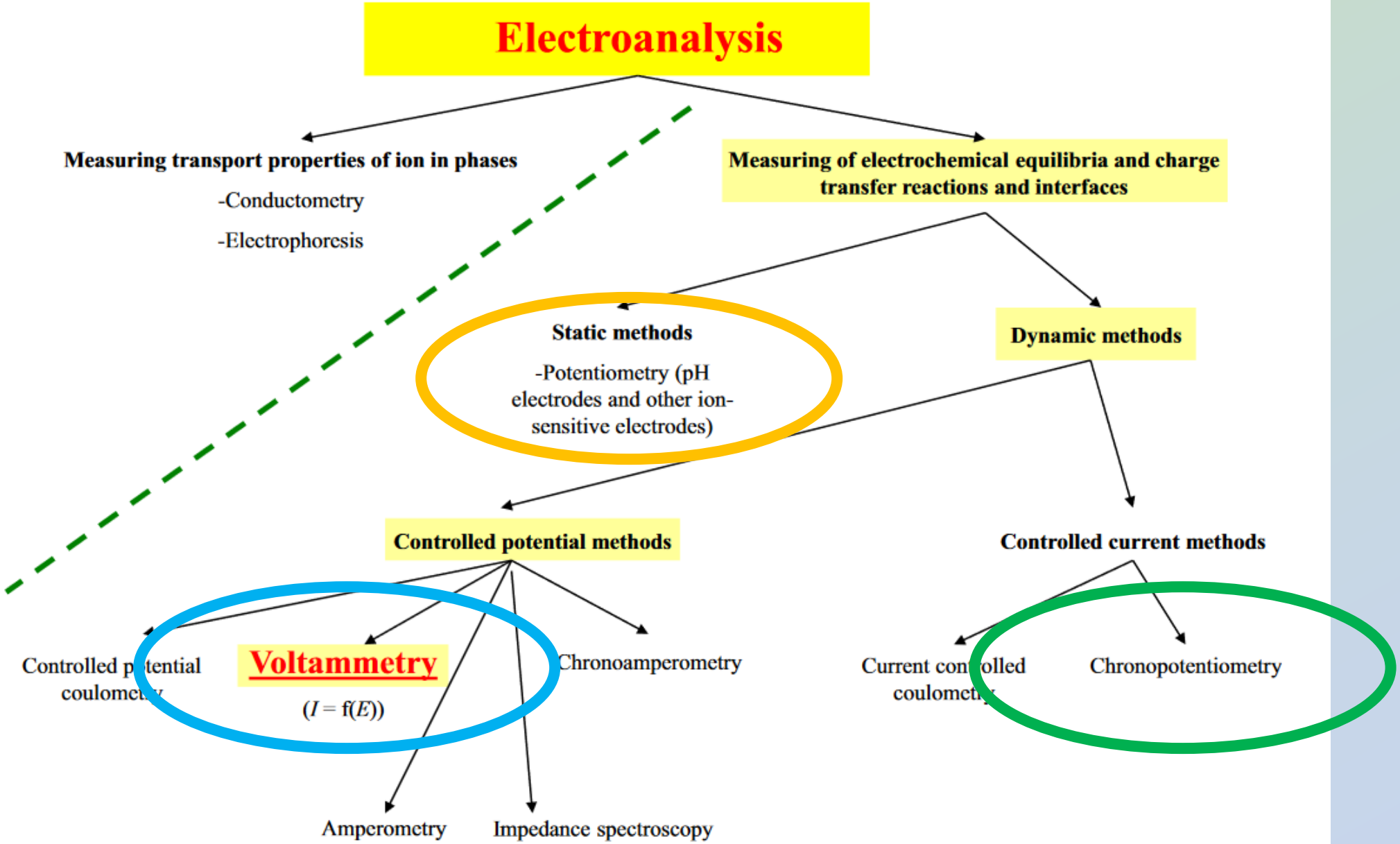
High sensitivity and selectivity

Miniaturisation, mass production

Simple instrumentation

Simple automation

Low costs



Fritz Scholz: Voltammetric techniques of analysis: the essentials. *ChemTexts* (2015) 1:17, DOI 10.1007/s40828-015-0016-y

Requirements:

Robust electrochemical cell

Long-life electrodes

On-line sample treatment

Voltammetry

Advantages

- Linear response
- Broad concentration range
- Charging currents can be eliminated
- Proven applications

Limitations

- iR drop compensation not trivial
- Switching of current ranges

Chronopotentiometry

Advantages

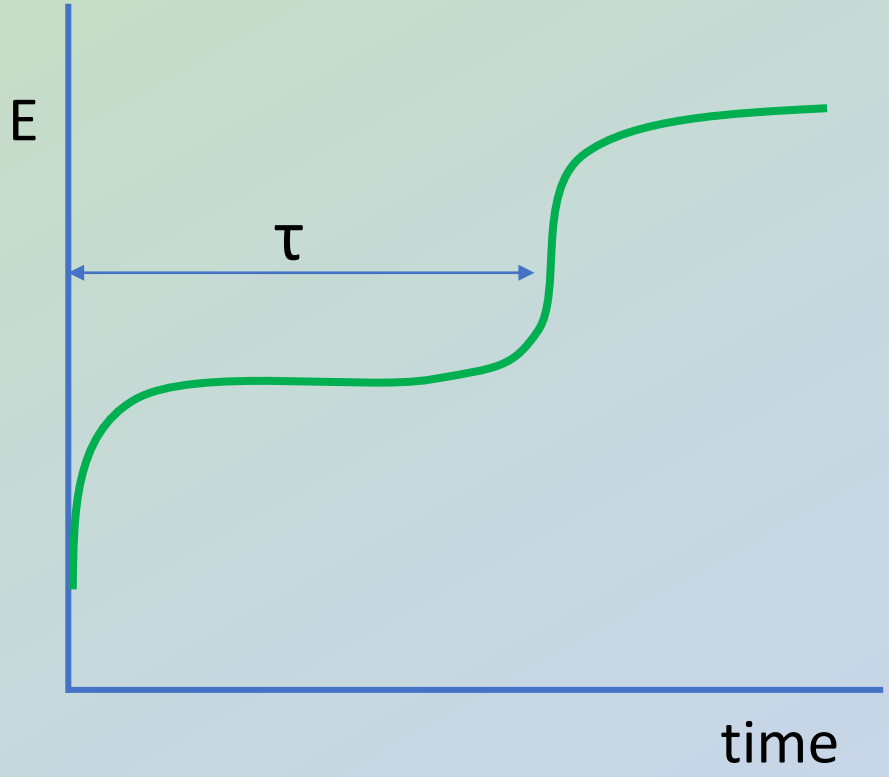
- Broad concentration ranges
- Response linearity in thin layer arrangements and stripping mode
- Direct coulometric titrations
- Simple iR drop compensation
- Simple instrumentation

Limitations

- Nonlinear concentration dependences in some cases
- Charging currents cannot be simply eliminated
- Constant current CP not working on individual microelectrodes
- Few applications available

Chronopotentiometry

In chronopotentiometry, a current step is applied across an electrochemical cell (usually without stirring) and the potential of the working electrode is monitored against a reference electrode. The potential-time dependence resembles an oxidation-reduction titration curve which it actually is.



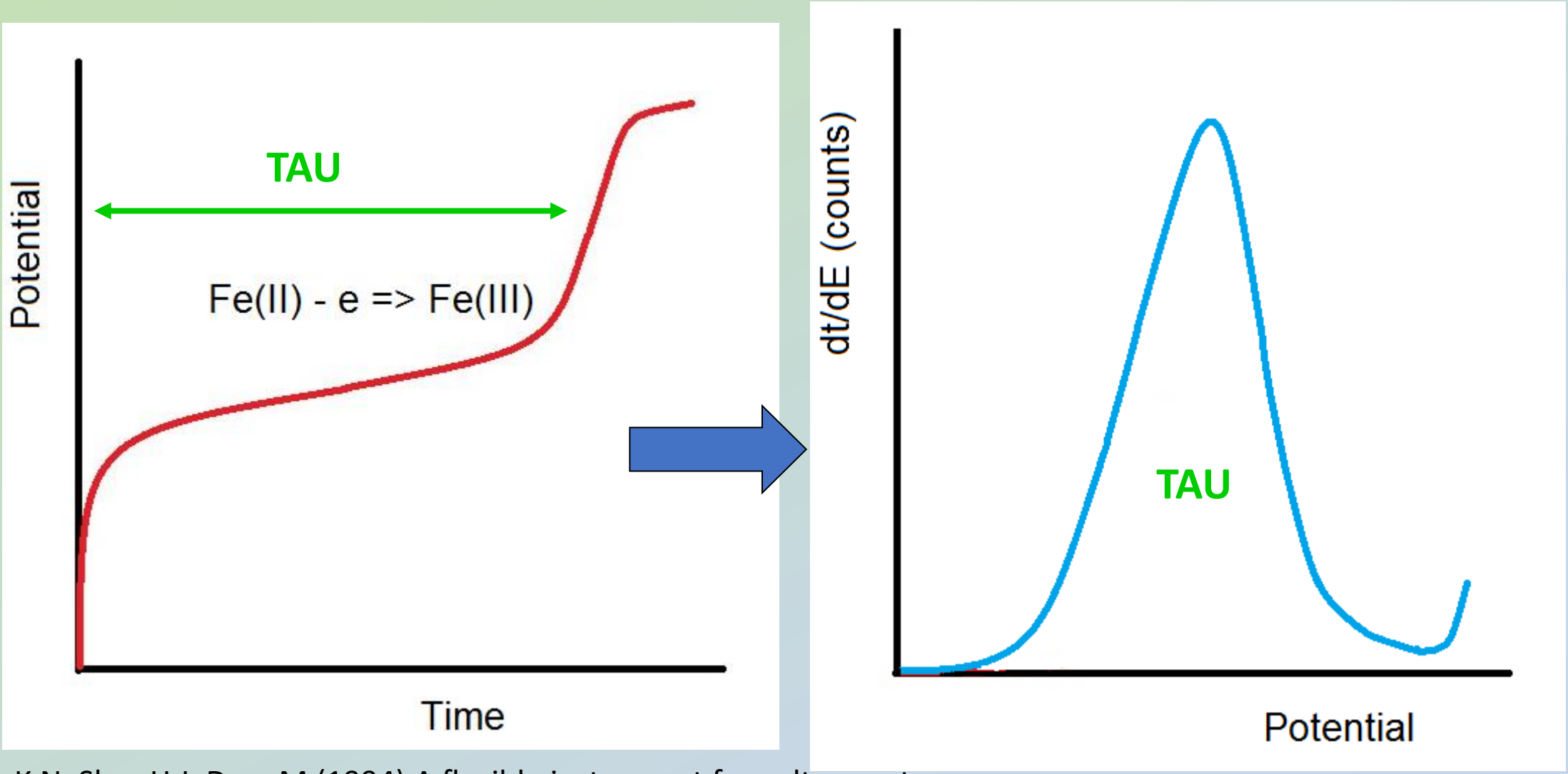
Sand equation:

$$i\tau^{1/2} = \frac{nFAC\pi^{1/2}D^{1/2}}{2}$$

$$\tau = k\, c^2$$

H. J. S. Sand : *About the concentration at the electrodes in a solution, with special consideration of the hydrogen evolution through electrolysis of a mixture of copper sulfate and sulfuric acid* . In: *Journal of Physical Chemistry* . tape 35 , No. 1 , October 1900, p. 641-651 , doi : 10.1515 / zpch-1900-0143

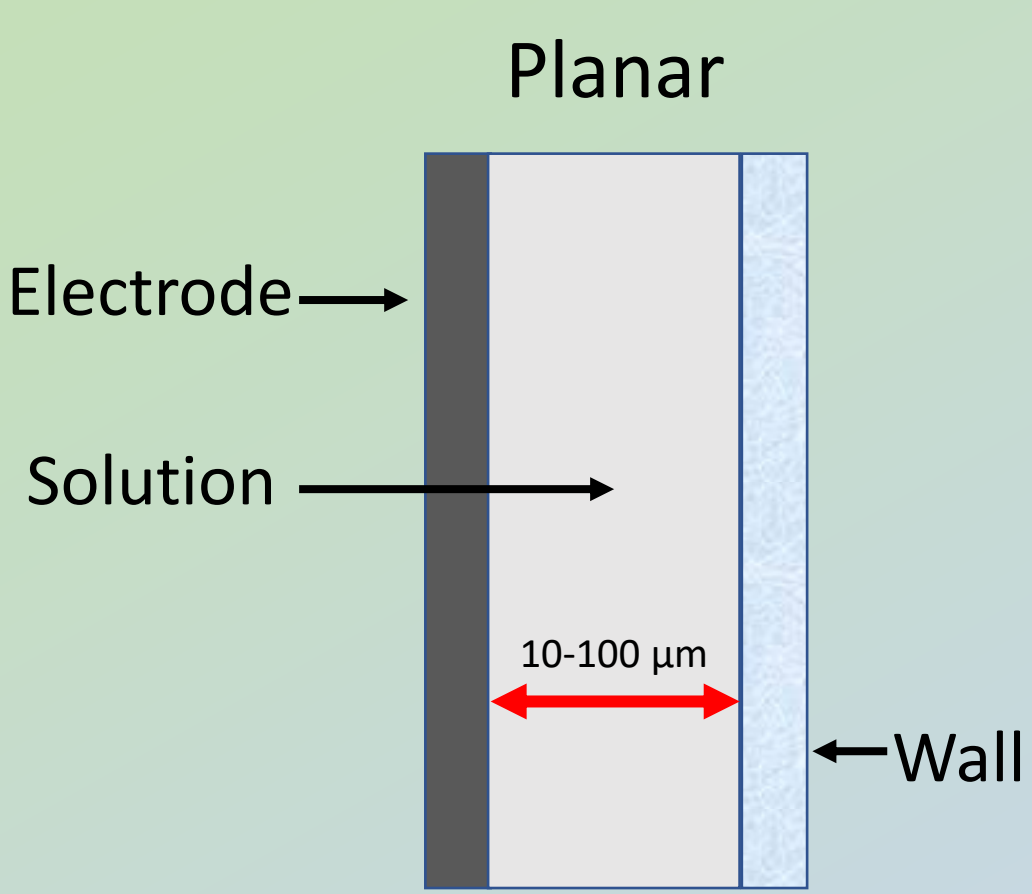
Measurement principle: “Memory mapping”

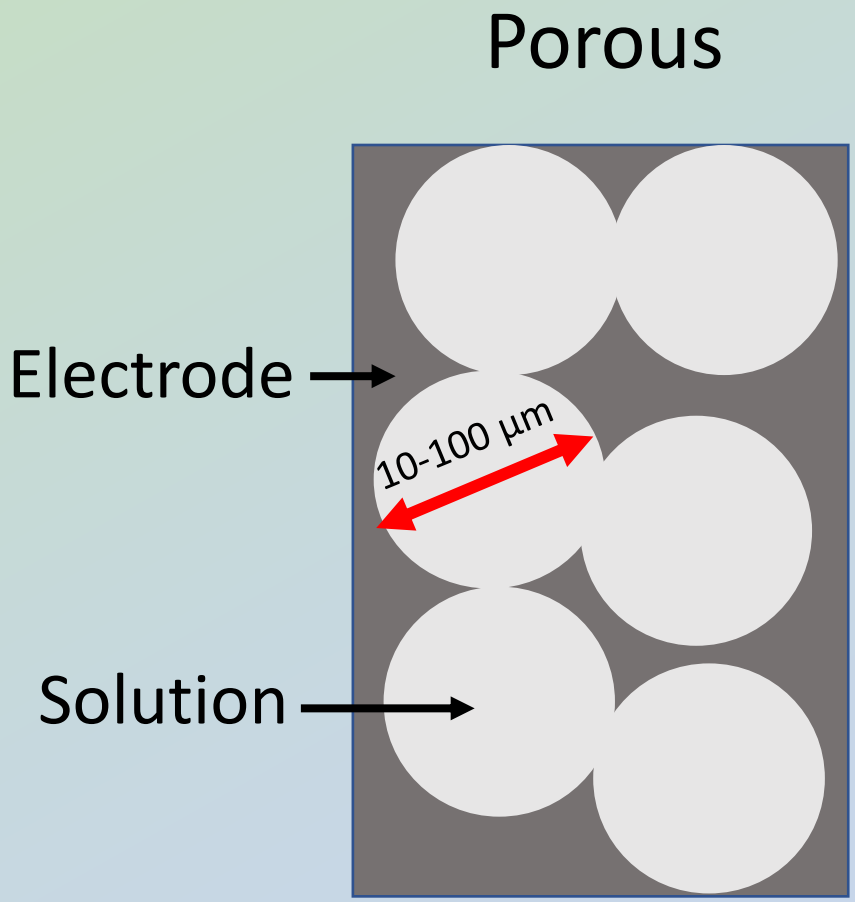


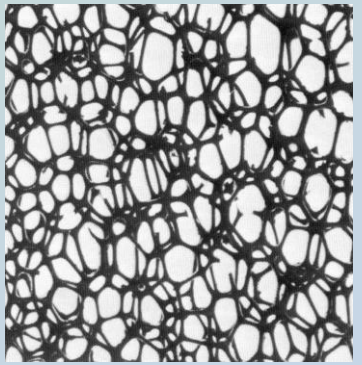
Thomsen K N, Skov H J, Dam M (1994) A flexible instrument for voltammetry, amperometry and stripping potentiometry. Anal Chim Acta 293: 1

Chronopotentiometry: Linearity

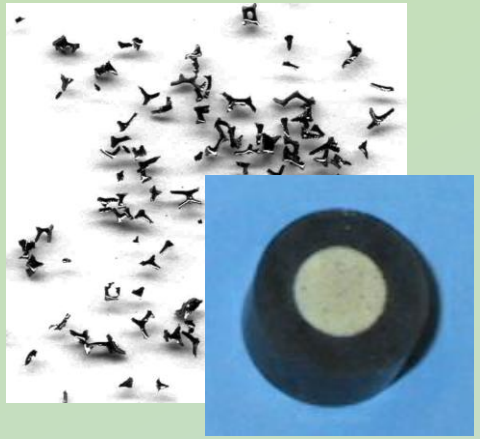
Thin layer cell design:





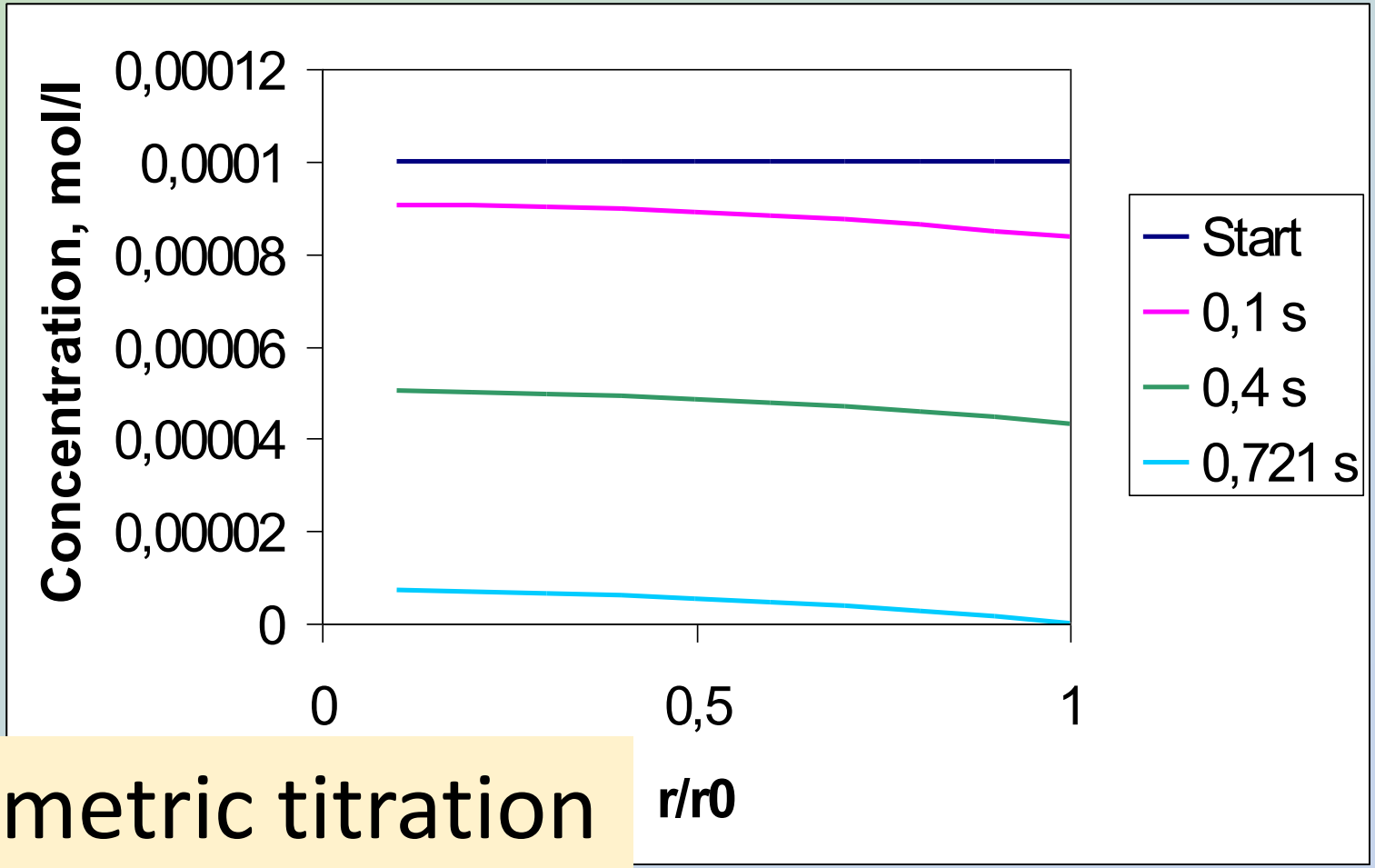


Chronopotentiometry: Linearity



Pore diameter: 15 μm

Current density: 5 μA/cm²



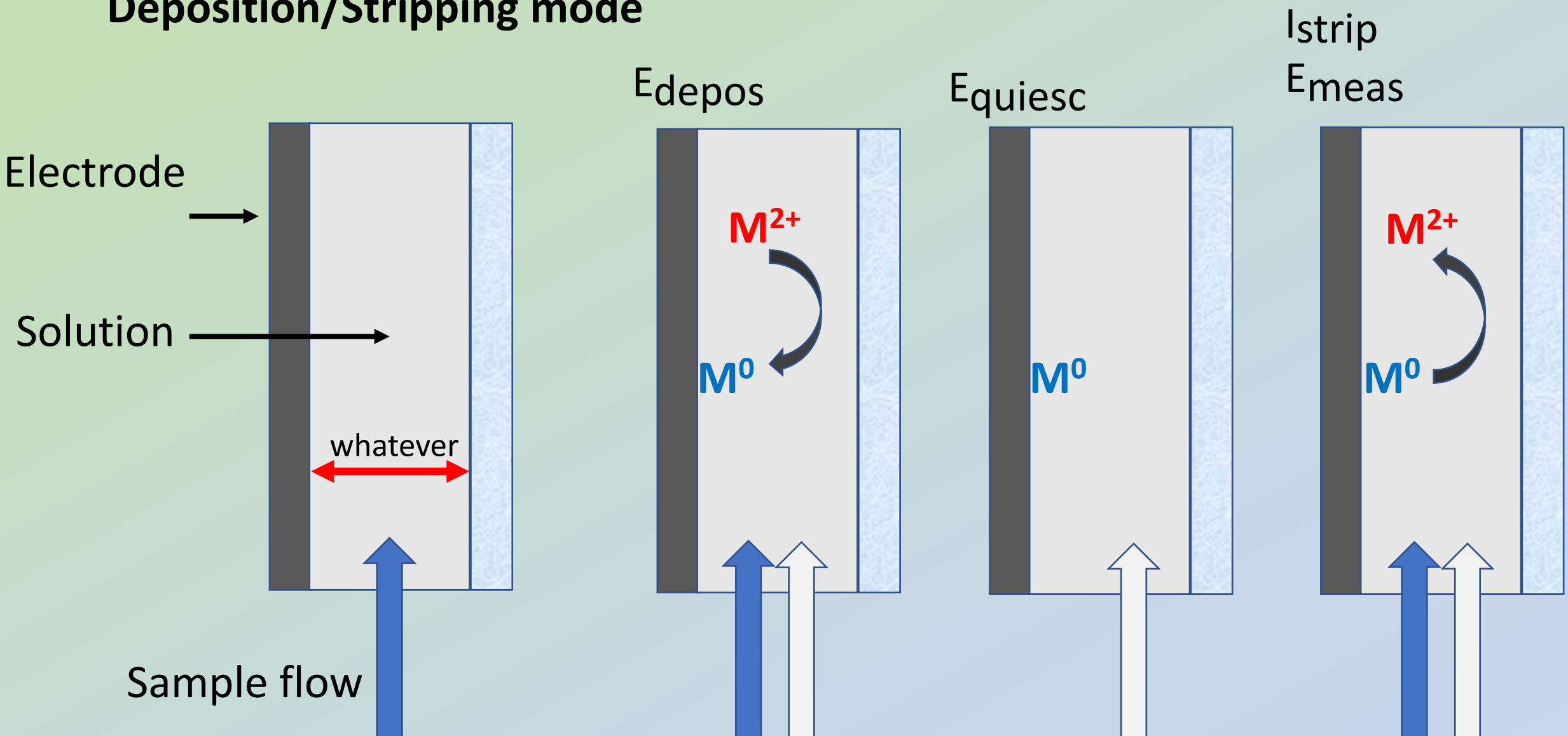
$\tau = r\ z\ F\ c\ V/i$

In-electrode coulometric titration

Chronopotentiometry: Linearity

$\tau = r\ z\ F\ c\ V/i$

Deposition/Stripping mode



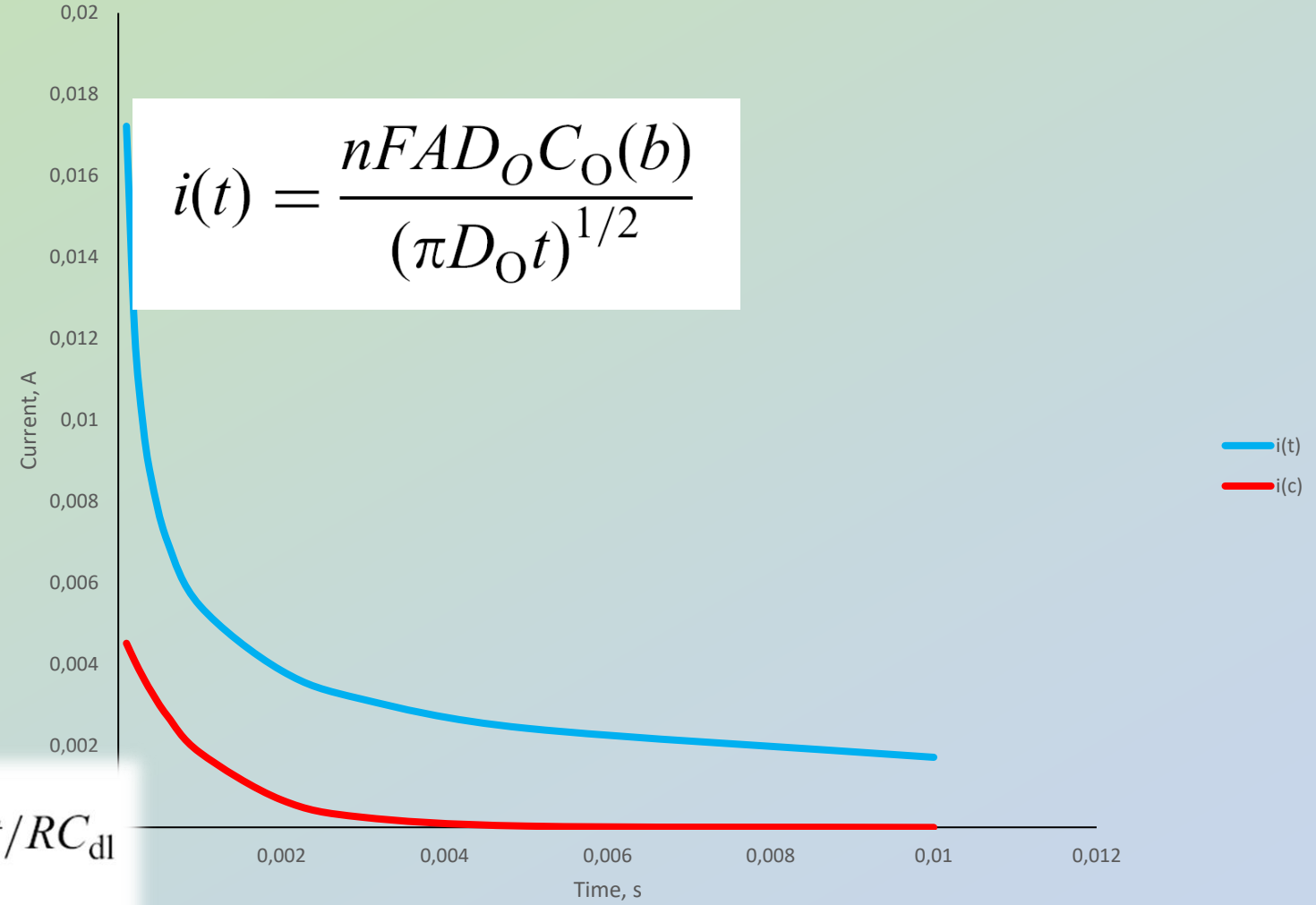
Background compensation

A fraction of the applied current is consumed by other procedures than the electrode reaction of the analyte species:

i) Reaction of the electrode surface
ii) Electrode reactions of matrix components (interfering species, impurities)
iii) Double layer charging

E = 500 mV
R = 100 Ω
C_{dl} = 10 μF
D = 10^{-5} cm^2 s^{-1}
A = 1 cm^2
c = 0.001 mol/l

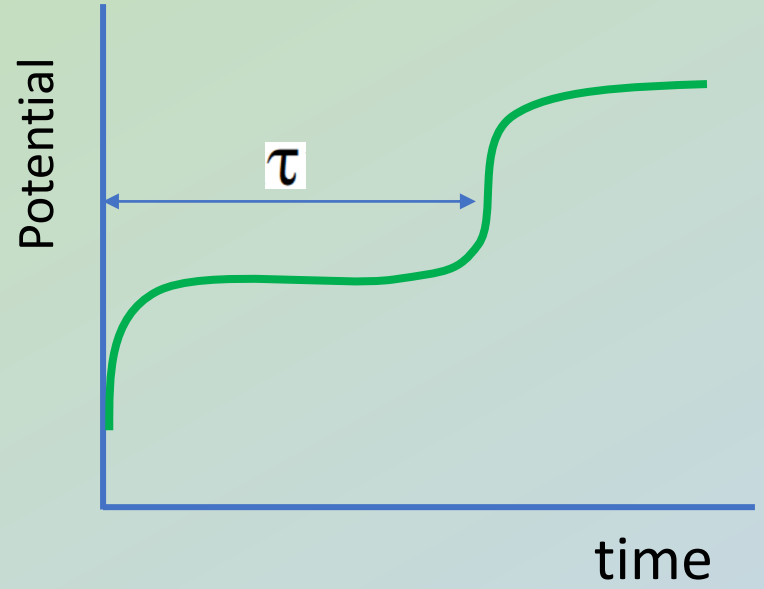
$$i(t) = \frac{nFAD_O C_O(b)}{(\pi D_O t)^{1/2}}$$

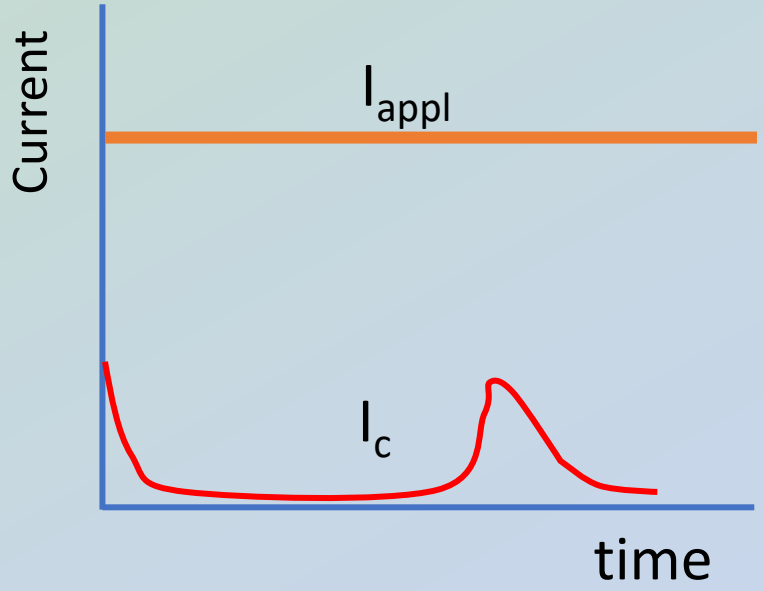


$$i_c = \frac{E}{R_S} e^{-t/RC_{dl}}$$

Cottrell, F. G. (1903-01-01). "Der Reststrom bei galvanischer Polarisation, betrachtet als ein Diffusionsproblem". Zeitschrift für Physikalische Chemie (in German). Walter de Gruyter GmbH. 42U (1): 385. doi:10.1515/zpch-1903-4229

Chronopotentiometry



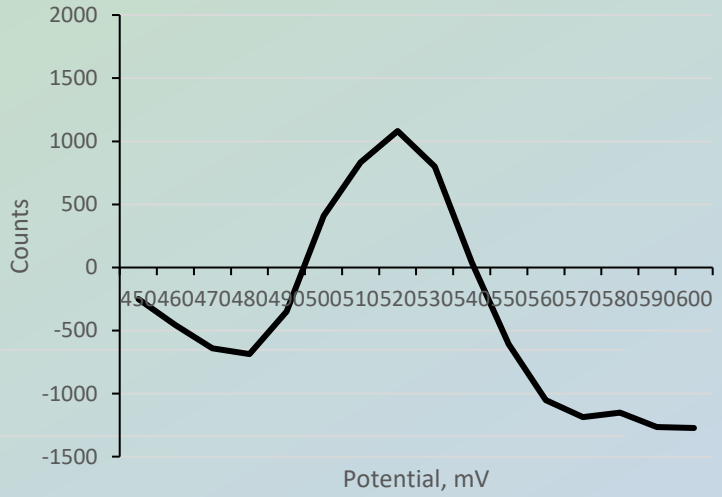


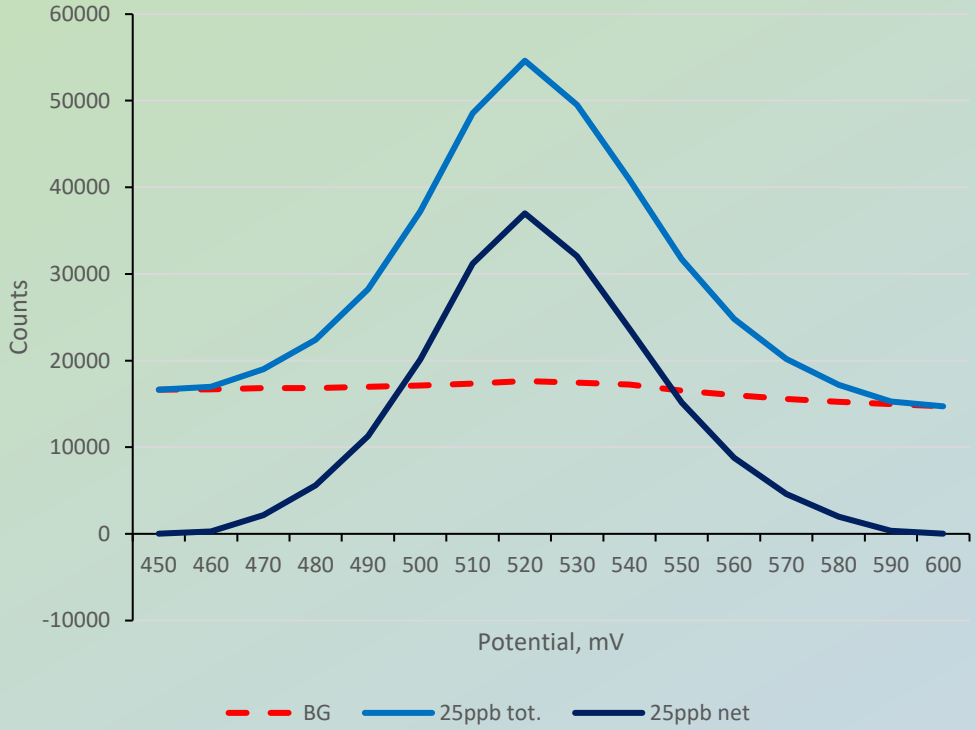
$$\tau = r\ z\ F\ c\ V/i$$

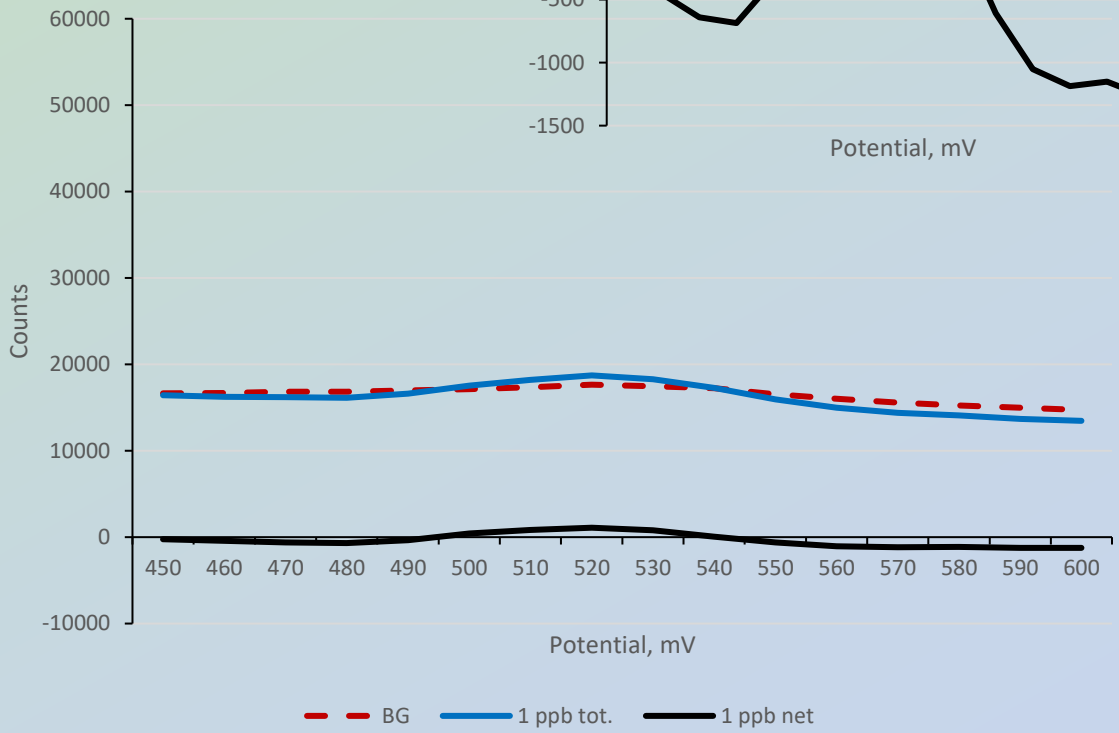
Chronopotentiometry

Background compensation: Blank sample

Hg^{2+} deposition/stripping on gold wire electrode in HCl media







Chronopotentiometry

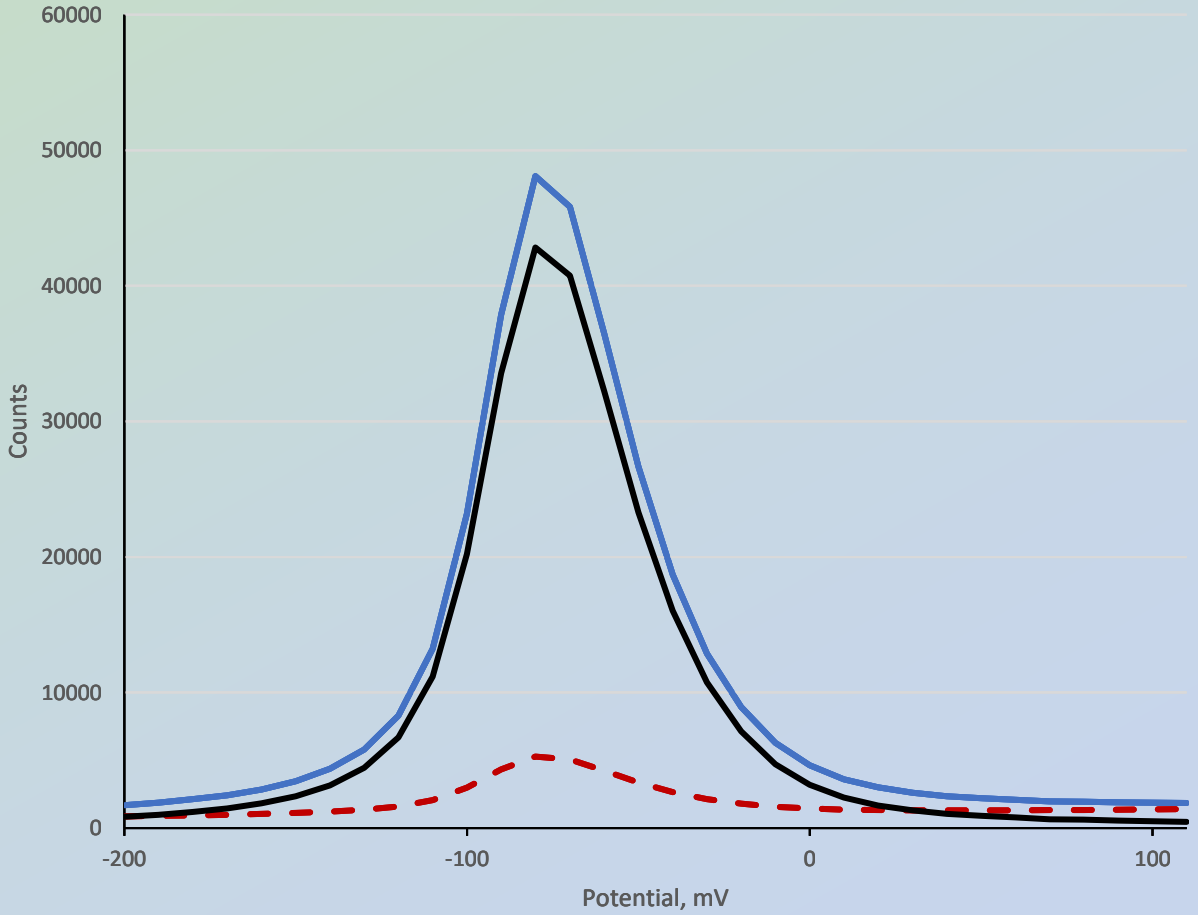
Background compensation: On the sample

Copper determination:

Electrode: Au wire

Deposition/stripping:
$Cu^{2+} + 2\ e^{-} \leftrightarrow Cu^{0}$

Stripping at +1 µA



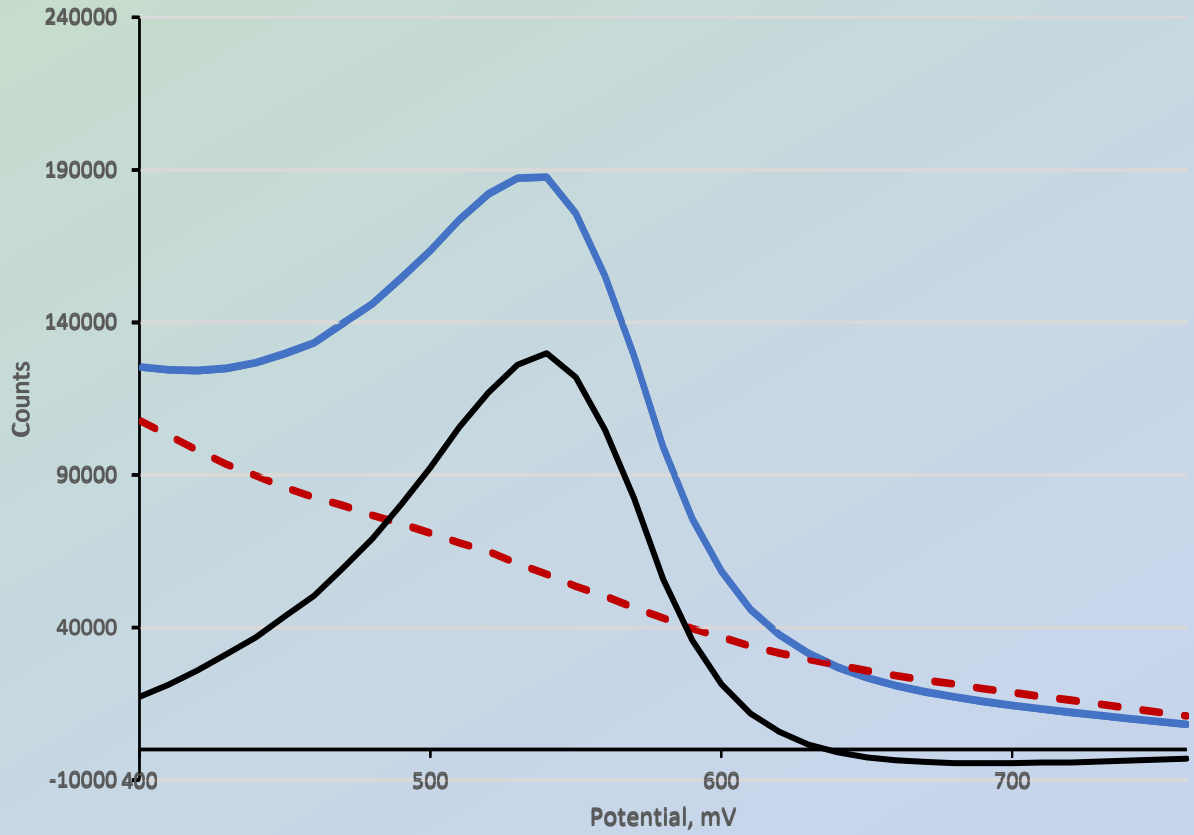
Chronopotentiometry

Background compensation: “SelfBlanking”

Chromium(VI) determination:

Electrode: Porous RVC 100ppi
In-electrode coulom. titration:
$CrO_4^{2-} + 8\ H^+ + 3\ e^- = Cr^{3+} + 4\ H_2O$

Reduction at -10 µA



Manova A., et al: Determination of chromium(VI) and total chromium in water by in-electrode coulometric titration in a porous glassy carbon electrode. Microchim Acta 000, 1–7 (2007) DOI 10.1007/s00604-007-0751-x

Chronopotentiometry

Background reduction

Enhancing the Signal to Background (S/B) ratio significantly contributes to the improvement of the detection limit of any analytical method.

Signal enhancement:

- Deposition/stripping approach
- Enhancement of the electrochem. recovery (WJ vs normal flow, thinning the diffusion layer)

Background reduction:

- Electrodes with lower BG (BDD)
- MEA with overlapping diff. layers

Flow-through cell

Fresenius J Anal Chem (1992) 343:566–575

Fresenius' Journal of Analytical Chemistry

Design and characterization of flow-through coulometric cells with porous working electrodes made of crushed vitreous carbon

E. Beinrohr [1,*], M. Németh [2], P. Tschöpel [1], and G. Tölg [1]

[1] Max-Planck-Institut für Metallforschung, Laboratorium für Reinststoffanalytik, Bunsen-Kirchhoff-Strasse 13, W-4600 Dortmund 1, Federal Republic of Germany
[2] Department of Analytical Chemistry, Slovak Technical University, CS-812 37 Bratislava, Czechoslovakia

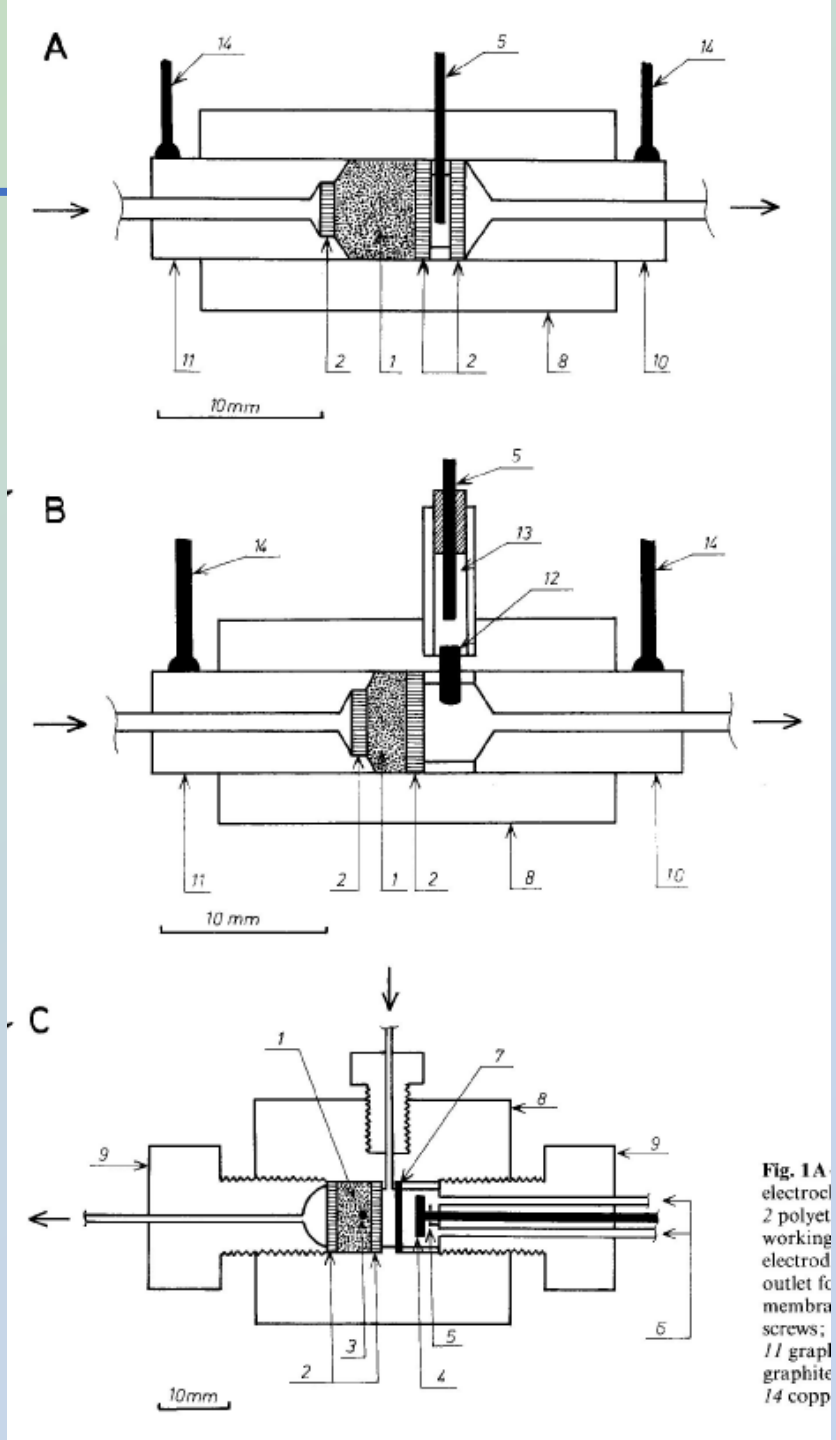


Fig. 1A
electrocl
2 polyet
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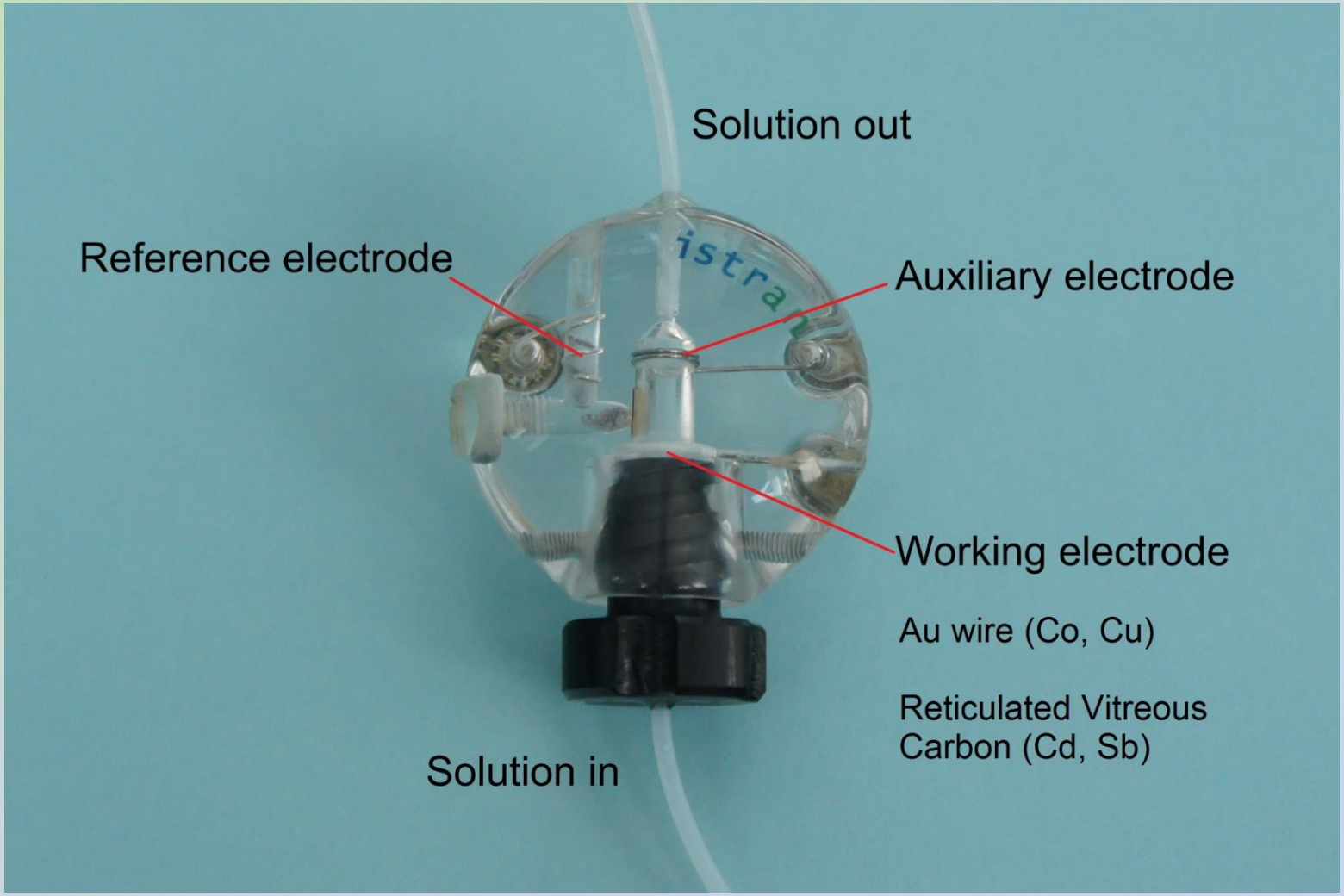
screws;
11 grapl
graphite
14 copp

Flow-through cell



Beinrohr E.: Flow-through coulometry in waste water analysis. In:Waste water. Evaluation and management, Ed. Einschlag F. S. G., Intech 2011, p. 71

Electrodes

Wire electrodes

0.5 and 4 mm in diameter and length., resp.

Material: Au, Pt, Ag

Electrodes

Porous electrodes

Reticulated vitreous carbon with 100 ppi and less porosity

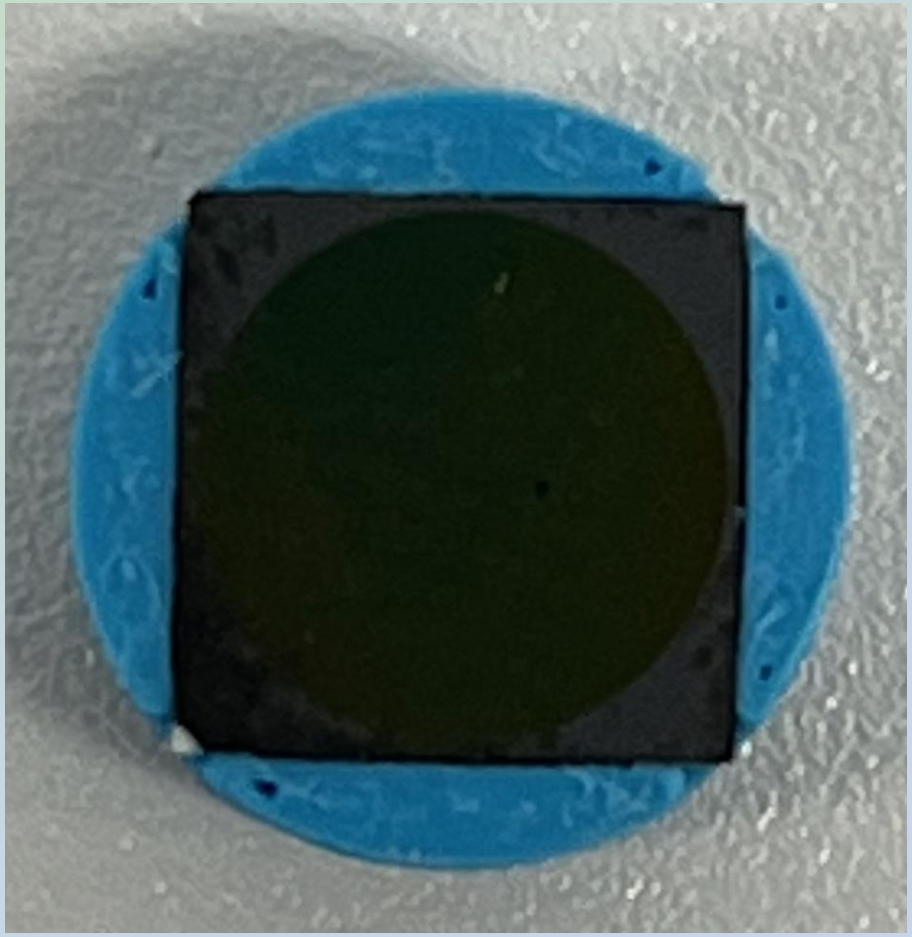
Material: Glassy carbon

Electrodes

Diamond electrodes

Microcrystalline boron doped diamond layer with bare surface or with microelectrode array design on ceramic support

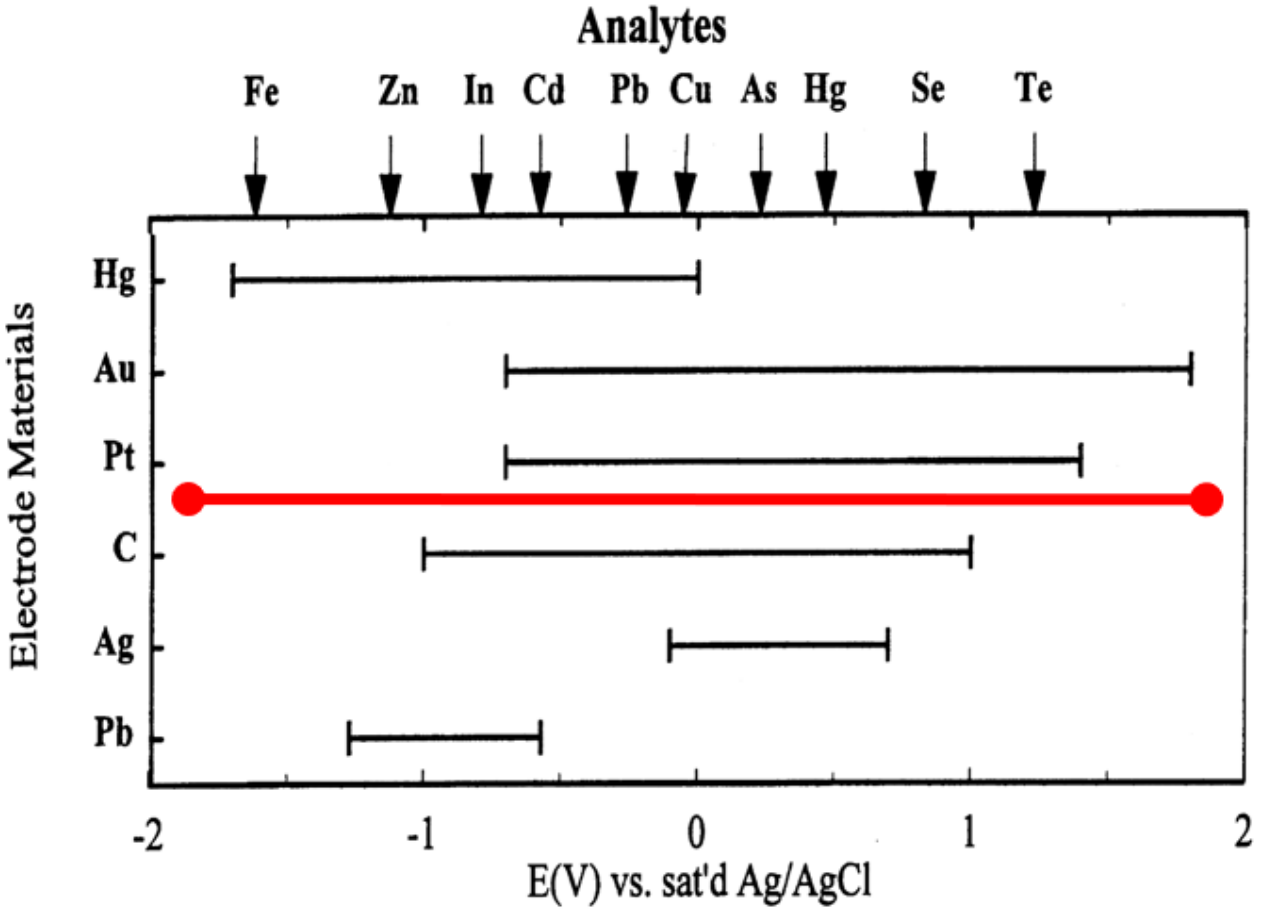
Material: BDD



Electrodes

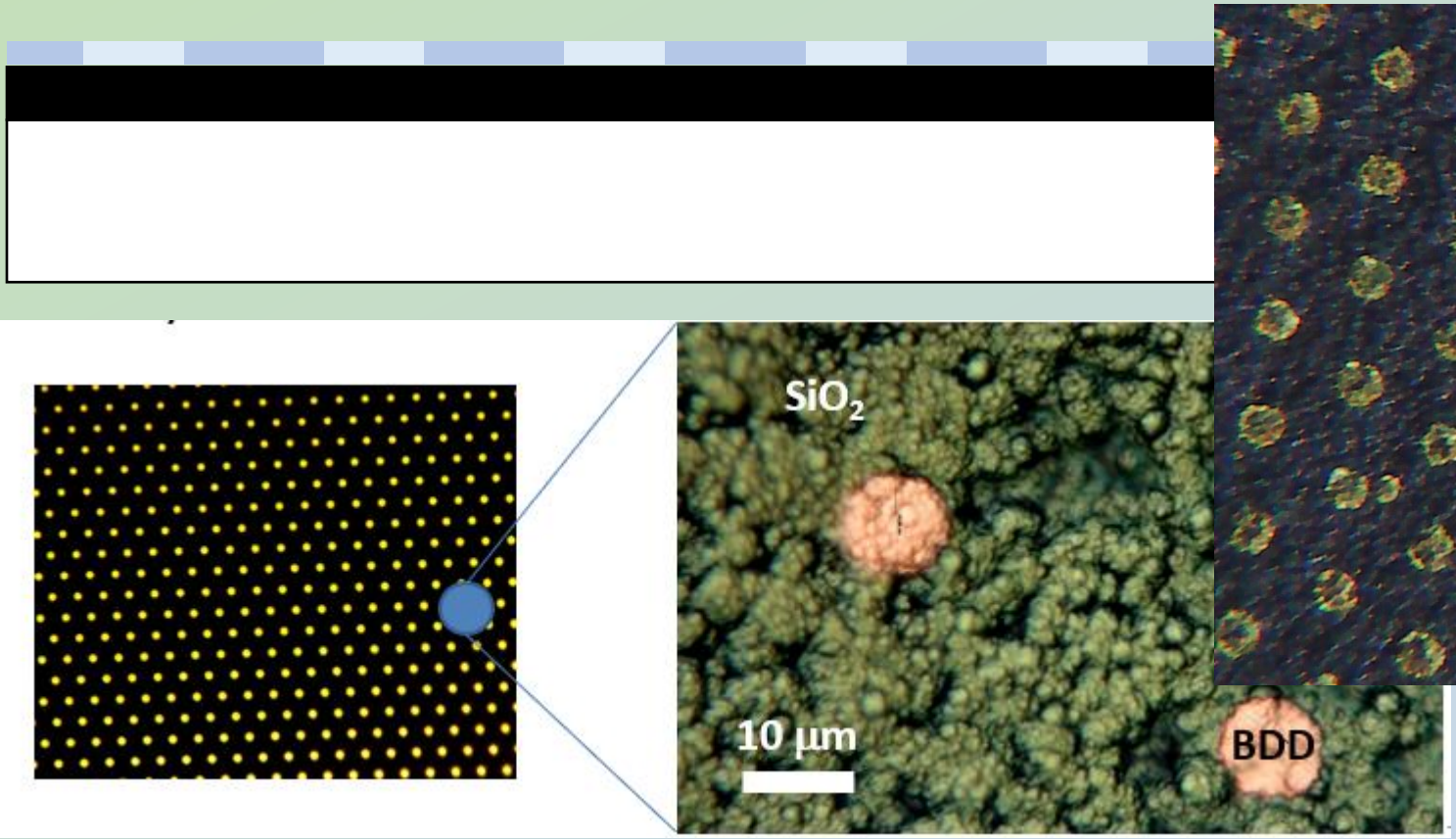
Diamond electrodes

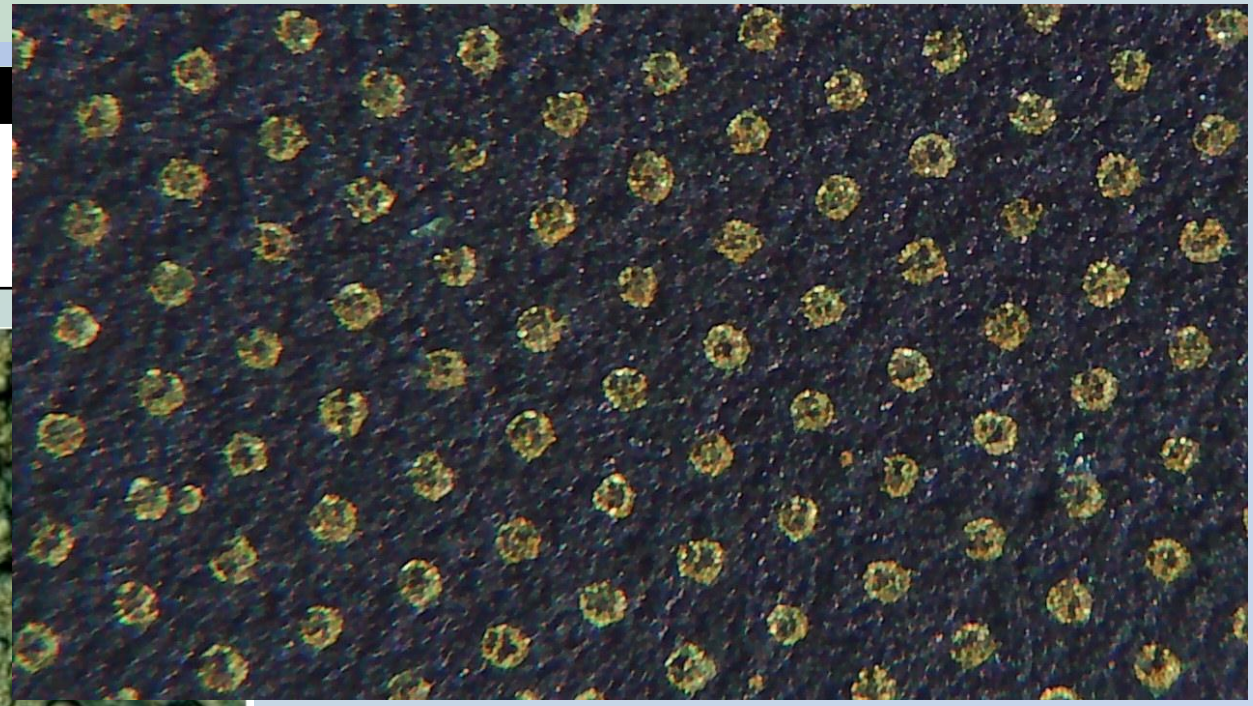
Properties
Mechanical stability
Electrical conductivity (boron doped diamond)
Wide potential window
Biological compatibility
Chemical inert
High ratio Signal to Noise, Signal to background (SBR)



Electrodes

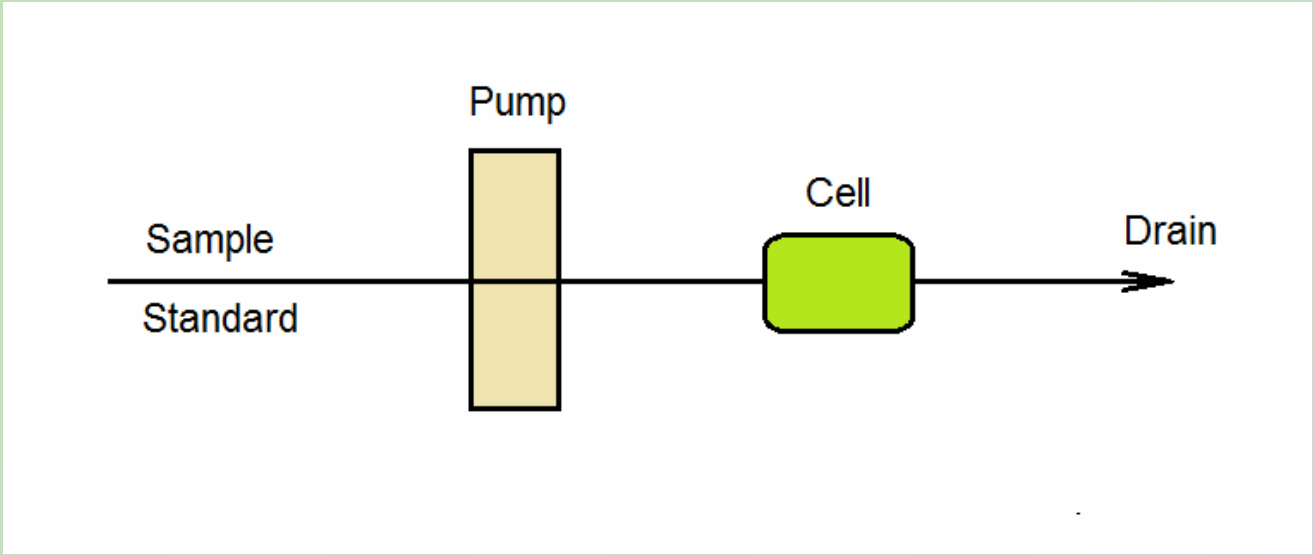
Diamond microarray electrodes (BDD-MAE) fabricated by the chemical vapour deposition technology





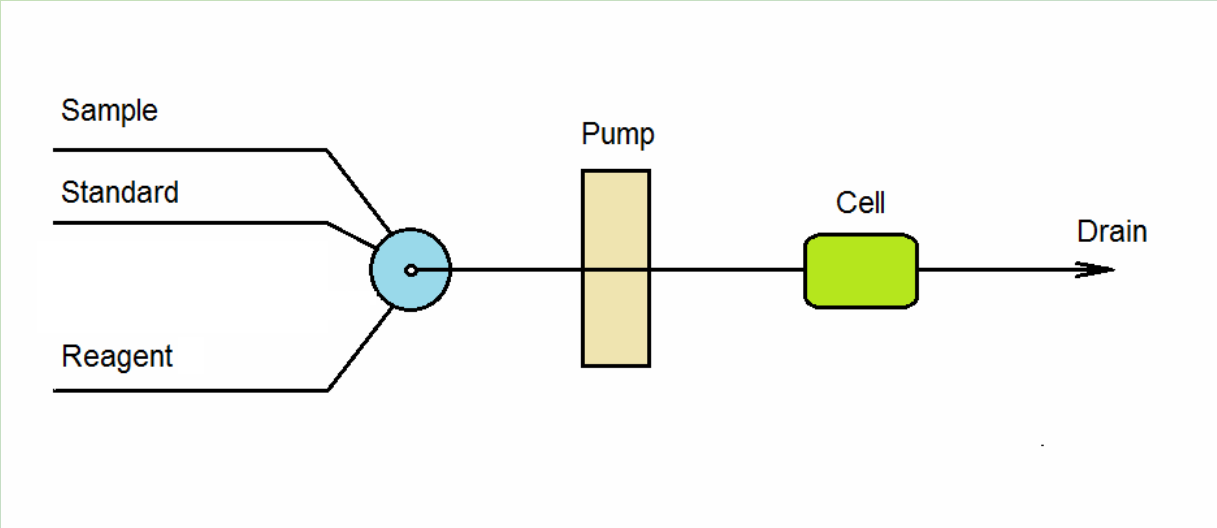
Flow systems

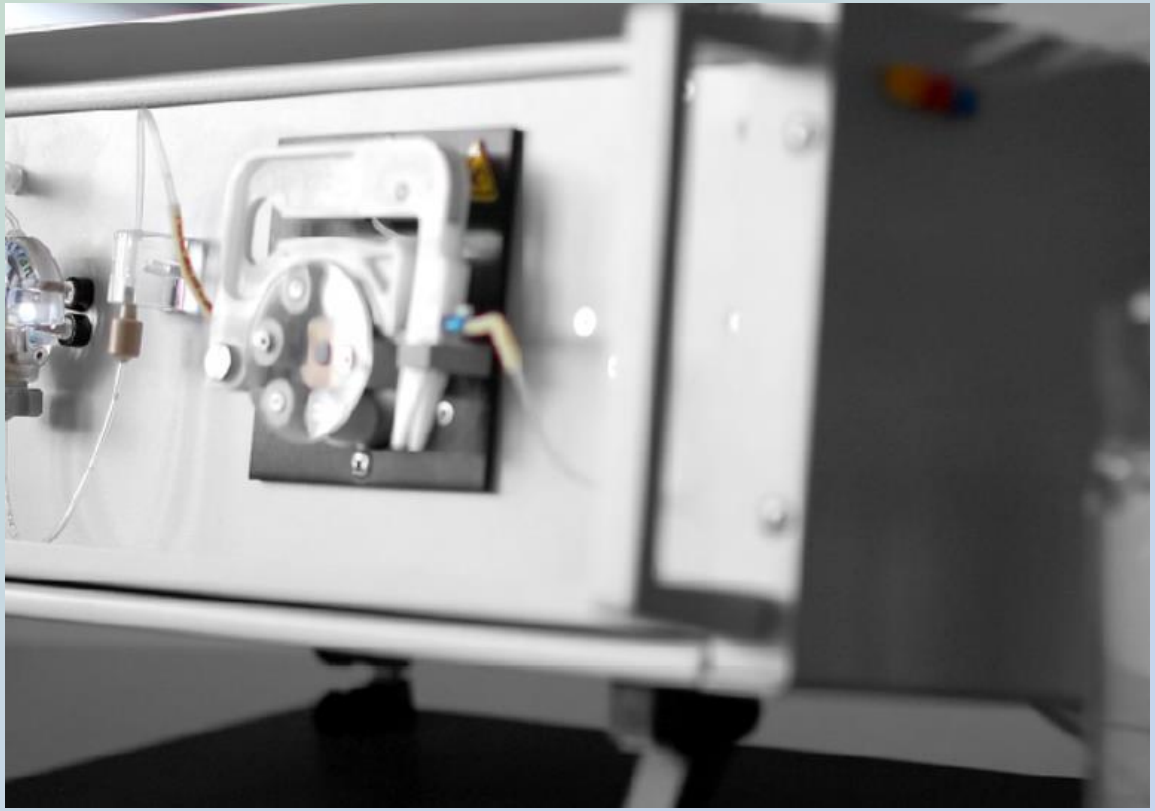
Single line



Flow systems

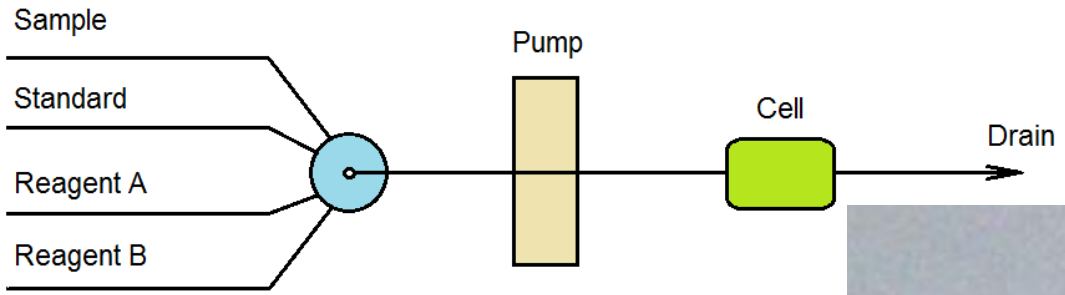
Three lines

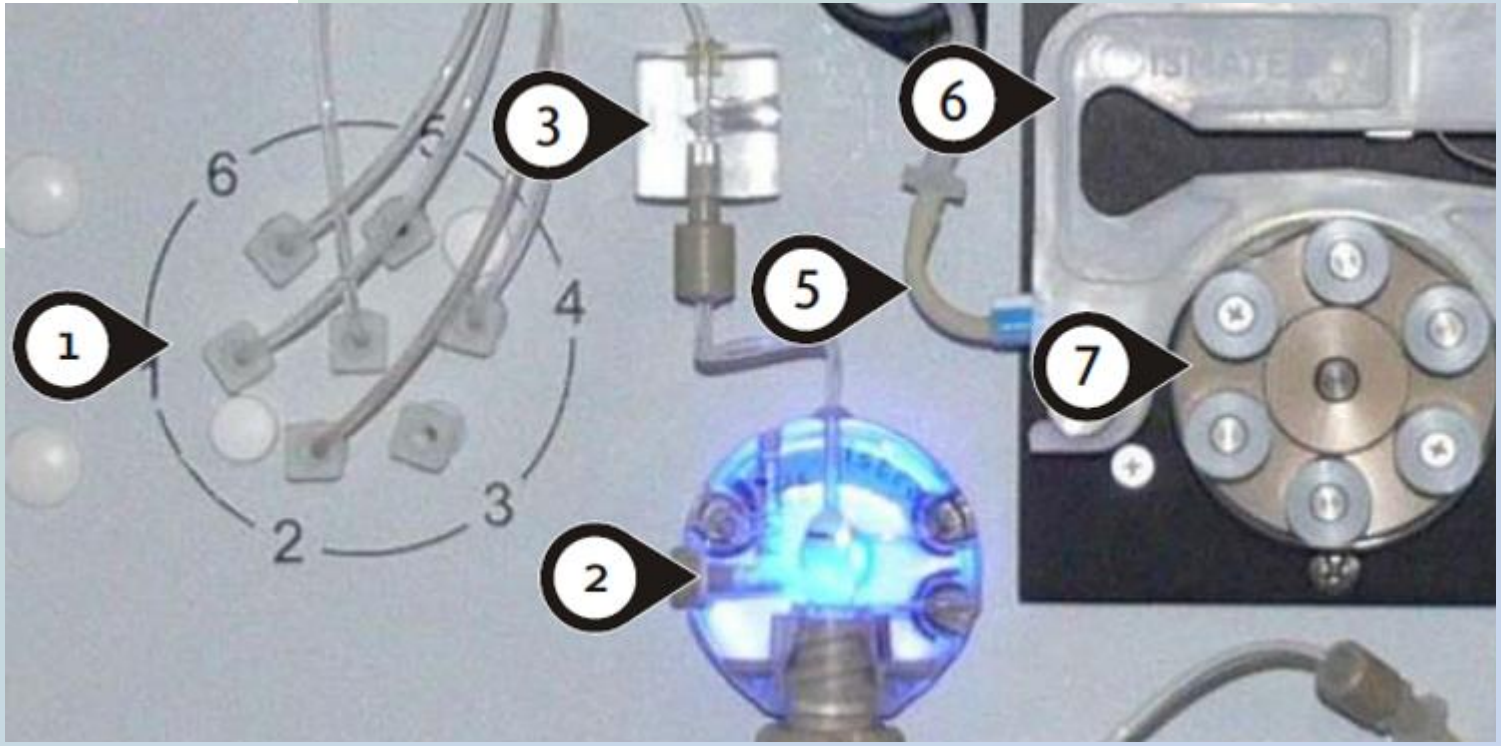




Flow systems

Four and more versatile lines





Sample pre-treatment

Filtration

Diffusion

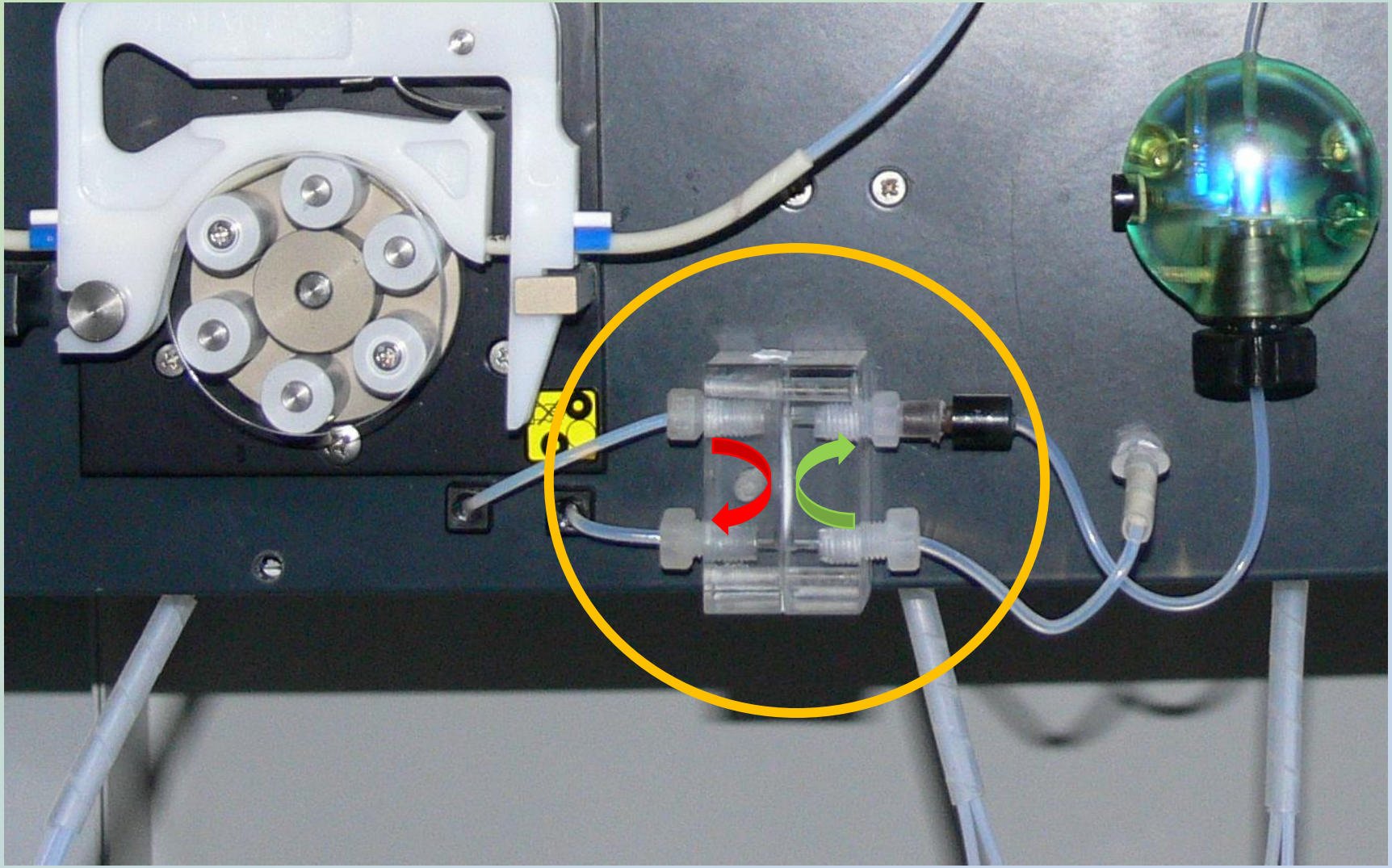
Ion exchange, sorption

Digestion

Diffusion

Volatile small molecules:

NH_3, SO_2, HCN, Cl_2, ClO_2 …



Josef Dvořák, et. al: Determination of Total Sulphur Dioxide in Beer Samples by Flow-Through Chronopotentiometry. *J. Inst. Brew.* 112(4), 308–313, 2006

Ion exchange

Task: **As** determination in the range of 10 to 200 µg/l in industrial **Cd** solutions containing 0.5 to 50 g/l Cd.

The sample is flowing through a column packed with an Catex-type sorbent which traps the $Cd2^{+}$ ions whereas let the AsO_3^{3-} anions through to the cell and are measured.
In the next step, the column is rinsed with NaCl solution to elute the Cd^{2+} ions which are determined as well.

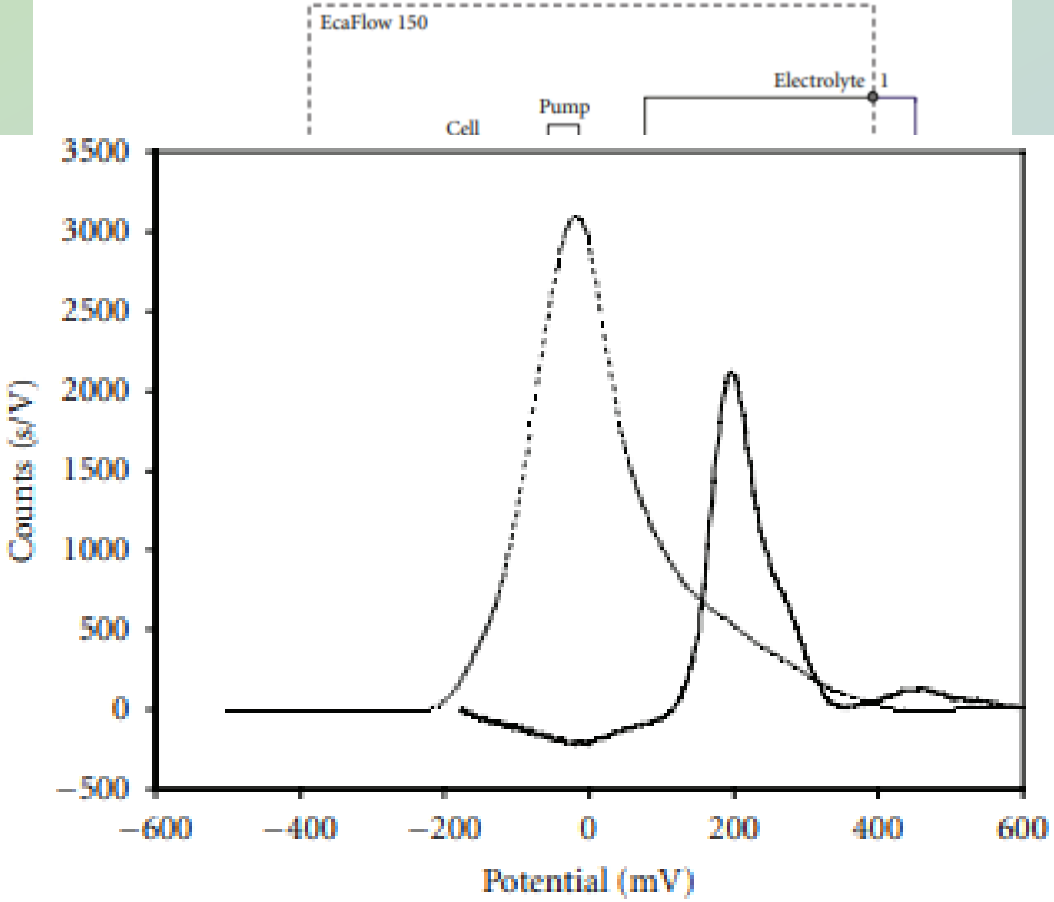


FIGURE 2: Background corrected chronopotentiometric signals obtained successively for As (full line) and Cd (broken line) by analysing a cadmium sulphate solution containing 100 µg/L and 20 g/L of As and Cd, respectively. See experimental parameters in Section 2.

FIGURE 1: Flow chart diagram of the Cd/As measuring system. See explanation in the text.

Cacho F. et al: Sequential Determination of Total Arsenic and Cadmium in Concentrated Cadmium Sulphate Solutions by Flow-Through Stripping Chronopotentiometry after Online Cation Exchanger Separation. *J. Analyt. Meth. Chem.* Volume 2012, Article ID 814983, doi:10.1155/2012/814983

Digestion:

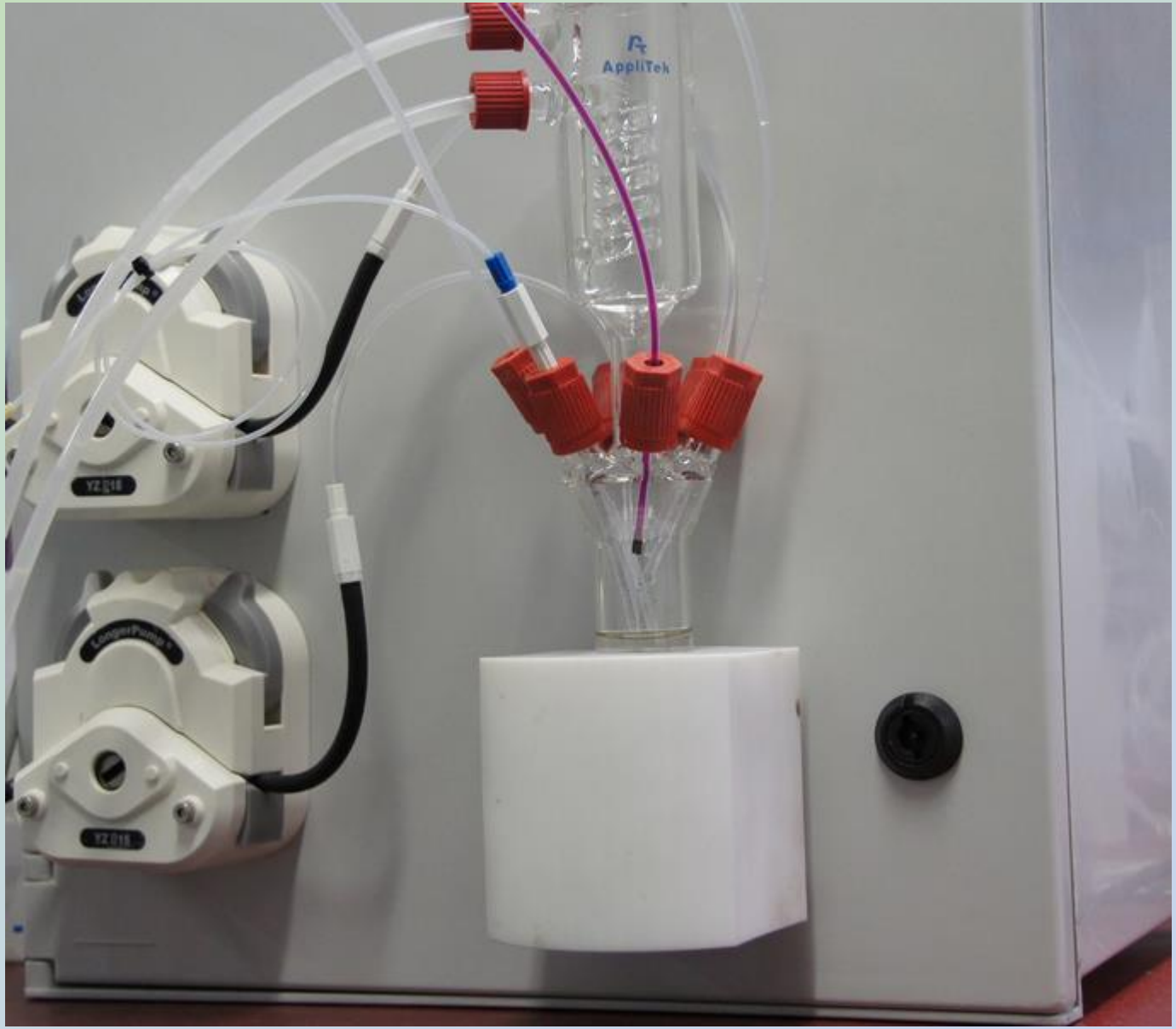
“Soft” digestion

UV digestion

Microwave assisted digestion

Thermal digestion

Digestion



Digestion

Applications

- **Metals and semi-metals** (Ag, As, Au, Cd, Cu, Cr, Fe, Hg, In, Mn, Ni, Pb, Se, Sb, Tl, Zn)
- **Nonmetals** (Fluoride, chloride, chlorite, chlordioxide, chlorine, bromide, bromate, iodide, sulfide, sulfite, sulfate, ammonia, hydrazine, nitrate, nitrite, cyanide, phosphate, acids, bases)
- **Organics** (methanol, ethanol, formaldehyde, antioxidants, EDTA)

  - Waste water
  - Underground water
  - Surface water
  - Drinking water
  - Technological aqueous solutions

Bromates (BrO_3^-) in disinfected water

Principle

Conversion to bromine:

$BrO_3^- + 5\ Br^- + 6\ H^+ = 3\ Br_2 + 3\ H_2O$

Electrochemical reduction:

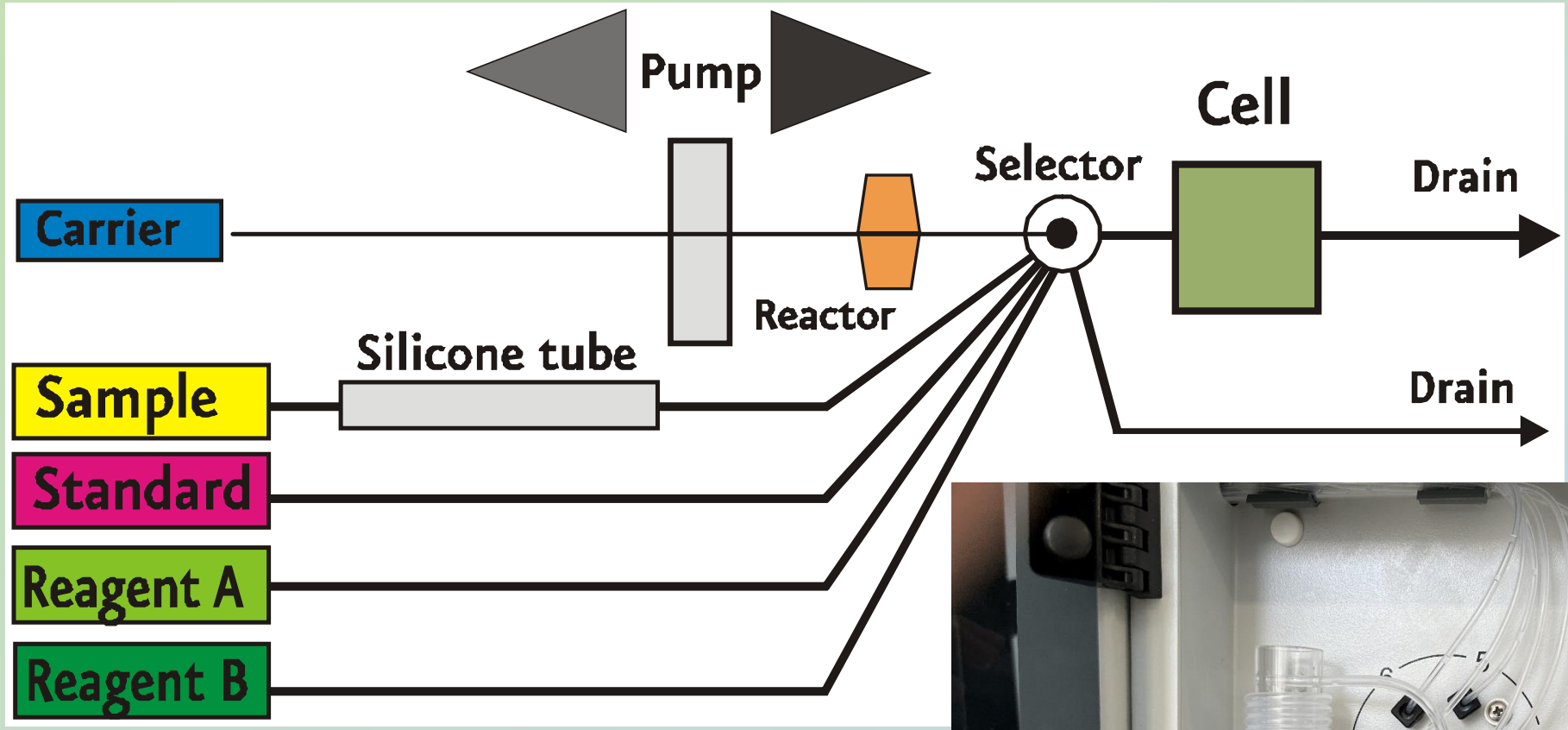
$Br_2 + 2\ e^- = 2\ Br^-$

Interferences

Oxidising species (Cl_2, ClO^-, ClO_2, ClO_2^-, O_3 …)
Unstable reagents (Fe^{2+}, Br^-)

Removal:

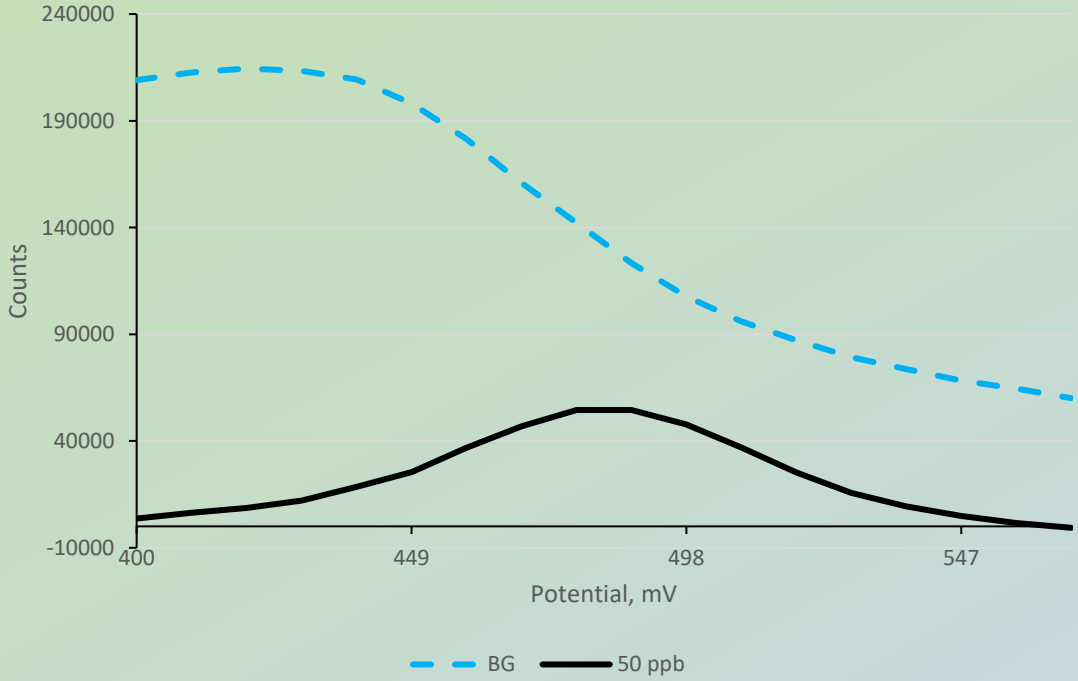
On-line diffusion
pH adjustment and addition of Fe(II)
<u>In-situ reagent regeneration</u>



Carrier: 0.1 mol/l HCl

Reagent A: Fe(II) in H_2SO_4

Reagent B: KBr


240000
190000
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90000
40000
-10000
Counts
400
449
498
547
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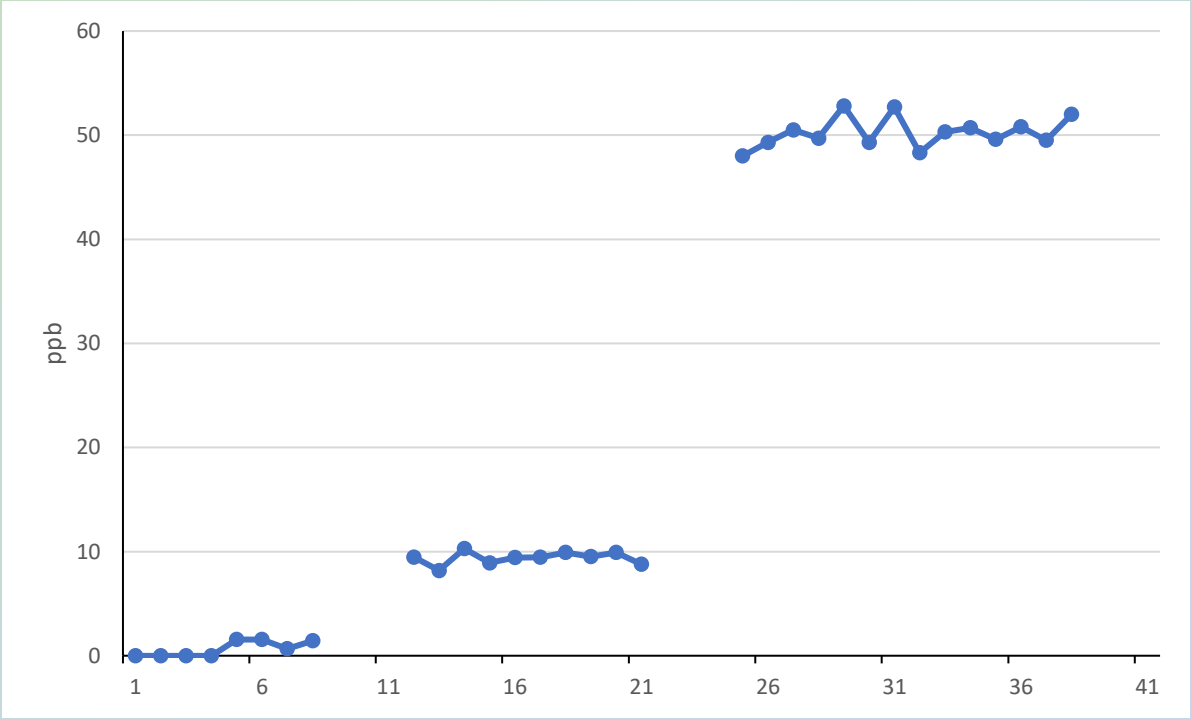
BG
50 ppb


60
50
40
30
20
10
0
ppb
1
6
11
16
21
26
31
36
41

Bromates in drinking water

Sample	Found μg/L	Reference HPLC
Brescia tap water	< 5	n.d.
Brescia tap water + 20 μg/L BrO_3^-	18 ± 5	22
Kuwait tap water	44 ± 8	45
Mineral water (Fe removal by ozone)	52 ± 8	49

Outlooks

- Micro- and nanoelectrode arrays (S/N enhancement)
- Microfluidics (“green” chemistry)
- “Reagentless” procedures (“green” chemistry)
- Modified electrodes (selectivity enhancement)
- In-line analysers (immersable voltammetric sensors)

- **Thank you for your attention**