

Capillary Electrophoresis with Microwave-Enhanced Electrochemical Detection

Frank-Michael Matysik

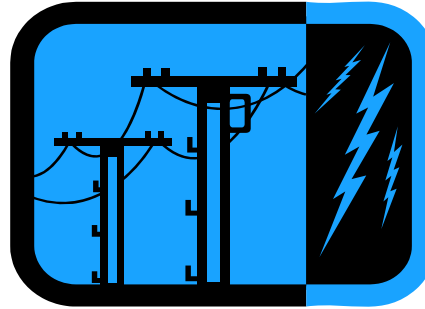
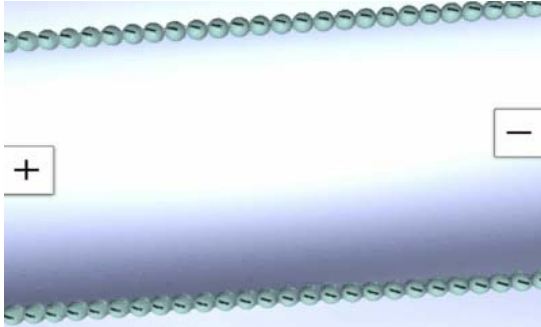
Institute of Analytical Chemistry

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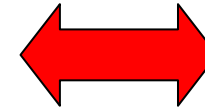
Potential of microfluidic systems

- Analysis of small samples
- Short analysis times (*high throughput analysis*)
- Small transportable apparatus (*point-of-care analysis*)
- Considerable reduction of solvents and reagents
- Integration of various miniaturized functional components (*lab-on-a-chip*)

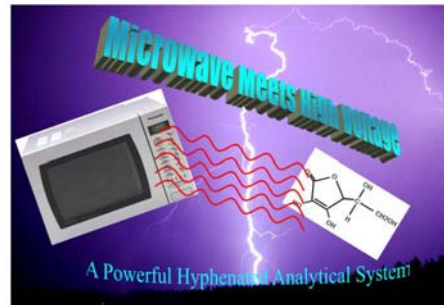
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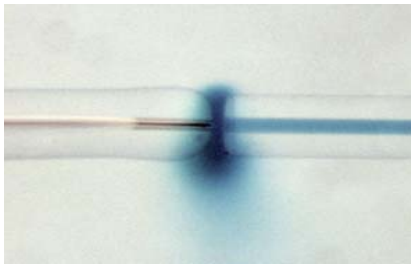
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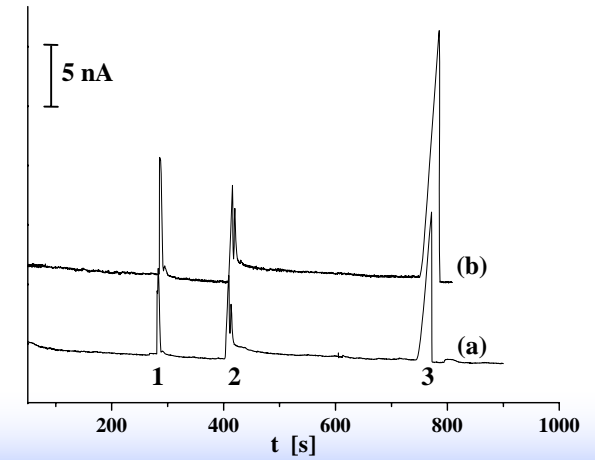
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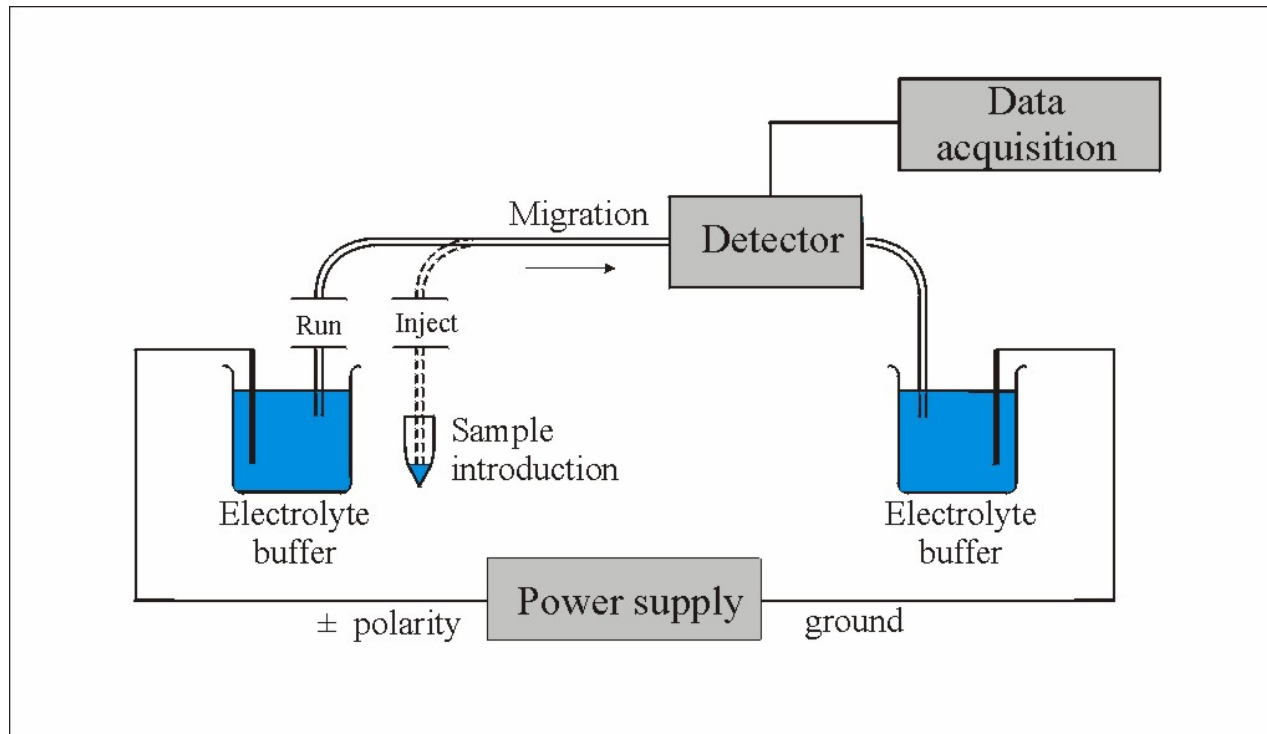
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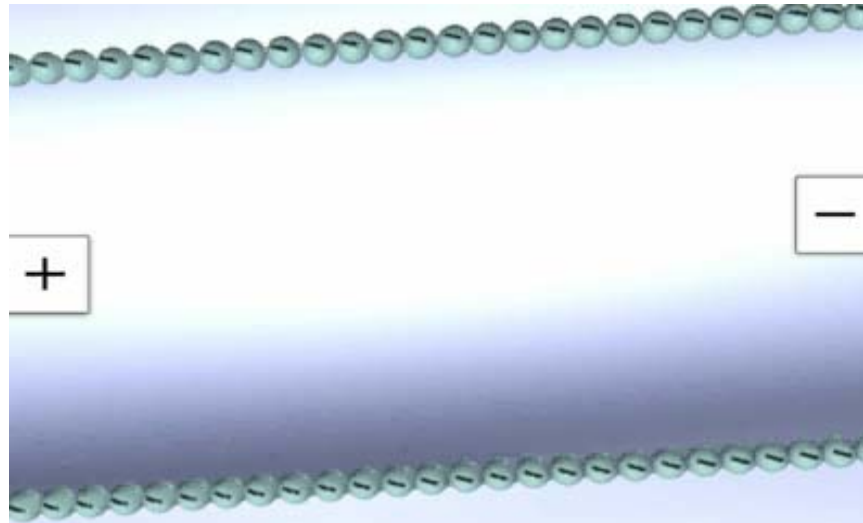
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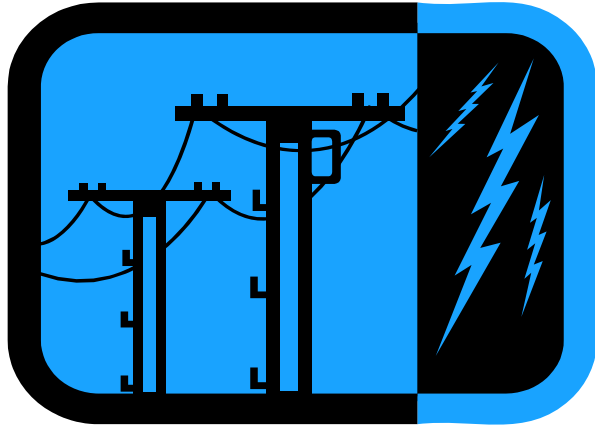
Capillary electrophoresis system



Principle of capillary electrophoresis

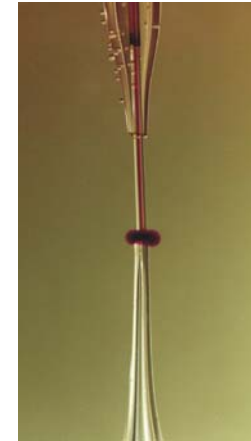


Electrophoresis system



- Separation voltage: 10 – 30 kV
- Electrophoretic current: μA - mA

Electrochemical detection



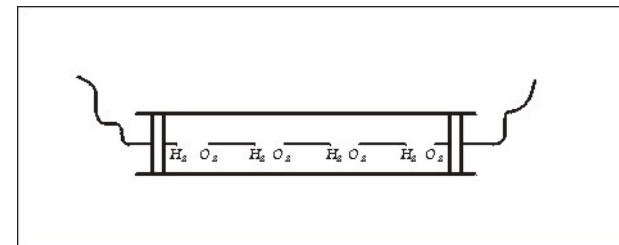
- Detection potential: ≤ 2 V
- Detection signal: pA - nA

Capillary electrophoresis + Electrochemical detection

Experimental challenges



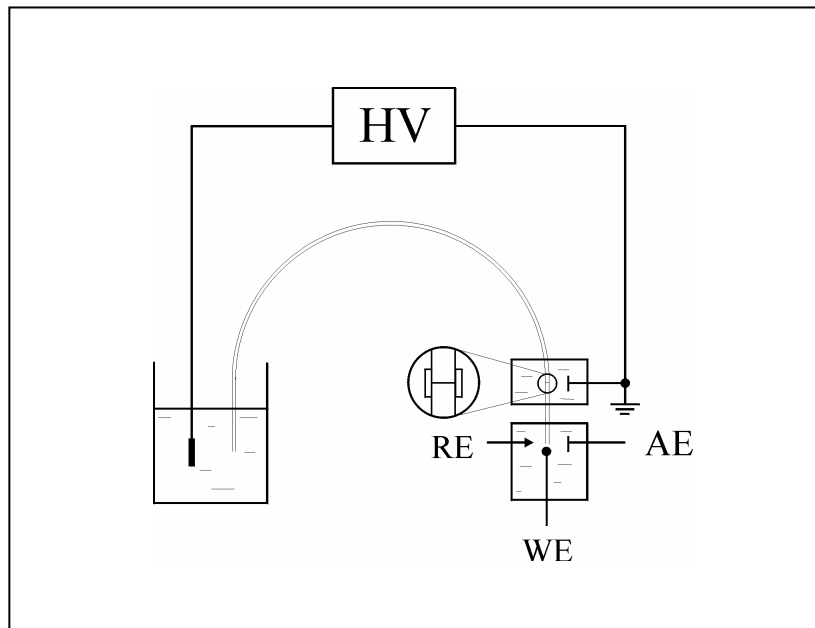
Paul Erman



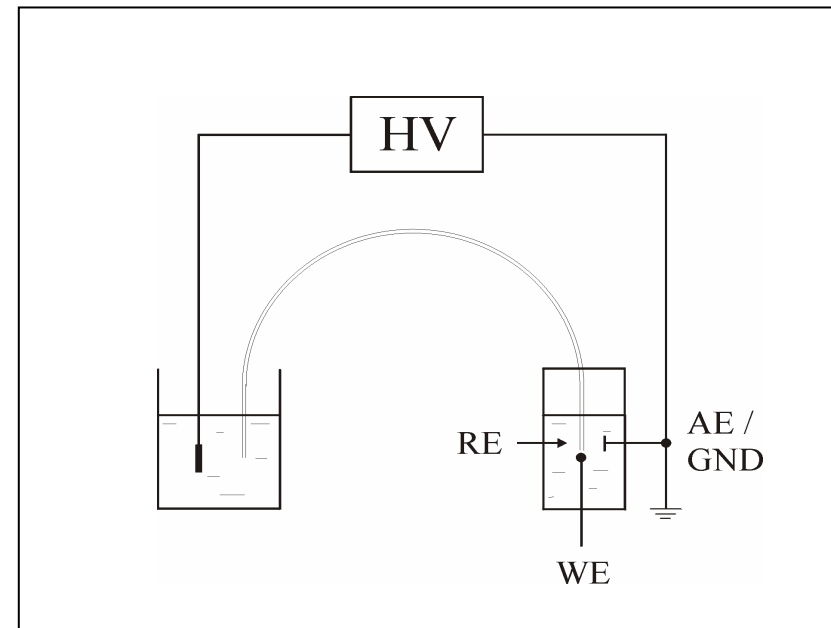
Historical experiment by Erman (1802)

Capillary electrophoresis + Electrochemical detection

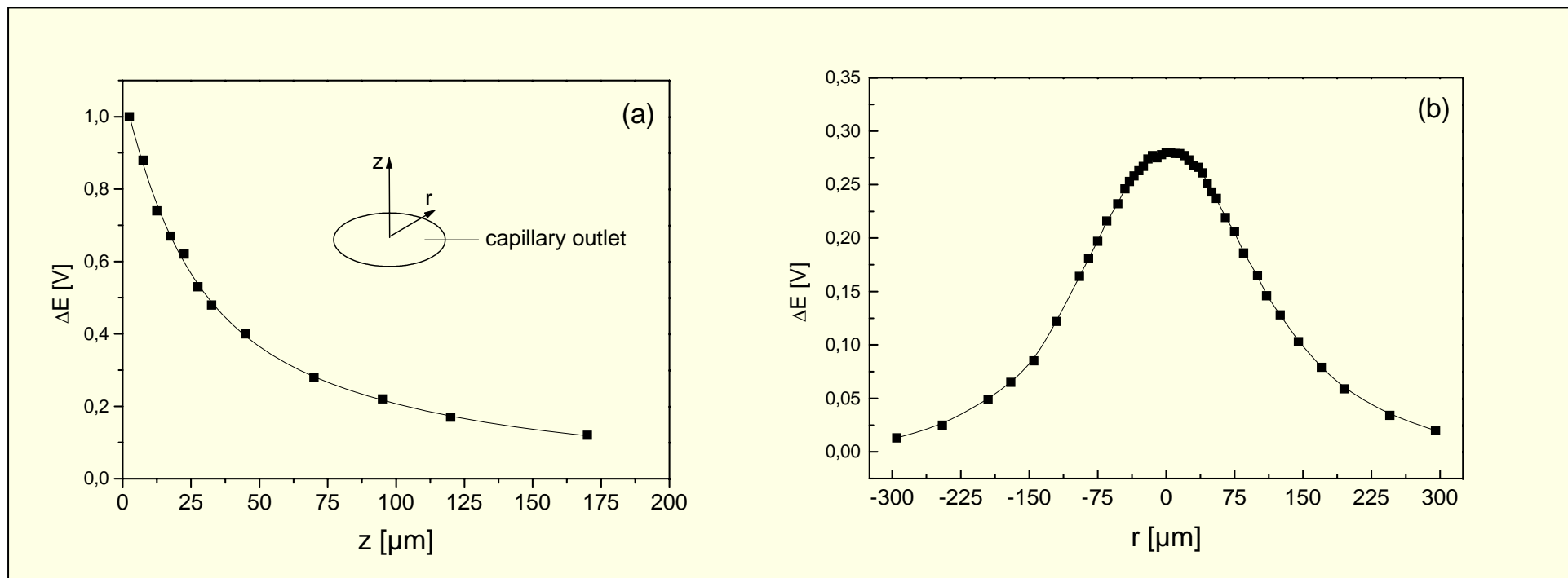
with HV decoupler



without HV decoupler



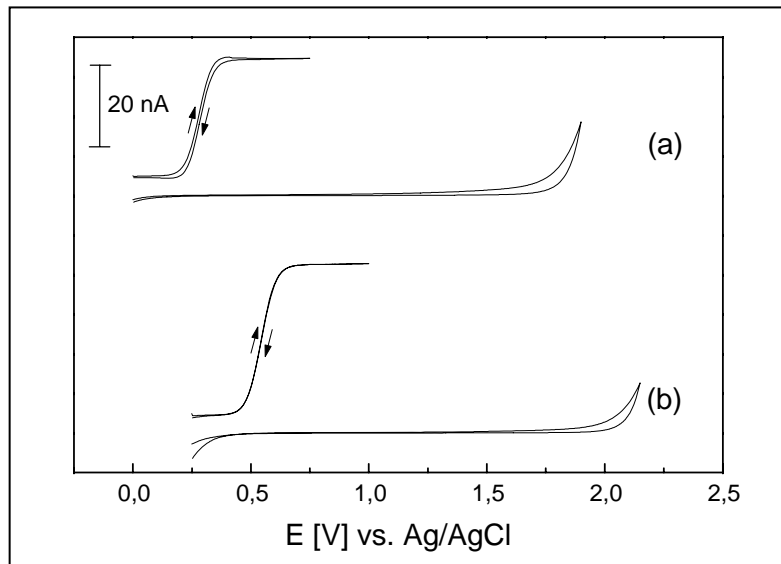
Influence of the high voltage electrical field on electrochemical detection



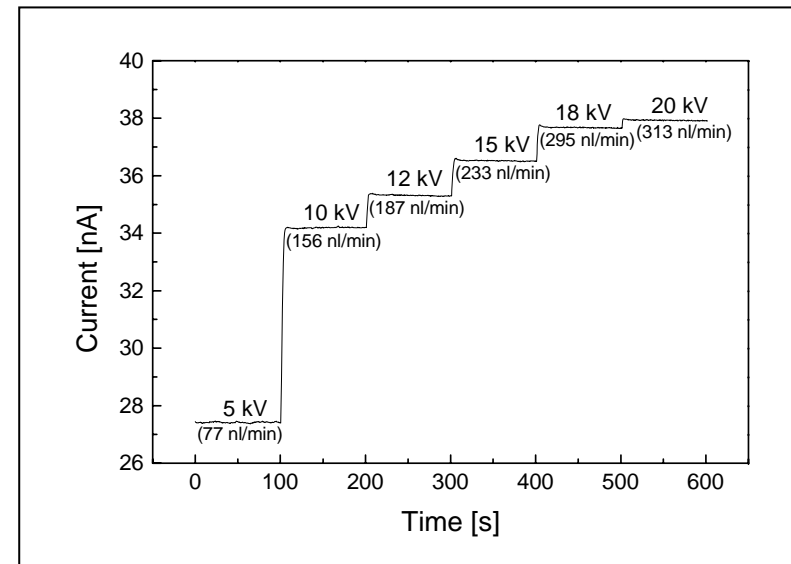
Experimental conditions: electrolyte, acetonitrile / 1 M HAc / 10 mM NaAc / 1 mM ferrocene; high voltage, 20 kV; capillary dimensions, 75 μm x 85 cm

➤ *Anal. Chem.* 72 (2000) 2581

Hydrodynamic voltammetry with electrokinetic systems



CV of (HAc, NaAc in AN) and 2 mM ferrocene (a) in absence (b) in presence of high voltage (20 kV)

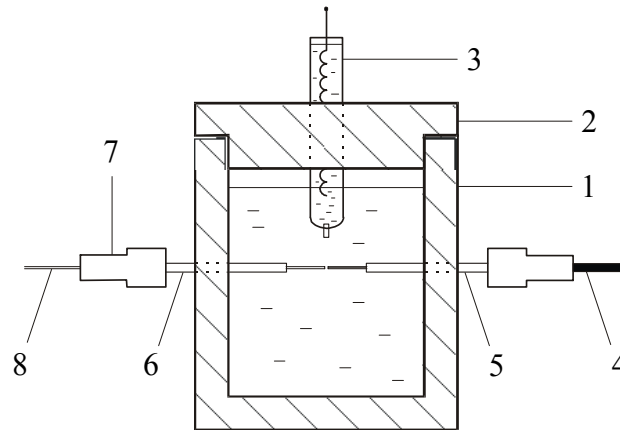
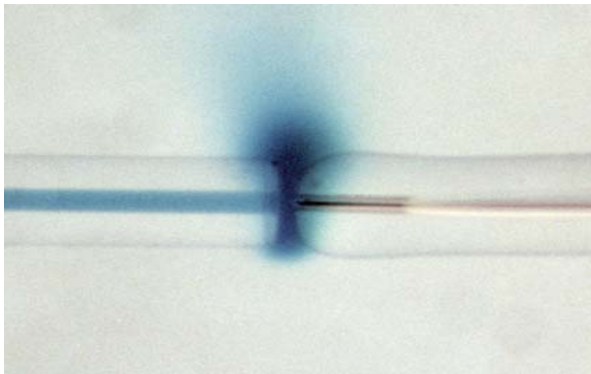


Dependence of the amperometric signal (2 mM ferrocene) on EOF

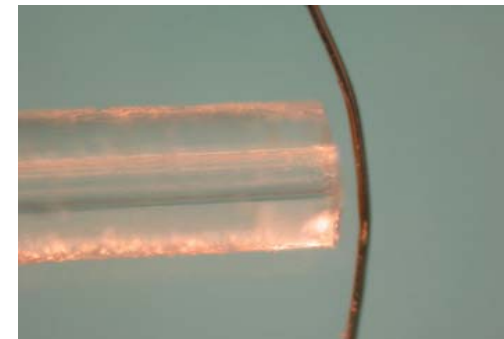
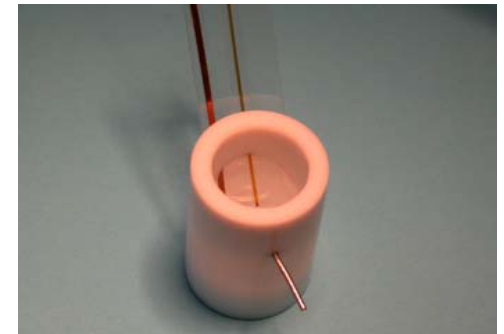


Development of electrochemical detectors for capillary electrophoresis

Microdisk detector



Laminated disposable detectors



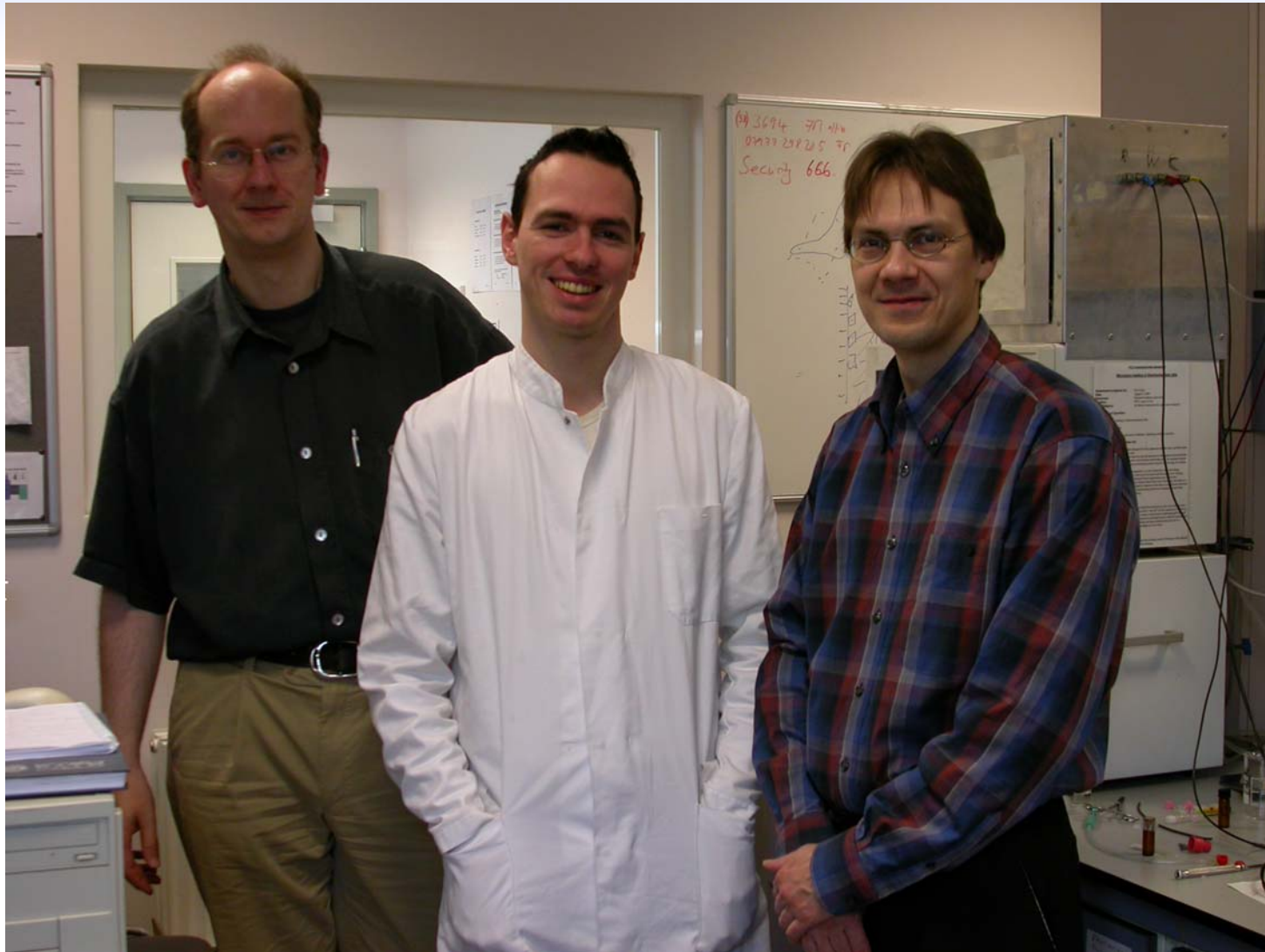
➤ DE 195 38 597 A1

➤ Electroanalysis 17 (2005) 1187

Capillary electrophoresis + Electrochemical detection

Applications

- Neurotransmitters (catechol compounds, serotonin, acetylcholine)
- Alkaloids (in particular tobacco alkaloids)
- Dyes
- Illicit drugs (amphetamines, cannabinoids)
- Speciation of tinorganic compounds
- Hydrazine compounds ➤ *Electrophoresis 26 (2005) 3341*
- Neuropeptides ➤ *Electrophoresis 27 (2006) 1199*



STSM February 2006

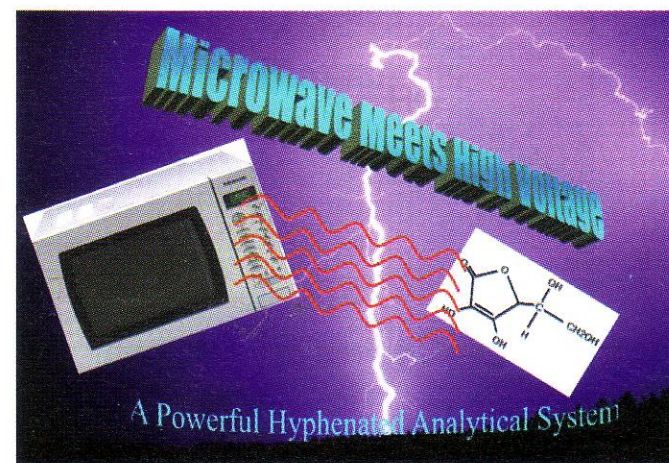
Microwave-Assisted Capillary Electrophoresis with Electrochemical Detection (MW-CE-ED)

1210

Capillary electrophoresis with microwave-enhanced electrochemical detection

Sascha Förster, Frank-Michael Matysik,*
Mohamed A. Ghanem and Frank Marken*

A new experimental development concerning microwave-assisted electrochemical detection in conjunction with capillary electrophoresis is presented.



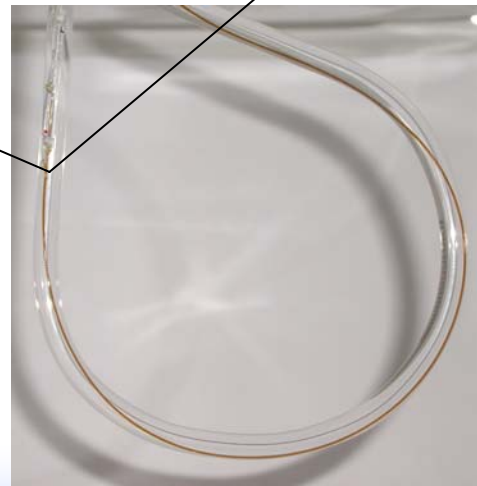
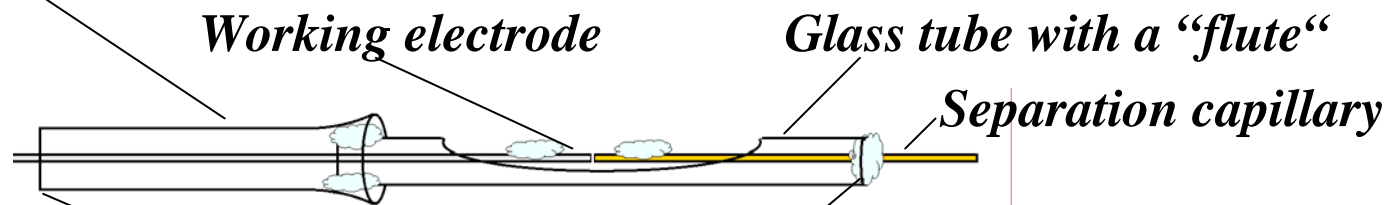
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➤ Analyst 131 (2006) 1210



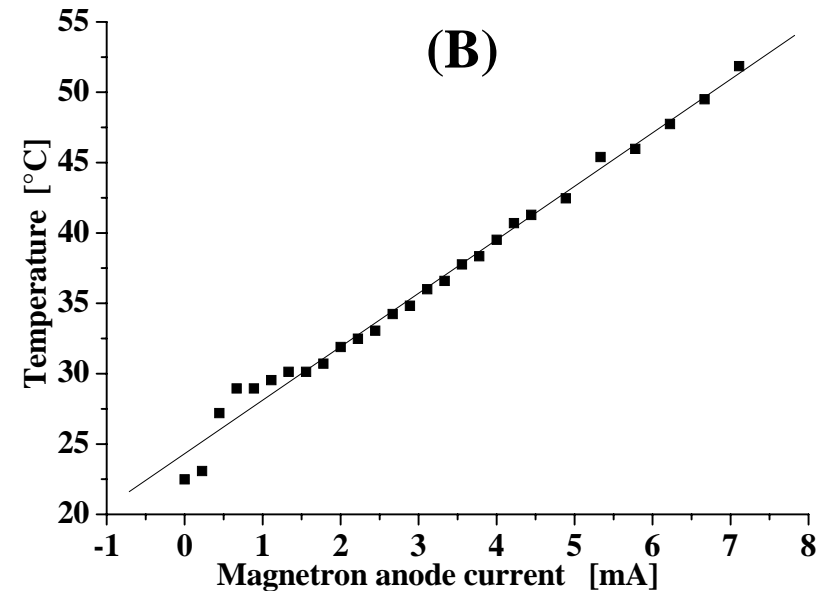
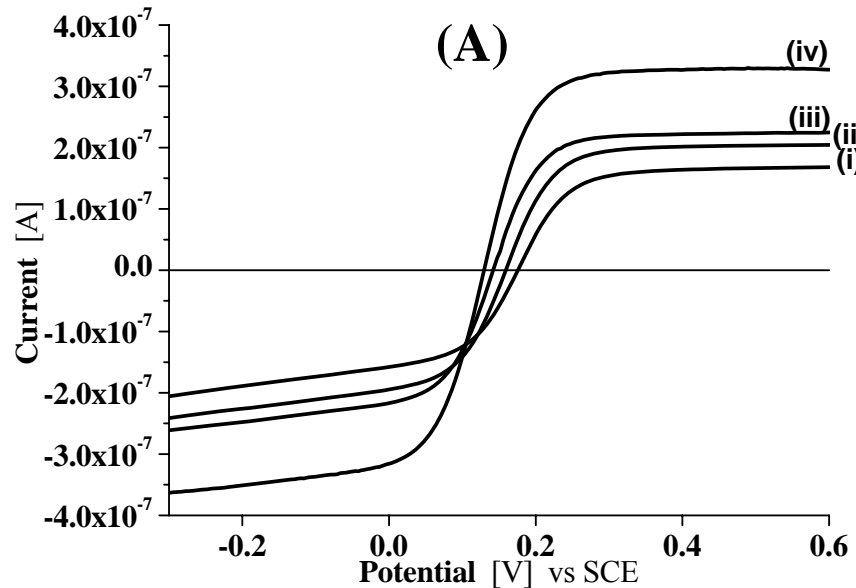
Microwave-Assisted Capillary Electrophoresis with Electrochemical Detection (MW-CE-ED)

Glass tube with tapered inner diameter



➤ Analyst 131 (2006) 1210

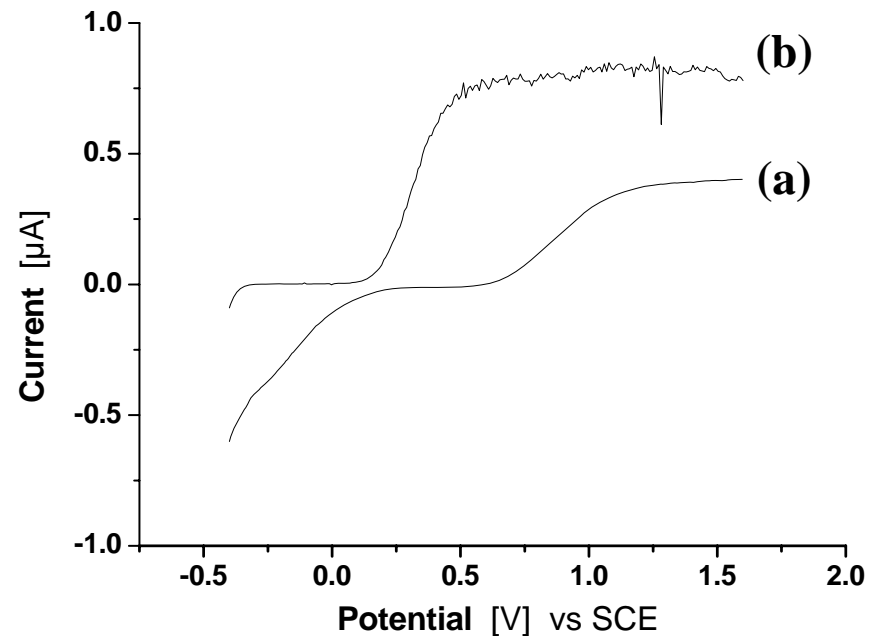
Microwave-Assisted Capillary Electrophoresis with Electrochemical Detection (MW-CE-ED)



Voltammograms for 4 mM $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ in 50 mM phosphate buffer recorded with the detection system in presence of microwave radiation (magnetron anode current (i) 0, (ii) 2.22, (iii) 4.45, (iv) 6.67 mA)

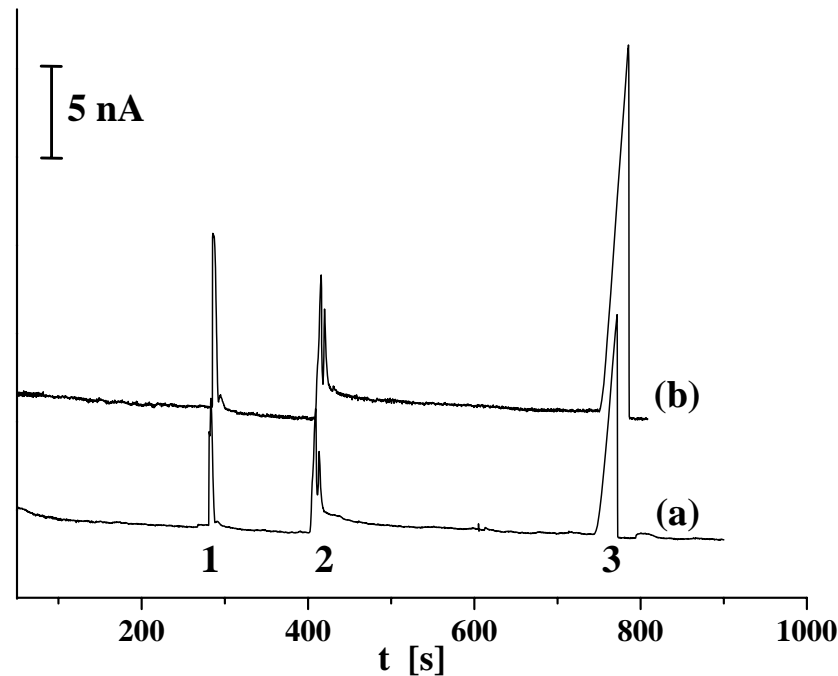
Calibration of the electrode temperature in dependence on the microwave power

Microwave-Assisted Capillary Electrophoresis with Electrochemical Detection (MW-CE-ED)



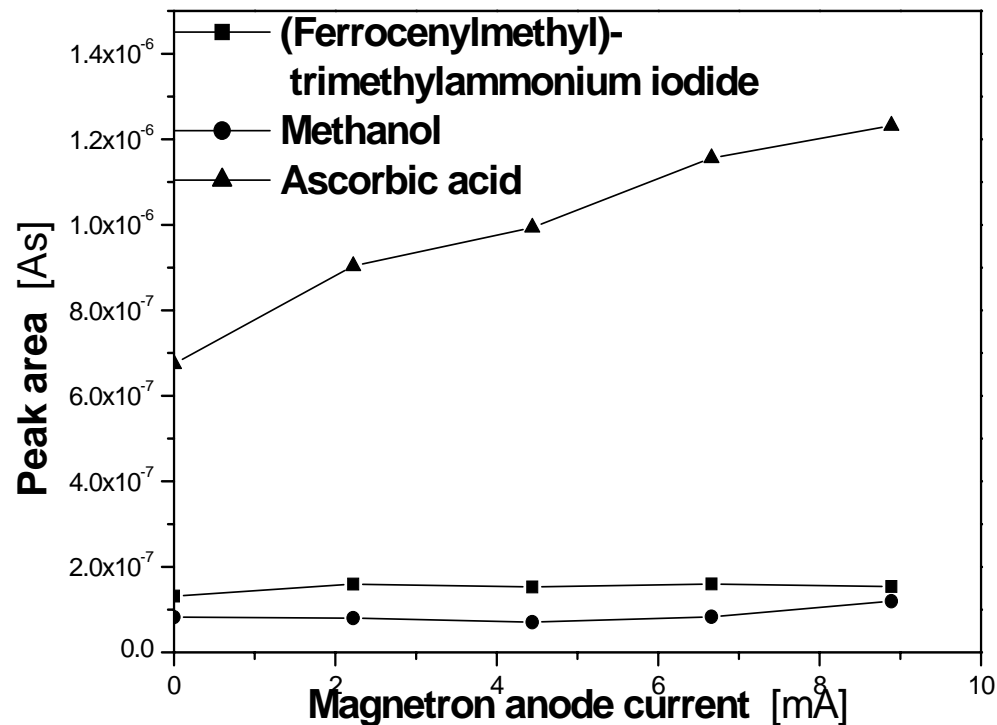
Influence of MW on the voltammetric oxidation of 1 mM ascorbic acid in 50 mM phosphate buffer (pH = 7) using a 25 μm Pt electrode; scan rate, 20 mV/s; (a) without MW (b) with MW, magnetron anode current: 8,89 mA

Microwave-Assisted Capillary Electrophoresis with Electrochemical Detection (MW-CE-ED)



Effects of MW radiation on CE-ED measurements using (1) 1 mM FcMTMA⁺, (2) 5% methanol, (3) 10 mM ascorbic acid (a) without MW, (b) in presence of MW, magnetron anode current: 8.89 mA. Conditions: capillary, 80 cm x 50 μ m; separation voltage, 25 kV, detection potential, +1V.

Microwave-Assisted Capillary Electrophoresis with Electrochemical Detection (MW-CE-ED)



Dependence of peak area of separated signals on the MW power

Conclusions

Microwave-assisted capillary electrophoresis with electrochemical detection is characterized as follows:

- Local thermal activation in the vicinity of the sensing electrode can be exploited
- No significant convective mass transport effect
- Dramatic enhancement of detection performance for species with sluggish kinetics of the electrode reaction (increase in sensitivity, reduction of overpotential)