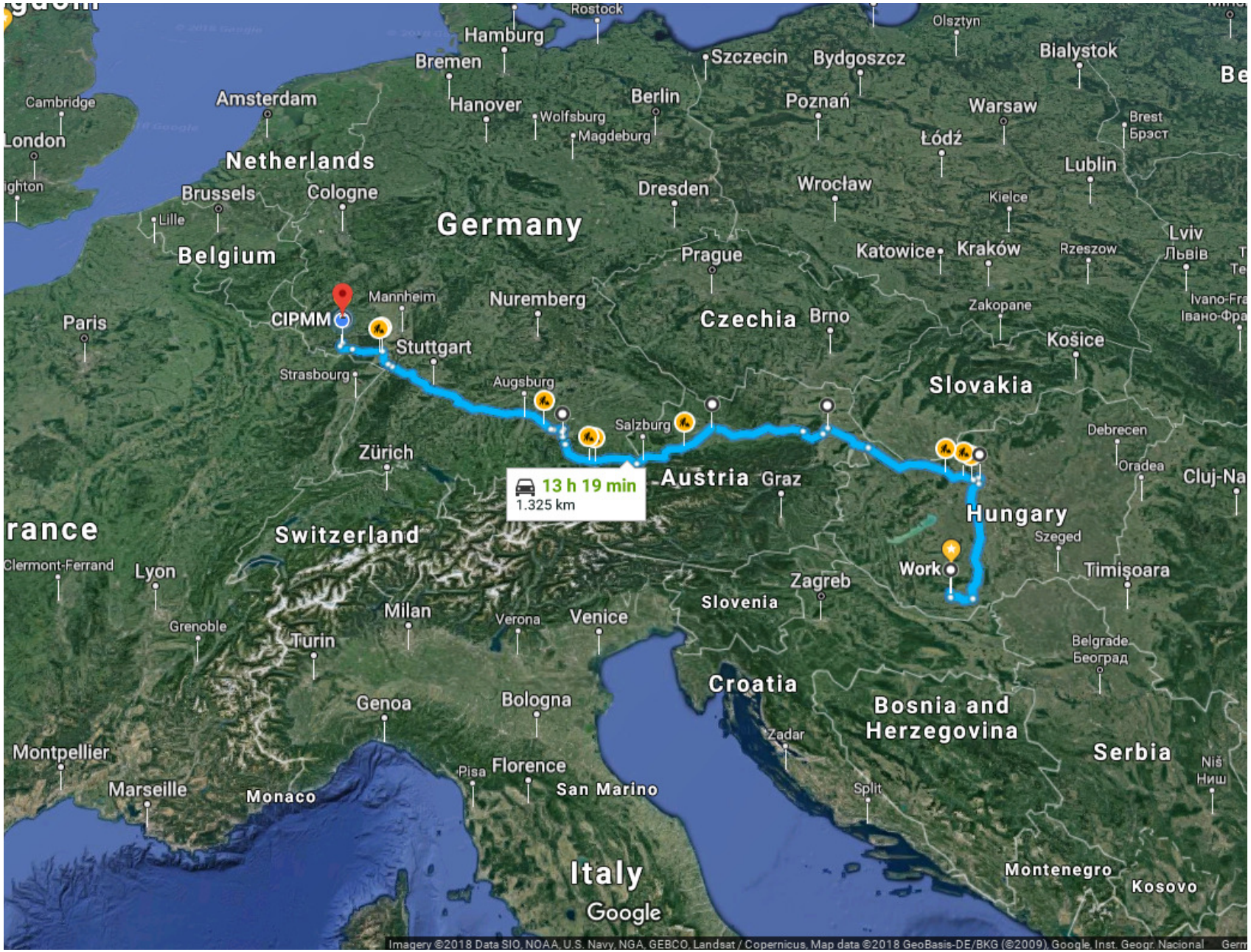
Deconvolution in Scanning Electrochemical Microscopy

Dr. András Kiss

Department of General and Physical Chemistry
University of Pécs, Hungary

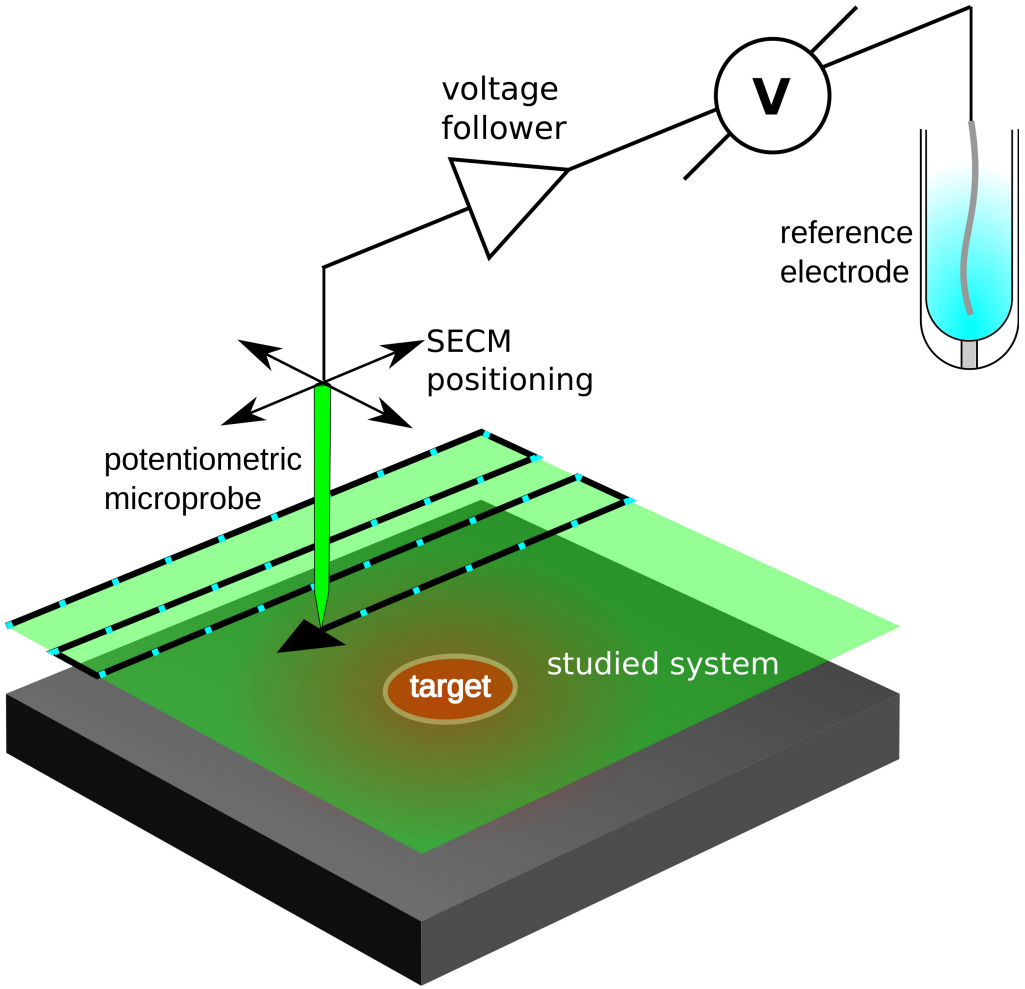
Center for Integrative Physiology
and Molecular Medicine
Universität des Saarlandes, Homburg, Germany


Rostock
Hamburg
Bremen
Amsterdam
Hanover
Berlin
Wolfsburg
Magdeburg
Szczecin
Bydgoszcz
Olsztyn
Białystok
Poznań
Warsaw
Łódź
Brest
Брэст
Lublin
Cambridge
London
Netherlands
Brussels
Cologne
Lille
Belgium
Germany
Dresden
Wrocław
Kielce
Lviv
Львів
Katowice
Kraków
Rzeszow
Prague
Zakopane
Ivano-Fra
Івано-Фра
Paris
CIPMM
Mannheim
Nuremberg
Czechia
Brno
Košice
Stuttgart
Strasbourg
Augsburg
Slovakia
Salzburg
Debrecen
Oradea
Cluj-Na
Zürich
13 h 19 min
1.325 km
Austria
Graz
Hungary
rance
Switzerland
Szeged
Clermont-Ferrand
Lyon
Work
Timişoara
Zagreb
Slovenia
Milan
Verona
Venice
Grenoble
Turin
Belgrade
Београд
Croatia
Genoa
Bologna
Bosnia and
Herzegovina
Zadar
Montpellier
Serbia
Pisa
Florence
Niš
Ниш
Marseille
Monaco
San Marino
Split
Italy
Montenegro
Kosovo
Google
Imagery ©2018 Data SIO, NOAA, U.S. Navy, NGA, GEBCO, Landsat / Copernicus, Map data ©2018 GeoBasis-DE/BKG (©2009), Google, Inst. Geogr. Nacional

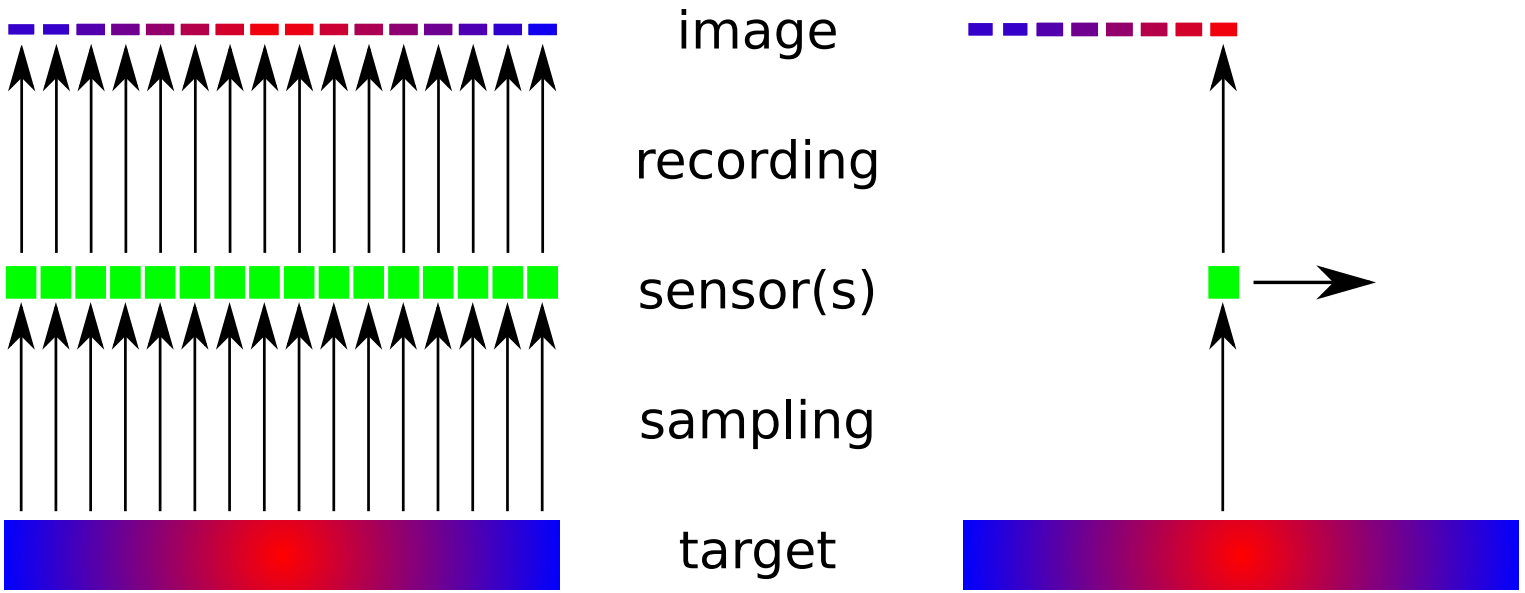

University of Pécs, Hungary
General and Physical Chemistry
Lívia Nagy
Prof. Géza Nagy
András Kiss
Zsuzsanna Őri

Potentiometric Scanning Electrochemical Microscopy

A Scanning Probe Microscopic technique



Difference between conventional and scanning microscopic techniques

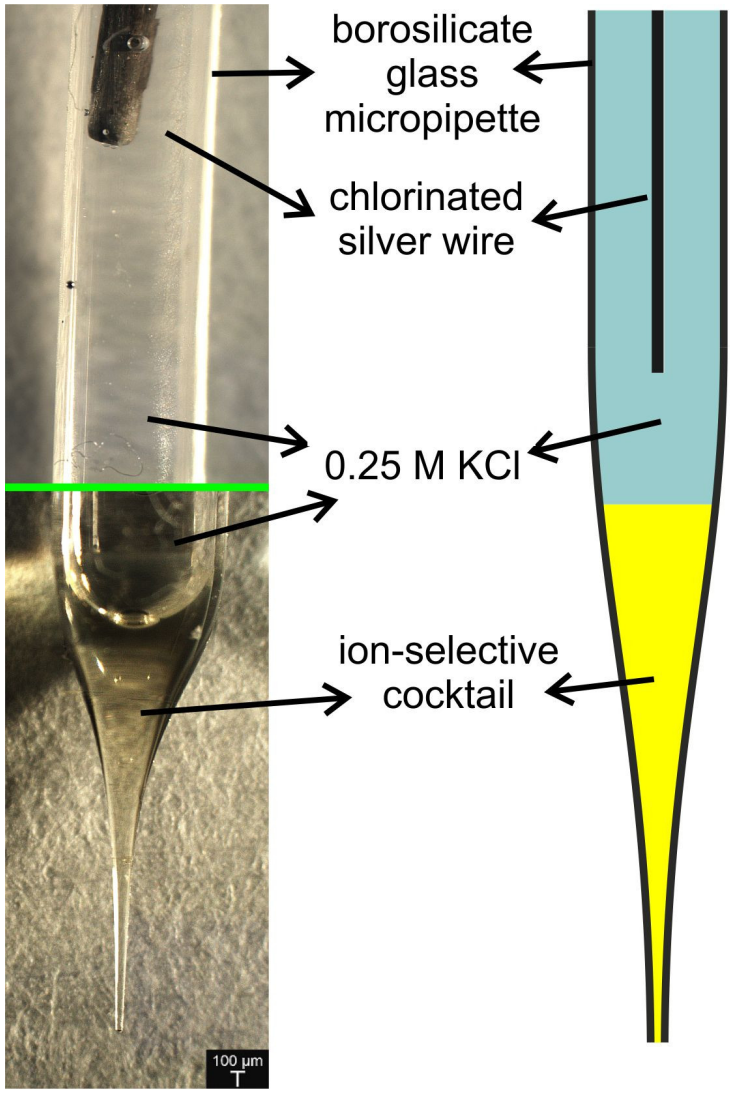


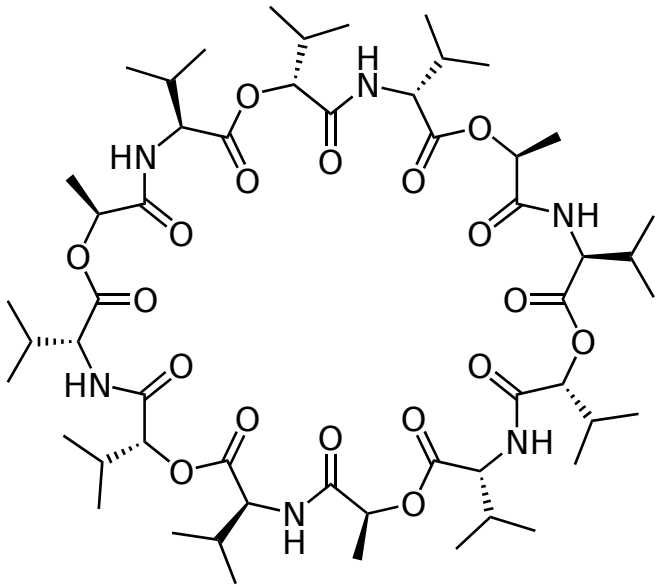
non-scanning technique

scanning technique

Ion-selective micropipettes

As SECM probes





Valinomycin

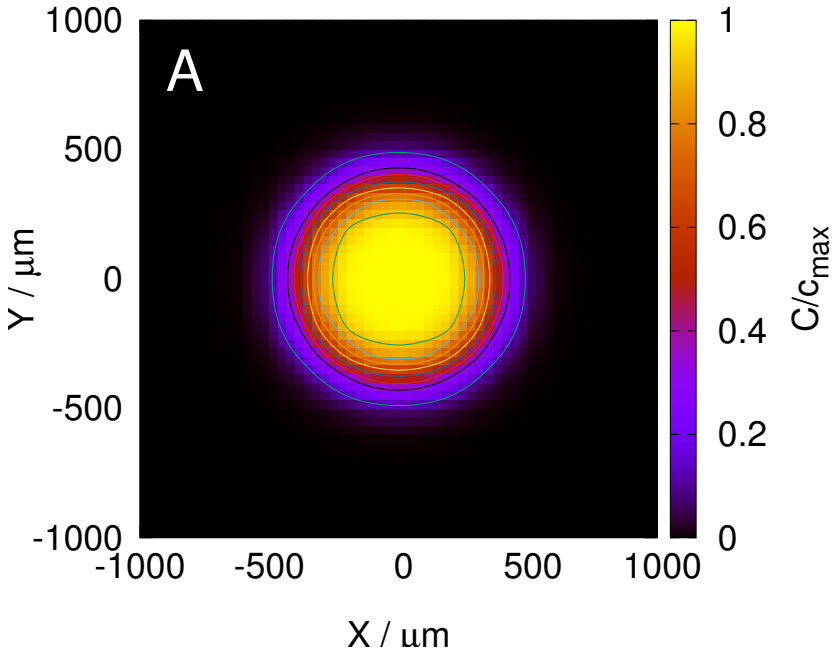
$$E = E^{\theta} + \frac{RT}{z_i F} \ln \left[a_i + \sum_j \left(k_{ij} a_j^{z_i/z_j} \right) \right]$$

Nikolsky–equation

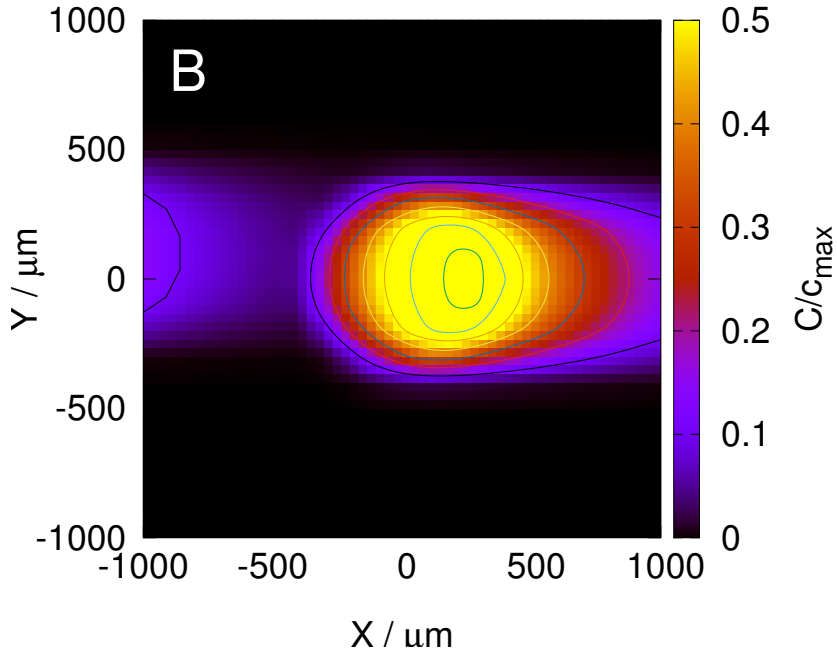
The problem with potentiometric SECM

Distortion at high scan rate

Slow

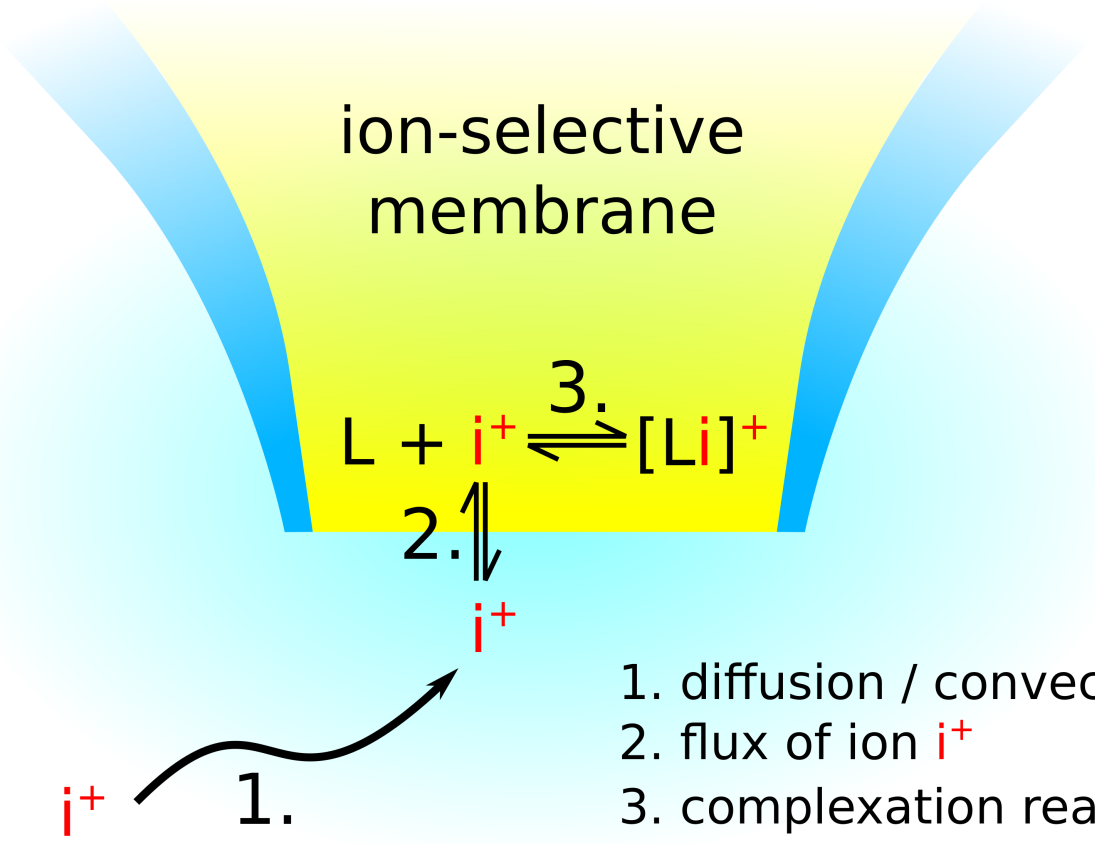


Fast



Why is the image distorted?

Possible contributors to the lag



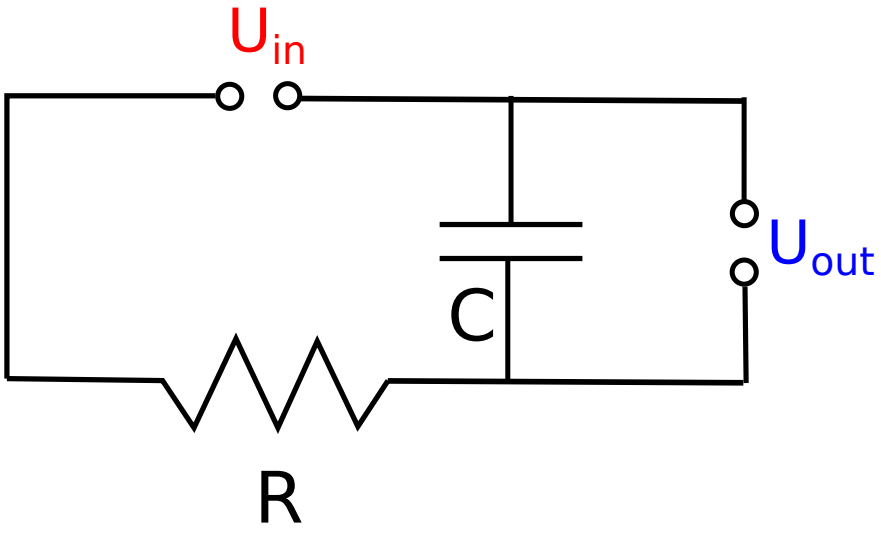
1. diffusion / convection
2. flux of ion i^+
3. complexation reaction

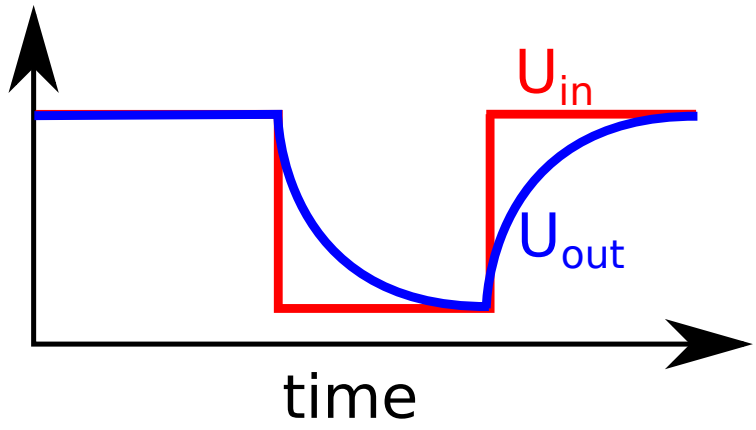
L: ligand

i^+: measured ion

Why is the image distorted?

The RC time constant

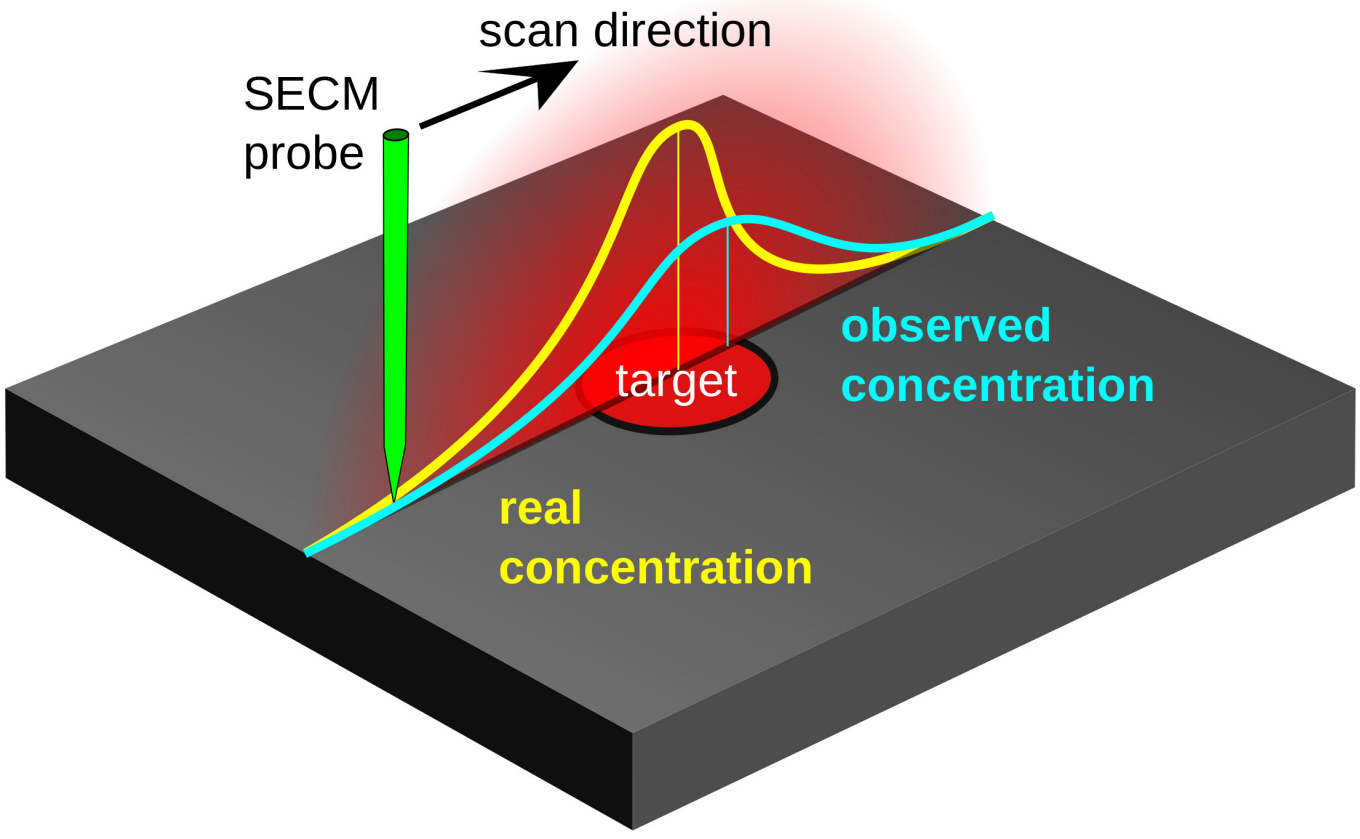




τ is the time that is required to charge the capacitor by $\approx 37\%$ $(1/e)$.

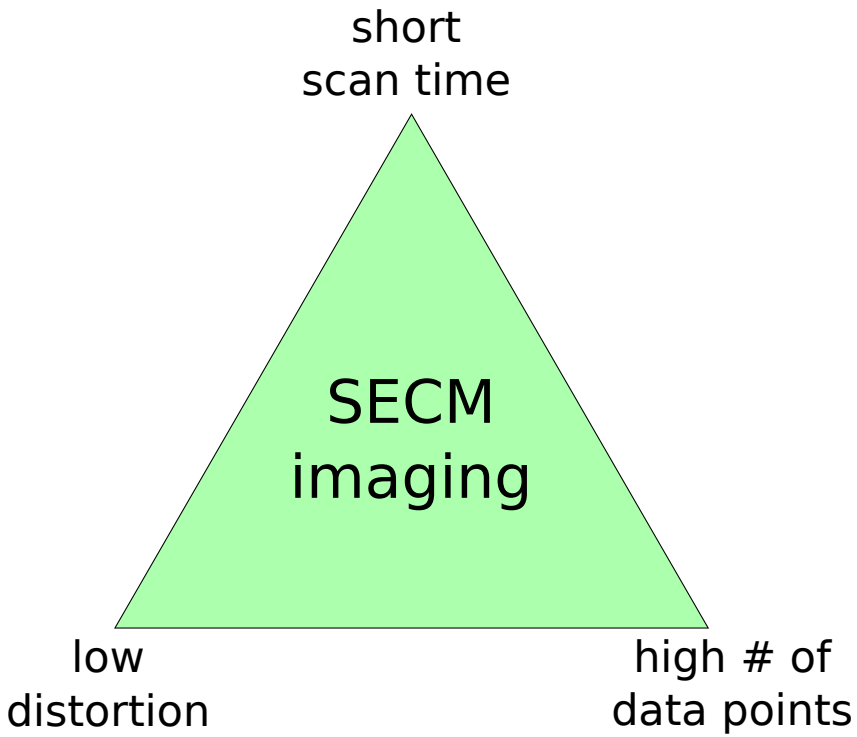
Distortion of potentiometric imaging

In the case of a linescan

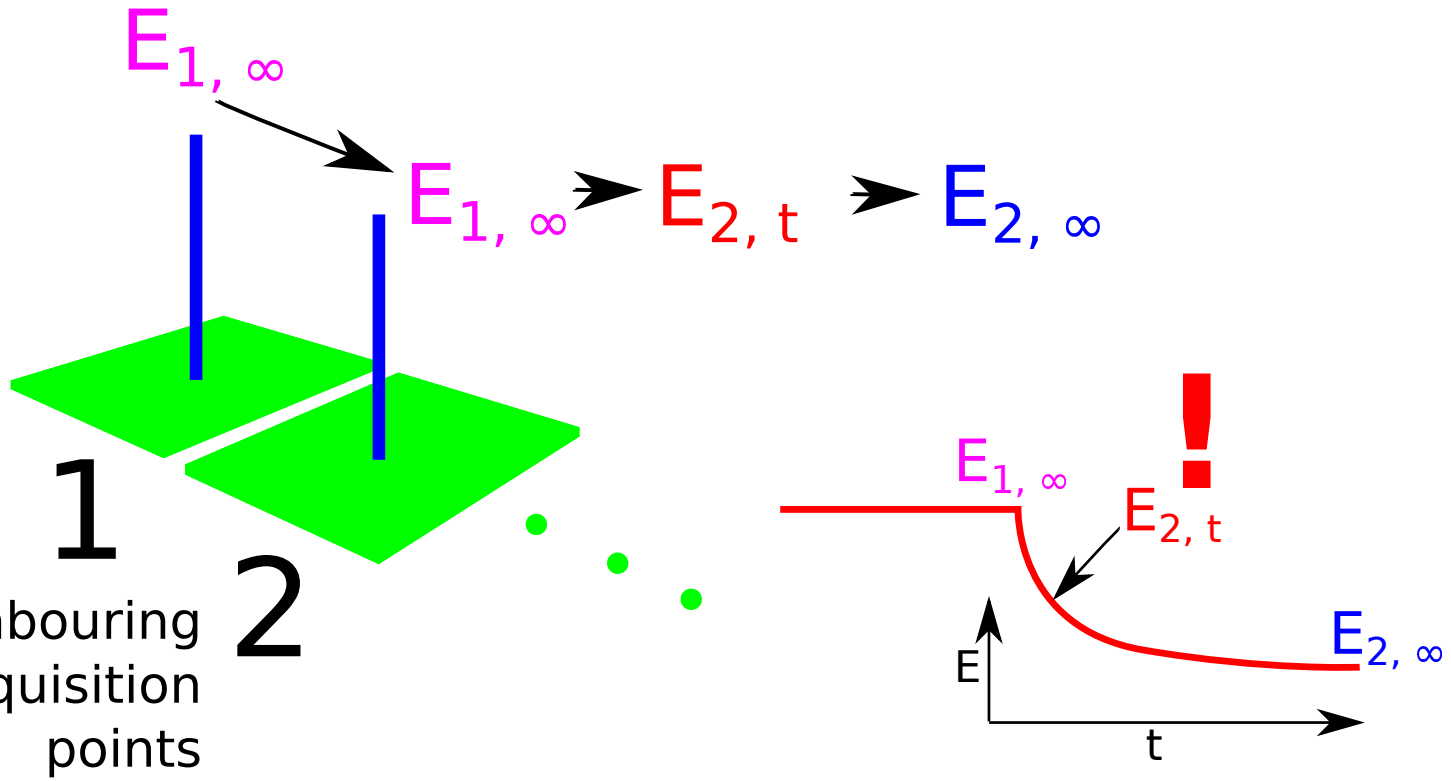


Trade-off triangle of potentiometric SECM

Compromise between the three desired competing properties

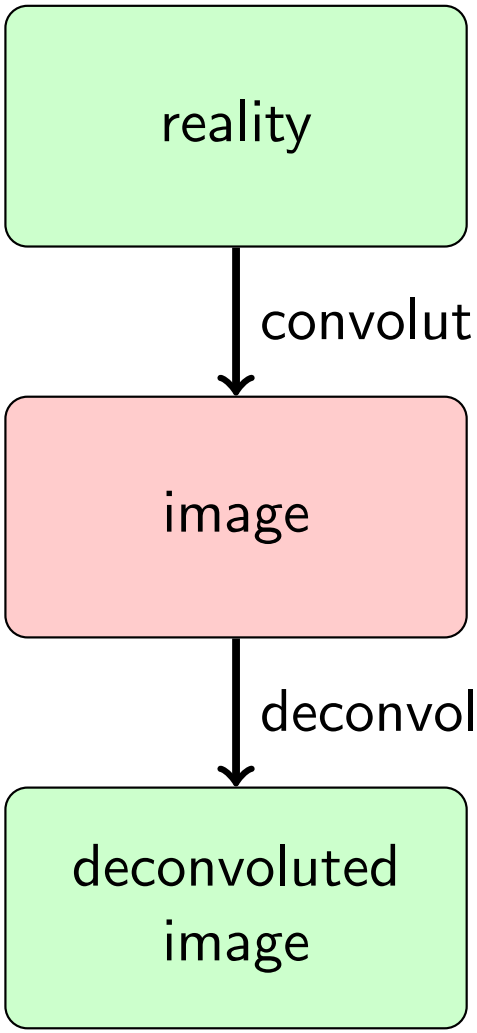


The convolution function of the distortion



$$E_{cell}(t) = E_{cell}(\infty) + [E_{cell}(0) - E_{cell}(\infty)]e^{-t/\tau}$$

Convolution and deconvolution

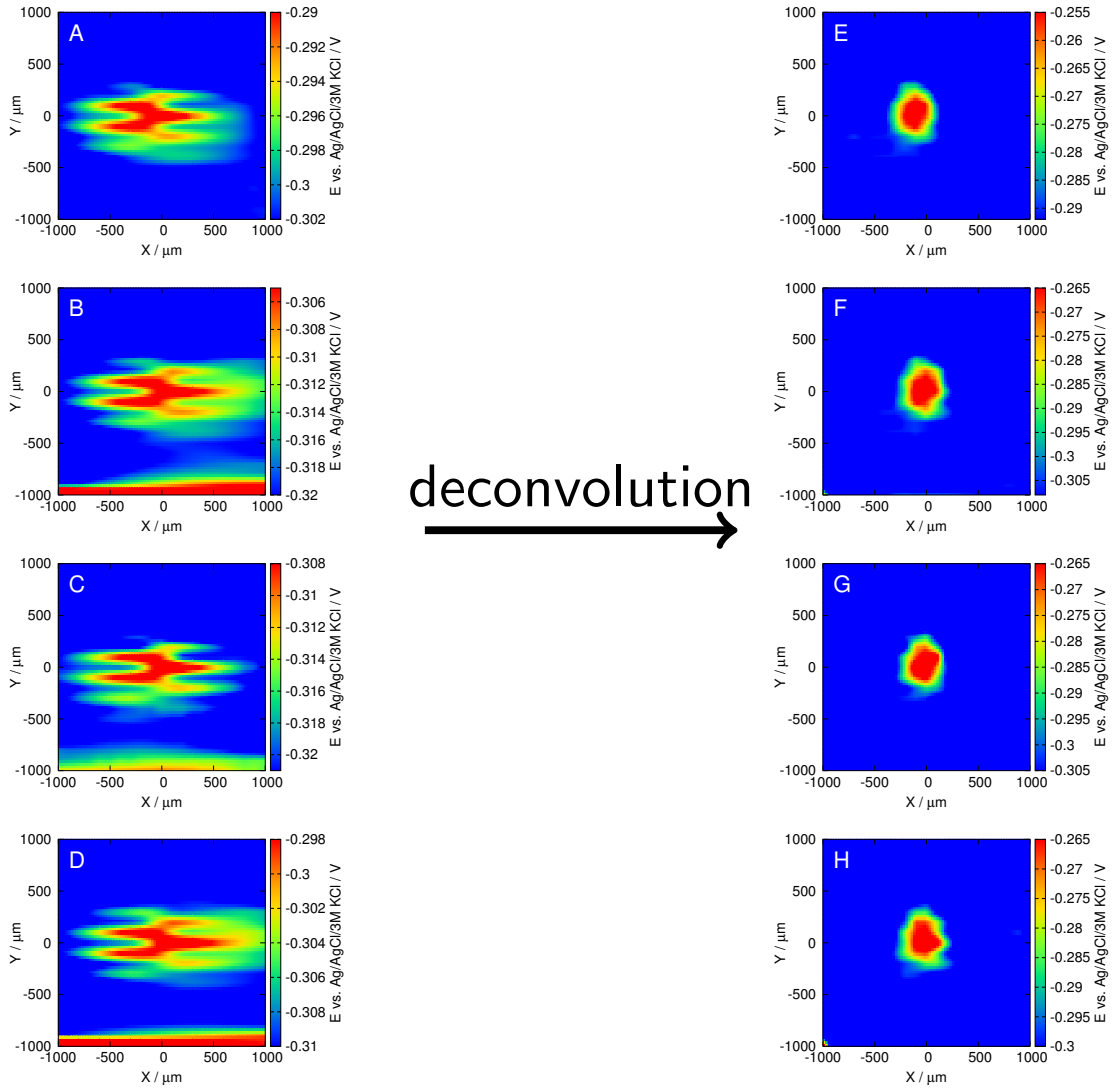


convolution : $E_{cell}(t) = E_{cell}(\infty) + [E_{cell}(0) - E_{cell}(\infty)]e^{-t/\tau}$

deconvolution : $E_{cell}(\infty) = \frac{E_{cell}(t) - E_{cell}(0)e^{-t/\tau}}{1 - e^{-t/RC}}$

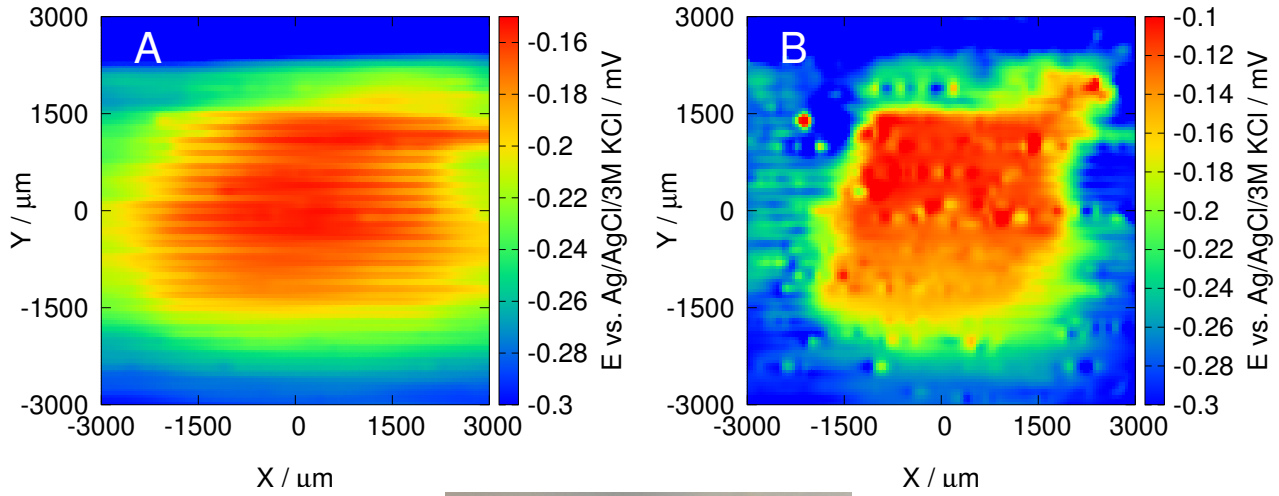
Deconvolution of potentiometric SECM images

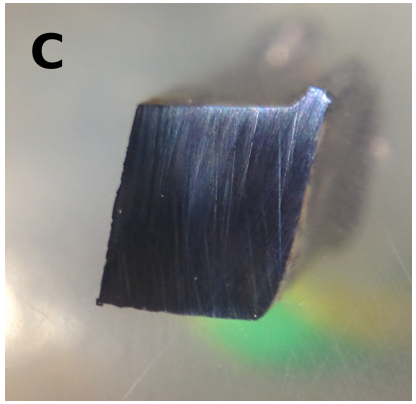
Recorded using the antimony microelectrode following the meander algorithm



Practical example: corroding carbon steel sample

Scanned with an antimony microelectrode





9th Workshop on Scanning Electrochemical Microscopy and Related Techniques

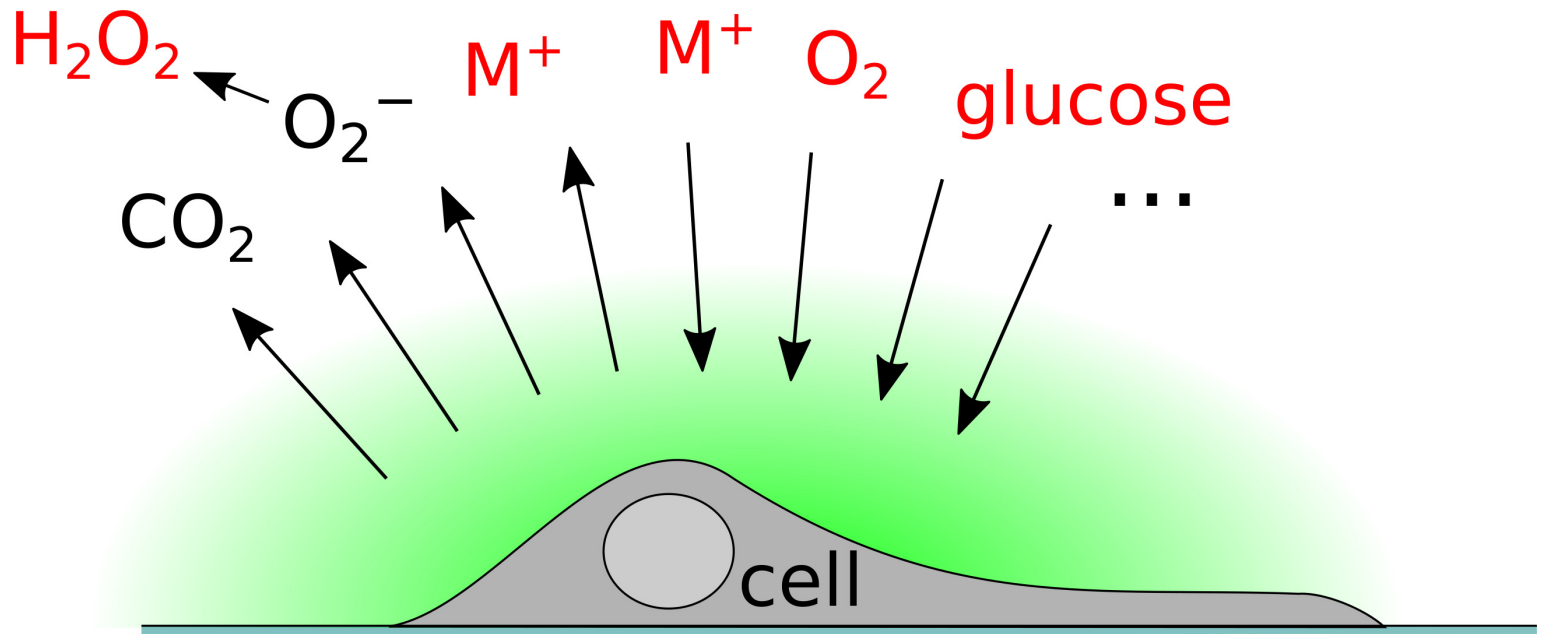
Warsaw, Poland, August 13-17, 2017.

Can it be done with amperometric SECM images?


DAAD
Deutscher Akademischer Austausch Dienst
German Academic Exchange Service

Why would you want to do SECM imaging of a cell?

It's an easy way to make *in situ*, real-time, selective, non-invasive, high resolution, single cell experiments



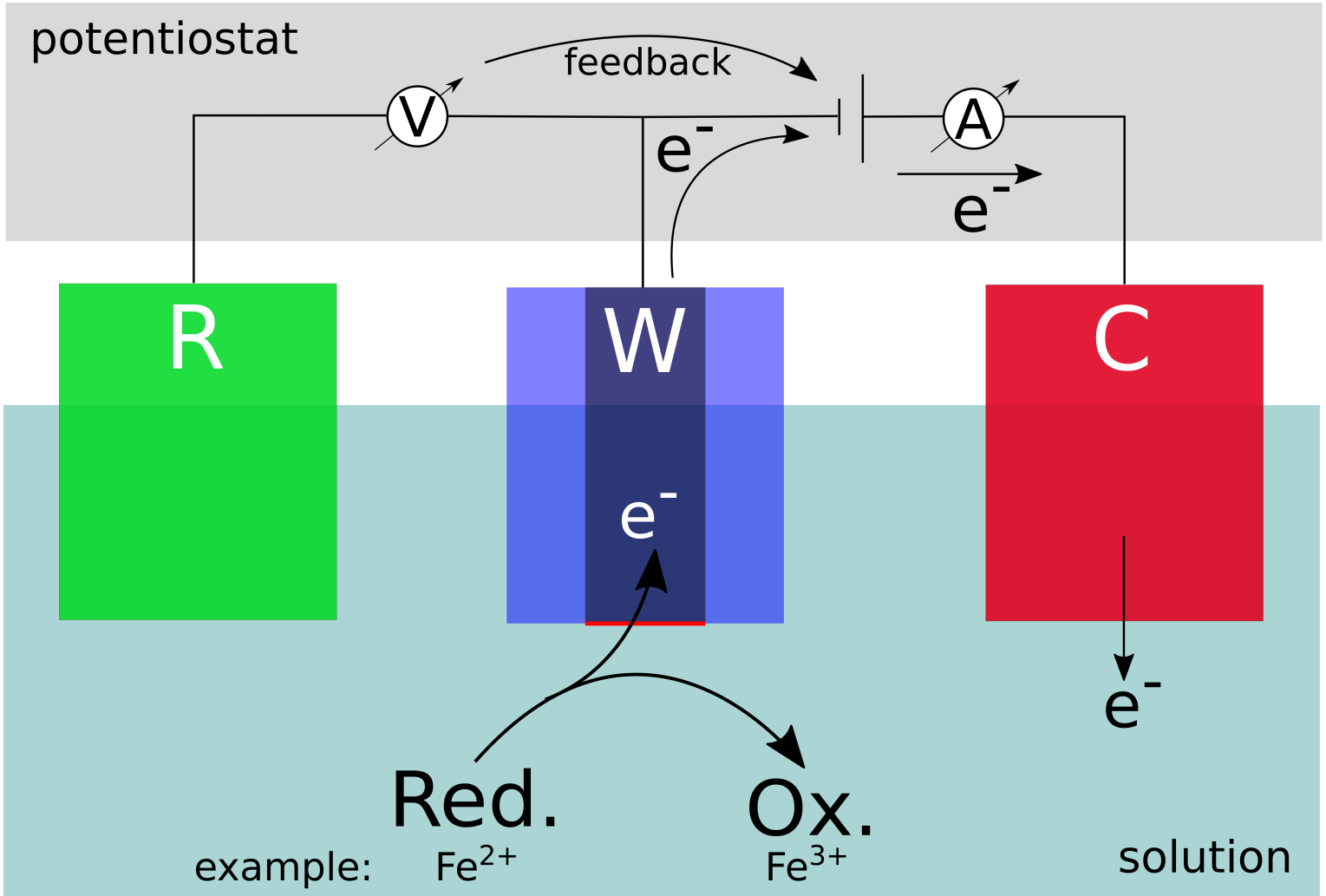
ANTIOXIDANTS & REDOX SIGNALING
Volume 29, Number 6, 2018
Mary Ann Liebert, Inc.
DOI: 10.1089/ars.2016.6840

FORUM ORIGINAL RESEARCH COMMUNICATION

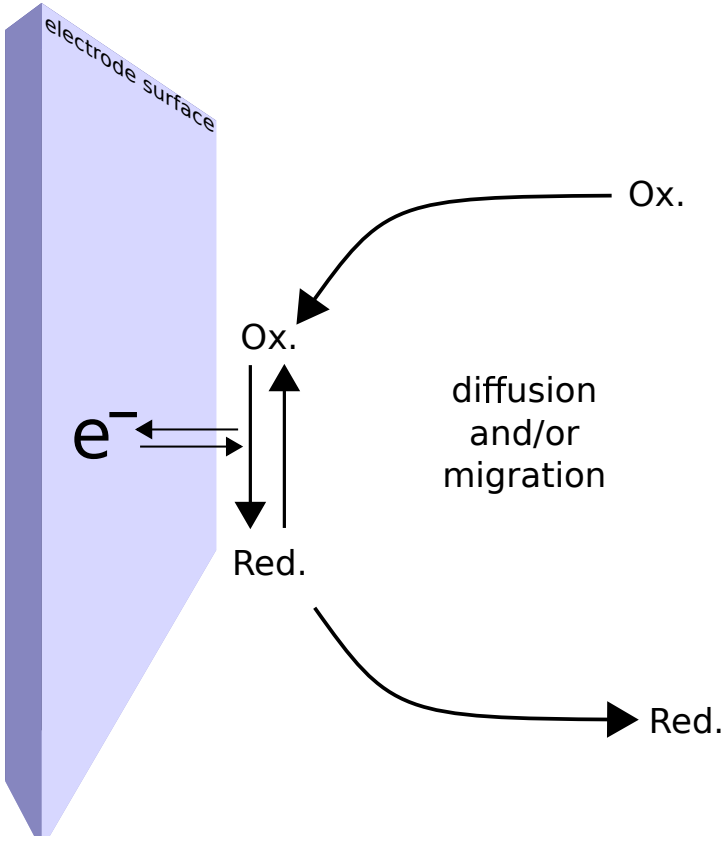
Electrochemical Quantification of Extracellular Local H_2O_2 Kinetics Originating from Single Cells

Monika Bozem,[1] Phillip Knapp,[1] Valentin Mirčeski,[2] Ewa J. Slowik,[1] Ivan Bogeski,[1,3] Reinhard Kappl,[1] Christian Heinemann,[4] and Markus Hoth[1]

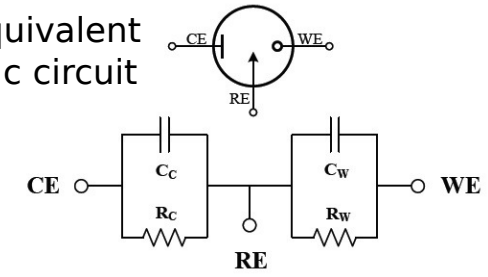
The amperometric measuring cell

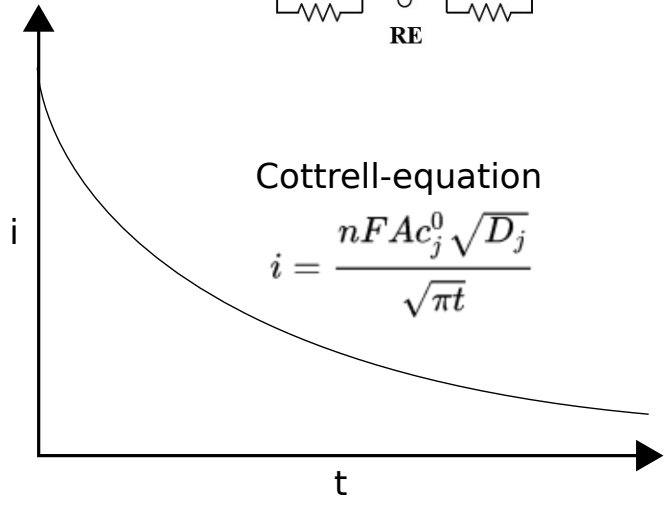


Amperometric transient response



Simplified equivalent amperometric circuit



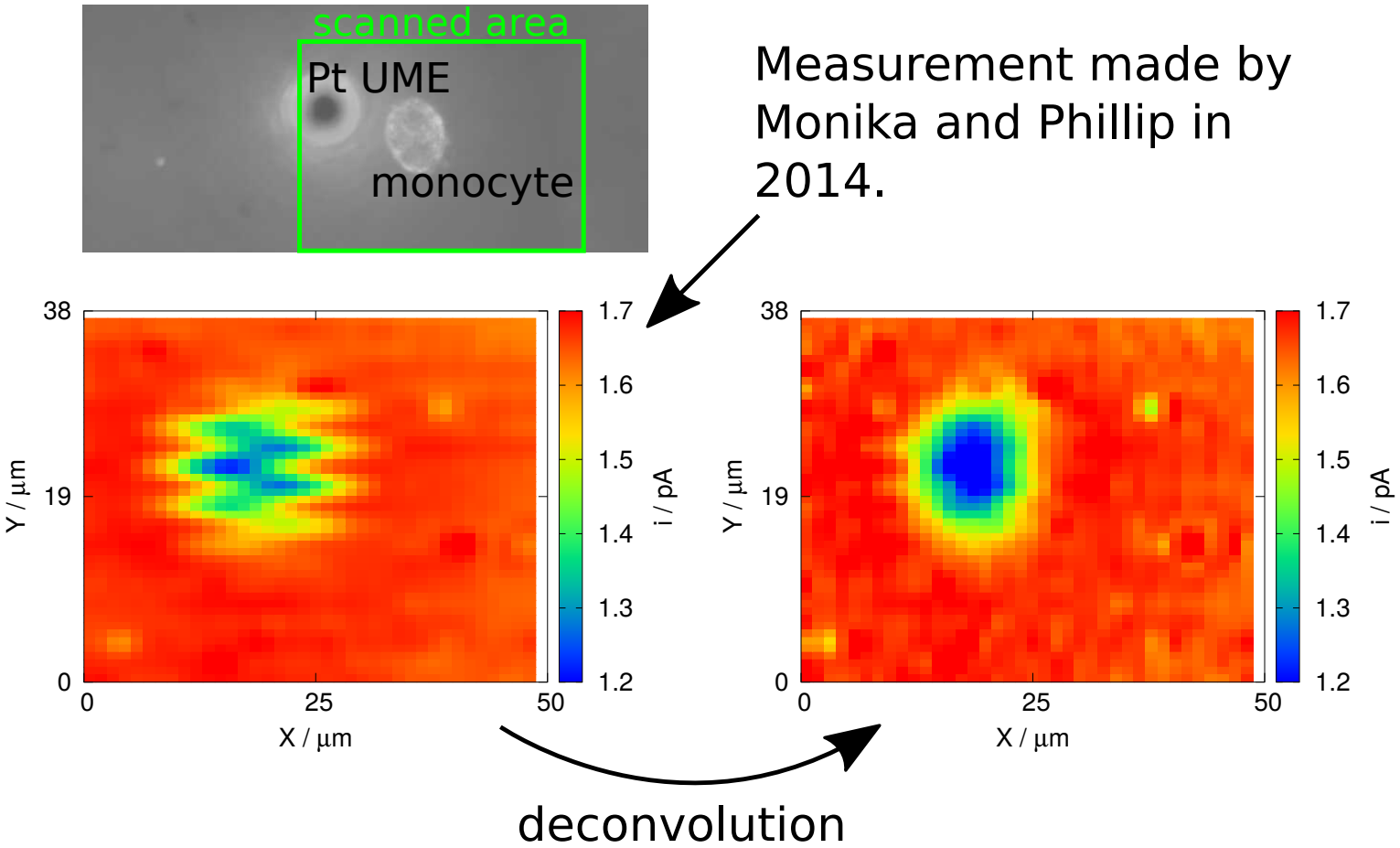


Cottrell-equation

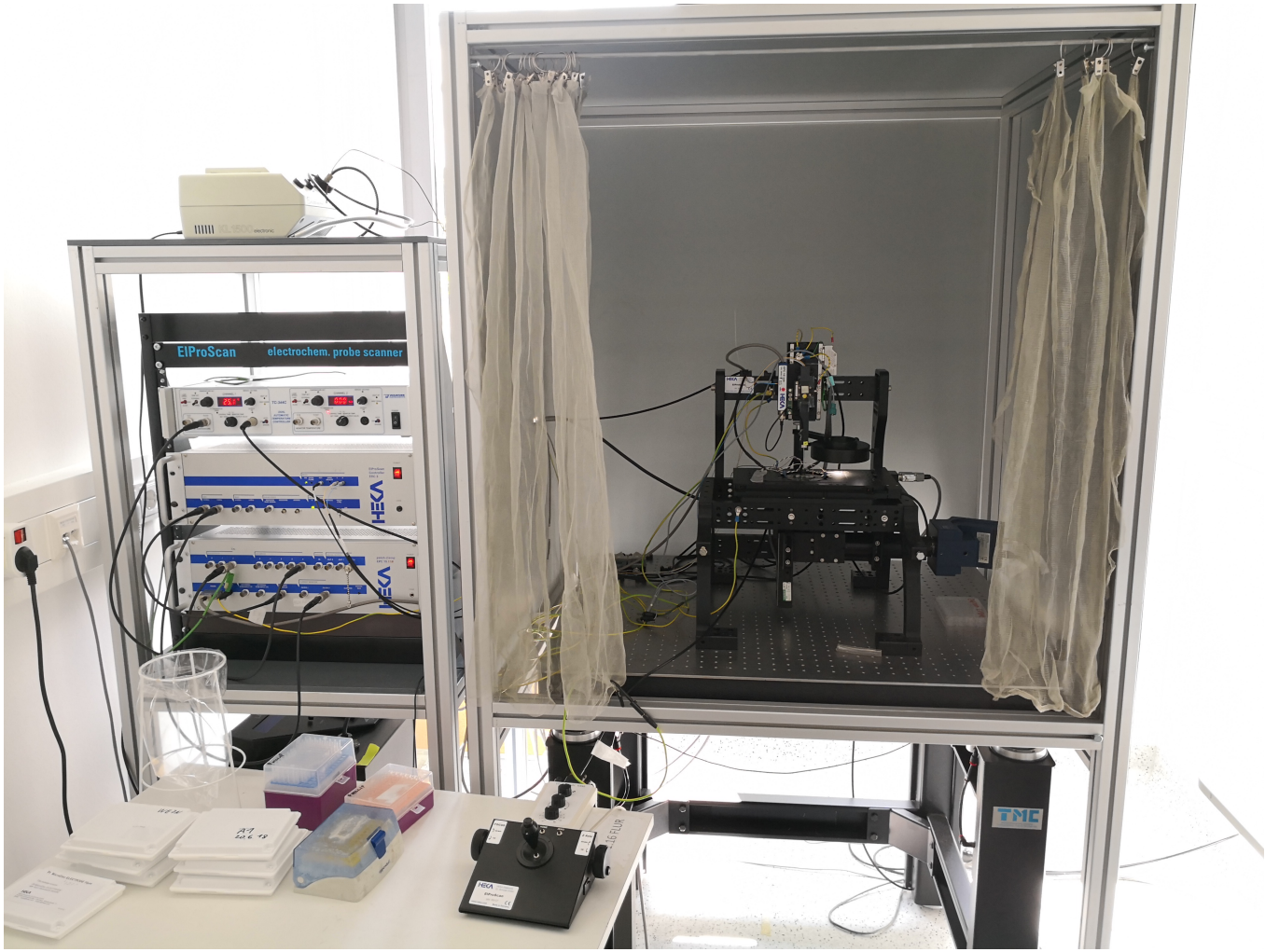
$$i = \frac{nFAc_j^0\sqrt{D_j}}{\sqrt{\pi t}}$$

Deconvolution of an amperometric image.

H_2O_2 oxidation current above a monocyte exposed to extracellular H_2O_2 (10 µM).

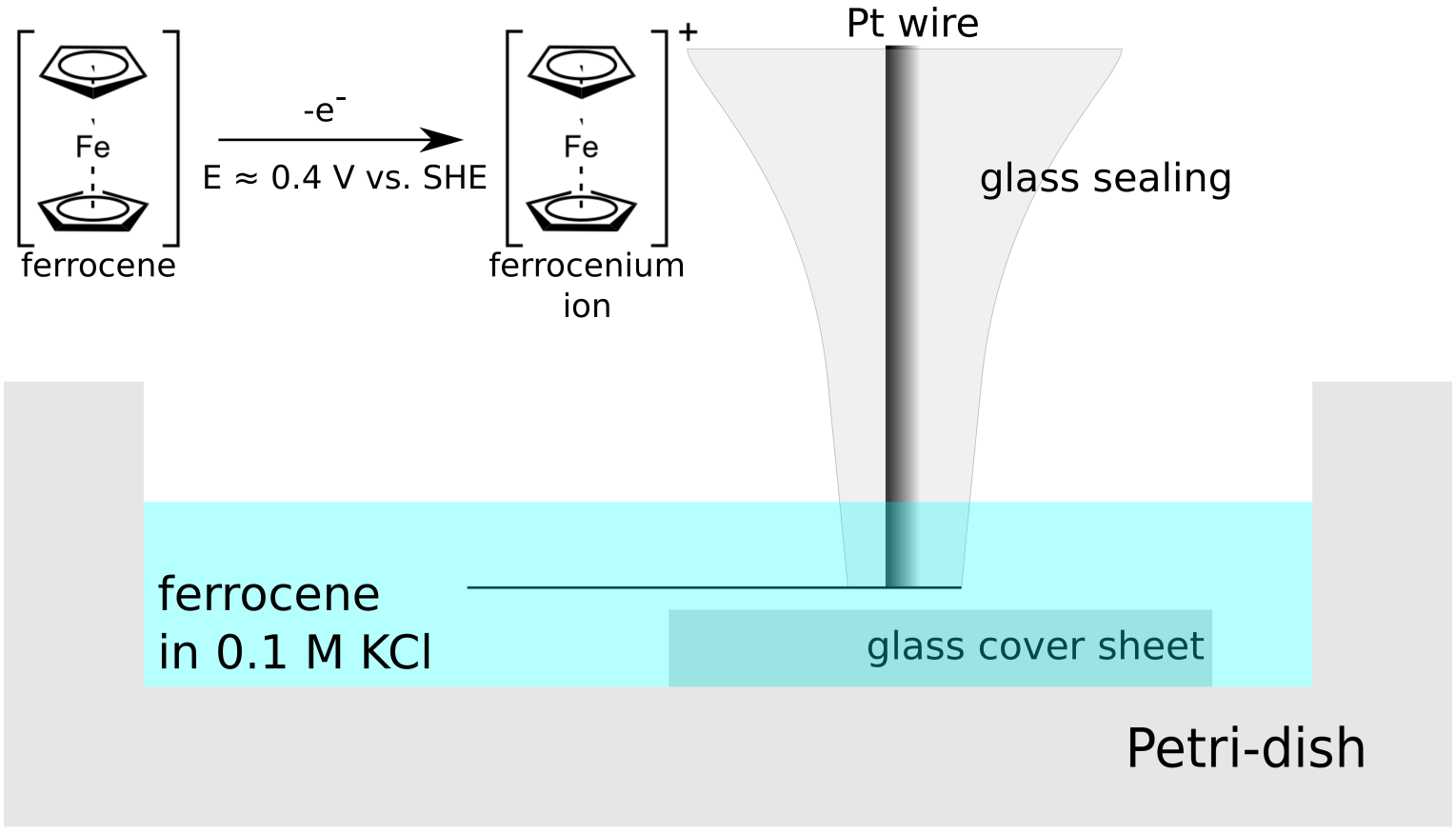


The HEKA ElProScan.



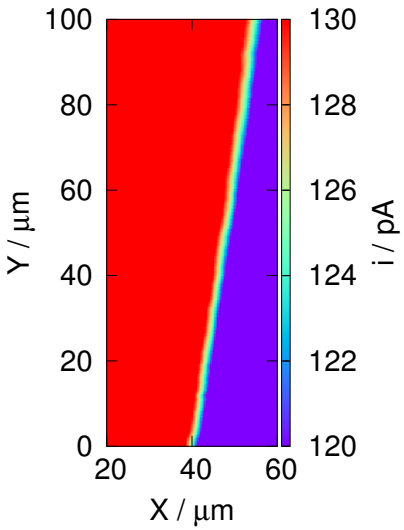
Investigating a step response over a glass sheet edge.

With the ferrocene/ferrocenium system.

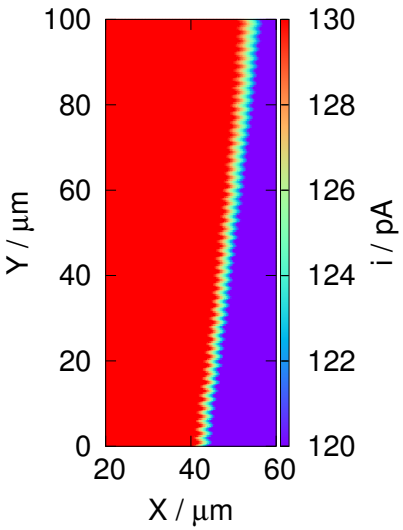


Investigating a step response over a glass sheet edge.

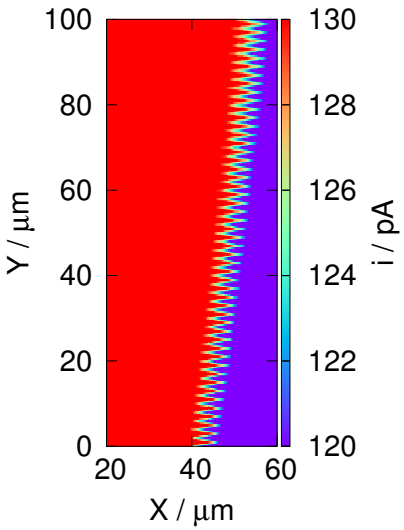
Results.



5 µm/s



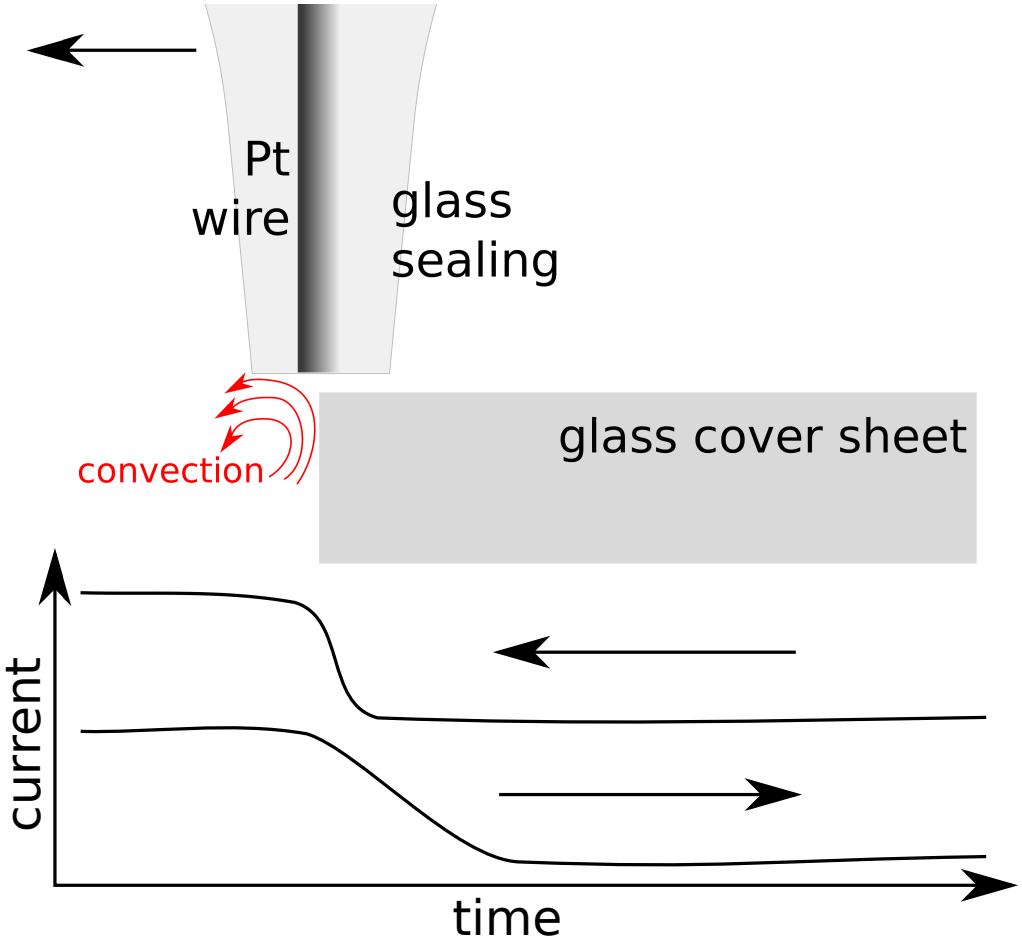
10 µm/s



10 µm/s deconvoluted

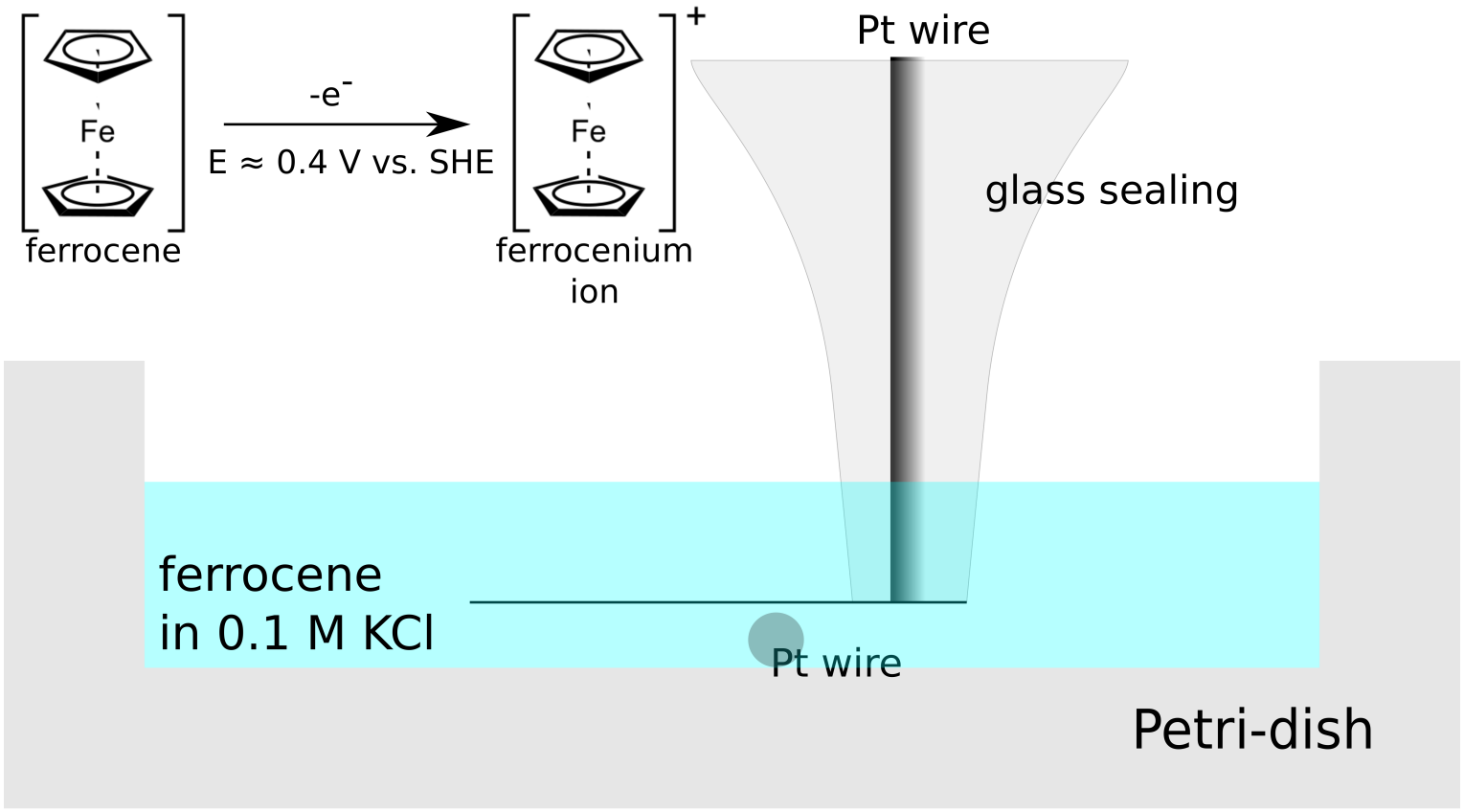
Investigating a step response over a glass sheet edge.

Discrepancy caused by convection.



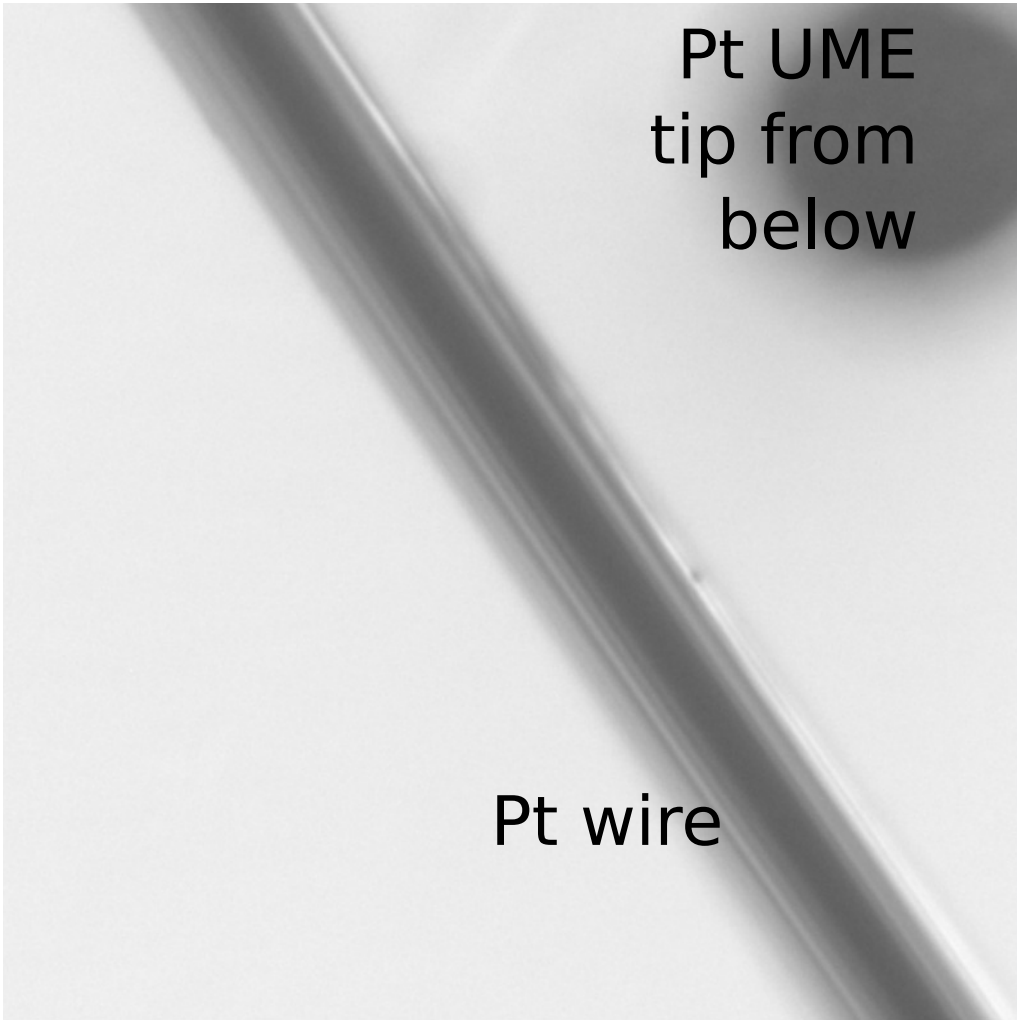
Investigating a step response over a d = 10 μm Pt wire.

With the ferrocene/ferrocenium system.



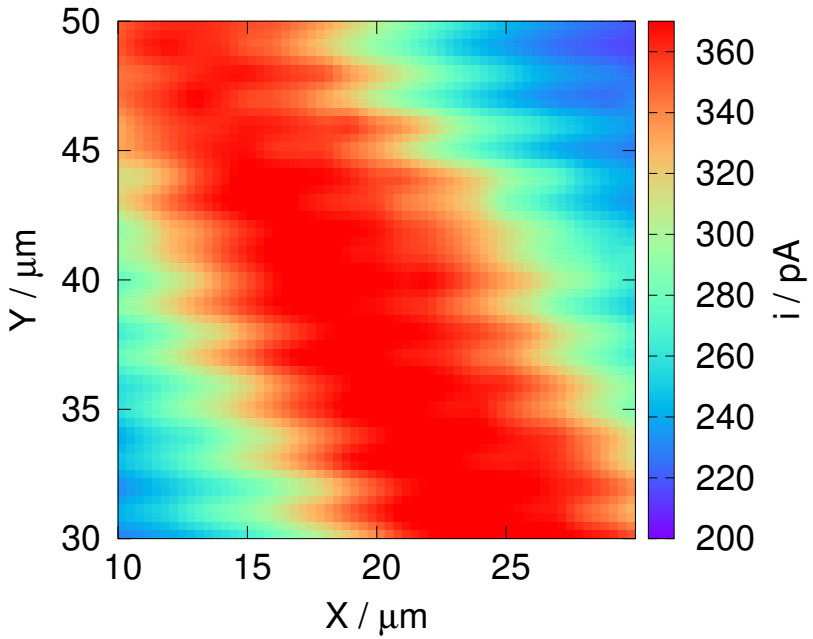
Investigating a step response over a d = 10 μm Pt wire.

Microphoto of the model system from below.

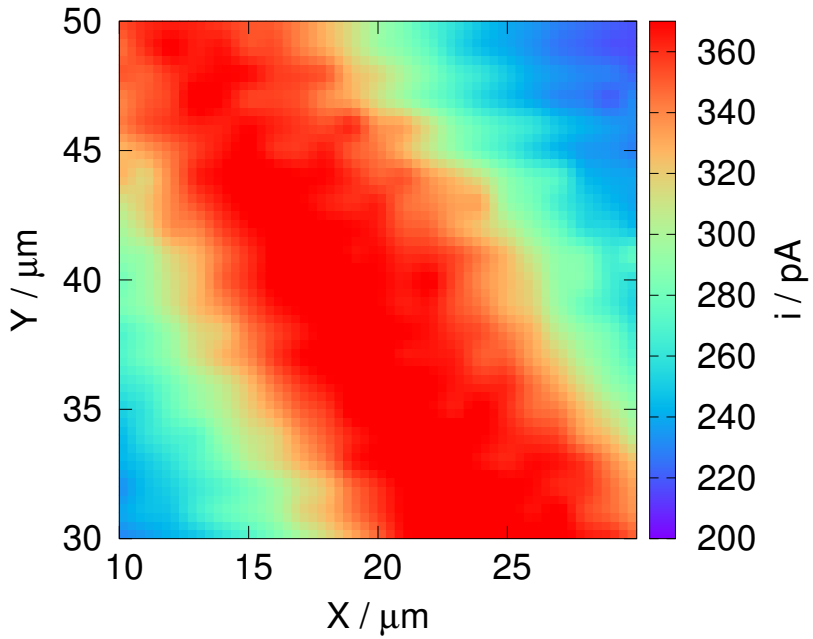


Investigating a step response over a d = 10 µm Pt wire.

Results.



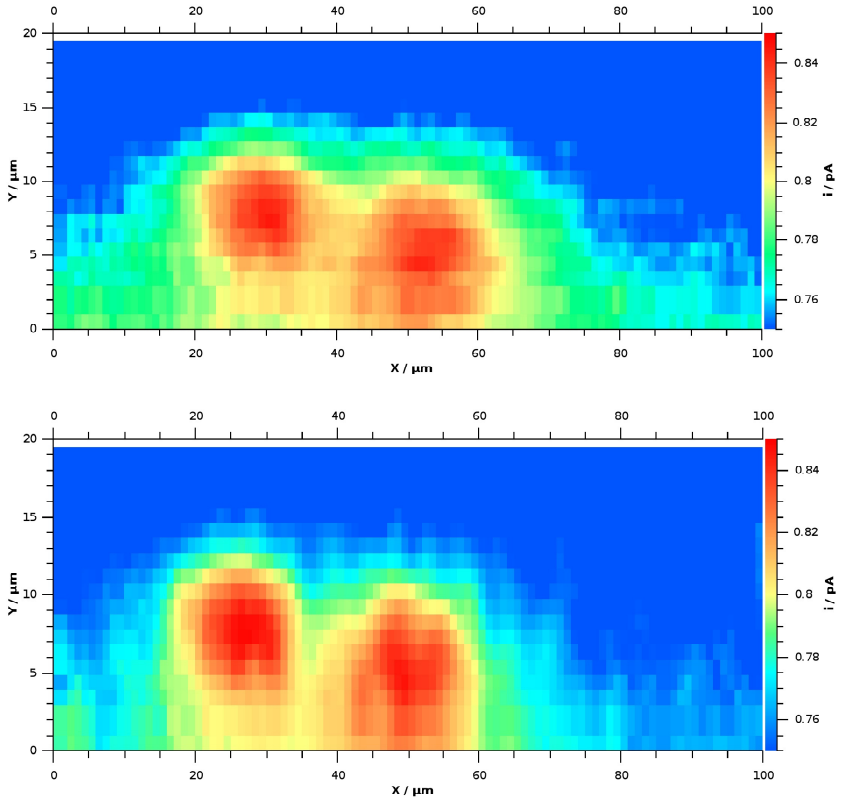
10 µm/s



10 µm/s deconvoluted

H_2O_2 measurement over a TPA stimulated monocyte.

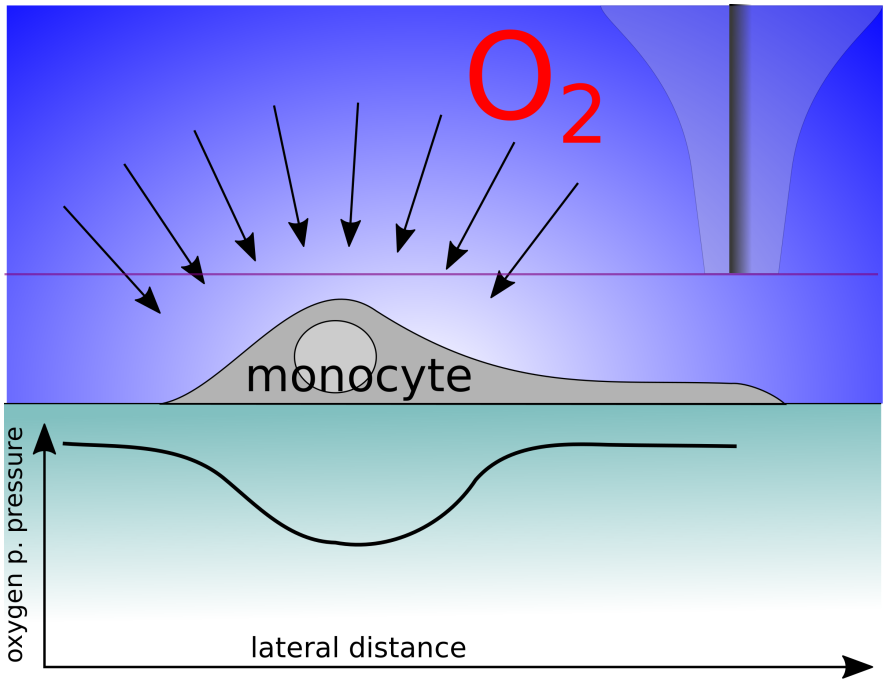
Results.

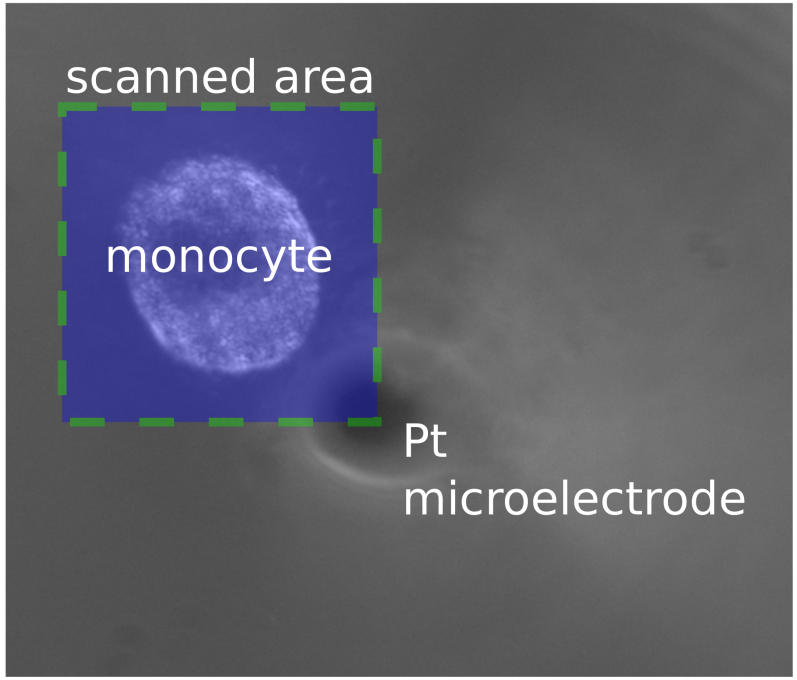


Top image: original measurement, made by Monika in 2014. Scanning speed was 2 µm/s. Bottom image: deconvoluted image.

Oxygen reduction current above a monocyte.

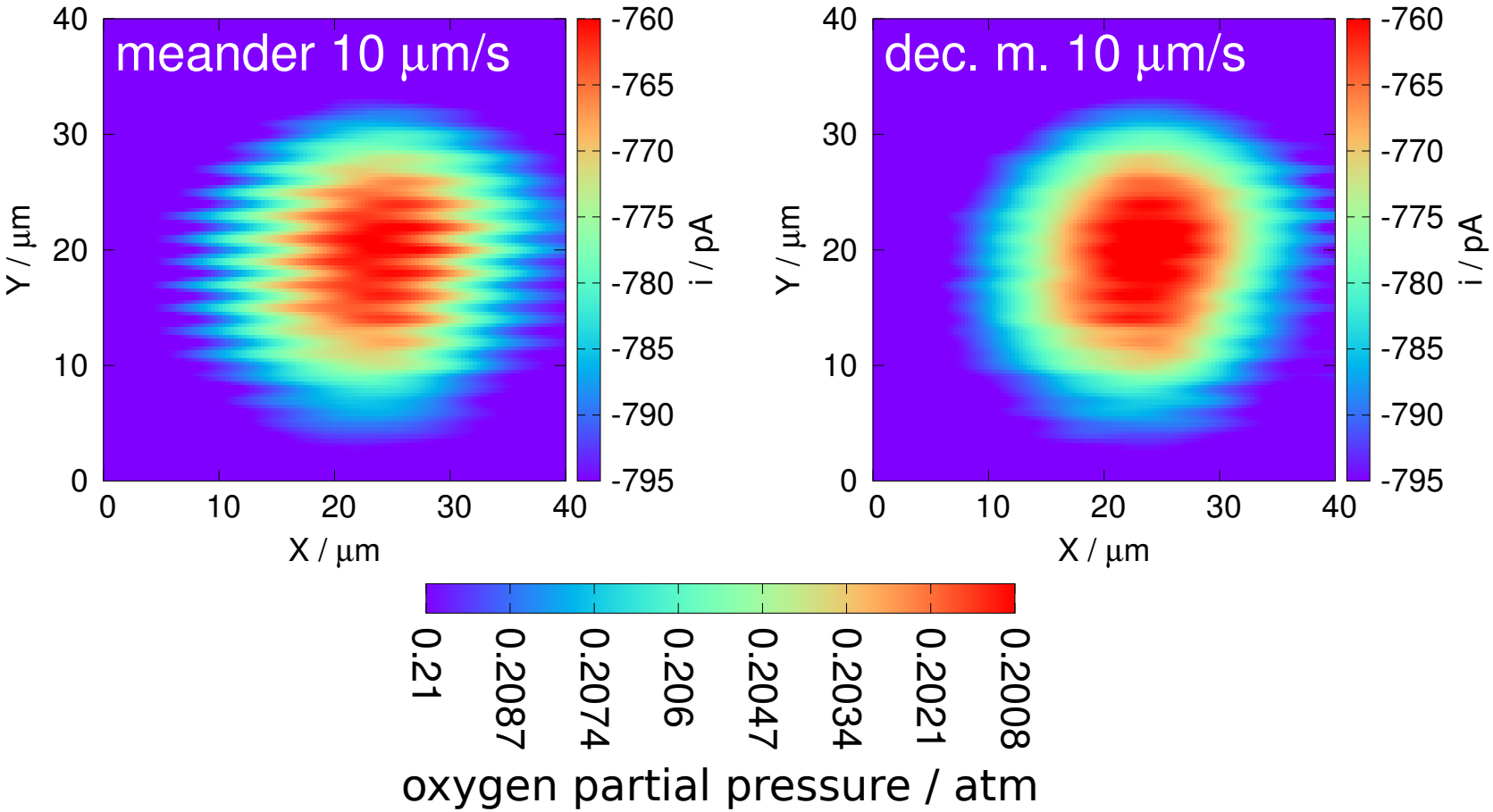
Experimental setup.





Oxygen reduction current above a monocyte.

Results.



Conclusion

1. **SECM is a powerful tool. Many systems can be studied best with this technique.**
2. **However, it suffers from low scan speeds and high distortion.**
3. **Previously I have worked out a deconvolution technique to solve this problem for potentiometric SECM.**
4. **During my stay here I have worked out a similar method for amperometric SECM.**
5. **I have used the technique to restore images recorded by Monika and Phillip previously.**
6. **I have introduced single cell oxygen measurements here with the SECM, and successfully applied the deconvolution to those images as well.**

Thank you!

Dr. Monika Bozem
Prof. Dr. Markus Hoth
Phillip Knapp
Katerina Stankoska
Rüdiger Stumpf
Staff of CIPMM

DAAD

Thank you for your kind attention!