Deconvolution in Scanning Electrochemical Microscopy

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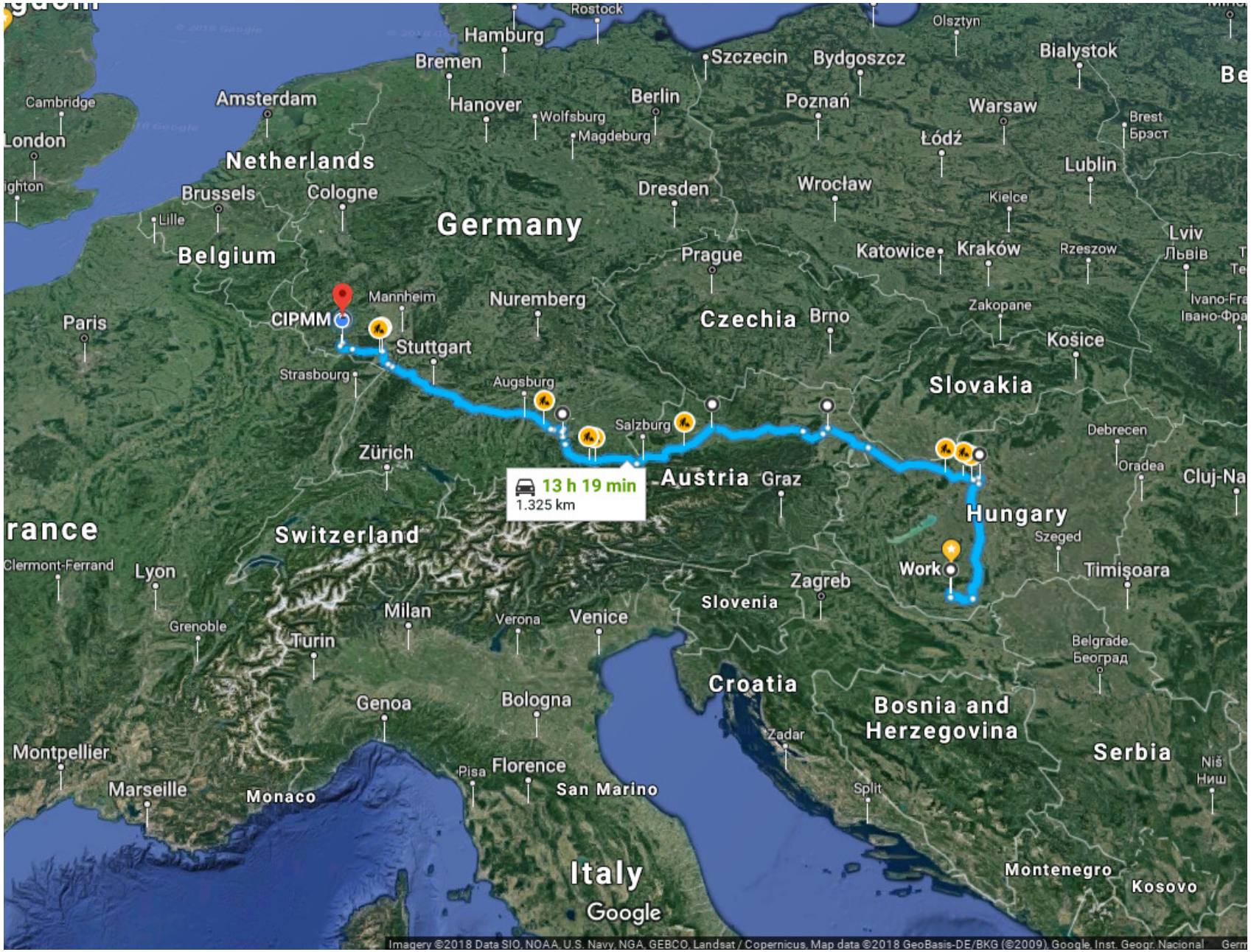
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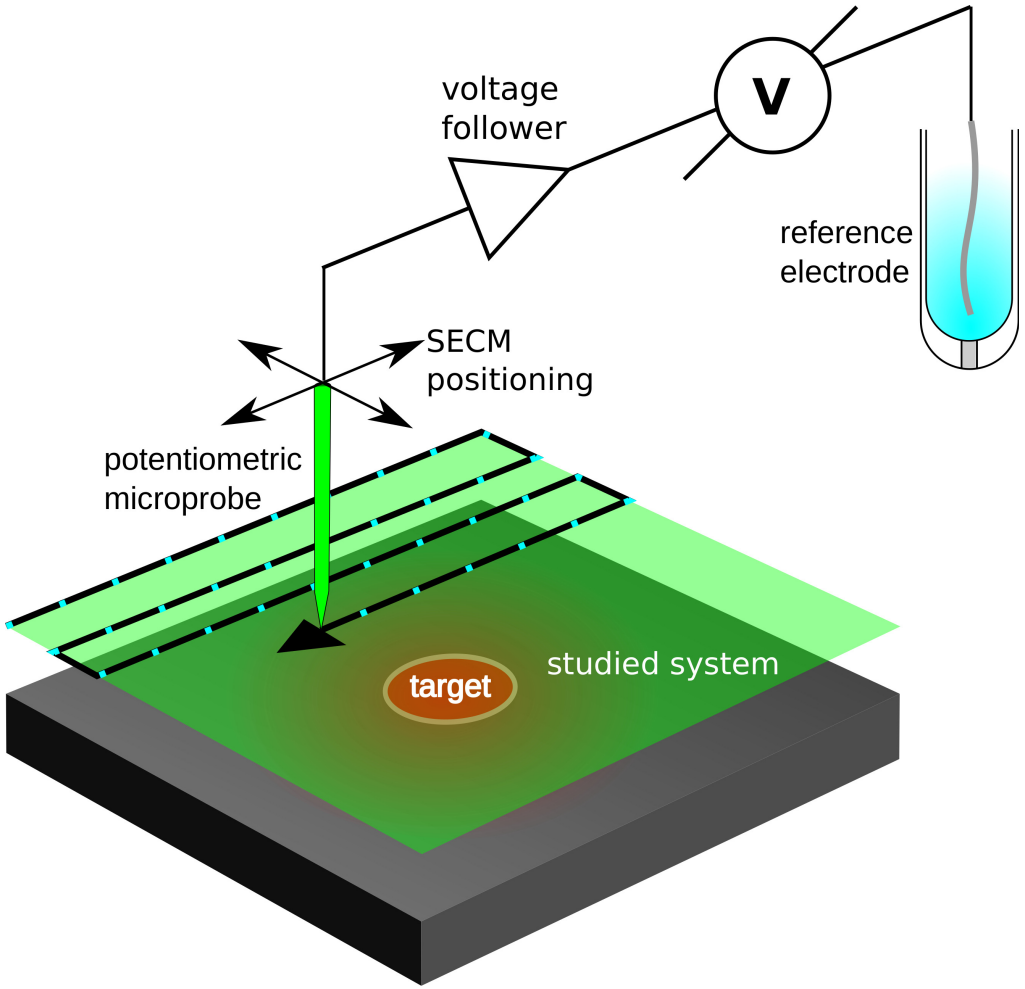
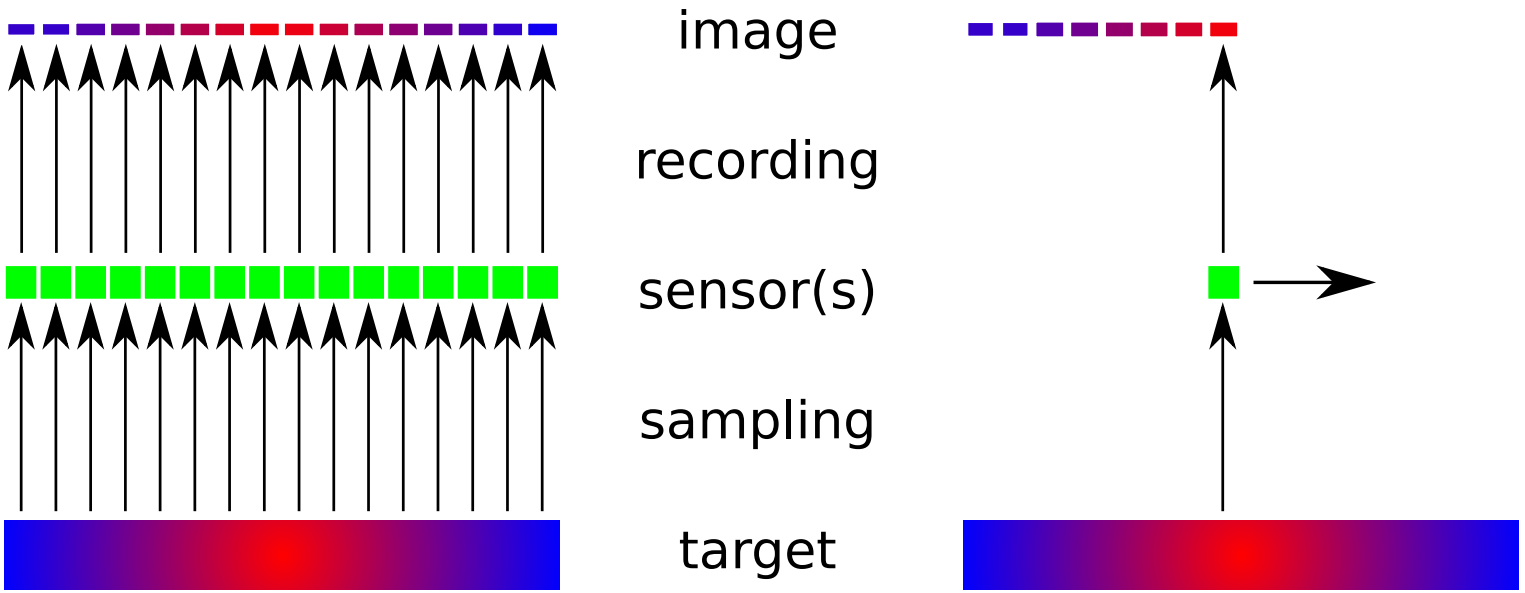
András Kiss
Zsuzsanna Őri

Potentiometric Scanning Electrochemical Microscopy

A Scanning Probe Microscopic technique



Difference between conventional and scanning microscopic techniques

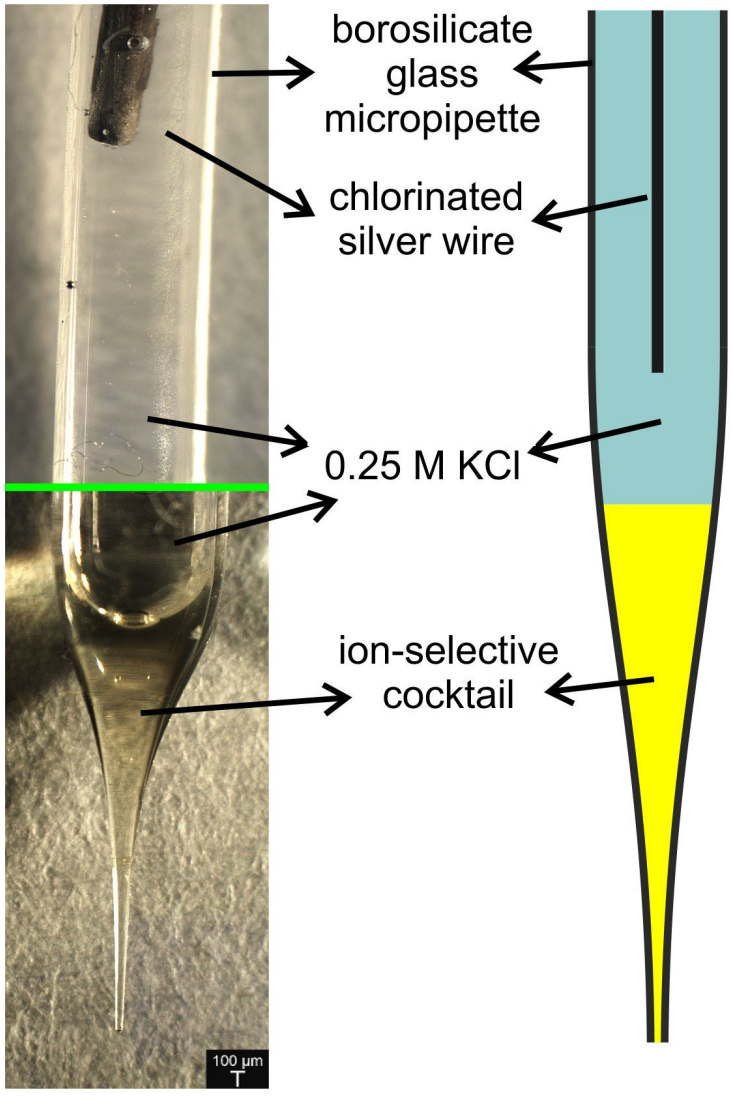


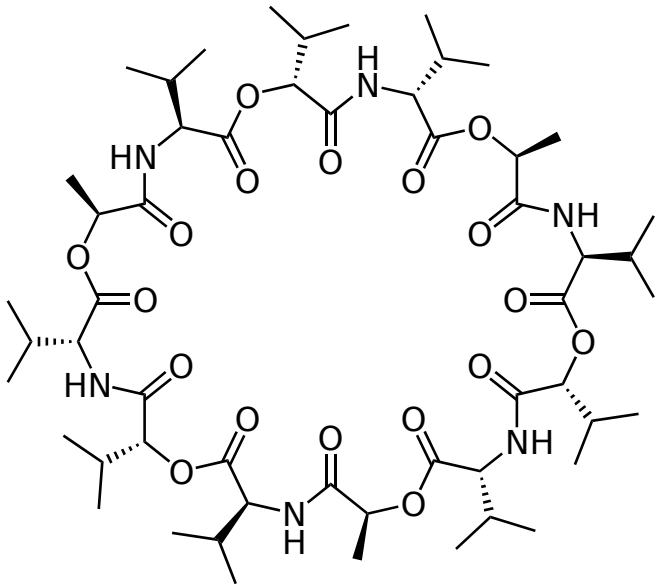
non-scanning technique

scanning technique

Ion-selective micropipettes

As SECM probes





Valinomycin

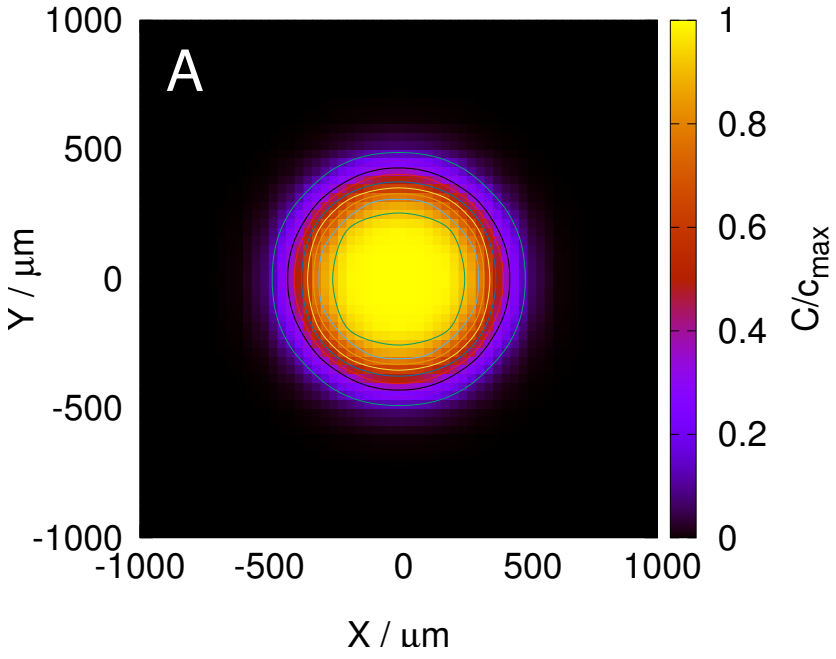
$$E = E^{\theta} + \frac{RT}{z_i F} \ln \left[a_i + \sum_j \left(k_{ij} a_j^{z_i/z_j} \right) \right]$$

Nikolsky–equation

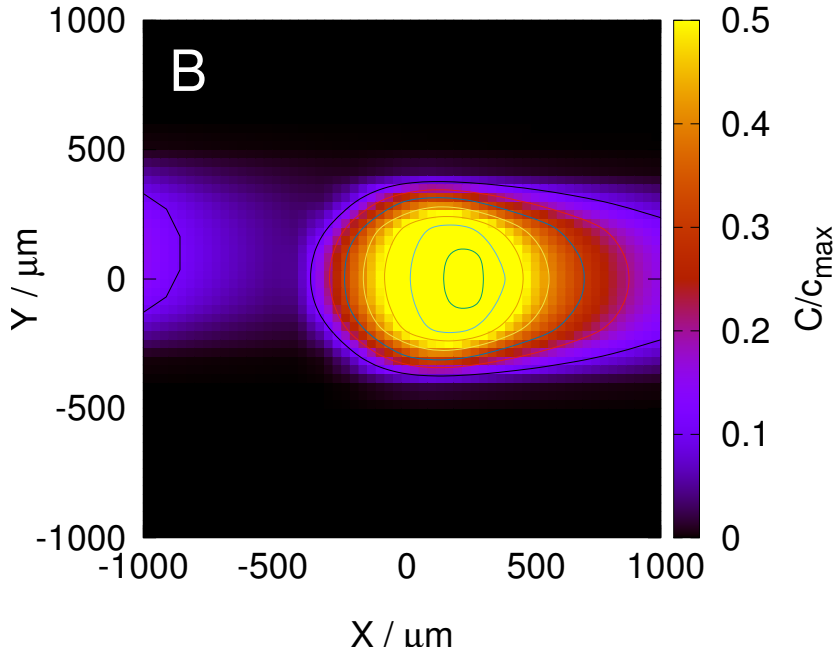
The problem with potentiometric SECM

Distortion at high scan rate

Slow

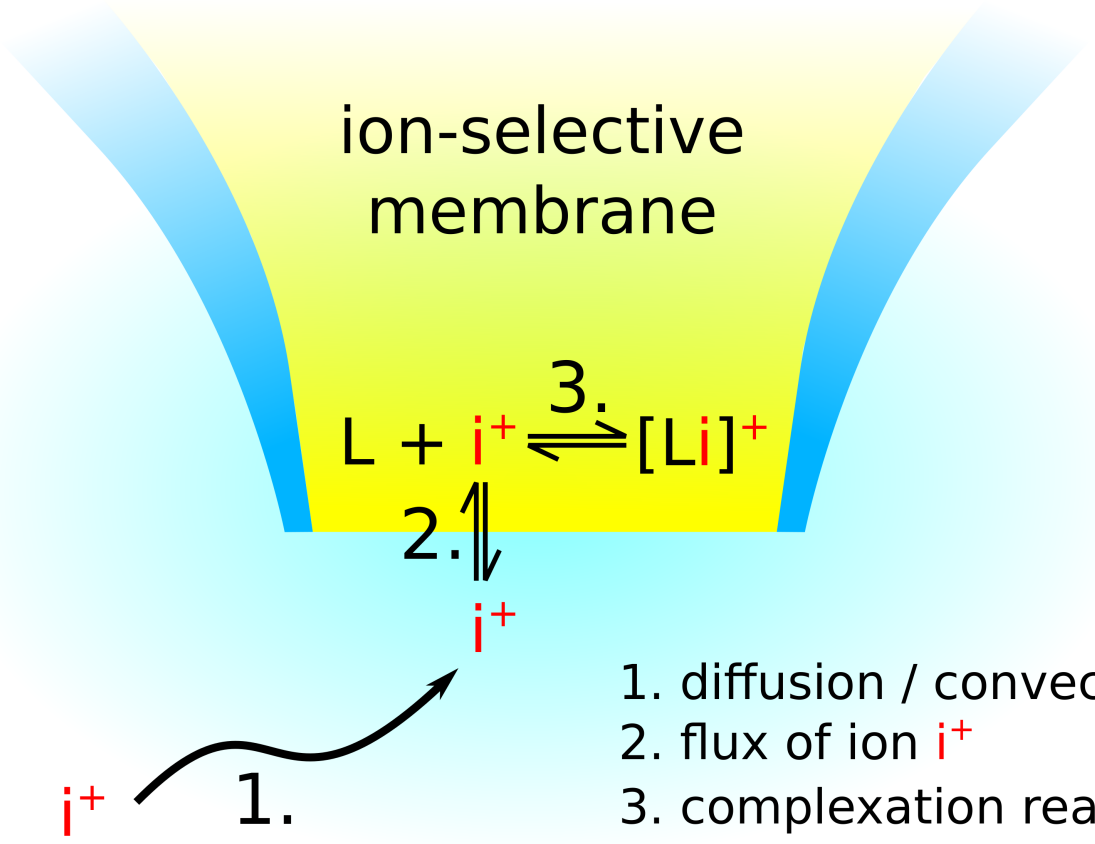


Fast



Why is the image distorted?

Possible contributors to the lag



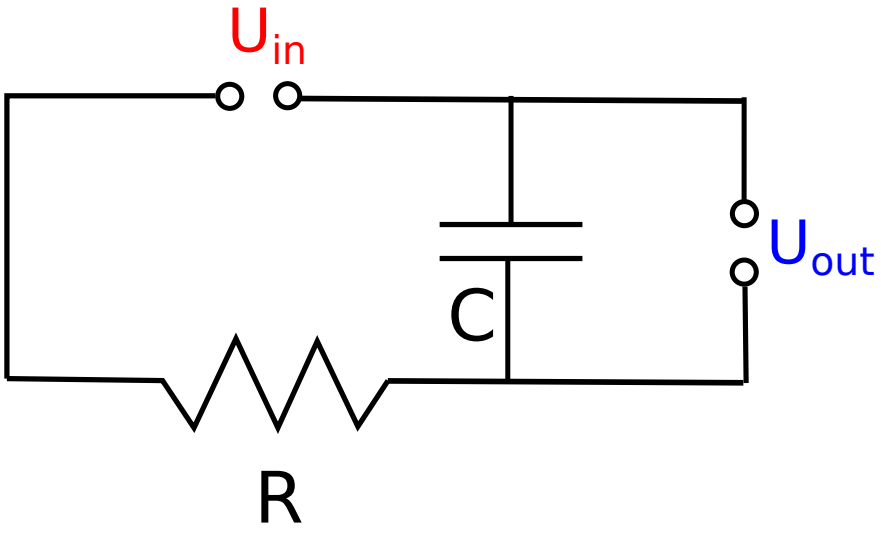
1. diffusion / convection
2. flux of ion i^+
3. complexation reaction

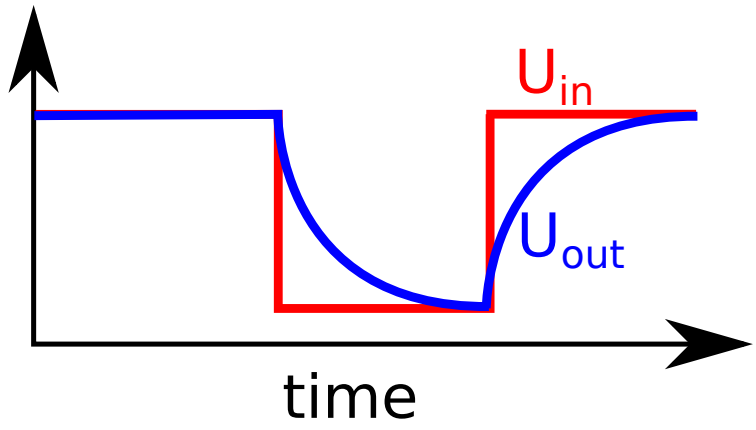
L: ligand

i^+: measured ion

Why is the image distorted?

The RC time constant

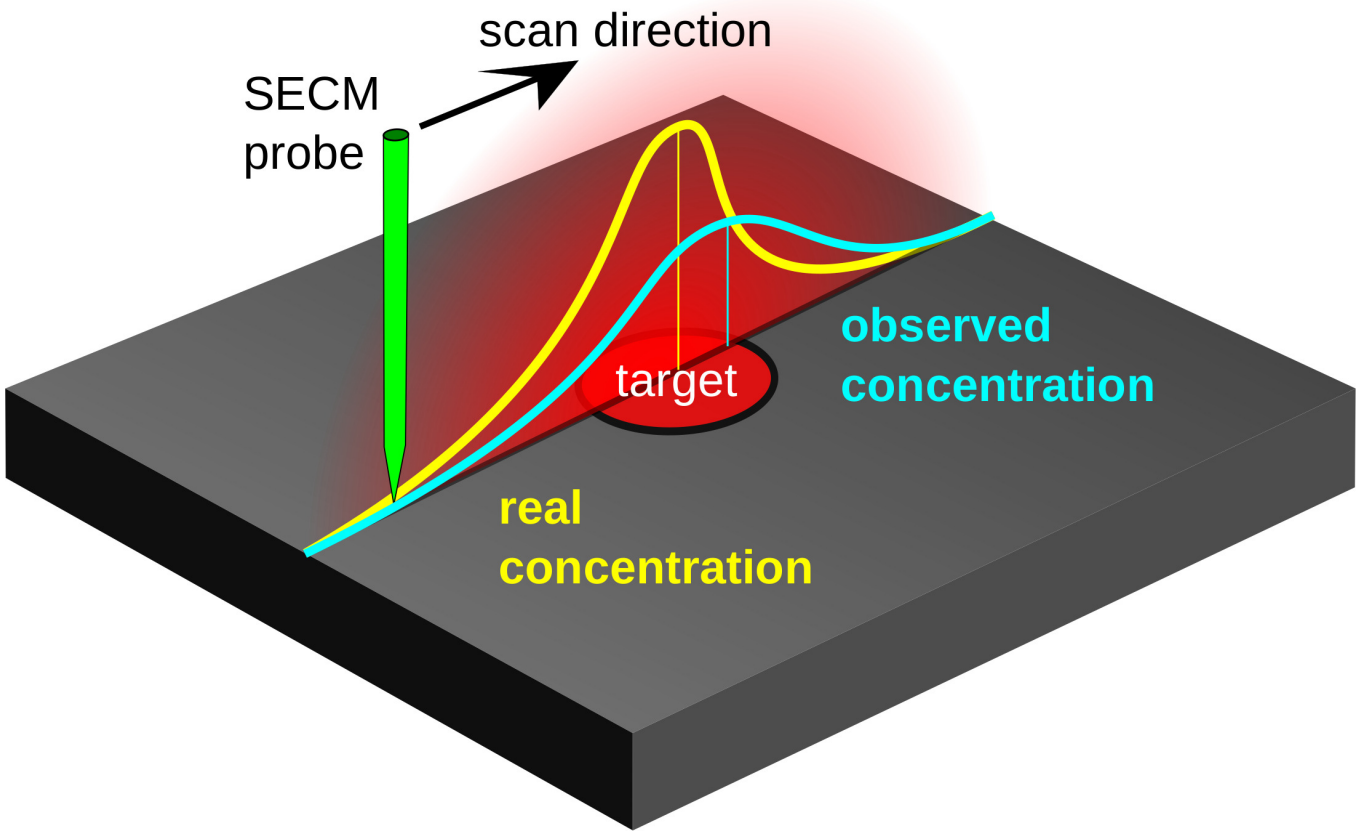




τ is the time that is required to charge the capacitor by $\approx 37\%$ $(1/e)$.

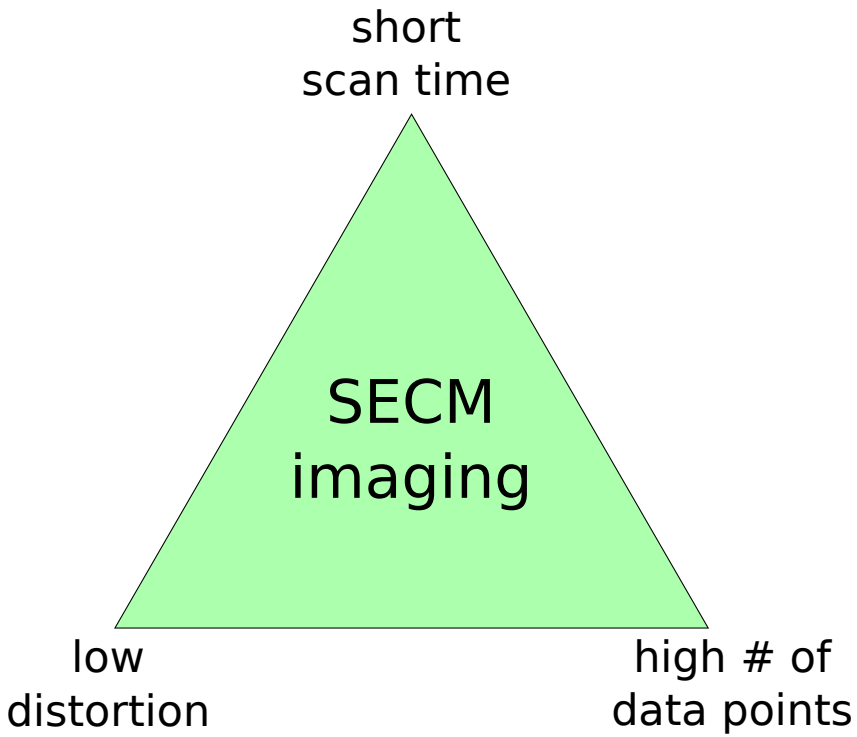
Distortion of potentiometric imaging

In the case of a linescan

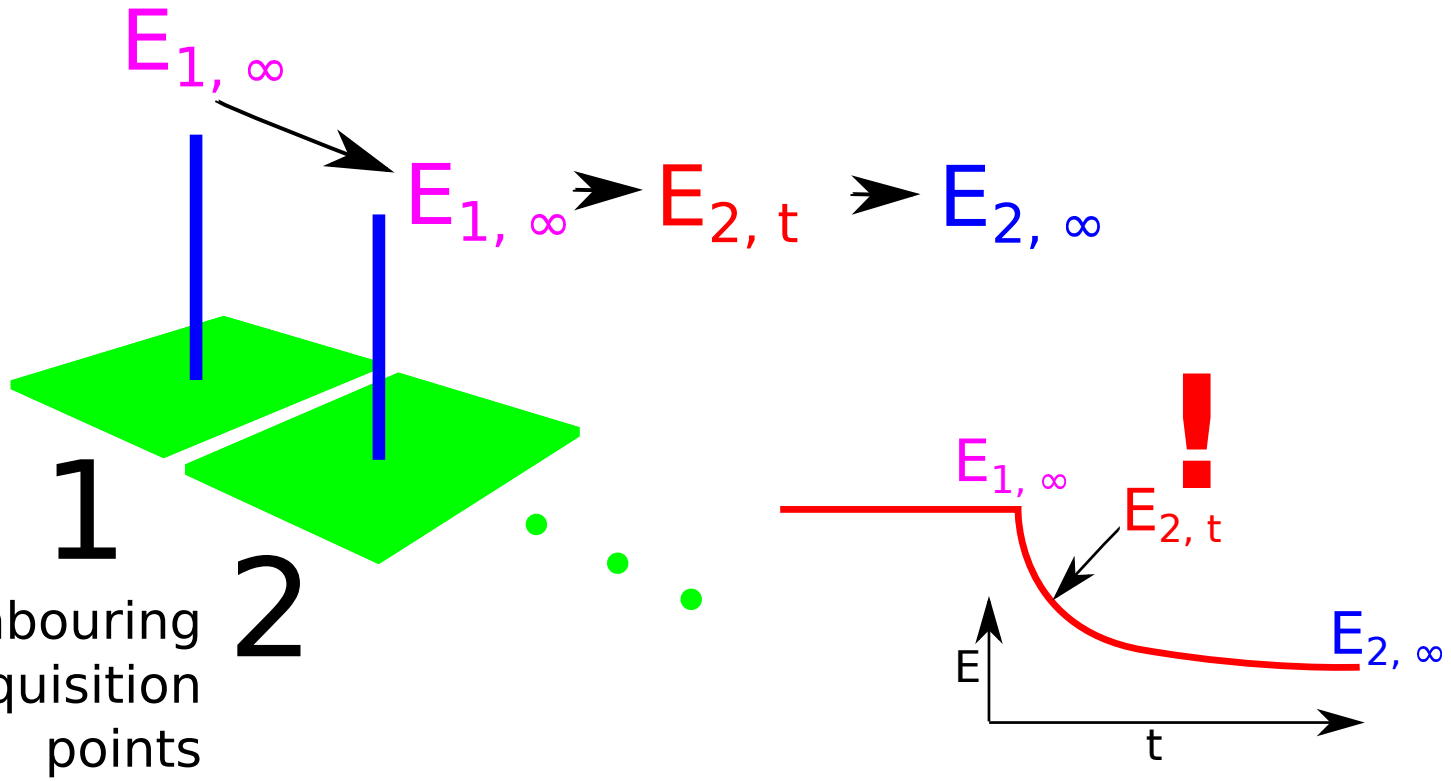


Trade-off triangle of potentiometric SECM

Compromise between the three desired competing properties

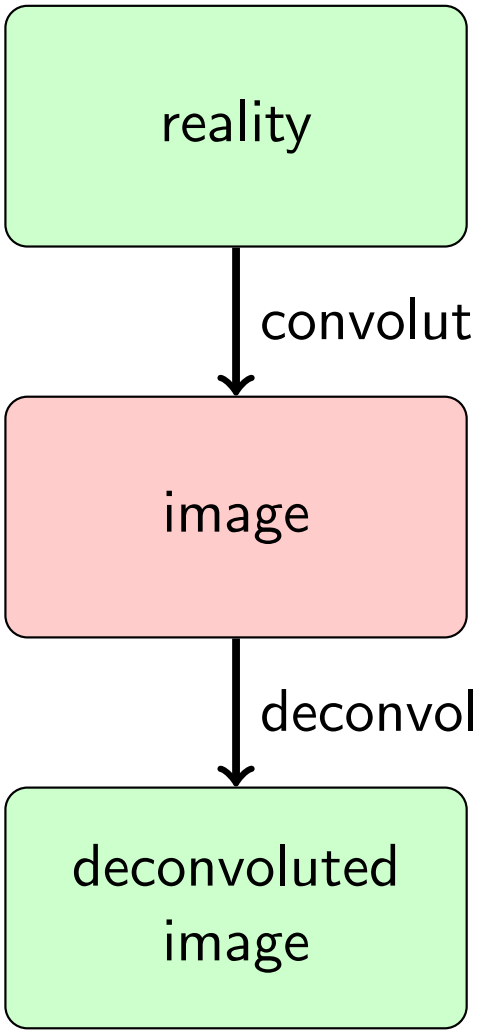


The convolution function of the distortion



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

Convolution and deconvolution

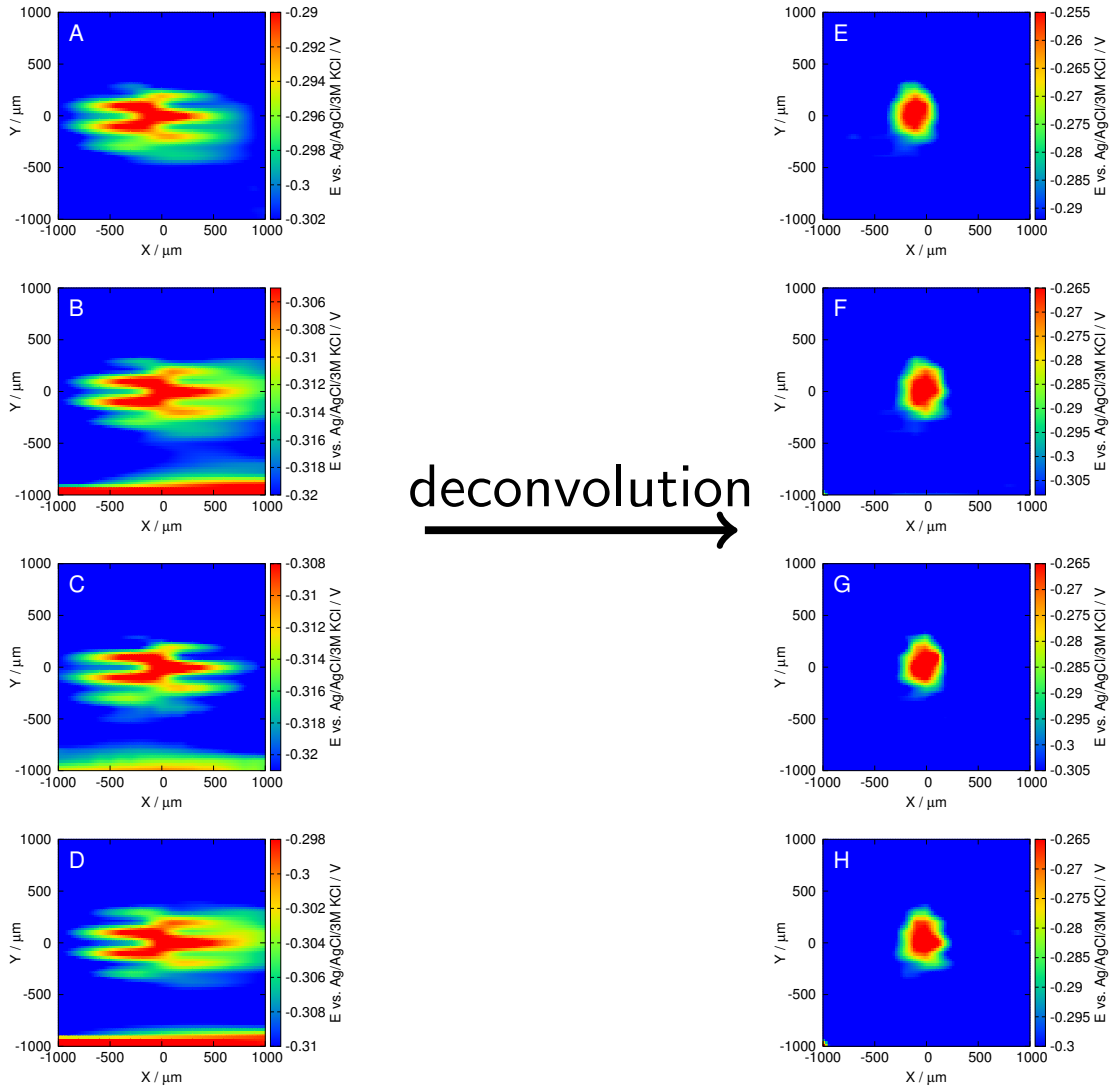


convolution : $E_{cell}(t) = E_{cell}(\infty) + [E_{cell}(0) - E_{cell}(\infty)]e^{-t/\tau}$

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

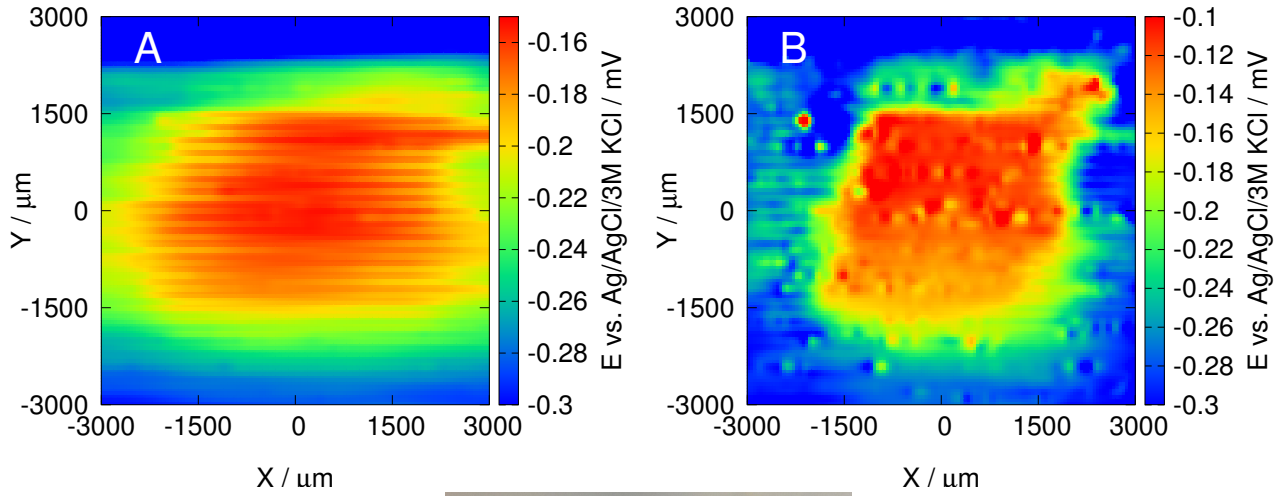
Deconvolution of potentiometric SECM images

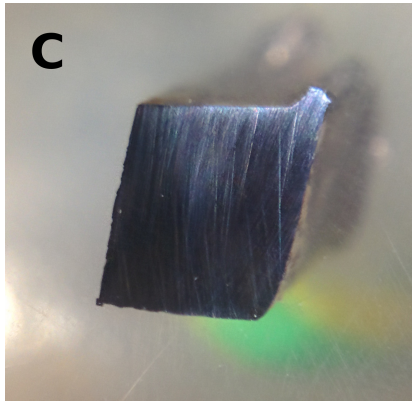
Recorded using the antimony microelectrode following the meander algorithm



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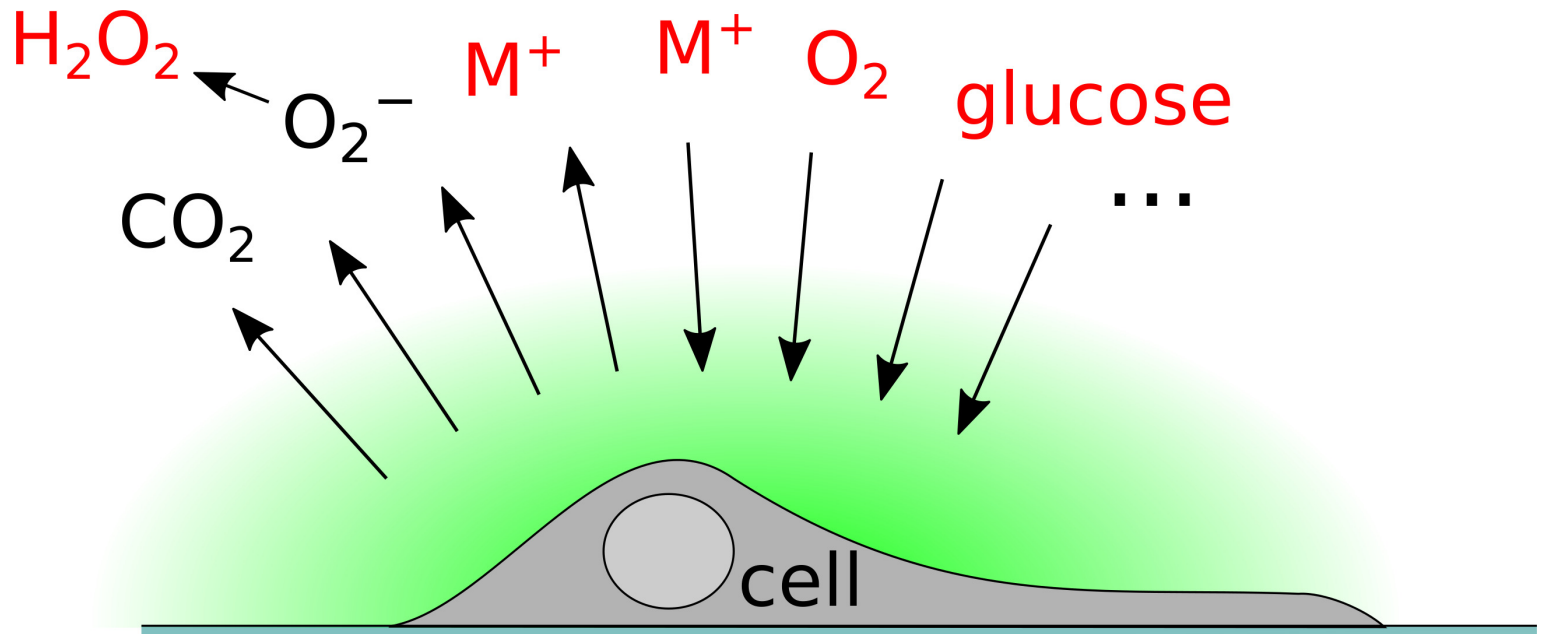
Why would you want to do SECM imaging of a cell?

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



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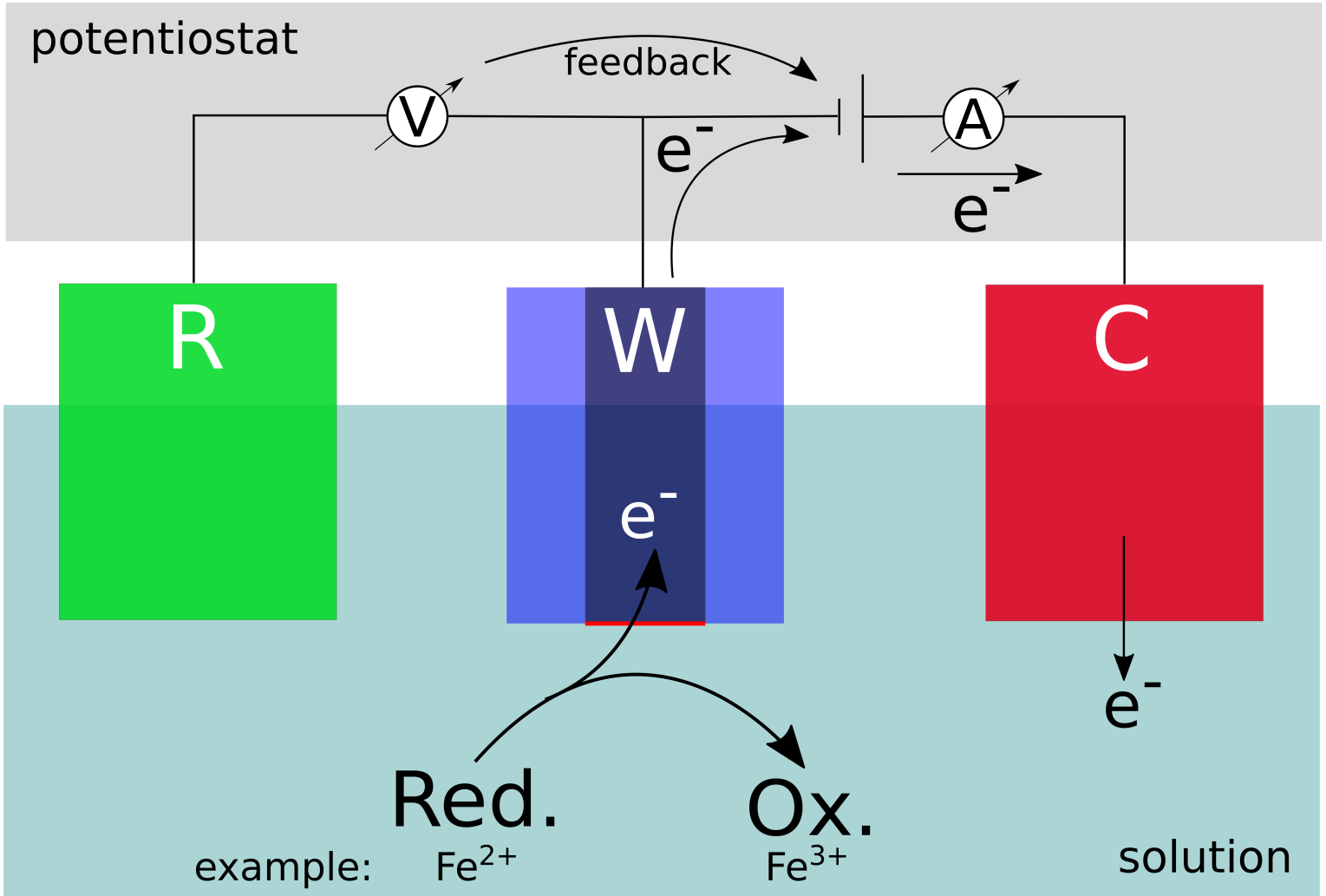
FORUM ORIGINAL RESEARCH COMMUNICATION

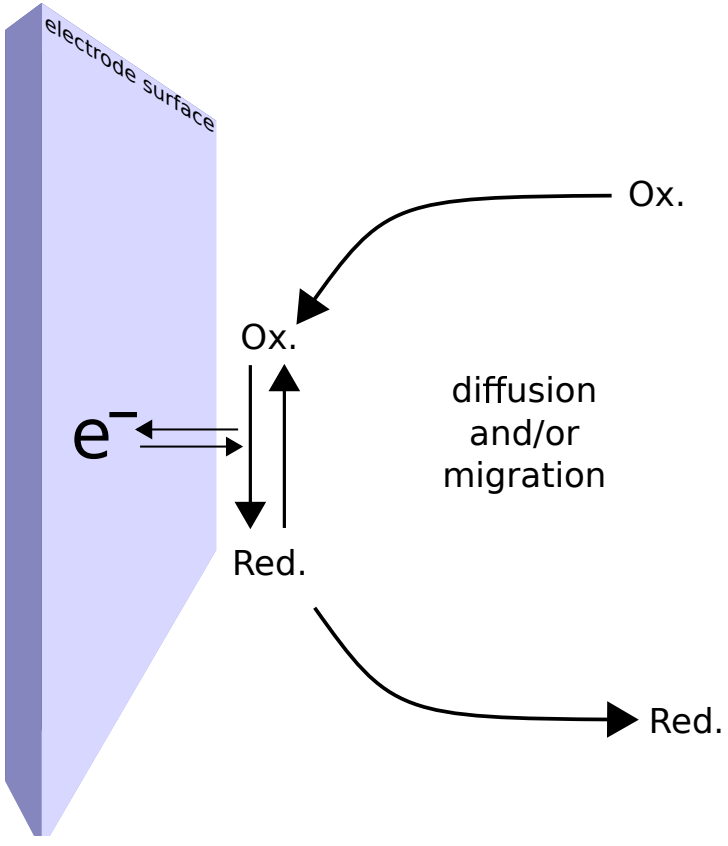
Electrochemical Quantification of Extracellular Local H_2O_2 Kinetics Originating from Single Cells

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]

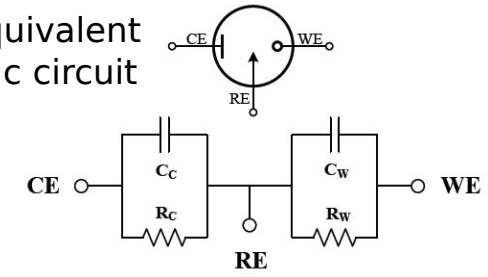
The amperometric measuring cell

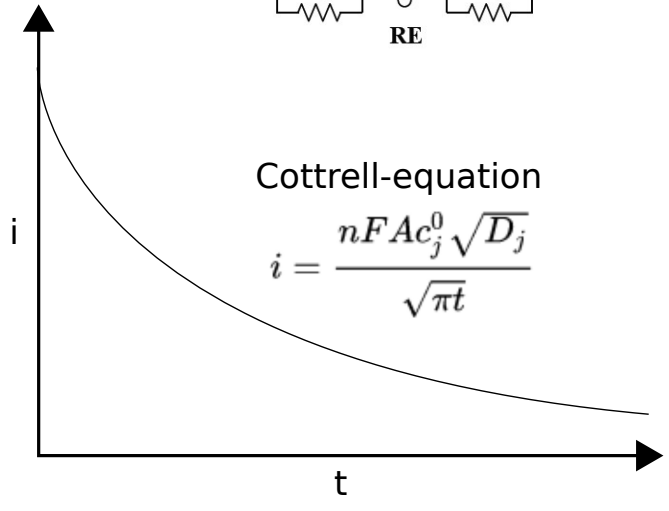


Amperometric transient response



Simplified equivalent amperometric circuit



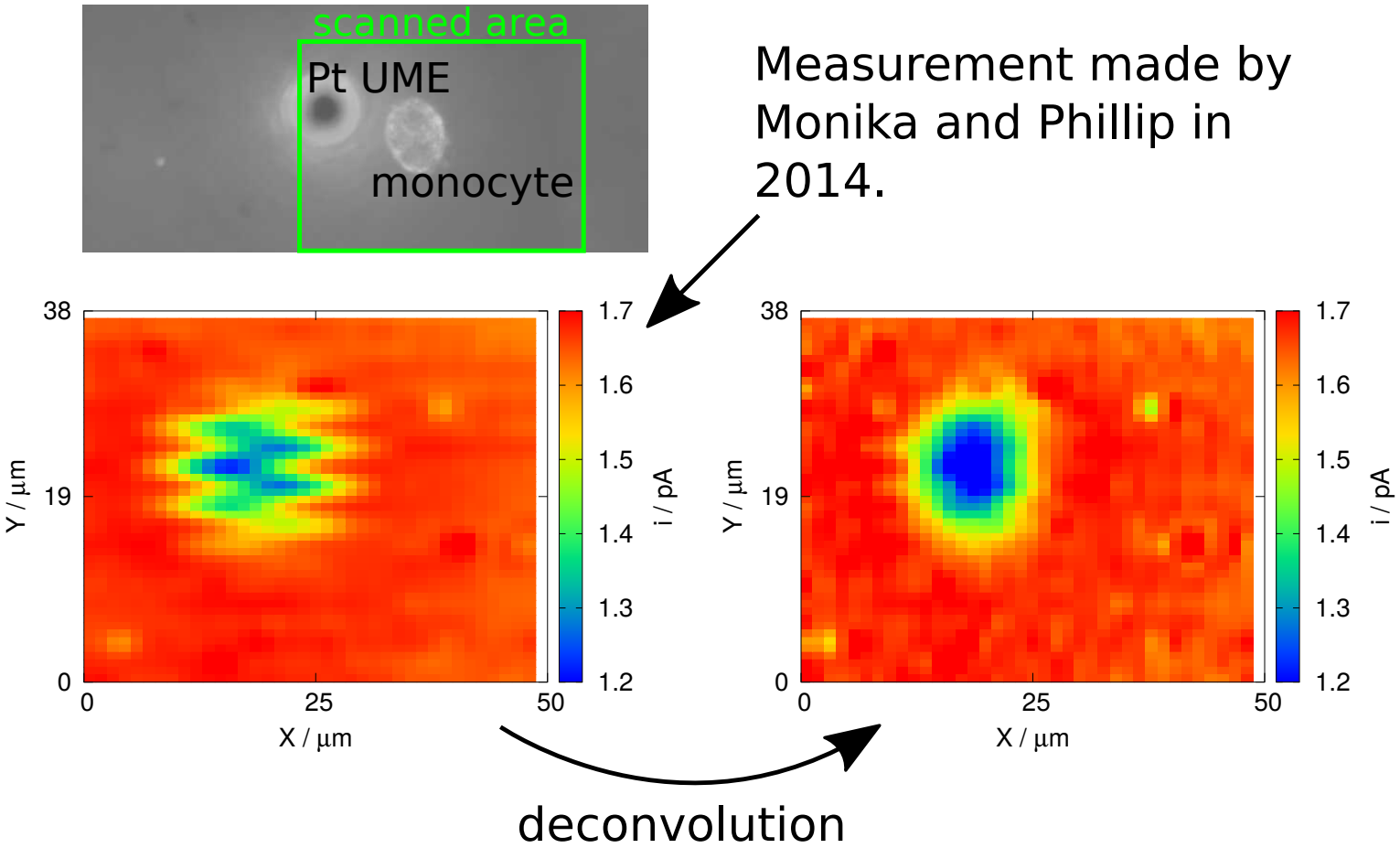


Cottrell-equation

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

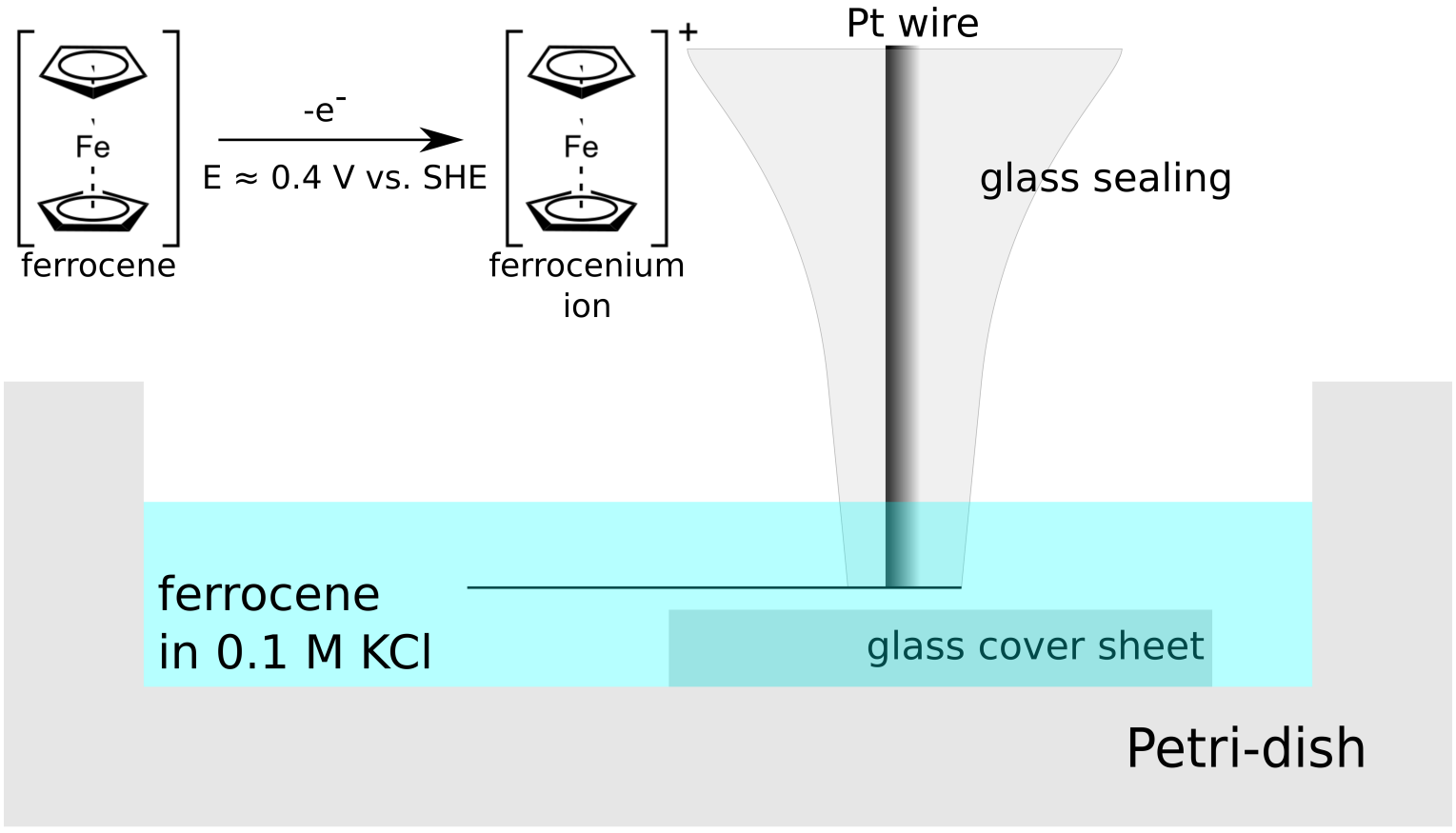
Deconvolution of an amperometric image.

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



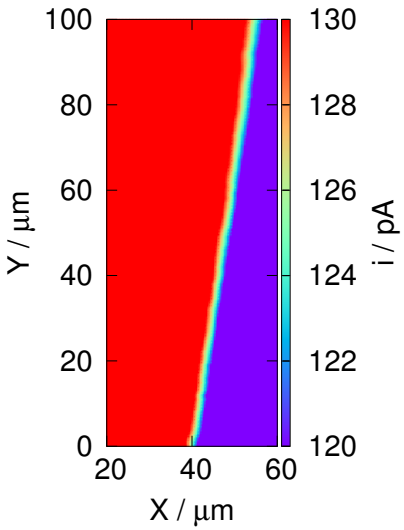
Investigating a step response over a glass sheet edge.

With the ferrocene/ferrocenium system.

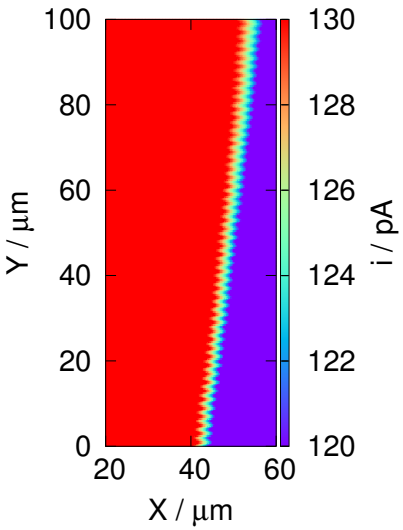


Investigating a step response over a glass sheet edge.

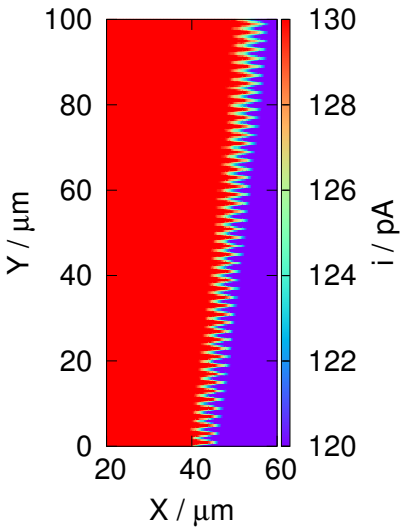
Results.



5 µm/s



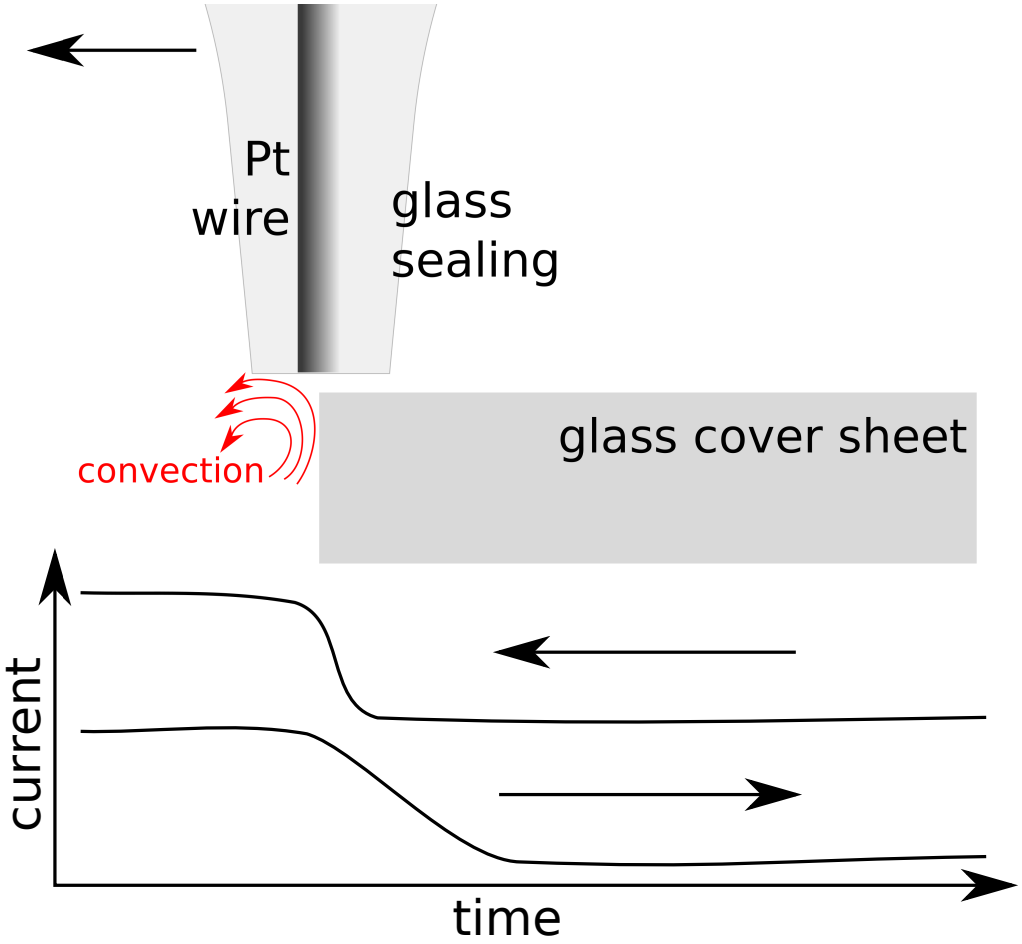
10 µm/s



10 µm/s deconvoluted

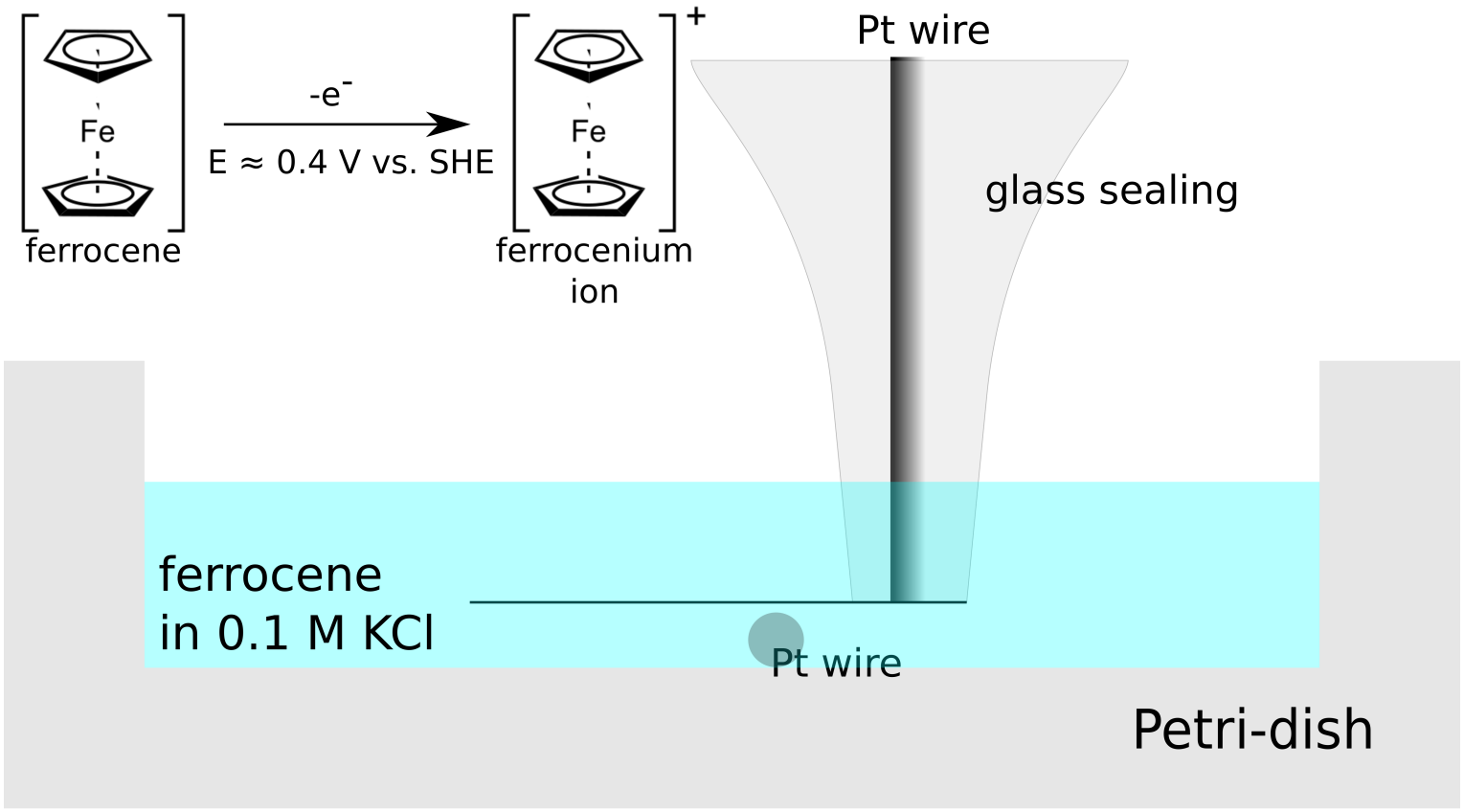
Investigating a step response over a glass sheet edge.

Discrepancy caused by convection.



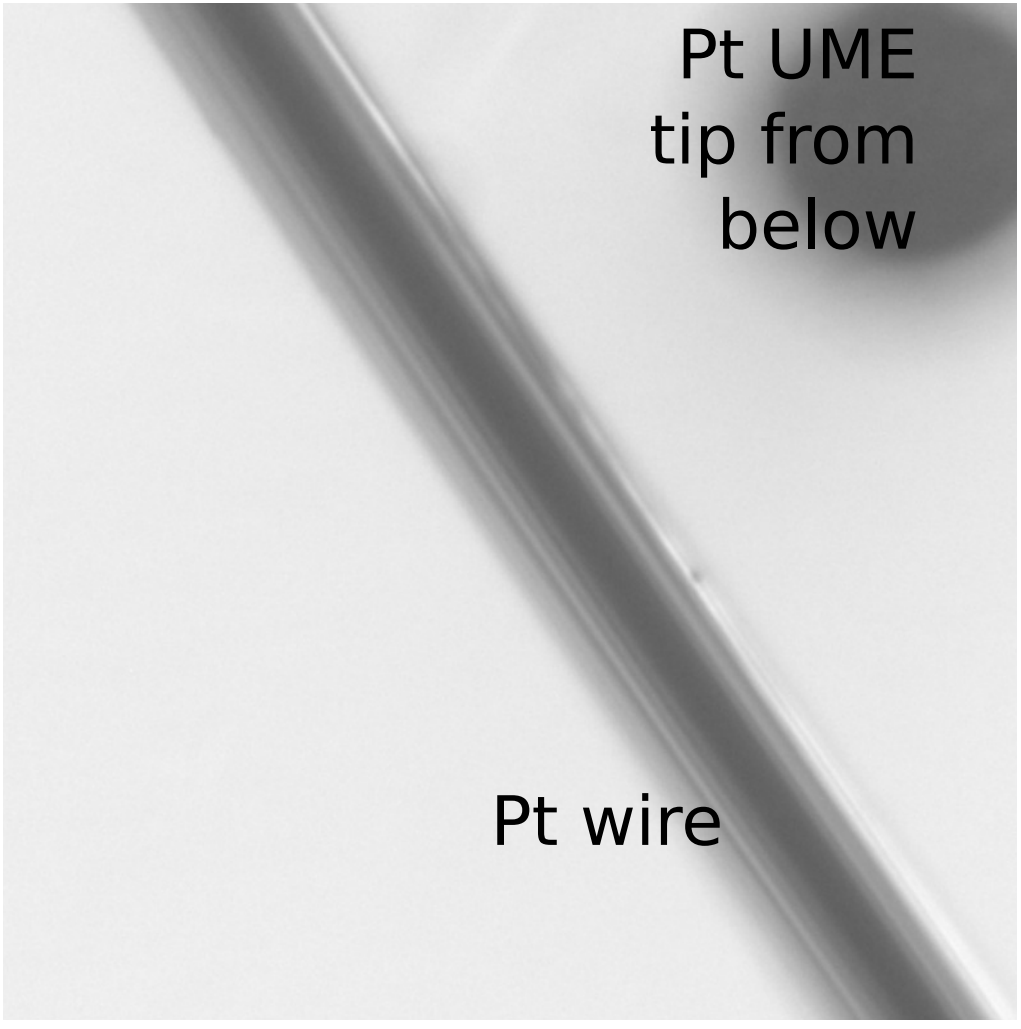
Investigating a step response over a d = 10 μm Pt wire.

With the ferrocene/ferrocenium system.



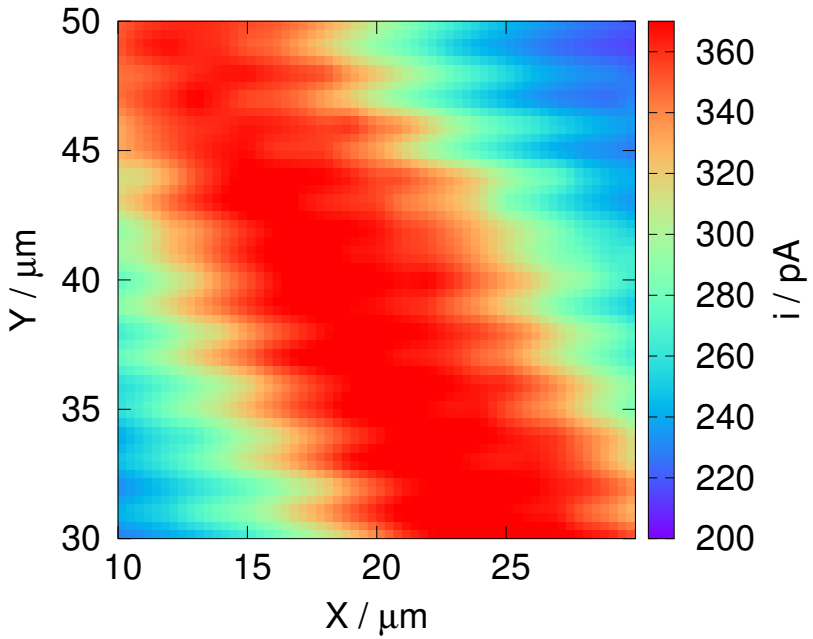
Investigating a step response over a d = 10 μm Pt wire.

Microphoto of the model system from below.

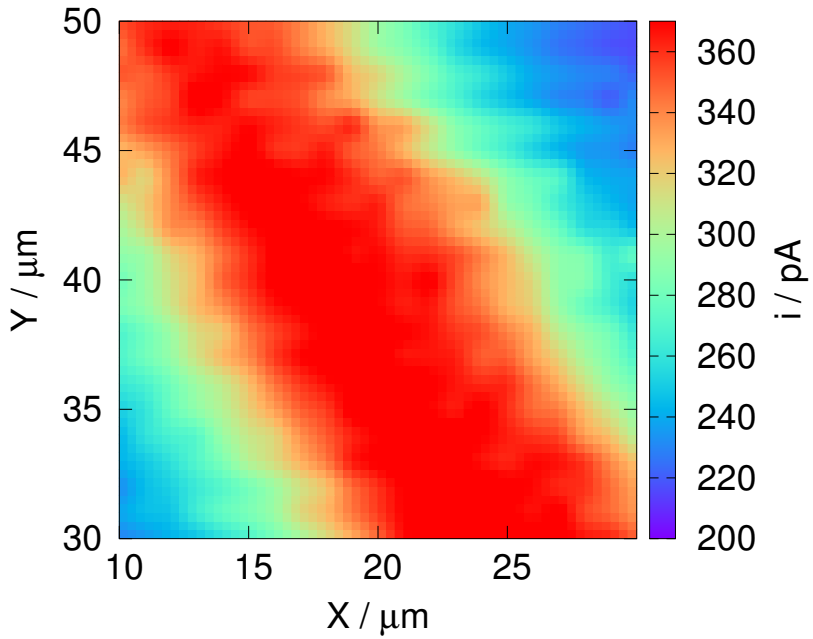


Investigating a step response over a d = 10 µm Pt wire.

Results.



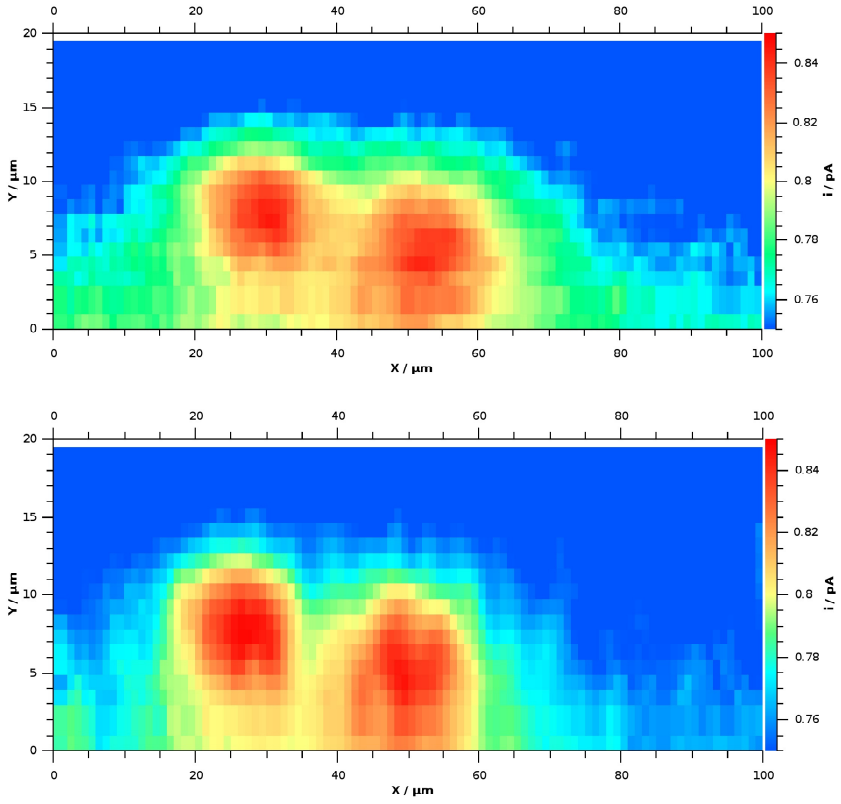
10 µm/s



10 µm/s deconvoluted

H_2O_2 measurement over a TPA stimulated monocyte.

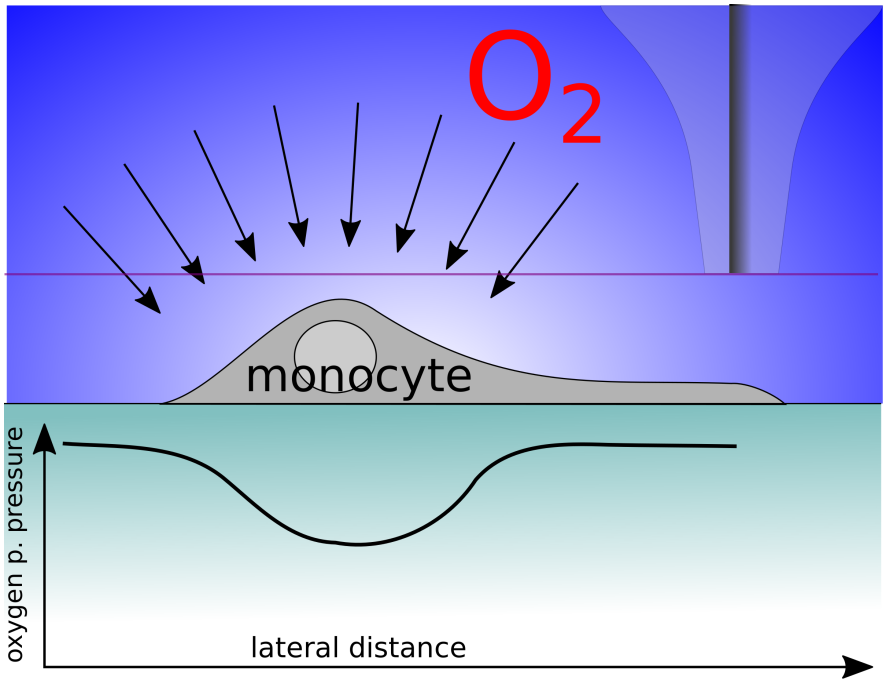
Results.

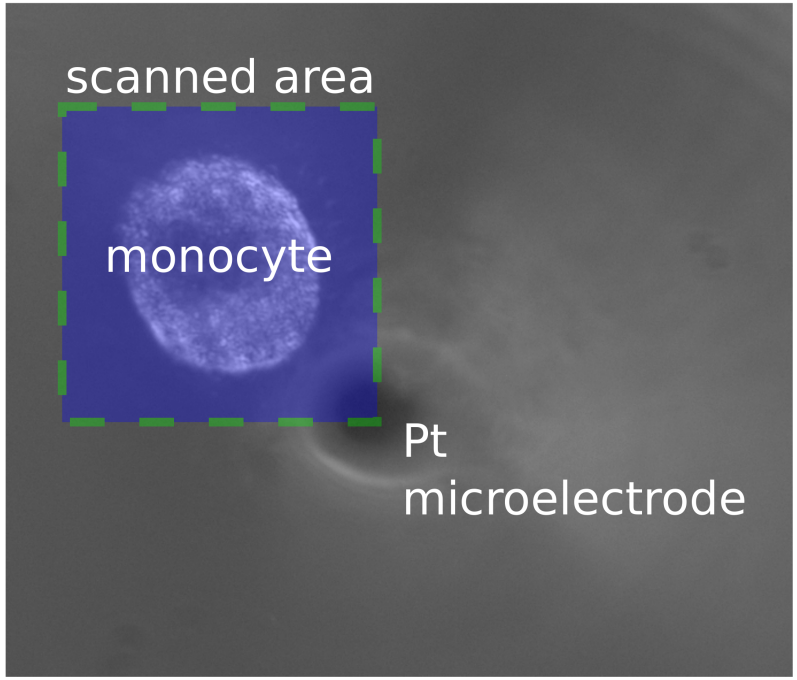


Top image: original measurement, made by Monika in 2014. Scanning speed was 2 µm/s. Bottom image: deconvoluted image.

Oxygen reduction current above a monocyte.

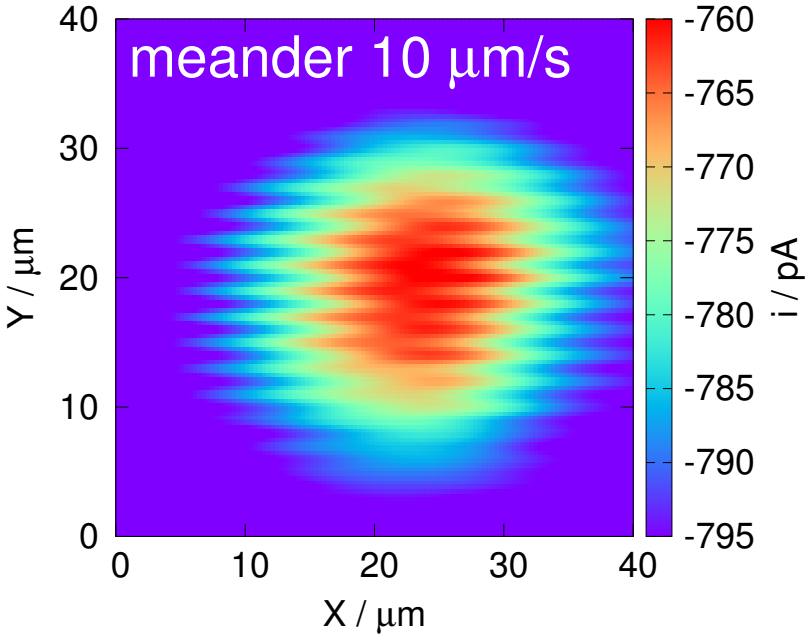
Experimental setup.

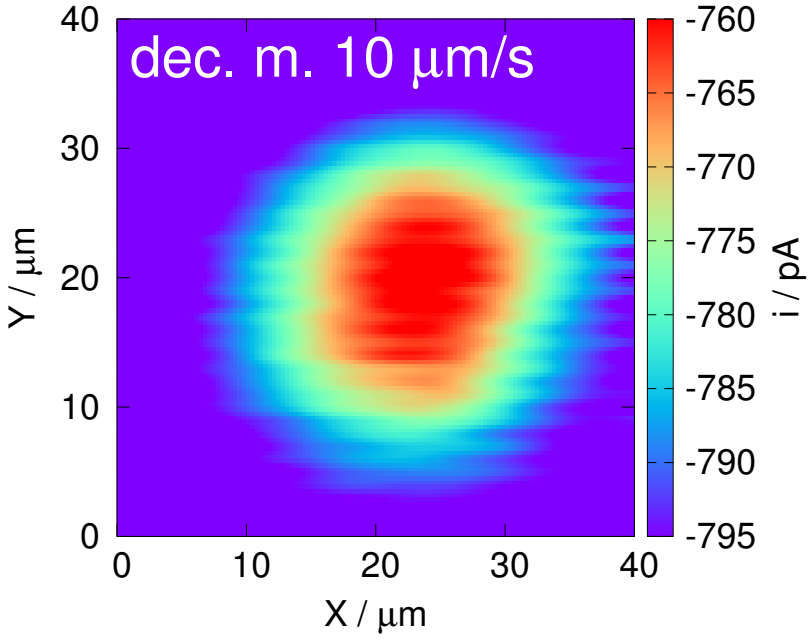




Oxygen reduction current above a monocyte.

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!