Recent Advances in Potentiometric Scanning Electrochemical Microscopy

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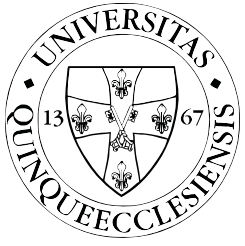


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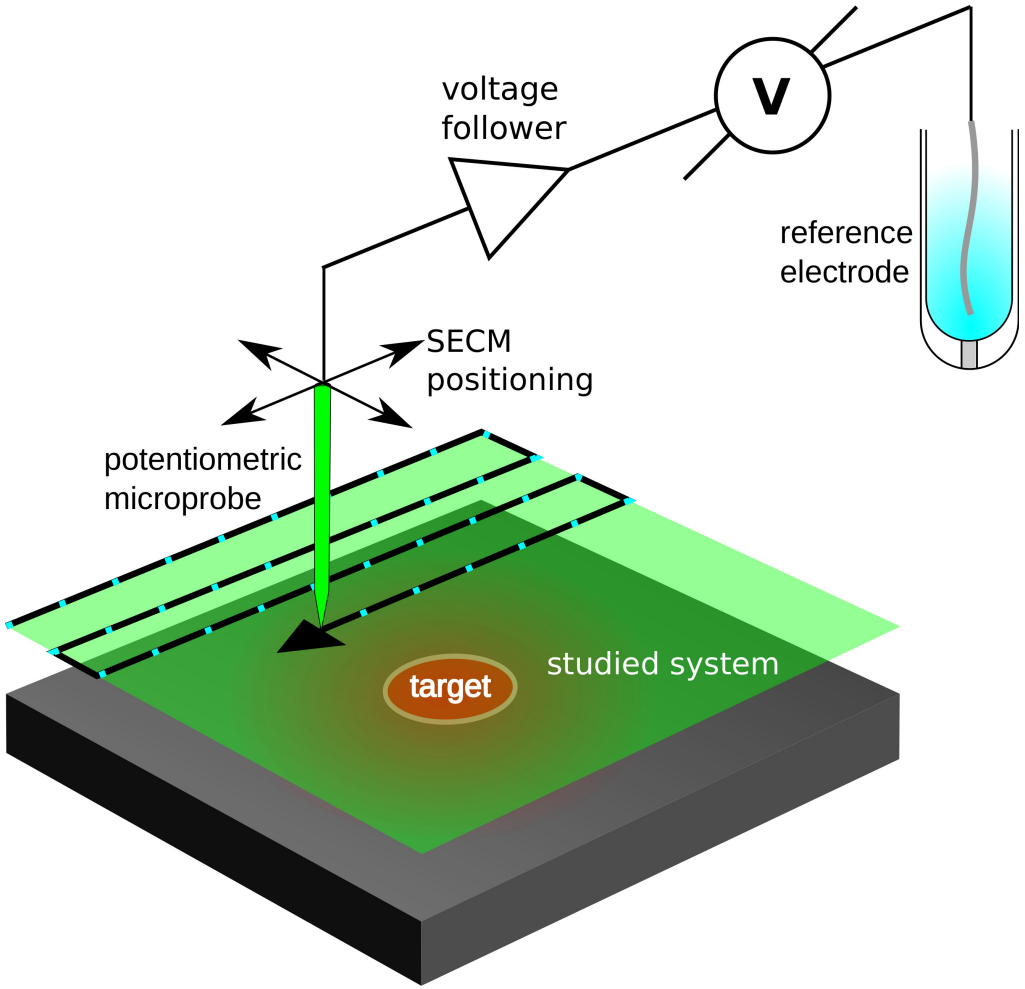
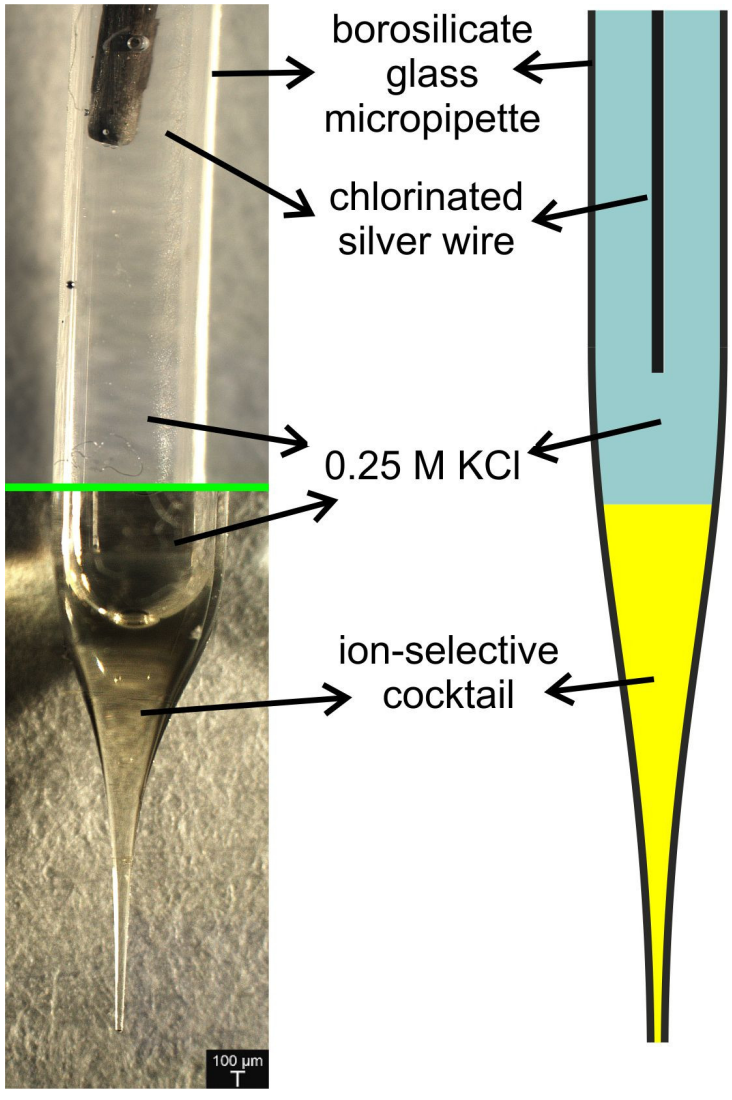
Potentiometric Scanning Electrochemical Microscopy

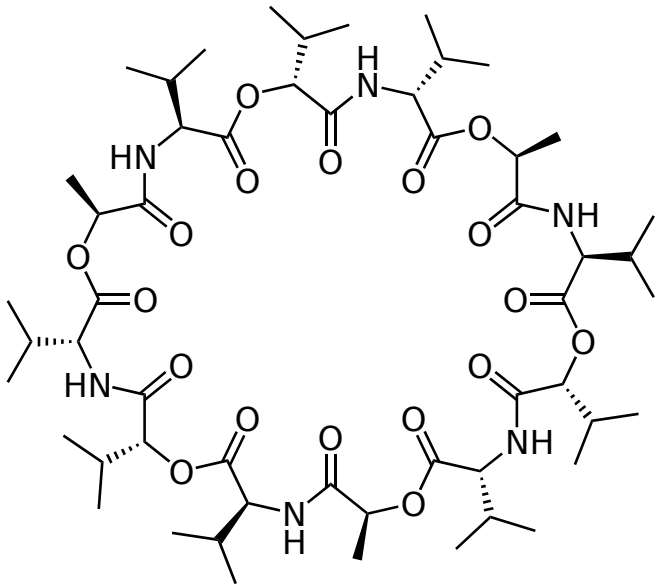
A Scanning Probe Microscopic technique



Ion-selective micropipettes

As SECM probes





Valinomycin

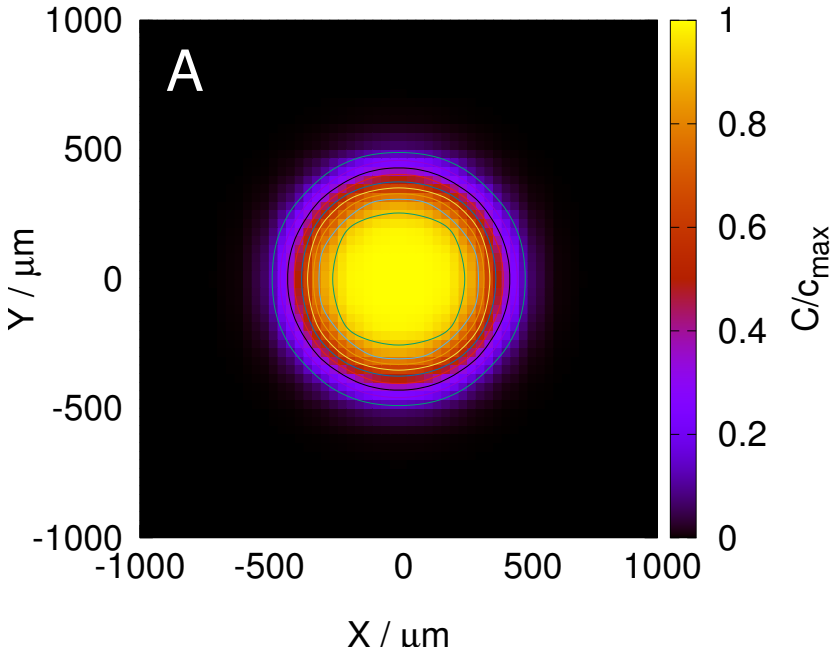
$$E = E^{\theta} + \frac{RT}{z_i F} \ln \left[a_i + \sum_j \left(k_{ij} a_j^{z_i/z_j} \right) \right]$$

Nikolsky–equation

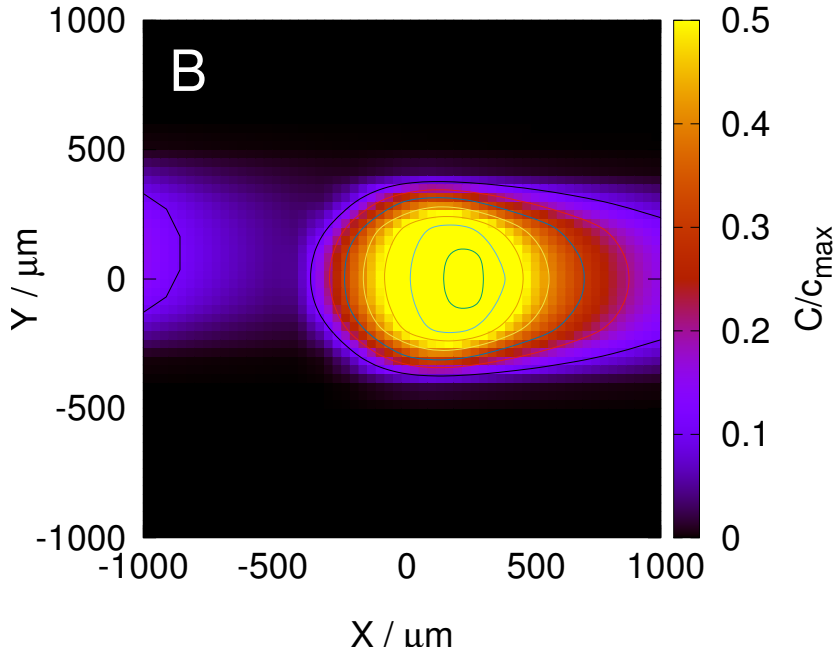
The problem with potentiometric SECM

Distortion at high scan rate

Slow

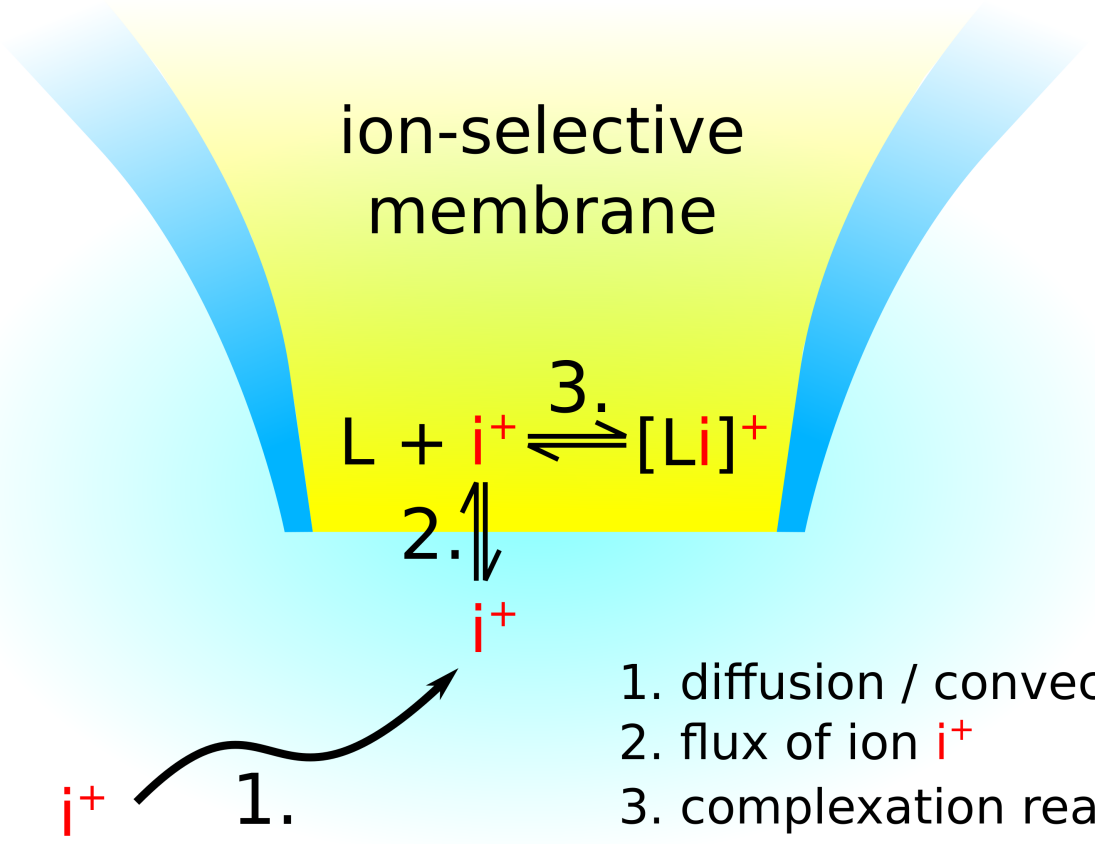


Fast



Why is the image distorted?

Possible contributors to the lag



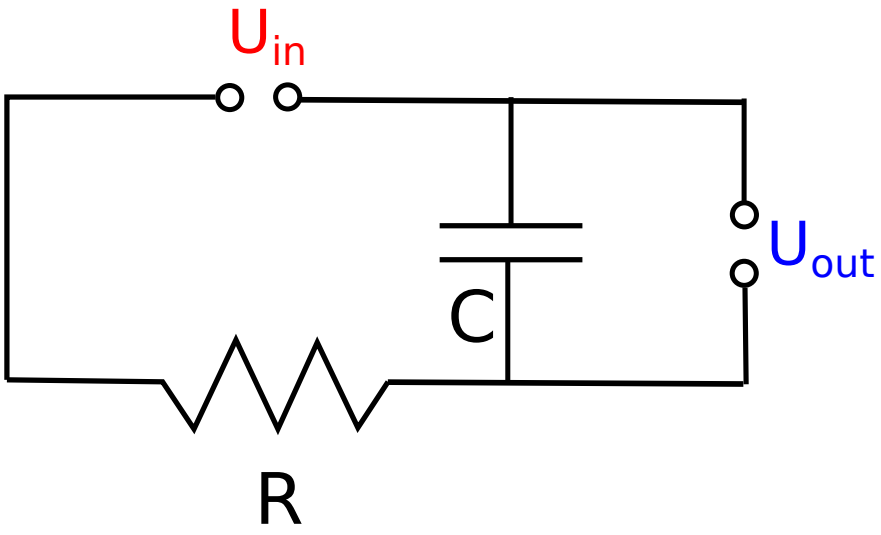
1. diffusion / convection
2. flux of ion i^+
3. complexation reaction

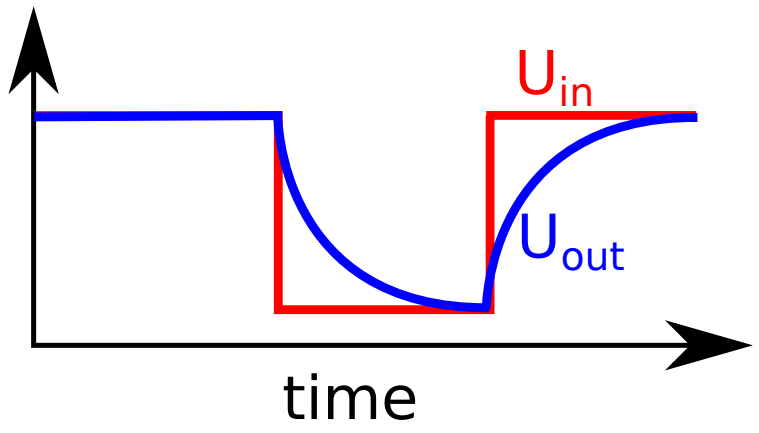
L: ligand

i^+: measured ion

Why is the image distorted?

The RC time constant





The time that is required to charge the capacitor by $\approx 63\%$ $(1 - 1/e)$.

$$\tau = R \cdot C$$

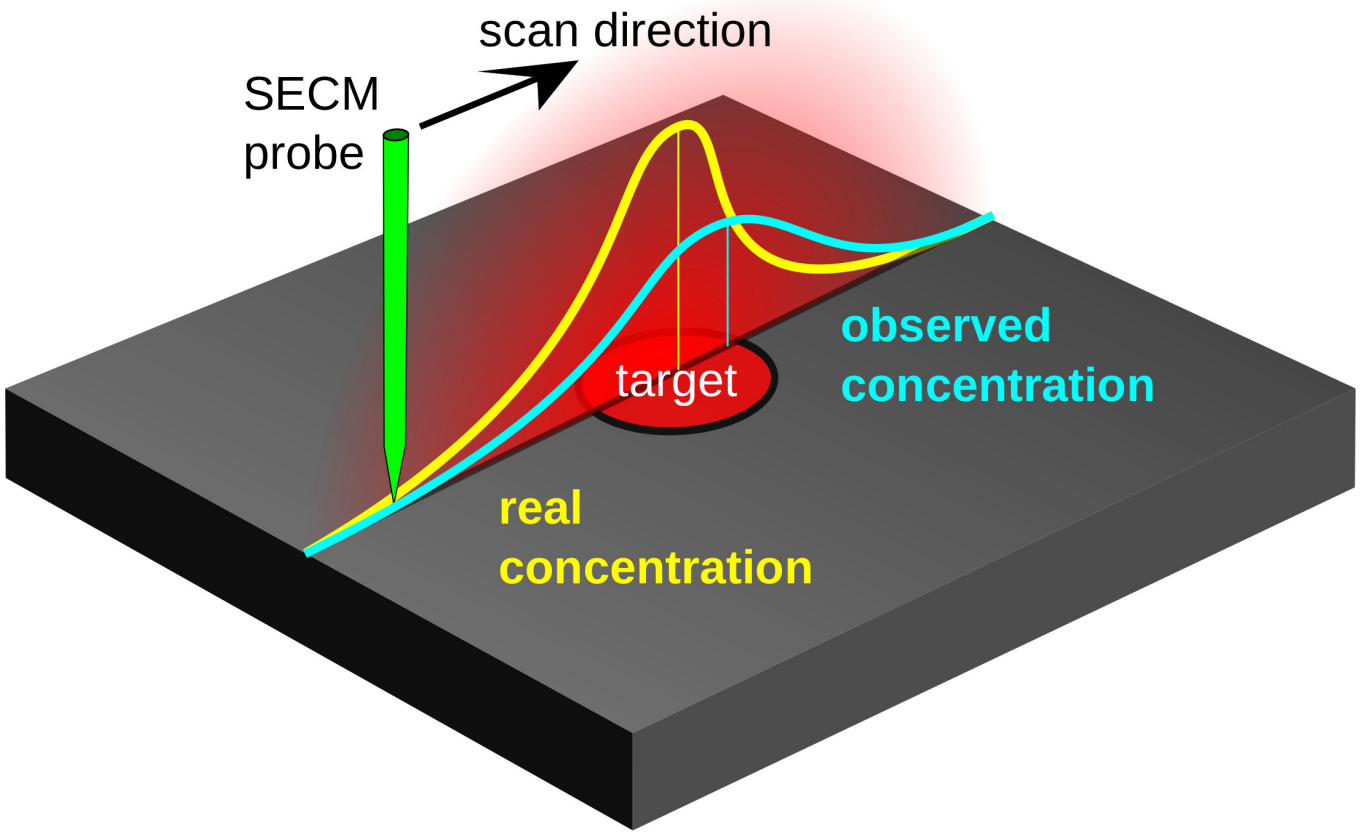
$$R = 5\ \text{G}\Omega$$

$$C = 500\ \text{pF}$$

$$\tau = 2.5\ \text{s}$$

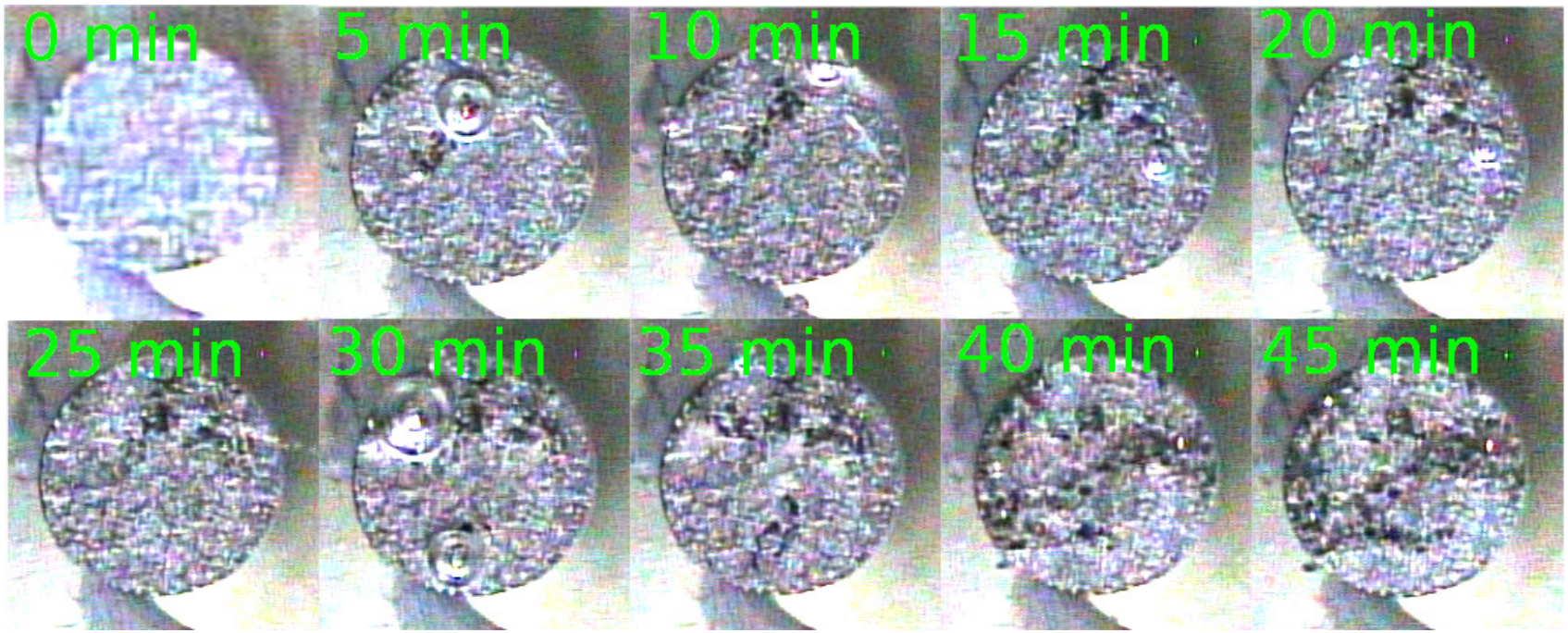
Distortion of potentiometric imaging

In the case of a linescan



Why is it so important to complete the scan quickly?

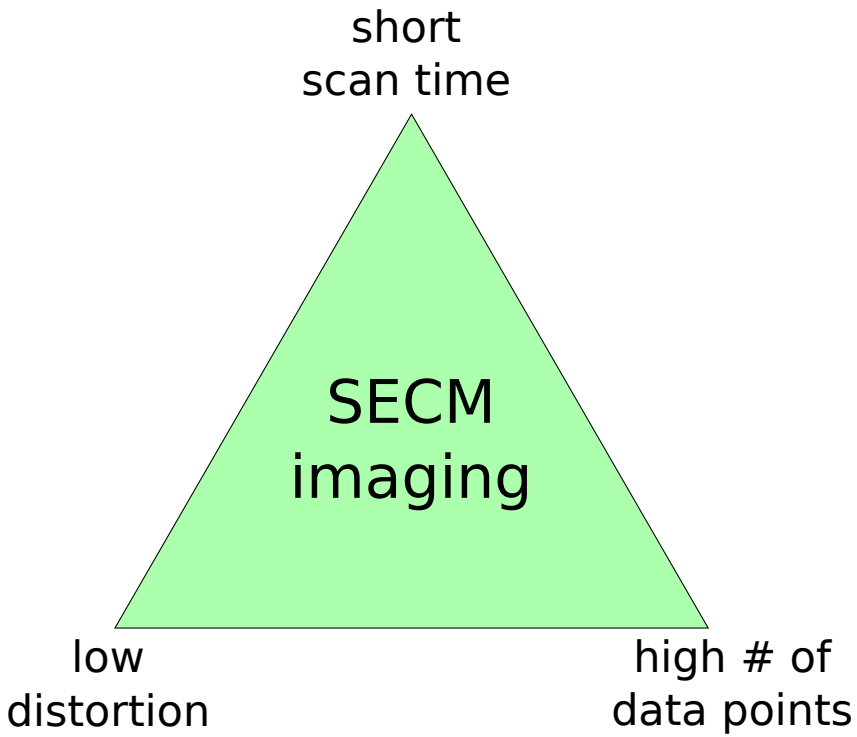
Example: corrosion of a magnesium alloy



Corrosion of the AZ63 magnesium-aluminium-zinc alloy.

Trade-off triangle of potentiometric SECM

Compromise between the three desired competing properties

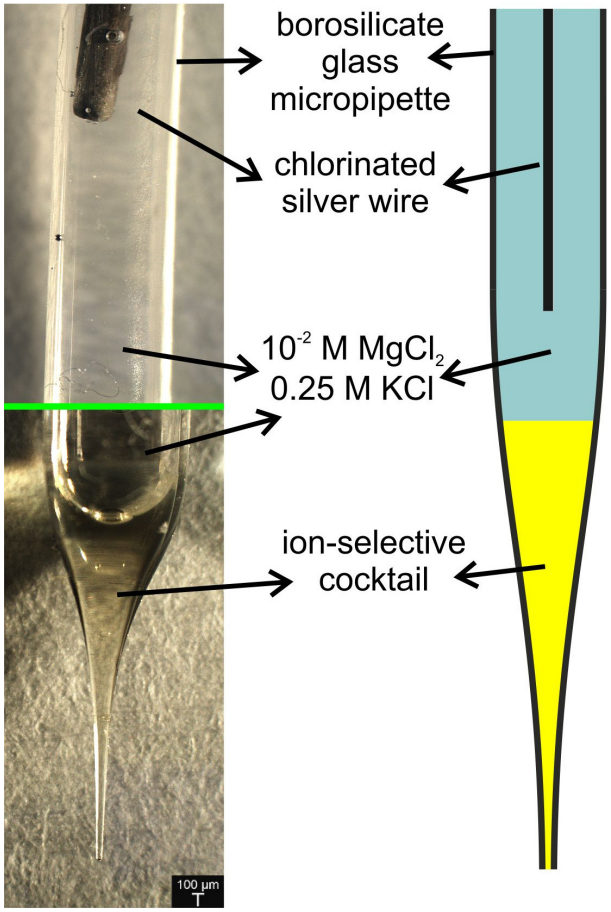


Solution #1: Solid contact micropipettes as SECM probes.

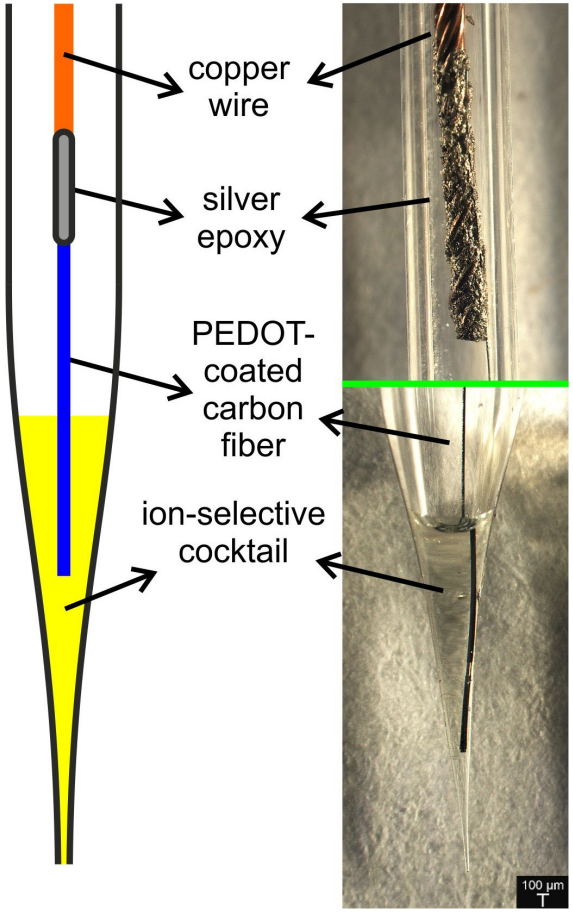
Liquid vs. solid contact micropipettes

Comparison of construction

Liquid contact

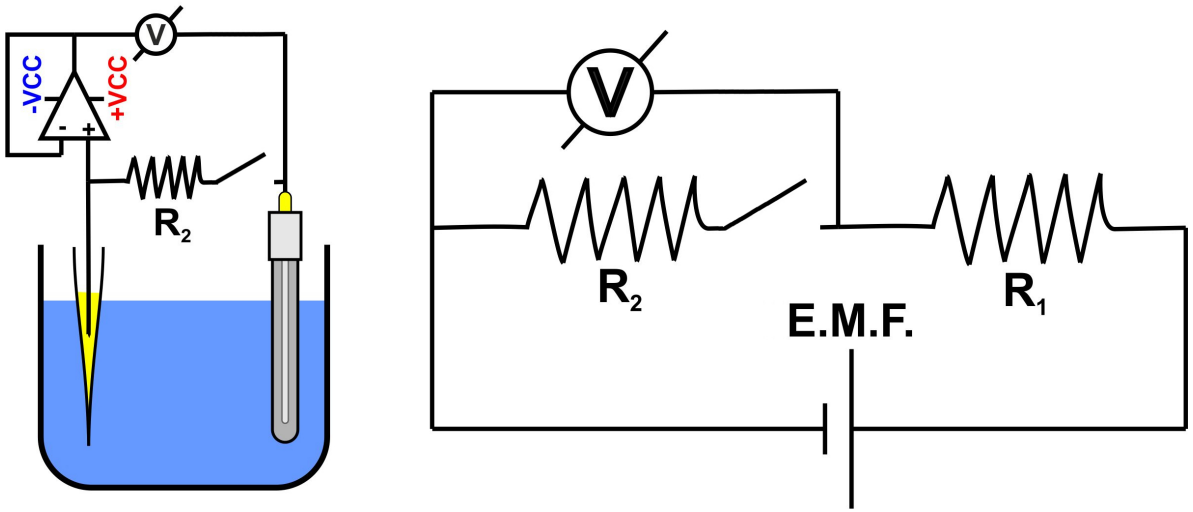


Solid contact



Comparison of the electrodes' resistance

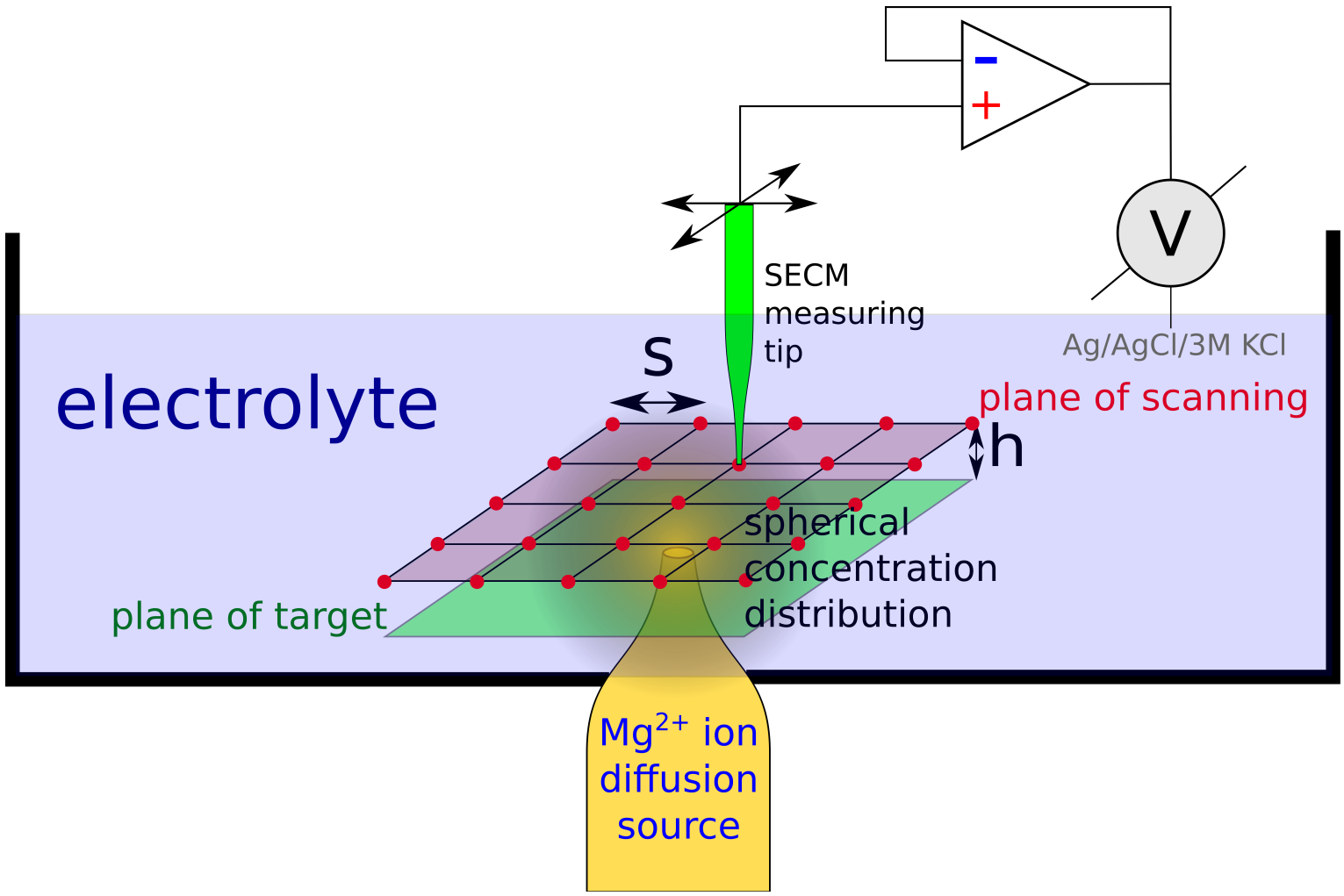
Voltage divider method and result



Type	R_{ISME} / GΩ
Liquid contact	**4.80**
Solid contact	**0.56**

Comparison of the electrodes' performance

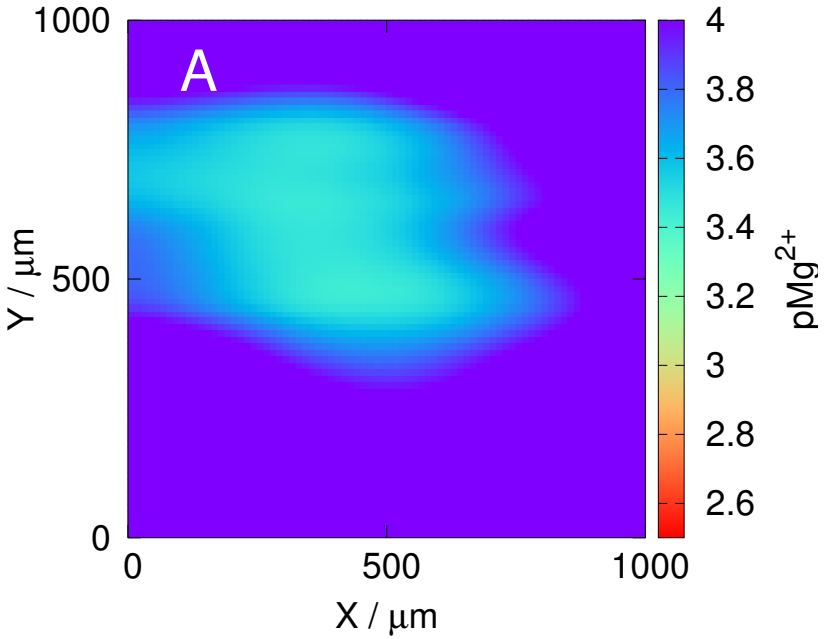
Experimental setup



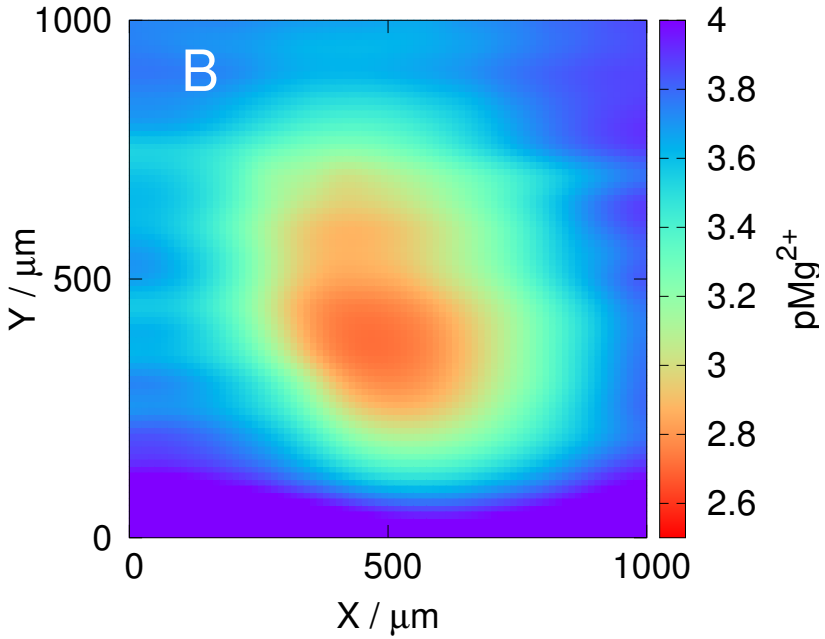
Comparison of the electrodes' performance

Results

Liquid contact

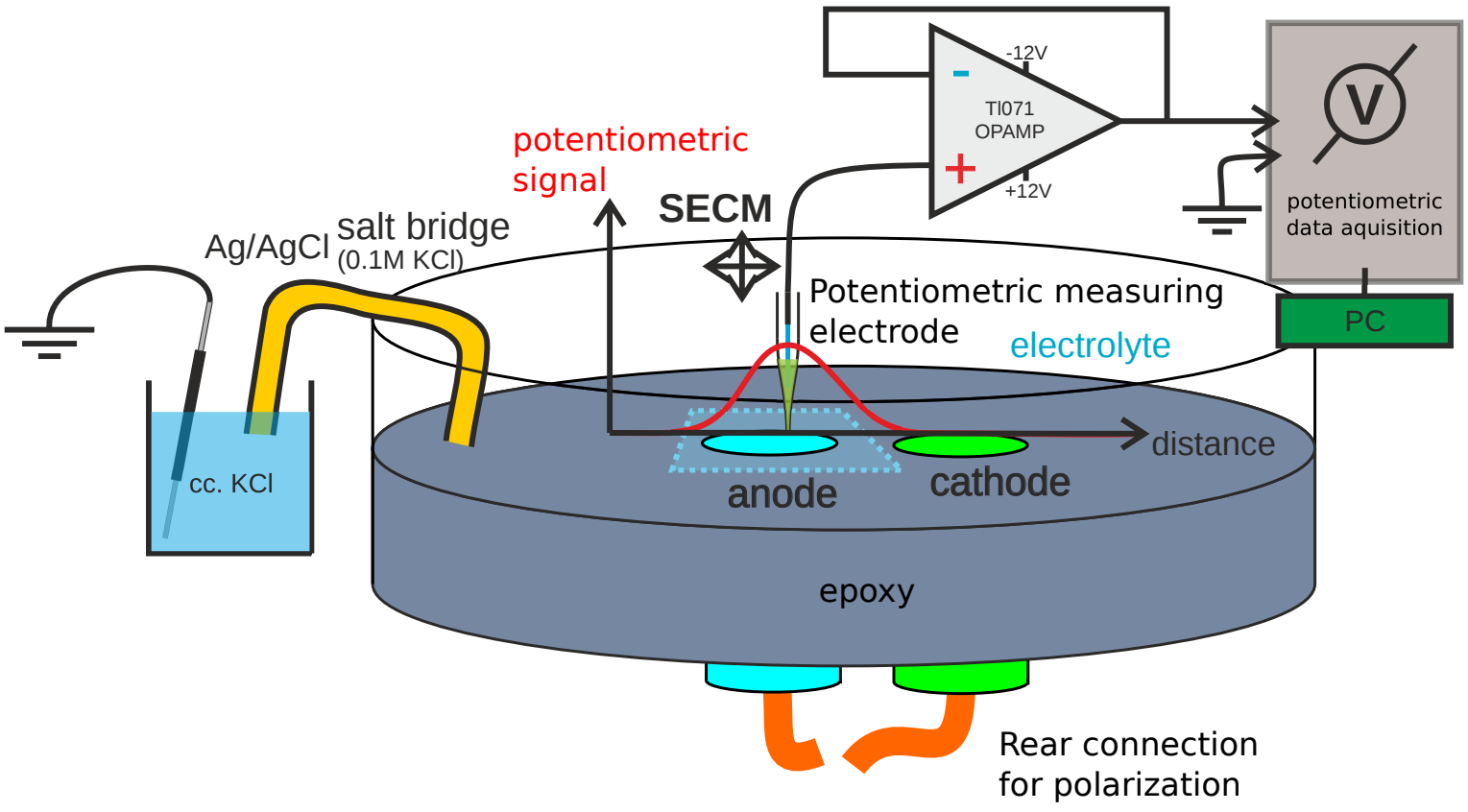


Solid contact



Application in corrosion science: galvanic corrosion of Mg

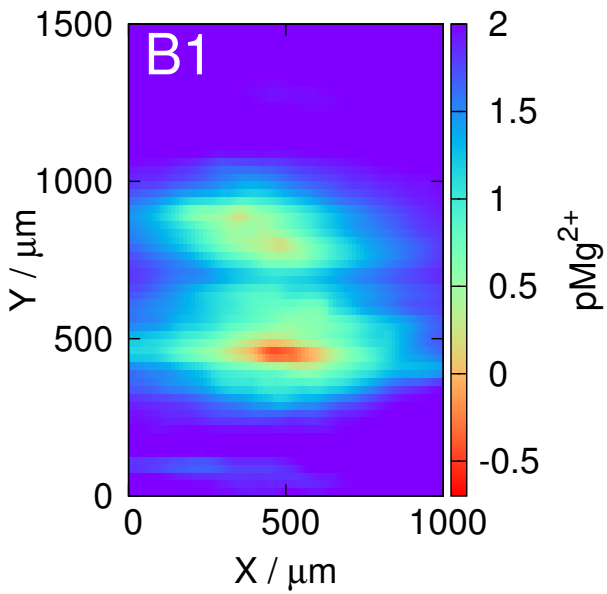
Experimental setup



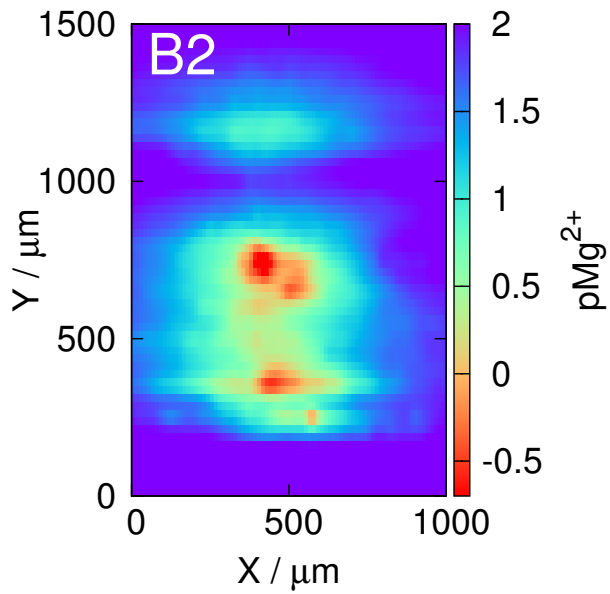
Application in corrosion science: galvanic corrosion of Mg

Results

Liquid contact



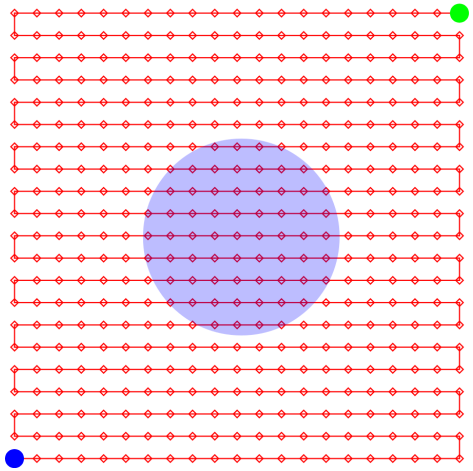
Solid contact



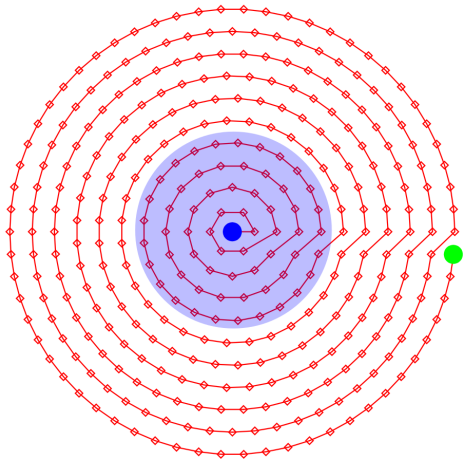
Solution #2: Optimizing scanning patterns and algorithms.

New SECM scanning patterns based on the polar-coordinate system

Cartesian coordinate system based scanning pattern



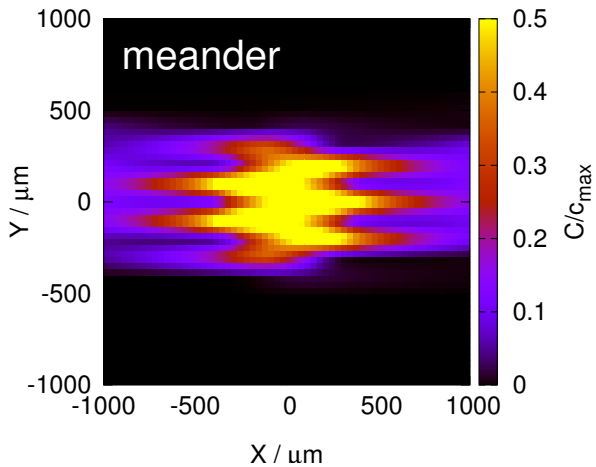
Polar coordinate system based scanning pattern



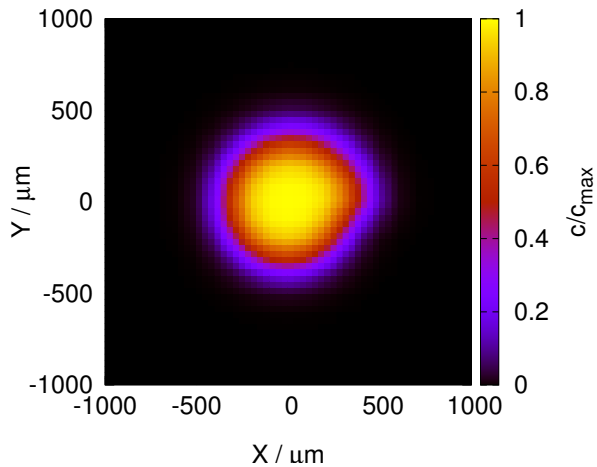
Simulated SECM scans

Using the Cartesian and the polar coordinate system based algorithms

Cartesian



polar



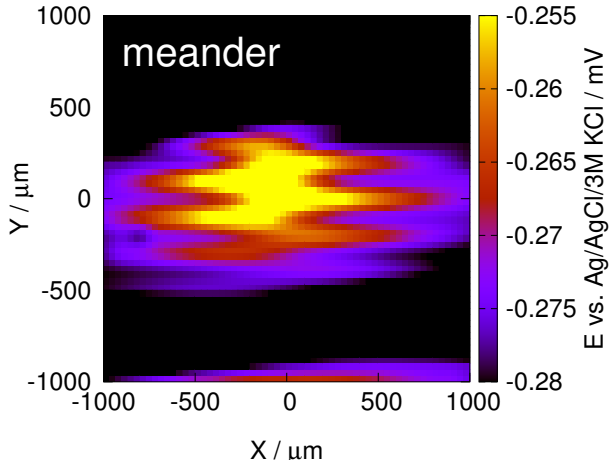
Comparison of the simulated scans

Algorithm	n	time (s)	mean squared error
Meander	441	440	2.75×10^{-2}
Fast comb	441	520	2.07×10^{-2}
Comb	441	881	2.75×10^{-2}
Web	110	109	9.63×10^{-3}
Arc	341	340	2.95×10^{-3}

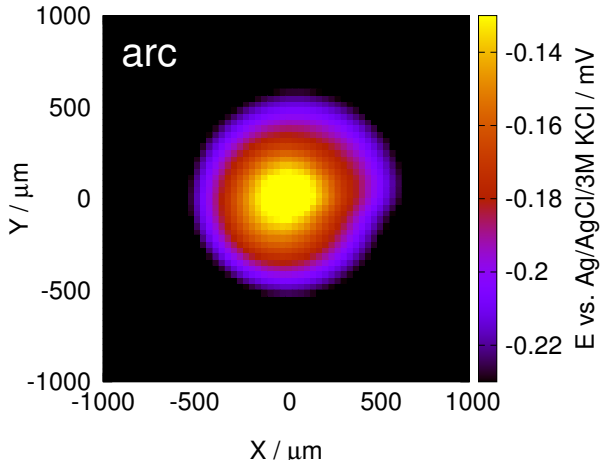
Confirmation with experimental SECM scans

Recorded using the antimony microelectrode

440 seconds



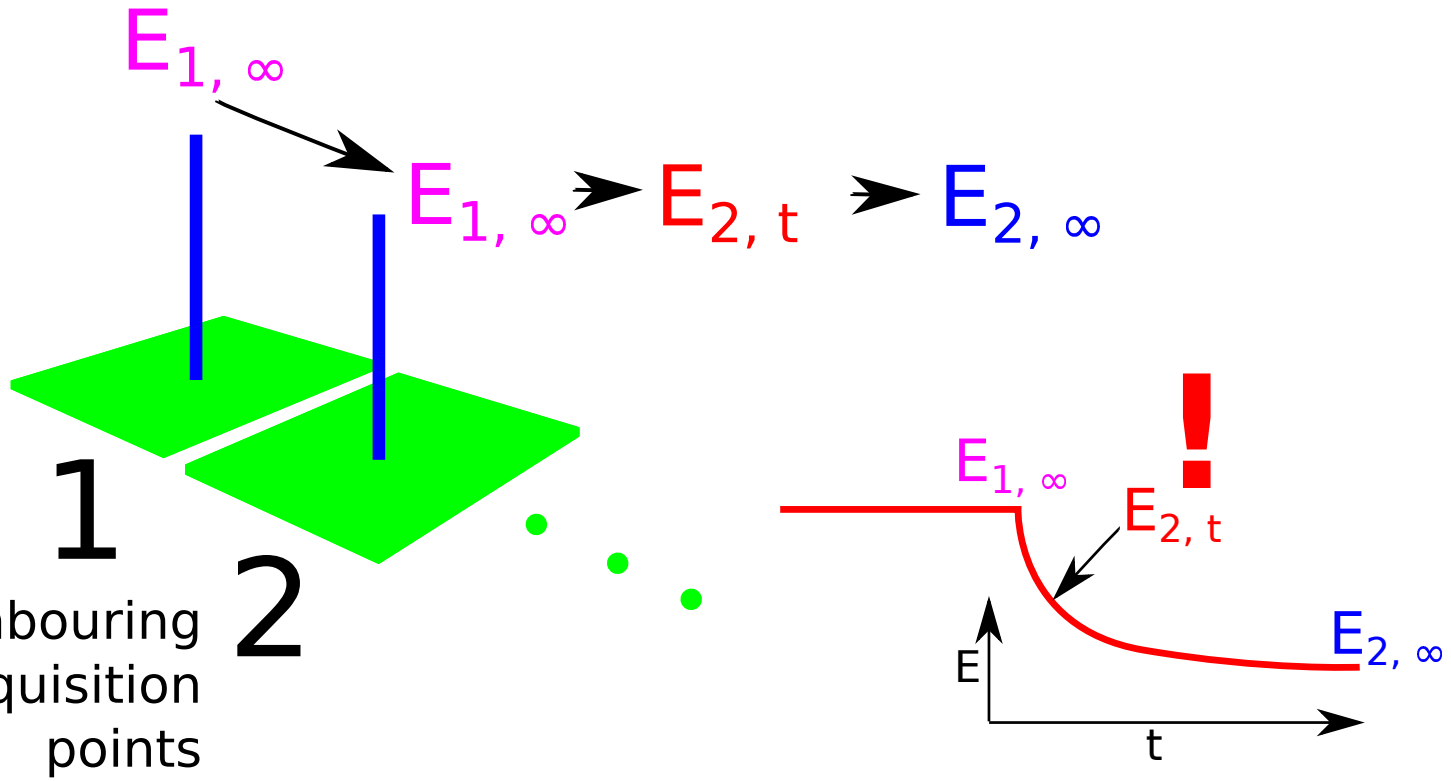
340 seconds



Scans are completed almost 2 times faster,
images have almost 10 times less distortion.

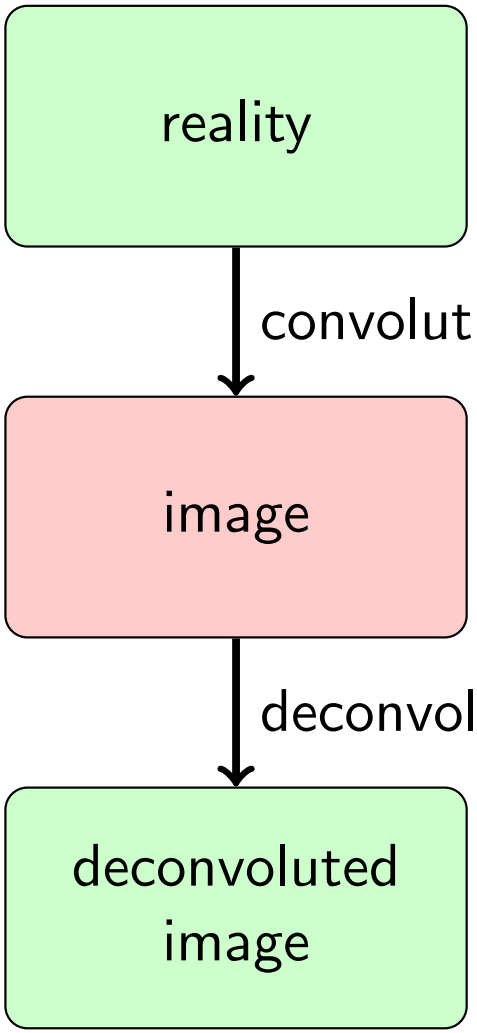
Solution #3: Signal processing.

The convolution function of the distortion



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

Convolution and deconvolution

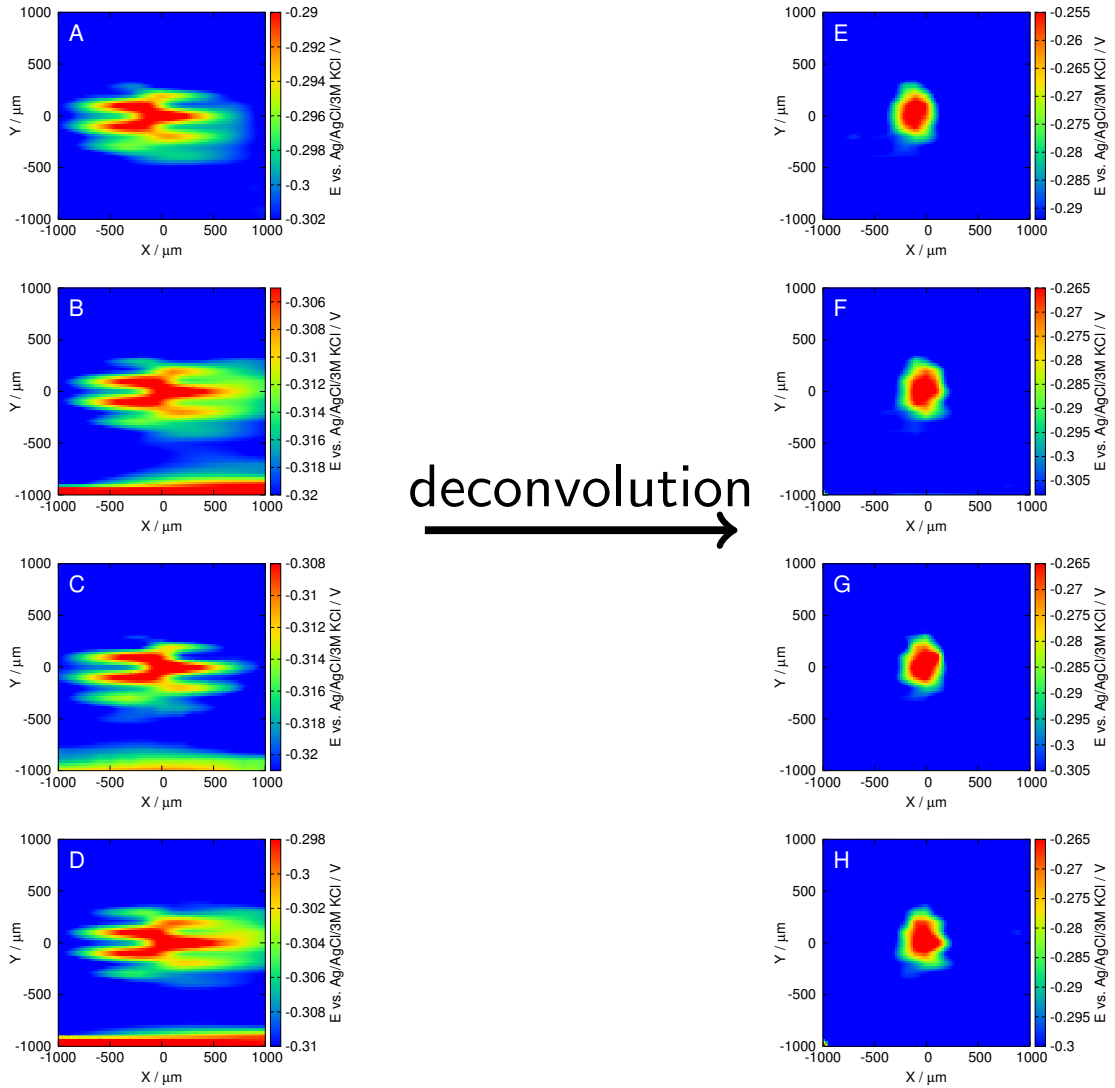


convolution : $E_{cell}(t) = E_{cell}(\infty) + [E_{cell}(0) - E_{cell}(\infty)]e^{-t/\tau}$

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

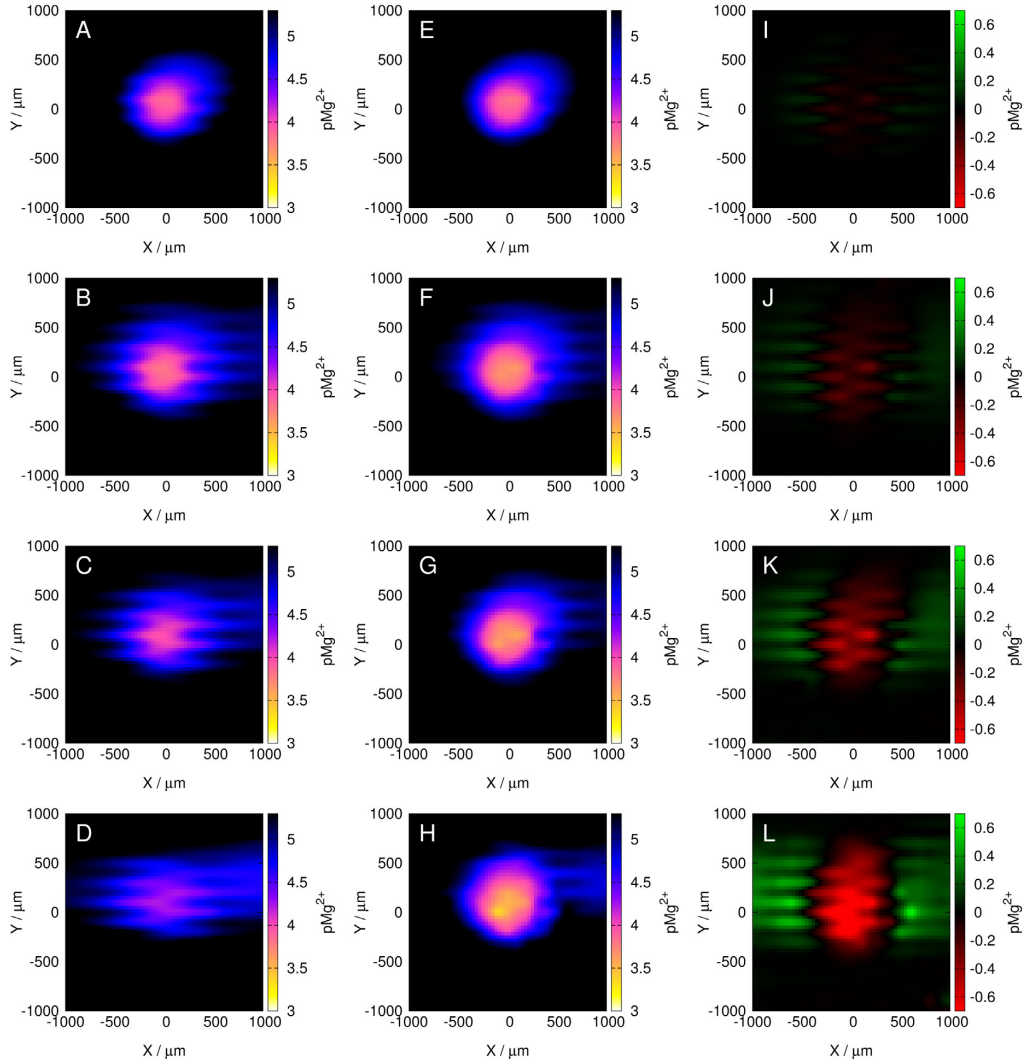
Deconvolution of potentiometric SECM images

Recorded using the antimony microelectrode following the meander algorithm



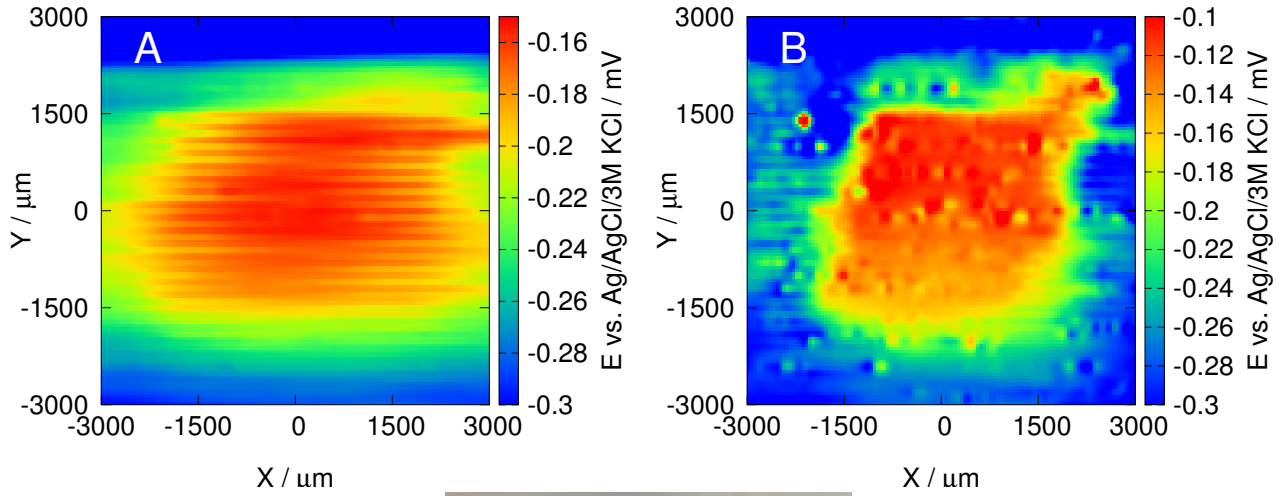
Deconvolution of potentiometric SECM images

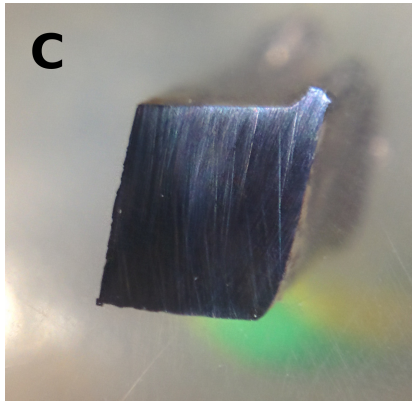
Recorded using the magnesium ISME following the meander algorithm



Practical example: corroding carbon steel sample

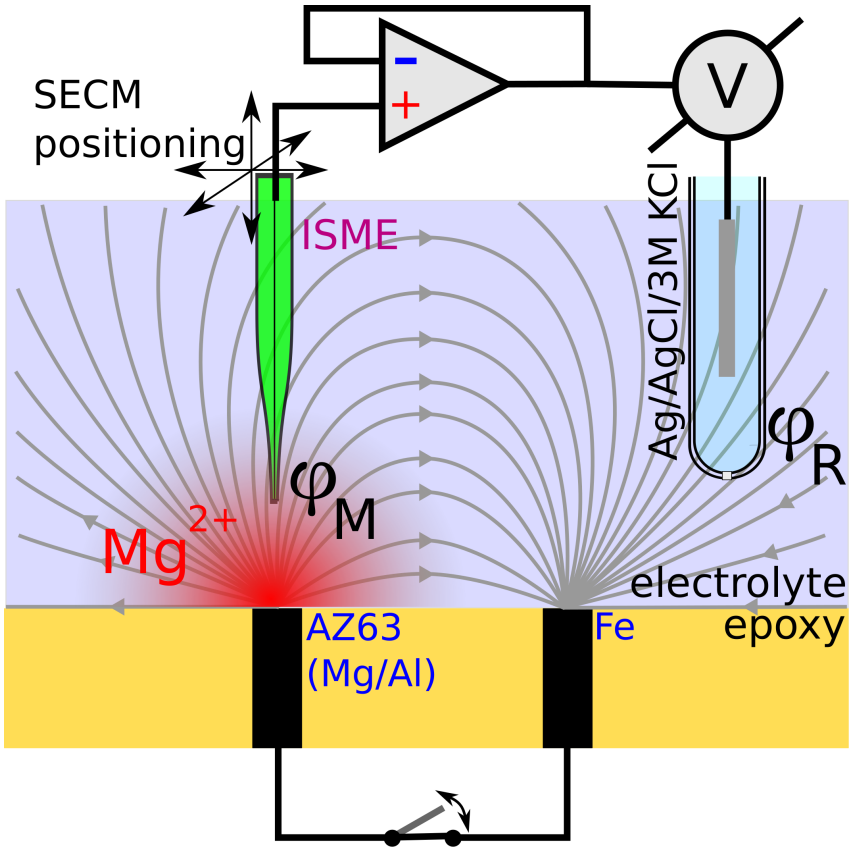
Scanned with an antimony microelectrode





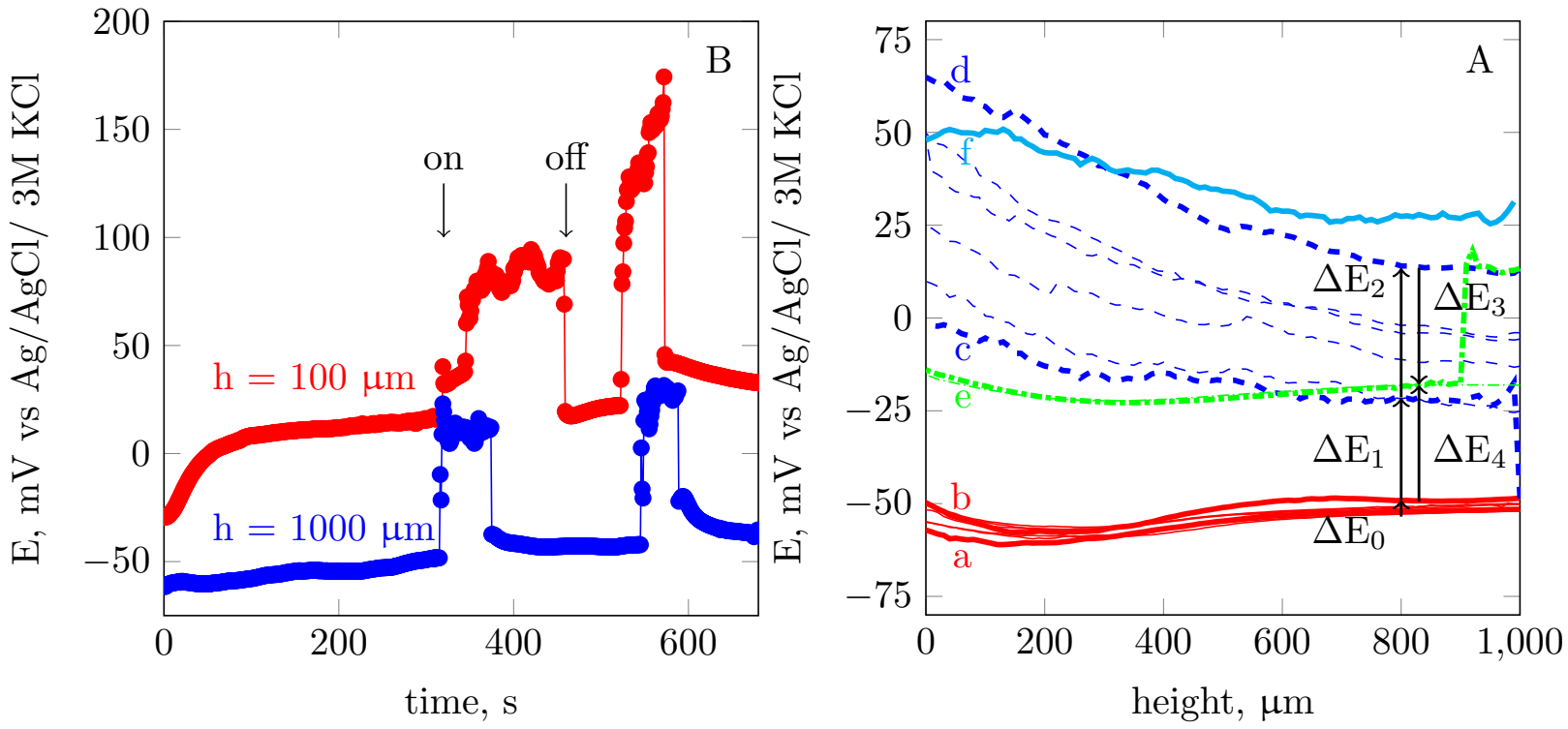
The effect of electric field on potentiometric SECM imaging.

The electric field during galvanic corrosion

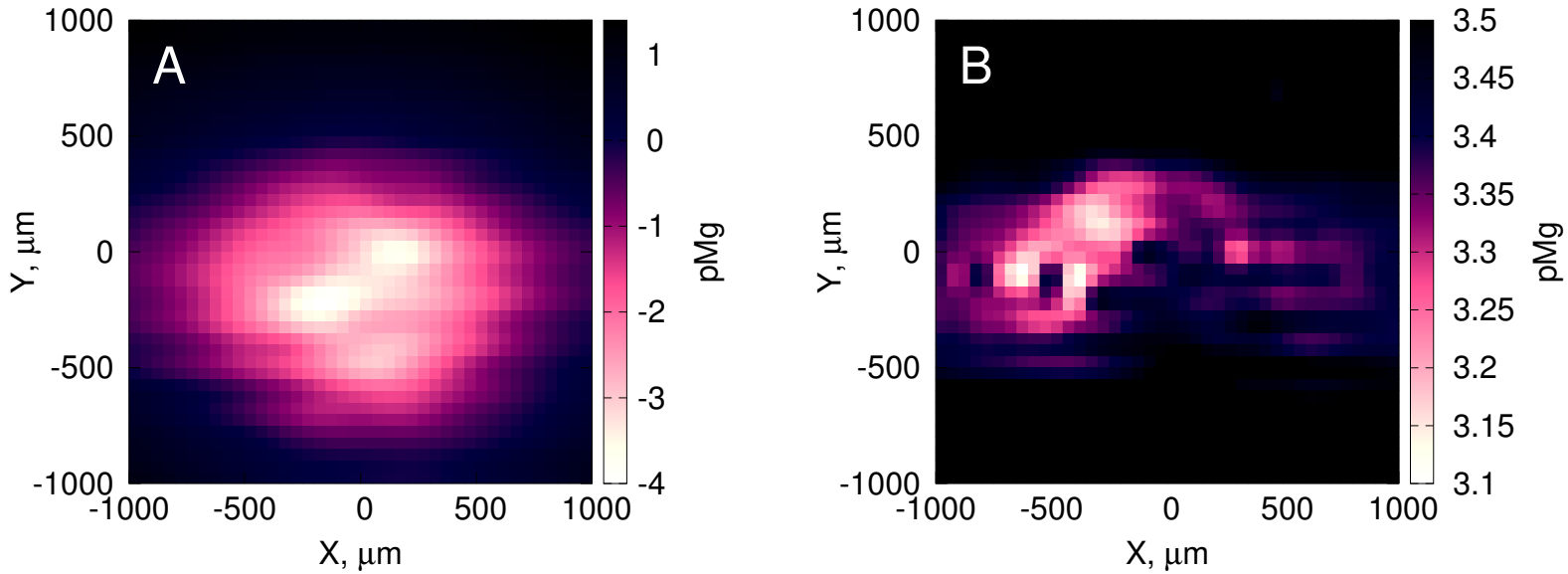


$$\Delta E = E_M - E_R + (\phi_M - \phi_R)$$

The effect of electric field on the measured potential



The effect of electric field on potentiometric SECM imaging



Conclusion

1. **I have shown the improved quality of potentiometric SECM images recorded with low resistance, solid-contact magnesium ion-selective microelectrodes.**
2. **Taking advantage of the new solid-contact microelectrodes, I have studied the galvanic corrosion of magnesium by mapping the concentration of dissolving ions.**
3. **I have proven that with the new patterns and algorithms that I have designed, image distortion is lower compared to the conventional ones, by numerical simulations and experimental SECM scans.**
4. **I was the first to use deconvolution to reduce distortion in potentiometric SECM images.** To prove the validity of the technique, I have compared deconvoluted images to equilibrium images scanned at a rate which allowed to record equilibrium potentials.
5. **I have successfully used deconvolution to restore potentiometric SECM images about a corroding carbon steel sample.** Evaluation of this data was possible, because scanning time *and* distortion was reduced at the same time.
6. **I have successfully resolved the observed discrepancy in recent papers about impossibly high ion activities.** The electric field present in many studied systems – galvanically corroding ones in particular – has a direct influence on the measured potential. In the system I have studied, the error was almost four orders of magnitude.

Acknowledgements

I wish to express my sincere gratitude to **professor Dr. Géza Nagy** for introducing me to the fascinating field of electrochemistry, and for the continuous support and guidance during the work.

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Many thanks are due to all my colleagues and friends with whom I have worked during my years as an undergraduate and doctoral student.

Thank you for your attention.