Recent Advances in Potentiometric Scanning Electrochemical Microscopy

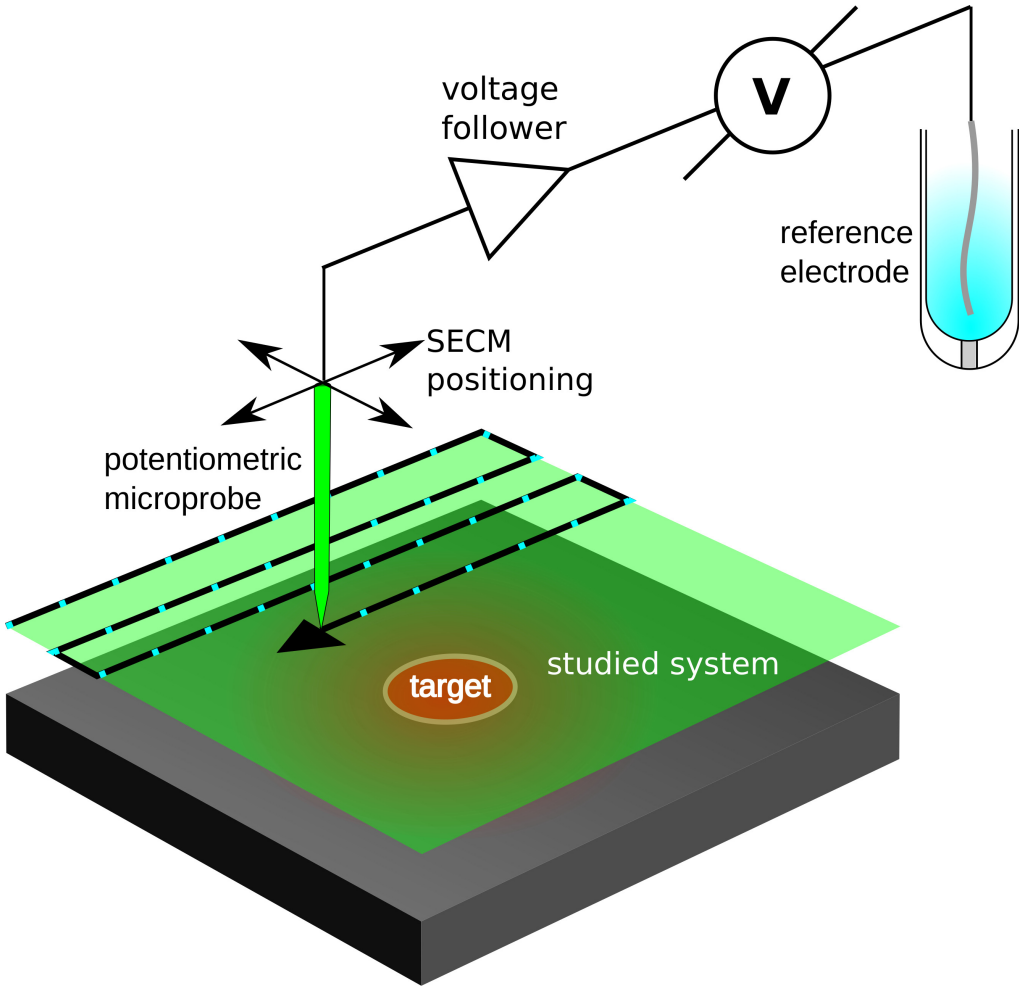
9^{th} Workshop on Scanning Electrochemical Microscopy and Related Techniques, Warsaw

András Kiss, Géza Nagy

Department of General and Physical Chemistry
University of Pécs, Hungary

August 16, 2017

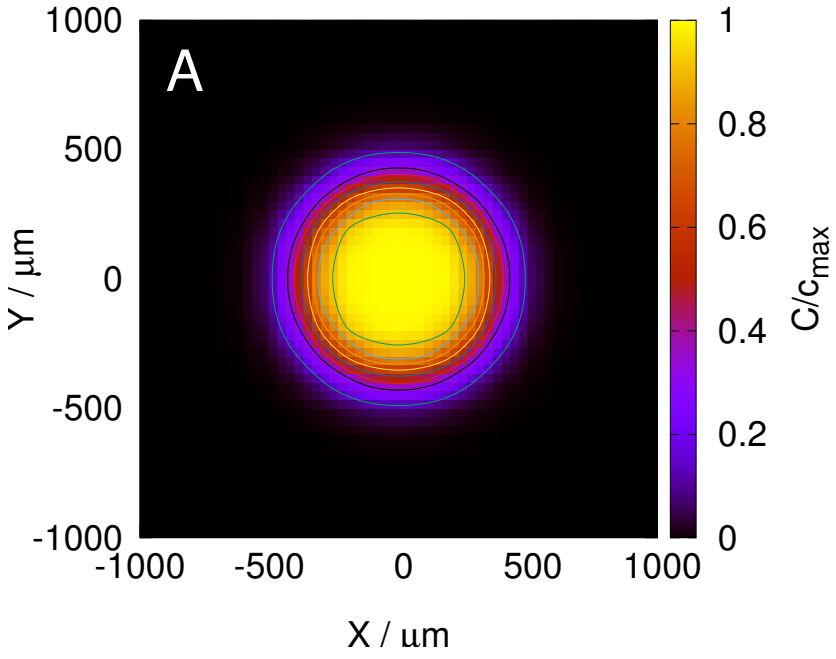
Potentiometric SECM



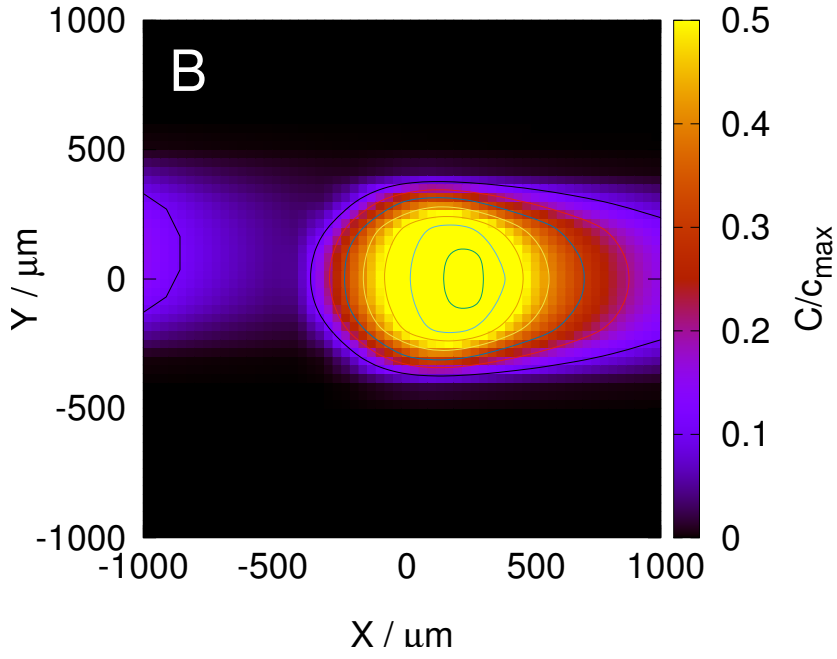
The problem with potentiometric SECM

Distortion at high scan rate

Slow

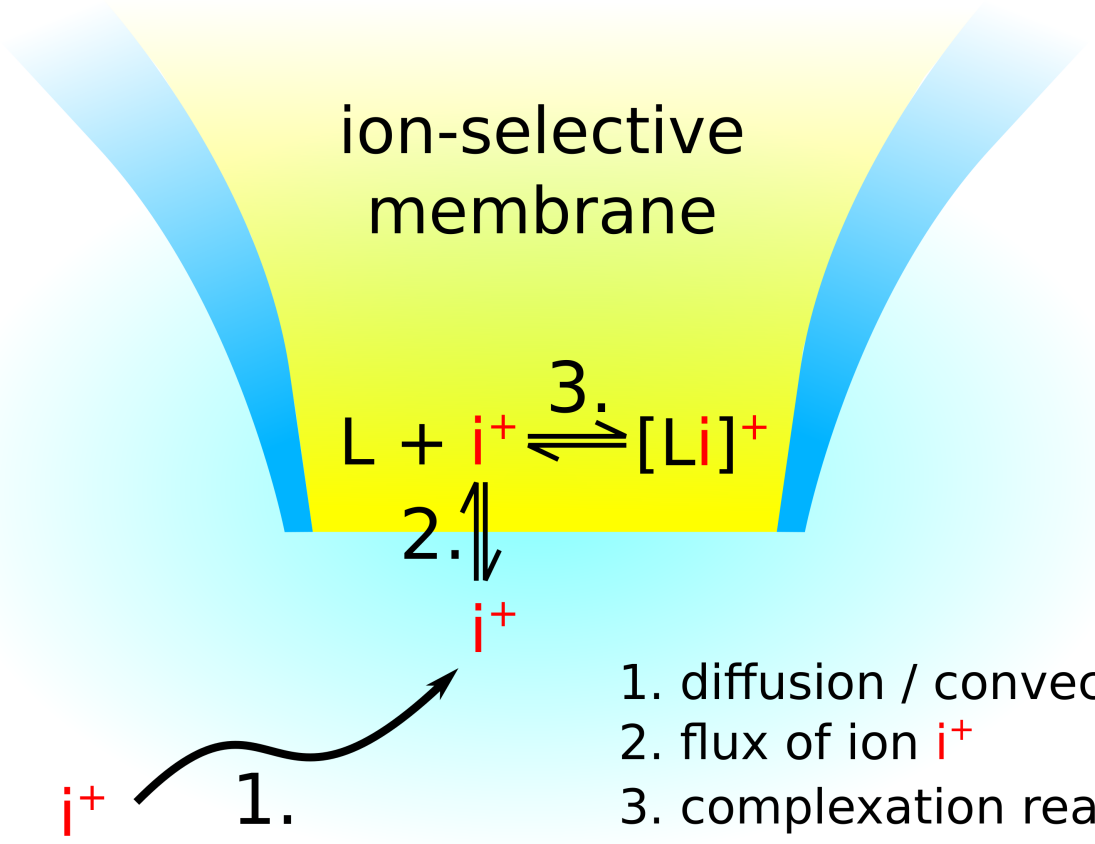


Fast



Why is the image distorted?

Possible contributors to the lag



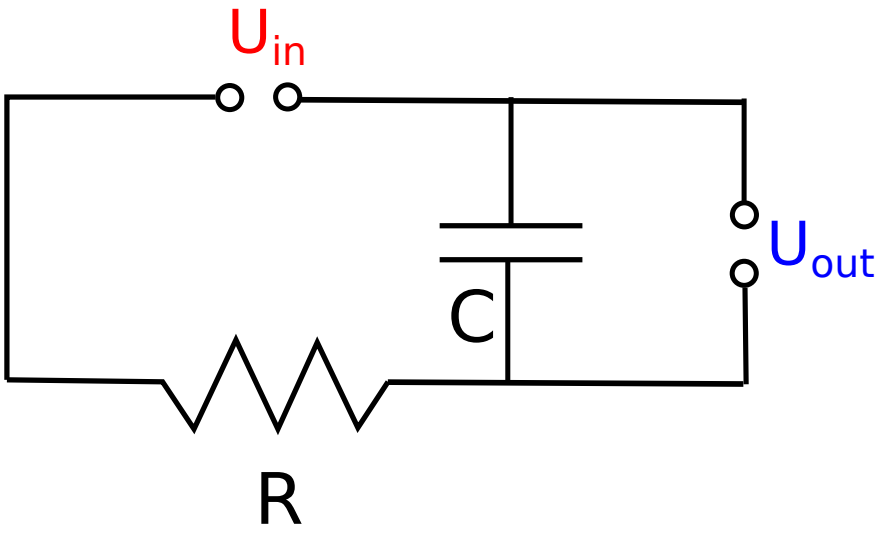
1. diffusion / convection
2. flux of ion i^+
3. complexation reaction

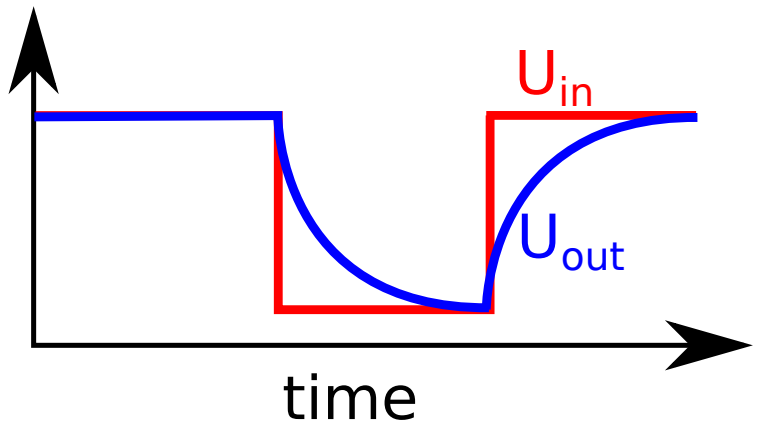
L: ligand

i^+: measured ion

Why is the image distorted?

The RC time constant





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

$$\tau = R \cdot C$$

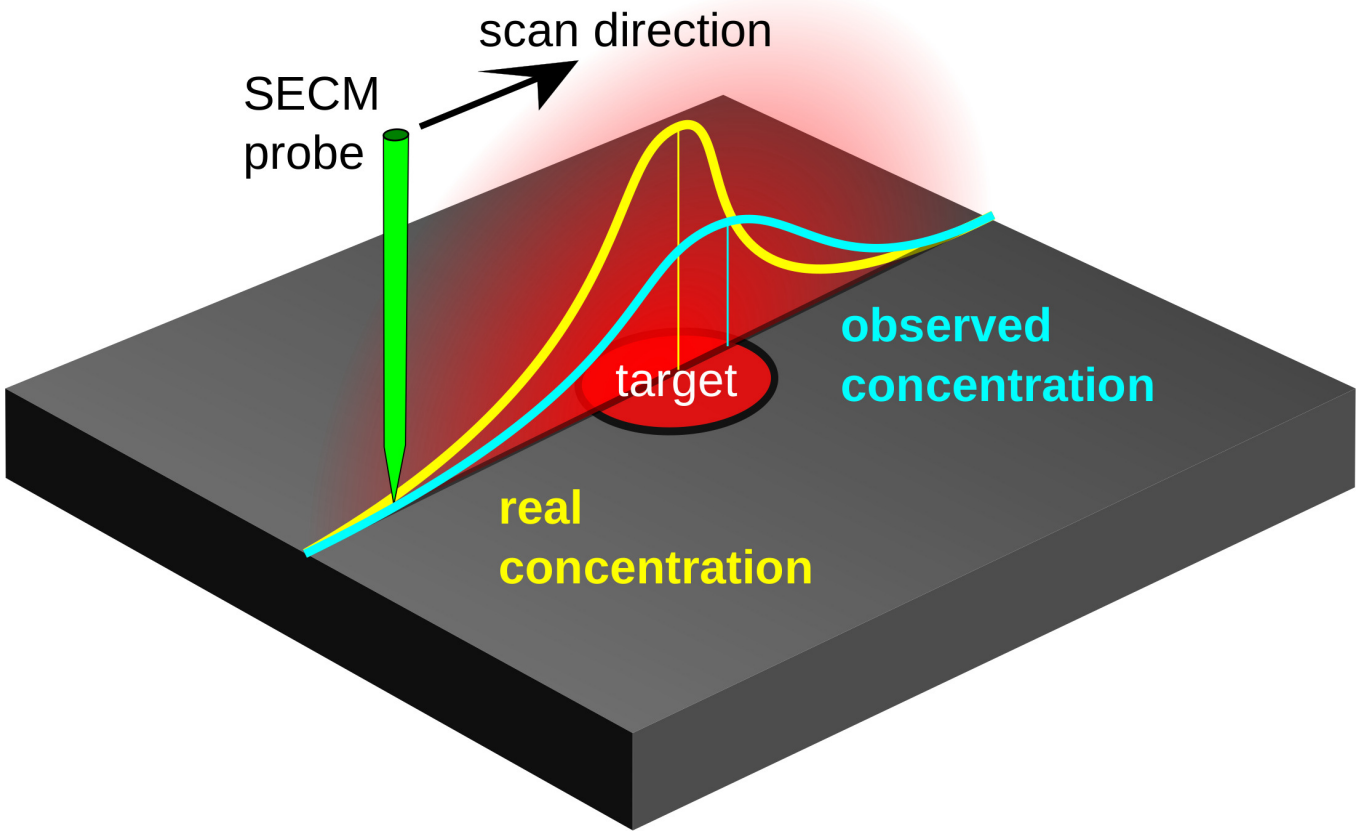
$$R = 5\ \text{G}\Omega$$

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

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

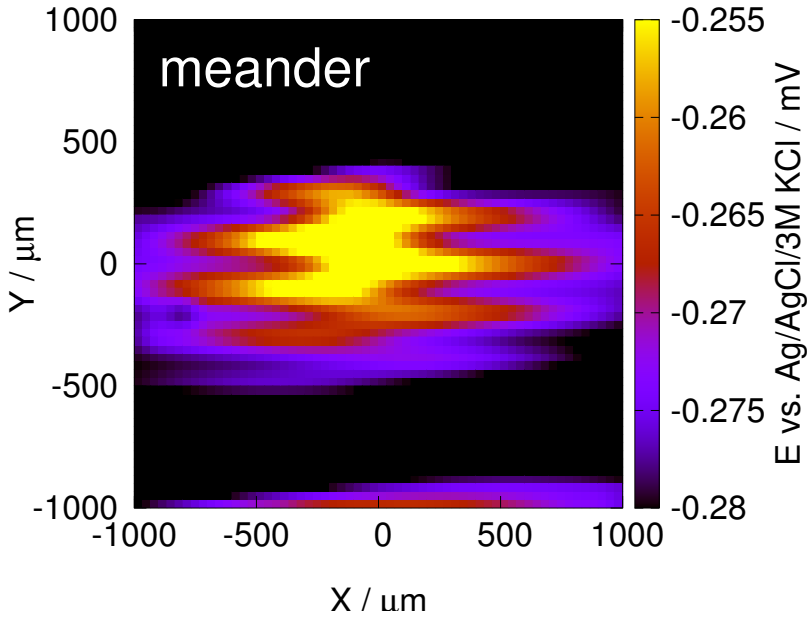
Distortion of potentiometric imaging

In the case of a linescan



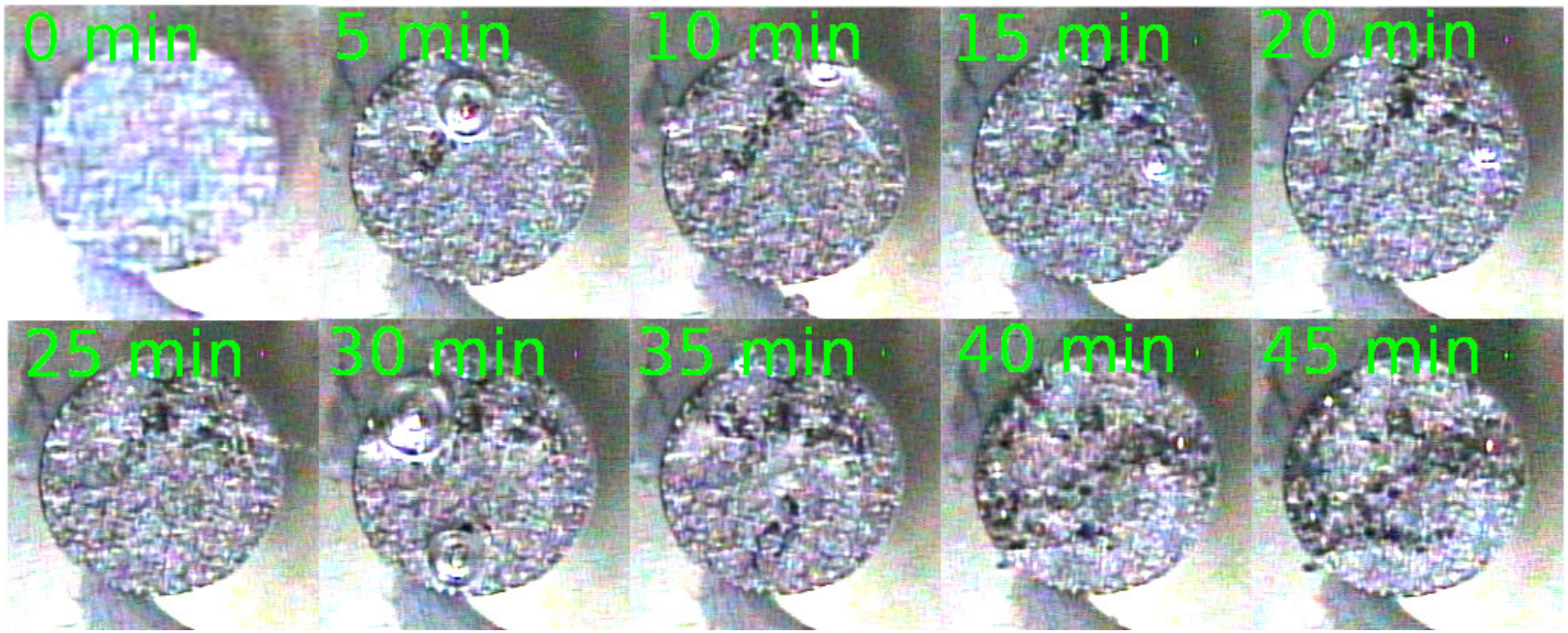
Imaging distortion

Using the meander algorithm



Why is it so important to complete the scan quickly?

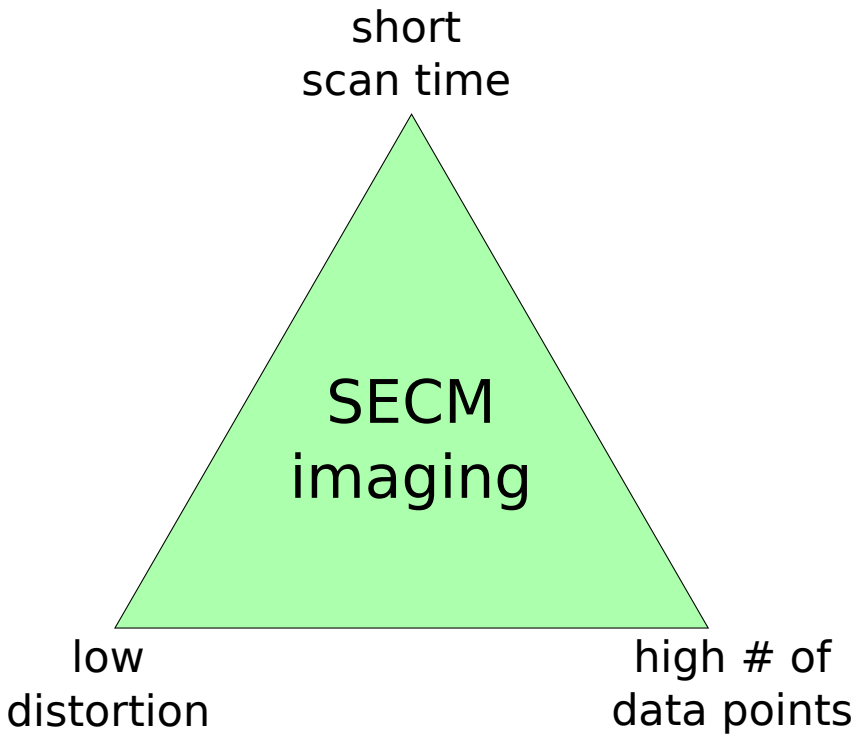
Example: corrosion of a magnesium alloy



Corrosion of the AZ63 magnesium-aluminium-zinc alloy.

Trade-off triangle of potentiometric SECM

Compromise between the three desired competing properties

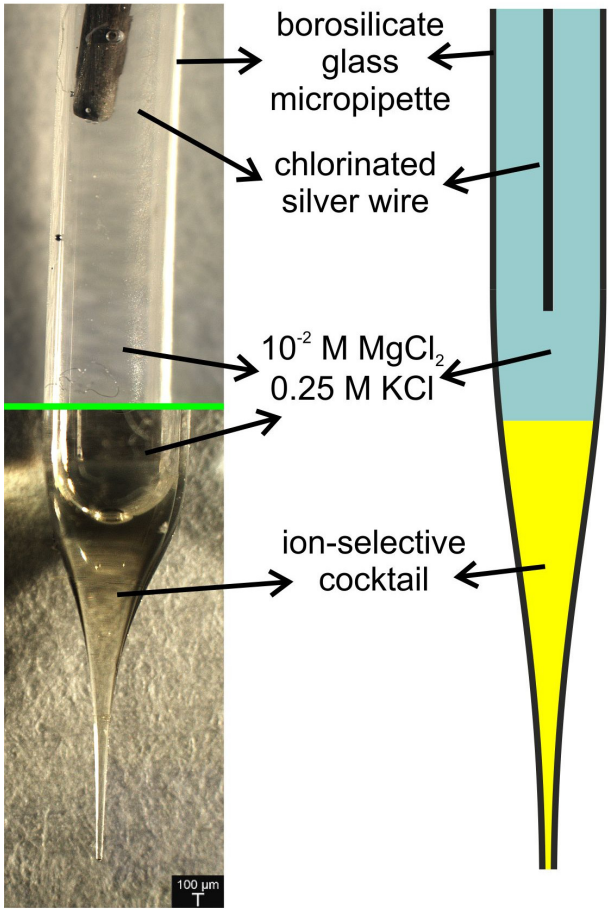


Solution #1: Solid contact micropipettes as SECM probes.

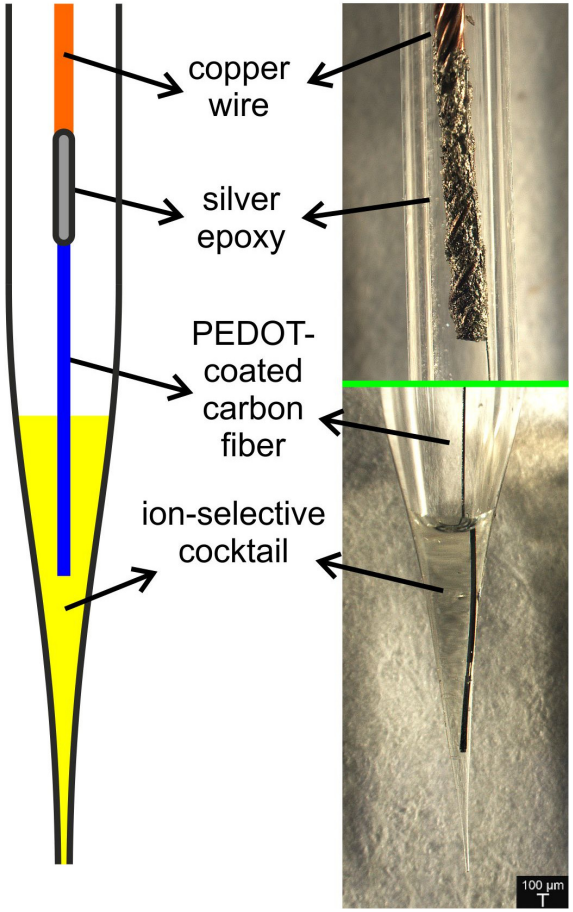
Liquid vs. solid contact micropipettes

Comparison of construction

Liquid contact

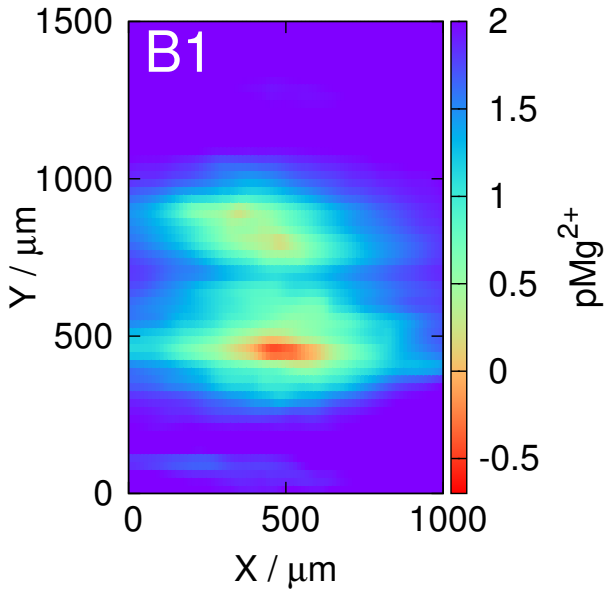


Solid contact

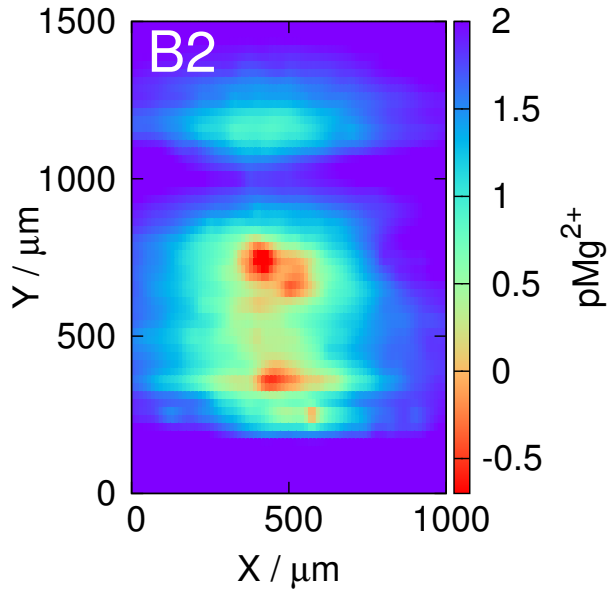


Application in corrosion science: galvanic corrosion of Mg

Liquid contact



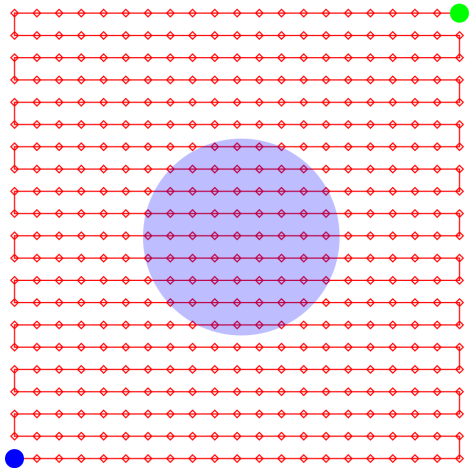
Solid contact



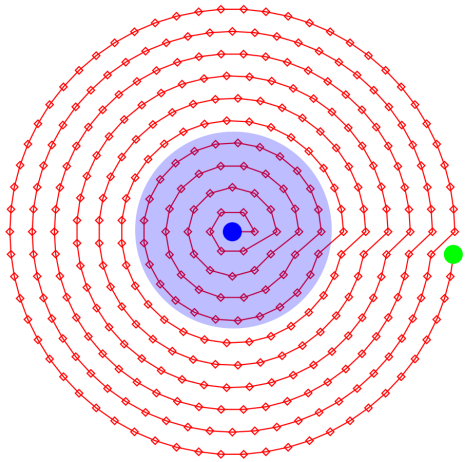
Solution #2: Optimizing scanning patterns and algorithms.

New SECM scanning patterns based on the polar-coordinate system

Cartesian coordinate system based scanning pattern



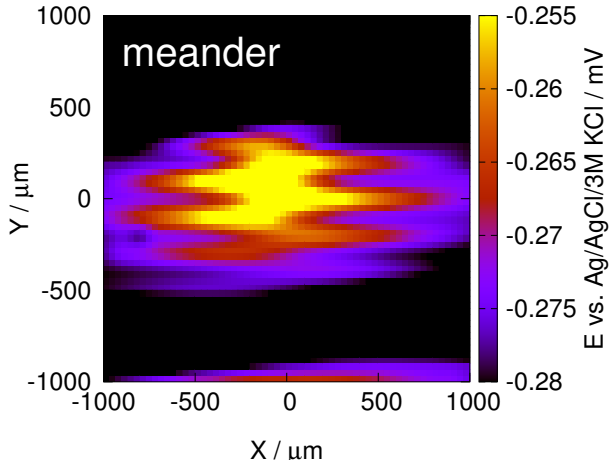
Polar coordinate system based scanning pattern



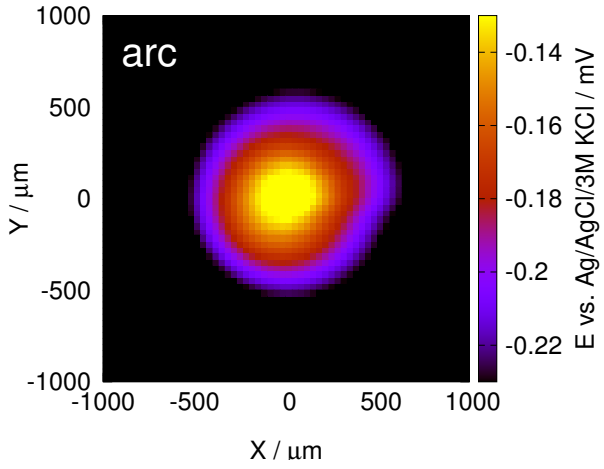
Confirmation with experimental SECM scans

Recorded using the antimony microelectrode

440 seconds



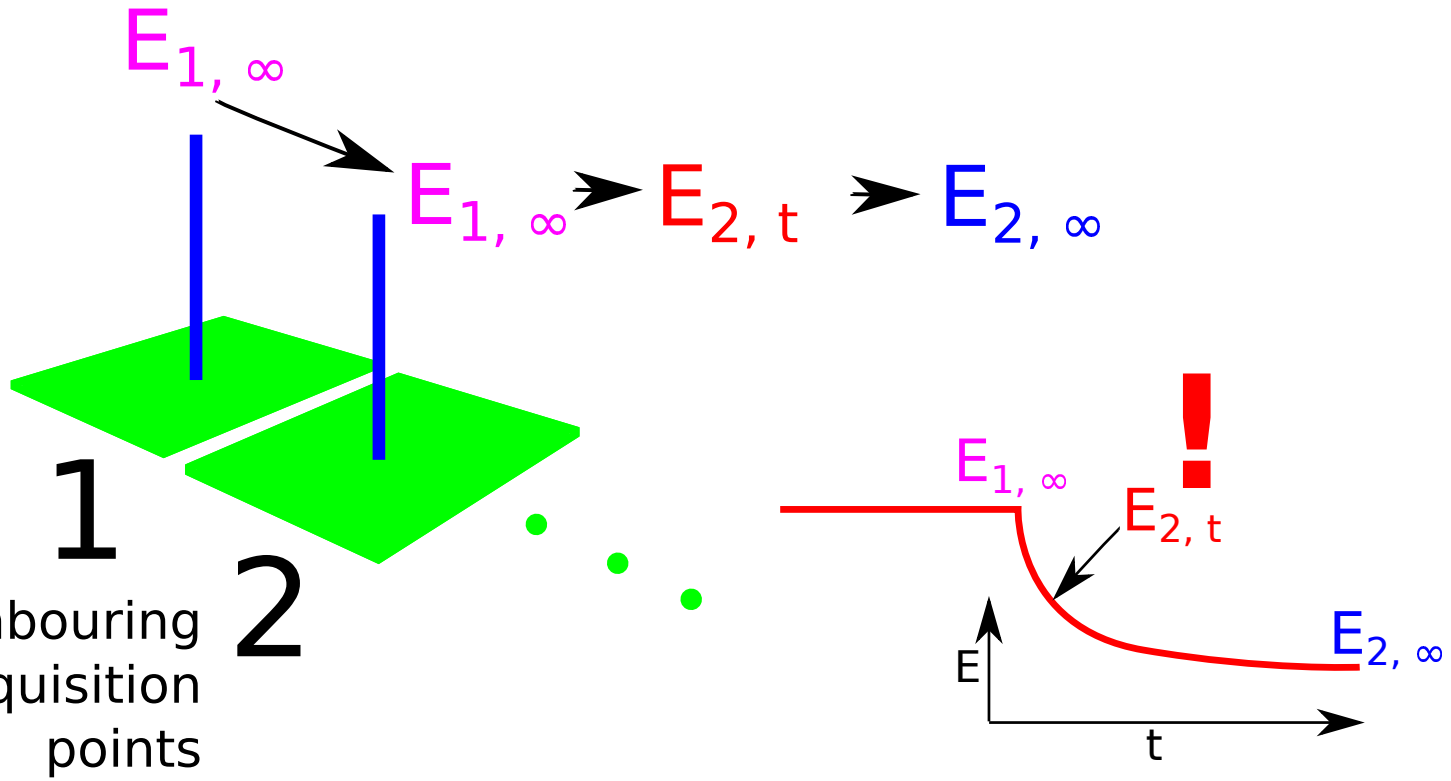
340 seconds



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

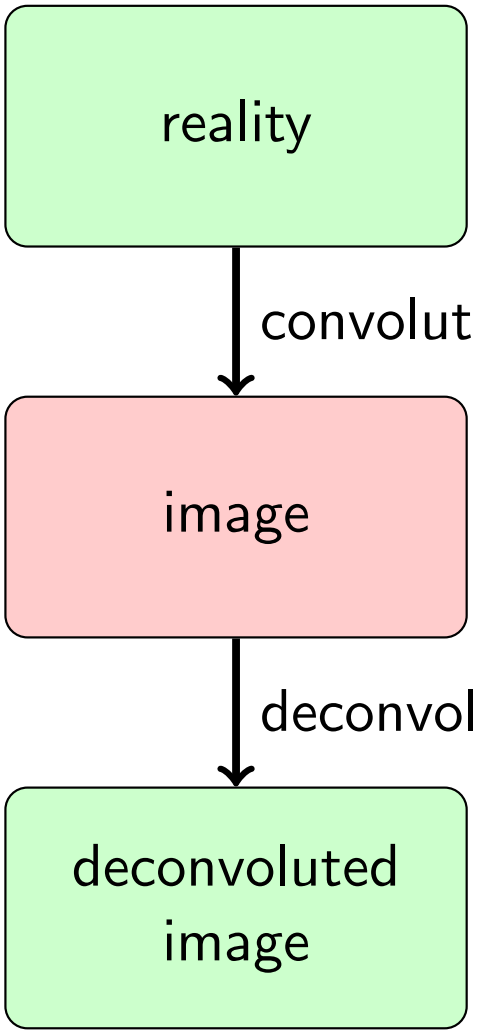
Solution #3: Signal processing.

The convolution function of the distortion



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

Convolution and deconvolution

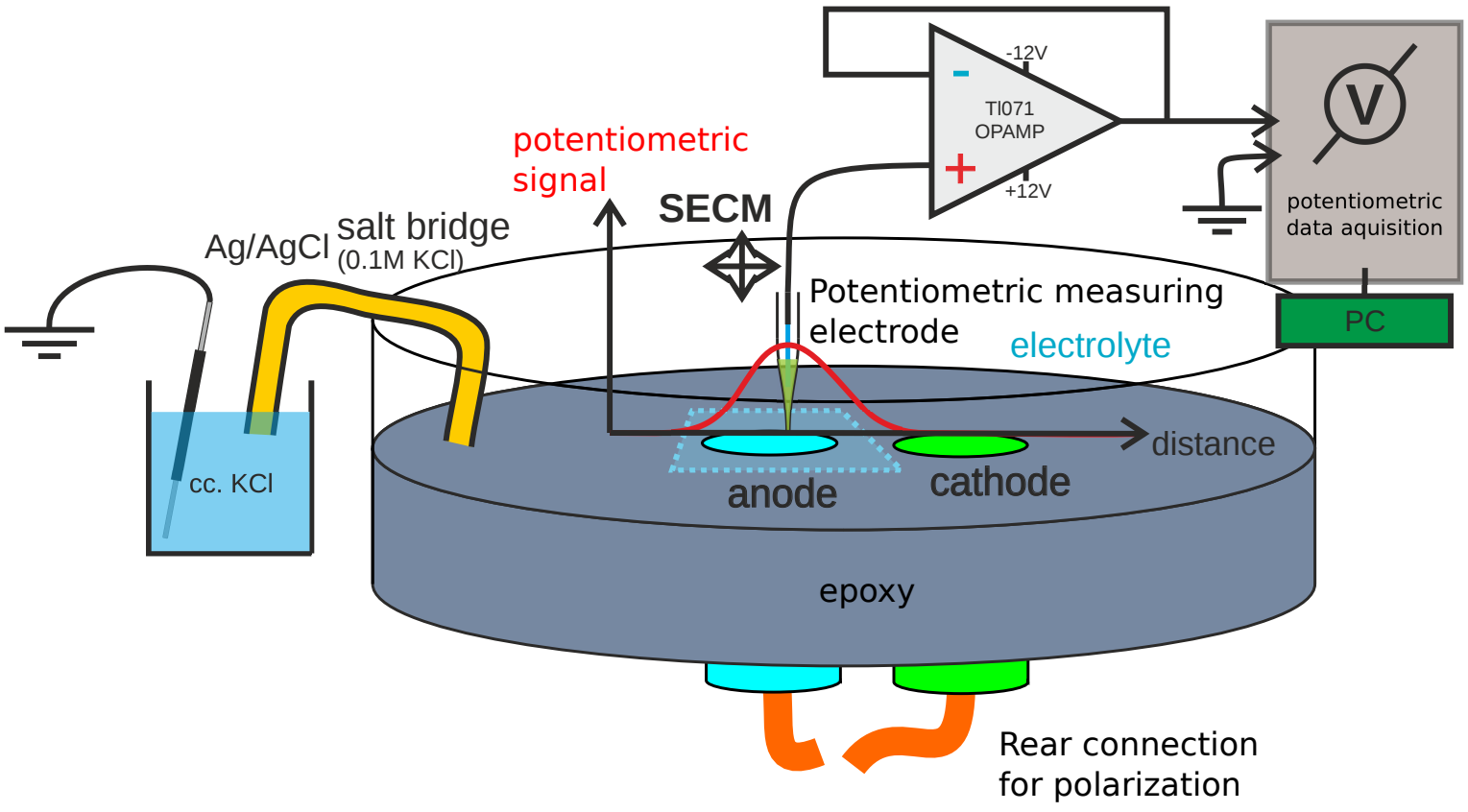


convolution : $E_{cell}(t) = E_{cell}(\infty) + [E_{cell}(0) - E_{cell}(\infty)]e^{-t/\tau}$

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

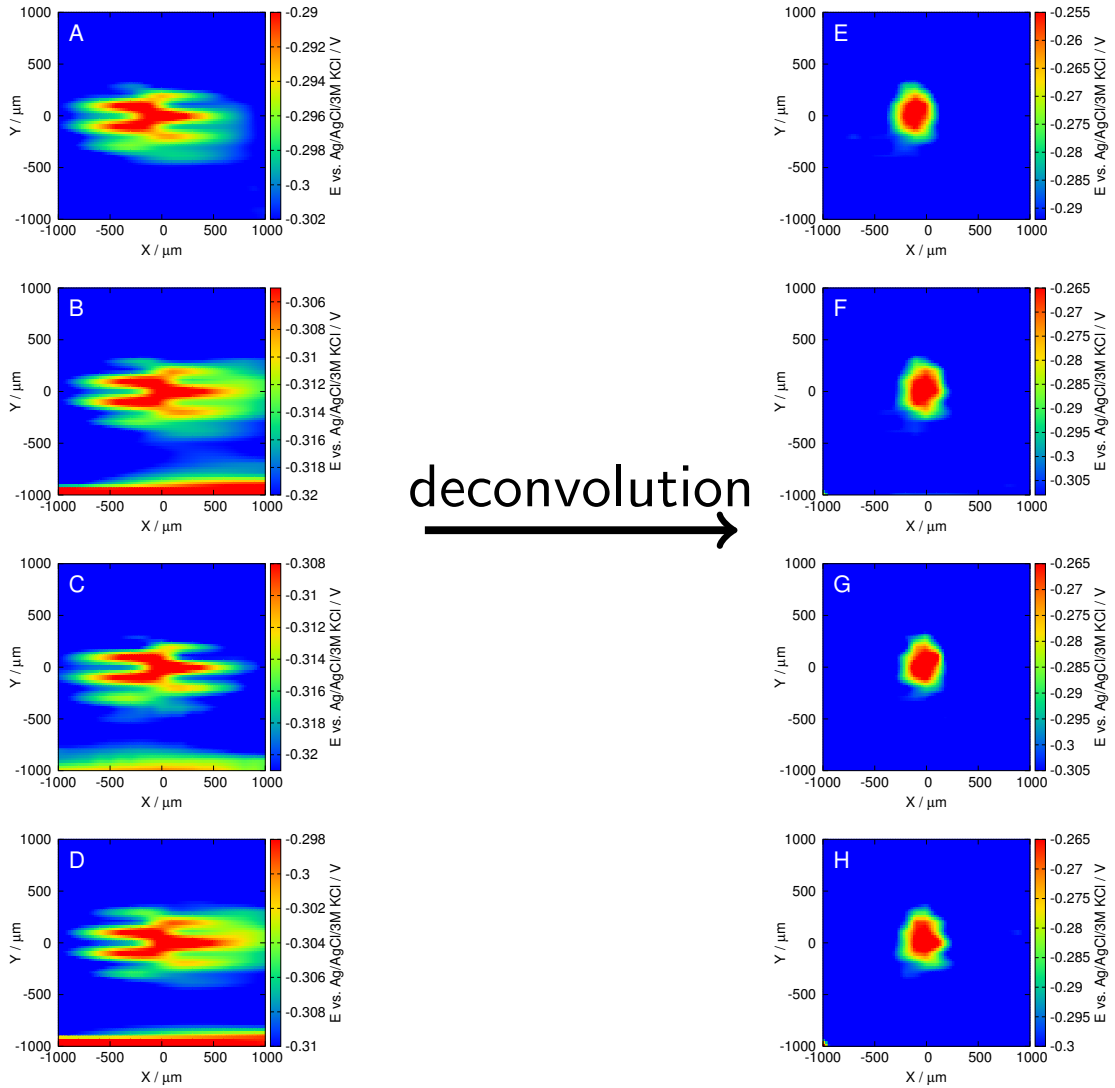
Demonstartion with a model system

Experimental setup



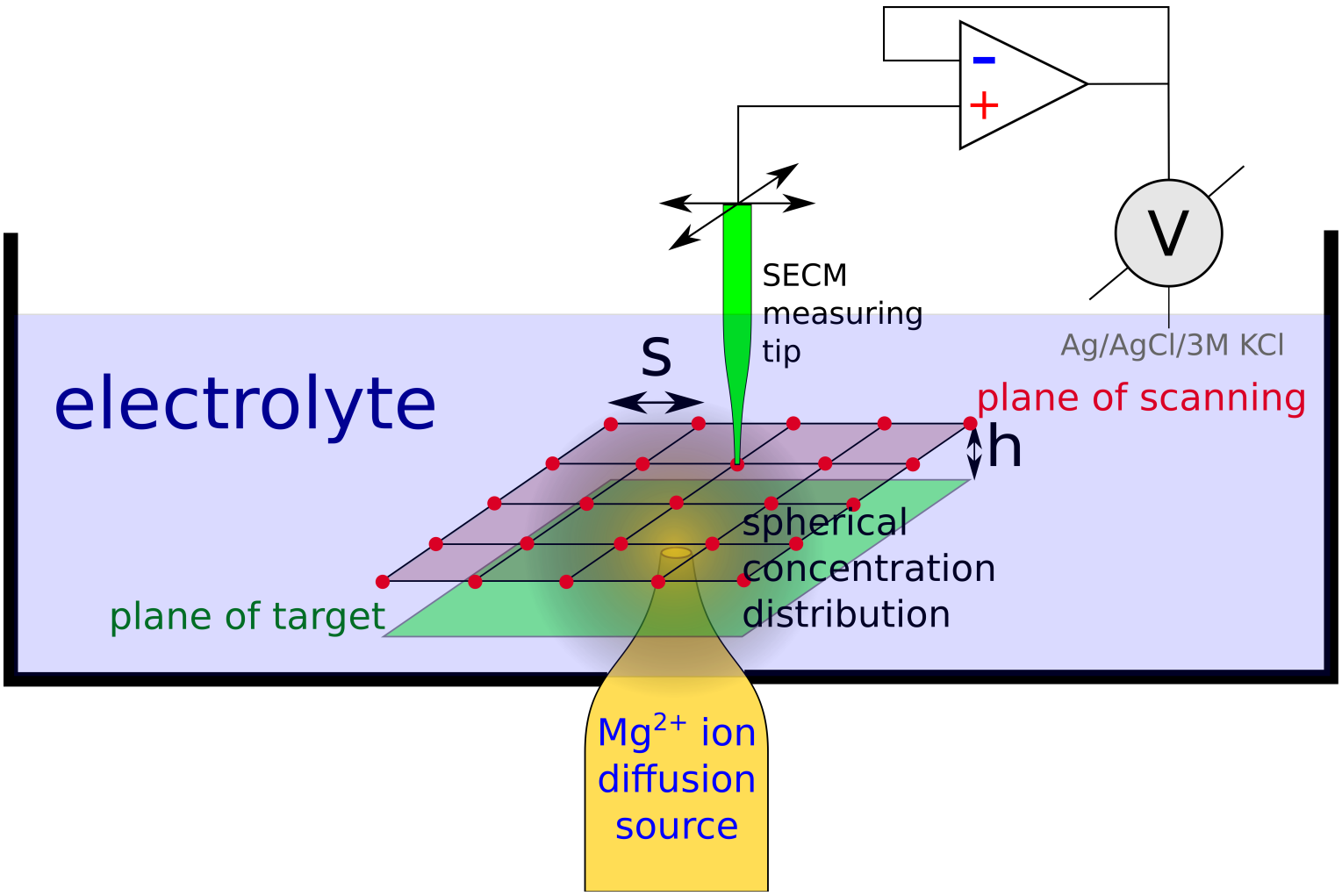
Deconvolution of potentiometric SECM images

Recorded using the antimony microelectrode following the meander algorithm



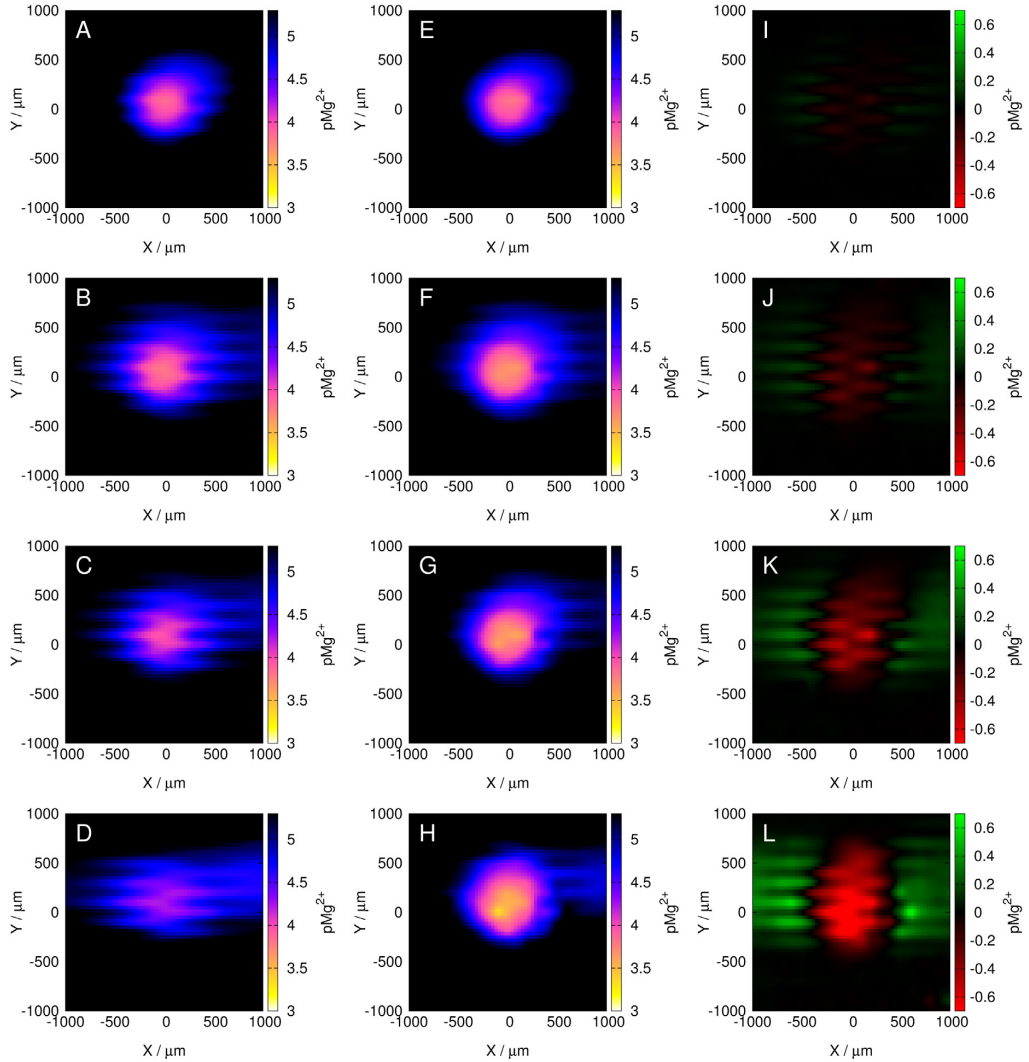
Deconvolution of potentiometric SECM images

Experimental setup



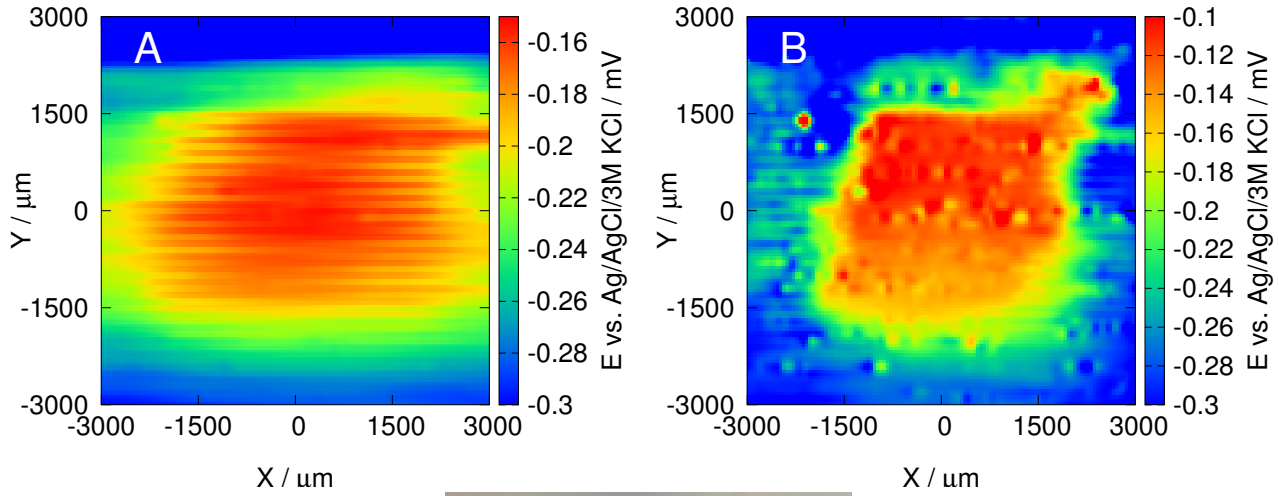
Deconvolution of potentiometric SECM images

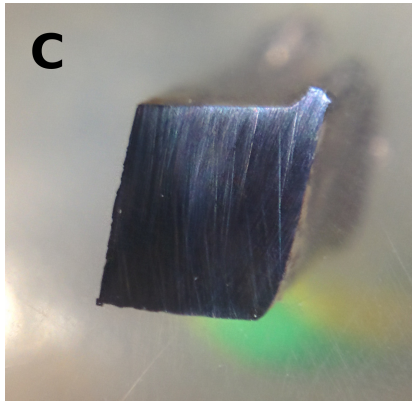
Recorded using the magnesium ISME following the meander algorithm



Practical example: corroding carbon steel sample

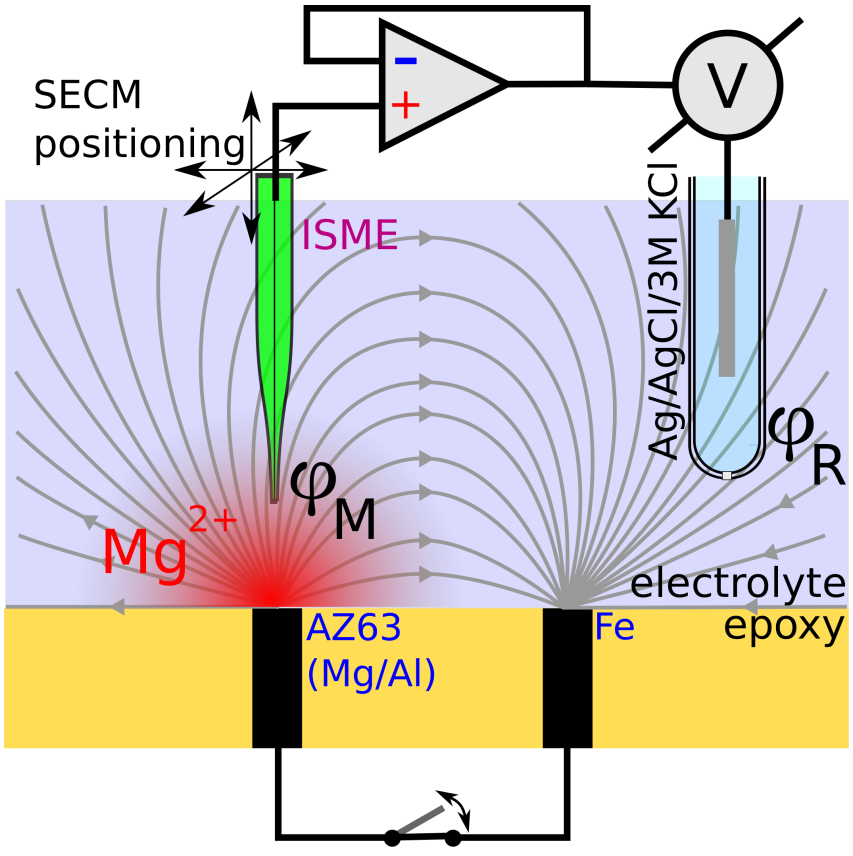
Scanned with an antimony microelectrode





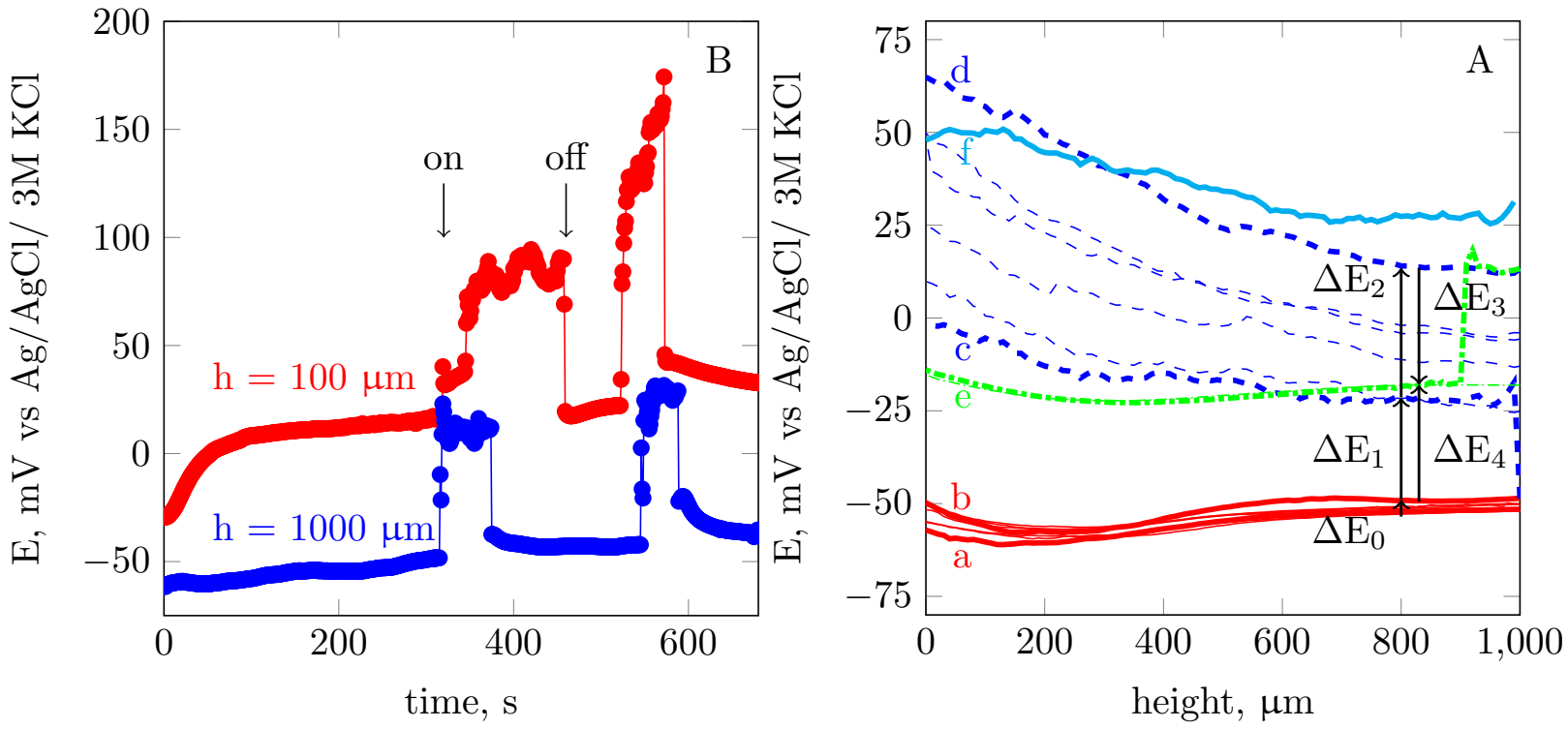
The effect of electric field on potentiometric SECM imaging.

The electric field during galvanic corrosion



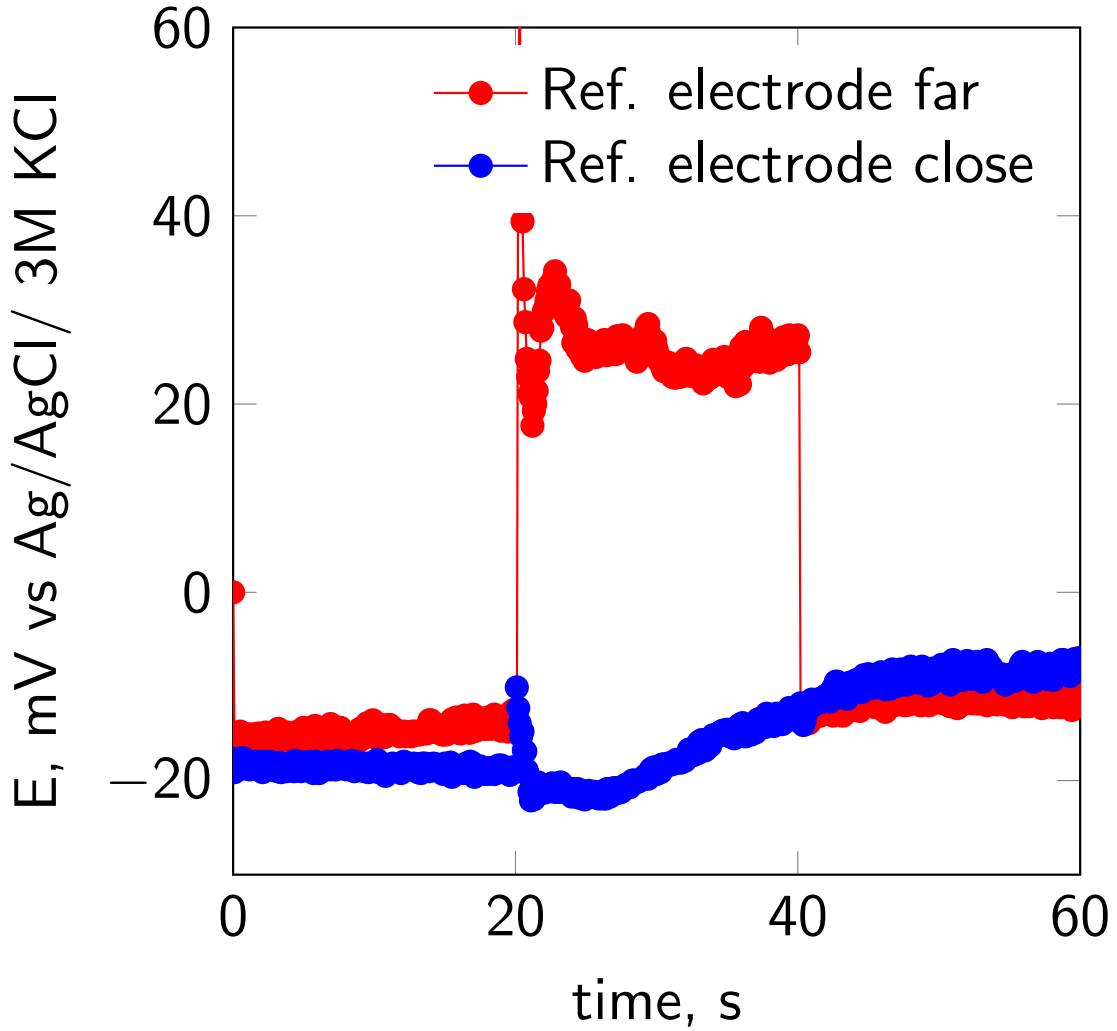
$$\Delta E = E_M - E_R + (\phi_M - \phi_R)$$

The effect of electric field on the measured potential

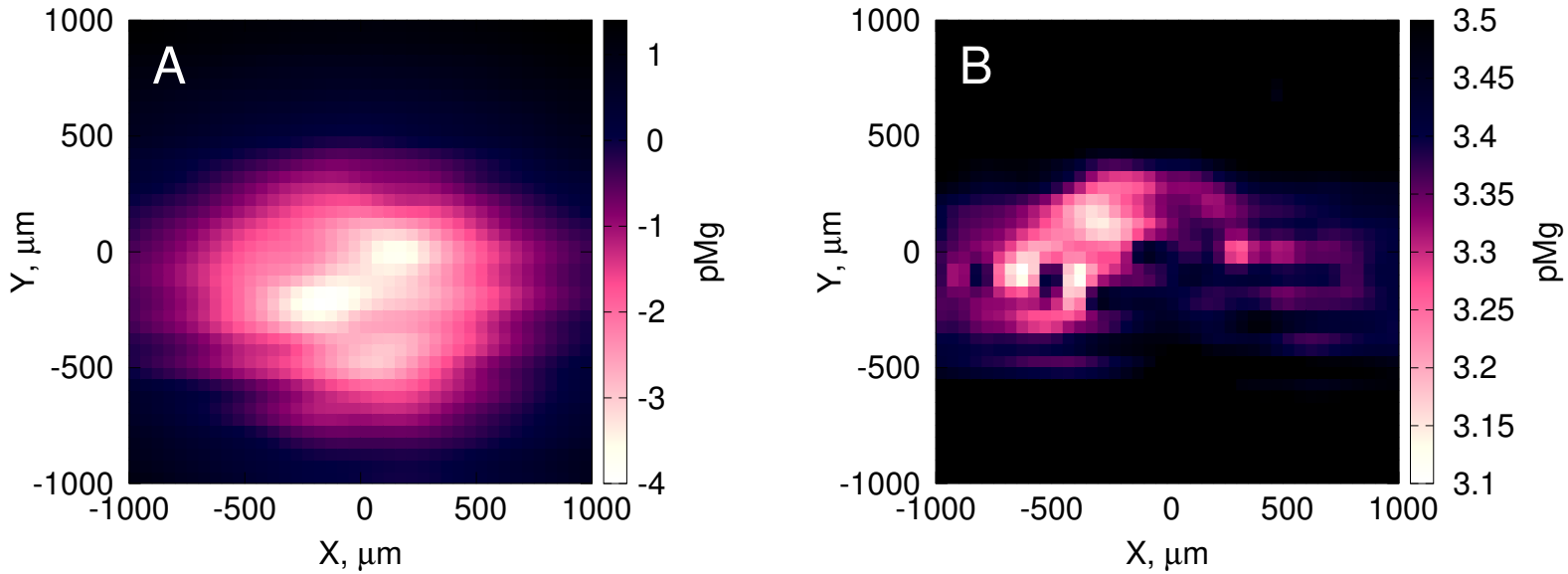


Eliminating the effect of the electric field

By careful reference electrode positioning



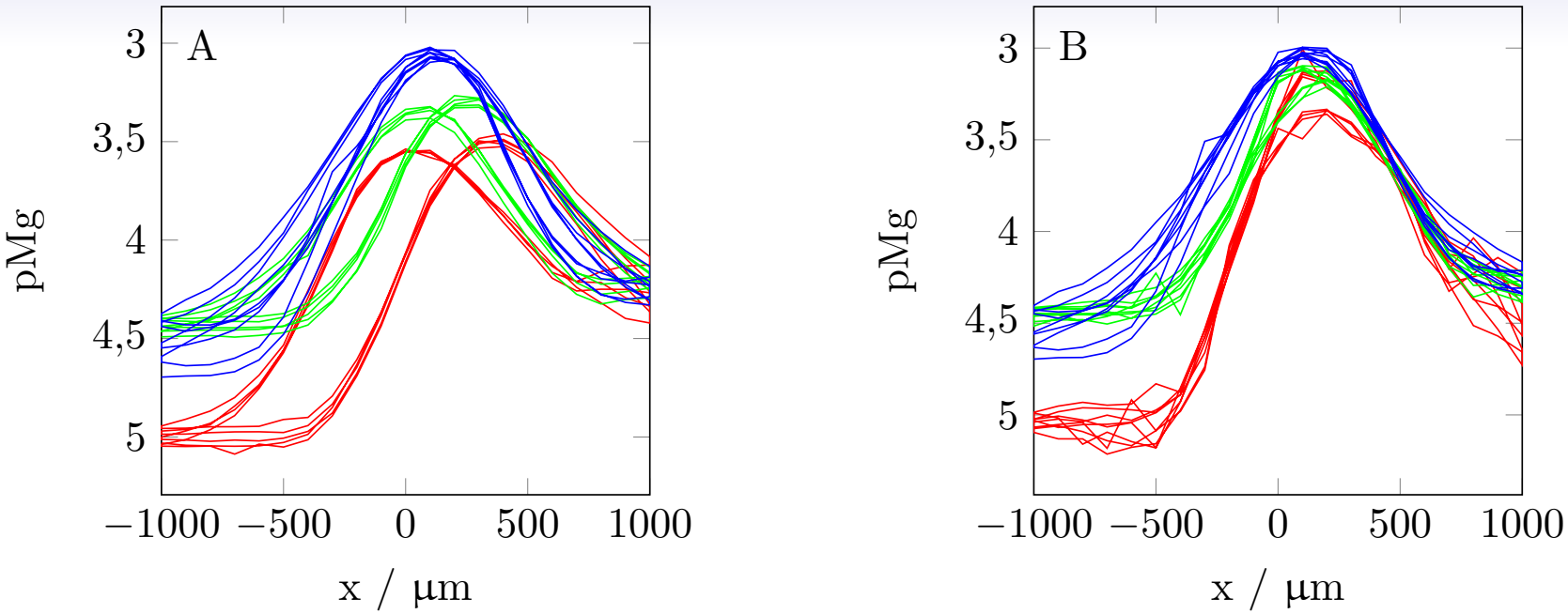
The effect of electric field on potentiometric SECM imaging



Conclusions

1. **Distortion in potentiometric SECM images can be reduced with deconvolution.** To prove the validity of the technique, deconvoluted images have been compared to equilibrium images scanned at a rate which allowed to record equilibrium potentials.
2. **The observed discrepancy in recent papers about impossibly high ion activities was resolved.** 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. By taking this effect into account, a more accurate conclusion can be drawn.

Thank you for your attention.



(A) Raw scan lines recorded $h = 100$ µm over the center of the pipette orifice, which served as a Mg^{2+} ion diffusion source. (B) Scan lines obtained after deconvolution. t_e equilibration intervals were 4.9 s (blue), 1.9 s (green), and 0.4 s (red). Probe movement speed was 1000 µm/s, and probe movement interval was 0.1 s. 8 scan lines were recorded in each case, 4 forward, 4 reverse scans.