

# Recent Advances in Potentiometric Scanning Electrochemical Microscopy

9<sup>th</sup> Workshop on Scanning Electrochemical Microscopy and  
Related Techniques, Warsaw

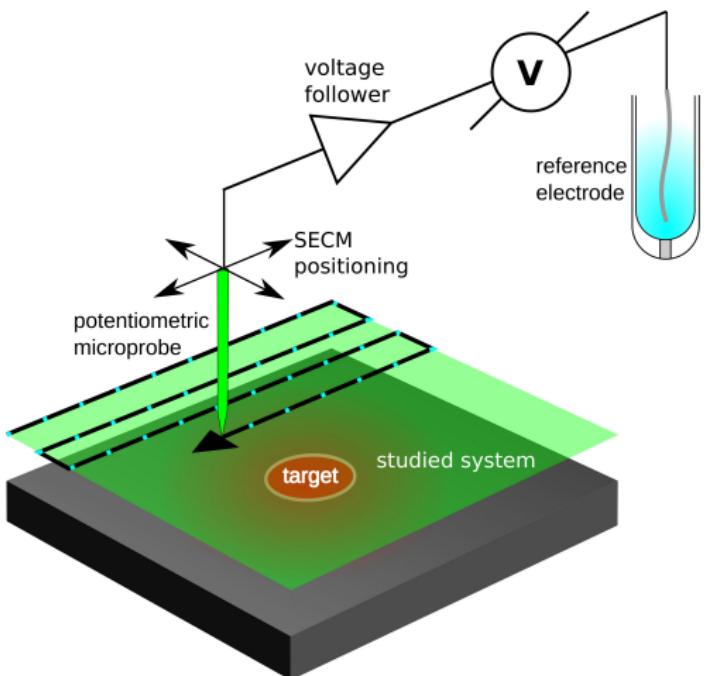
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August 16, 2017

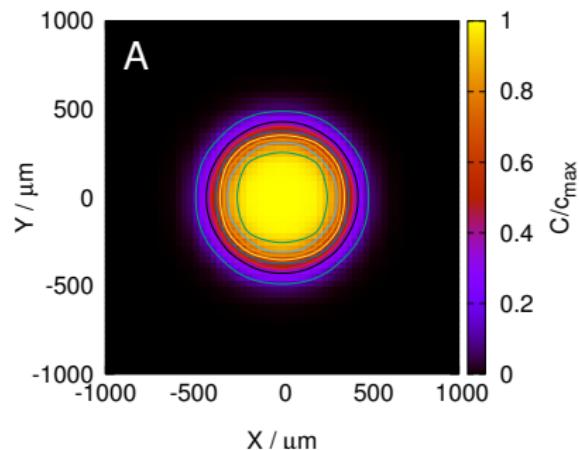
# Potentiometric SECM



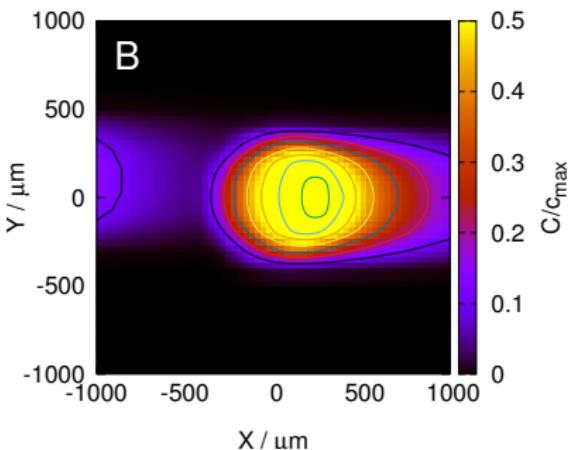
# The problem with potentiometric SECM

Distortion at high scan rate

Slow

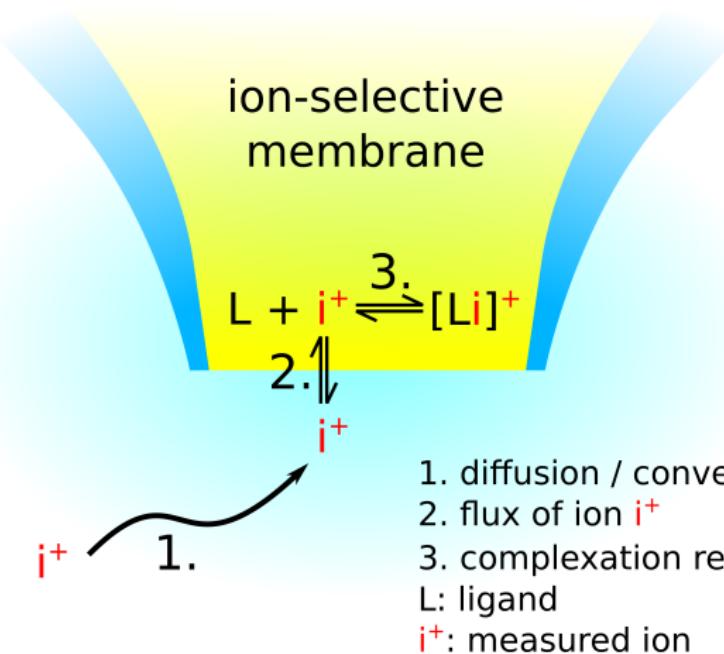


Fast



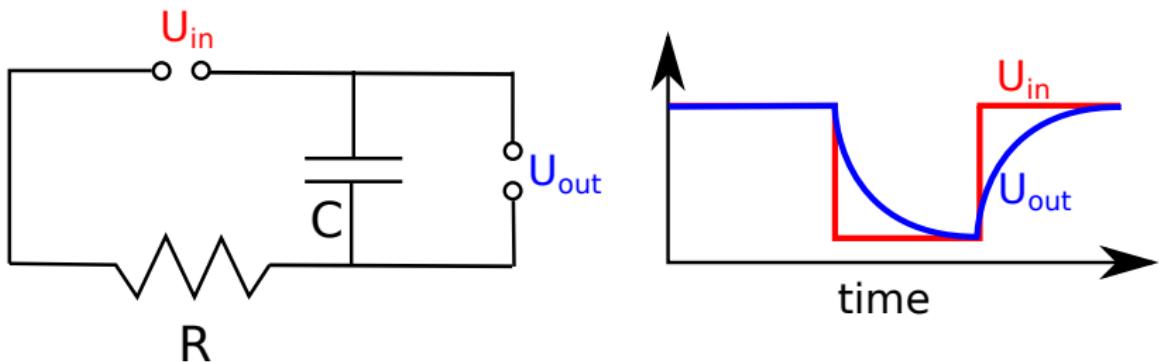
# Why is the image distorted?

Possible contributors to the lag



# Why is the image distorted?

The RC time constant



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

$$\tau = R \cdot C$$

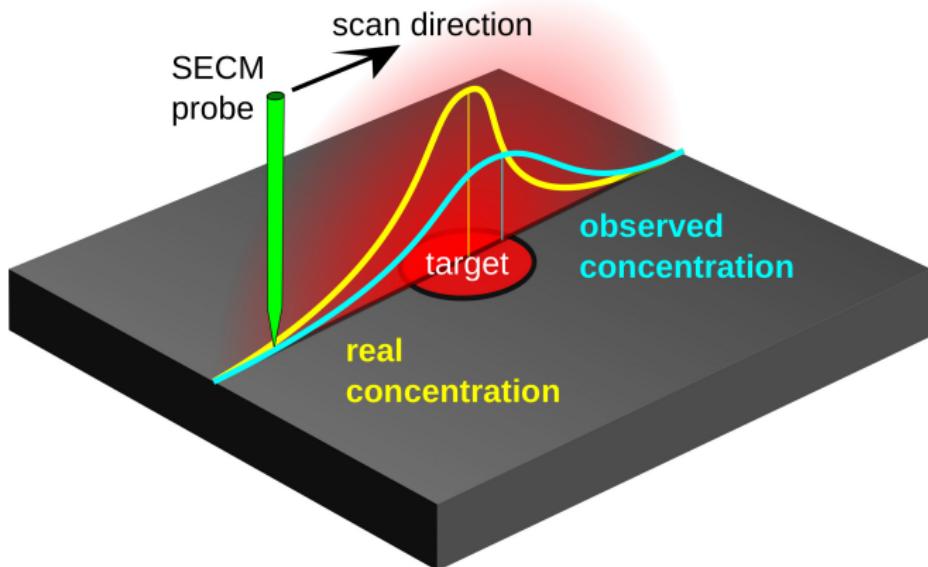
$$R = 5 \text{ G}\Omega$$

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

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

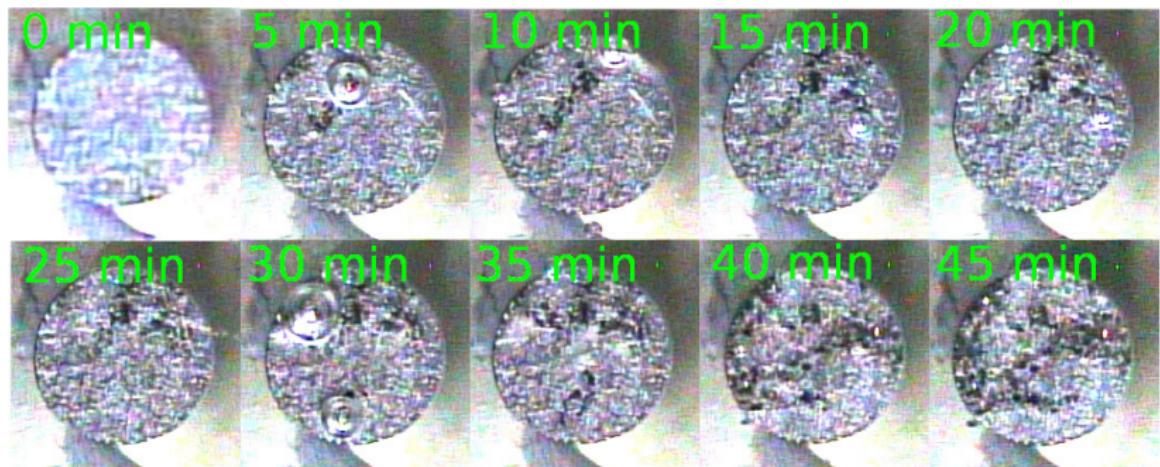
# Distortion of potentiometric imaging

In the case of a linescan



# Why is it so important to complete the scan quickly?

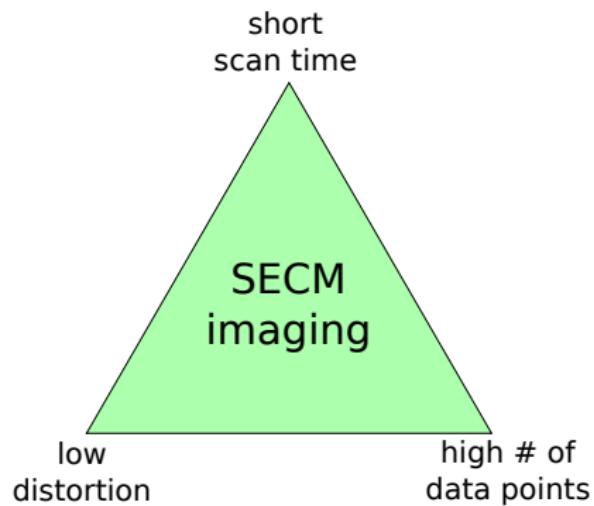
Example: corrosion of a magnesium alloy



Corrosion of the AZ63 magnesium-aluminium-zinc alloy.

# Trade-off triangle of potentiometric SECM

Compromise between the three desired competing properties

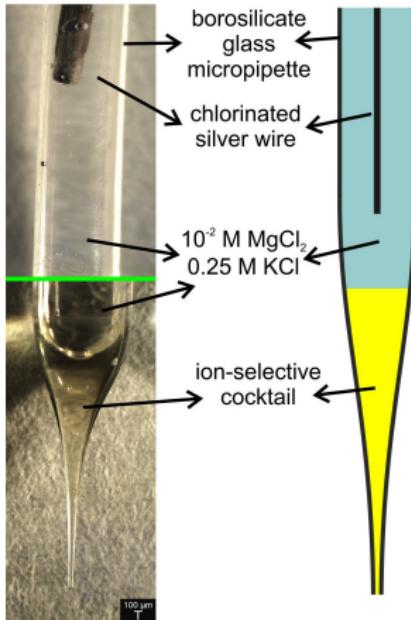


Solution #1: Solid contact micropipettes as SECM probes.

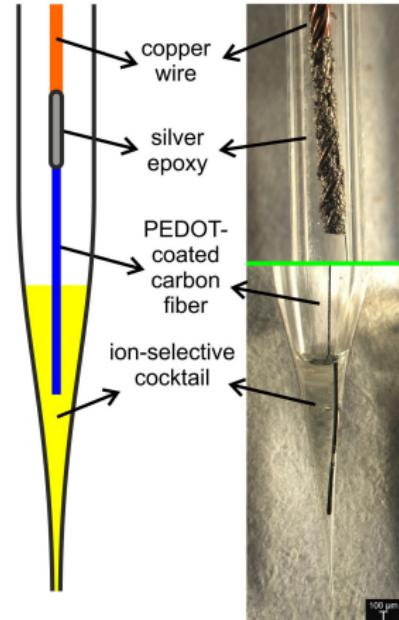
# Liquid vs. solid contact micropipettes

## Comparison of construction

Liquid contact

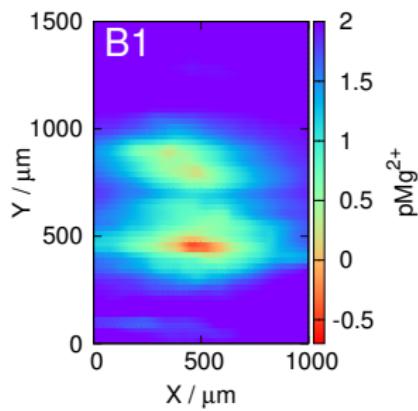


Solid contact

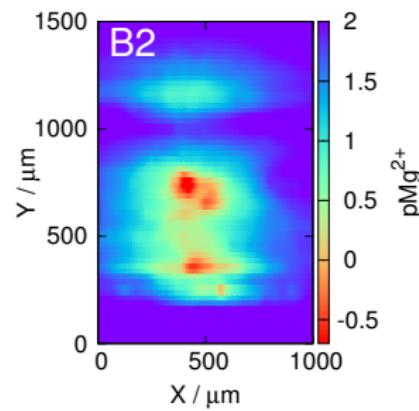


# Application in corrosion science: galvanic corrosion of Mg

Liquid contact



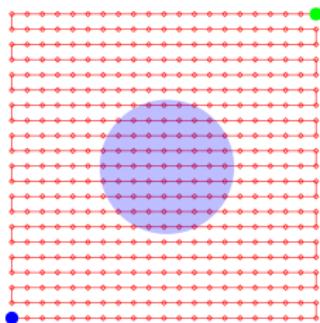
Solid contact



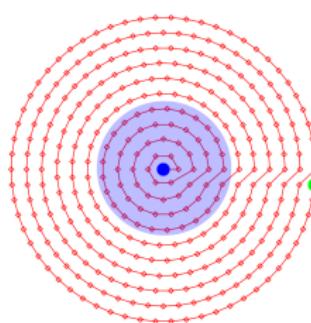
Solution #2: Optimizing scanning patterns and algorithms.

# New SECM scanning patterns based on the polar-coordinate system

Cartesian coordinate  
system based scanning  
pattern



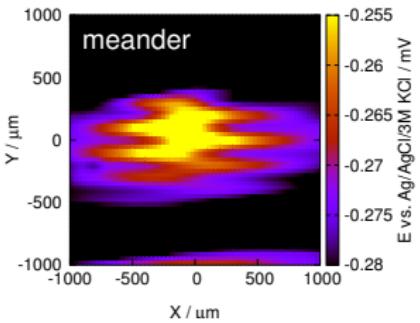
Polar coordinate  
system based scanning  
pattern



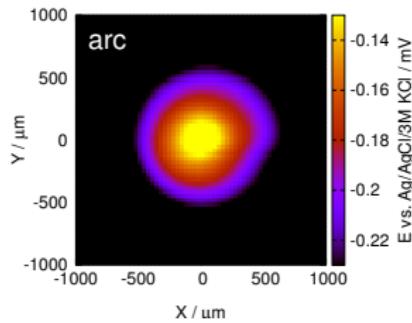
# Confirmation with experimental SECM scans

Recorded using the antimony microelectrode

440 seconds



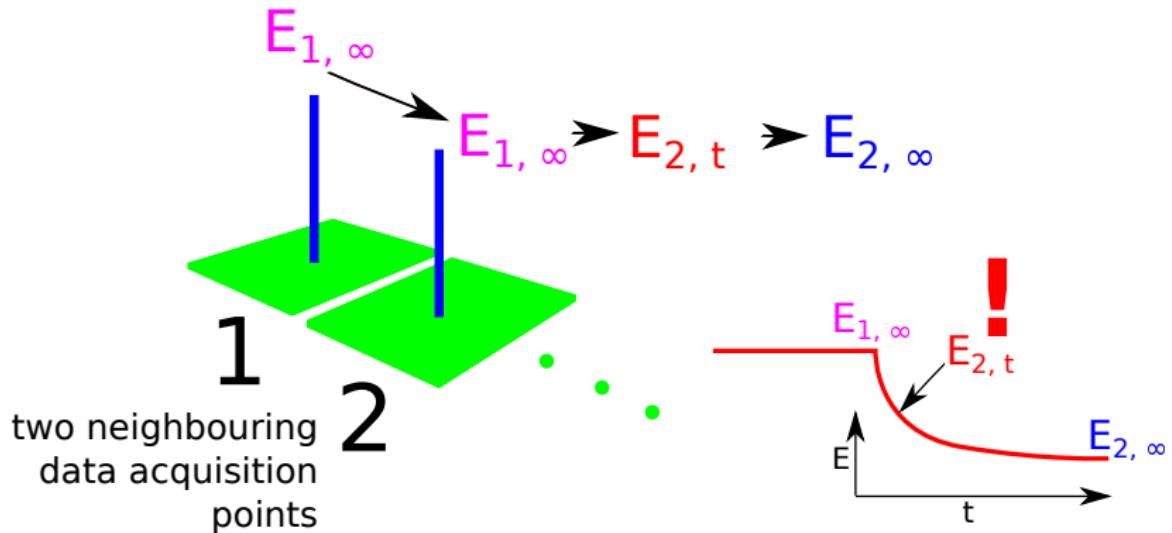
340 seconds



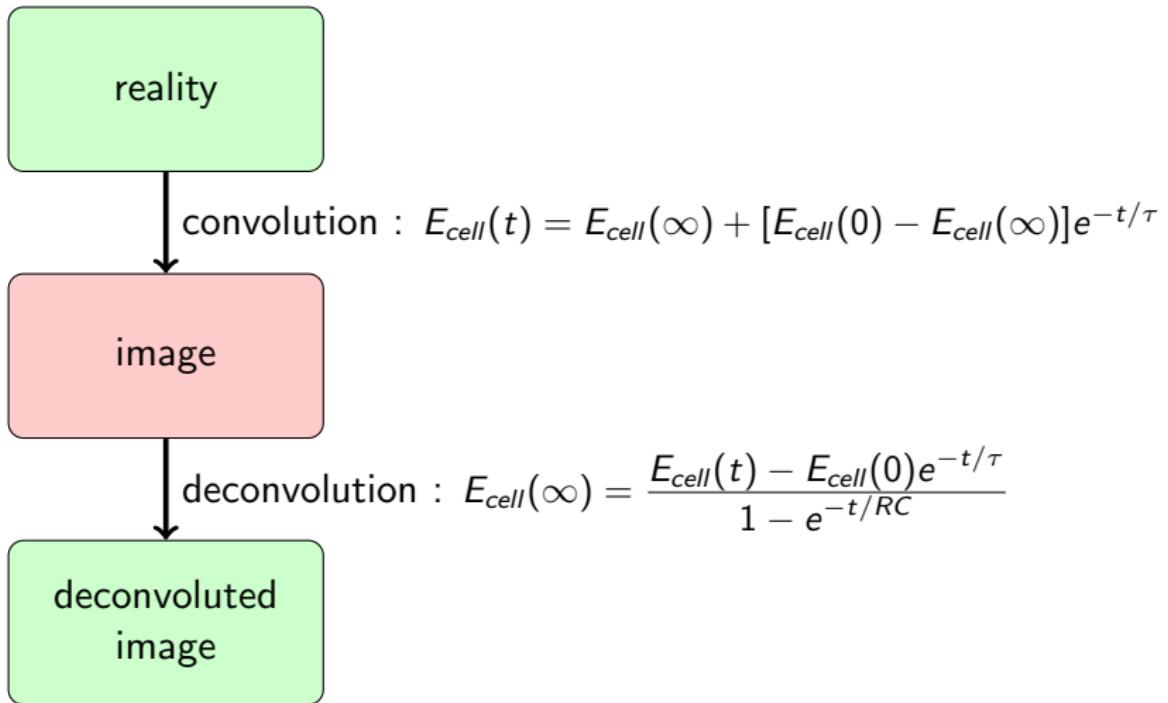
Scans are completed almost 2 times faster,  
images have almost 10 times less distortion.

Solution #3: Signal processing.

## The convolution function of the distortion

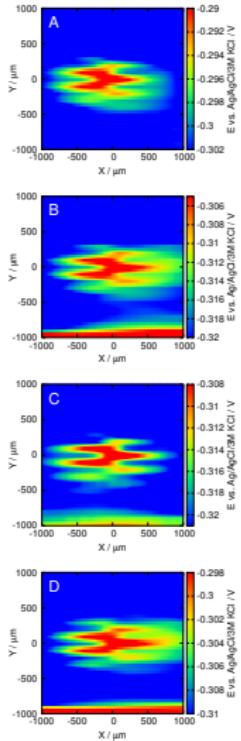


# Convolution and deconvolution

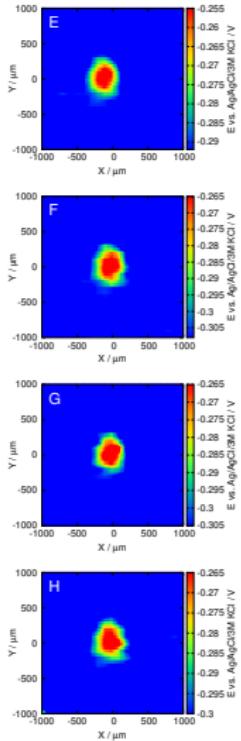


# Deconvolution of potentiometric SECM images

Recorded using the antimony microelectrode following the meander algorithm

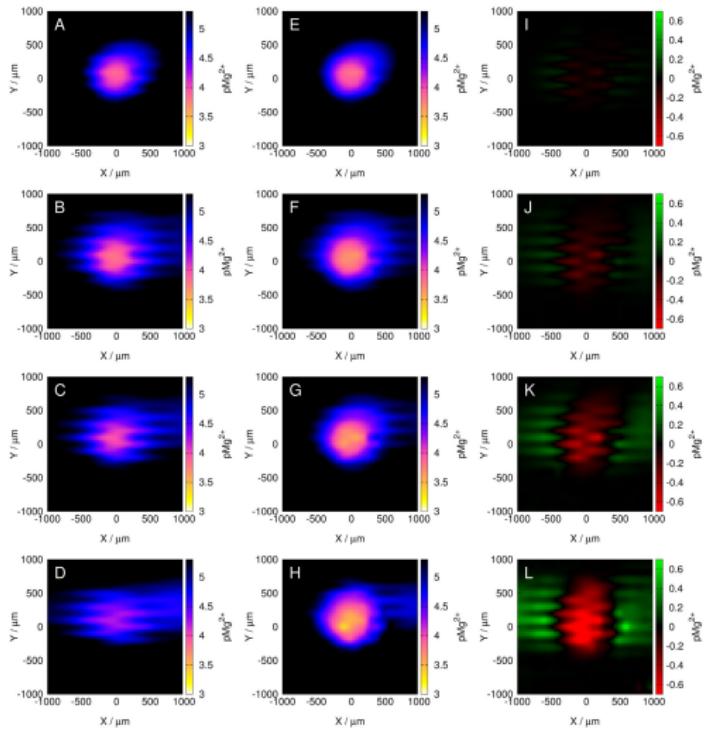


deconvolution  
→



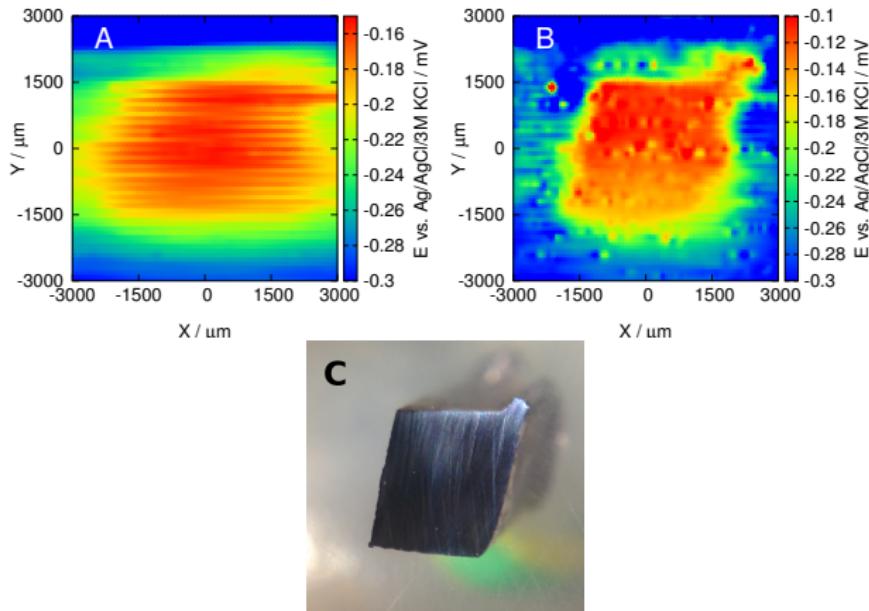
# Deconvolution of potentiometric SECM images

Recorded using the magnesium ISME following the meander algorithm



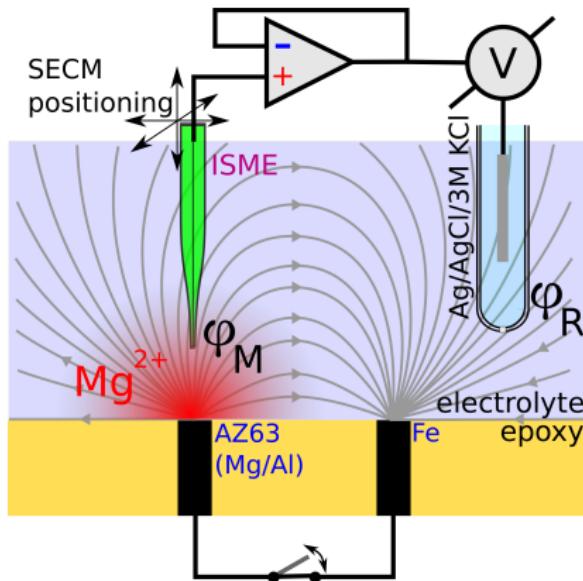
# Practical example: corroding carbon steel sample

Scanned with an antimony microelectrode



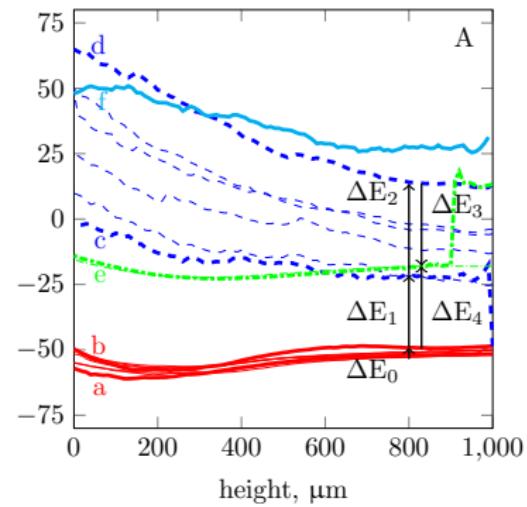
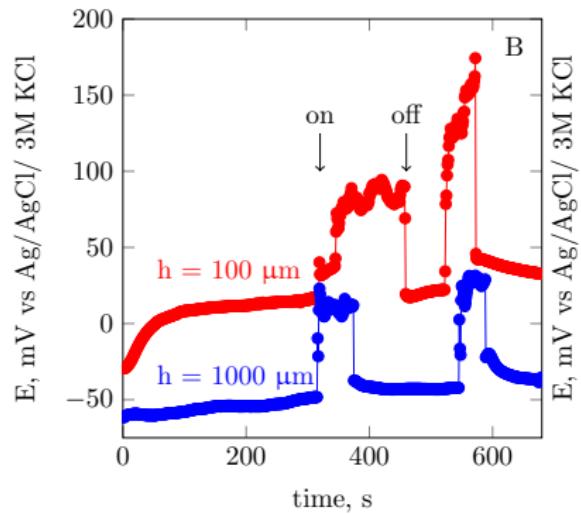
The effect of electric field on potentiometric SECM imaging.

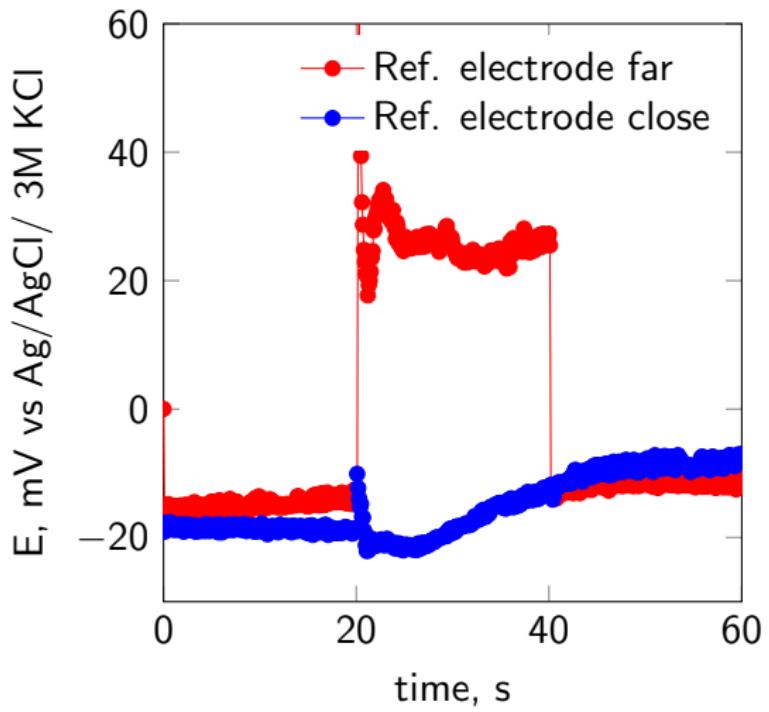
# The electric field during galvanic corrosion



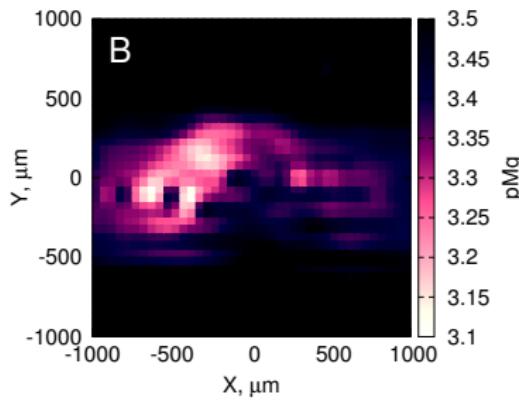
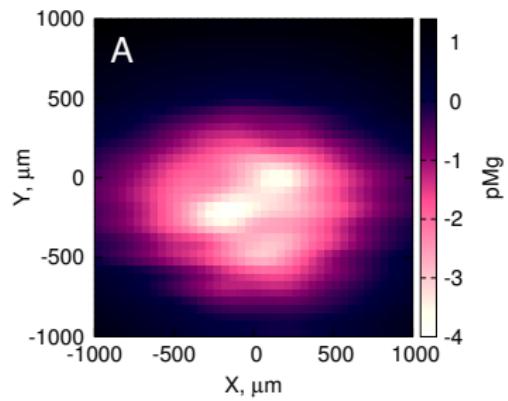
$$\Delta E = E_M - E_R + (\phi_M - \phi_R)$$

# The effect of electric field on the measured potential





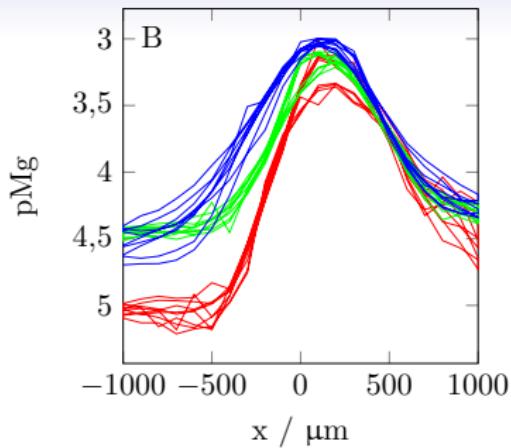
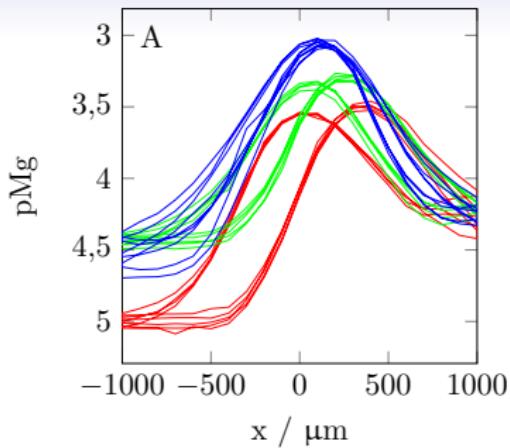
# The effect of electric field on potentiometric SECM imaging



# Conclusions

- 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.
- 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.
- 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. I have shown how big of an error can it cause. 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  $h = 100 \mu\text{m}$  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  $1000 \mu\text{m}/\text{s}$ , and probe movement interval was 0.1 s. 8 scan lines were recorded in each case, 4 forward, 4 reverse scans.