# Recent Advances in Potentiometric Scanning Electrochemical Microscopy

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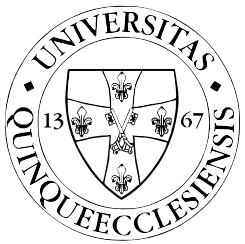
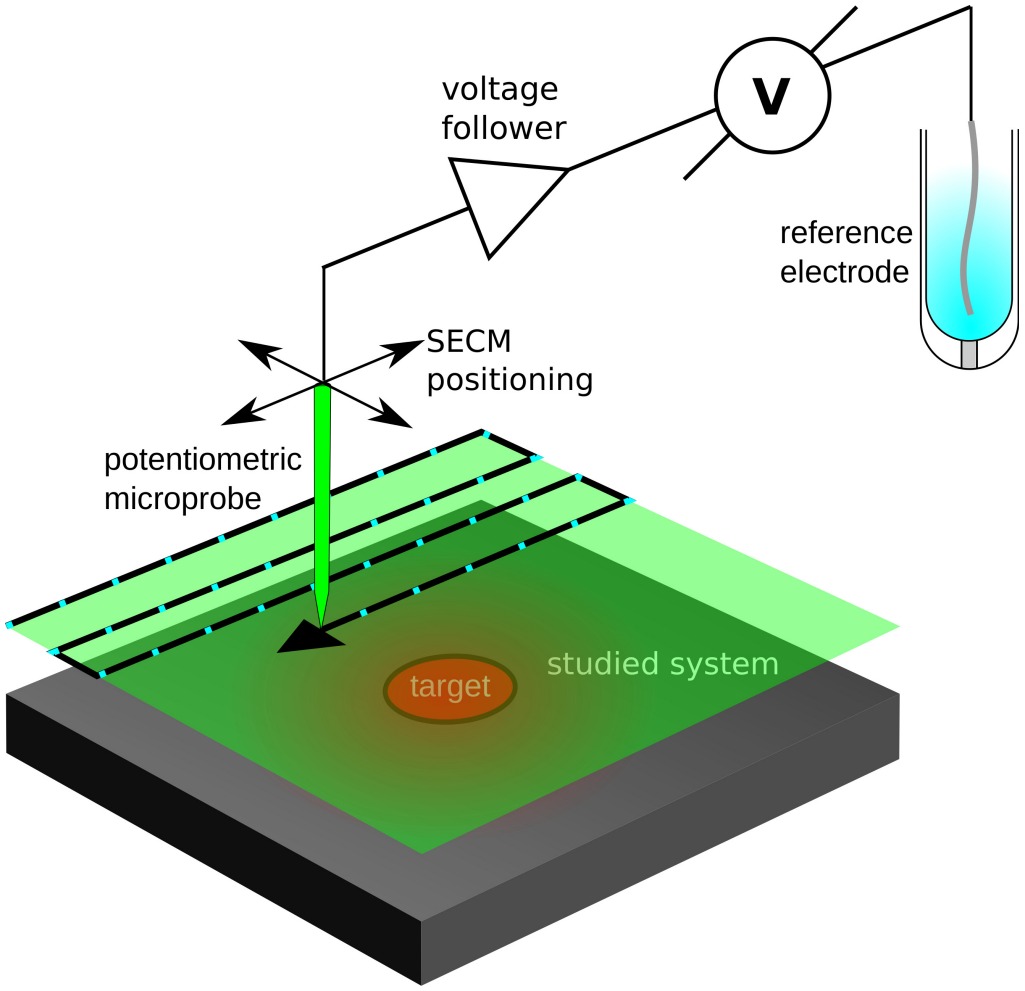



April 18, 2017

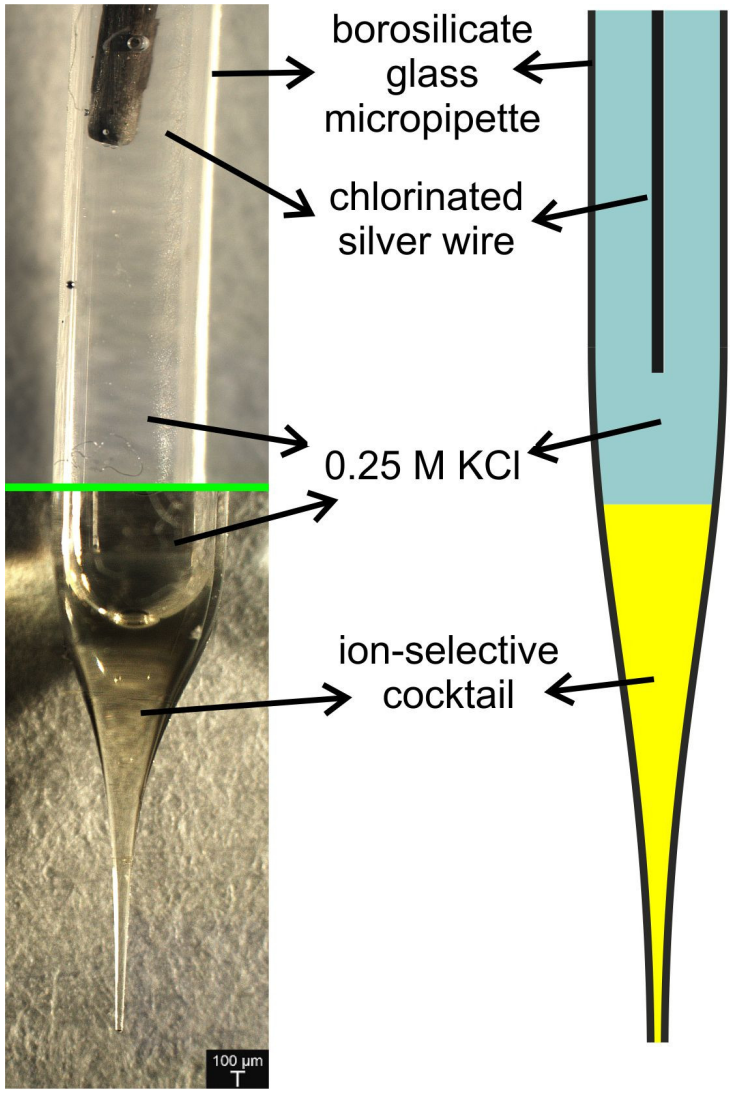
# Potentiometric Scanning Electrochemical Microscopy

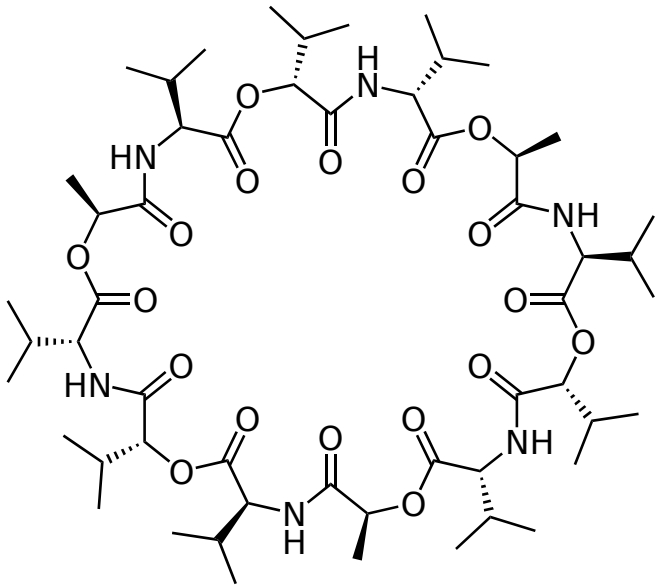
## A Scanning Probe Microscopic technique



# Ion-selective micropipettes

## As SECM probes



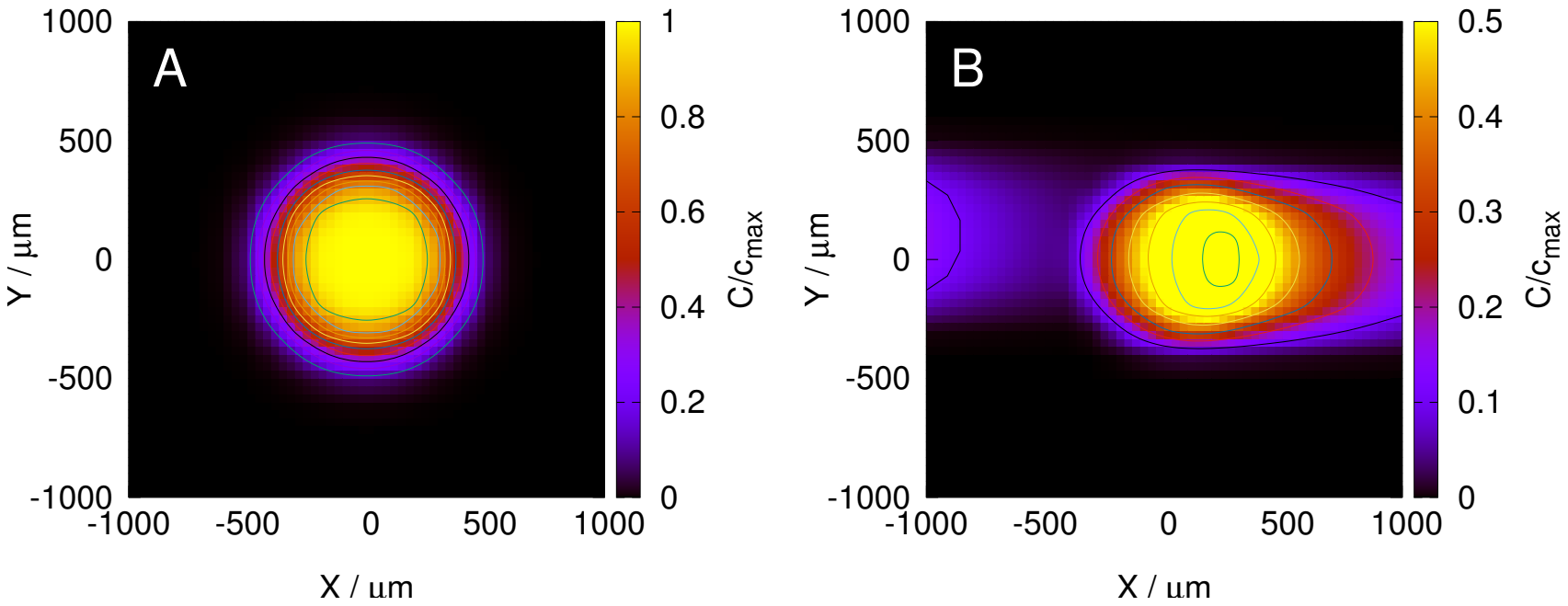
Valinomycin

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

Nikolsky–equation

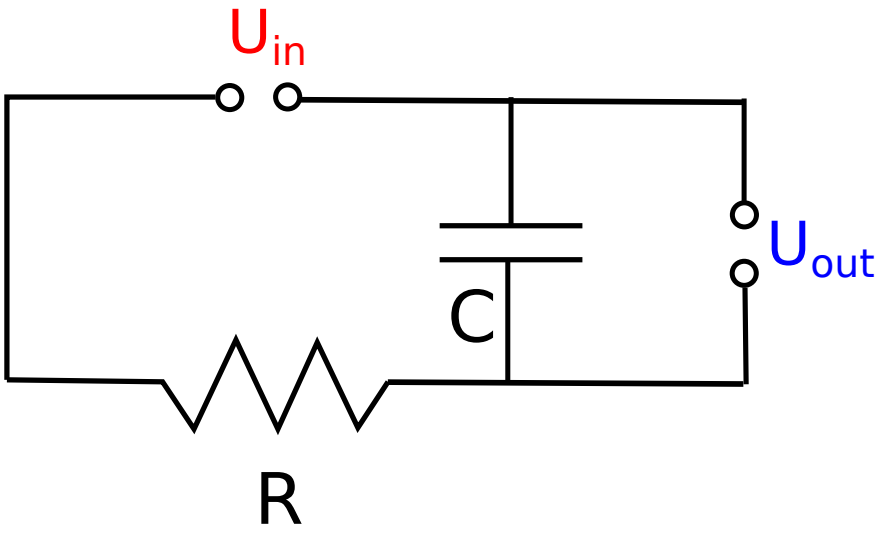
# The problem with potentiometric SECM

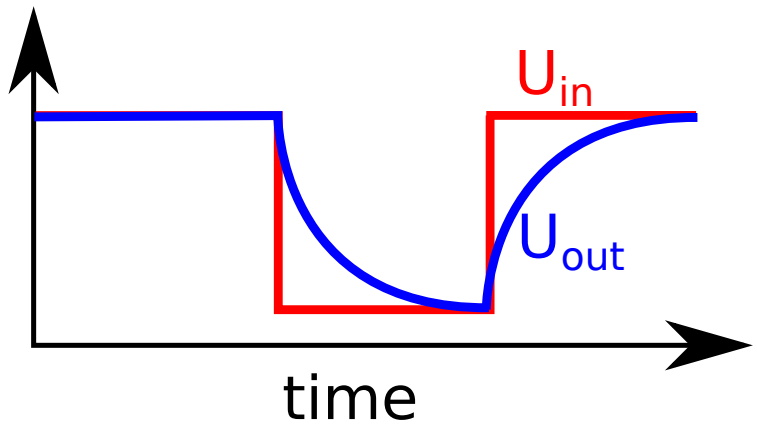
## Distortion at high scan rate



# Why is the image distorted?

## The RC time constant



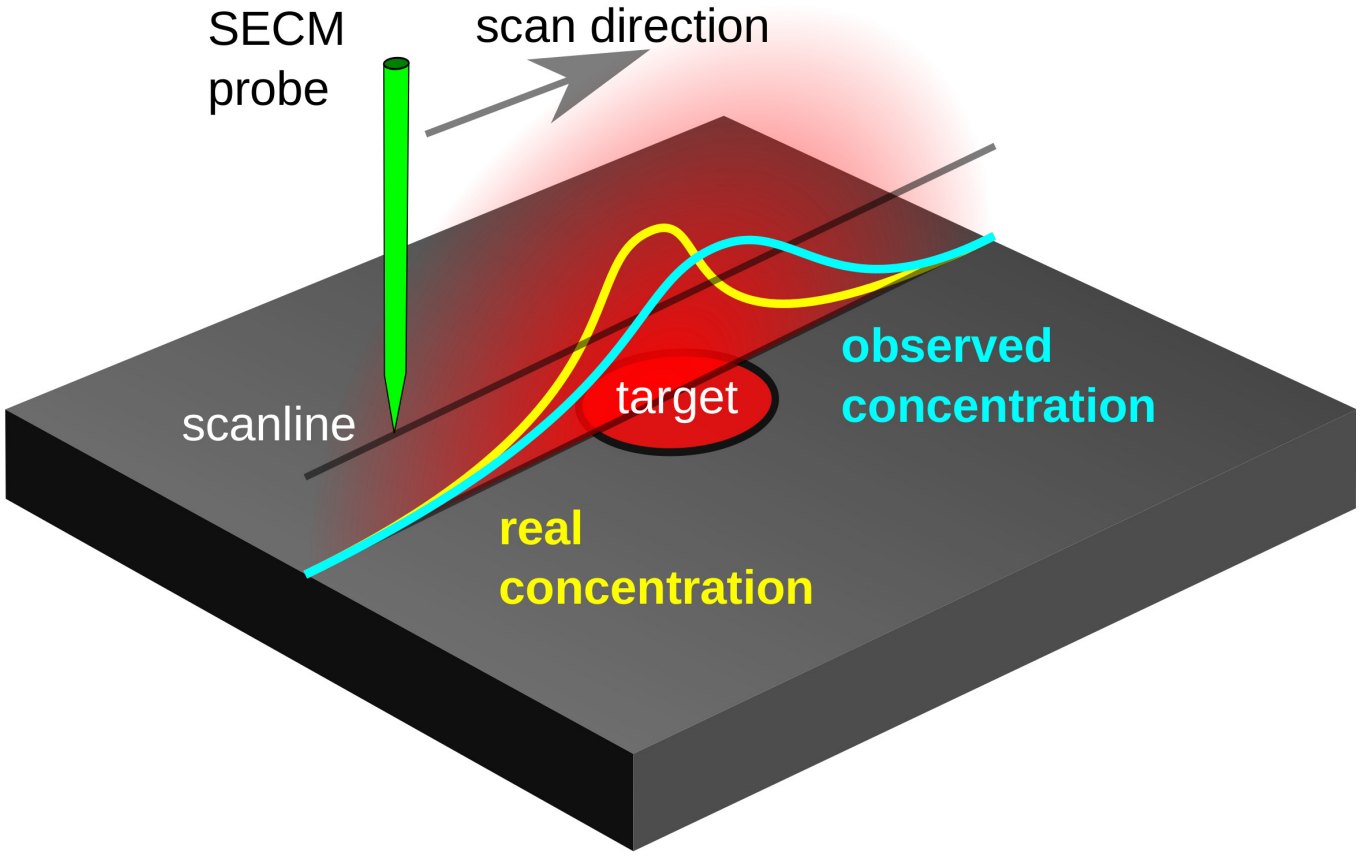




The time required to discharge the capacitor by $\approx 37\%$ $(1/e)$.
Or to charge it by $\approx 63\%$ $(1 - 1/e)$.

$$\tau = R \cdot C$$
$$R = 5\ \mathrm{G\Omega}$$
$$C = 500\ \mathrm{pF}$$
$$\tau = 2.5\ \mathbf{s}$$

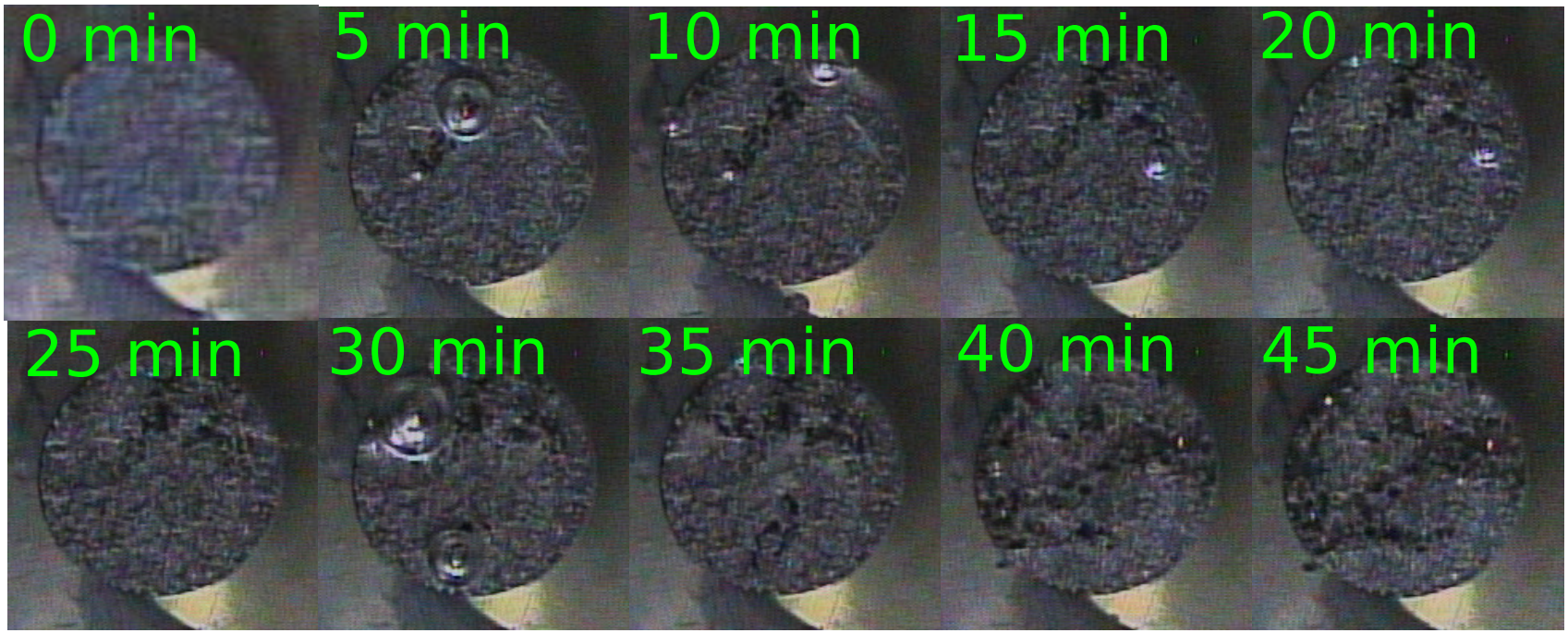
# Distortion of potentiometric imaging

## In the case of a linescan



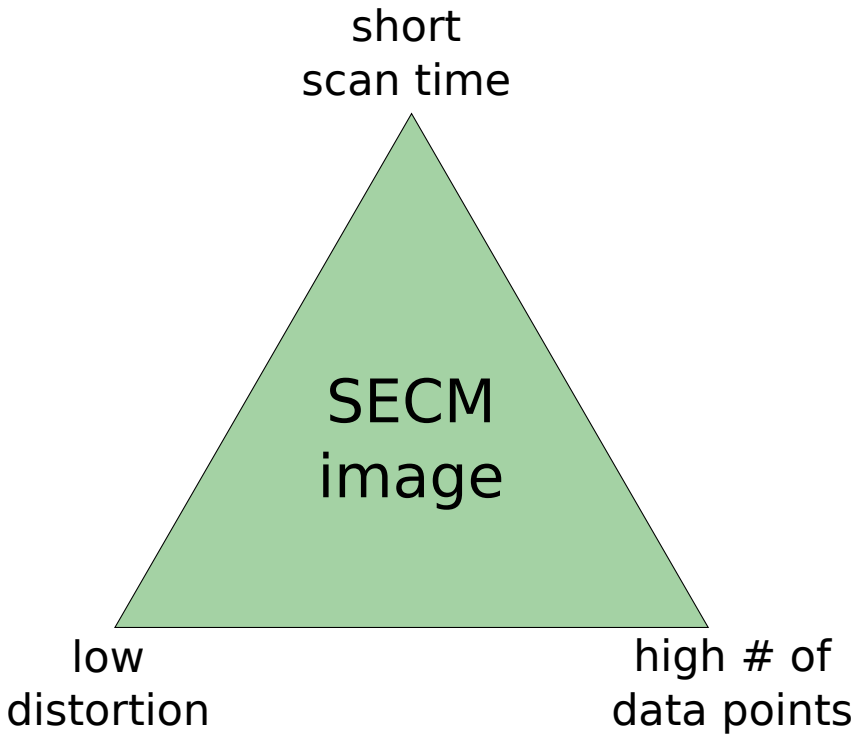
# Why is it so important to complete the scan quickly?

Example: corrosion of a magnesium alloy




Corrosion of the AZ63 magnesium-aluminium-zinc alloy.

# Trade-off triangle of potentiometric SECM

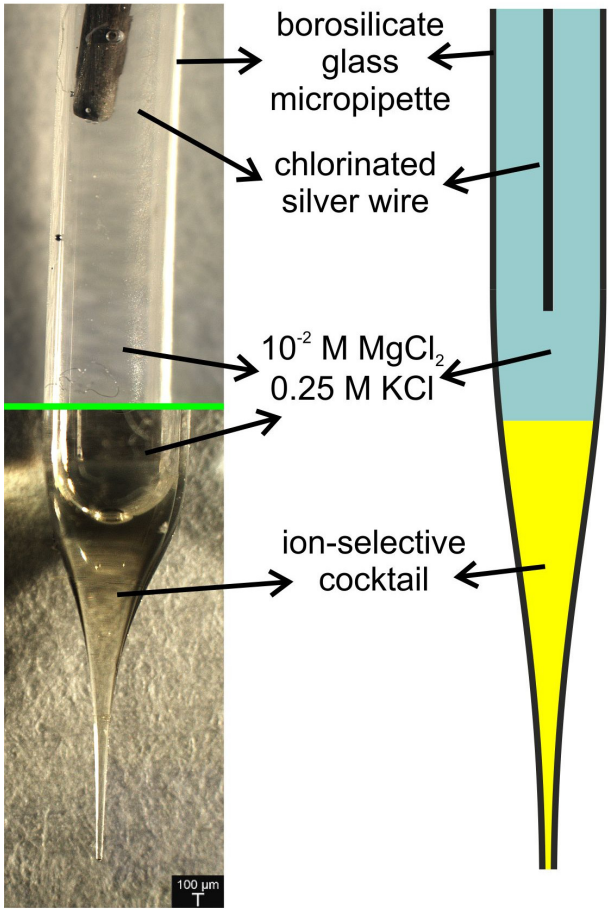


Solution #1: Solid contact micropipettes as SECM probes.

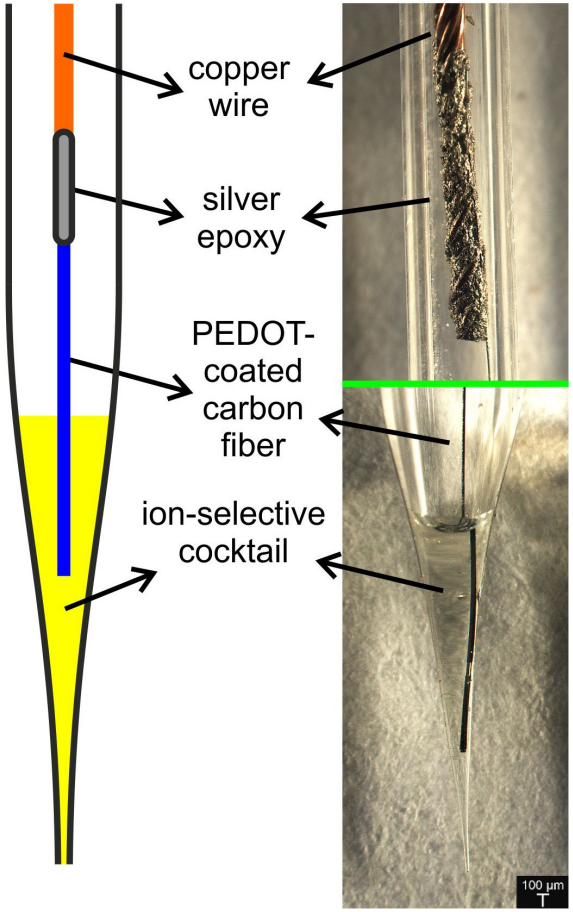
# Liquid vs. solid contact micropipettes

## Comparison of construction

### Liquid contact

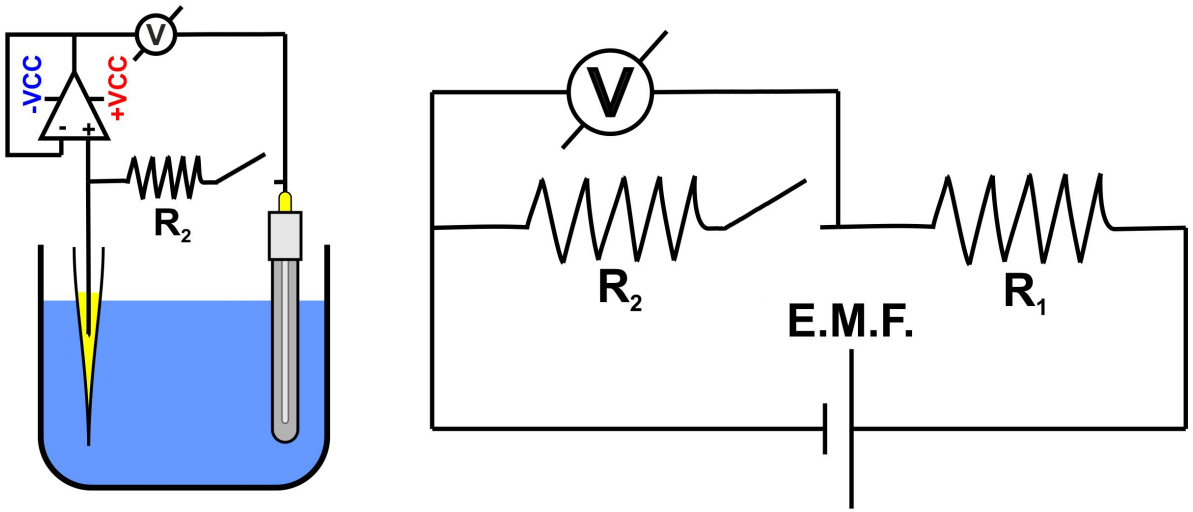



### Solid contact



# Comparison of the electrodes' resistance

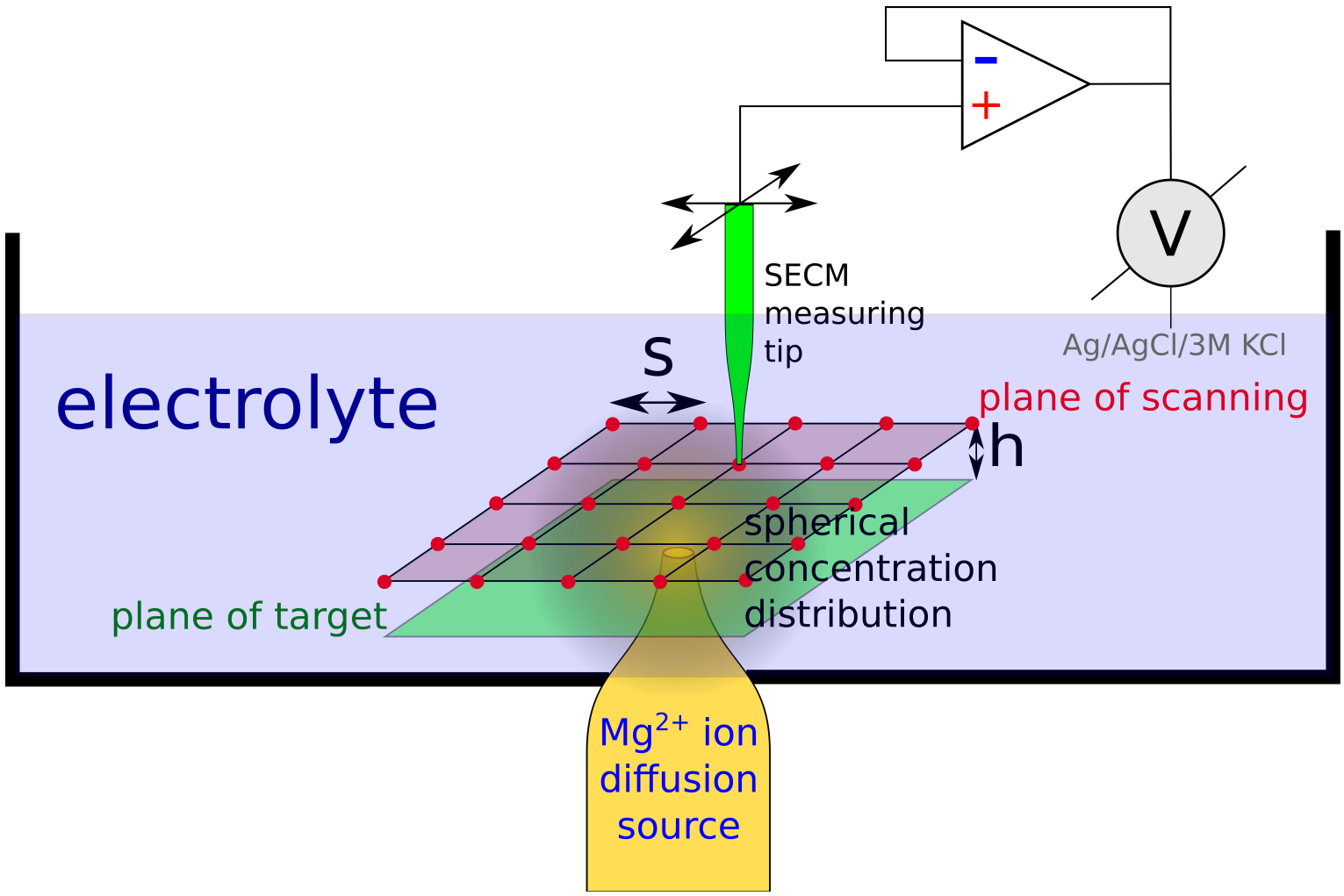
## Experimental setup and result




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

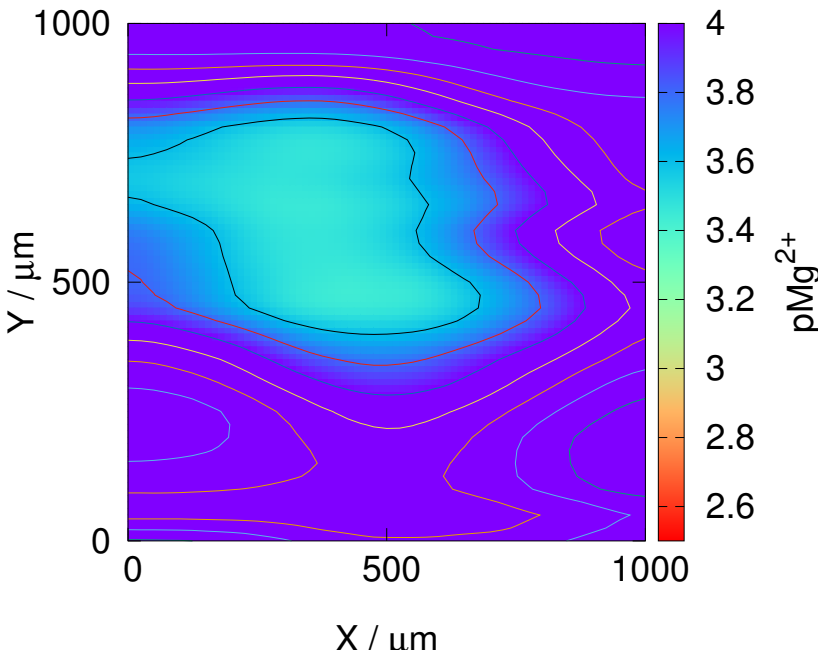
# Comparison of the electrodes' performance

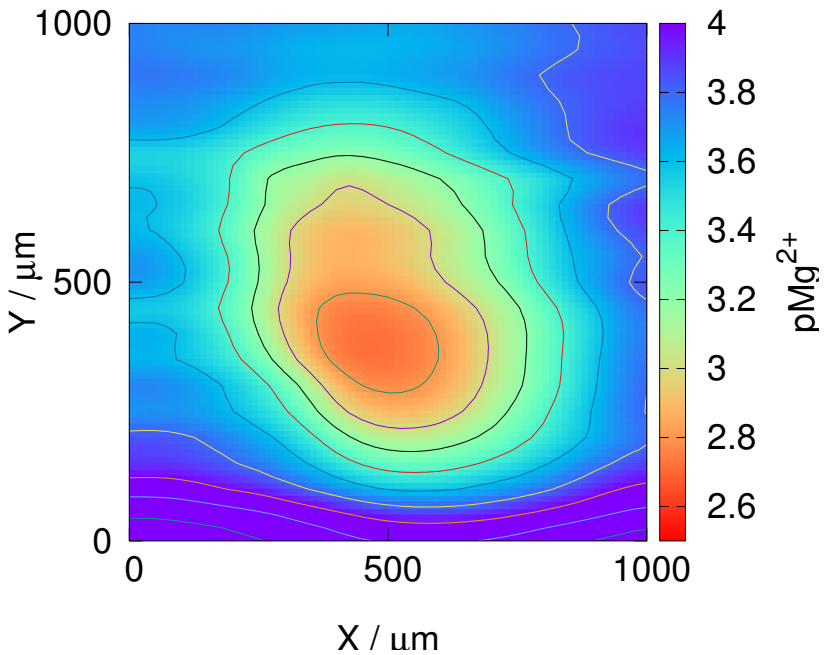
## Experimental setup



# Comparison of the electrodes' performance

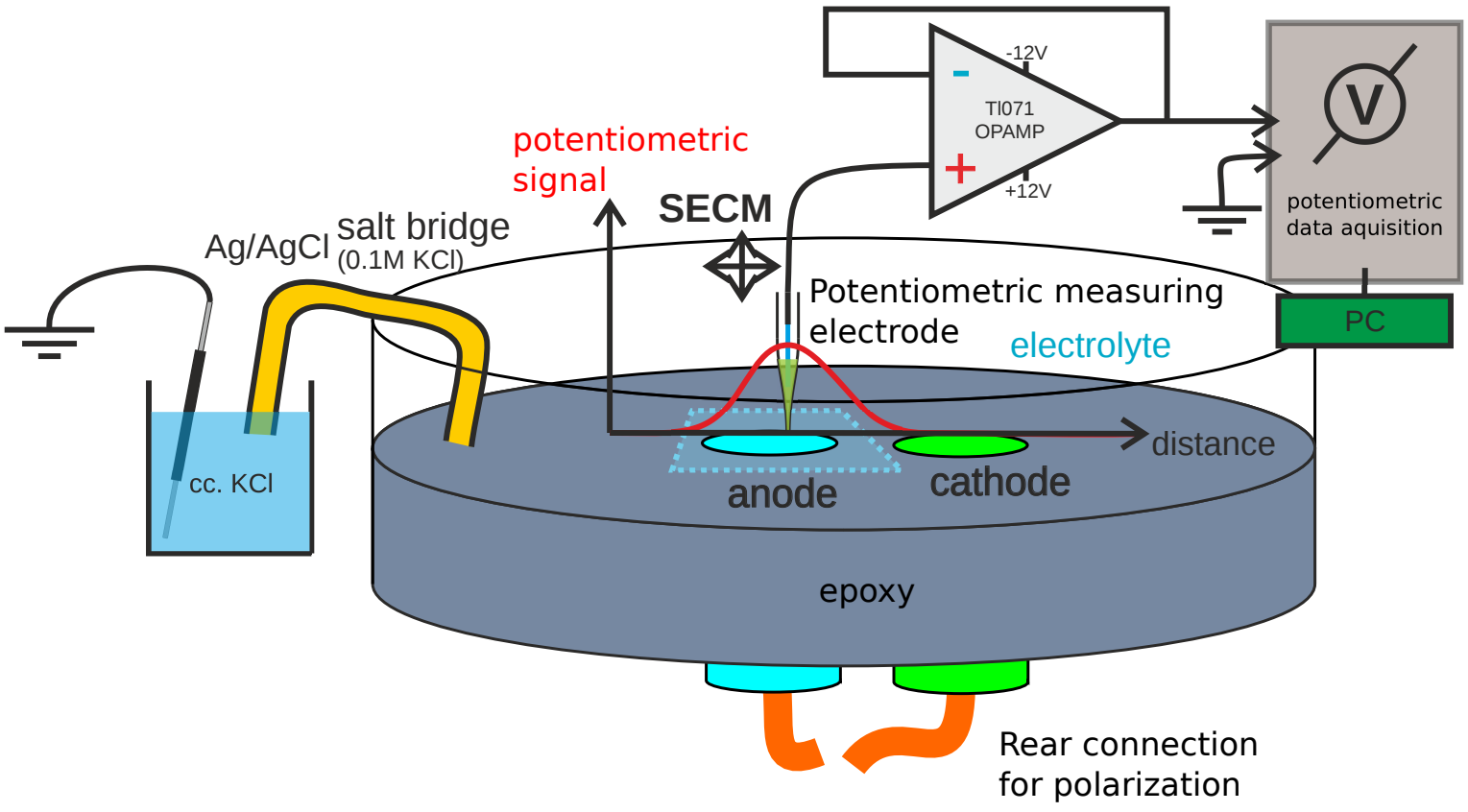
## Results



# Application in corrosion science: galvanic corrosion of Mg

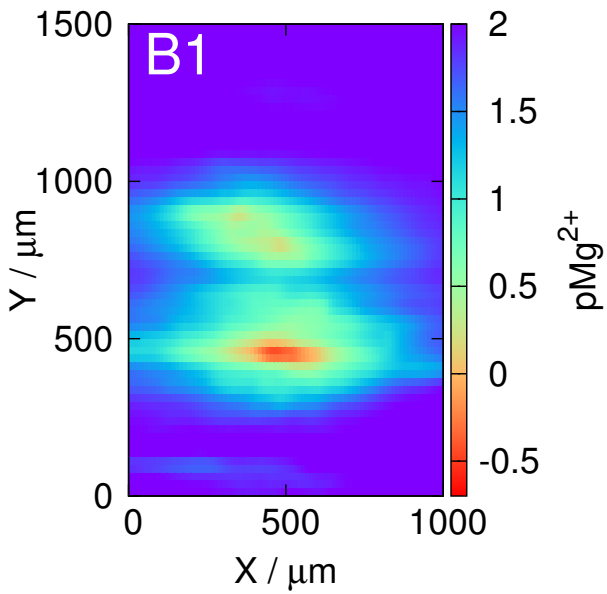
## Experimental setup



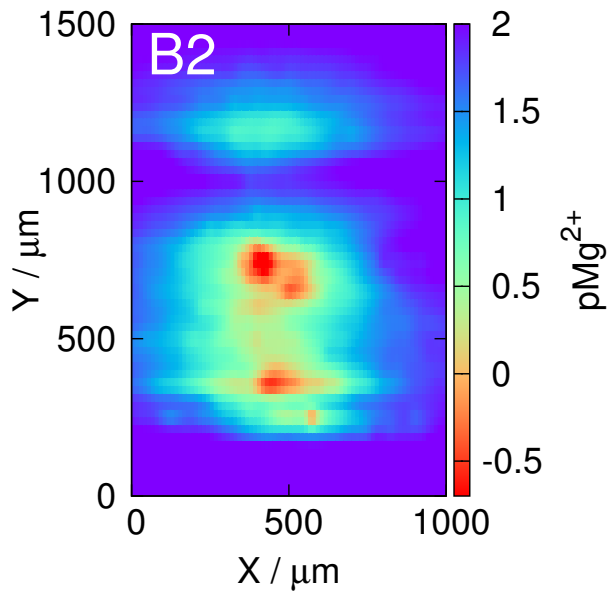
# Application in corrosion science: galvanic corrosion of Mg

## Results

Liquid contact



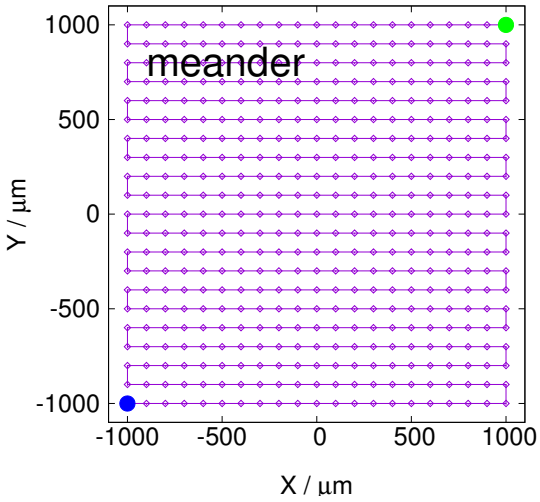

Solid contact

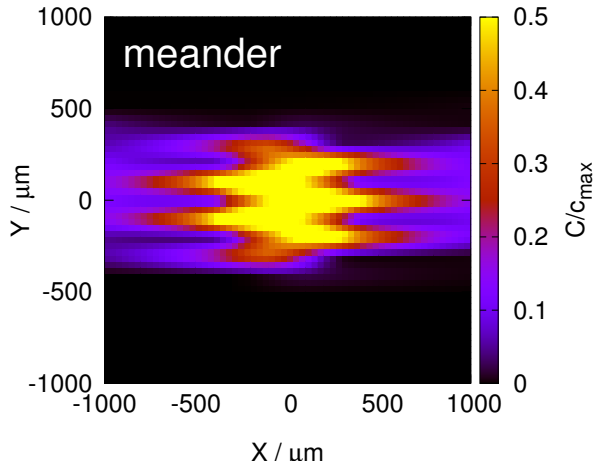


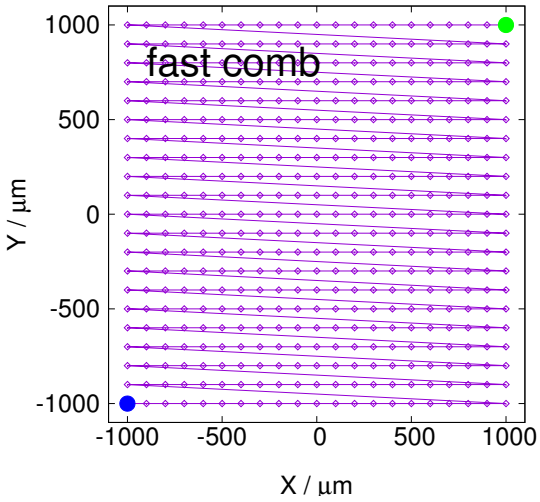
Solution #2: Optimizing scanning patterns and algorithms.

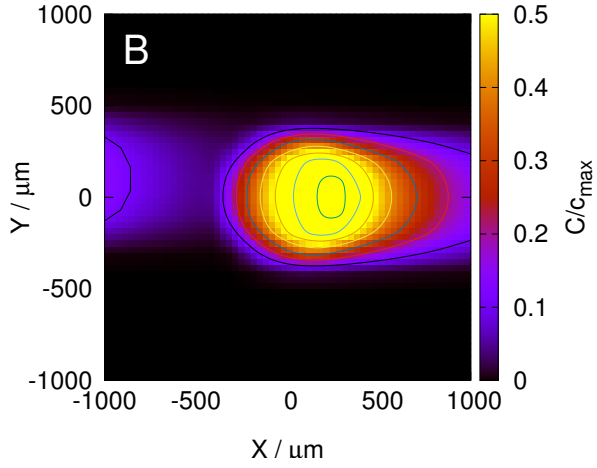
# "Traditional" scanning algorithms for the 2D raster pattern

## 1. "Meander" and "fast comb" scanning algorithms



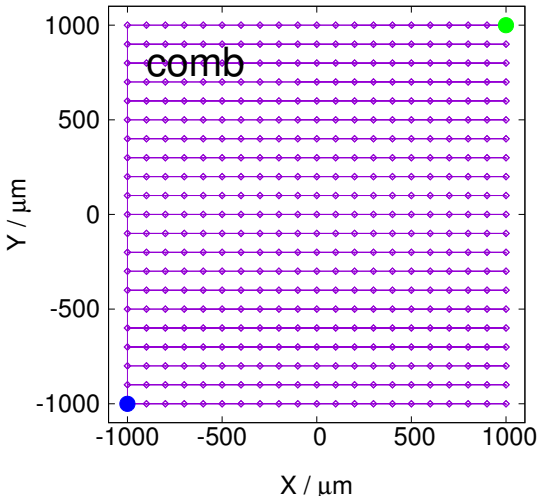



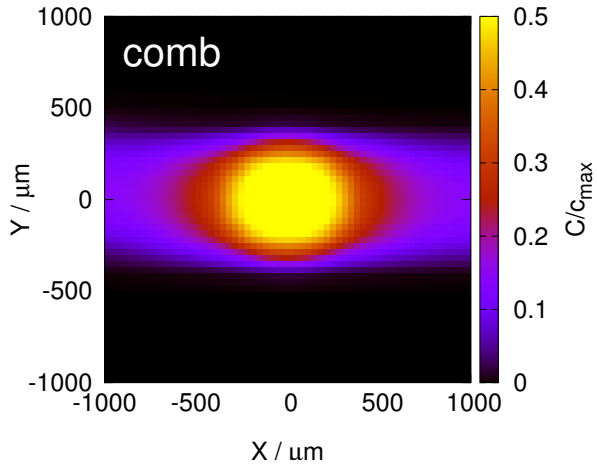



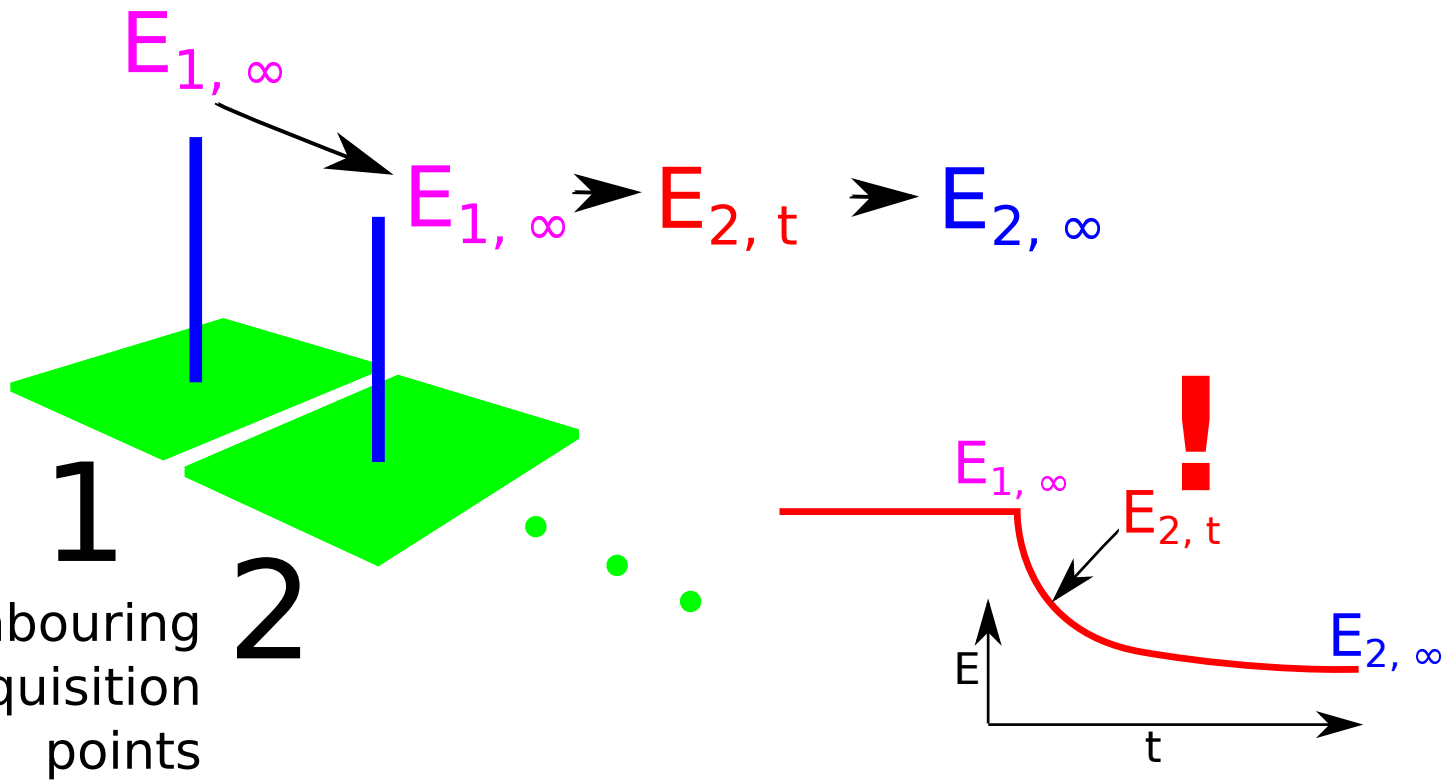
# "Traditional" scanning algorithms for the 2D raster pattern

## 2. "Comb" scanning algorithm



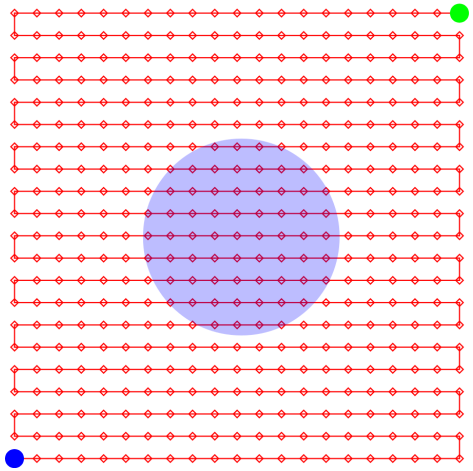



# The RC time constant

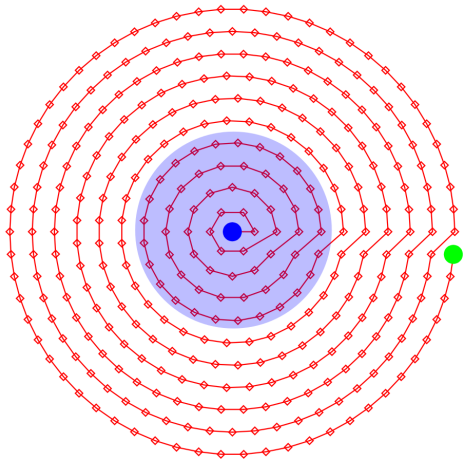


# New SECM scanning patterns based on the polar-coordinate system

Cartesian coordinate system based scanning pattern

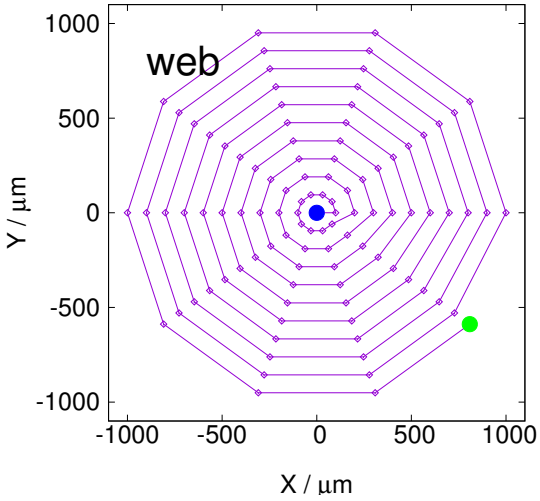


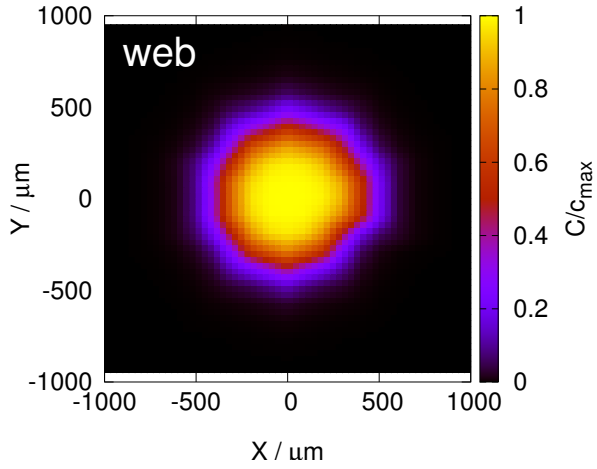
Polar coordinate system based scanning pattern

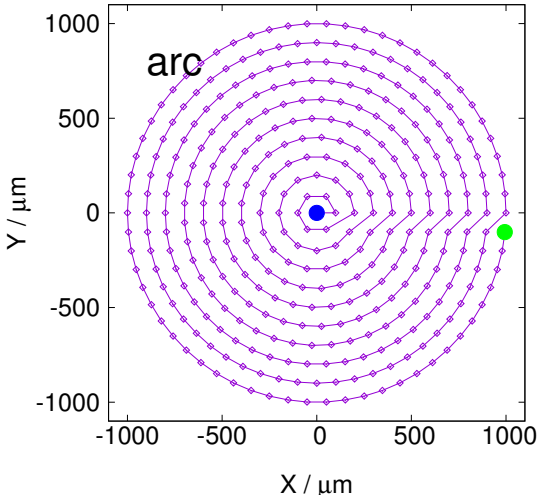


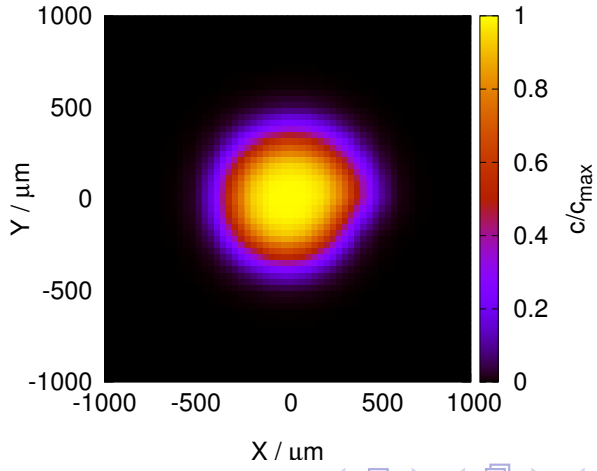
# New SECM scanning patterns based on the polar-coordinate system

## Simulated scans with the "web" and the "arc" algorithms



# Comparison of the simulated scans

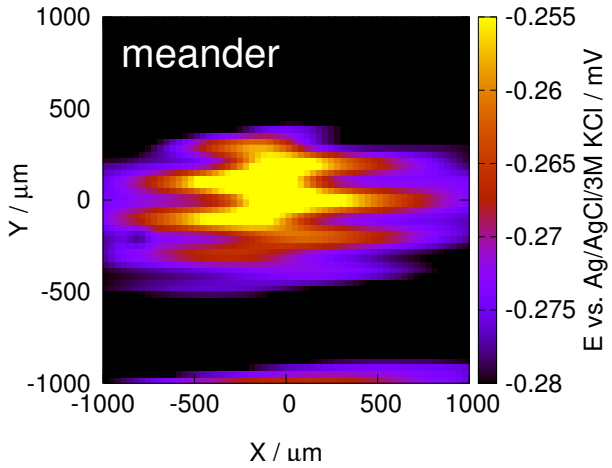
Parameters of the simulations:

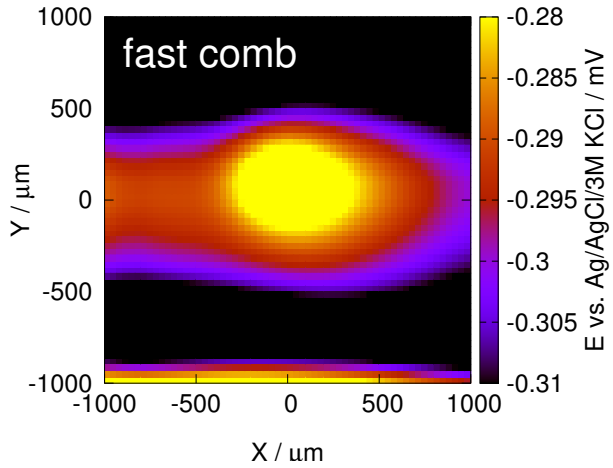
- 2000 $\mu$m $\times$ 2000 $\mu$m scan area,
- 100 $\mu$m $\times$ 100 $\mu$m resolution,
- 1 s for each data aquisition point,
- 500 $\mu$m/s probe positioning speed.

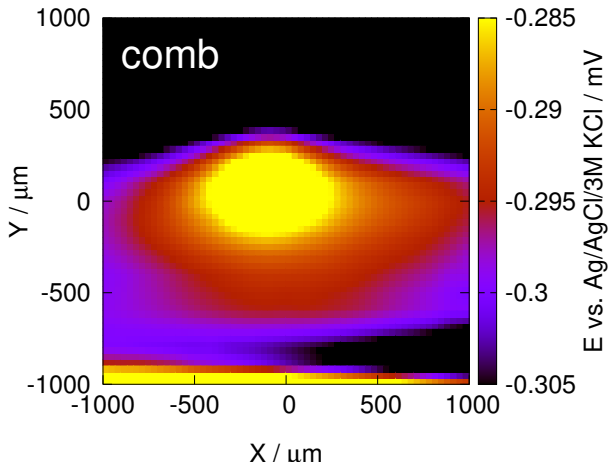
| Algorithm | #n | time (s) | mean squared error |
|---|---|---|---|
| Meander | 441 | 440 | $2.75 \times 10^{-2}$ |
| Fast comb | 441 | 520 | $2.07 \times 10^{-2}$ |
| Comb | 441 | 881 | $2.75 \times 10^{-2}$ |
| Web | 110 | 109 | $9.63 \times 10^{-3}$ |
| Arc | 341 | 340 | $2.95 \times 10^{-3}$ |

# Confirmation with experimental SECM scans

## Traditional scanning algorithms



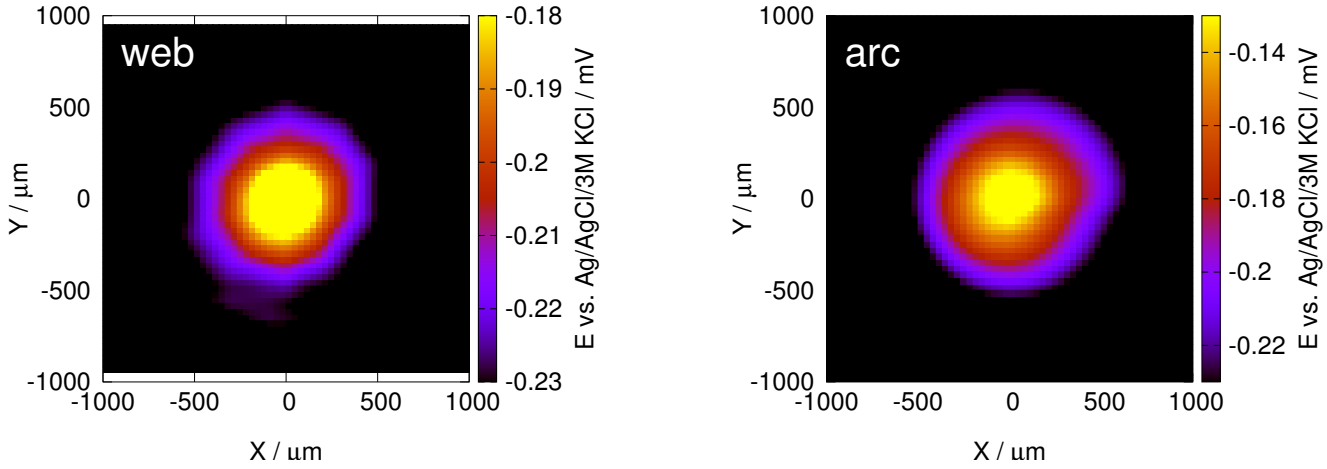




Images recorded with the meander, fast comb, and comb algorithms.

# Confirmation with experimental SECM scans

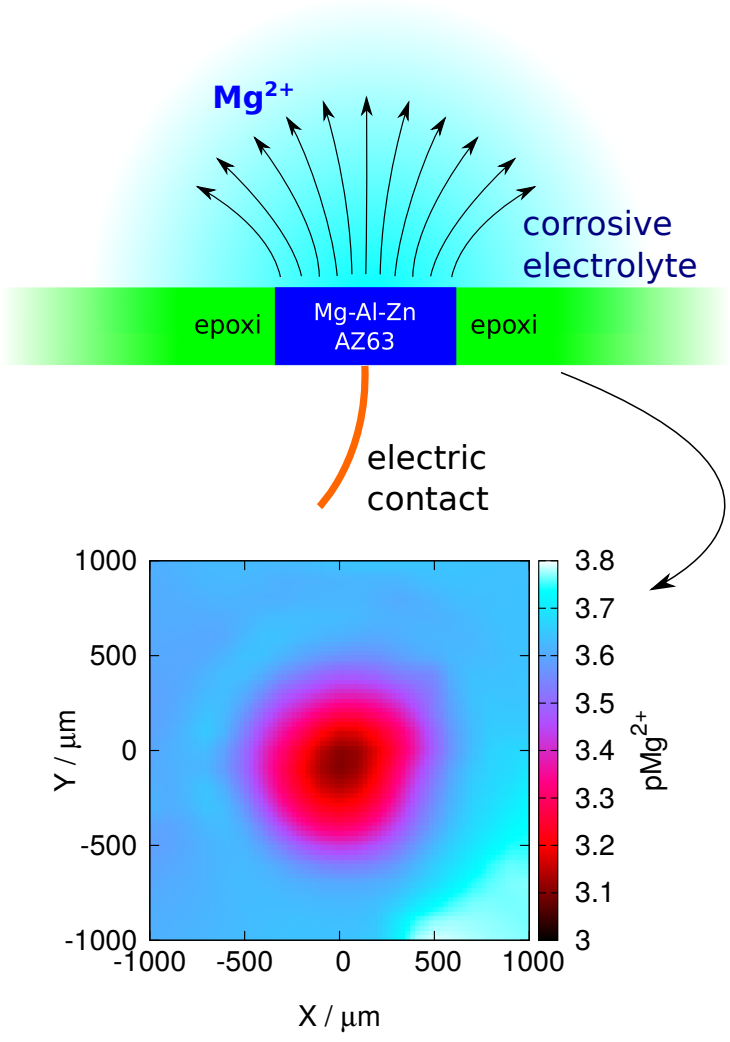
## New scanning algorithms

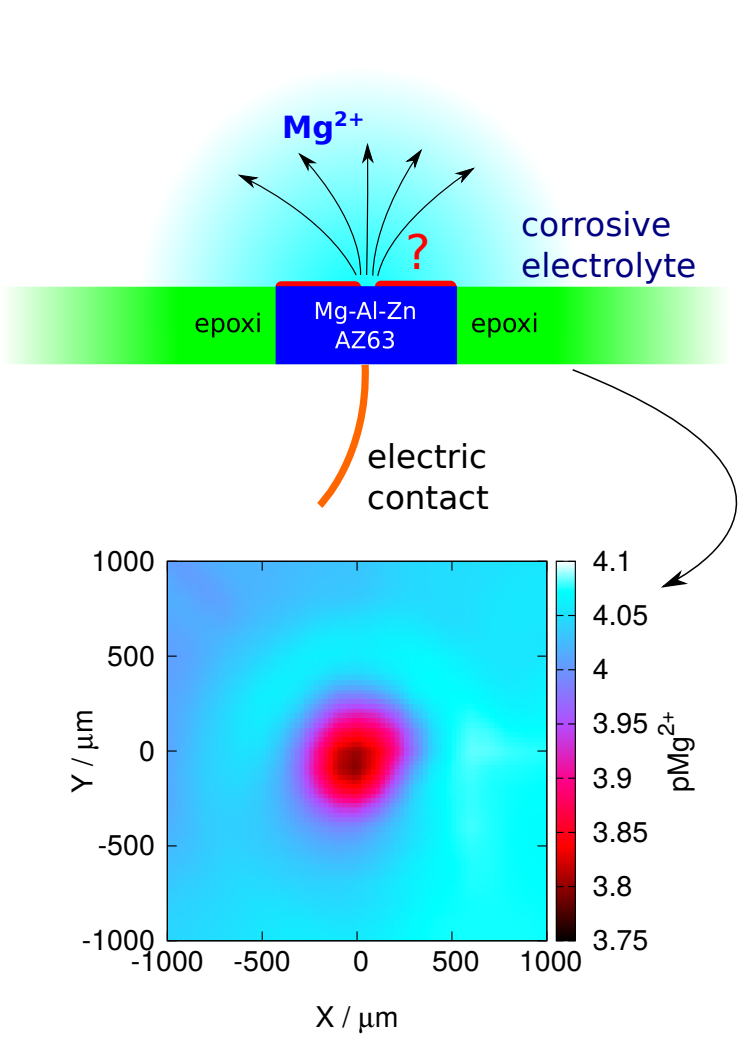



Images recorded with the web, and the arc algorithms.

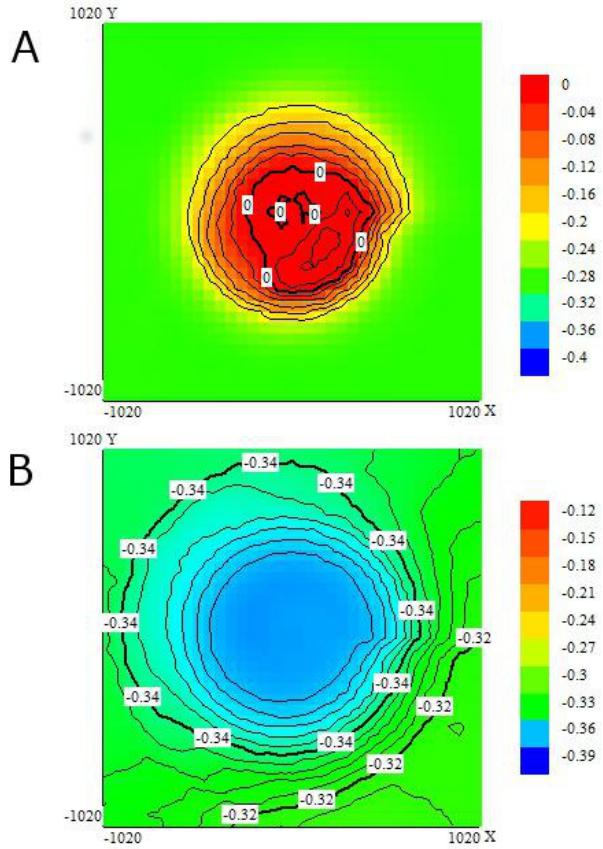
Scans are completed 75% and 20% faster, images have almost 10 times less distortion.

# Example 1: SECM study on the effectiveness of corrosion protection coatings using the arc scanning pattern



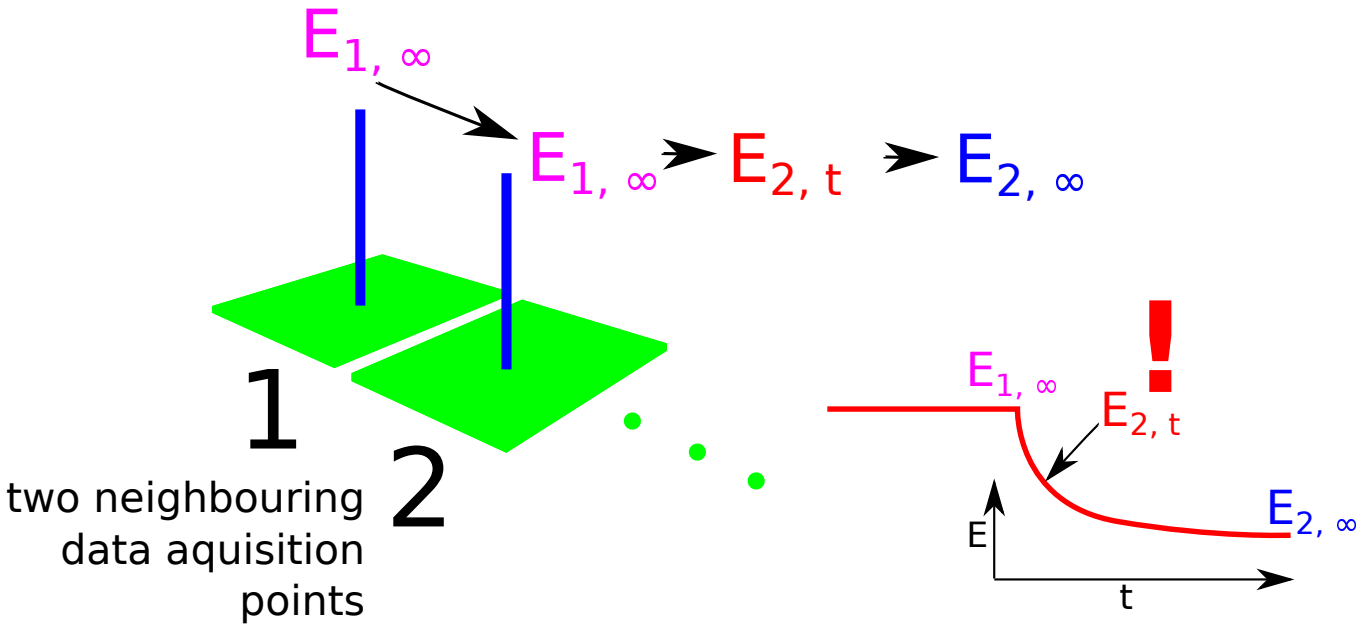
# Example 2: SECM study on the galvanic corrosion of the AZ63 alloy and iron, using the arc scanning pattern




pH-dependent potential map above the corroding (A) magnesium, and (B) iron samples.

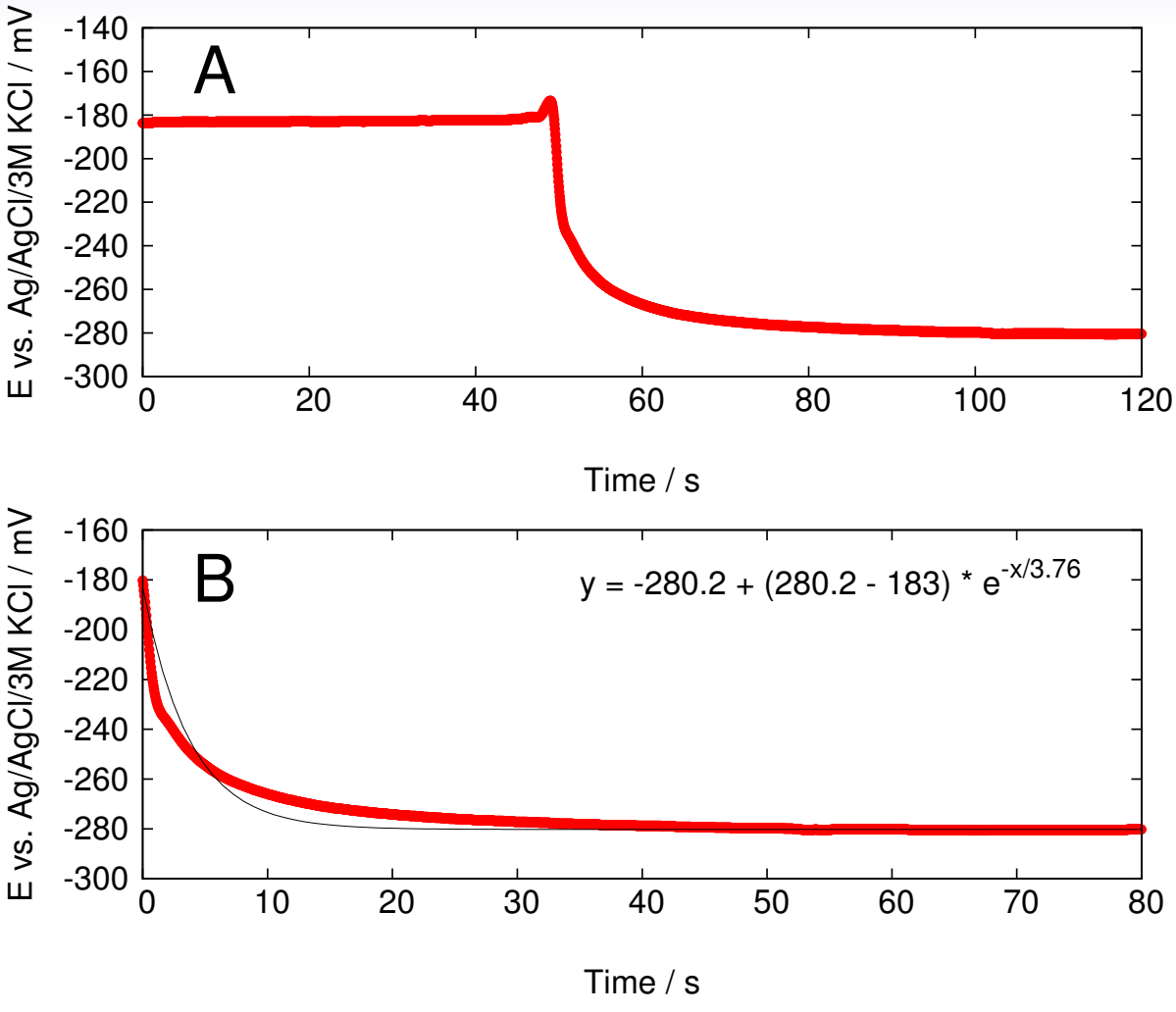
Solution #2: Signal processing.

# Deconvolution of the distorted image




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

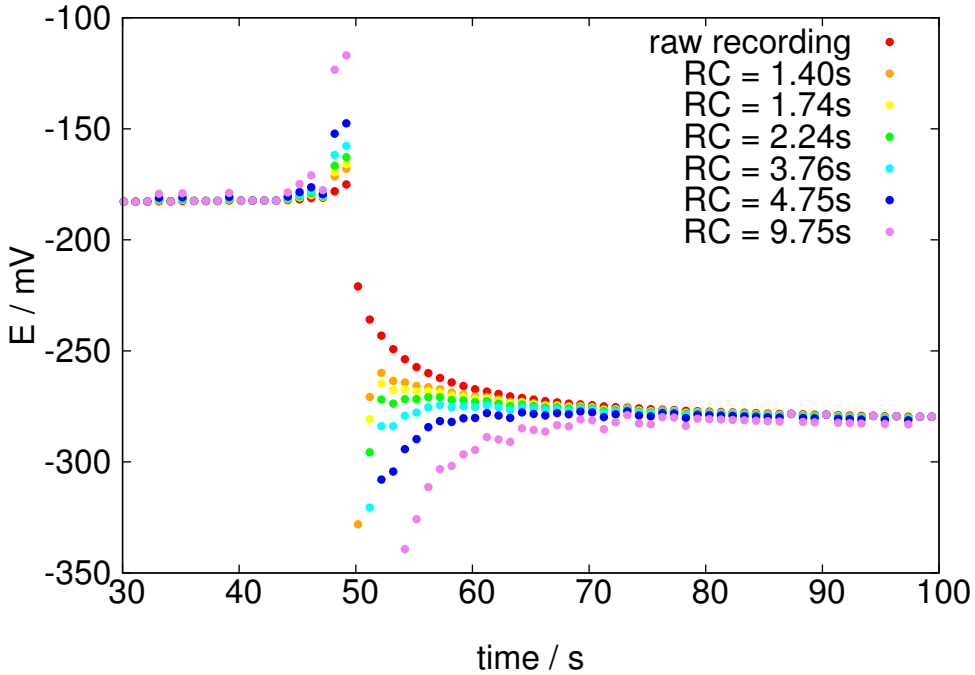
$$E_{cell}(\infty) = \frac{[E_{cell}(t) - E_{cell}(0)]e^{-t/RC}}{1 - e^{-t/RC}}$$




Response of an antimony/antimony-oxid - Ag/AgCl/3M KCl cell when pH changes from 4 to 6. RC time constant was determined from the fit.

# Minimal working example:

## Deconvolution of a response to activity step



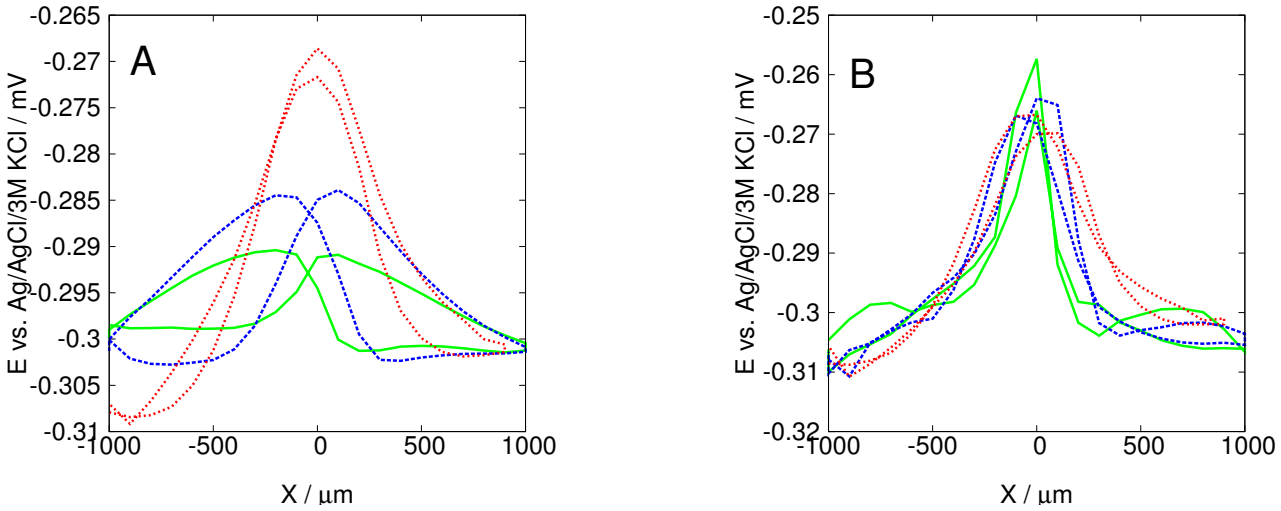

Transient response of the antimony microelectrode to analyte activity step (red), and deconvolutions performed with different $RC$ time-constants. The measured time-constant was $\tau = 3.76s$ (cyan).

# Comparison of the deconvoluted time-potential recordings.

| $e^{-0.5/RC}$ | $RC(s)$ | Mean squared error |
|---|---|---|
| raw recording (0) | raw recording (0) | 53.43 |
| 0.7 | 1.4 | 22.03 |
| 0.75 | 1.74 | 15.88 |
| 0.8 | 2.24 | 9.01 |
| **0.8755** | **3.76** | **3.83** |
| 0.9 | 4.75 | 16.99 |
| 0.95 | 9.75 | 781.94 |

# One step further

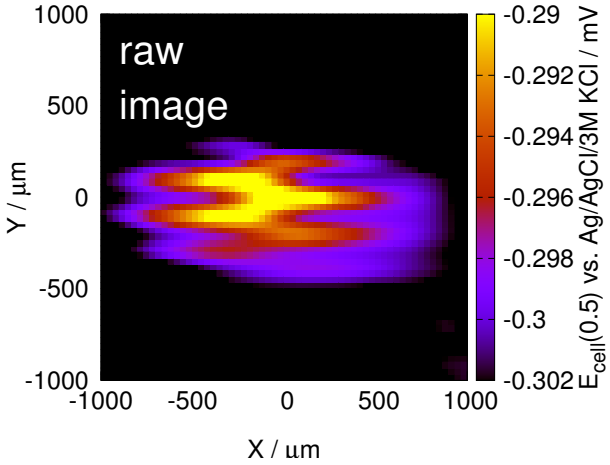
## Deconvolution of linescans

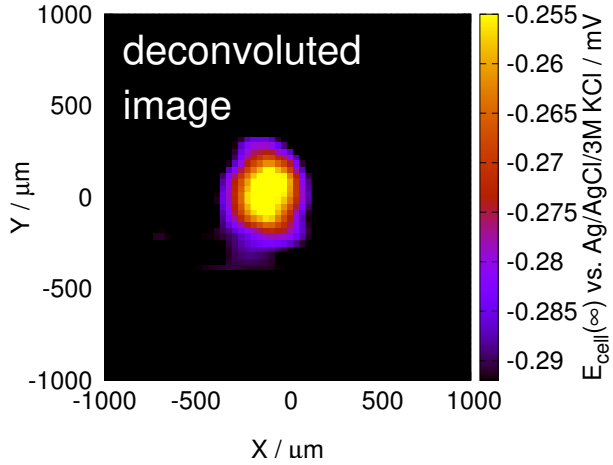



(A) Raw, and, (B) deconvoluted SECM linescans above the center of the target, at h = 100 mm height, using three different equilibration periods: 0.5 s, (green), 1 s, (blue), and 5 s, (red).

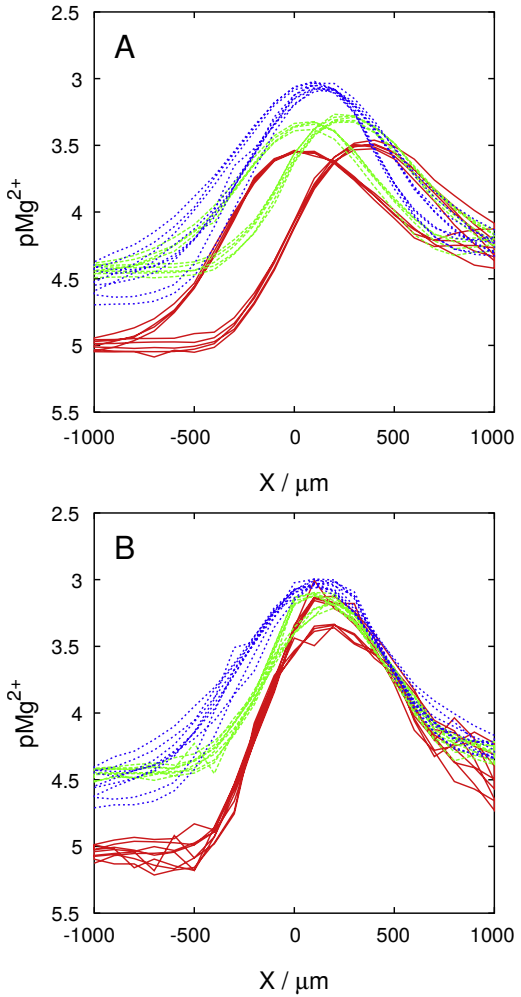
# Deconvolution of the distorted image

## pH microscopy with antimony microelectrode

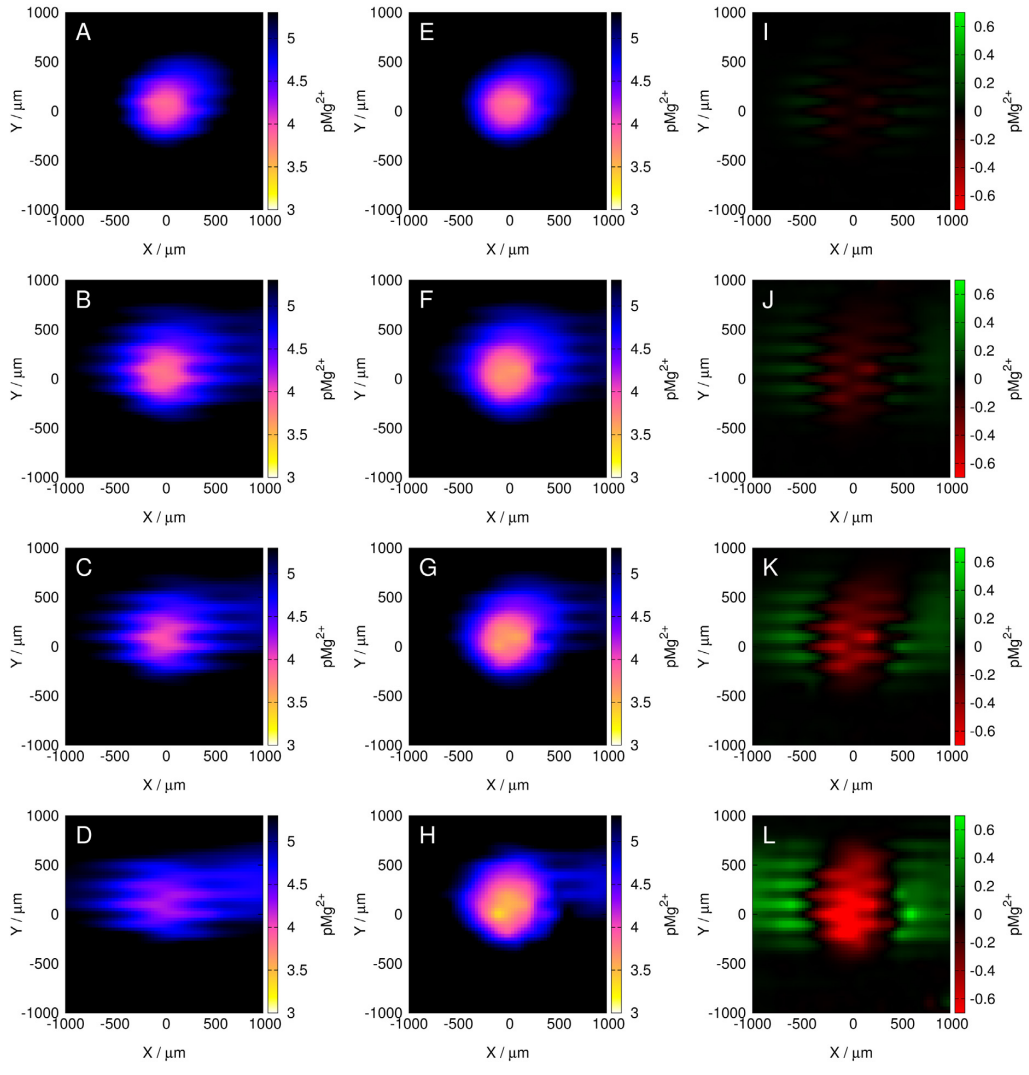


# Linescans with magnesium-ion selective micropipettes, and their deconvolution

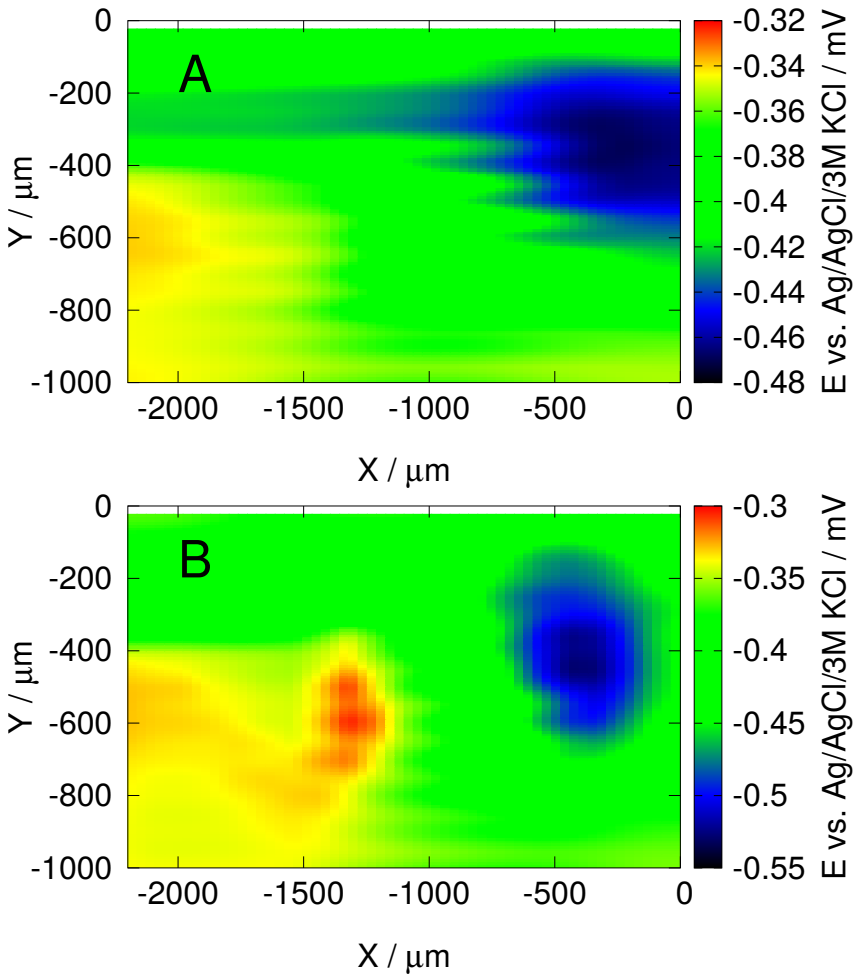


# 2D scans with magnesium-ion selective micropipettes, and their deconvolution



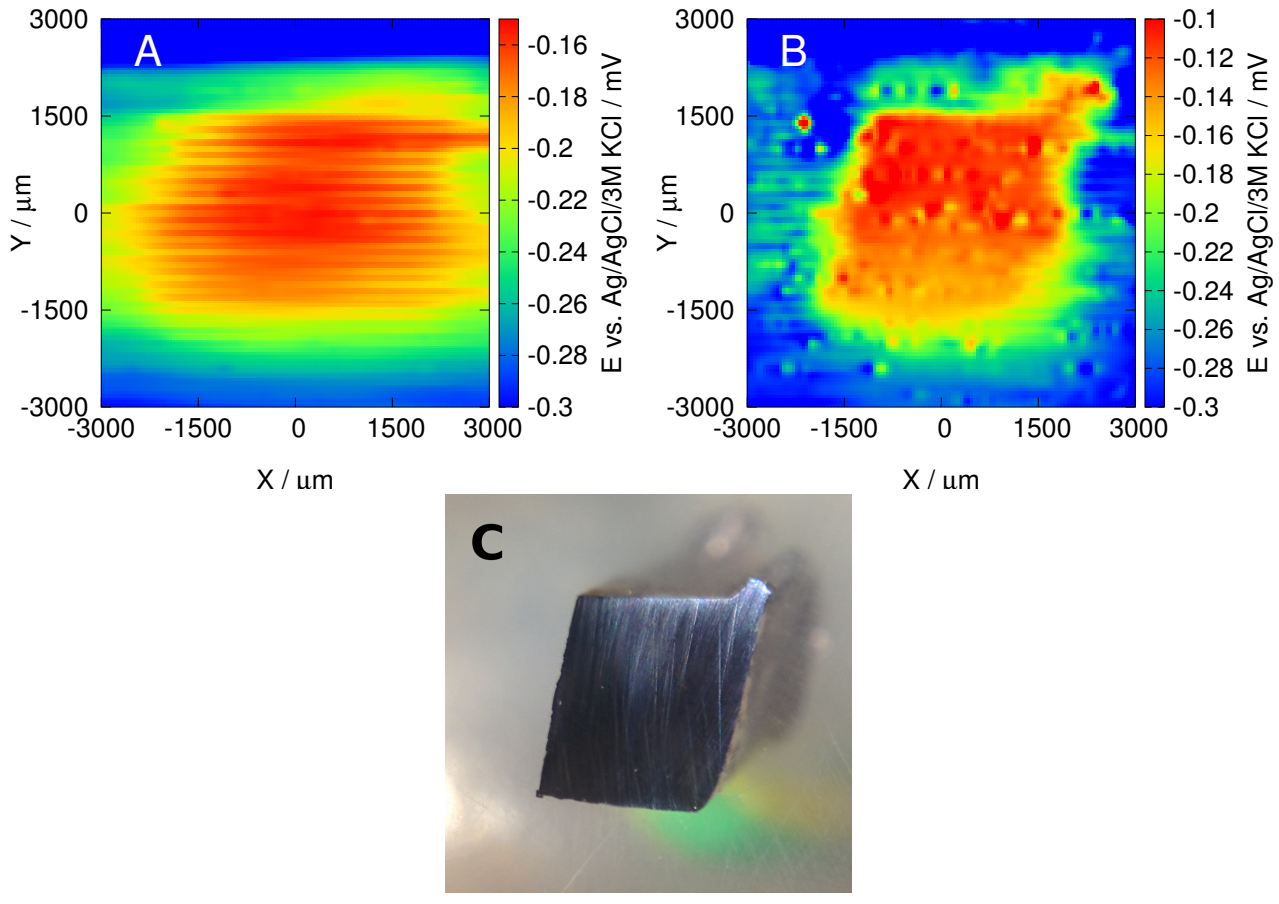
# Example 3: SECM study on the galvanic corrosion of a zinc - copper galvanic pair

## With antimony microelectrode



# Example 4: Raw, and deconvoluted SECM image and microphoto of a corroding carbon-steel sample.

## With antimony microelectrode



# Summary

- Compromise between image quality and scan time in potentoimetric SECM.
- I've demonstrated two approaches to alleviate this compromise.
- With optimized scanning patterns and algorithms, scans are faster up to 4 times, imaging distortion is 10 times less.
- These algorithms work only with radially symmetric targets.
- Another approach is to deconvolution. Can be applied to any system. Image quality is drastically improved, and scan time is shorter.


Thank you for your
kind attention!
Pécs, Hungary