BioLogic

How to get clear images in Scanning Electrochemical Microscopy (SECM)*

Part 1: Practical Considerations

Version 1.0

*Advice made throughout this tutorial can be applied to SECM measurements on the M470, SECM150, and M370 instruments

Aim.

This two part tutorial aims to provide users with the information they need to obtain clear images using Scanning Electrochemical Microscopy (SECM). In this part we address a number of practical factors which can affect the SECM image:

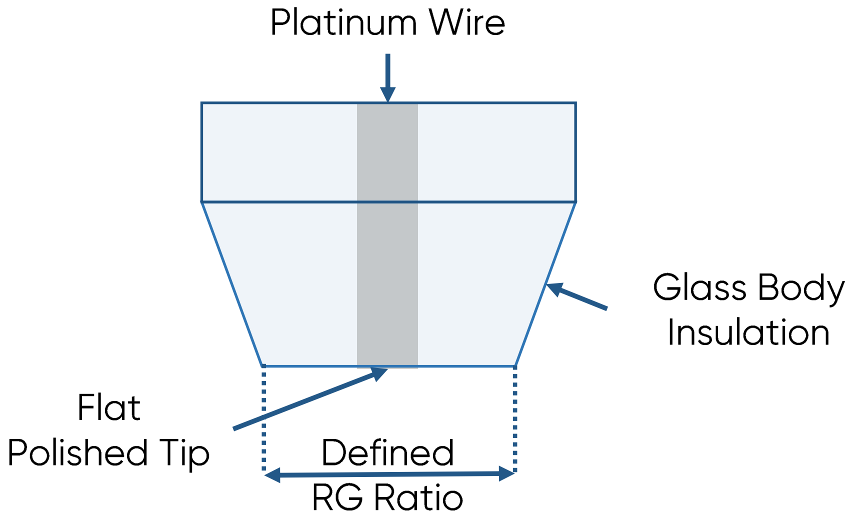
- The probe
- Sample mounting
- Sample tilt and topography
- Probe positioning
- Movement configuration

Once mastered users will be able to measure model and novel samples.

The SECM Probe

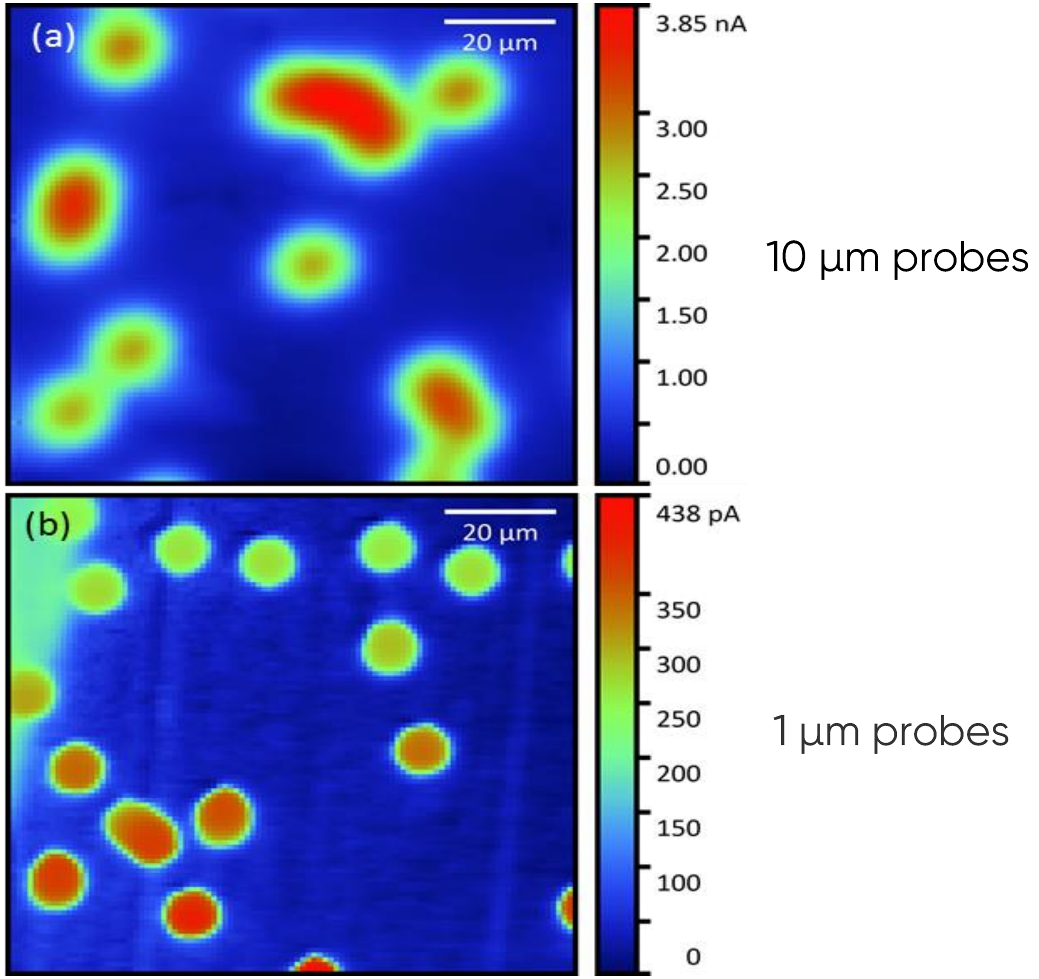
SECM probe background.

The SECM probe is a flat disc UltraMicroElectrode (UME). The active material, commonly Pt, is surrounded by an insulator, typically glass. The ratio of the radius of active to insulating material, the RG Ratio, is strictly controlled. The final image quality is determined by the active diameter and material, as well as the RG ratio.



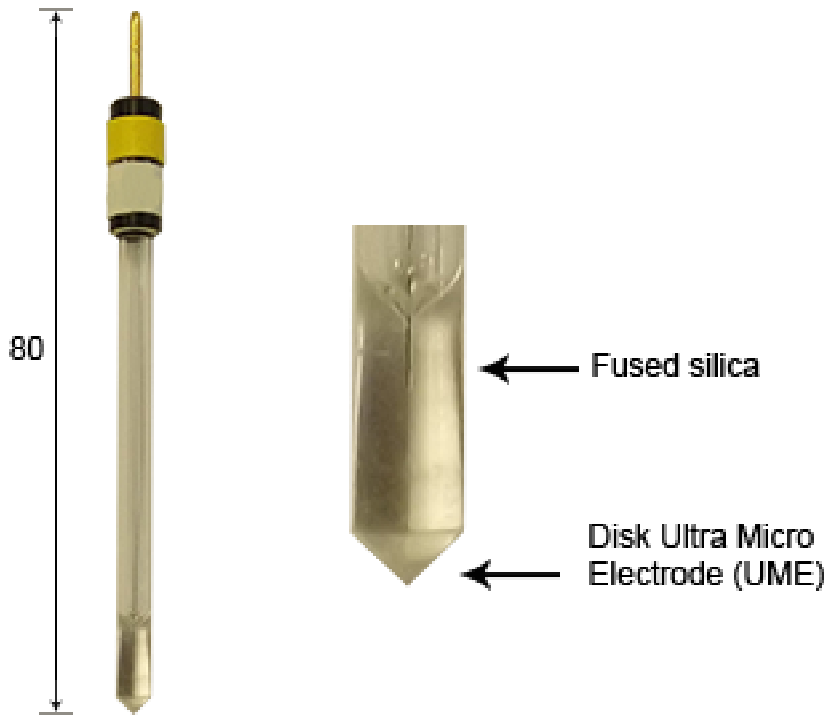
Selecting a probe: Active diameter.

- Probe size determines final measurement resolution
- Sharpest images will be obtained from the smallest probes
- Ideally the probe active diameter will be the same size as, or smaller than the feature of interest
- The signal is proportionally smaller for smaller probes therefore the measurement may have more noise



Selecting a probe: Active material.

- **BioLogic offers Pt probes covering most SECM applications**
- **Homebuilt and third party probes can be used**
- **Material is dependent on:**
  - Active electrochemical range of interest
  - Mediator under study



Tips to keep the probe clean.

- **Properly select redox mediator**
  - Further information can be found in Part 2: Experimental Considerations
- **Properly select measurement potential**
- **Do not measure too close the surface**

In some cases a minor decay in signal cannot be avoided

Cleaning the SECM Probe.

Mechanical Polishing

Pt probes ≥ 10 µm:

- Uses napped cloth & ≤ 1 µm Al_2O_3 suspension
- Apply Al_2O_3 suspension to cloth and wet w/ DI water
- Polish probe in small figure-of-8 for 30-60 seconds
- Rinse thoroughly with DI water
- Test cyclic voltammetry
- Repeat if necessary

Electrochemical Polishing

All Pt probes:

- Performed in measurement solution
- Retract probe far from sample
- Step probe potential from -1.5 to 1 V *vs* Ag/AgCl 10-25 times
- Remove bubbles with pipette
- Test cyclic voltammetry
- Repeat if necessary

Mounting the sample.

Mounting the sample.

Blu-Tac

Useful for constant height measurements, in neutral aqueous electrolytes

Beeswax

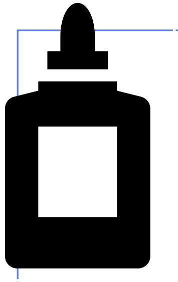
Can be used in constant height SECM, and ic-SECM. Sample should not be porous, or adversely affected by heating.

Epoxy Resin

Should only be used for samples which are polished before measurement.

Compression Mounting

Can be achieved with Foil Cell or µTriCell. Sample should be relatively flat to ensure seal.

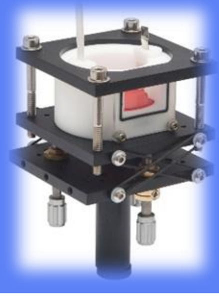
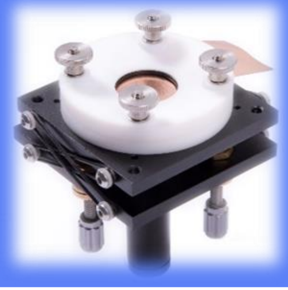


Other

PTFE tape, parafilm, double sided tape, glue, adhesive medical tapes…

Selecting the SECM Cell.

There are three cell options compatible with the M470 and M370, each suited to different experiments. A single cell type is provided with the SECM150.

	µTriCell 	Shallow µTriCell 	Foil Cell 
Solution Volume	7 ml	6 ml	1 ml
Internal Diameter	26 mm	44 mm	20 mm
Internal Depth	18 mm	5 mm	2 mm
Sample Mounting	Designed for standard metallurgical samples mounted in epoxy or on supplied PTFE blank.	Designed for standard metallurgical samples mounted in epoxy or on supplied PTFE blank.	Designed for use with flat foil type samples. Seal is formed by compression mounting.

Sample tilt and topography.

Dealing with sample topography – 1.

SECM signal is dependent on sample activity and topography. To reduce topography effects the probe can track the sample surface:

- With Intermittent Contact (ic)-SECM which follows sample topography whilst simultaneously measuring sample activity.
- With a Height Tracking (HT) SECM measurement in which topography is measured first by OSP, ic-SECM, or SKP.

Dealing with sample topography – 2.

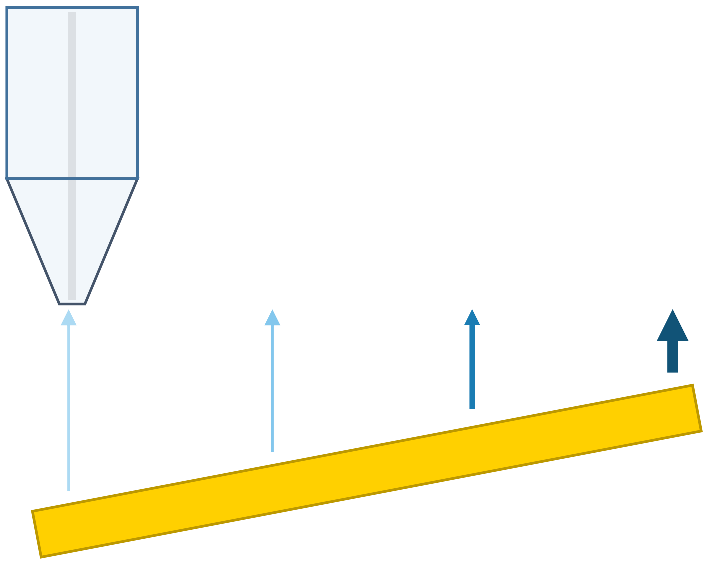
SECM signal is dependent on sample activity and topography. To reduce topography effects in a constant height measurement:

- **Bias the sample to reduce topographic effect if possible**
- **Measure insulating samples, like cells, on conductive backgrounds to increase contrast**
- **Use the probe as near the surface as possible without risk of probe crash**

A separate study of sample topography allows correlation of activity and features

Sample tilt.

- Too much sample tilt causes partial or complete loss of SECM signal.
- Aim for sample tilt in measurement area to be no more than one to two probe diameters for the best results.



Dealing with sample tilt: During setup.

A spirit level is supplied to help level the sample in the (Shallow) µTriCell using the micrometre screws.

Dealing with sample tilt: Pre-experiment.

Bring probe near surface and zero z position

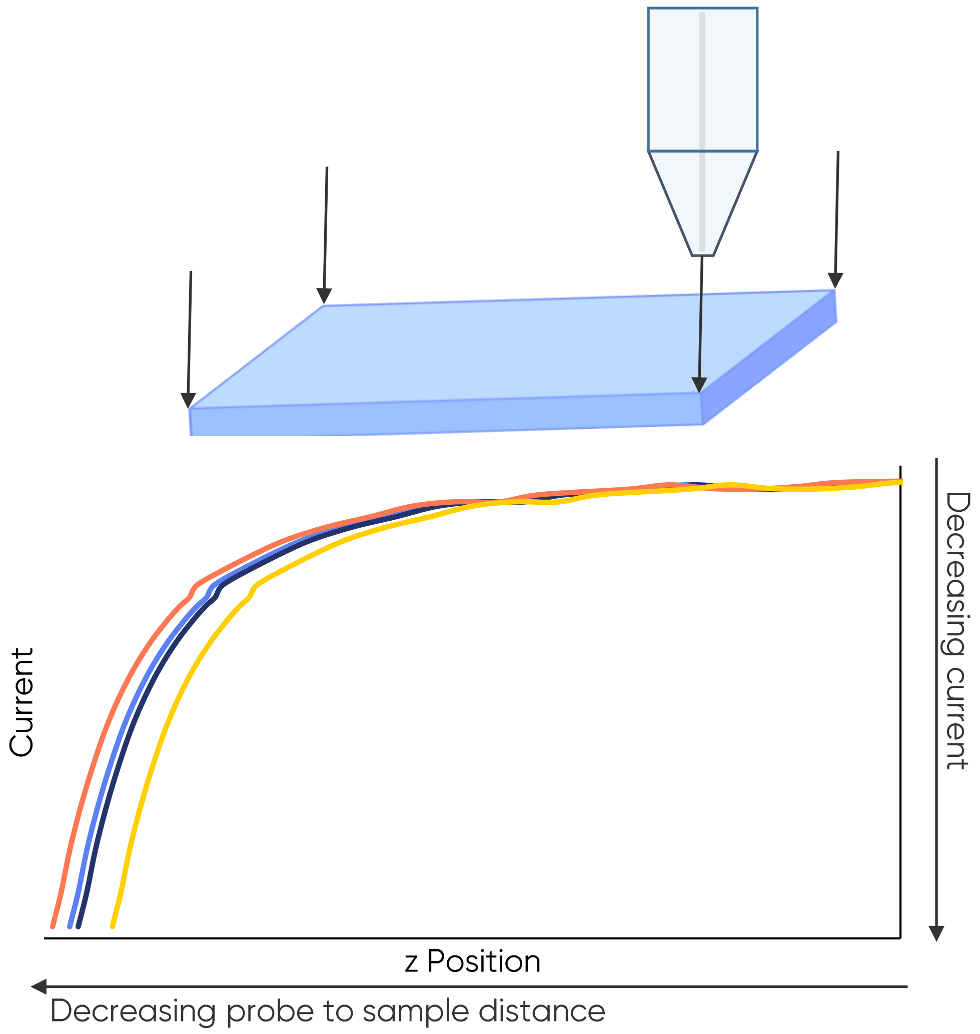
Measure approach curve at each corner

Compare:
Small final z is highest point
Large final z is lowest point

Retract probe from surface

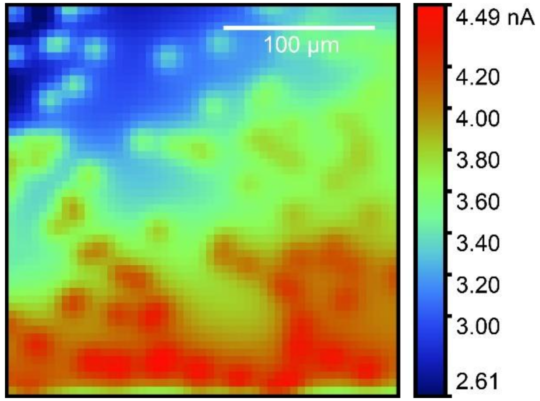
Adjust sample with micrometres of µTriCell

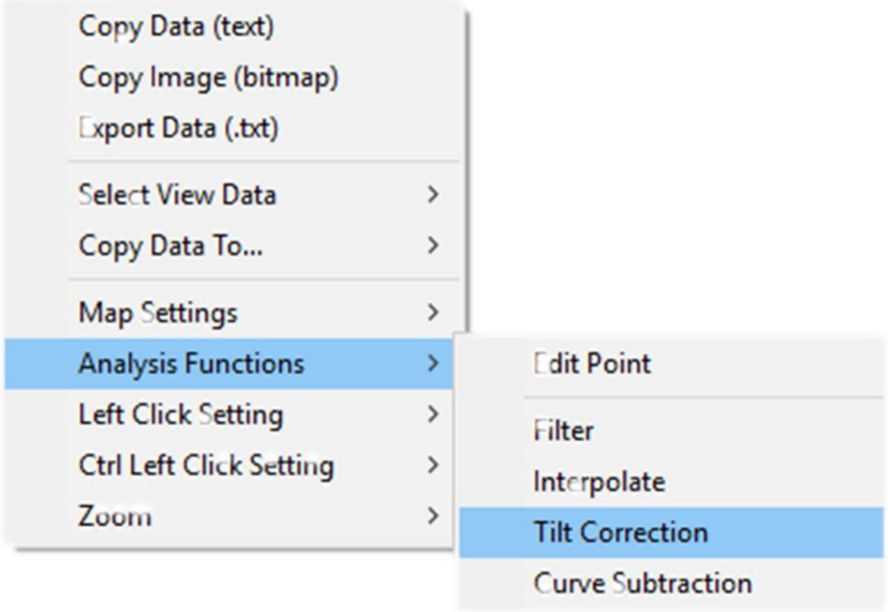
Tilt adjustment complete:
Highest and lowest point are within 1-2 probe diameters of each other

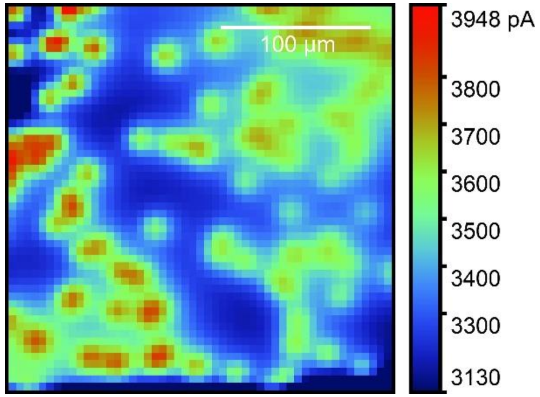


Dealing with sample tilt: Post experiment.

If sample tilt is apparent in an area scan it may be possible to correct for this in the SECM150, M470 and M370 software.





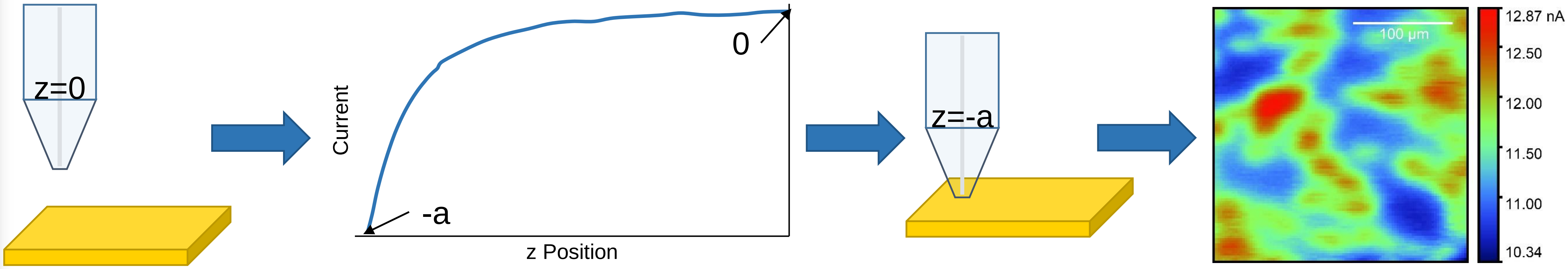


If the signal has returned to bulk values over large regions sample tilt should be adjusted and the experiment repeated.

Probe height.

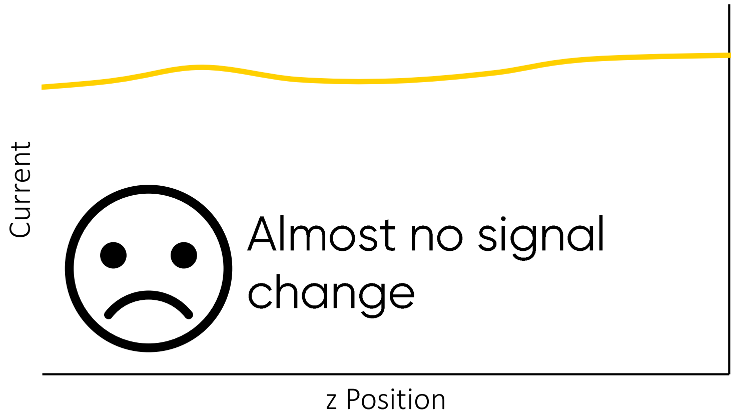
Determining probe height.

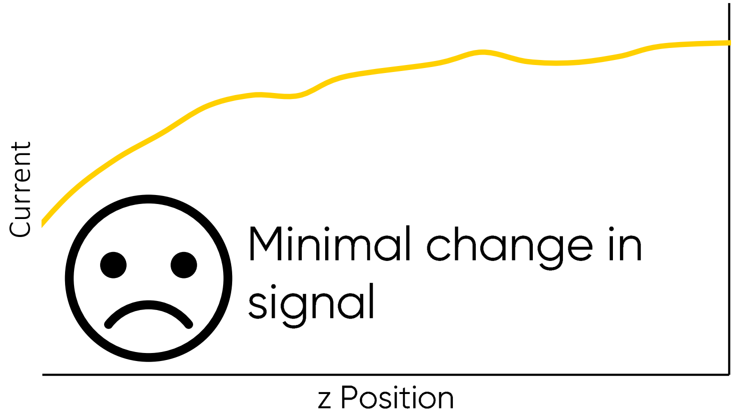
In a constant height SECM experiment the probe is set at a fixed position in z throughout the measurement. Prior to performing a line and/or area scan a probe approach curve is performed to determine this fixed z position.



When to keep approaching – 1.

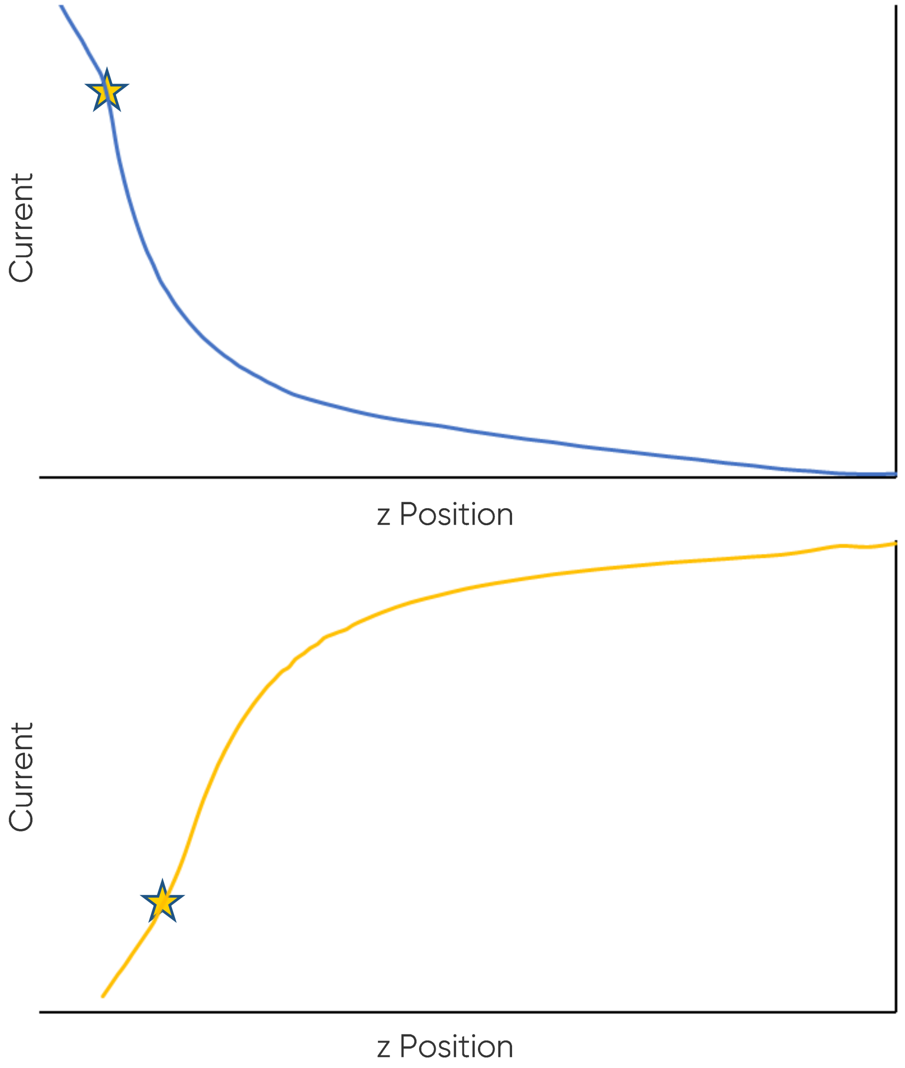
- During an approach an exponential decay or growth of signal will be seen
- If little to no change in signal has been measured the probe should be moved toward the surface, its position zeroed, and the approach restarted.





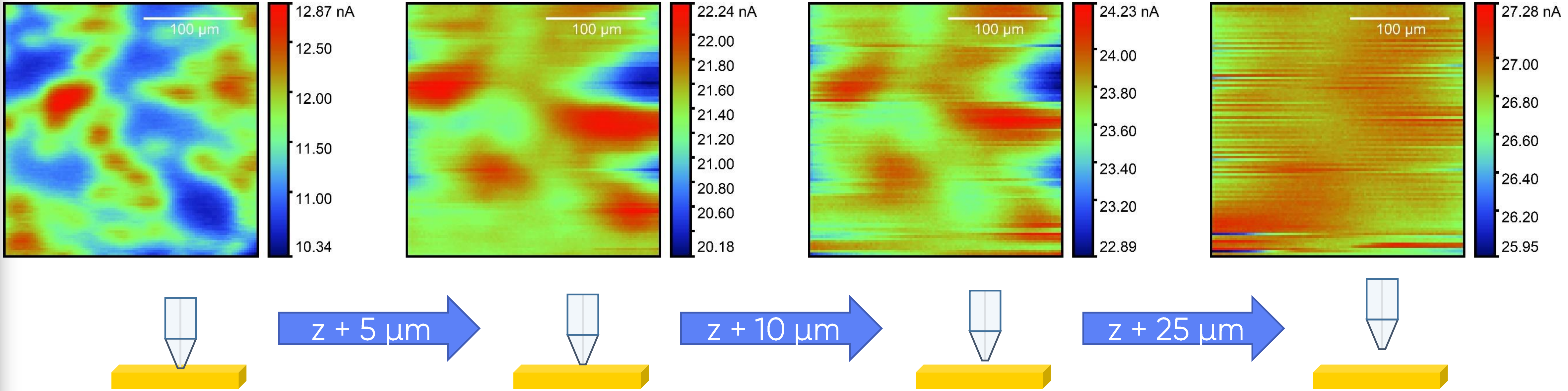
When to stop approaching – 2.

- Large change in signal
- Overload in signal
- Change in slope of approach curve



Probe position.

- To measure a strong signal the probe should be near the surface
- It should not be close enough to touch the surface at any point



Measurements performed with 10 µm probe

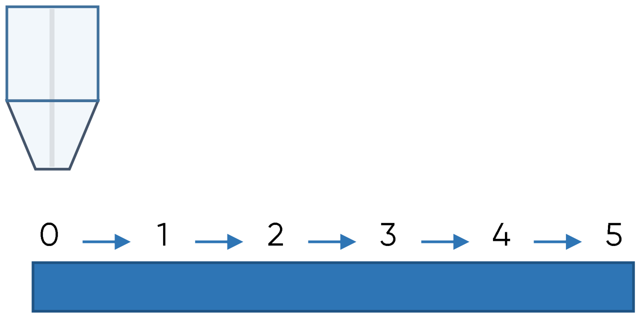
Movement parameters.

Step scan or sweep scan.

In constant height dc-SECM both step scan and sweep scan are available

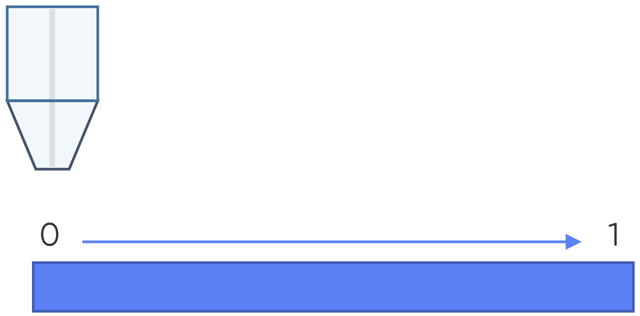
Step scan:

- Probe pauses at each point to collect data
- Lower noise measurement, with reduced solution stirring

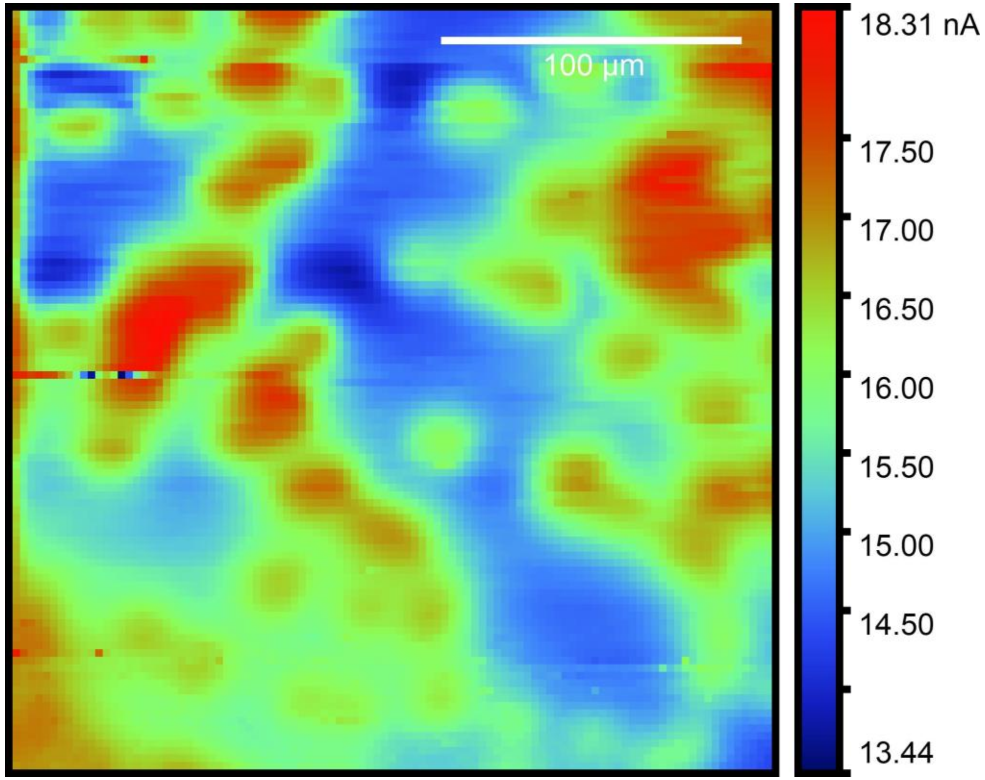


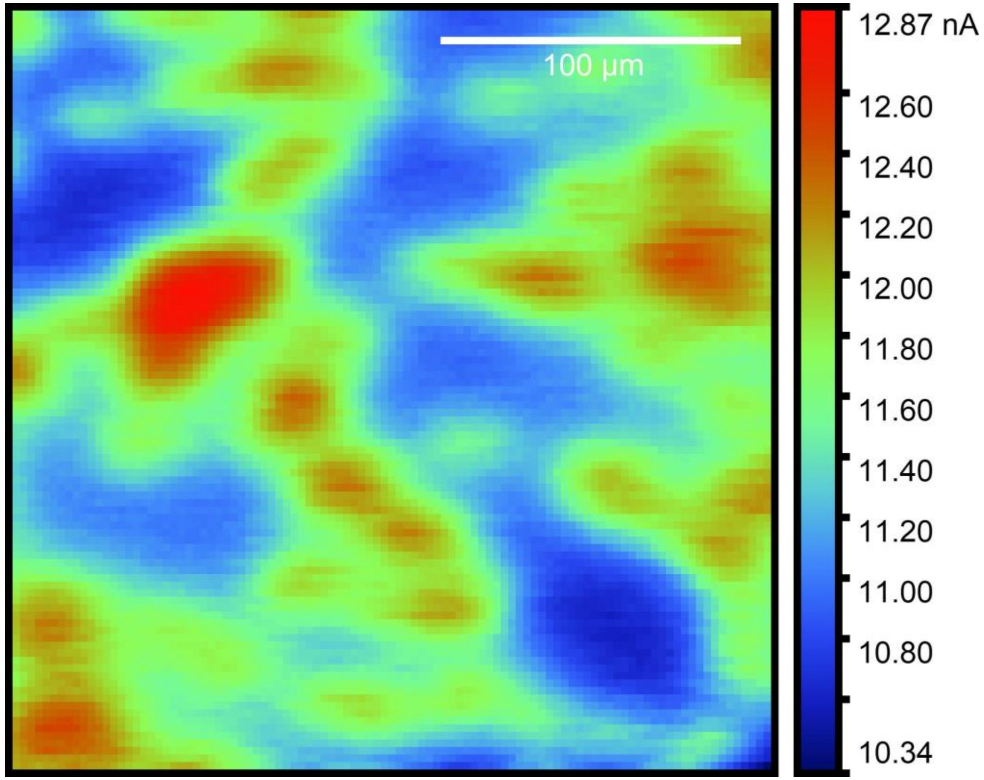
Sweep scan:

- Probe does not stop during a line, measuring at given time intervals
- Faster measurement



Step scan vs sweep scan example.



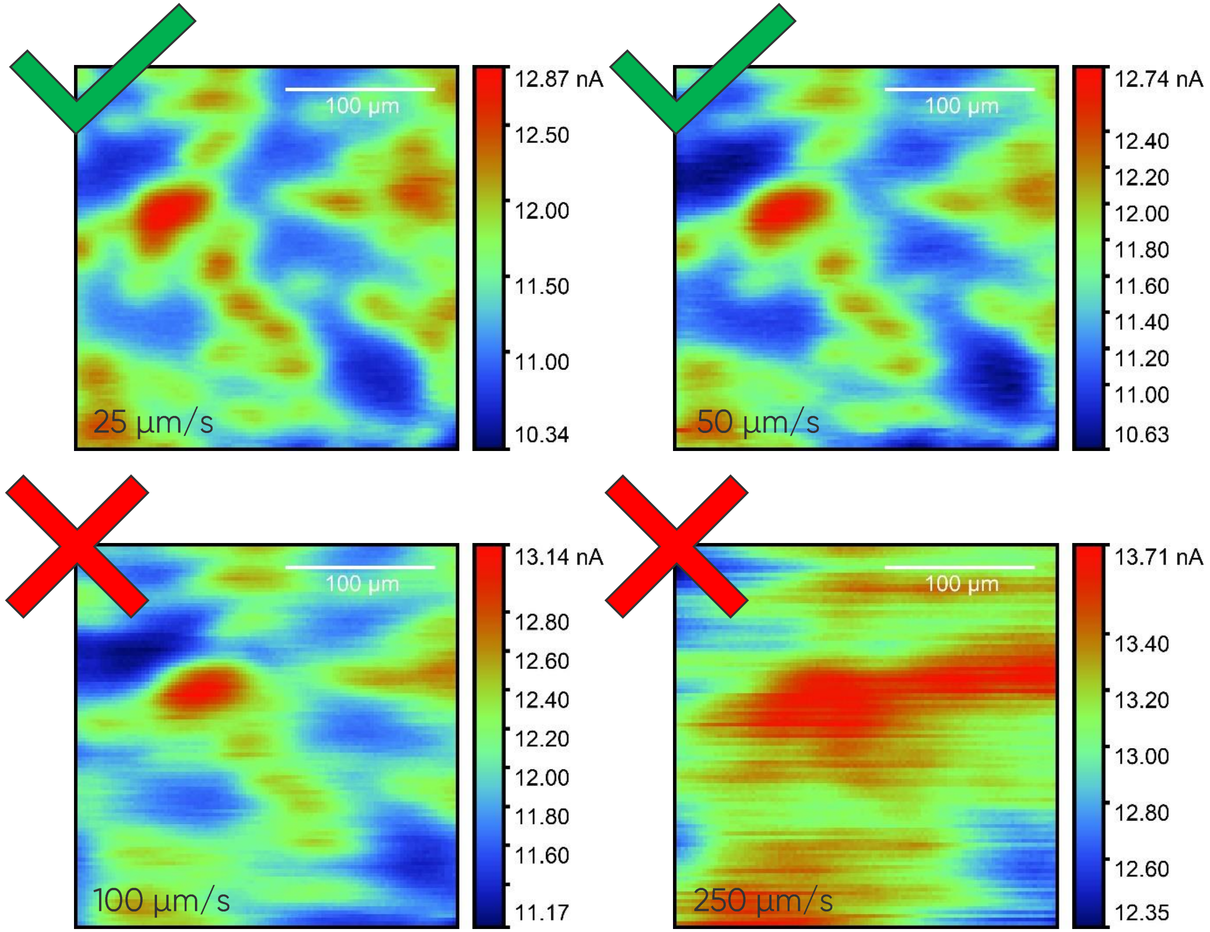


Step scan will typically result in better images than sweep scan. However a step scan experiment will take longer to perform than a sweep scan experiment.

Selecting positioning scan rate.

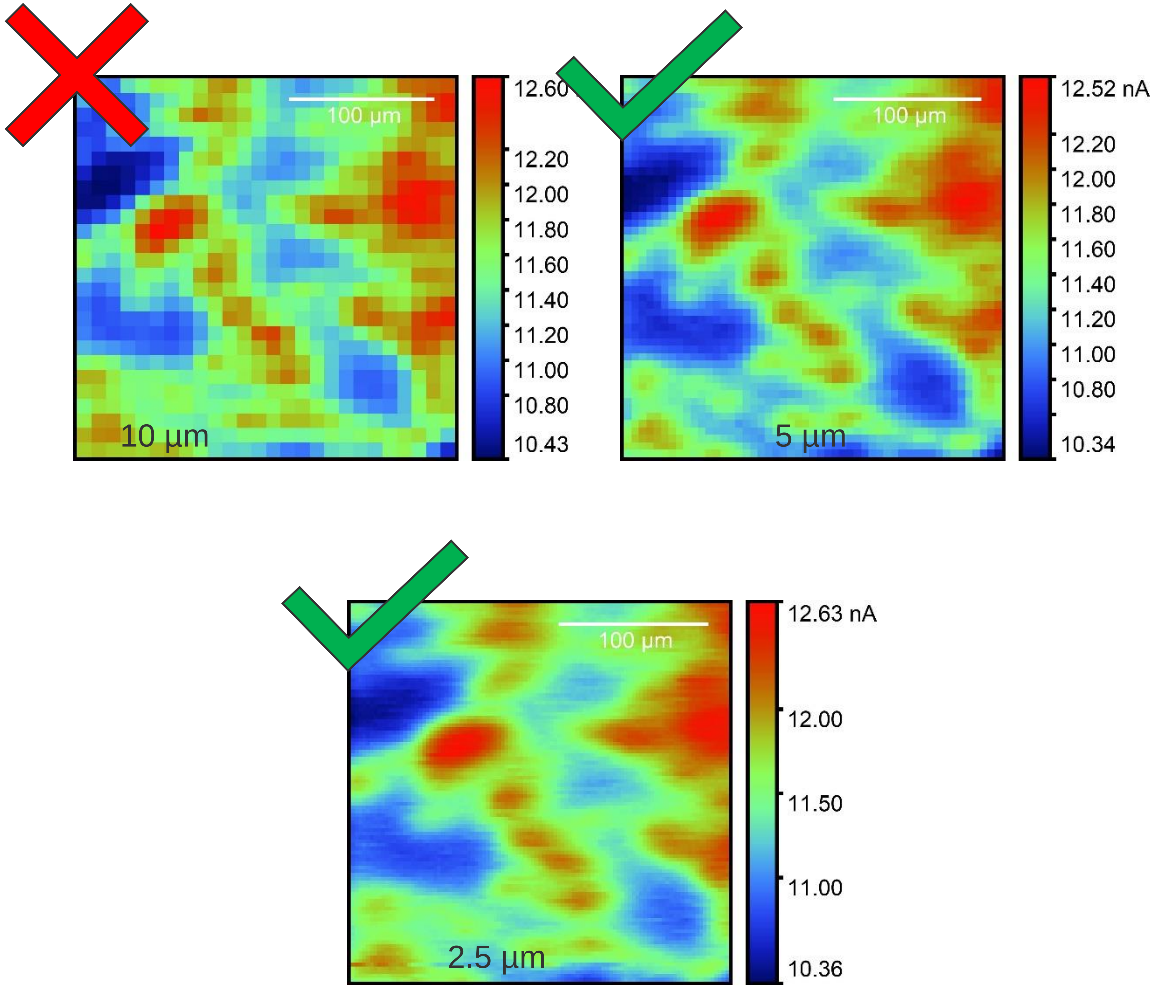
Positioning scan rate selected based on:

- **Maintaining accuracy**
- **Avoiding solution stirring**
- **Avoiding excess noise**
- **Reducing experiment time**
    - Key for dynamic samples



Selecting a step size.

- While resolution is ultimately dependent on probe size, step size also matters
- Oversampling, where the step size is smaller than the probe, is common
- Smaller step sizes lead to clearer images but increase experiment times



Conclusion.

Conclusion.

A number of practical considerations have been discussed with the aim of optimising the SECM measurement. These considerations relate to the probe, sample mounting, sample tilt and topography, and movement settings. Understanding how to control each of these settings will allow users to measure standard and novel samples.

More information.

BioLogic Support: https://www.biologic.net/support/

BioLogic Contact: https://www.biologic.net/contact/

Glossary.

- RG ratio: The ratio of the radius of the inactive probe region (R) to the radius of the active probe region (r) ($RG=R/r$).
- Redox Mediator: Electrochemically active compound which transfers electrons in SECM, allowing measurement of Faradaic current.
- Pre-delay: The length of the pause before measuring a point or line in SECM.

Thank you!

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