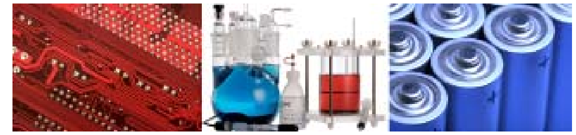
M370
Princeton Applied Research

A unique multi-technique scanning electrochemical workstation

PAR M370

The goal of the M370 is to provide spatial resolution to electrochemical measurements. Bulk measurements give bulk responses….local measurements give local responses.

Pictured here is the M370 platform configured for a SECM experiment – including the MicroTricell and the VCAM2 (now a LCD display)



Expandable Platform… Customized Solution

Available Techniques with the M370

- Scanning Electrochemical Microscopy (SECM)
- Scanning Vibrating Probe (SVP, SVET)
- Local Electrochemical Impedance Spectroscopy (LEIS)
- Scanning Kelvin Probe (SKP)
- Scanning Droplet System (SDS)
- Non-contact Optical Scanning Profiler (OSP)

Positioning System

- A key advantage to the M370
- Closed Loop, Zero Hysteresis system
  - Linear encoders (100-nm resolution) on **all axes** independently read the true position of the probe.
  - This ensures requested and actual position are the same, through position feedback.
  - Stepper motors have 8-nm resolution.

Installation and Support

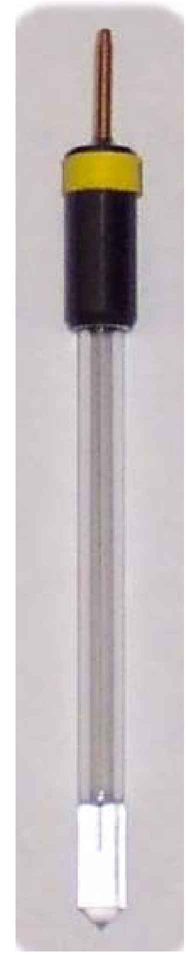
- Included with the 370BASE is professional on-site installation.
- A laptop computer is included to control the system
- The M370 is supported by the Princeton Applied Research global network
- Manufactured by Uniscan Instruments, UK.

Scanning Electrochemical Microscopy (SECM)

- Ability to **control and monitor** local reduction-oxidation reactions.
- An ultramicroelectrode (tip) is positioned within a few probe diameters of a substrate.
- An electrochemically active molecule in solution (*the mediator*) generates a measurable response (*e.g., current*) at either the tip or the substrate.

Available Tips/Probes

- Probes are available with Platinum diameters of either 25-, 15-, or 10-micron.
- Both the 25- and 15-micron probes are supplied with the SECM370.
- The RG ratio (glass diameter to electrode diameter) is 10 for each type.
- User can manufacture their own SECM probes. Practical limitations may become a issue at diameters of less than 2 microns.



Available Standard Experiments

Scanning Experiments

- Approach Curve
- Area Scan
- Line Scan
- Constant-Current*
- Sloping Correction*
- Area OCP*
- Auto-Approach*

Stationary Experiments

- Cyclic Voltammetry
- Chronoamperometry
- Chronopotentiometry
- Differential Pulse Voltammetry
- Linear Sweep Voltammetry
- Normal Pulse Voltammetry
- Square Wave Voltammetry

*Available via provided Macros

Modes of Operation and Data Acquisition

- Two (2) electrically-isolated potentiostats are supplied to allow operation in either Feedback or Generation-Collection Imaging Modes.
- Data is acquired by:
  - Constant-Height,
  - Constant-Current (by supplied macro),
  - Constant-Distance (with OSP module).
- Data can be acquired as:
  - Sweep Mode: Data sampled as probe is moving.
    - Faster experiments. Sample exploration.
  - Step Mode: Data is over-sampled and averaged, reducing noise.
    - User Defined:
      - Pre-Delay,
      - Acquisition Rate,
      - and Number of Samples.

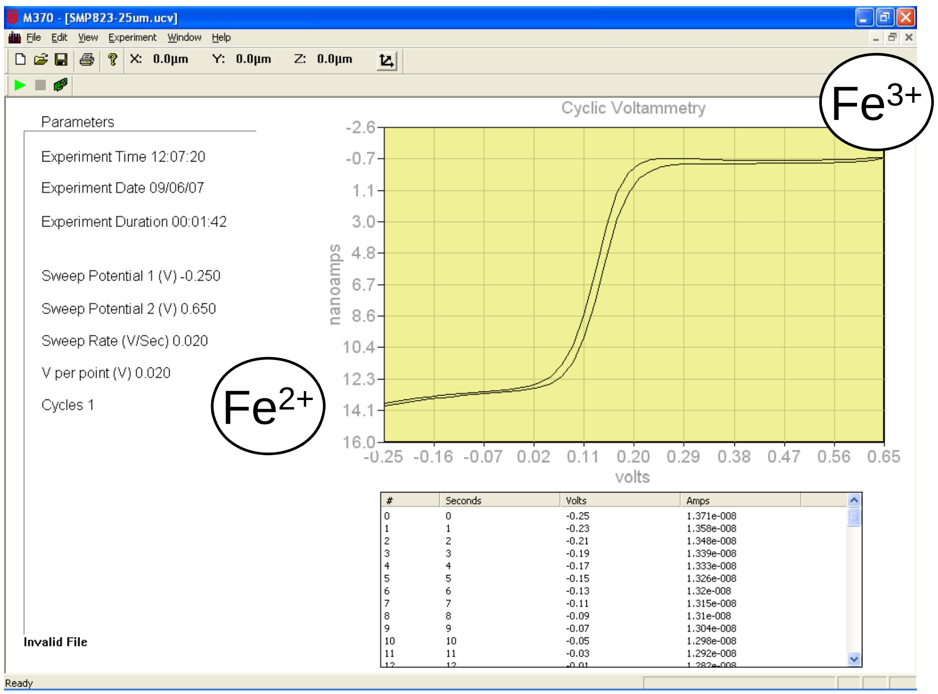
Specifications of the PG580R

2 x PG580 supplied with SECM370

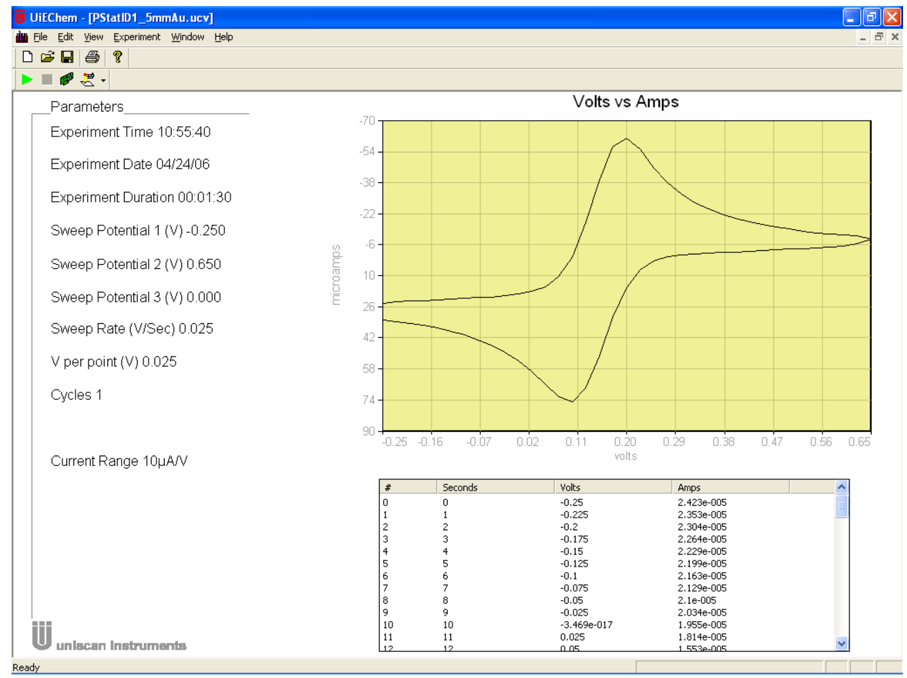
Specifications of the PG580R	
Current Ranges	1 nA to 10 mA/V in 8-decades
Current Resolution	61 fA
Maximum Current	+/- 20 mA
Applied probe potential	+/- 2 V at 16-bits (61 µV res). Option to 8 Volts
Applied substrate potential	+/- 2 V at 16-bits (61 µV res). Option to 8 Volts
Compliance Voltage	+/- 8 Volts
ADC Resolution	16-bit at > 100 kHz
Current Measurement Accuracy	< 0.5 %
I/E input bias	< 10 pA
Rise Time	1 V/µsec into 1 kOhm
Floating	Yes
Mode	2- and 3- terminal
EIS capable	No

Cyclic Voltammetric Responses

Microelectrode (Probe/Tip)



Macroelectrode (Sample)



Potassium FerriCyanide(Hexacyanoferrat(III)) - $K_3Fe(CN)_6$ – 5mM
Potassium Chloride – KCl – 100mM

The bulk mediator exists as Fe^{3+}.

These CVs determine the appropriate potential to apply when imaging.

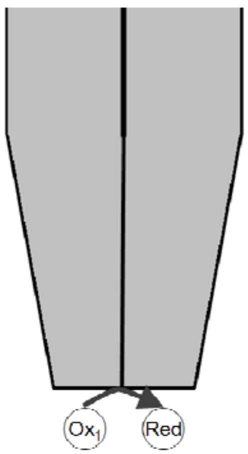
The reducing potential (here -0.25 Volts) causes the current to flow.

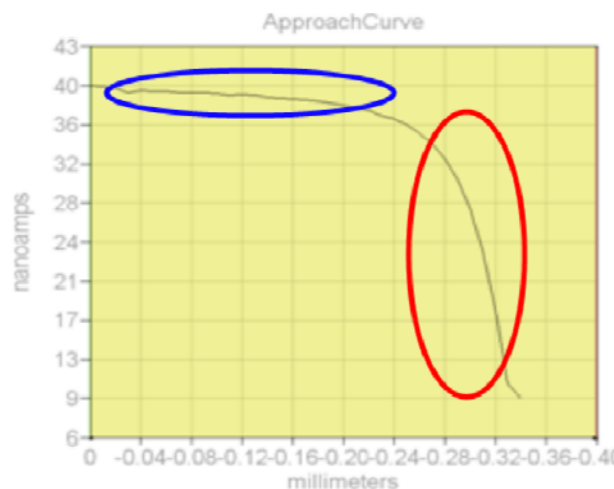
The Approach Curve Experiment

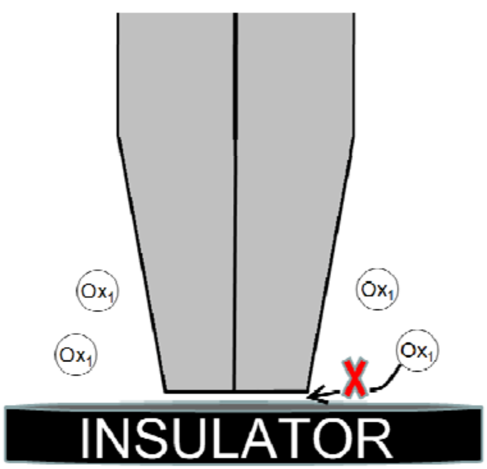
- **Goal:** Position probe in the Z-axis appropriately close to the sample.
- **Process:** (this example assumes the bulk mediator is in Ox state).
  - Position the Tip in X, Y over a known insulating area.
  - Connect Active Potentiostat to the Tip and polarize it sufficiently to cause the reduction: $Ox + e^- \rightarrow Red$ (as determined by CV).
  - Record the current at the Tip as the probe approaches the sample (increments in the –Z direction).
  - Return the tip to a bulk distance.
  - Reposition in X,Y over a conductive area of the sample.
  - Record the current in a separate experiment as the tip approaches the sample.

Negative Feedback: Hindered Diffusion

Bulk





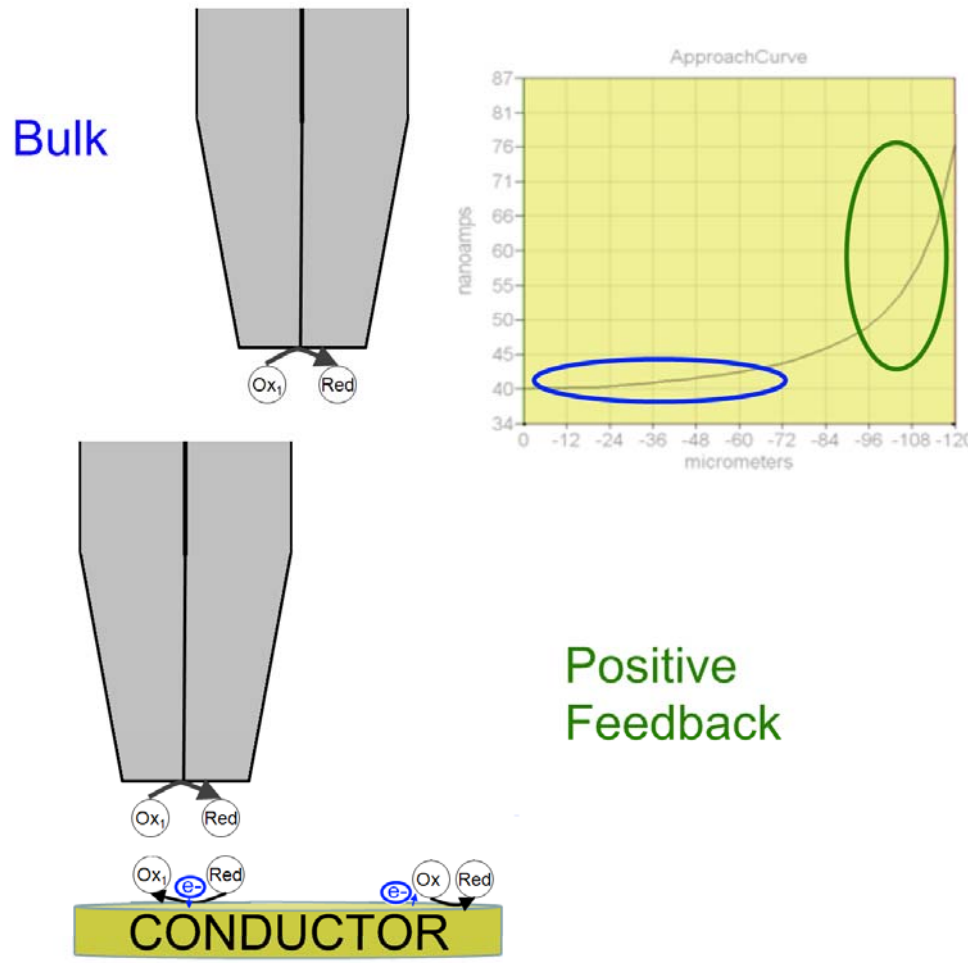


Negative Feedback

- As the tip approaches an insulating surface diffusion of the mediator to the electrode is hindered.
- As a result the current quickly approaches zero.
- Blue circle is bulk response; red is local.
- Remember :

  No Ox at the electrode's surface = no current

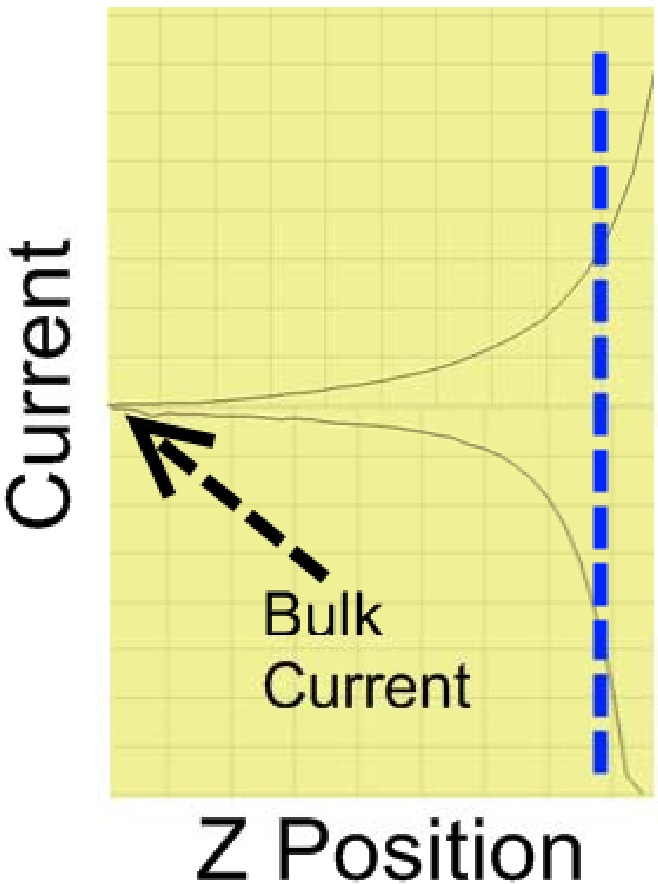
Positive Feedback: Enhanced Diffusion



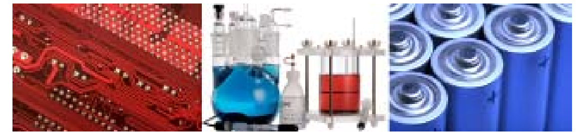
- As the tip approaches a conducting surface, the current is enhanced, due to the thermodyamics of the non-polarized substrate.
- Another balancing reaction happens at the sample, but that is outside the area locally "seen" by the tip.
- This mechanism creates more Ox in the local area for the tip to reduce = higher current.

<u>This effect happens even though the substrate is not polarized.</u>

Positioning Probe for Imaging

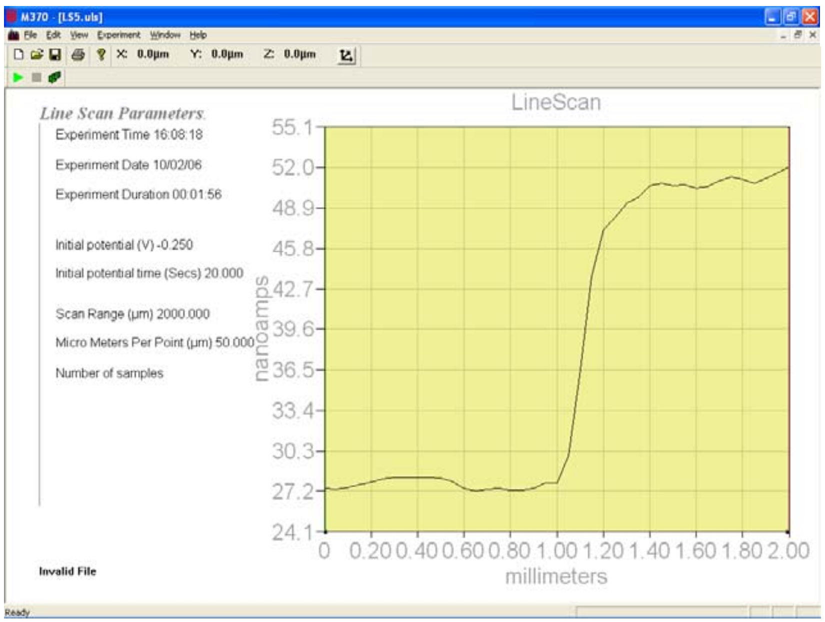


By first running 2 Approach Curve experiments (one over a insulator and one over a conductor) and comparing the results, you can determine the Z position that gives the greatest differential (blue dashed line)

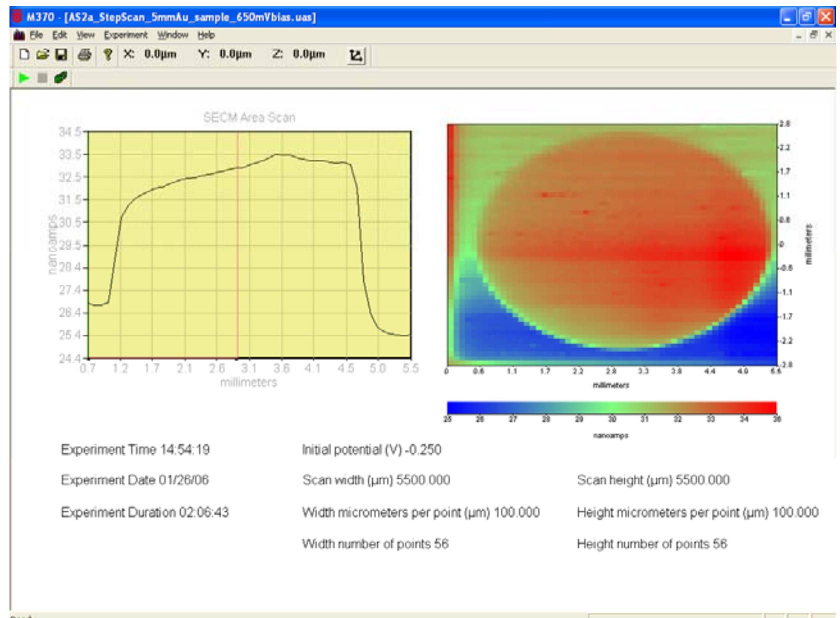


Imaging of Insulator/Conductor Surface

Line Scan



Area Scan



Comparing Imaging Modes

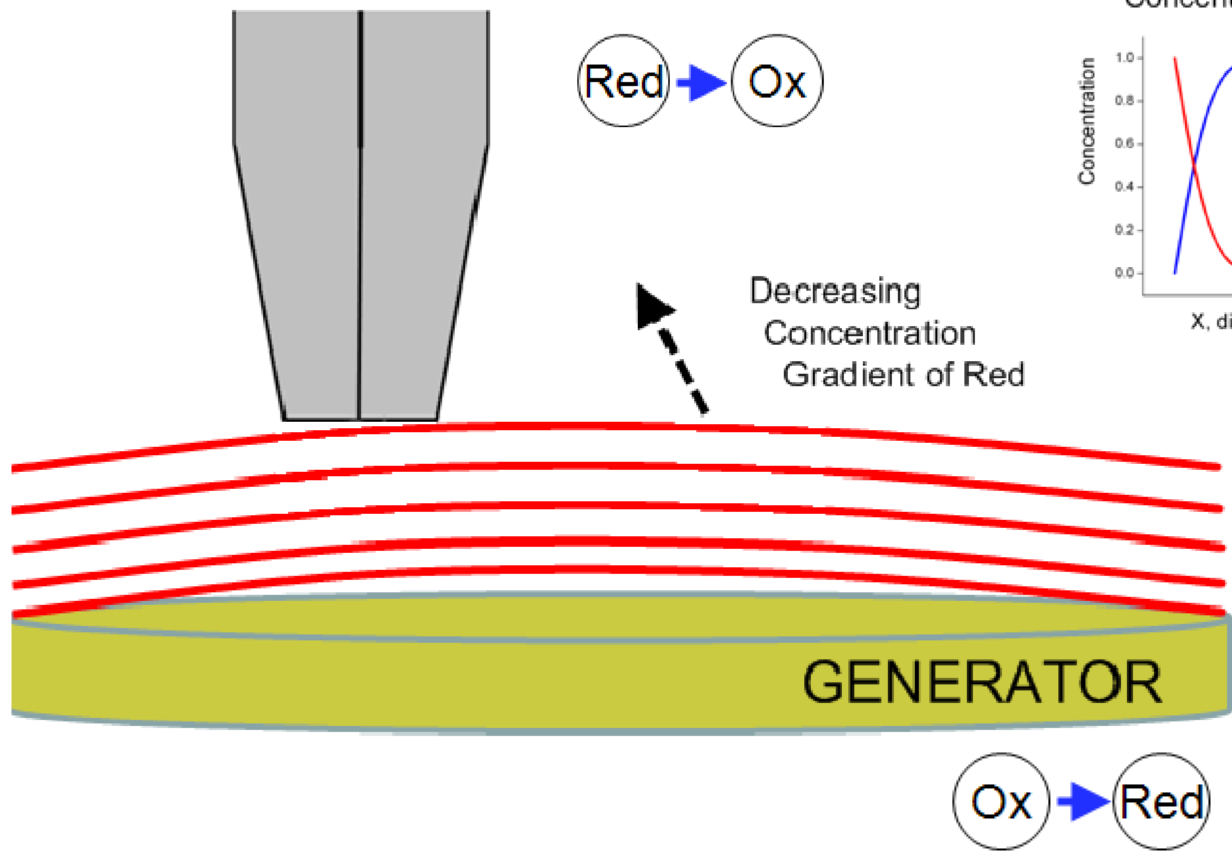
Feedback Mode

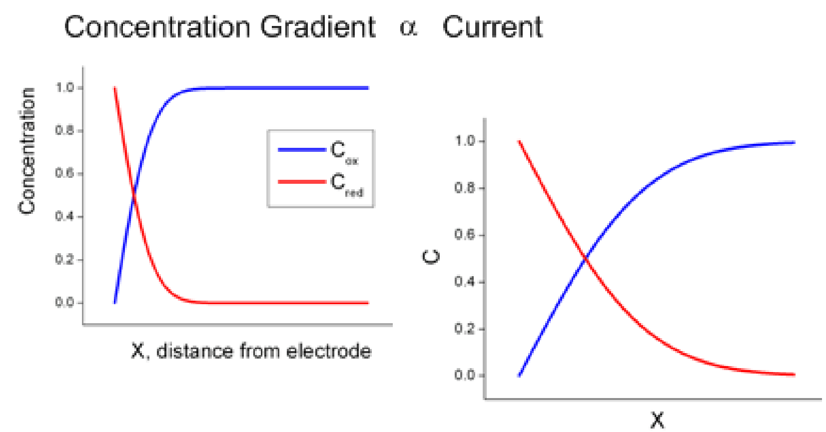
- Single potentiostat
- Monitor current at Tip
- Use a redox "mediator" (e.g., Ferricyanide)
- Connection to sample may not be required

Generator-Collector Mode

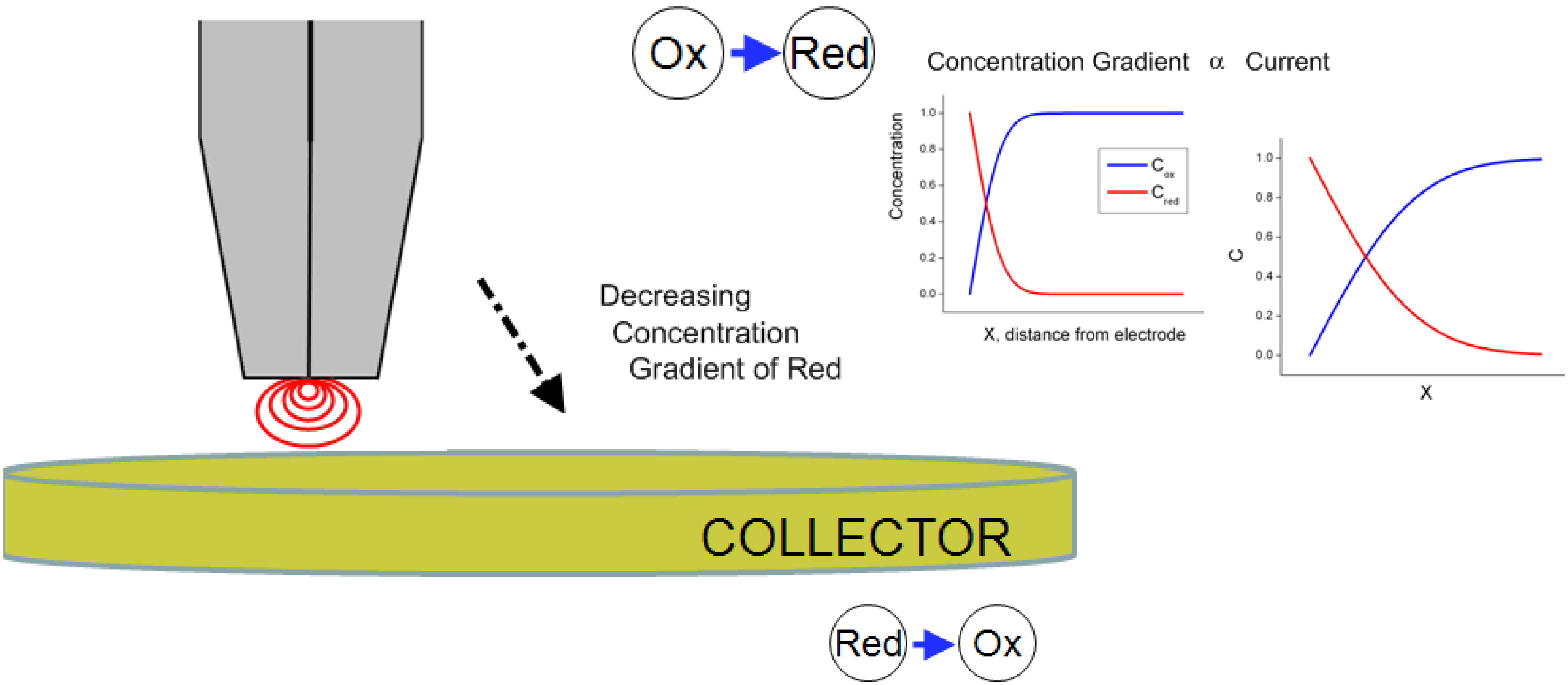
- Two potentiostats
- Monitor current at either electrode, but more common at the Tip.
- May have redox molecule in solution; inherent mediator
- Decreased spatial resolution due to random diffusion walk

Substrate-Generation Tip-Collection SG-TC





Tip-Generation Substrate-Collection
TG-SC



Topographic Effects, Complications

- Approach Curves demonstrate have the probe-to-sample distance affects the measured current.
- In a *constant-height* experiment, the current may be a convolution of surface reactions and topography of the sample.
- A *constant-distance* experiment ensures the probe-to-sample distance is the same throughout the scan.

The SECM-SYS

Goal:

Provide a solution for users interested in only SECM, the most popular scanning probe technique.

Restrictions:

No other techniques should be added to this 370BASE for a period of 1 year.

Includes:

370BASE

SECM370 module

MicroTricell

Recommendations:

VCAM2

Isoplot

SECM versus Atomic Force Microscopy (AFM)

- SECM has similar information with a different dimensionality and focus.

  SECM images localized electrochemical processes happening to the specimen that cannot be obtained in any other way, not just the topography

- SECM can probe a larger area an AFM
- SECM cannot achieve the molecular resolution of AFM

Some Resolution Considerations

- Accuracy/Resolution of Current Measurement
  - Accuracy: <0.5 %; Resolution: 61 fA
- Accuracy/Resolution of Positioning System
  - Accuracy: Determined by speed; Close-Loop on all axes
  - Resolution: 100-nm on the linear encoders.
- Probe diameter
  - Available in 25-, 15-, 10-micron Pt probes. User-made probes will work as well.
- Topographic Effects
  - Height-Tracking (constant-distance) with OSP technique
  - Sample Tilt Macro
- Probe-to-Sample Distance
  - Probe should be positioned with 2-4 probe diameters from the surface.
- Random-walk of ionic diffusion

Example SECM Applications

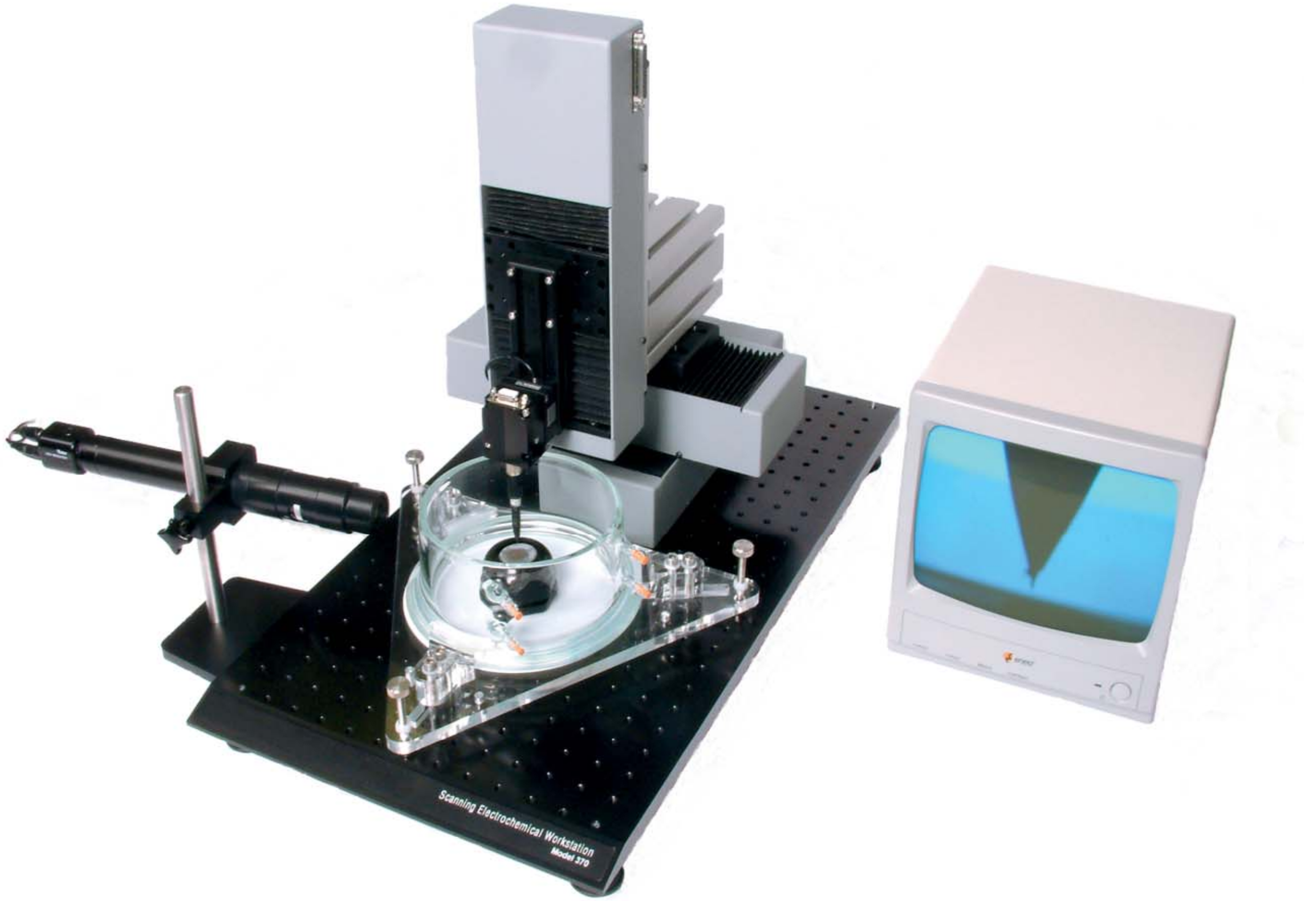
- Imaging
- Ultramicroelectrode Shape Characterization
- Heterogeneous Kinetics
- Homogenous Kinetics
- Biological Systems
- Liquid/Liquid Interfaces
- Membranes and Thin Films
- Surface Reactions
- Semiconductor Surfaces
- Electrochemistry in Small Volumes
- Fabrication

- Using Tip scan sample for decrease in molecular oxygen to image a live cell.
- Using Tip scan sample for increase in molecular oxygen to image photosynthesis
- Sensors.
- Kinetics of electrochemical reactions; fuel cells.

SECM Library

- Application Notes:
  - Area Open Circuit Potential Scan 
  - Constant Current Macro 
  - Tilted Sample Correction 
  - OSP-SECM for Constant-Distance for Corrosion 
  - OSP-SECM for Constant-Distance for Sensors/Electrodes 
- Documented Check-Out (Install) Procedure 

Scanning Vibrating Probe (SVP/SVET)



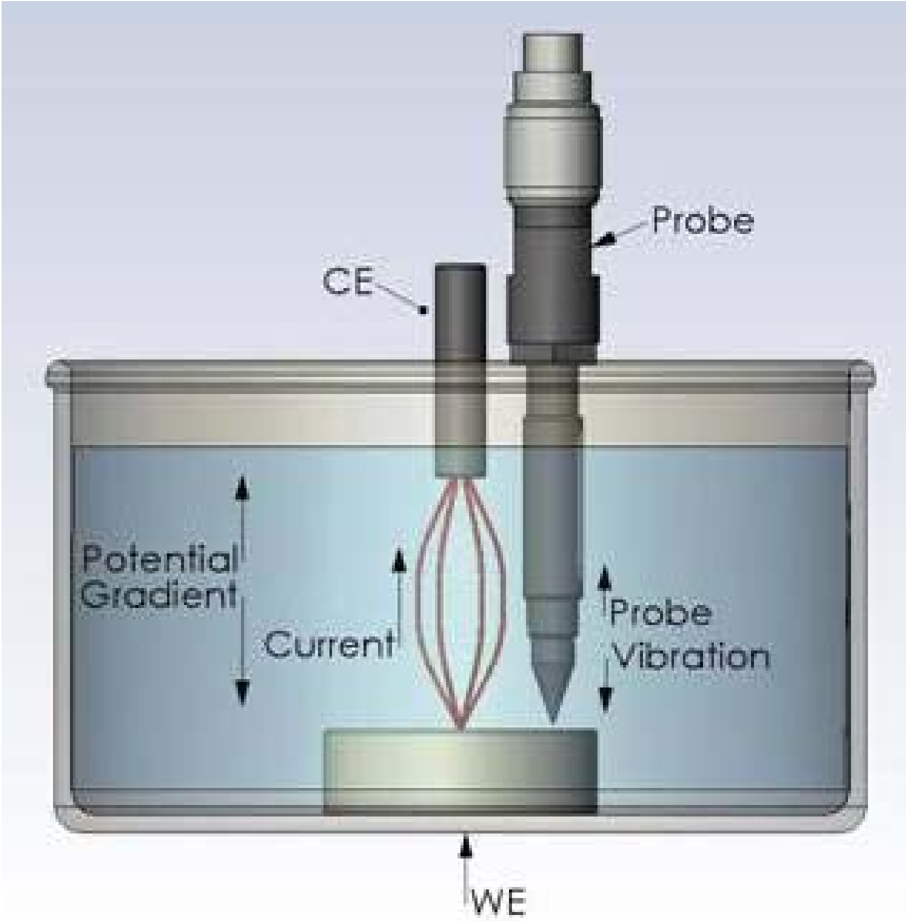
SVP Theory

- SVP maps local current density variations over an active (corroding) sample surface by measuring the voltage-drop variations close to the surface.

- A vibrating probe is used with a lock-in amplifier to eliminate noise occurring at any frequency other than the frequency of probe vibration.

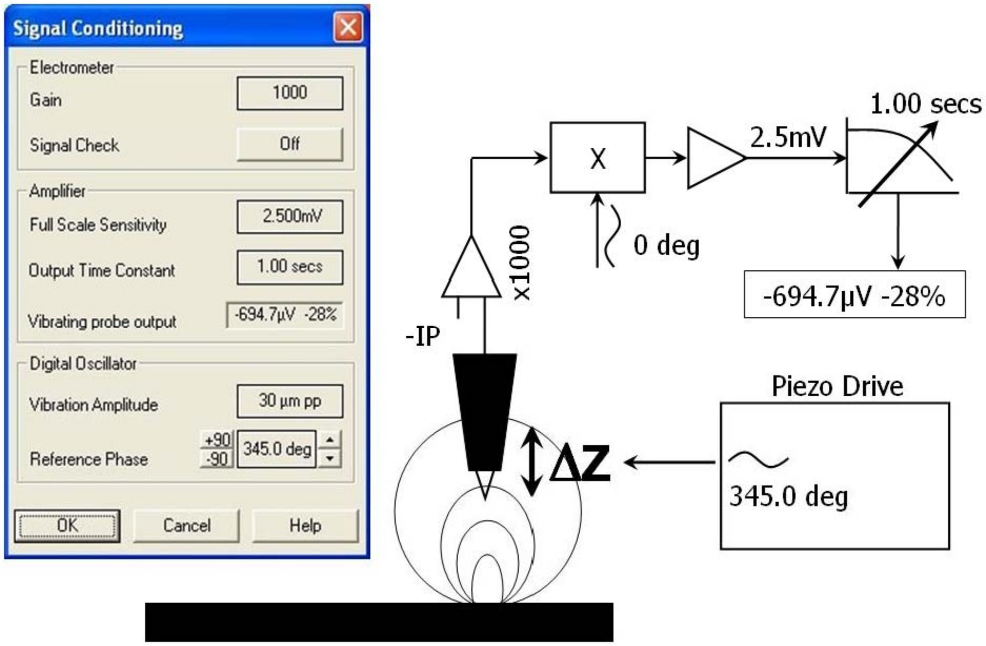
SVP Technique

- In an electrochemical process, reactions occur at the sample's surface.
- A CE is an inert, conductive surface in the same solution, which balances the reactions of interest at the WE.
- Flow of ions result in a current (and potential gradient) in the electrolyte.

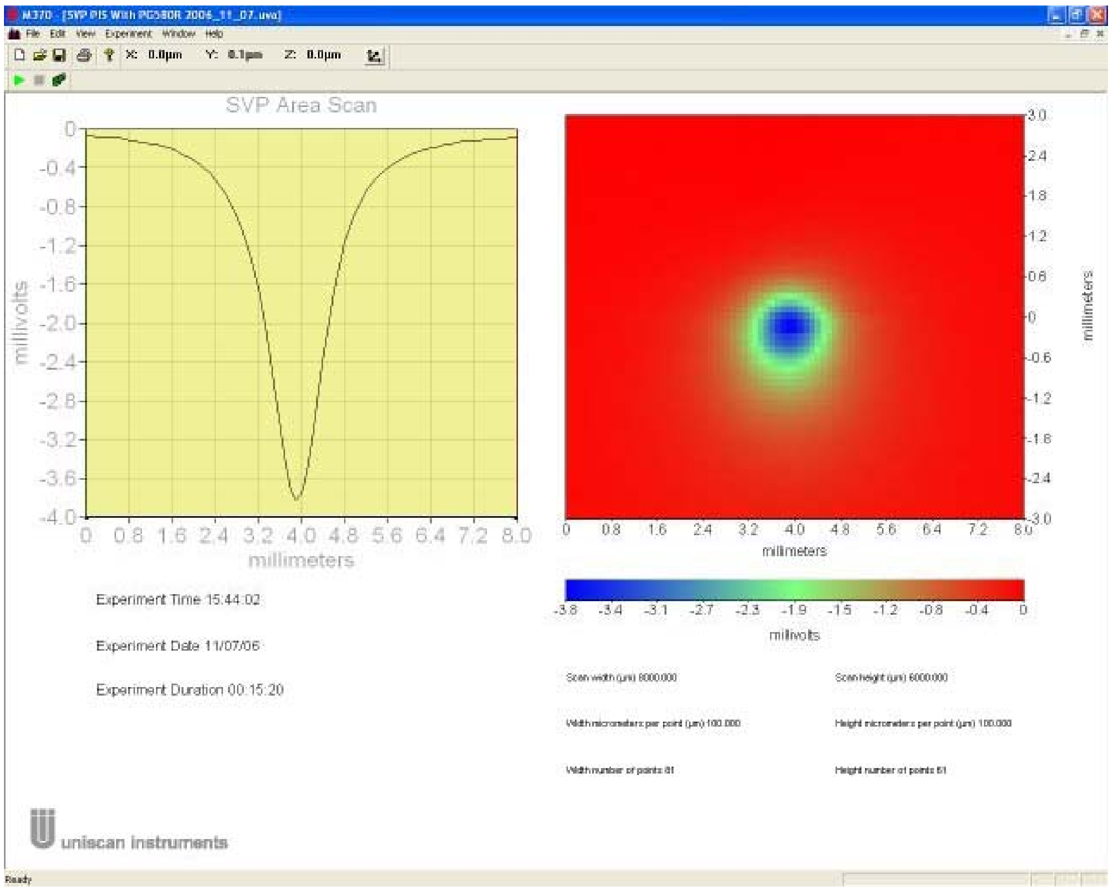


SVP Technique

- The probe is vibrated at a constant, user-defined amplitude (*e.g.*, 30-microns p-to-p),
- The probe is rastered over the sample's surface. Successive line scans build an area map.
- The AC vibration is captured by an electrometer and built-in LIA to provide a sensitive measurement of the electrochemical activity of the sample's surface
- Though SVP uses AC coupling for a more sensitive measurement, it is still inherently a DC measurement (in contrast to LEIS).



SVP Data



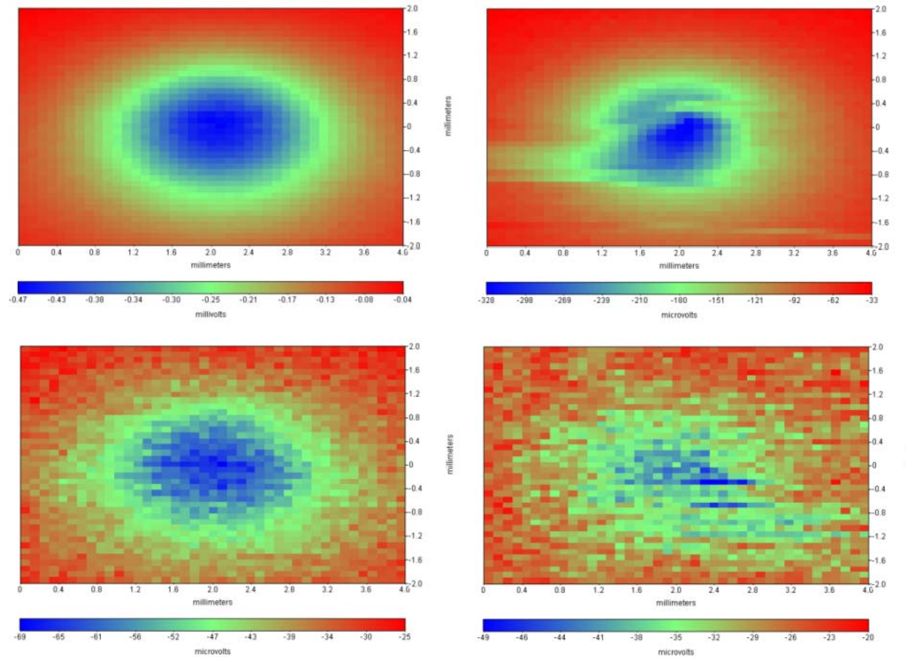
200-micron gold
Point-In-Space Test Sample
with -10 μA applied.

Measured in Tap Water.

AMETEK®

Optimum Solution Conductivity

- **Solution conductivity plays an integral role in the SVP response.**
- Tap Water in my lab is ~ 150 µS/cm.
- Too conductive and potential gradients are too disperse (negatively affects resolution).
- Too resistive and can overload the compliance of the potentiostat.



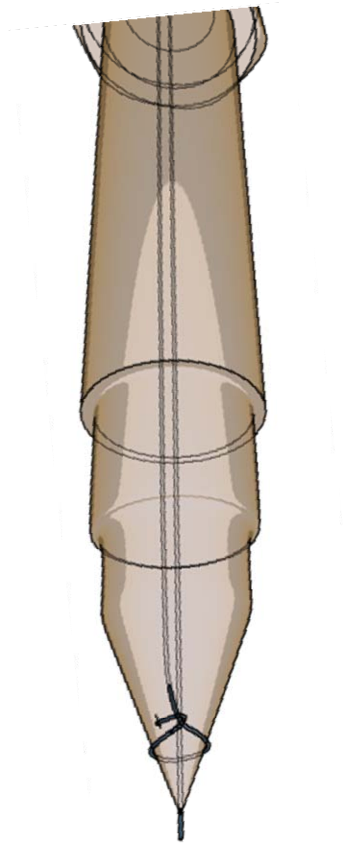
SVP results on the Gold PIS at different solution conductivity.
Top-left is 122 uS/cm (tap water).
Top-right is 600 uS/cm.
Bottom-left is 1400 uS/cm.
Bottom right is 4000 uS/cm
(this one is our seawater analog).

SVP Probe

- The tips start as 200-micron Pt wires.
- These are then etched to a point.
- The tip is then platinized to increase the surface area open to solution (and reduce the solution-metal interface resistance).
- The dimension of this probe varies by between probes, but the tip is in the region of 5μm – 50μm. This is a range and not options.

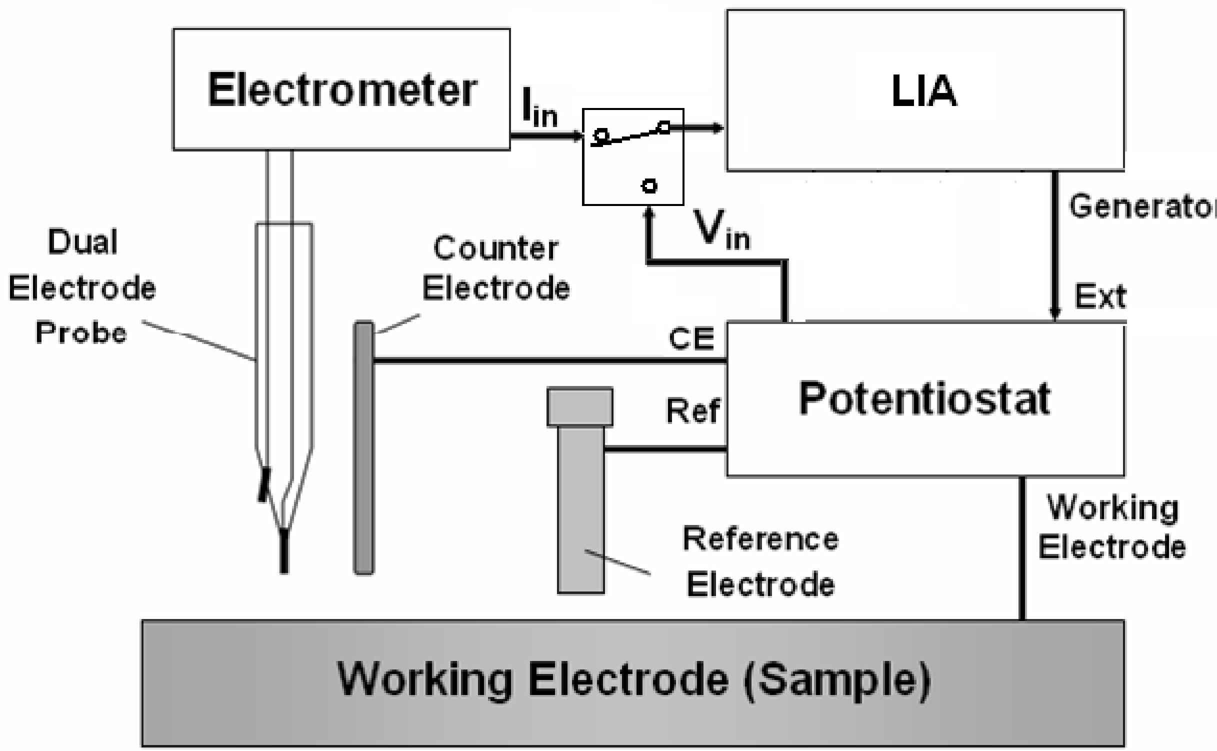
Local Electrochemical Impedance Spectroscopy (LEIS)

- Uses Dual-Element Probe
- Requires external Pstat and FRA/LIA
- Applies global ***v*** and measures local ***i***…by voltage drop through electrolyte.
- LEIS software is different than the M370 program



LEIS Setup using an External LIA

Probe with circular CE.



Compatible External Instrumentation for LEIS

Potentiostats, one of:

PAR 263A

PAR 273

PAR 273A

Solartron 1286

Solartron 1287

FRA/LIA, one of:

Solartron 1250

Solartron 1255

Solartron 1255B

Solartron 1260

PAR 5210

(Solartron 1252)

Existing instrumentation should be verified by dummy cell, if planned on being used.

Modes of Data Acquisition
Fixed Position versus Fixed Frequency

- Point-scan:

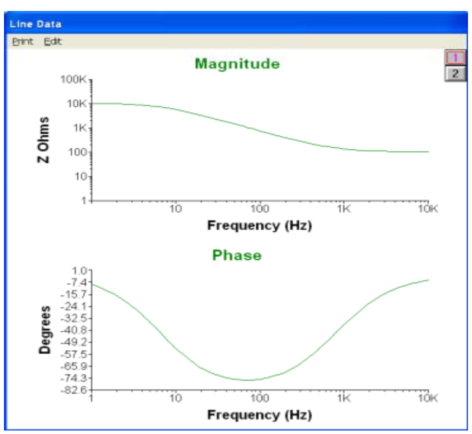
  Fixed probe position, frequency swept.
  - Bode: |Z| and phase versus frequency.
  - Nyquist: $Z_{imaginary}$ versus Z_{real}.

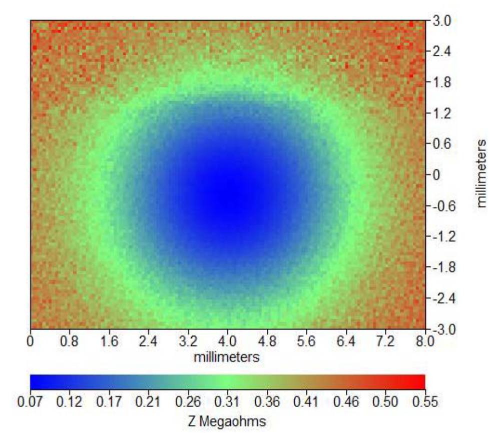
- Line-scan:

  Fixed frequency,

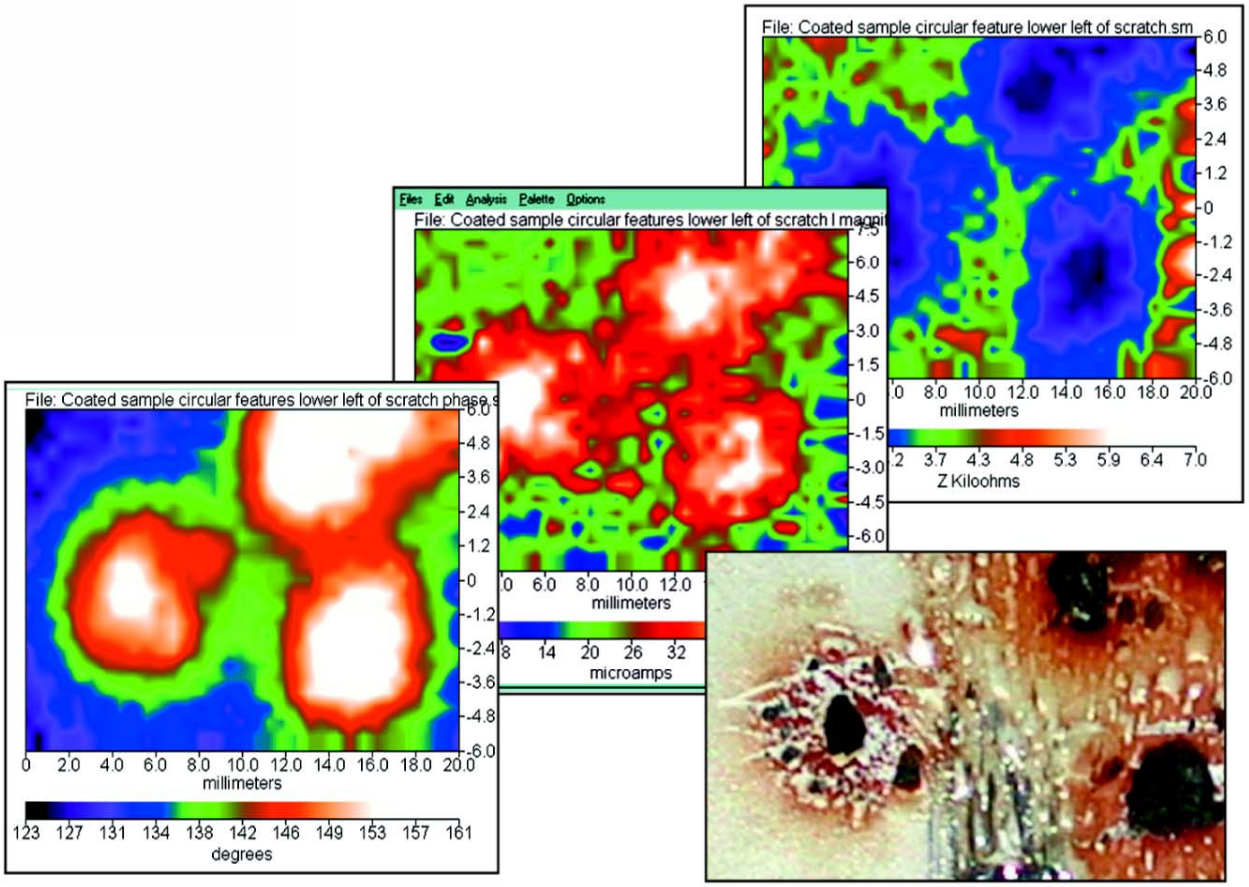
  probe position swept.
  - Magnitude / phase versus position.

- Area-scan: Same





Data from a LEIS Area Scan Experiment



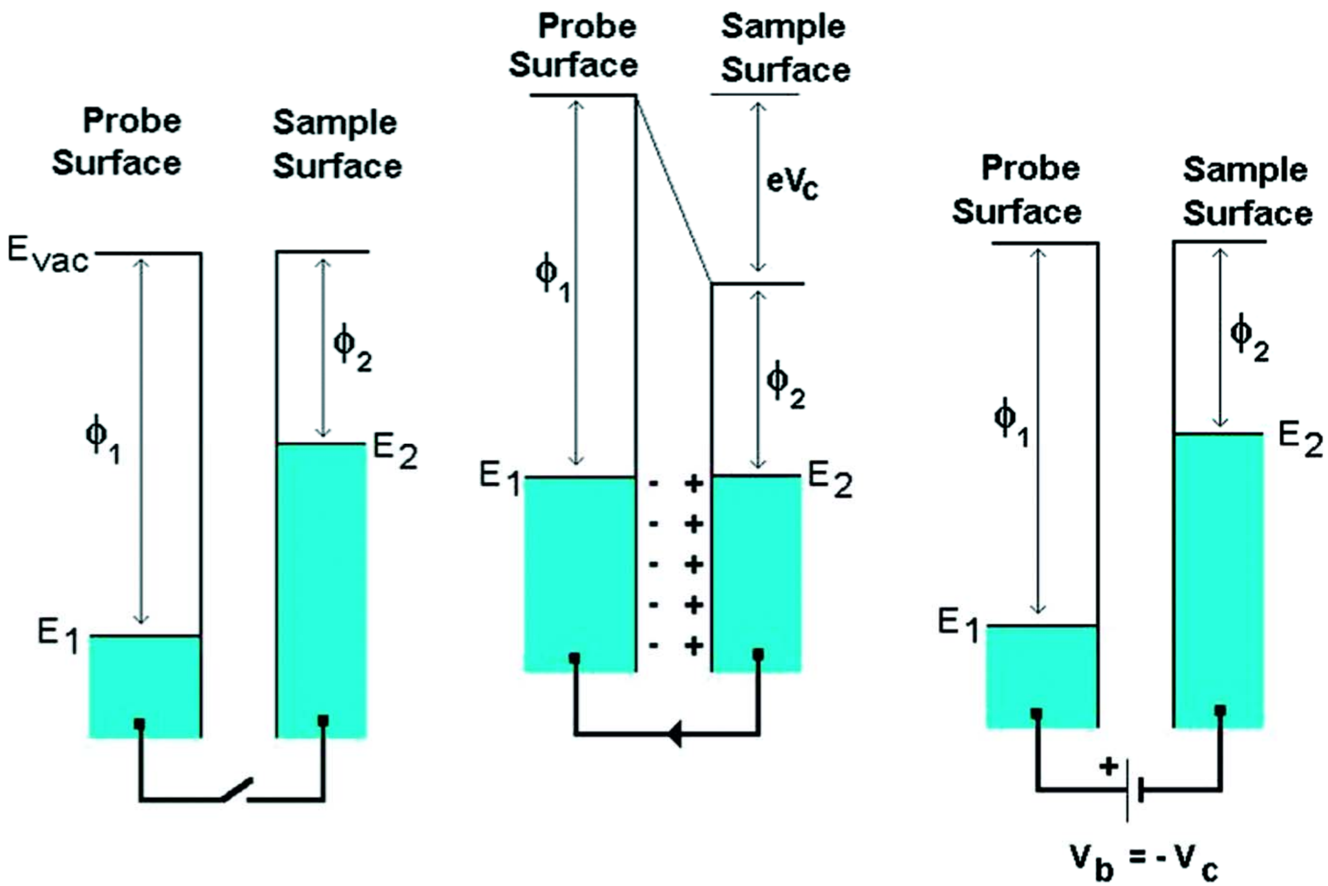
Similar to SVP, but with the advantages of an AC measurement

….particularly in watching the thinning of a coating.

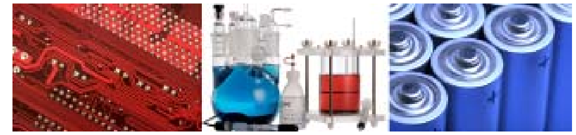
Applications of LEIS

- Inorganic / organic coatings research
- Localized corrosion
- Coating integrity, *e.g.* delamination, defects, bubbling.
- Variations in coating thickness
- Surface contamination
- Inhibitor studies

Scanning Kelvin Probe Theory



Work Function = Energy required to liberate electron from the surface of a conductor



SKP Technique

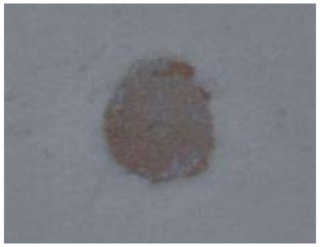
- Non-destructive
- Non-contact
- Measures Work Function difference being probe and sample**
- Typically measured in atmospheric conditions
- Measures over conducting surface…even with a insulating coating over it

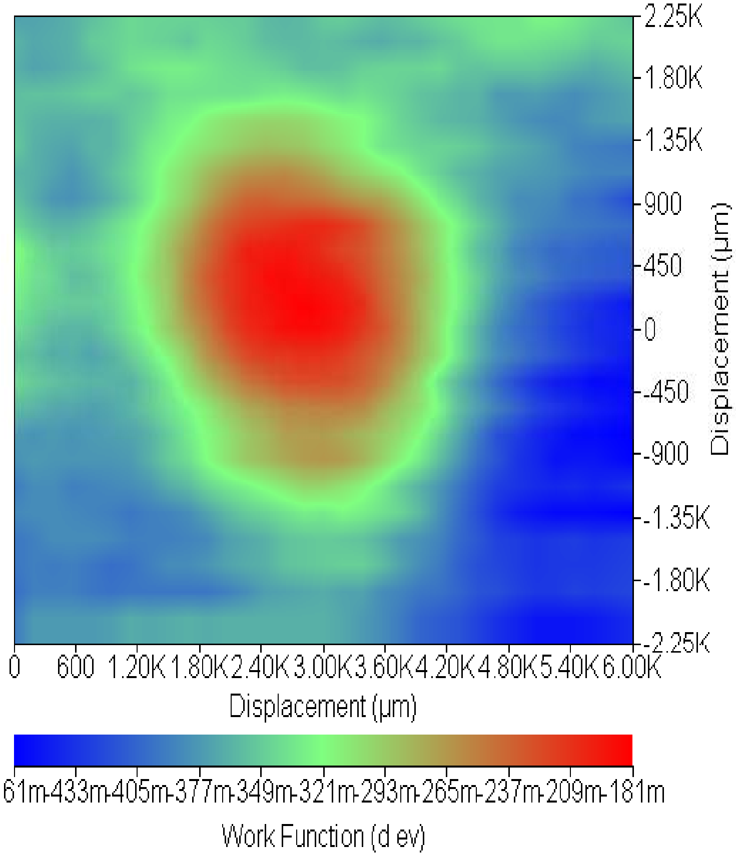
**This work function difference can be related to Ecorr by building a calibration curve

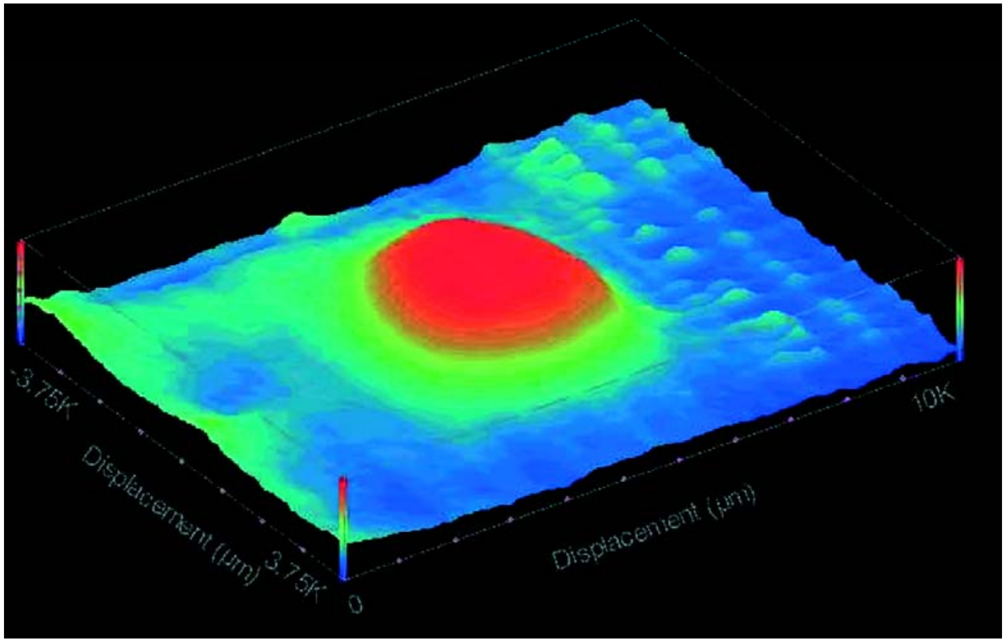
The SKP370

- The SKP370 vibrates the probe to be less destructive and uses a supplied Lock-In Amplifier for enhanced signal recovery.
- Can measure topography via CHM or CTM
- With rubber Gaiter Tricell can be outfitted with other gases.
- Probe is a 500-micron Tungsten wire
- PID controlled microprocessor system

SKP Data



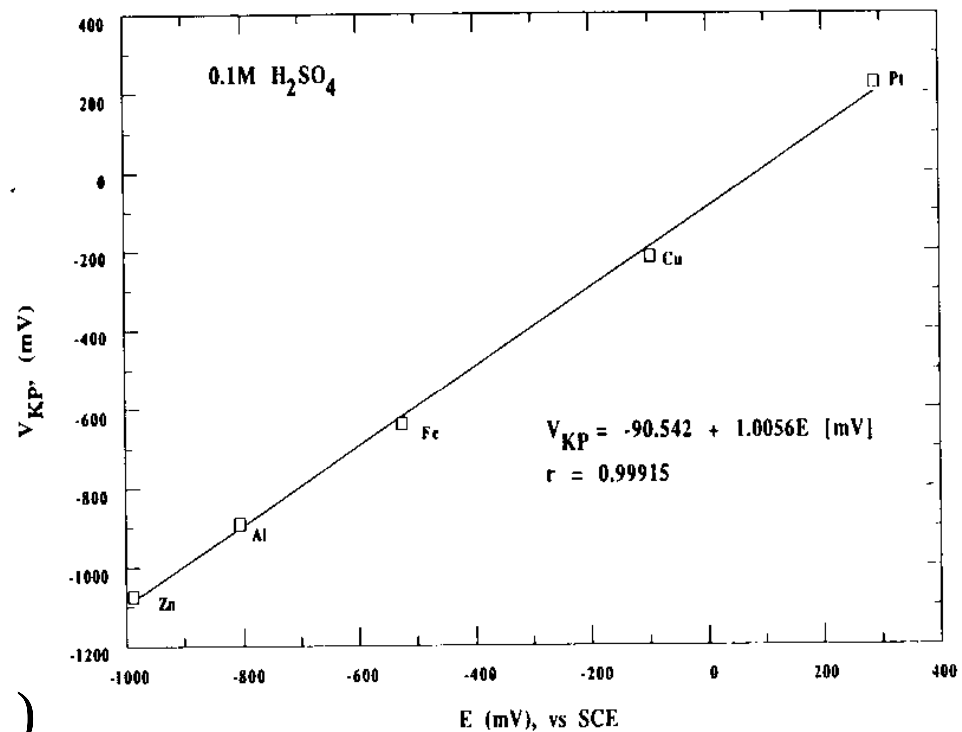




Results of Test Sample (Zn-anodized steel, Zn coating removed with conc. HCl)

SKP Results → Ecorr

E_{corr} can be calculated from the measured difference in work function using the following equation*



$$E_{corr} = \text{Constant} + (\Phi_{probe} - \Phi_{sample})$$

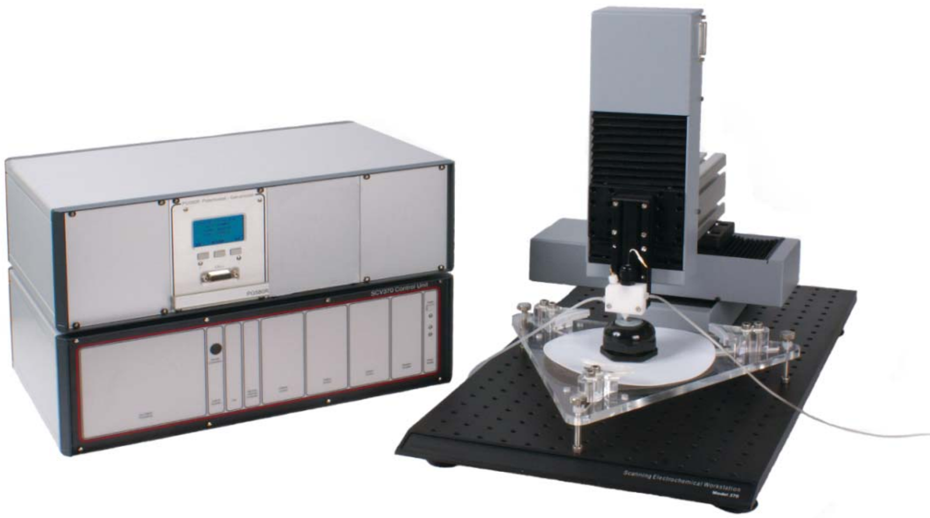
*M. Stratmann and H. Streckel, *Corrosion Science* Vol. 30, No. 6, Pg. 681

Height-Tracking with the SKP370

- The probe-to-sample distance is an important parameter in all techniques of the M370.
- However, this is crucial in the capacitance-based SKP.
- **Using the same probe**, run a scan in topography mode,
- Run a separate SKP experiment using that file as a background file to maintain a constant-distance of the probe to sample.

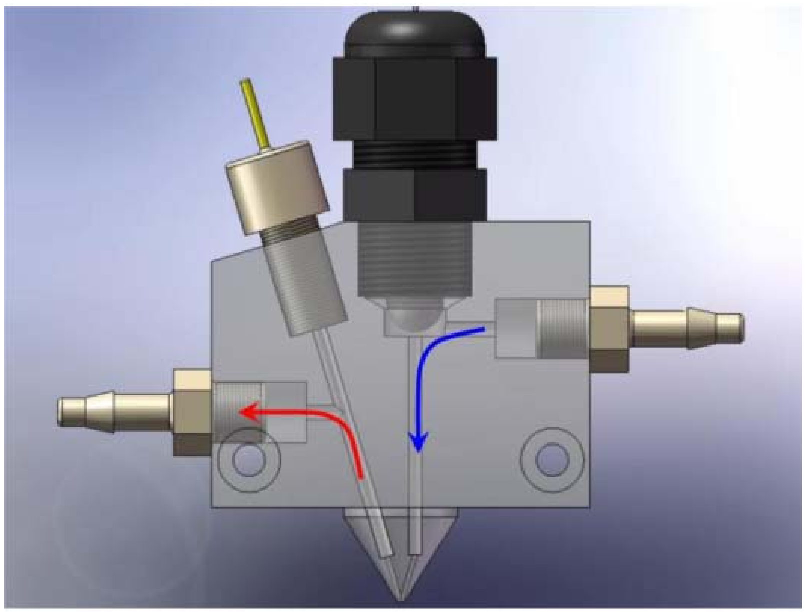
See Application Note demonstrating the importance and different methods to accomplish this.

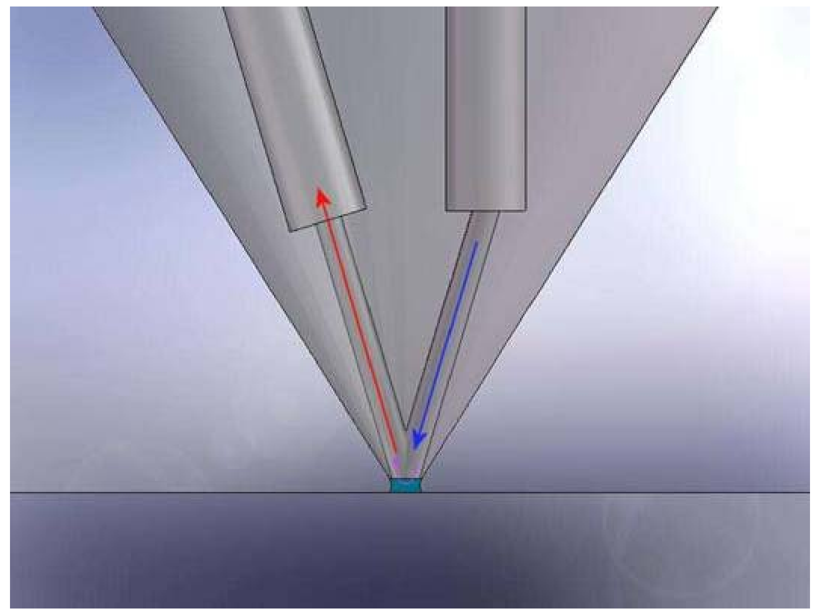
Scanning Droplet System (SDS)



SDS Head and Electrolyte Path

Note: Aperture = 0.5 mm diameter, ~0.196 mm^2.

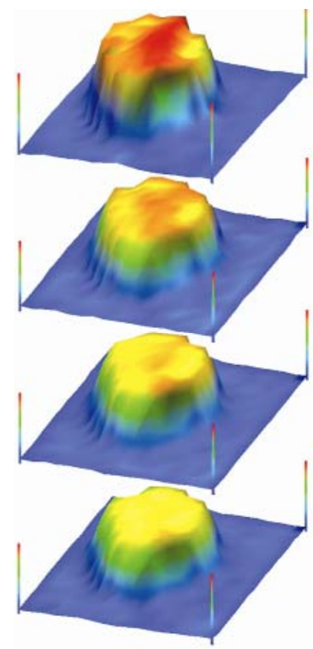




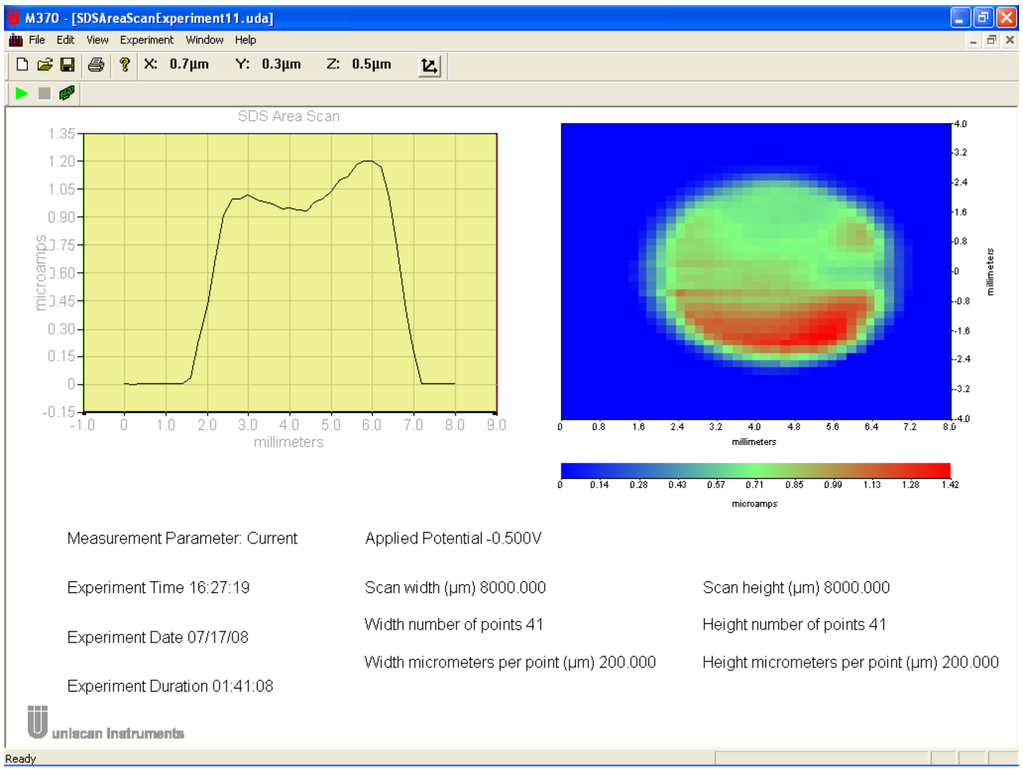
Electrolyte flows into the SDS head (blue arrow) past the Ag/AgCl Reference Electrode…
forms a droplet on the surface (interacts with sample)…
is pumped past the Pt wire CE and out.

SDS Modes of Data Acquisition

- Changing Position:
  - Use supplied potentiostat to apply a constant signal (*e.g.*, potential) and scan the surface looking for changing response (*e.g.*, current).
- Sweeping Signal:
  - Position the SDS head and run a dynamic signal experiment (*e.g.*, Tafel) at a fixed position.
- Changing Flow Rate:
  - Scan the flow rates of electrolyte.

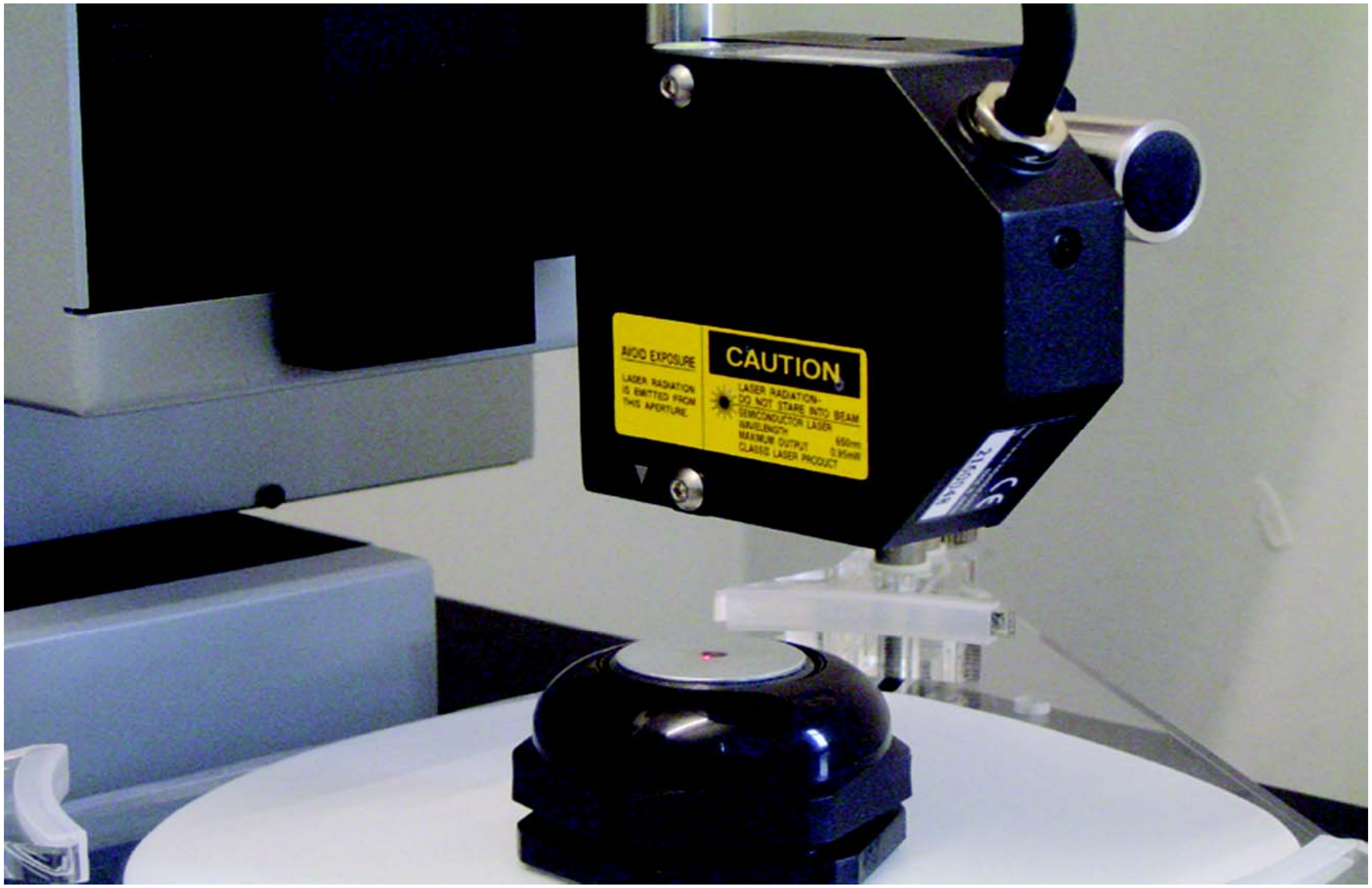


SDS results on Au Test Sample

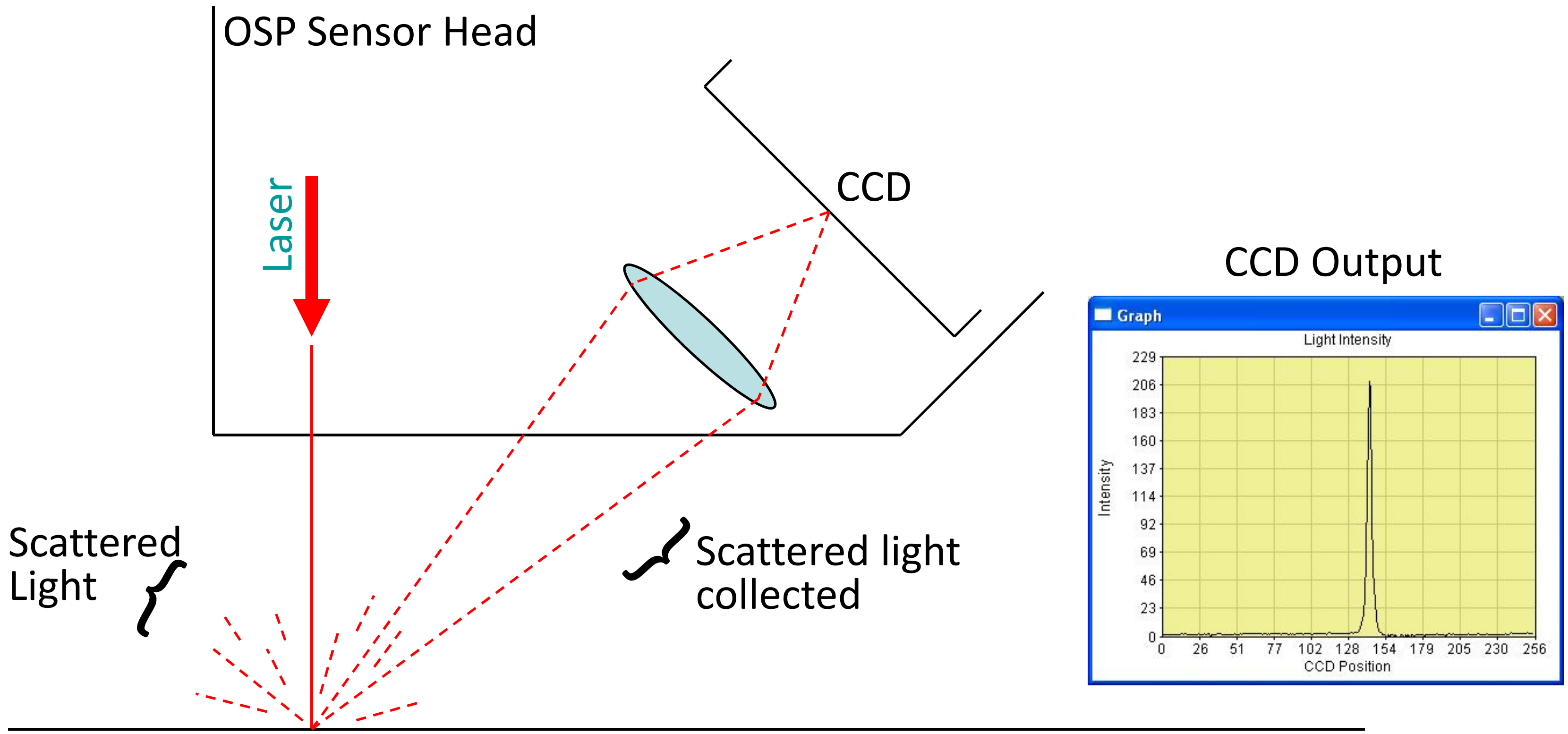


- Micro-physical electrochemistry
- Micro-corrosion
- Micro-OCP measurements

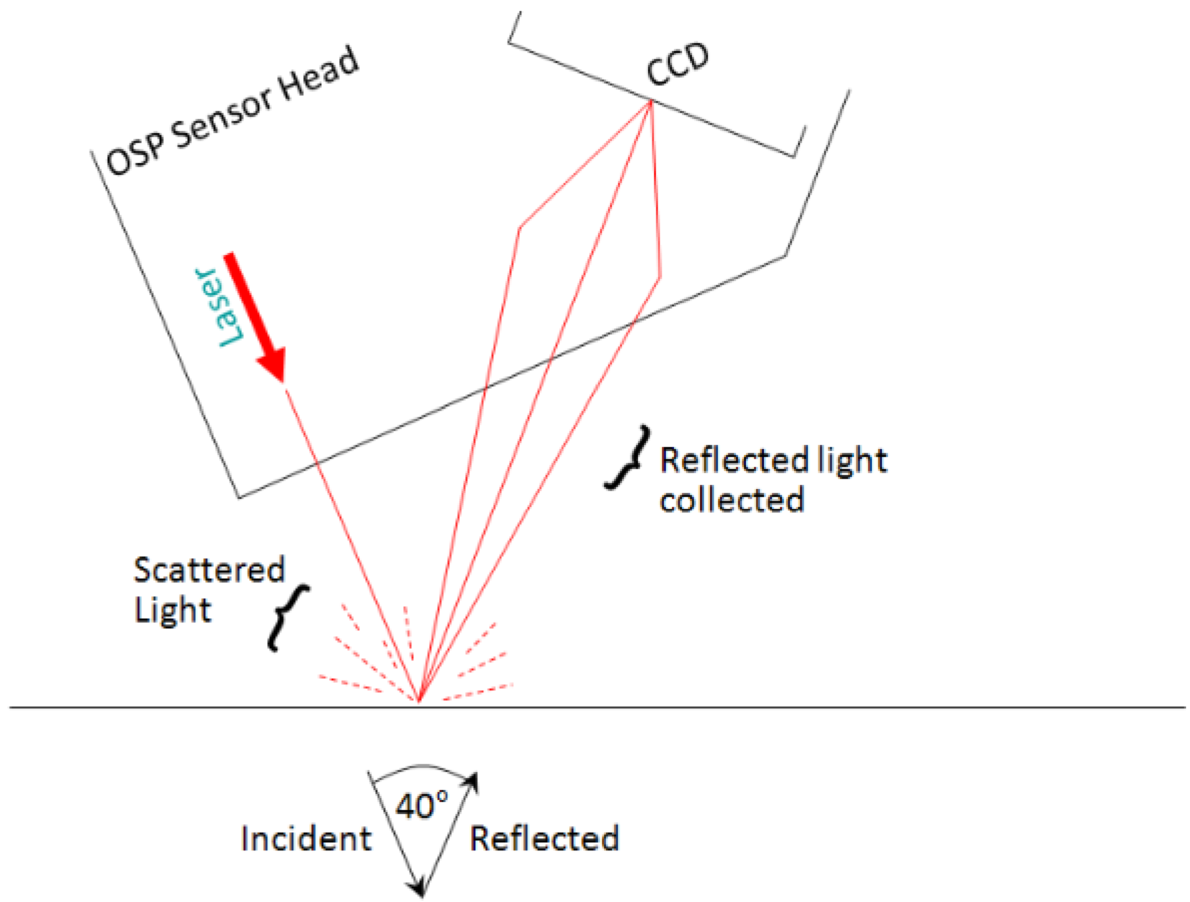
Optical Scanning Profiler (OSP)



Principle of Operation: Diffusely scattered light

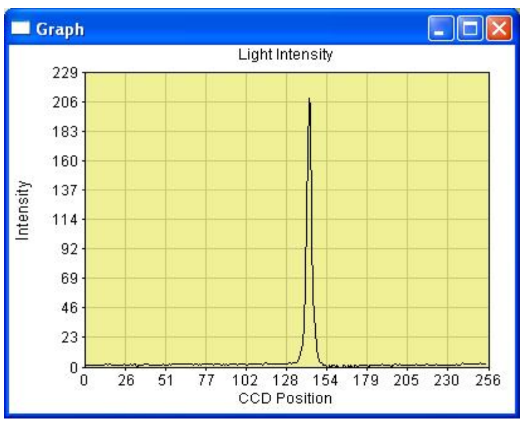


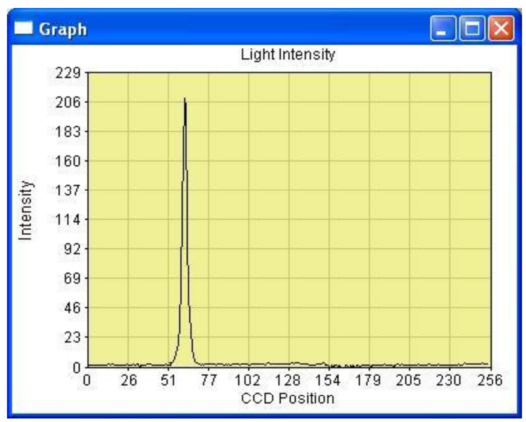
Principle of Operation: Spectural reflected light

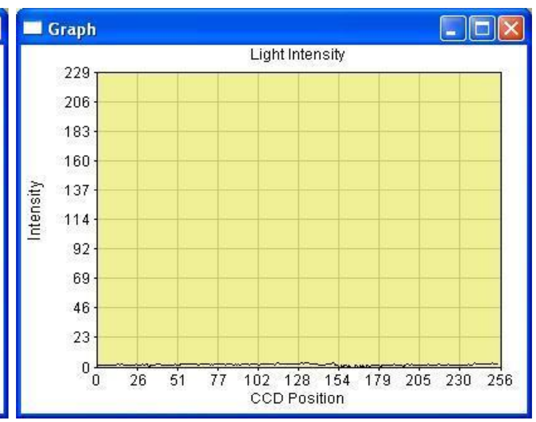


Signal Quality Indicator

Green Light. Amber Light. Flashing Amber Light.





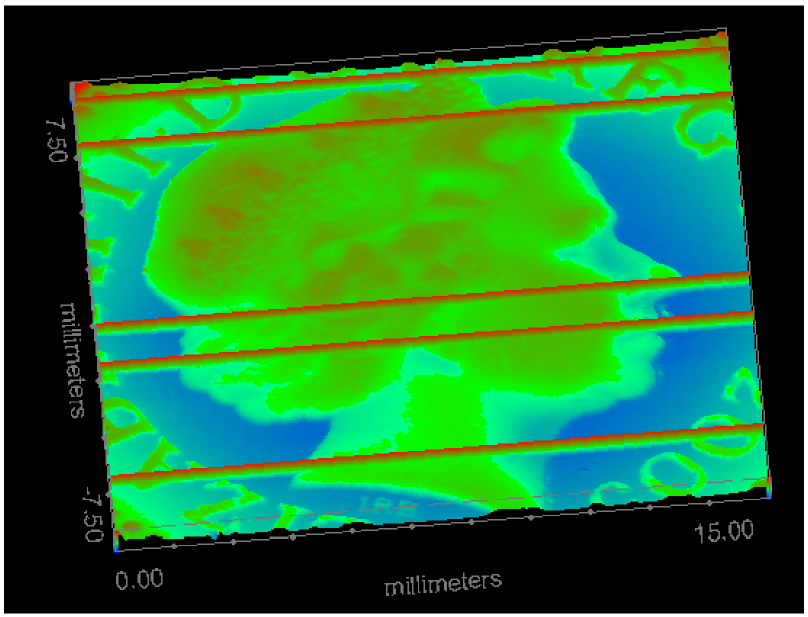


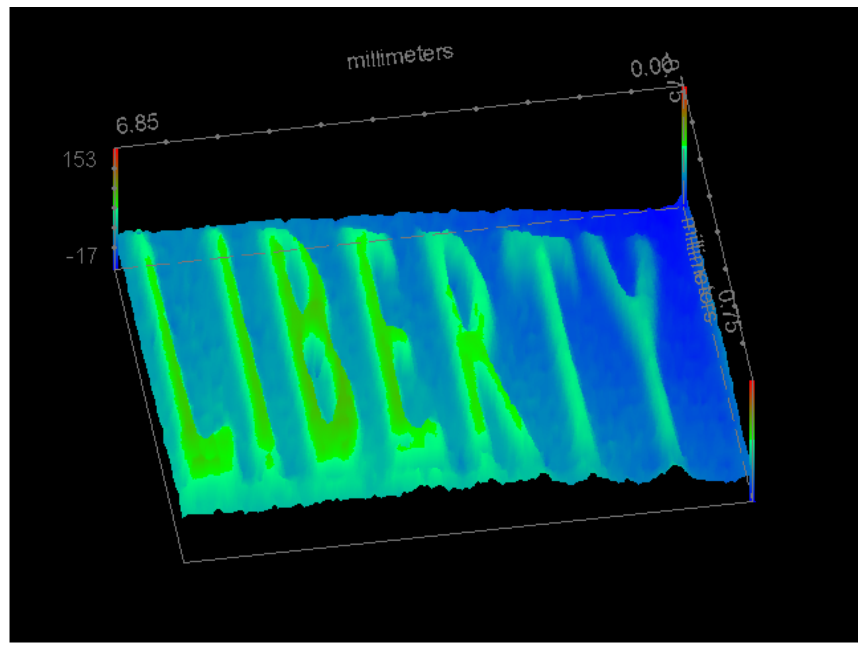
±250µm of zero

Beyond ±250µm
Less than ±5mm

No signal
Beyond ±5mm

OSP results on a GBP and a US Quarter



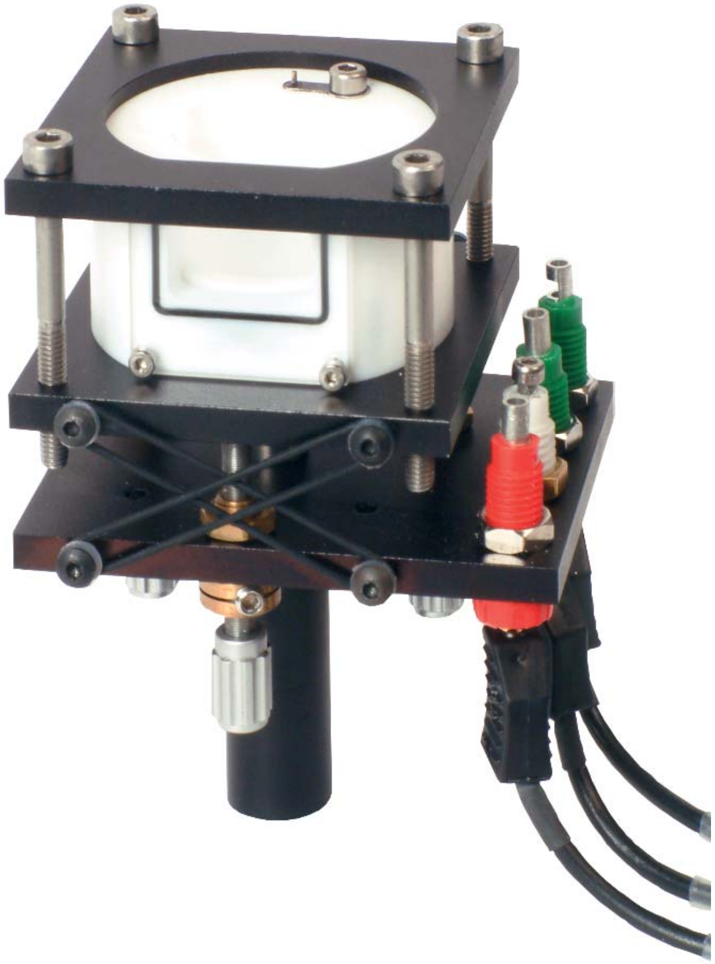


Tricell (Environmental Tricell)

- Holds ~ 1L of electrolyte
- Provides means to level sample
- Mounts a 32-mm diameter sample
- Mounts directly to M370 table
- 4 external ports and rubber cover to control environment

MicroTricell

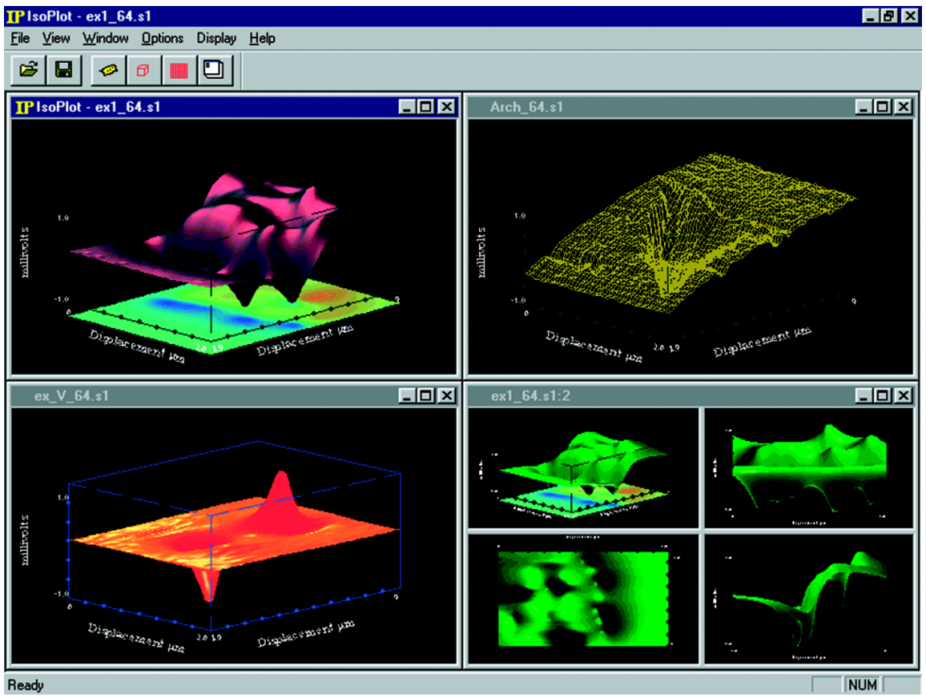
- Small electrolyte volumes
- Provides means to level sample
- Quartz window to help probe positioning
- Wide range of samples (32-mm, blanks and area reducers supplied)



VCAM2

- Long Working Distance Video Microscope
- Helps visualize probe/sample during positioning
- A LCD display

Isoplot



- 3-D rendering software
- Gives user full control to change viewing angle, lighting etc.
- Makes presentation quality graphs
- Dongle-authorized