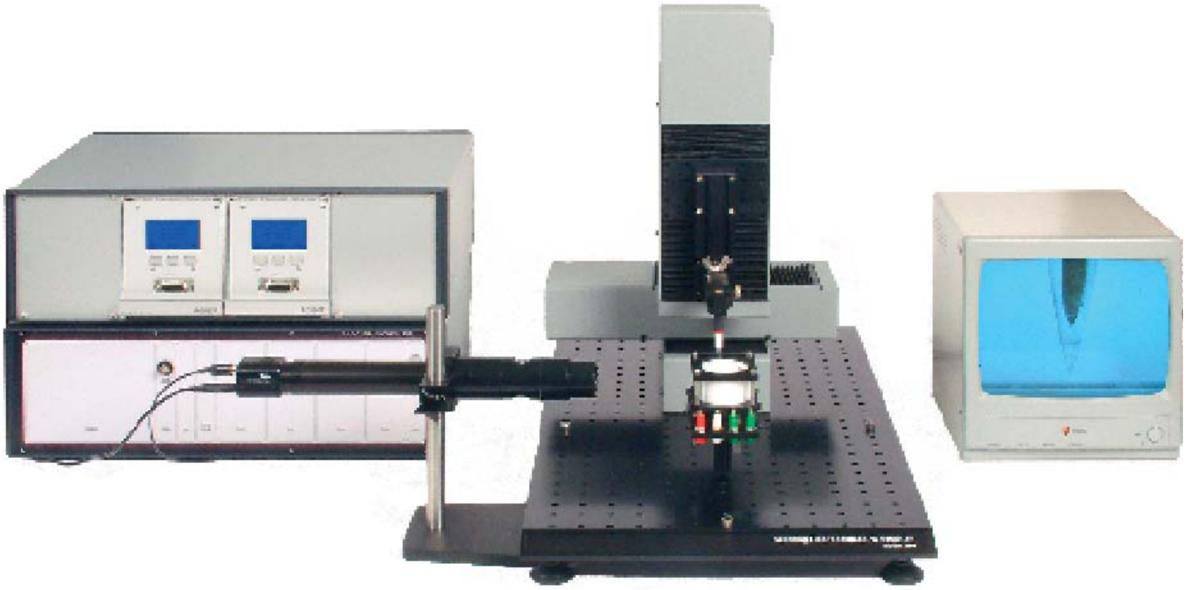
Princeton Applied Research

Model 370 Scanning Electrochemical Workstation



- Scanning Electrochemical Microscopy (SECM)
- Scanning Vibrating Electrode (SVET)
- Scanning Kelvin Probe (SKP)
- Localized Impedance Spectroscopy (LEIS)
- Scanning Droplet System (SDS)
- Non-contacting Surface Profiling (OSP)

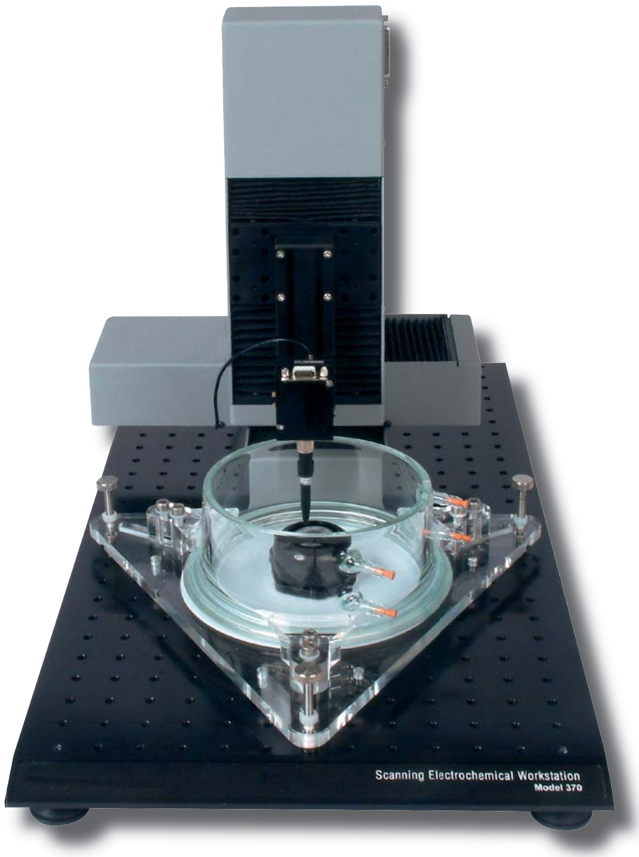
AMETEK

Model 370 Scanning Electrochemical Workstation

The Model 370 Scanning Electrochemical Workstation is a new concept in Scanning Probe Electrochemistry designed for ultra-high resolution, spatially resolved electrochemical and non-contact surface topography measurements.

The Model 370 is a modular configurable system which will perform all the key Scanning Probe Electrochemical techniques plus laser based non-contact surface profiling:

- Scanning Electrochemical Microscopy (SECM)
- Scanning Kelvin Probe (SKP)
- Scanning Vibrating Electrode Technique (SVET)
- Localized Electrochemical Impedance Spectroscopy (LEIS)
- Scanning Droplet System (SDS)
- Non-contact Surface Profiling (OSP)



The Model 370 utilizes a fast and precise closed loop x, y, z positioning system with nanometer resolution, along with a flexible data acquisition system enabling the user to select the configuration most suited to their experiments. The system is designed with flexibility in mind and the design ergonomics insure convenient cell, sample and probe access.

Scanning System Specification

Description	Model 370 Specification
Scan range (x, y, z) mm	70 mm x 70 mm x 70 mm
Scan motor resolution	8 nanometers
Position encoder type	Linear, zero hysteresis
Closed loop positioning	Yes
Linear position encoder resolution	100nm
Maximum scan speed	2 mm/sec
Limit switches on all axes	Yes
Measurement resolution	16 Bit @ 100kHz
Techniques	SECM, LEIS, SKP, SVET, SDS, OSP
Long WD optical microscope (model VCAM2)	Option
Cell mount	Optical table standard screw fitting
Environmental TriCell^{TM} support	Yes
µTriCell^{TM} SECM style electrochemistry cell support	Yes
Aux analog input	Yes
Computer interface	USB
Software - computer operating system	Windows XP^{TM} Proffesional or Vista^{TM} Business
Software - macro programming	Yes
Software - multi-document	Yes
UiECorr^{TM} corrosion software module	Yes
IsoPlot^{TM} 3D rendering software	Option

The Model 370 is available in any or all of the six configurations (SECM, SVET, SKP, LEIS, SDS, OSP) and may be upgraded at a later date by subsequent purchase of any combination of the available options.

A wide variety of optional accessories are available, including various probe options, cell options (Environmental TriCell™ and µTriCell™), long working distance optical video microscope (VCAM2) and 3D shaded surface rendering software (IsoPlot™). The ability to configure to a specific application and upgrade at a later date makes the Model 370 uniquely flexible, while maintaining ultimate performance.

The Model 370 control and analysis software is Windows™ 32 bit MDI with the following features as standard:

- User defined scan parameters (displacement, velocity, step scan/continuous scan mode, step size, number of data points)
- Direct real-time readout of displacement in x, y, and z via 100nm linear encoders
- Post data acquisition x, y, z measurement at any point
- Surface maps acquired at up to 70,000 data points in each axis
- Height tracking in any map experiment using topography data from any source (SKP topography, OSP or Constant current SECM macro)
- Fully programmable macro language for non-standard experiments
- Easy to use, user configurable visual templates
- User definable 16,777,216 color palette via easy to use palette editor
- ASCII exportable data files
- Full Windows™ clipboard support

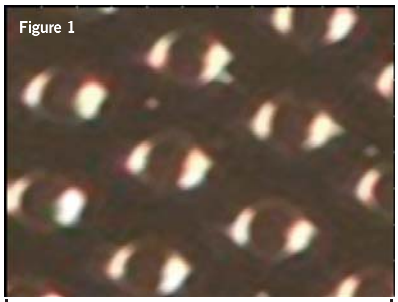
SECM370 Scanning Electrochemical Microscope System

The SECM370 is a precision scanning micro-electrode system which can be used to monitor (or impose) current flowing between a micro-electrode and a specimen surface in solution at extremely high spatial resolutions. It can be used to examine, analyze, or alter the surface chemistry of a sample solution. This equipment has many potential applications in the study of fundamentals of surface reactions in fields as diverse as corrosion science to enzyme stability studies.

The specification of the SECM370 incorporates an integrated versatile bi-potentiostat/galvanostat system with the Model 370 Scanning Electrochemical Workstation. All scanning parameters, variables, control, data acquisition and post data acquistion analysis are performed on a PC via a direct, single connection to the USB port. Using our proven, powerful, and user-friendly software, all scan cycles are automated and are user definable, including linescan, repeat linescan, z-approach scan, area map scan, constant current area map, as well as all standard electrochemical techniques. The unique Macro experiment feature of the M370 software (included) allows the researcher total control of the scanning stage and potentiostats in order to devise even more complex experiments.

Examples included: area open-circuit potential measurement, constant current area scan, auto approach curve, and sloping area scan macros.

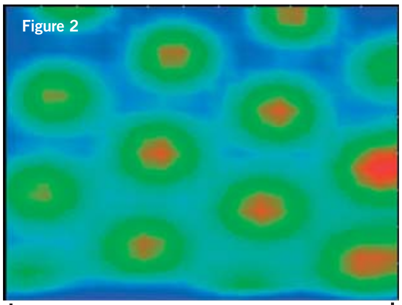
Figure 1



0 60µm

Optical micrograph of Gold on Silicon micro-electrode array.

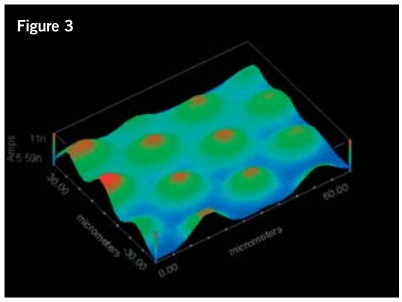
Figure 2



0 60µm

SECM image in tip-generation/substrate-collection mode of area shown in figure 1.

Figure 3



Isometric 3D projection of SECM image shown in figure 2. Peak current differences around 6nA.

SECM

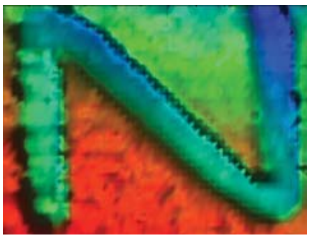
Floating electrochemical cell, allows connection in bipotentiostat or other mixed configurations	
Current ranges	1 nA to 10 mA/V in 8 decade ranges
Current resolution:	15 fA
Maximum current	± 20 mA
Applied probe potential	± 2 V at 16 bits (61µV res) Factory option to ± 8 V*
Applied substrate potential:	± 2 V at 16 bits (61µV res) Factory option to ± 8 V*
Compliance voltage:	± 8 V
ADC resolution	16 bit at > 100 kHz
Rise time	1 V/µsec into 1kOhm
Current measurement accuracy	<0.5%
I/E input bias:	<10 pA
Full computer control of all parameters	
Potentiostat or Galvanostat modes of operation	

* Resolution will vary with option specified

Potentiostat - Galvanostats

The SECM370 system includes a precision bi-potentiostat system, allowing full control and measurement of electrochemical processes at the micro-electrode tip and substrate independently to the above specification.

The SECM370 can be specified with either the µTricell™ or four port environmental TriCell™. Both cells can be accomadated in the standard screw fitting optical table mounts of the Model 370 Scanning Electrochemical Workstation.

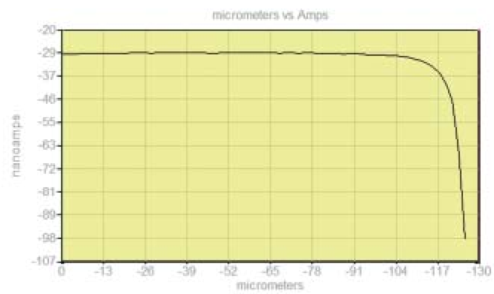


0 millimeters 2.75

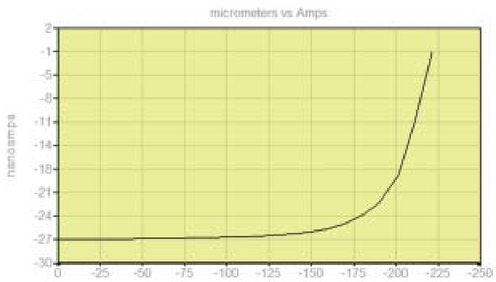
0 millimeters 2.75

Application areas:

- Studying flow through membranes
- Monitoring biological activity
- Determining kinetic parameters
- Imaging immobilized enzymes
- Monitoring living cells
- Liquid - liquid interfaces
- Chemical imaging of biosystems
- Materials for fuel cell research
- Localized ISE
- Surface modification
- Corrosion science



SECM approach curve to conducting surface for 10µm diameter probe.



SECM approach curve to insulating surface for 10µm diameter probe.

SECM370 Software

The SECM370 incorporates our own Windows™ based M370™ 32 bit MDI control and analysis sofware, with the following:

- Scanning probe techniques including x, y, and z line and area scans, z-probe approach curve, constant current area map
- Standard electrochemical techniques including: cyclic voltammetry, linear voltammetry, chronoamperometry, chronopotentiometry, square wave voltammetry, normal and differential pulse voltammetry
- User defined experiments via powerful Macro program experiments. Standard macros shipped with the software include Area OCP, Constant Current Area Scan, Sloping Area Scan, and Auto-Approach techniques

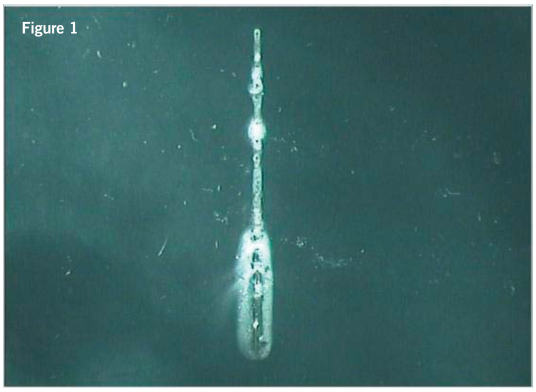
SVP370 Scanning Vibrating Electrode System

The Scanning Vibrating Electrode Technique (SVET) operates with a non-intrusive scanning, vibrating probe measuring and mapping the electric field generated in a plane above the surface of an electrochemically active sample. This enables the user to map and quantify local electrochemical and corrosion events in real time.

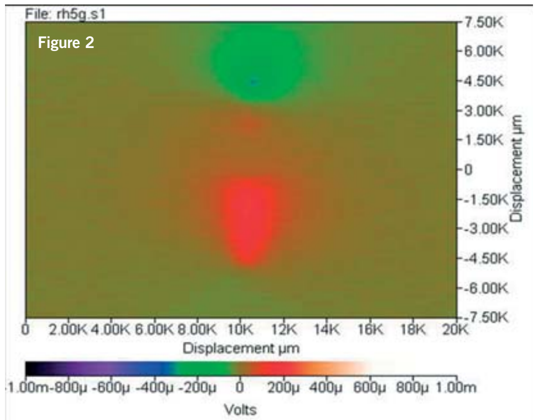
The SVP370 vibrating probe provides you with increased electrical sensitivity as well as enhanced system stability. Localized corrosion events of less than 5 µA/cm² can be measured with this extremely sensitive technique.

The probe vibration is controlled by a piezo-ceramic displacement device allowing vibration amplitudes from 1-30 µm (perpendicular to the sample surface). It is an AC technique, thus, high system sensitivity can be achieved via a differential electrometer in conjunction with a lock-in amplifier.

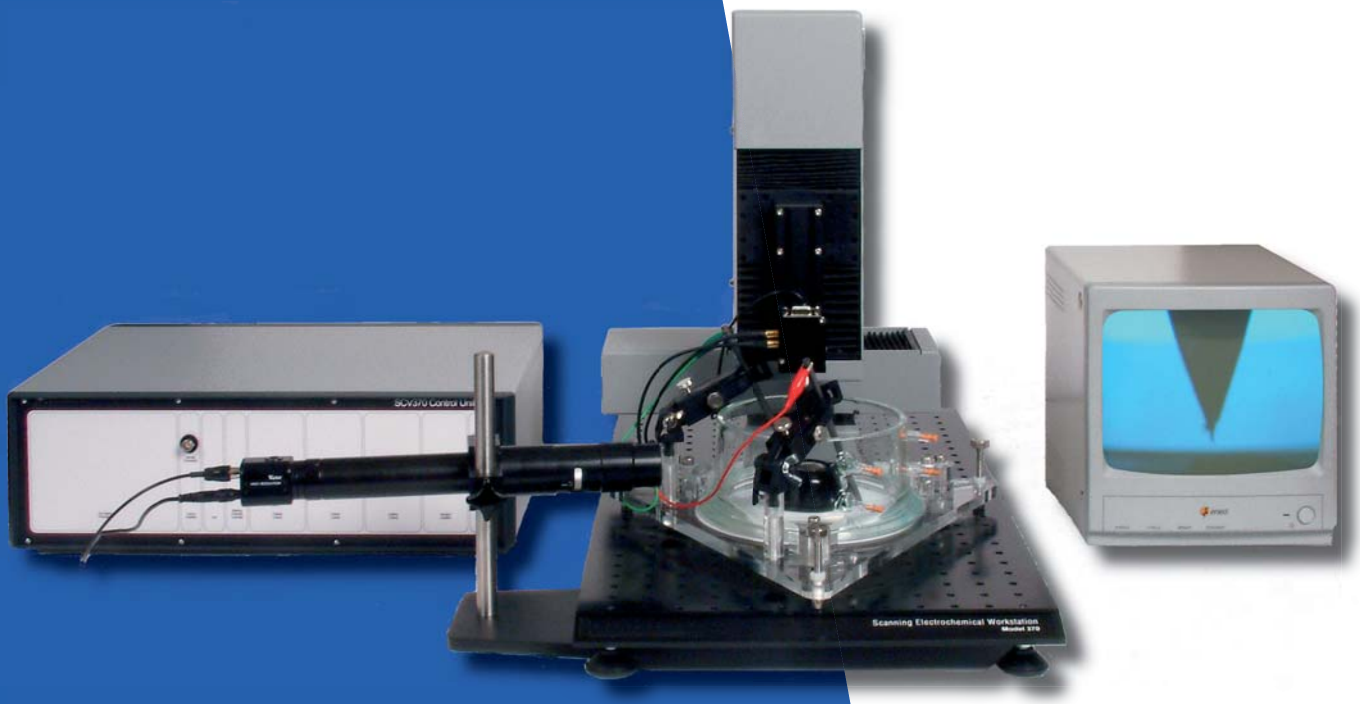
All system parameters, including the xyz scanning mechanism, piezo actuator, and lock-in amplifier are controlled via a PC under the user-friendly Windows™ Operating system.



Optical micrograph of laser ablated, coil coated, galvanized steel.

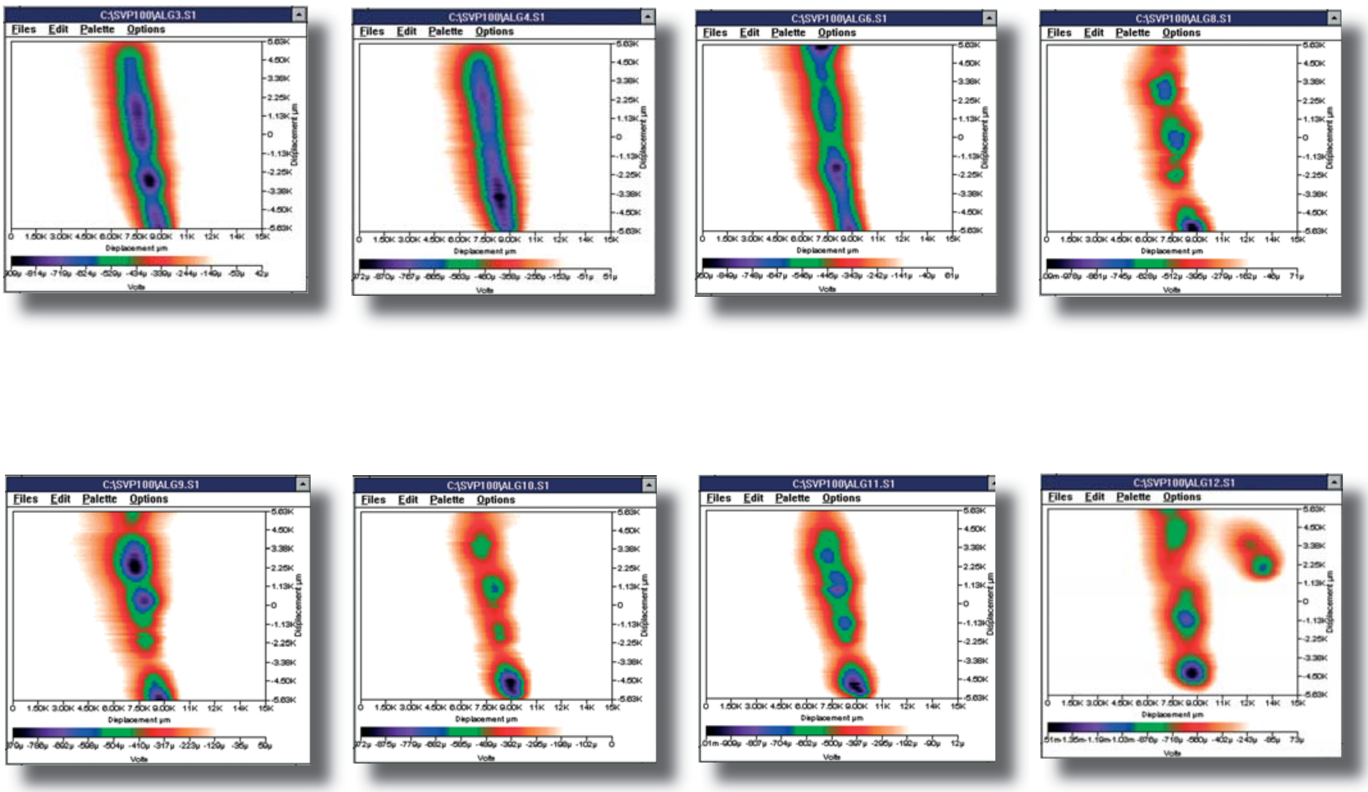


SVET image of region shown in figure1, showing alternating anodic and cathodic behavior of the defect. The red region is cathodic behavior, and the blue is anodic.



SVP

Signal chain	Phase sensitive detection using microprocessor controlled lock-in amplifier with digital dual phase oscillator and differential electrometer input.
Lock-in amplifier	Software controllable gain range. Gain 1-10^5. Maximum theoretical sensitivity 50 nA FSD. Output time constant 0.1, 1, 10 seconds.
Differential electrometer	10^{15} Ohms input impedance. Decade gain ranges 0 to 80dB. Common mode range ±12 V.
Vibration actuator	One dimensional low voltage piezo-electric actuator.
Vibration amplitude (±10%)	Software set from 0-30 microns perpendicular to sample surface.
Probe type	Standard SRET™ MKIII platinized platinum probe socket.
Electrochemical sensitivity	Better than 5 μA/cm² (using standard PIS test approach)



Time resolved SVET images representing current distribution associated with the development of corrosion activity in damaged coil coated steel. Images taken at one hour intervals.

SKP370 Scanning Kelvin Probe System

The Scanning Kelvin Probe (SKP) is a non- contact, non-destructive instrument designed to measure the surface work function difference between conducting, coated, or semi-conducting materials and a sample probe. The technique operates using a vibrating capacitance probe, and through a swept backing potential, the work function difference is measured between the scanning probe reference tip and sample surface. The work function can be directly correlated to the surface condition. A unique aspect of the SKP is its ability to make measurements in a humid or gaseous environment.

The principal of operation of the Kelvin Probe is illustrated in Figure (1).

The figure depicts three energy level diagrams depicting two metals having a constant separation and work functions and Fermi levels of (ϕ_1, E_1) and (ϕ_2, E_2), respectively. The first diagram shows the metals with no electrical contact and differing Fermi levels. When electrical contact is made (center diagram) the flow charge allows the Fermi levels to equalize and gives rise to a surface charge. The potential difference, V_c, is related to the difference in work function:

$$-eV_c = \phi_1 - \phi_2 \qquad (1)$$

where e is the electron charge. The inclusion of an external backing potential, V_B (final diagram), allows for a nulling of the surface charge at a unique point where $V_B = V_C$. This point represents the work function difference between the two materials.

When capacitance is at a minimum, the sample potential, V_B is varied automatically to ensure that the nullpoint is always maintained and thus the potential at which nulling occurs equates to the work function difference between the probe and sample. Therefore, the values presented in the analyses are opposite to the actual work function being measured.

Work function can then be used to determine the corrosion potential (E_{corr}) at a specific point using the relationship:

$$E_{corr} = \text{Constant} + (\phi_1 - \phi_2) \qquad (2)$$

where (ϕ_1 - ϕ_2) is the measured work function between the probe and the sample. The constant can be determined by measuring the corrosion potential using a conventional reference electrode in an electrolyte. Once the constant is known for a particular sample, E_{corr} can be calculated directly from the SKP data

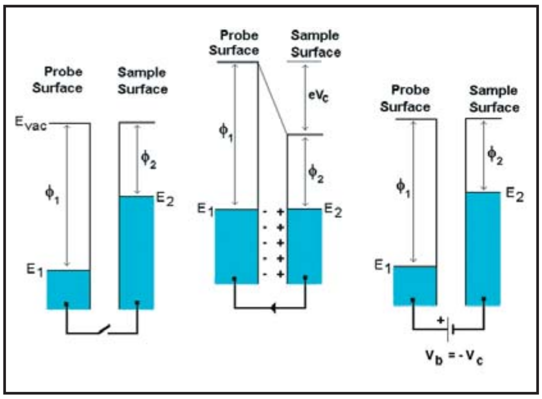


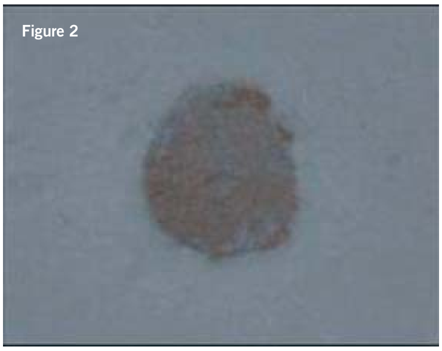
Figure 1

Application areas:

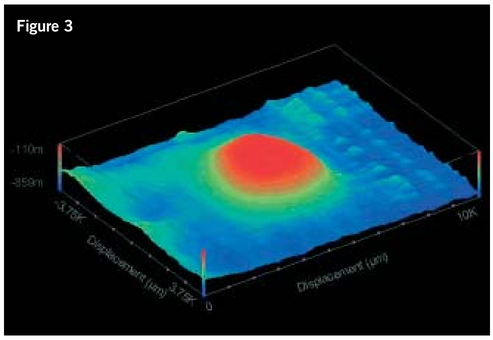
- Energy Systems
- Dipole layer formation
- Display technologies
- Charge analysis
- Fermi-level mapping
- Photo voltage spectroscopy
- Corrosion
- Coatings
- Sensors
- Solar cells

SKP

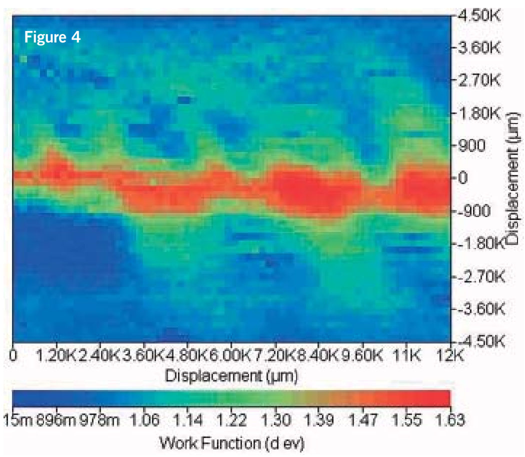
Signal chain	Phase sensitive detection using microprocessor controlled lock-in amplifier with digital dual phase oscillator and differential electrometer input.
Lock-in amplifier	Software controllable gain range. Gain 1-10^5. Maximum theoretical sensitivity 0.5μV FSD. Output time constant 0.1, 1, 10 seconds.
Differential electrometer	10^{15} Ohms input impedance. Decade gain ranges 0 to 80dB. Common mode range ±12 V.
Vibration actuator	One dimensional low voltage piezo-electric actuator.
Vibration amplitude (±10%)	Software set from 0-30 microns perpendicular to sample surface.
Backing potential controller potential range	±10V.
Backing potential controller DAC resolution	300μV.
Backing potential controller sampling	0.1 to 1000Hz.
Backing potential controller type	PID Controller.
Probe type	SKPR Tungsten air gap.
Electrochemical sensitivity	Better than 0.15 meV.



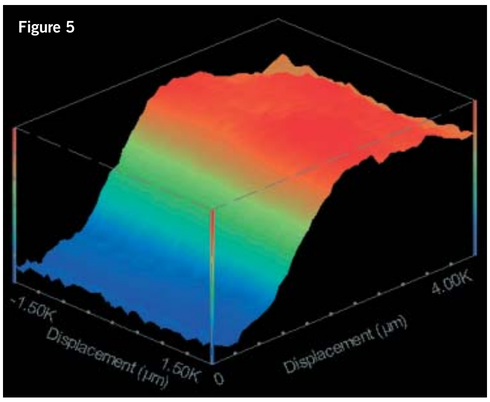
Optical image of an area of etched zinc coated steel



Surface map of Scanning Kelvin Probe signal recorded over area of sample shown in Figure 2.



Scanning Kelvin Probe measurement of filiform corrosion on Aluminium.

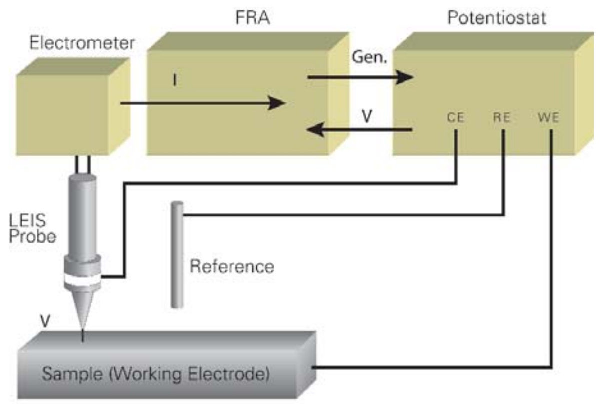


Scanning Kelvin Probe measurement over Indium Tin Oxide (ITO) / Organic LED interface

LEIS370 Localized Electrochemical Impedance System

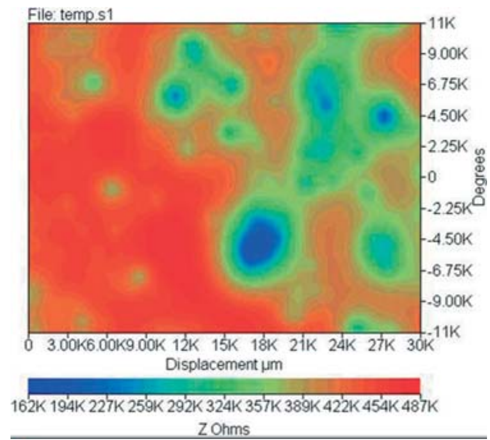
The LEIS370 allows spatially resolved impedance measurements to be made, combining established principles of EIS measurements with scanning probe technology.

The principles of LEIS are similar to those employed in traditional bulk EIS, in that a small sinusoidal voltage perturbation is applied to a working electrode sample and the resulting current is measured to allow the calculation of the impedance. However, rather than measure the bulk current, a small electrochemical probe is scanned close to the surface, measuring the local current in the electrolyte.

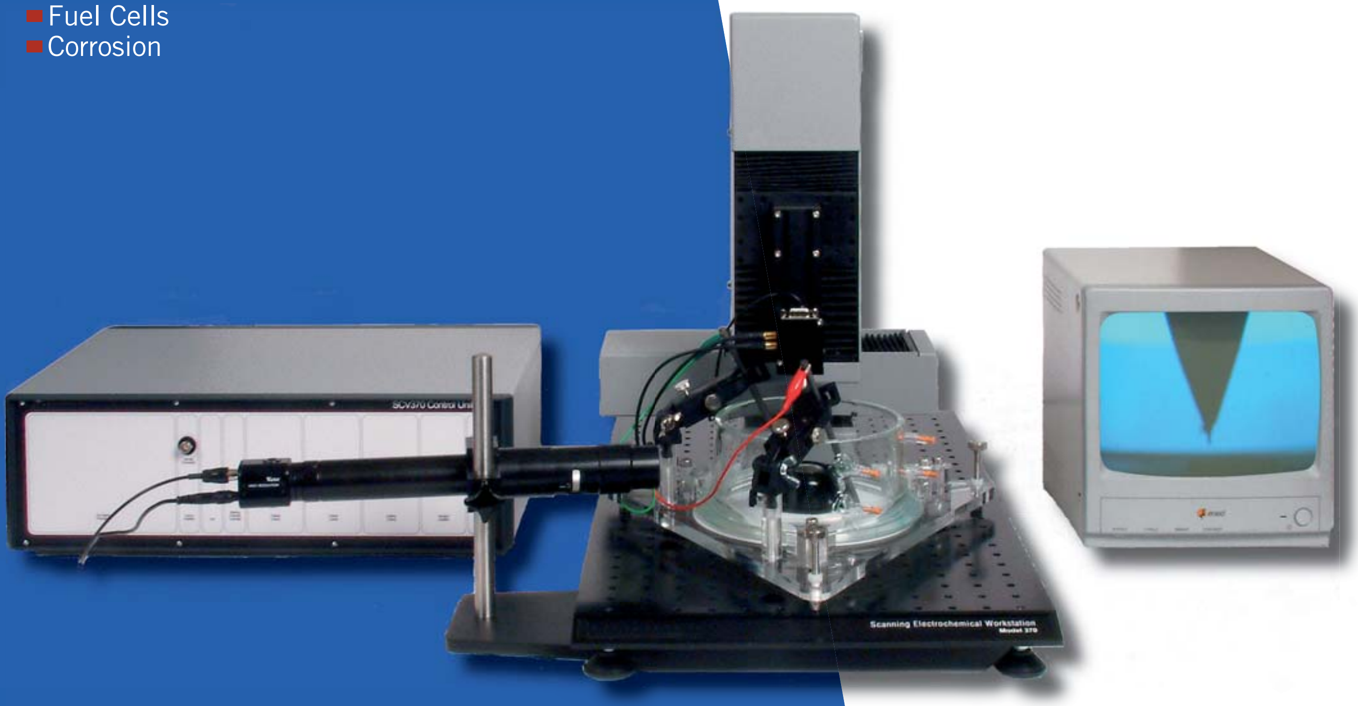


Application areas:

- Imaging complex impedance of thin films
- Direct imaging of cell growth media
- Characterization of photoelectrochemical reactions
- Photo voltage spectroscopy
- Passivated metals and alloys
- Batteries
- Sensors
- Fuel Cells
- Corrosion

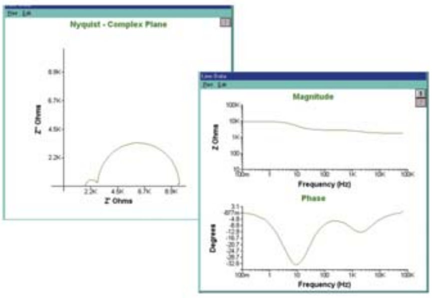


Localized impedance map of intact coating on mild steel with sub-film chloride contamination.



LEIS

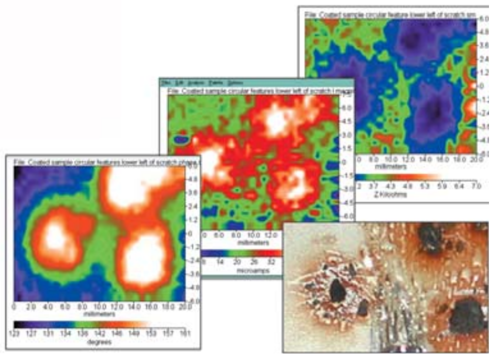
Frequency range	**Dependent on FRA / LIA.**
Display modes	**Impedance line-scan, area scan, point frequency scan, Bode and Nyquist.**
Differential electrometer	**10^{15} Ohms input impedance. Common mode range ±12V.**
Probe type	**Twin probe socket. RSP type probe.**
Compatible instruments	**Princeton Applied Research:** **5210 Lock-In Amplifier** **273, 273A, and 263A Potentiostats.** **Solartron:** **1250, 1255, 1255B, and 1260 Frequency Response Analyzers.** **1286 and 1287 Potentiostats.**

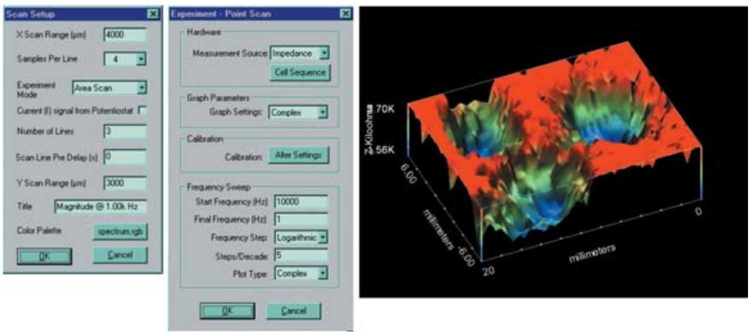


Software control

The LEIS370 software is 32-bit, Microsoft® Windows™ based, and provides the user with complete control of the potentiostat / galvanostat and lock-in amplifier / FRA as well as the LEIS370. Full frequency sweeps of individual points of interest or a feature on the surface of a sample are easily set with a few clicks of the mouse.

Mapping of impedance data over the surface of the sample at a single frequency has never been easier. Real-time display of the data provides the user with instant feedback on the phase or magnitude of the impedance values measured. As an alternative, it is possible to measure the magnitude and phase of the voltage, current or admittance as well. In addition, the LEIS370 allows the user to make galvanic or bulk impedance measurements simply by choosing which mode the potentiostat is operating in, and the software does the rest.





The LEIS370 software provides the user with a high degree of control over the experimental parameters as well as graphical features. The area scan images are easily exported into a text document as a bitmap image, or the data can be exported into a data spreadsheet for further analysis. The optional IsoPlot™ 3-D Surface Rendering Software allows the user to control viewing, light angles, color and plotting parameters.

SDS370 Scanning Droplet System

The Scanning Droplet System is a technique which confines a liquid in contact with a sample surface in order to measure electrochemical and corrosion reactions over a limited region where the droplet is actually in contact with the sample. This offers the ability to spatially resolve electrochemical activity and to confine it exclusively to a quantifiable area of the sample.

An additional feature of the Scanning Droplet System is the inclusion of a pumped fluid handling system to vary the flow rate of electrolyte over the surface sample. This allows the standard measurements to be made versus flow-rate and adds the ability to remove any reaction product from the sample surface, resulting in constantly refreshed solution in the microcell.

The Scanning Droplet technique allows the positioning of a small drop of electrolyte from the PTFE machined capillary onto the sample surface. The wetted surface area under investigation acts as the working electrode and the capillary contains the counter and reference electrodes which are electrically connected to the surface through the drop. The wetted area is approximately determined by the capillary radius. The small distance between the counter electrode and the sample allows high current densities due to the small ohmic resistance. The electrolyte drop is then scanned at high resolution across the surface sample.

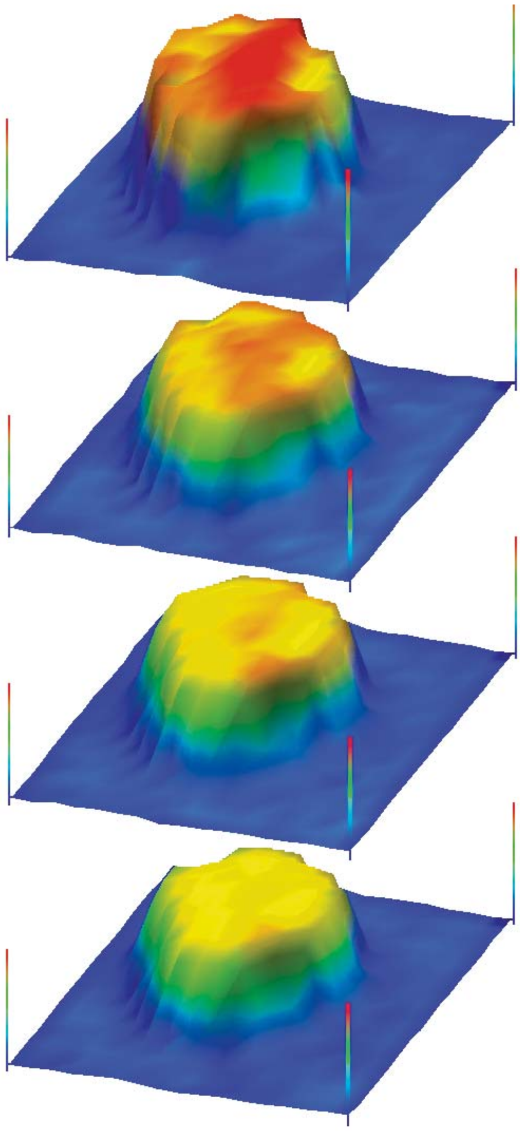
The Scanning Droplet System allows a spatially resolved, in-situ investigation by the standard electrochemical techniques such as line scans, area maps, potentiostatic pulse steps, and open circuit measurements. The electrolyte flow through the cell is controlled via a precision peristaltic pump thus ensuring a good reproducibility of the free droplet wetted area.

Application areas:

- Characterization of surface oxides
- Investigation of coatings
- Characterization of ISFETs
- Investigation of pitting corrosion
- Localized corrosion versus flow rate

SDS

Reference electrode	Ag/AgCl mounted within sensor head
Counter electrode	Pt wire inside the capillary
Micro pump	Peristaltic Pump type, 4-channels
Head construction	PTFE head with silicon rubber tubing
Aperture	i.d 0.5 mm, 0.196mm^2
Resolution	<1mm depending on solution/surface
Supported techniques	CV, CA, Ecorr vs. T, LPR, Line Scan, Area maps



Ecorr changes due to flow rate variation on mild steel sample.

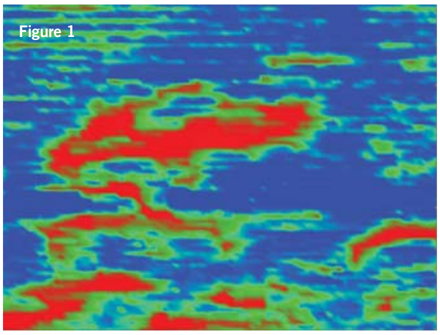


Figure 1. Polarized partially zinc-coated mild steel sample. Red areas show coating retained intact. (SDS370)

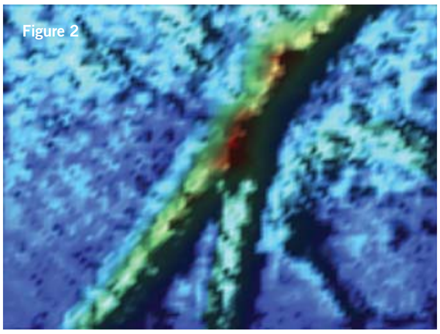
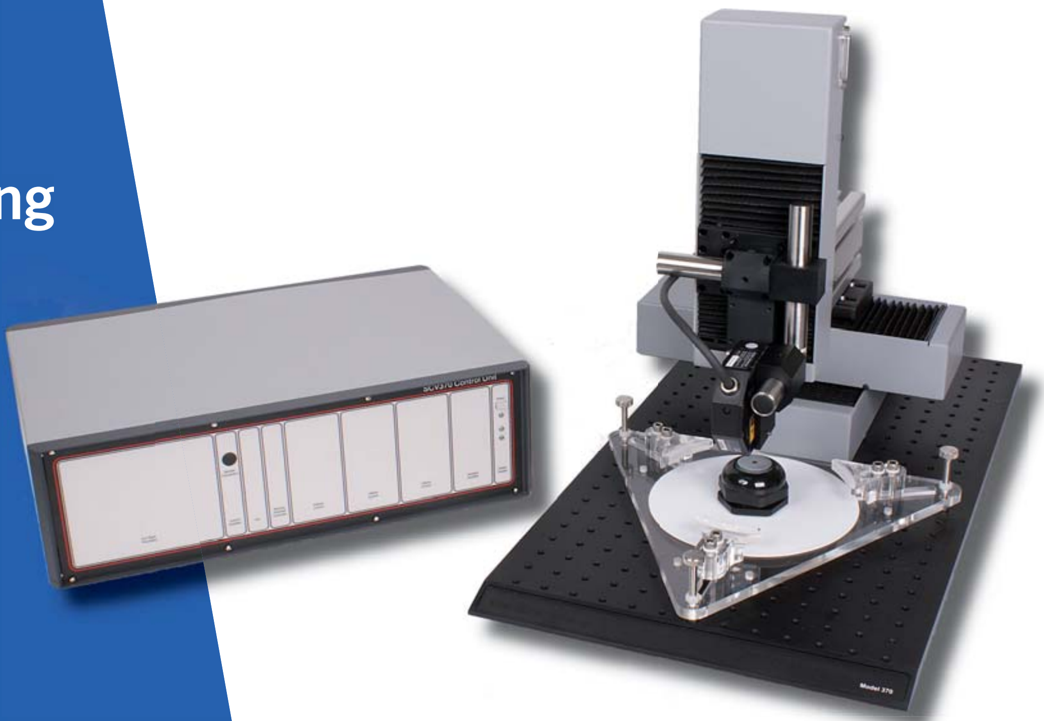


Figure 2. Open-circuit potential changes over zinc-coated sample due to scoring. (SDS370)

Figure 3. Optical surface profile of the scored zinc sample shown in figure 2. (OSP370)

OSP370 Non-contact Surface Profiling



Utilizing a non-contact laser displacement sensor, the OSP370 module allows fast and accurate non-contact surface measurement to a very high accuracy. Features of less than one micrometer can be imaged and measured over a height measurement range of 10 mm without touching the sample surface.

The OSP370 incorporates a CCD displacement sensor mounted on the scanning head of the M370 workstation. A small spot of laser light at 650nm is projected down onto the sample surface and the scattered light is focused on to the CCD aray allowing the direct displacement measurement of the diffuse scattered light.

This allows very accurate surface height profile of the entire surface to be generated, and thus measurement of the surface roughness, and topography features. Most importantly, the OSP370 module will allow the use of the generated data subsequently to alter the height of the probe in any of the other electrochemistry techniques, so the probe can scan over uneven surfaces while maintaining a constant distance of the probe from the sample.

OSP

Measurement range	10mm
Reference distance	30mm
Maximum vertical resolution (static)	100nm
Spot size	30µm at focus
Scan speed	2mm/sec
Multiple readings averaged	Yes
Correct positioning	Red light / Green light
Scan range (x, y, z)	70mm
Light source	650nm class 2 semiconductor laser max. 0.95mW

Surface Topography

- 32 bit MDI control and analysis software running under Microsoft™ Windows™. Control functions include precise speed and position of height measurement sensor, all automatic scanning facilities for single linescan and two dimensional calibrated surface map
- Data resolution up to 64,000 samples per line
- Dynamic data display of all displacement (x,y,z) parameters via optical encoder readouts displayed on floating toolbar
- Curved surface removal
- Macro-analysis language for automatic signal processing of data files including: tilt correction, digital filtering, thresholding, arithmetic, statistics, and autothresholding
- Export of 1:1 tiff files (Bi-color in threshold mode)
- Area map analysis with precise post data acquisition measuring spatial displacement and surface height at any point
- Dimensional measurement including point to point, angle, radius of curvature, etc.
- Full line and surface roughness statistics including Ra, Rp, Rq, Rv, Rt, Sa, Sp, Sq, Sv, St, Sst, Sku
- Storage of area maps for subsequent probe height control

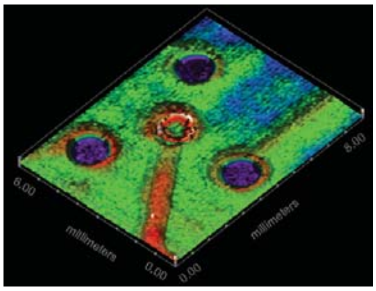


Figure 1. Non-contact surface profile of electrochemical sensor surface - sample courtesy of Oncoprobe Ltd.

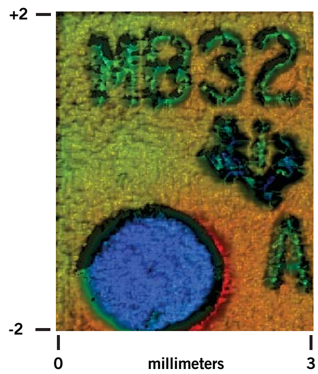


Figure 2. Non-contact surface profile of integrated circuit packaging (OSP370).

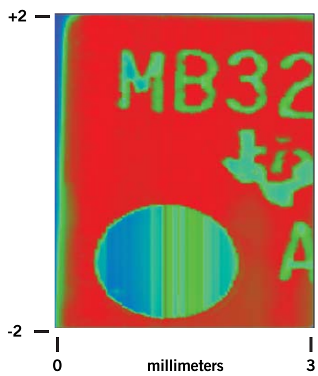


Figure 3. SECM area scan of same area of integrated circuit as figure 2 (SECM370).

Options: Environmental TriCell™

The Environmental TriCell™ screws directly into the Model 370 Scanning Electrochemical Workstation optical table base, and provides for large samples and various electrode configurations. It comes with a flexible rubber cover through which a probe can be inserted in order to allow control over the environment. The cell has four external ports, tilt glass cell, and adjustable electrode holders.

- Easy sample access and connection
- External level adjustment
- Enables experiments under controlled atmoshphere
- Enables experiments under liquid flow
- Accomodates a wide range of sample geometry's including sheet metal and 32mm diameter metallurgical mount

Options: µTriCell™

The µTriCell™ screws directly into the Model 370 Scanning Electrochemical Workstation optical table base, and provides for small samples with low electrolyte volumes and various electrode configurations. It has a PTFE body, and comes with a quartz window to allow optical and viewing access.

- Easy sample access and connection
- External level adjustment
- Accomodates a wide range of samples (32 mm and non standard options)

Options: Long Working Distance Video Microscope, VCAM2

Optical microscope, camera, and monitor for probe imaging / postioning, parfocal through zoom range. Working distance 108mm. Field of view at 0.7x position 8.6mm. Field of view at 4.5x position 1.4mm. Recommended for use with all scanning probe techniques.

VCAM2 specifications:

1/2" B&W CCD Image sensor
Field of view: 0.75° (x4.5) to 4.6° (x0.7)
Number of Pixels: 420K Pixels
Resolution: 570 TV Lines
Operation Temperature: -30° ~ +70°C
Camera Dimensions: 34 mm x 34 mm x 46 mm

Features:

- Very Low Light Operation, Min. Illumination: 0.0003 lux - f1.4
  Compact size: 1.8" Long w/out Lens
- CS- Mount Lenses or C-Mount Lenses w/5mm Adapter
- Power: 12V DC +10%, 160mA

Options: IsoPlot™ 3D surface rendering software

The IsoPlot Scientific Graphics Software produces quality 3D images of data matrices in excess of 200,000 data points. This 32 bit Windows™ application employs a camera and light model to give the user full control over viewing angle, lighting angle, lighting color, and material characteristics.

Software options include:

- Shaded surface rendering
- Depth shading
- Isometric split screen views
- User definable color palette
- Wire frame plots
- Full control of materials optical characteristics

Please consult technical sales engineer if in any doubt of system requirements. These specifications are subject to change without prior notice.

Dimensions and Weights

Model370 Scanning Electrochemical Workstation physical parameters:
Scanning Head:
350mm wide x 470 mm high x 660 mm deep. 17 kg
Control Unit SCV370:
450mm wide x 140mm high x 330mm deep. 6kg
Bi-Potentiostat:
450mm wide x 140mm high x 330mm deep. 6.5kg

Computer Specifications

The minimum hardware and operating software requirements of the 370 system are:

1.5 GHz Pentium IV™ processor

- 2 GB RAM
- 50 MB free disk space
- USB Port
- MIcrosoft™ Windows™ XP Professional
- or Vista Business

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