



**Princeton
Applied
Research**

AMETEK®

VersaSCAN™

Electrochemical Scanning System



- Scanning Electrochemical Microscopy (SECM)
- Scanning Vibrating Electrode Technique (SVET)
- Localized Electrochemical Impedance Spectroscopy (LEIS)
- Scanning Kelvin Probe (SKP)
- Scanning Droplet Cell (SDC)
- Non-Contact Optical Surface Profiling (OSP)
- VS Stylus - Constant Distance SECM

Introducing...

The VersaSCAN is a single platform capable of providing spatial resolution to both electrochemical and materials-based measurements. Traditional electrochemical experiment measure an average response over the entire electrode/electrolyte interface. Rarely is a sample homogenous. Samples often consist of local sites of passivate/active nature or sites of anodic/cathodic character. This need to investigate localized phenomenon led to the emergence of scanning probe electrochemistry.

By making the measurement at a probe above the surface of the sample, the response is taken from a subset of the sample. A small measurement probe positioned very close to the surface, but non-contact, reduces the sampling volume and provides a high spatial resolution. However, these small responses require superior measurement technology to record the measured parameter. The VersaSCAN integrates capabilities of proven models of Ametek instrumentation, such as the low-current measurement technology of the VersaSTAT and the high dynamic reserve of the Signal Recovery 7230-VS to extract these data.

The positioning system of the VersaSCAN is based entirely on piezoelectric motors. These motors give long travel (100-mm) and superior resolution (50-nm) in a small footprint.

Different auxiliary pieces interface to the positioning system to provide functionality for several different scanning probe experiments:

- Scanning Electrochemical Microscopy (SECM)
- Scanning Vibrating Electrode Technique (SVET)
- Localized Electrochemical Impedance Spectroscopy (LEIS)
- Scanning Kelvin Probe (SKP)
- Scanning Droplet Cell (SDC)
- Optical Surface Profiler (OSP)
- VS Stylus - Constant Contact SECM

A single scanning platform and software is used for any of these techniques.

Integration of a high-resolution, long-travel positioning system; different auxiliary pieces, such as measurement probes, piezo vibration stages, laser heads; and superior measurements devices such as potentiostats and lock-in amplifiers make the VersaSCAN possible.

SECM

Scanning Electrochemical Microscopy

The SECM integrates a positioning system, a bipotentiostat, and an ultramicroelectrode tip. The positioning system moves the tip close to the surface of the sample. The bipotentiostat polarizes both the sample and the tip independently and measures both resulting currents. The tip is an ultramicroelectrode with a specific tapered polish and active radius lower than 100 microns. The positioning system scans the measurement tip and charts position with measured electrochemical parameters, creating a data map of local activity.

Approach Curves are used as an electrochemical means by which to position the probe in Z sufficiently close to the sample to be in the local imaging zone. Current at the tip is charted as the tip is incremented towards the sample. When the probe is sufficiently close to the sample (a distance of 2-4 times that of the probe diameter) the measured current at the tip transitions from a bulk response to a local response. Over a region of high conductivity, a Nernstain response provides a local current enhanced over that of the bulk current. However, local current is decreased relative to bulk value over areas of insulating nature of the sample as mass-transport is hindered to the tip.

A common experiment in SECM is Generator-Collector Mode. Here one channel of the bipotentiostat polarizes the sample; where the other channel polarizes the tip. Similar to a Rotating – Ring Disk Electrode (RRDE) experiment, one electrode generates an electrochemical reaction, the products of which are subsequently measured at the other electrode. A SECM does this while adding the extra dimension of spatial resolution to the data, and being able to change from Sample Generation – Tip Collection (SG-TC) to Tip Generation – Sample Collection (TG-SC) often by simply changing polarization levels.

Applications

Since the imaging mechanism is electrochemistry, the applications of a SECM are as varied as the applications of electrochemistry itself. Some key fields that have already benefited are biological sensors, reaction kinetics, porous membrane study, fuel cell catalysts, and corrosion mechanisms.

Key Specifications

Several different models of potentiostats from Princeton Applied Research can serve as the channels of the bipotentiostat. As the default option, both channels will be the VersaSTAT 4A with the capability of “floating ground” operation.

- Polarization Voltage: $\pm 10V$
- Current Ranges:
VersaSTAT4A: 4nA to 2A
PARSTAT 4000A: 40pA to 4A
- VersaSTAT-LC expands to 4pA range and 122aA resolution for VersaSTAT 4A; 80fA range and 20aA resolution for PARSTAT 4000A
- AC-SECM now available

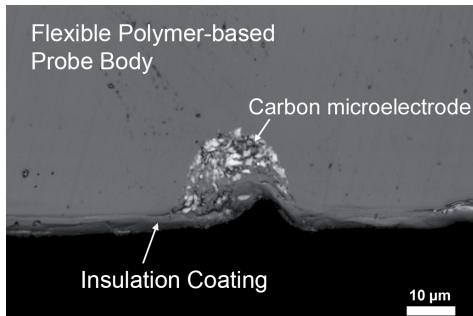
...the **VersaSCAN**

VS Stylus

Constant Distance SECM

The Soft Stylus Probe technology offers the following benefits:

- Constant distance SECM: SECM imaging without major topographic artefacts. Ideal for tilted, corrugated and rough samples.
- Soft contact with sample: with a contact force up to 1000 times less than hard probe technology, soft probes are ideal for studying biological samples in constant distance mode SECM.
- Low cost: no need for additional hardware and special feedback control electronics to control vertical position of the probe with respect to the sample
- Faster measurements: no need to measure topography before SECM scans. Fast approach curve to find the sample surface.
- Flexible and stable probes: no risk of damaging the probe or sample during positioning and scanning
- Small Tip: – Substrate better distance is easily achieved greatly enhancing contrast imaging and improving image resolution.
- Easy Electrode Preparation: The tip of the electrodes can be cut after each use ensuring a clean surface. Replacement probes can be purchased

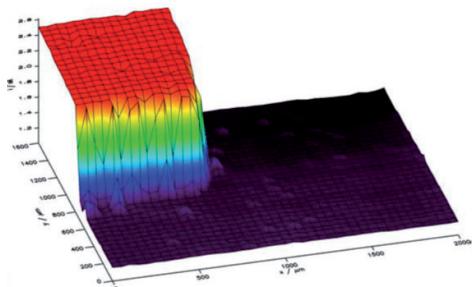


Cross section of Carbon Probe

Applications

Local Electrochemical Imaging

Since the tip is in constant contact with the sample, there is no need to apply tilt correction either before the scan or using post data correction techniques thus greatly simplifying the technique. Ideal for beginners to this field

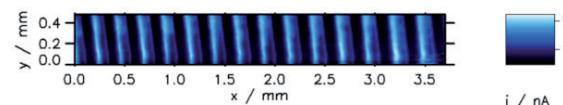


Gold Electrode (red) deposited on silicon substrate (purple) - no tilt correction required to produce resolved insulator/conductor SECM image.



Electrodeposition and Surface Science

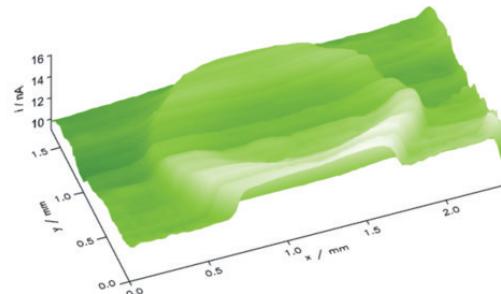
The soft probes simply follow the contours of corrugated and rough samples. Materials with high aspect ratios can be easily imaged.



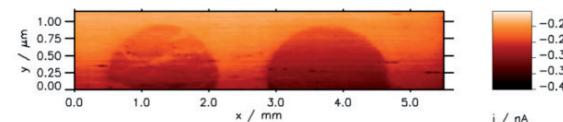
Silver Coated Curved Polyimide Sheet – Laser Ablated to Remove Ag (note regions of conducting Ag and insulating Polymer) Curvature radius 9 cm.

Biological Samples

Professor Hubert Girault and co-workers have shown that these probes are ideally suited to soft biological materials. Since the probe makes a soft contact with the material, the risk of damaging the sample is significantly reduced compared with hard probe contact techniques.



Spot of banana juice on a PVDF membrane. The enzyme tyrosinase (TyR) was detected in the sample generation - tip collection mode using L-DOPA.



Left Stage III melanoma (heterogeneous distribution and slightly reduced concentration of TyR) Right: Stage II melanoma (homogeneous distribution and higher concentration of TyR)

Key Specifications

- Soft disposable electrode (approx. 100 SECM experiments per probe)
- Graphite as electrode material
- Up to 10 μm minimum tip sample distance control
- Material: Polyimide with PDMS coated electrode body
- Modes of operation: Constant Distance and Constant Height
- Probe Contact Pressure approx. $2.55 \times 10^4 \text{ N m}^{-2}$

SVET

Scanning Vibrating Electrode Technique

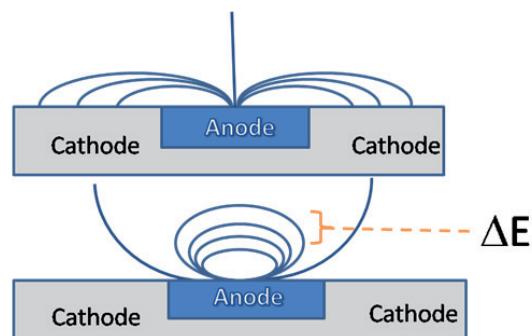
Introduction

The Scanning Vibrating Electrode Technique uses a single wire to measures potential field gradient drop in solution. This voltage drop is a result of local current at the surface of a sample. Measuring this gradient in solution images the current at the sample surface. Current can be naturally occurring from a corrosion or biological process, or the current can be externally controlled using a galvanostat.

A piezo unit vibrates the probe in Z-direction (axis perpendicular to the sample). The amplitude of vibration may be only 10s of microns peak-to-peak. This small vibration provides a very small voltage to be measured.

Therefore, the response (signal + noise) at the probe is then gained by the electrometer. The gained output of the electrometer is then input to a Lock-in Amplifier. This, in turn, uses a phase detector along with a Reference at the same frequency of vibration to extract the small AC signal from the entire measured response. The VersaSCAN capitalizes on Ametek's industry-leading Noise Characteristics of the Signal Recovery 7230-VS Lock-in Amplifier to provide superior measurement of these small signals.

The voltage recorded and the probe is repositioned. A data map results as voltage versus position are displayed.



Current path and resulting voltage-fields created from local electrochemical reactions on the surface of a sample. ΔE represents the measured value of the SVET experiment.

Applications

A key application of SVET is to study corrosion process of bare metals. These metals could be galvanic couples or these fields could occur from local non-uniform corrosion events, such as pits or crevices.

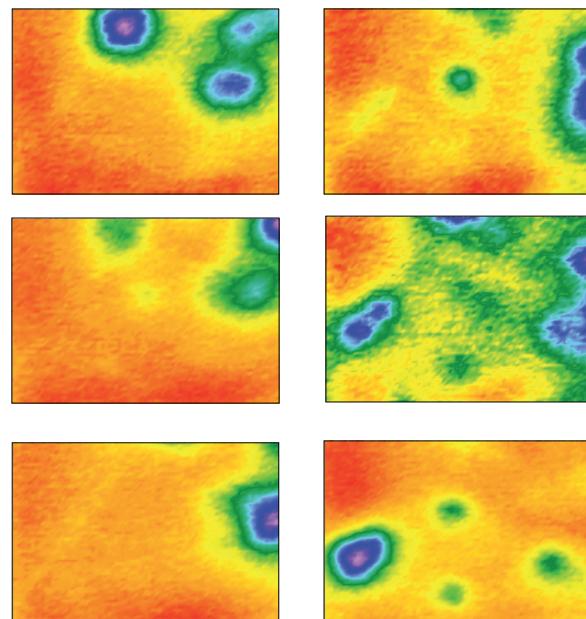
Time-lapse experiment series provide the capability to literally watch the corrosion events happen – as different areas passivate and activate.

Additionally, there are many applications and references for the use and results of SVET to study biological systems.



Key Specifications

- Probe Material: Pt/Ir
- Electrometer Range: $\pm 10V$
- Electrometer Gain: from 1x to 10,000x in decades
- Application based keys of the 7230-VS:
 - DSP Stability (not analog-based, impervious to temperature drift)
 - High Stability (no fan for failure)
 - Radically better Noise Sensitivity (13 fA/V/Hz)
- Piezo Unit: 0-30 μ m vibration perpendicular to sample
- Compatible Lock-in Amplifier: Signal Recovery 7230-VS



Time-resolved SVET images of the same area of an actively corroding sample taken at different exposure times in electrolyte.

LEIS

Localized Electrochemical Impedance Spectroscopy

Introduction

The VersaSTAT 4A applies an AC voltage to the sample emerged in electrolyte. This “global” voltage generates AC current to flow at the electrode / electrolyte interface. A dual-element probe is positioned in solution close to the surface of the sample. The electrometer measures a differential voltage measure between the two measurement elements as a measure of local voltage-drop in solution. This voltage-drop exists in solution because of current flow from local reactions at the sample, the resistance of the electrolyte and the spatial separation of the dual measurement elements.

The VersaSCAN’s electrometer inputs its measured voltage to the auxiliary differential voltage input available with the VersaSTAT 4A.

Software integration converts the measured local voltage-drop at the probe to local AC current.

The ratio of local measured current to the global applied voltage gives the localized impedance magnitude and phase shift.

Applications

There are two different test methods for the experimentalist to use LEIS to evaluate their samples

A) Chart the local response of a sample from a range of applied AC frequencies in a single location.

Data can be viewed in either a Bode or Nyquist representation.

B) Create a series of data maps to characterize an AC response as a function of probe position.

Data can be used to create a map, using either Magnitude or Phase as the response.

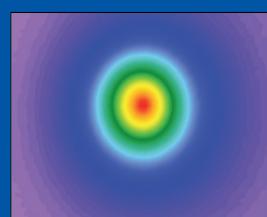
LEIS provides a spatially resolved impedance measurement that adds value to:

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

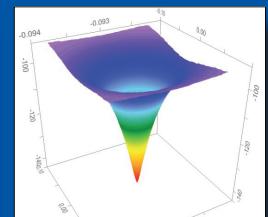


Key Specifications

- Probe Material: Pt/Ir pin; Pt ring.
- Electrometer Range: $\pm 10V$
- Electrometer Gain: from 1x to 10,000x in decades
- Compatible Potentiostats: VersaSTAT 4A with Differential Aux option
- Differential Aux:
 - Can be single-ended or differential
 - ADC: 16-bits
- ADC Voltage resolution: $305\mu V$ at X1 gain; $61\mu V$ at X5 gain; $30.5\mu V$ at X10 gain; $6.1\mu V$ at X50 gain.
- Bandwidth ≥ 3 MHz

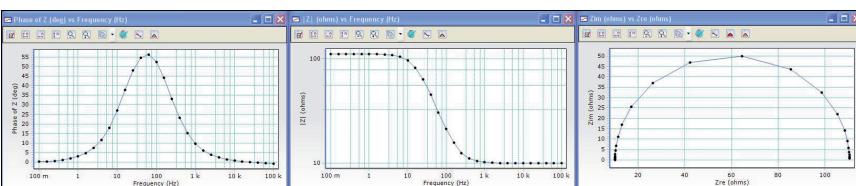


2-dimensional magnitude

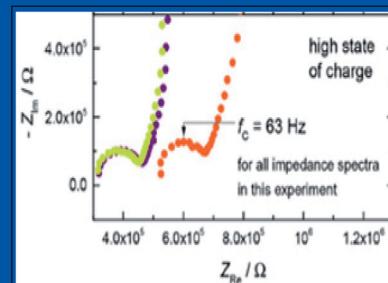


3-dimensional Plot

Area Scan experiment of LEIS. 200- μm gold wire with applied current to simulate local current event, such as a pinhole or pit.



Results of a fixed-position swept-frequency LEIS experiment. Results can be viewed as a bode plot of the phase or magnitude and a Nyquist plot.



LEIS mapping of local State-of-Charge of a Li-ion battery material

SKP

Scanning Kelvin Probe

Introduction

The Kelvin Probe experiment uses a nondestructive method to determine the relative work function difference between the probe and the sample. Work function describes the energy required to liberate an electron from the surface of a conductor; electrochemists often interpret this as the energy difference from an electrode's Fermi Level, average energy of electrons, and that of vacuum.

A metal microprobe is positioned close to the surface of the sample (on the order of 100-microns). If the microprobe and sample are of different metals, there is an energy difference between their electrons. The microprobe is then electrically shorted to the sample, through internal electronics of the system. As a consequence, one metal forms a positive charge on its surface and the other metal forms a negative charge on its surface. The probe and sample are separated by a dielectric (air), so a capacitor is formed. The probe is then vibrated and "backing potential" or "nulling potential" is then applied sufficient to minimize this capacitance. At the applied voltage that causes the capacitance to go to zero, the original state is achieved. This value is recorded and charted.

Experiments are typically performed in ambient gaseous conditions, but several published examples use humidified environments. The underlying conducting sample can have an organic coating or paint applied.

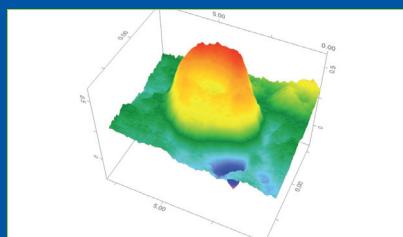
This relative work function can also be correlated to an Ecorr value.

Our SKP is also capable of functioning in Topography Mode. Without changing connections or probe, a reference voltage is applied to the sample. This reference voltage makes the surface of the sample uniform. Change in capacitance is then from a changing plate separation (via equation of a capacitor). This is the probe-to-sample distance.

This information can be used in 2 ways:

Position the probe a known distance from the sample, using a Calibration Coefficient.

Map topography for further use in Constant-Distance Mode SKP. This is particularly useful in studying welds or other samples of complex topography.

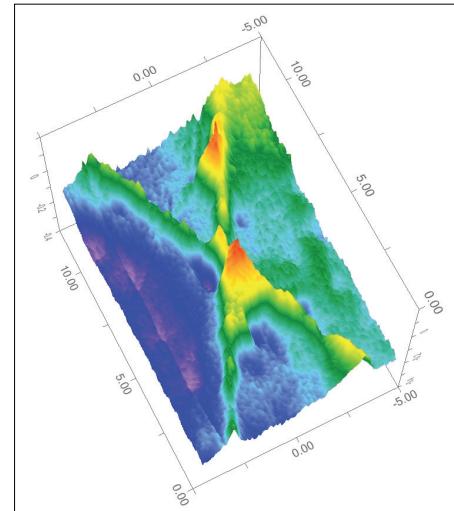


3-dimensional plot of SKP Area Scan data mapping response of a Zinc/Steel surface.

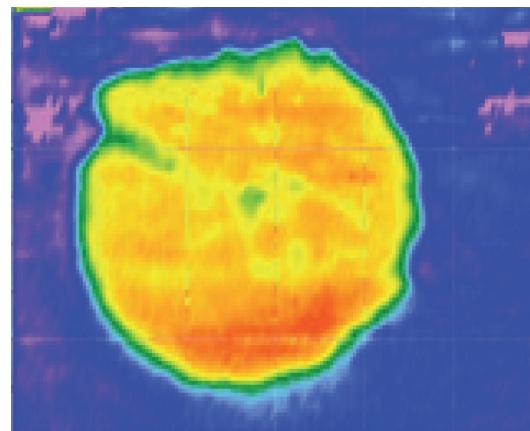


Key Specifications

- Probe Material: Tungsten. Multiple diameters available
- Electrometer Range: $\pm 10V$
- Electrometer Gain: from 1x to 10,000x in decades
- Compatible Lock-in Amplifier: Signal Recovery 7230-VS



SKP Area Scan experiment on a metal sample with an organic paint applied and a scribed "X".



High Resolution SKP Probe mapped response of a Zinc/Steel surface.

SDC

Scanning Droplet Cell

Introduction

Scanning Droplet System (SDC) uses a compact peristaltic pump to force electrolyte through a small diameter tube and into a specifically designed head. This PTFE-based SDC head is machined to allow electrolyte to flow past an installed Reference Electrode and then to a port at the base of the head. When the head is positioned sufficiently close to the sample a droplet forms between the head and sample. Tubing is also connected to an output port of the PTFE head. A second channel of the same peristaltic pump is then used to draw electrolyte past an installed Counter Electrode and out of the system. SDC experiments can be configured to either:

- Apply a constant bias (potential, current or open circuit) and increment position of the head creating a data map.
- Apply a static or dynamic electrochemical signal, such as a EIS experiment, a Tafel plot, or a Cyclic Voltammetry experiment as the head is kept in a fixed location.

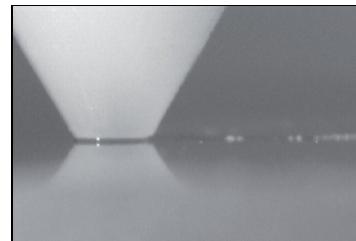
Since electrochemistry occurs at an electrode/electrolyte interface, only the portion of the sample that is in contact with the droplet is being measured. This allows experiments to study a small area of a large sample, without cutting the sample and thus limiting edge effects.

When running, the SDC pump creates a flowing droplet. SDC's pump velocity can be tuned to study effects of flow rate.



Key Specifications

- SDC Head Material: PTFE
- Tubing Material: Tygon
- Reference Electrode: Ag/AgCl
- Counter Electrode: Pt Wire
- Compatible Potentiostats: VersaSTAT 4A and PARSTAT 4000A



SDC head with its reflection pictured. Note : the droplet of electrolyte exists between this aperture and its reflection.

OSP

Non-contacting Optical Surface Profile

Introduction

The OSP experiment maps topographic changes on a sample surface. This is a laser-based technique.

Map topographic differences to characterize corrosion pits, sensors, etc.

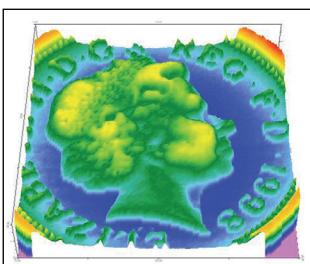
Create a topographic map for integration for other scanning probe technologies in Constant Distance Mode

Use as a highly accurate leveling mechanism before other scanning probe techniques.



Key Specifications

- Measurement Range: $\pm 10\text{mm}$
- Laser: Class 2, 650nm, 0.95mW
- Repeatability: $0.025\mu\text{m}$
- Spot Size: 50μ at reference distance of 50mm.



OSP results measuring topography of a British coin.

VersaSCAN options



VersaSCAN L-Cell

- Screws into optical table of VersaSCAN
- Approximately 1 Liter in volume
- Level adjustment mechanism
- Accepts large flat samples and 32mm diameter mounted samples
- Recommended for all techniques, particularly LEIS, SVET, SKP, SDC, OSP



VersaSCAN mL-Cell

- Screws into optical table of VersaSCAN
- Approximately 7 mL in volume
- Level adjustment mechanism
- Accepts a range of samples including 32mm diameter mounted samples and non-standard samples
- Specifically engineered for low-volume SECM applications



VersaCAM

- Camera:
 - Color
Number of Pixels: 795 (H) x 596 (V)
Minimum illumination 0.02 lx. F1.2
Power: 12V DC +/- 10%
CS-mount or C-mount with provided adapter.
 - Lens:
C-Mount
Manual focus.
 - Display:
8 inch color TFT display
PAL & NTSC auto selection
640 x 480 (307,200 pixels) screen resolution

Advantages of the VersaSCAN

Enhanced Technical Features:

- Single expandable platform capable of SECM, SVET, LEIS, SKP, SDC and OSP experiments
- Superior signal measurement and noise discrimination from integration of VersaSTAT 4A and PARSTAT 4000A Potentiostats and Signal Recovery 7230-VS Lock-in Amplifier
- Advanced positioning system provides long travel (100mm), high resolution (50nm) and improved repeatability (250nm)
- Vibration-resistant optical base employing both a honey-comb internal design and stiff steel surfaces.
- Ethernet connectivity between devices.

Installation and Training Features:

- Professional on-site installation and training provided, including assembly, verification, demonstration of both hardware and software.

Software Features:

- Preloaded on supplied high-quality laptop.
- Single software platform for all scanning probe techniques.
- Straight-forward configurations with step-by-step guides and easy-to-follow connection diagrams.
- Imbedded ability to rotate data view for an improved graphical presentation.
- Navigation tree design allows for setup of single experiments, building of both simple and complex sequences, and viewing of different data files within the project.
- Ability to export results as images or tables for importation into other analysis or report generating programs.

specifications

Dimensions

Scanning Head:
300mm W x 470mm H x 600mm D / 66.3lbs; 30kg

Control Unit (each):
360mm W x 120mm H x 300mm D / 9.3lbs; 4.3kg

Potentiostat:
421mm W x 89mm H x 387mm D / 10lbs; 4.5kg



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