



KH Design and Development

Electrochemical Corrosion Measurement and Control Consultancy

Implementation of Electrochemical Noise Measurement for Online Plant Condition Monitoring

Dr. Karel Hladky

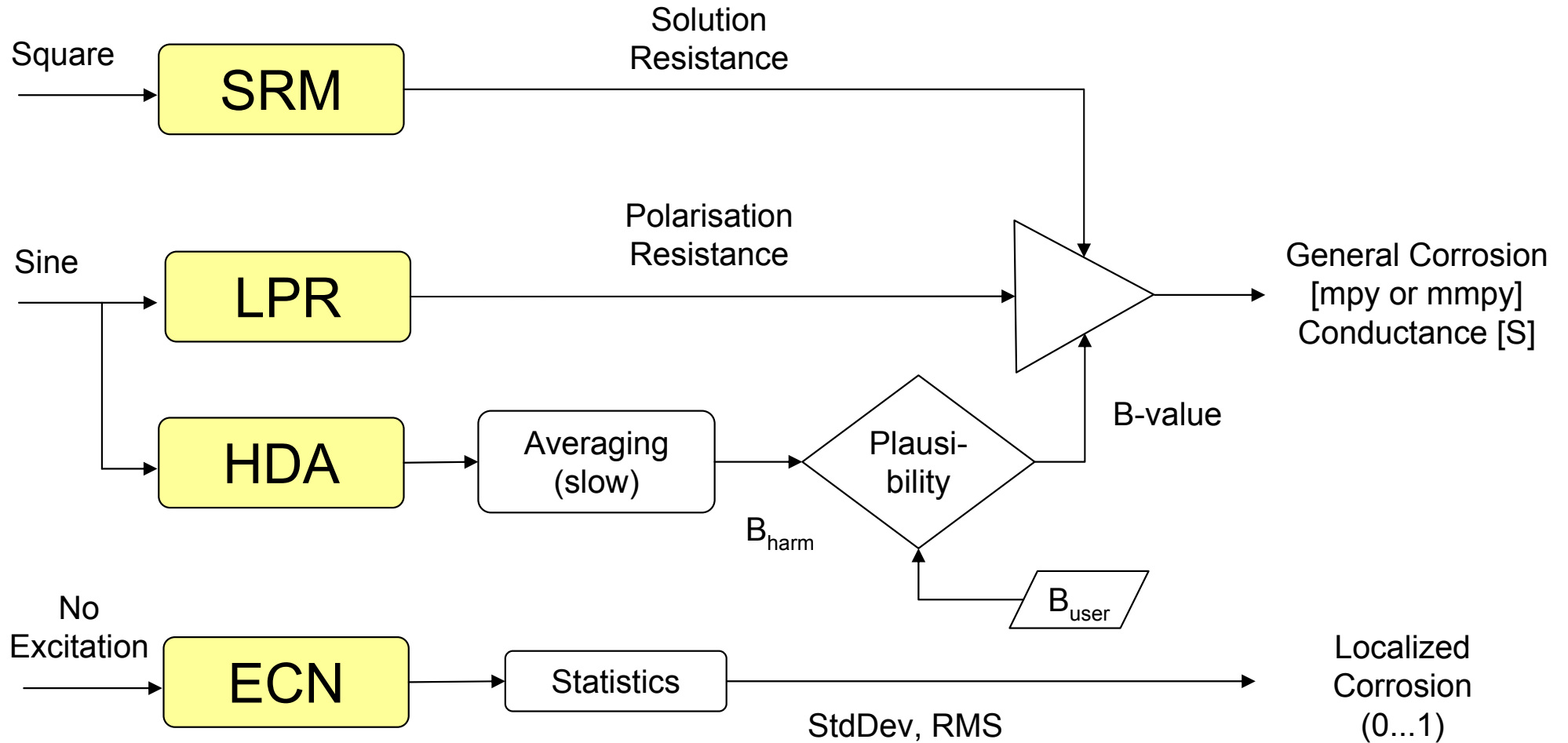
CorrTran MV

- Fresh design starting from first principles and using only public domain electrochemical measurement techniques and algorithms
- Proven hardware configuration (three electrode potentiostatic corrosion rate measurement, three electrode potential and current electrochemical noise measurement)
- Extensive configuration of measurement parameters
- Full diagnostic capability with non-volatile storage of 300 most recent 'raw' measurement results
- Active, ongoing product support resulting in continuous improvements of hardware, firmware and measurement algorithms
- Further products in the range are in active development

CorrTran MV Design Constraints and Aims

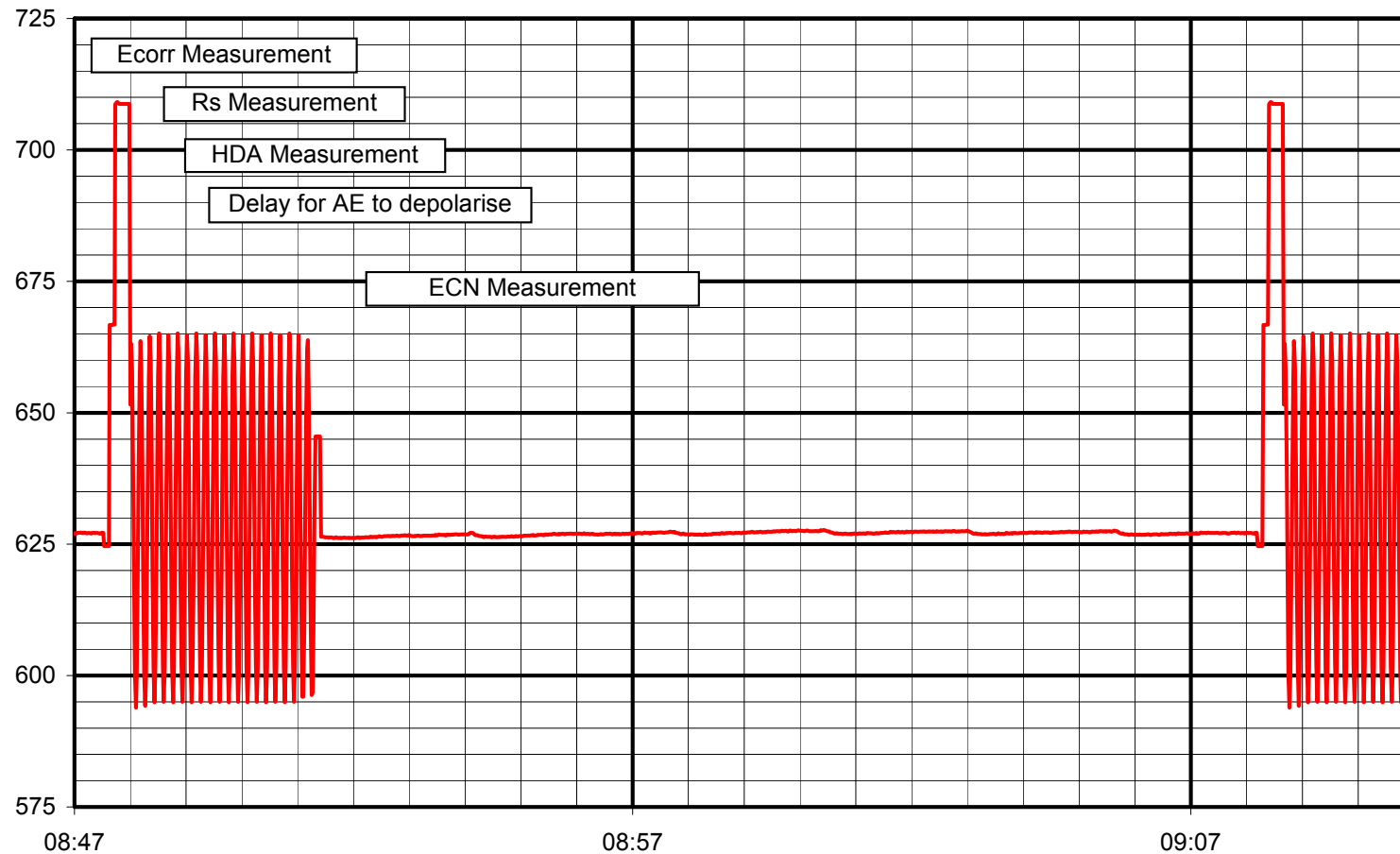
- Low power consumption (< 3mA) to enable 4-20mA loop power operation
- Electrical isolation from plant or 4-20mA loop ground
- Operation with existing industry standard three electrode probes
- Accurate measurement of electrolyte conductance
- Corrosion rate measurement using harmonic distortion analysis
- Potential and current electrochemical noise measurement
- Flexibility in setting operating parameters (sine amplitude, frequency, integration cycle count, electrochemical noise sampling rate etc.)
- Non-volatile memory recording of measurement results (300 point measurement history)
- HART interface
- Standards compliance
- Same physical size and housing as original CorrTran / SmartCET

CorrTran MV Measurement



CorrTran MV Measurement Cycle – R_s Measurement

- R_s (electrolyte conductance) measurement
- Corrosion rate measurement using harmonic distortion analysis (HDA)
- Localised corrosion measurement using electrochemical noise

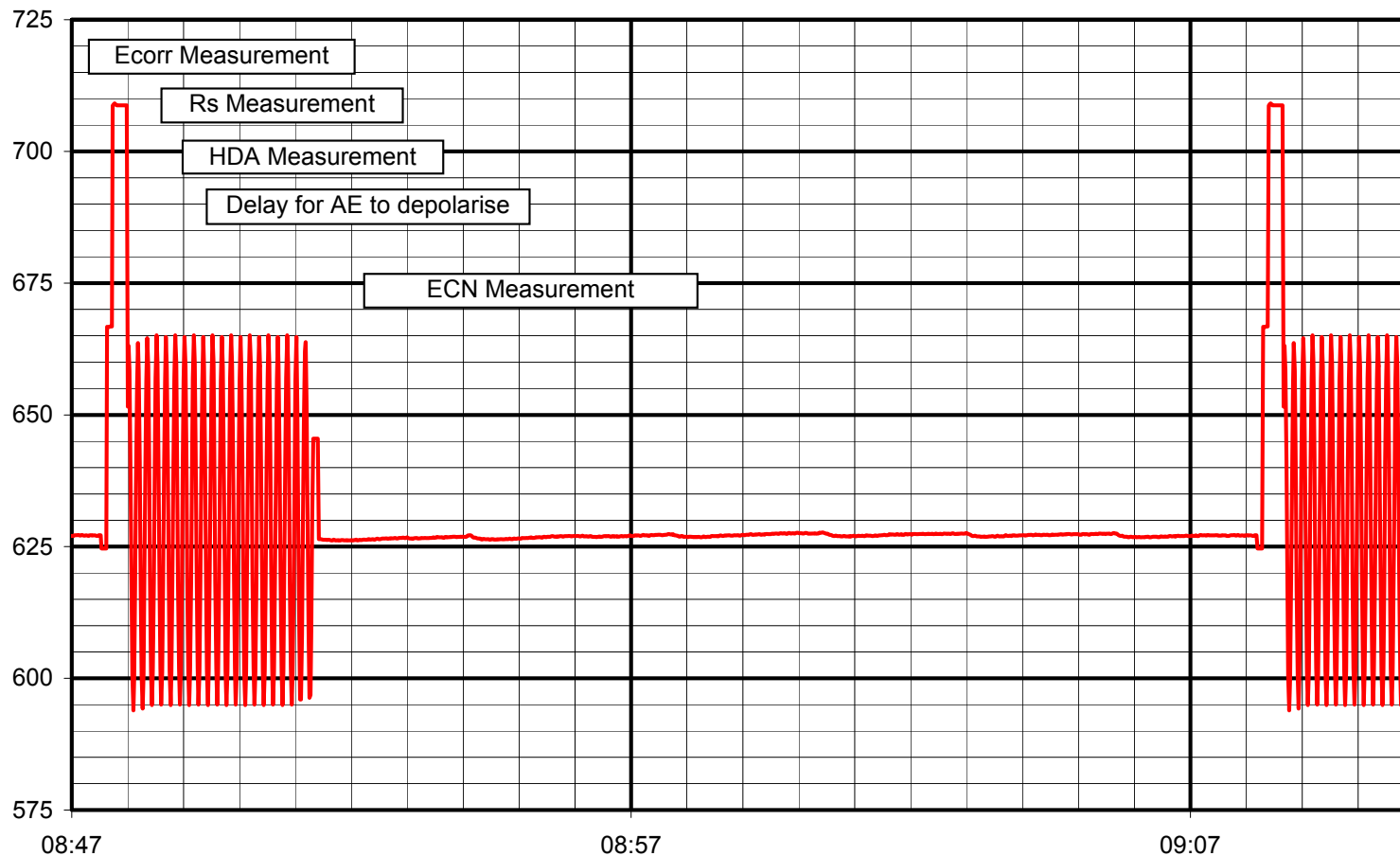


Electrolyte Conductance Measurement

- A.c. measurement using a 100 Hz to 1kHz bipolar square waveform
- Applied to the test probe using a three electrode potentiostatic circuit
- Autoranged waveform amplitude (3 to 50 mV peak) to minimise cell current demand
- Use of a synchronous rectifier circuit to reject dc and noise at frequencies other than the applied frequency
- Fast measurement (a few seconds)
- Gives an accurate value of R_s and conductance ($1/R_s$)

CorrTran MV Measurement Cycle – Corrosion Rate Measurement

- R_s (electrolyte conductance) measurement
- **Corrosion rate measurement using harmonic distortion analysis**
- Localised corrosion measurement using electrochemical noise



Harmonic Distortion Measurement

- Meszaros and Devay series of papers (1978)
- Mainly a mathematical exercise
- Many assumptions and approximations
 - Electrolyte resistance effects not considered
 - Near zero perturbation assumed
- Derives equation linking magnitudes of harmonic currents to corrosion current

Acta Chimica Academiae Scientiarum Hungaricae, Tomus 100 (1–4), pp. 183–202 (1979)

STUDY OF THE RATE OF CORROSION OF METALS BY A FARADAIC DISTORTION METHOD, I

J. DÉVAY and L. MÉSZÁROS

(Research Group of Electrochemistry of the Hungarian Academy of Sciences, Veszprém)

Received June 30, 1978

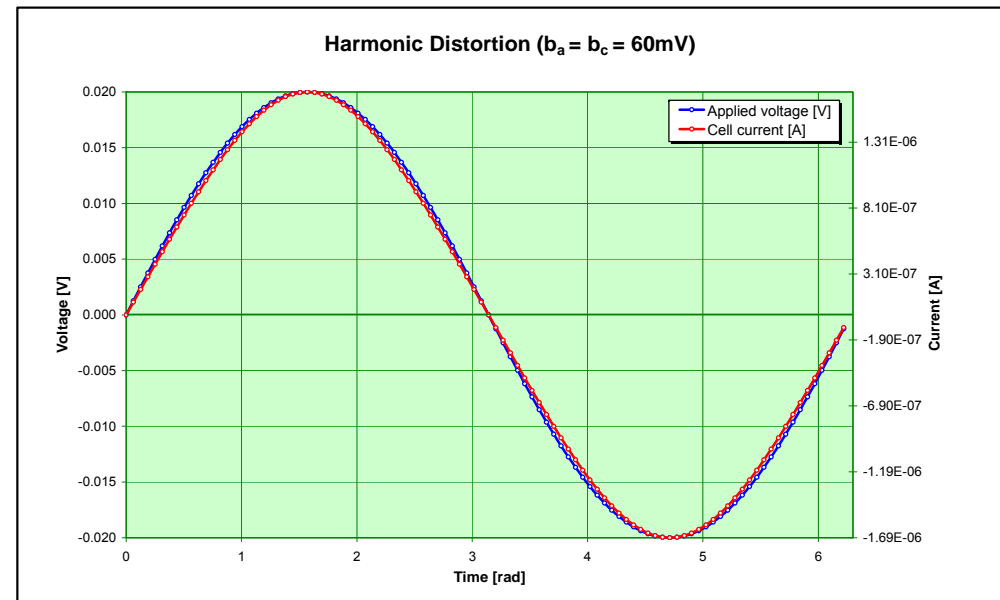
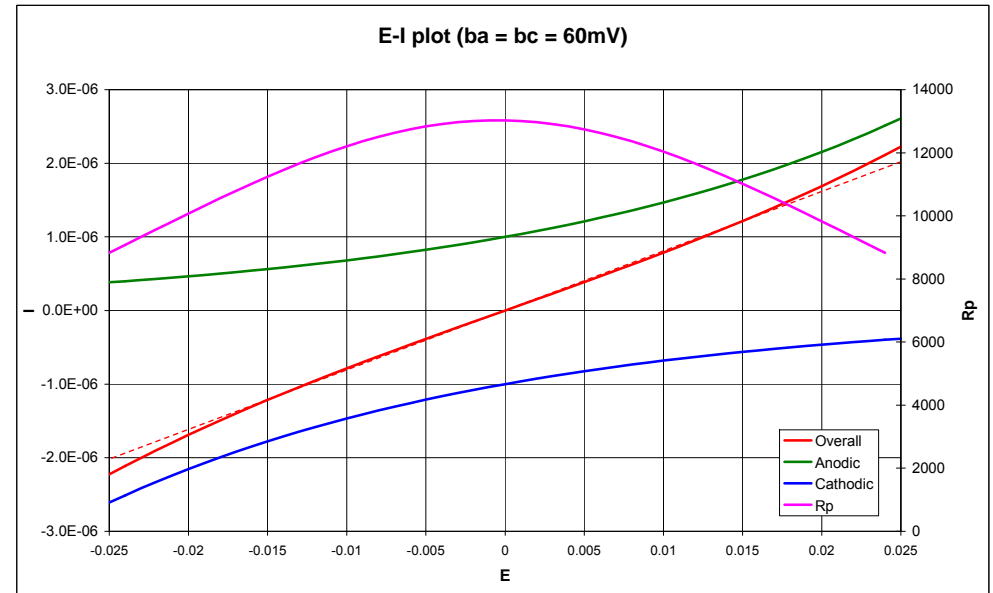
Accepted for publication August 8, 1978

A method based on faradaic distortion is presented for the study of the kinetics of corrosion processes for the case when the current-voltage characteristics of both the anodic and the cathodic reactions can be expressed by Tafel's equation. The harmonic components of the current flowing through the electrode under the effect of a sinusoidal alternating voltage superimposed on the polarizing direct voltage are examined as functions of the time-average value of the polarizing direct voltage and the amplitude of the alternating voltage. The corrosion current and the Tafel slopes of the anodic and cathodic reactions can be determined by measuring the first, second and third harmonic components of the faradaic current at one potential in each of the anodic and cathodic Tafel ranges. The Tafel slopes are determined from the Tafel slopes from the

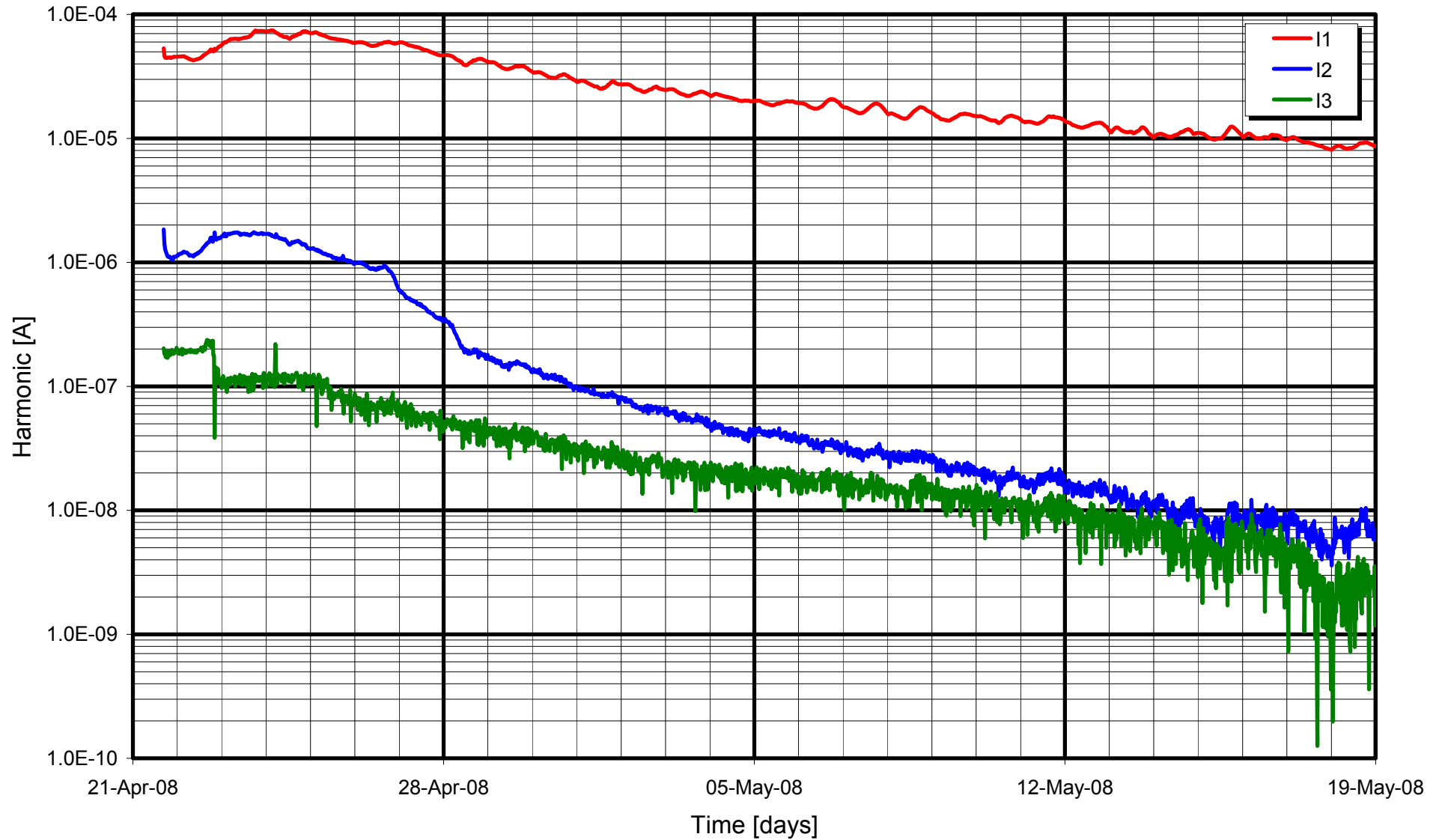
$$j_k = \frac{j_{i0}^2}{\sqrt{48} \sqrt{2j_{10}j_{30} - j_{20}^2}}$$

Harmonic Distortion Analysis

- Electrode E-I response is sum of two exponentials
- Response is near linear at E_{corr}
- Non-linearity distorts the applied voltage sine waveform
- Resulting current waveform contains harmonics of the fundamental frequency
- Magnitude of the harmonics is related to the curvature of the E-I response
- This is determined by I_{corr} and Tafel coefficient values
- Can use the harmonic magnitudes to calculate I_{corr} and Tafel coefficients

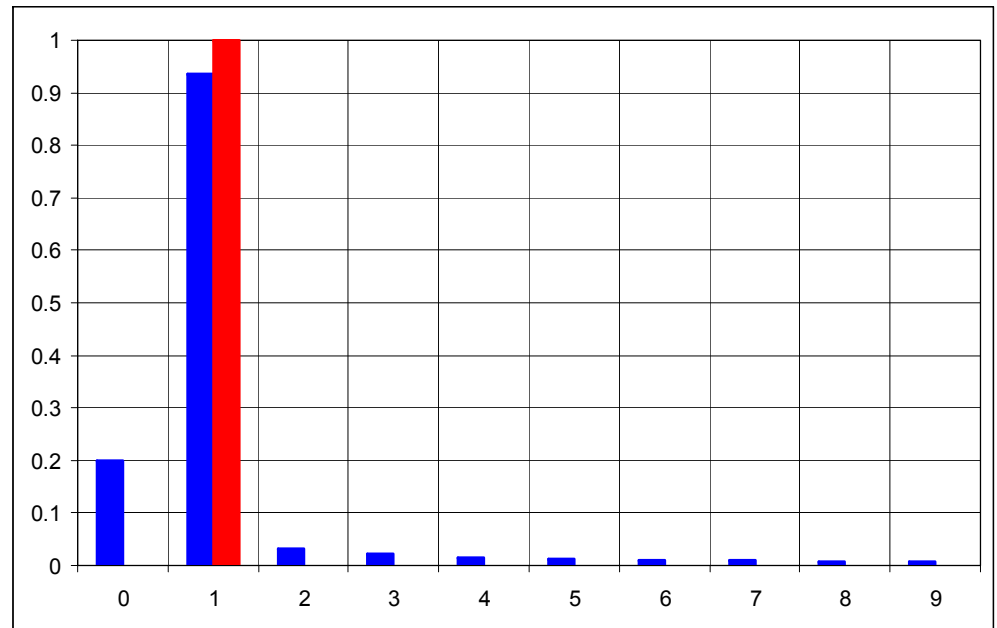
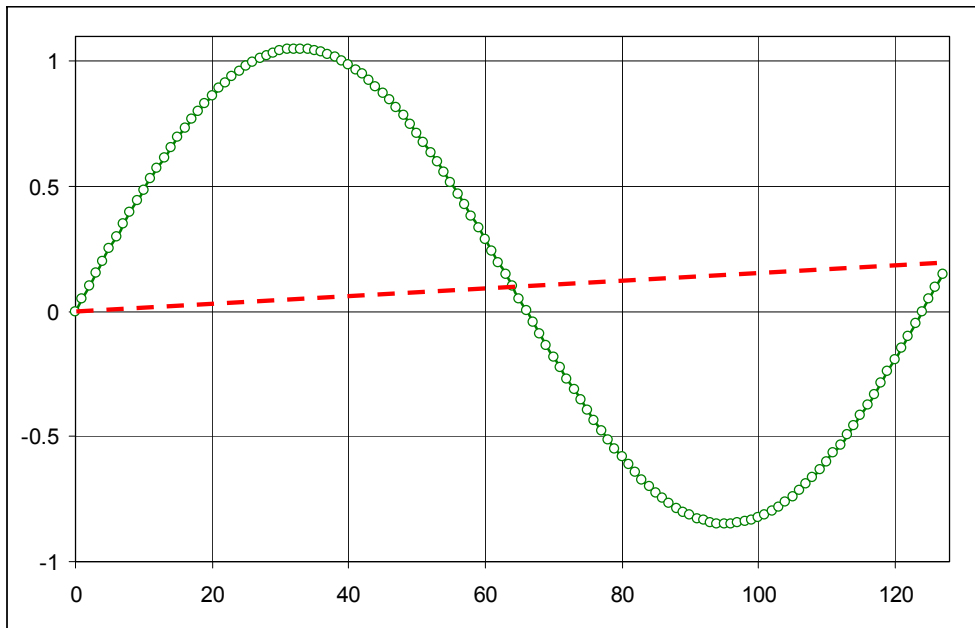


Typical Harmonic Distortion Component Magnitudes



DFT Errors

- Discontinuity between first and last sample appears as a step in the waveform, giving false harmonic values
 - Do trend removal ?
 - Use a window function ?
 - Increase perturbation amplitude ?
 - Integrate over a number of cycles of waveform ?



Trend of 20% of peak sine amplitude added. Fundamental amplitude is reduced to 94%, second harmonic appears at 3.2%, third harmonic at 2.1%

Harmonic Distortion Analysis Problems

- Electrolyte resistance tends to linearise the E-I response of the test electrode
 - Need to either compensate for R_s in hardware or measure R_s accurately and correct for its presence in firmware algorithms
 - Low conductivity environments ($R_s/R_p > 1$) present difficulties
- Amplitudes of harmonic components of cell current are of low level
 - Need to average over a number of sine wave cycles
 - Circuitry noise must be kept to very low levels
- Electrochemical noise makes measurement more difficult
 - $1/f$ spectral density behaviour of electrochemical noise reduces effectiveness of averaging
 - Need to measure at E_{corr} , unstable E_{corr} can invalidate measurement
- Choice of measurement frequency is important
 - Effects of C_{dl} , diffusion, adsorption etc.

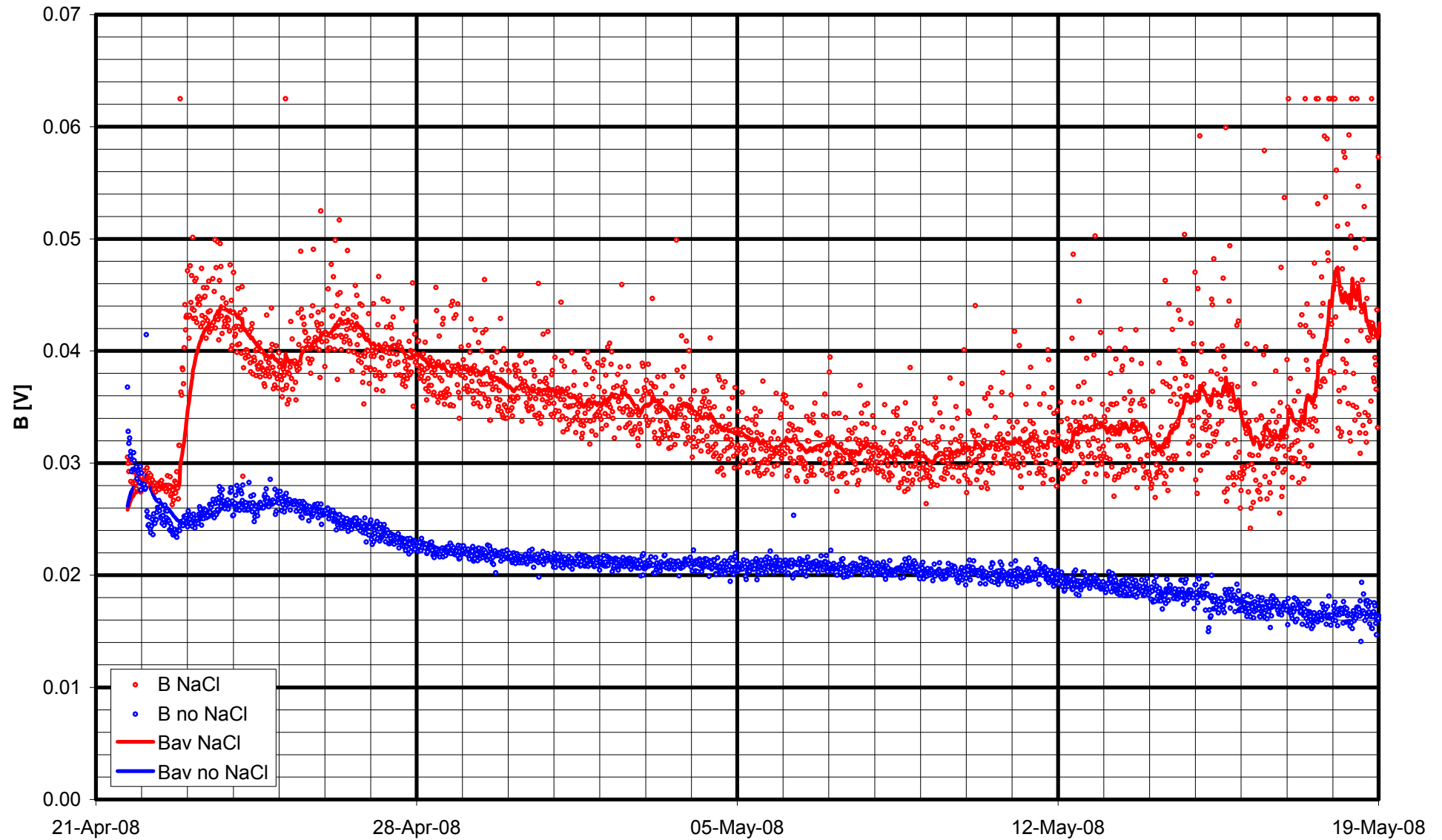
Harmonic Measurement Process

- Generate sine waveform as a series of small steps using a look-up table
- Apply as potentiostatic voltage cell perturbation with E_{corr} as datum
- Sample cell current just before each successive potential step
- Calculate Discrete Fourier Transform (DFT)
 - Multiply cell current value by appropriate look-up table value
 - Sum over one or more waveform cycles
- Results are real (in phase) and imaginary (90 degrees out of phase) components for I_1 , I_2 , I_3 etc.
- Use I_1 to calculate R_p
- Use I_1 , I_2 , I_3 to calculate I_{corr} (using the $\sqrt{48}$ equation) and to calculate B (using R_p)

CorrTran MV HDA Implementation

- Measure R_s accurately
- Determine E_{corr} by sampling and averaging over a short period of time
- Polarise test electrode to E_{corr}
- Apply 20 cycles of voltage sine waveform generated from a quarter-wave look-up table (96 steps per cycle)
- Use a 5 - 50 mV, 0.02 - 0.2 Hz sine waveform
- Using sine and cosine values from the look-up table calculate the real and imaginary components of fundamental, second and third harmonic cell currents
- Calculate R_p , I_{corr} and B , allowing for R_s and checking for plausibility
- Low pass filter B values to remove scatter
- Use low pass filtered B value and R_p to calculate output I_{corr}
- Convert to penetration rate in mm/y or mpy

CorrTran MV B Value Averaging

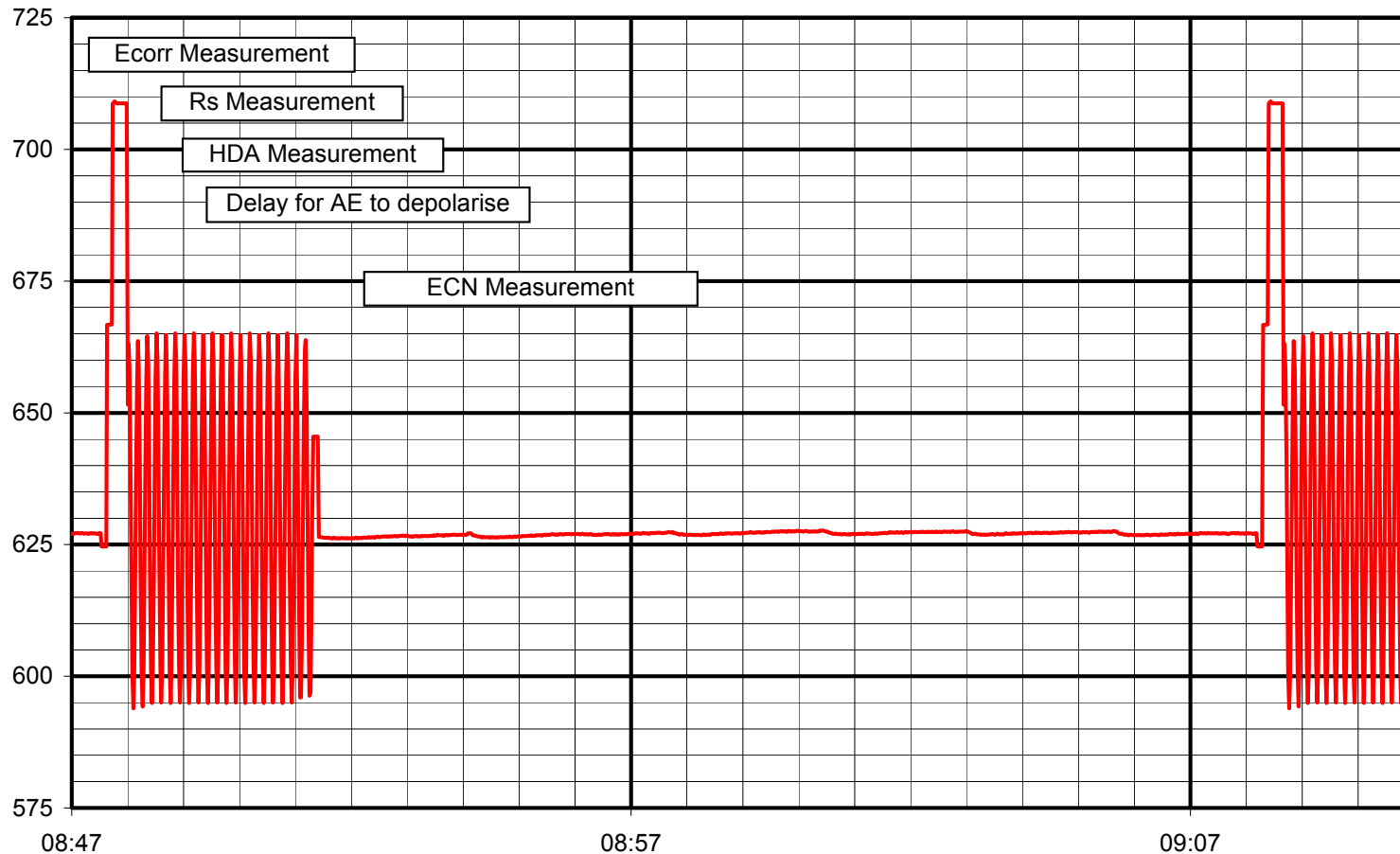


CorrTran MV HDA Trade-offs

- Measurement Frequency - Measurement Speed
 - Lower measurement frequency can give better accuracy (effects of C_{dl} etc.) but measurement time increases
 - Lower frequency measurement is more susceptible to interference by electrochemical noise and electrode condition or environmental changes
- Integration Cycle Count - Measurement Speed
 - Integrating over a larger number of waveform cycles improves accuracy but measurement time is increased
 - Longer integration time makes measurement more susceptible to electrode drift
- Perturbation Amplitude - Measurement Accuracy
 - Higher perturbation amplitude decreases susceptibility to interference by electrochemical noise and electrode condition changes
 - Approximations used in I_{corr} calculation are only valid at low perturbation amplitudes (need to use higher harmonics otherwise)

CorrTran MV Measurement Cycle – Localised Corrosion Measurement

- R_s (electrolyte conductance) measurement
- Corrosion rate measurement using harmonic distortion analysis (HDA)
- **Localised corrosion measurement using electrochemical noise**



Electrochemical Noise Measurement

- Iverson (1968)
 - Observed E_{corr} fluctuations
 - Attributed these to momentary charge imbalance between anodic and cathodic sites
- Hladky and Dawson (1981)
 - Amplified E_{corr} fluctuations
 - Found characteristic 'signatures' of pitting and crevice corrosion

Transient Voltage Changes Produced in Corroding Metals and Alloys

Warren P. Iverson¹

Fort Detrick, Detrick, Maryland

The formation of "hollow whiskers" by the action of slightly acidified potassium ferricyanide and ferro-cyanide solutions on metals and alloys (1) appeared to indicate that corroding metals produce bursts of metal ions from various point anodes. Since these bursts of ions appeared to be of a sporadic nature, it seemed possible that there might be transient fluctuations of the electrical charge on the metal. The present communication reports on the detection of such fluctuations in electrical charge.

The circuit shown in Fig. 1 was used. The voltmeter was of the high impedance type (11 megohms) with a chopper stabilized circuit. The electrodes consisted of an inert electrode of platinum foil

may also be due to transient changes in cathodic or anodic example, a corroding metal assumes increase in negative charge, the electrons would charge the plate of the capacitor in contact with it. An equal or opposite charge would develop on the other plate (flow of electrons away from the plate) thereby causing a difference in measurable potential across the resistance. The electrons might be expected to dissipate through the resistor to the platinum electrode and be removed as a result of reduction of the cations or neutral species in the solution. During a negative charge on the electrode

THE MEASUREMENT OF LOCALIZED CORROSION USING ELECTROCHEMICAL NOISE*

K. HLADKY and J. L. DAWSON

Corrosion and Protection Centre, UMIST, Manchester, England

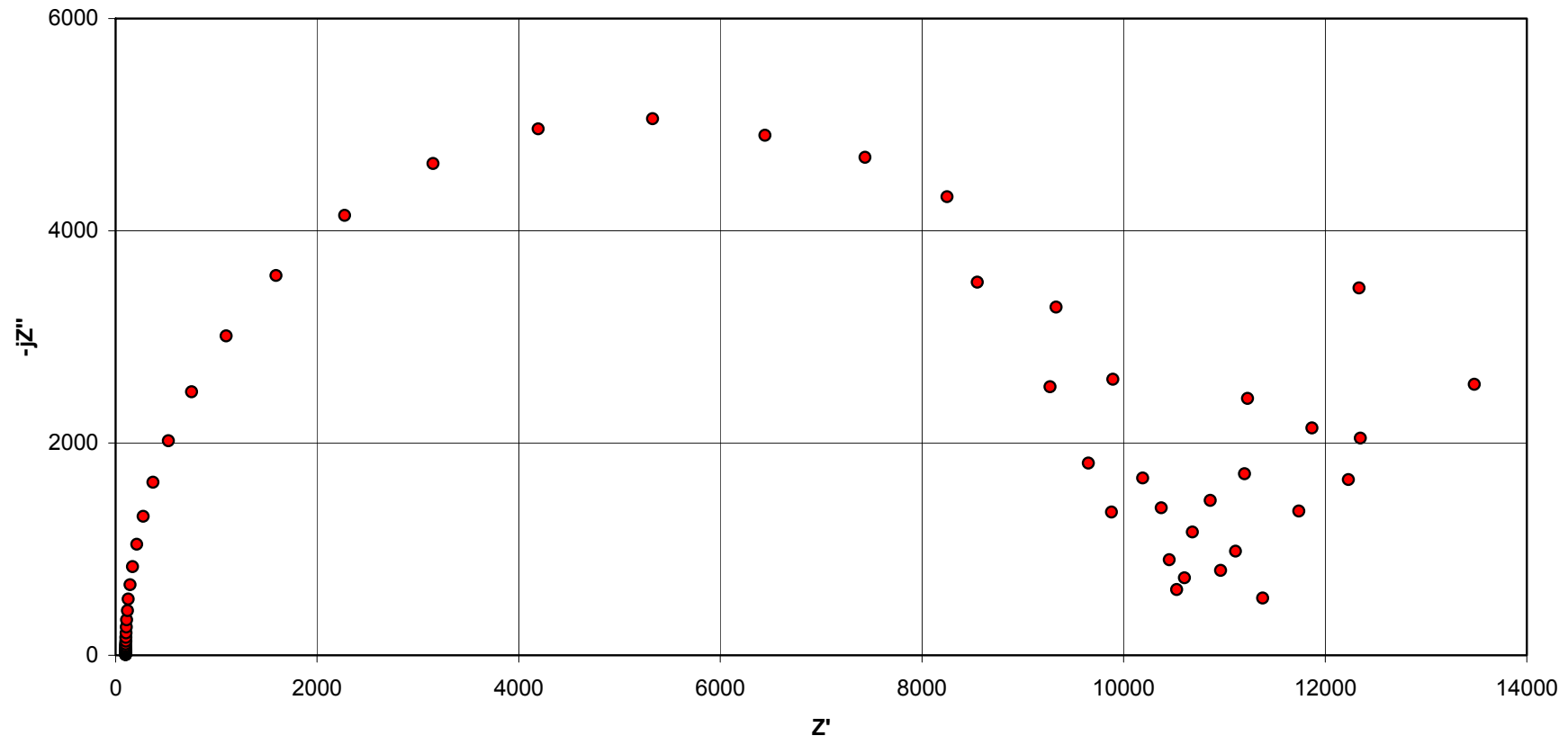
Abstract - Measurements of self-generated electrochemical potential fluctuations on electrodes undergoing either pitting or crevice corrosion show that these forms of localized attack have quite distinct noise "signatures" and that these two types of attack can be detected within seconds of their initiation.

INTRODUCTION

SEVERAL workers have investigated electrochemical noise related to electrode processes. Barker¹ concluded that noise measurements should be productive when applied to systems where charge transfer is catalyzed by a minor component of the interface or where the system is remote from its equilibrium. Blanc *et al.*² investigated the iron/sulphuric acid system using a cross-correlation technique. Prior³ observed free corrosion potential variations on

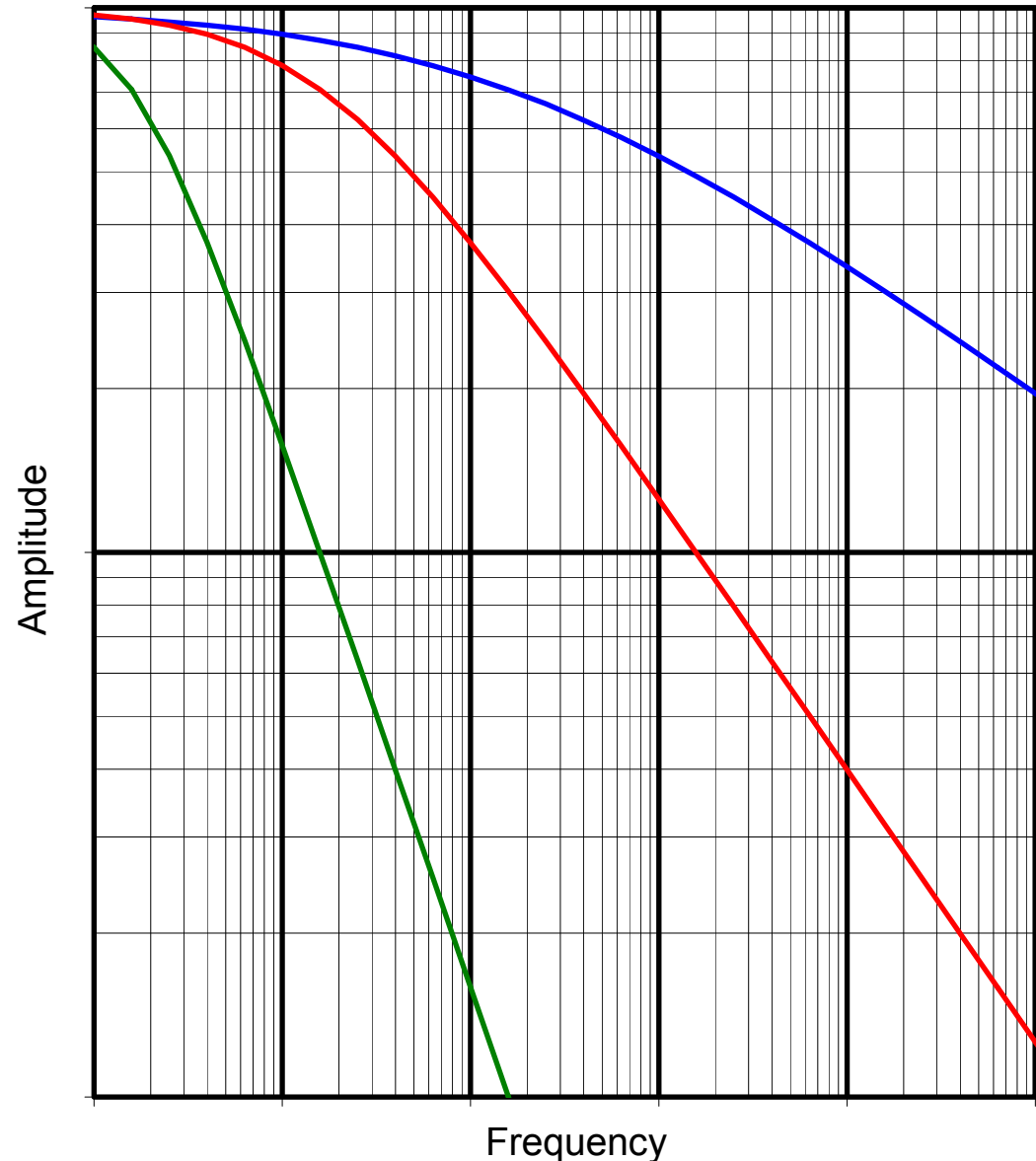
EIS Data Scatter

- EIS measurements on electrodes undergoing localised corrosion had data scatter at low frequencies
- Averaging over more sine cycles did not always improve results
- Why ?



1/f Spectral Density Behaviour

- Amplitude increases as frequency decreases
- Random signal - 'white noise' - would be flat
- Pitting – shallow slope (-10dB/decade)
- General corrosion – steep slope (-30dB/decade)
- The 1/f type of response is found in many natural phenomena



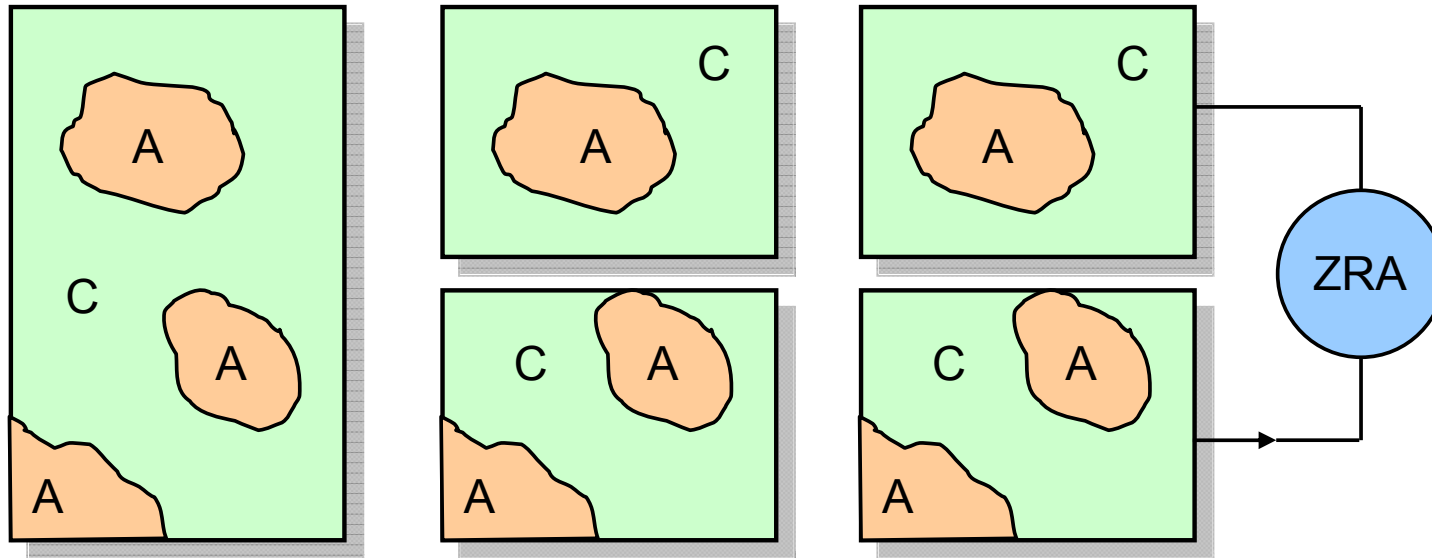
Electrochemical Potential Noise

- Fluctuations of E_{corr}
- Measured either as the potential difference between a test electrode and a stable reference electrode, or as the potential difference between two 'identical' electrodes
- Typical amplitudes of $1\mu\text{V}$ to $1000\mu\text{V}$
- Typical frequency range 0.001Hz to 1Hz
- Sensitive to passive film breakdown and re-growth
- Works well if electrode surface is mainly passive (large cathode)

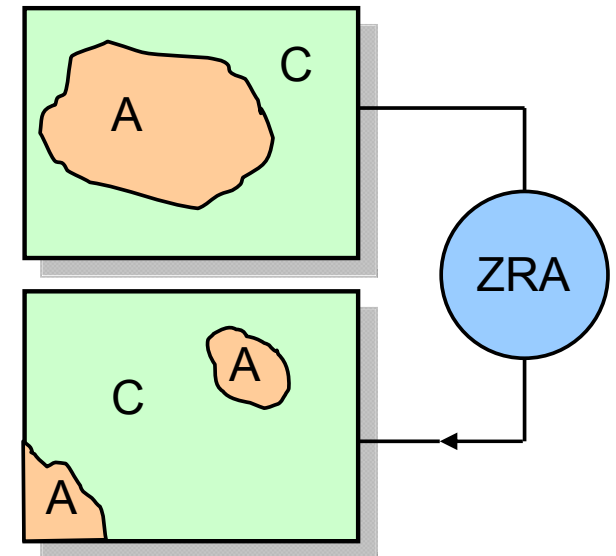
Electrochemical Current Noise

- Fluctuations of current between two 'identical' electrodes
- Measured as the current flowing between two electrodes electrically shorted through a current sensing circuit (zero resistance ammeter or a small resistor)
- Typical amplitudes of 10pA to 1mA
- Typical frequency range 0.001Hz to 1Hz
- Sensitive to differences between the two 'identical' electrodes
- Works well if separate anodic and cathodic areas exist on the electrodes

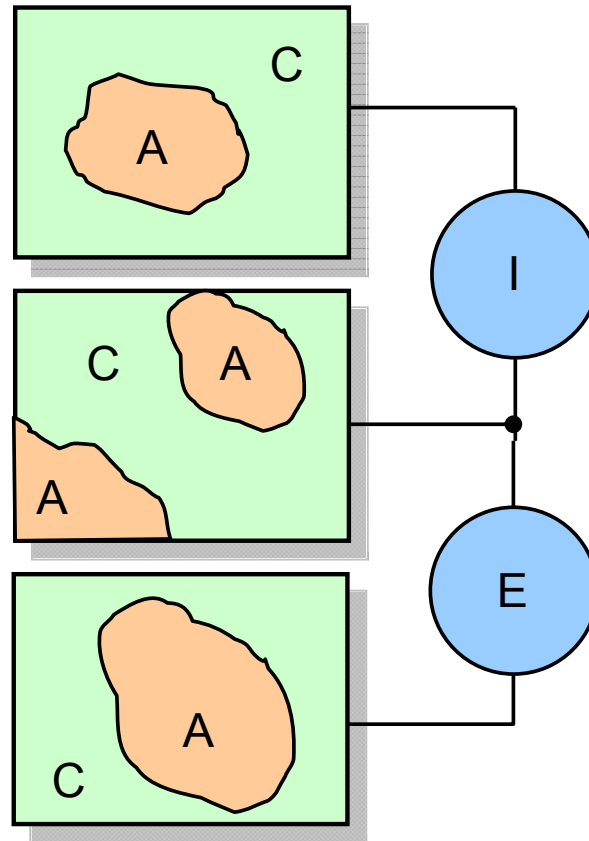
Electrochemical Current Noise Measurement



- Single corroding electrode with anodic and cathodic sites
- Cut electrode into two parts
- Connect two parts with a ZRA
- As anodic and cathodic sites change ZRA current also changes

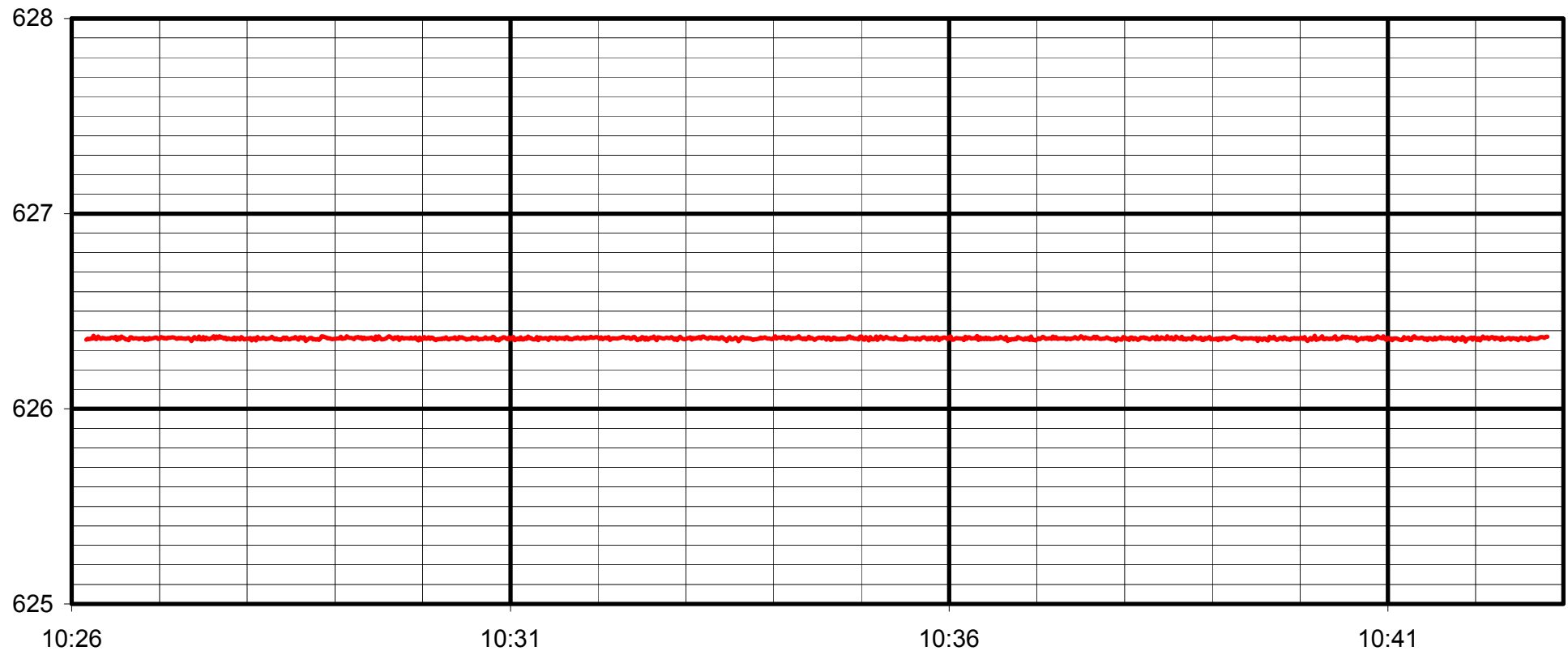


Combined Electrochemical Potential and Current Noise Measurement



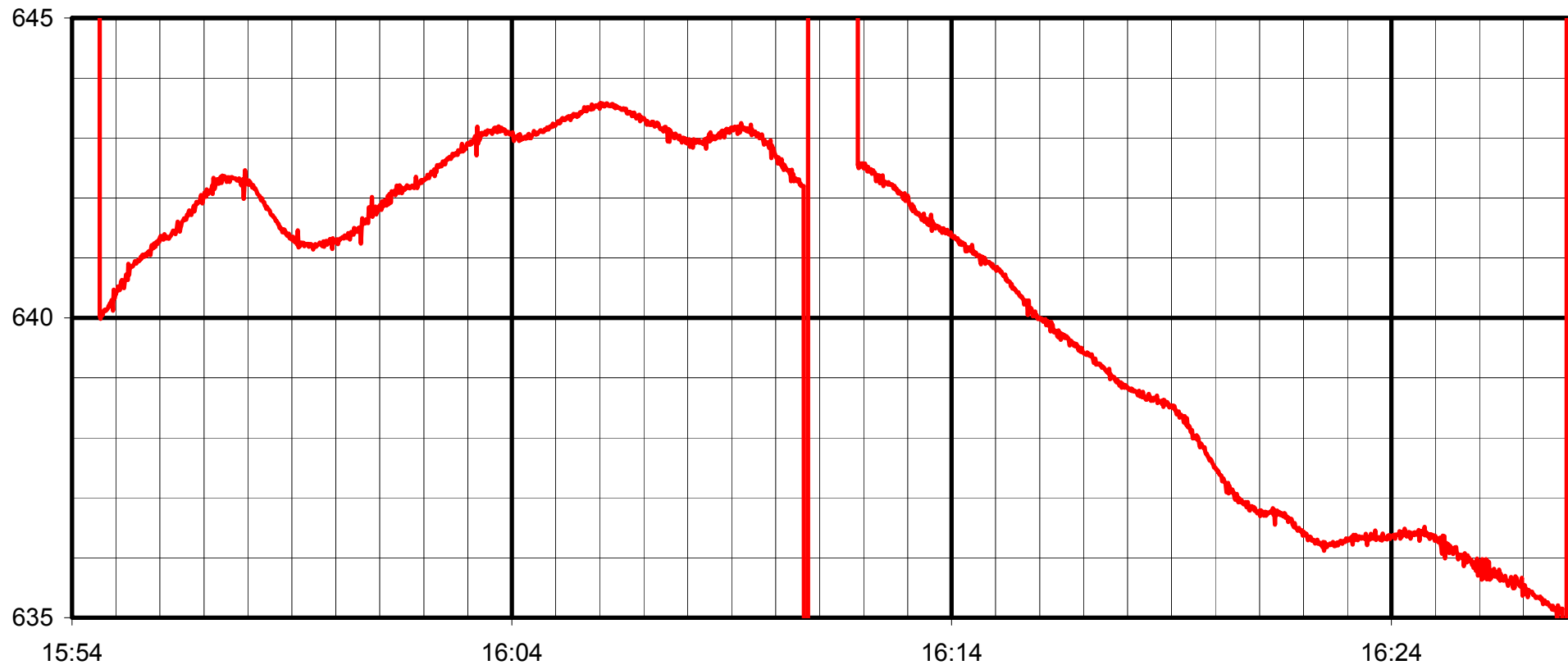
- Measure current noise between two of the electrodes
- Measure potential noise between this pair and the third electrode

Passive Electrode



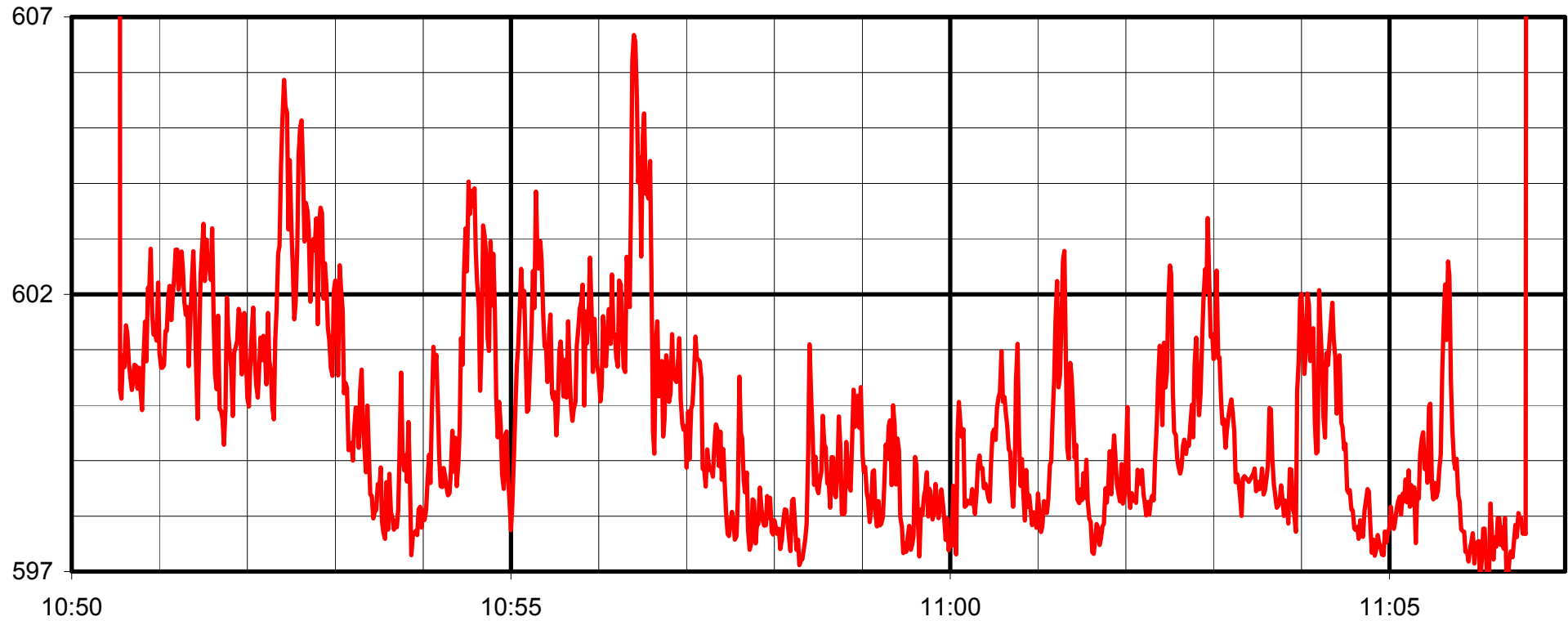
- CorrTran cell current on a passive test electrode
- Little or no fluctuation

General Corrosion



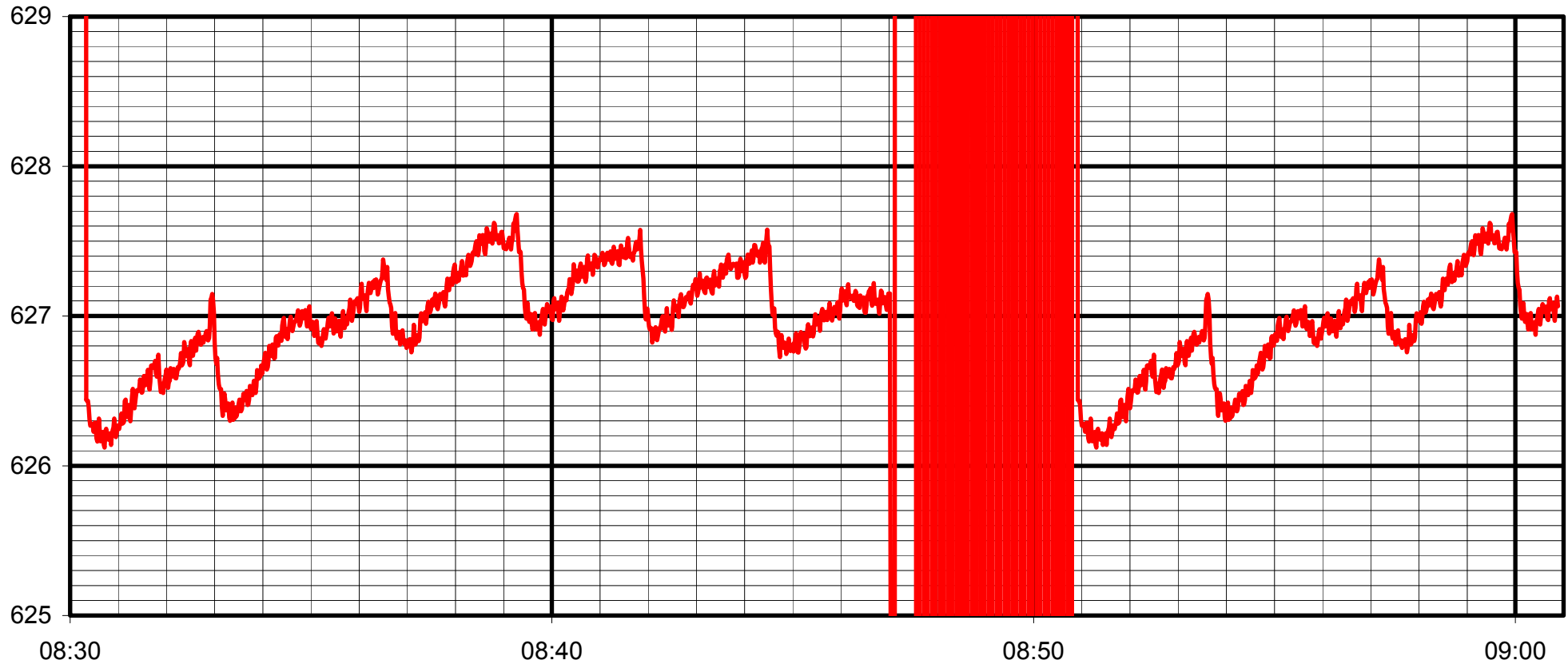
- CorrTran cell current on a uniformly corroding test electrode
- Slow long term high amplitude fluctuation
- Low amplitude higher frequency noise

Pitting Corrosion



- CorrTran cell current on a pitting test electrode
- High amplitude fast fluctuations

Crevice Corrosion Oscillations



- CorrTran cell current on a crevicing test electrode
- Crevice corrosion shows a characteristic periodic noise pattern

CorrTran MV ECN Calculation

- Use running moment formulae
- Latest noise sample number = n and latest noise sample value = x_n
- Previous first moment value is $m1$, second moment is $m2$ etc.
- Calculate delta as $d = (x_n - m1)$
- Calculate new moment values ($m1..m4$), for example :

$$m1 = m1 + \frac{d}{n} \qquad m2 = m2 + \frac{\left(d^2 \times \left(1 - \frac{1}{n} \right) - m2 \right)}{n}$$

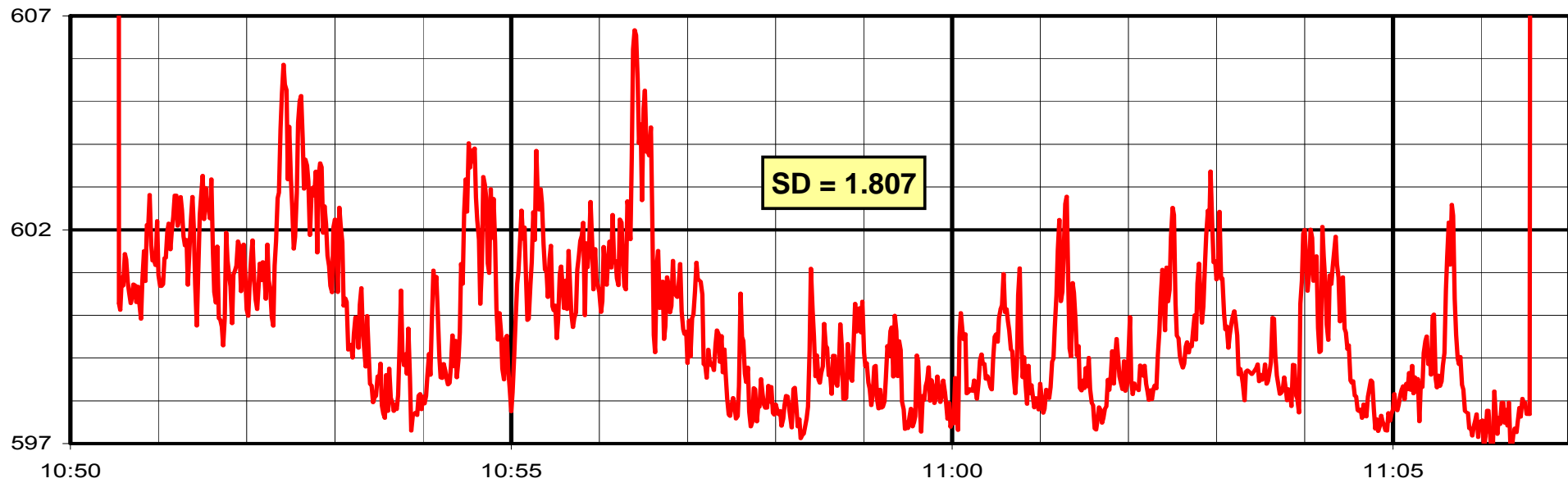
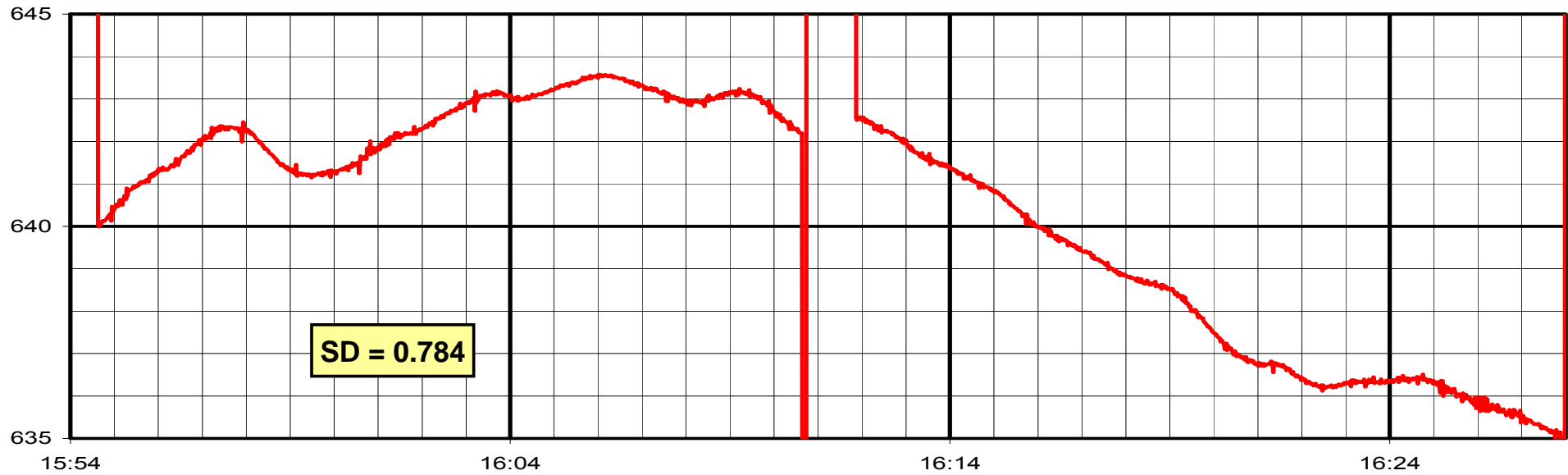
- Repeat for the required number of samples
- At the end of the measurement period calculate :
- Mean = $m1$
- Standard deviation = $\sqrt{m2}$
- Localised corrosion index = $\sqrt{(m2 / (m1^2 + m2))}$

Electrochemical Noise ‘Pitting Index’

- Search for a single parameter relating electrochemical noise to localised corrosion propensity

Standard deviation of potential noise	σ_E		1 μ V to 10mV
Standard deviation of current noise	σ_I		10pA to 10 μ A
Dc coupling current	I_I		about $\pm 0.1 * I_{corr}$ or less
Noise resistance	R_n	σ_E / σ_I	10 Ω to 100k Ω
SmartCET pitting factor	PF	σ_I / I_{corr} ?	Limited to 0.001 to 1.0
CorrTran localised corrosion index	LC	σ_I / I_{rms}	0 to 1
RMS of bandpass filtered potential			1 μ V to 1mV
Higher moments of fluctuations statistics (skewness or kurtosis)			
Spectral analysis of fluctuations			
AI identification of noise ‘signatures’			

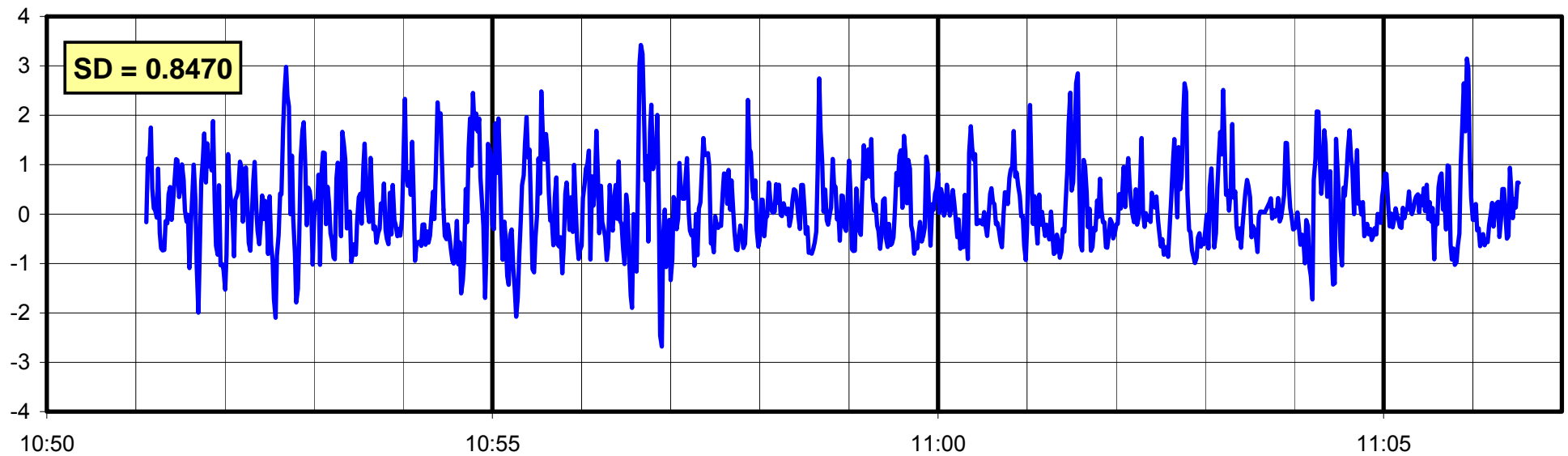
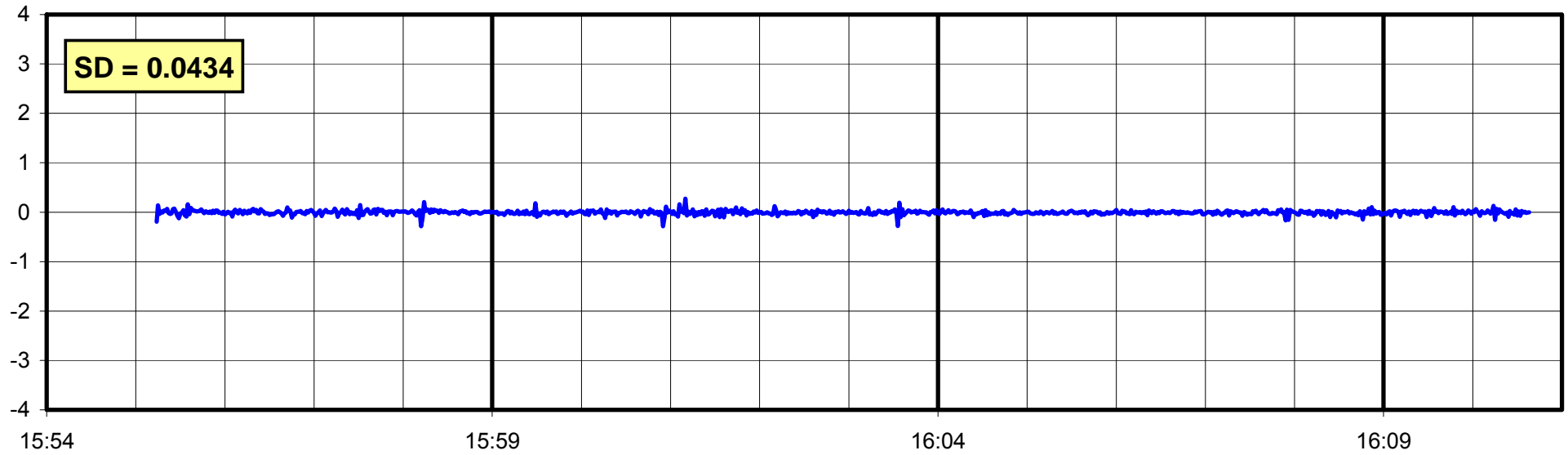
General Corrosion vs Localised Corrosion



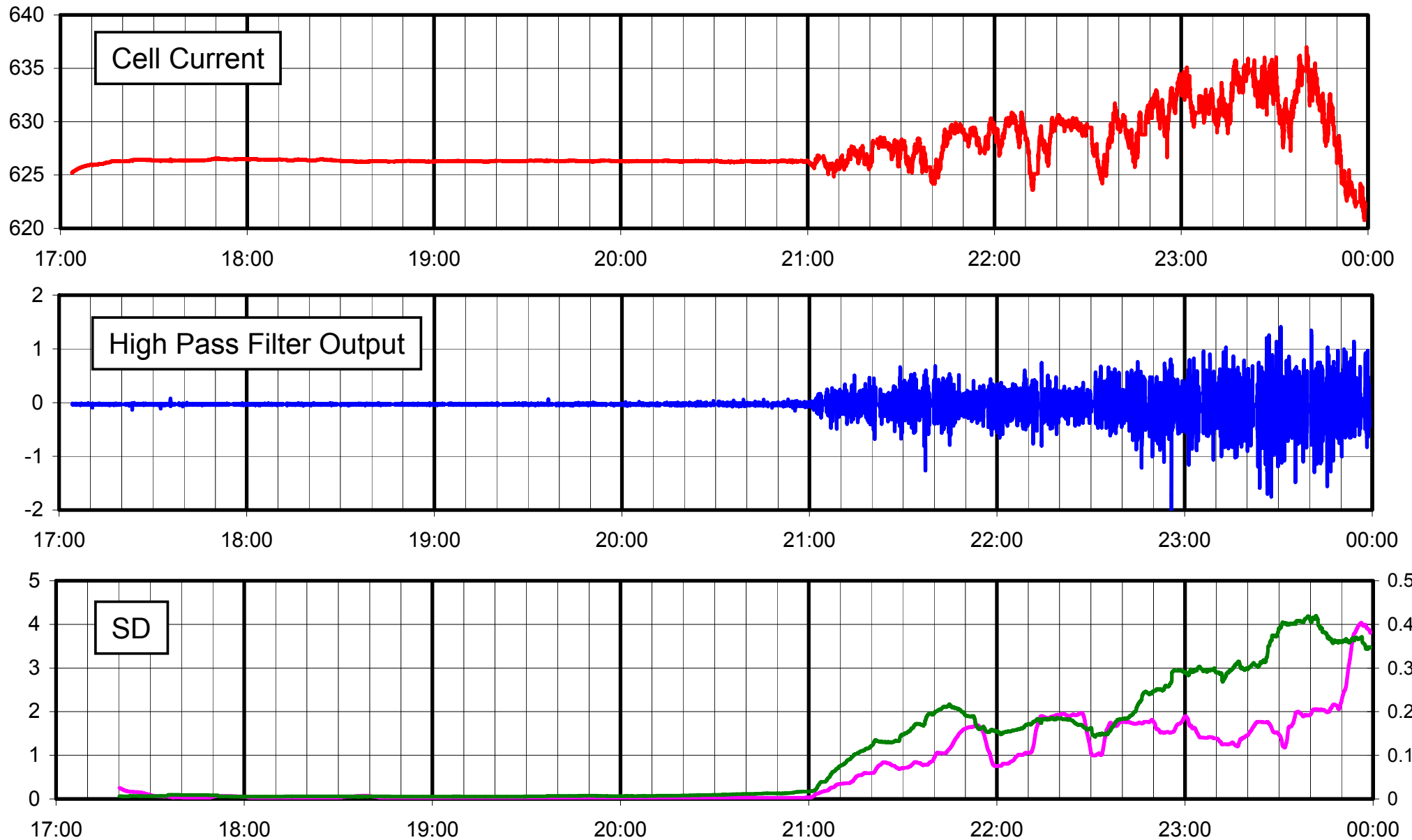
General Corrosion vs Localised Corrosion

- General corrosion gives current noise rich in low frequencies
- Localised corrosion gives current noise containing more high frequencies
- Simple standard deviation etc. calculation on a time record does not distinguish well between the two signal types
- Use high pass filter (e.g. digital 32 stage FIR HP filter, $f_c = 0.05$ Hz) to filter out low frequencies
- Then calculate standard deviation of time record
- Easy to differentiate between the two types of signal

General Corrosion vs Localised Corrosion



Pitting Corrosion Detection



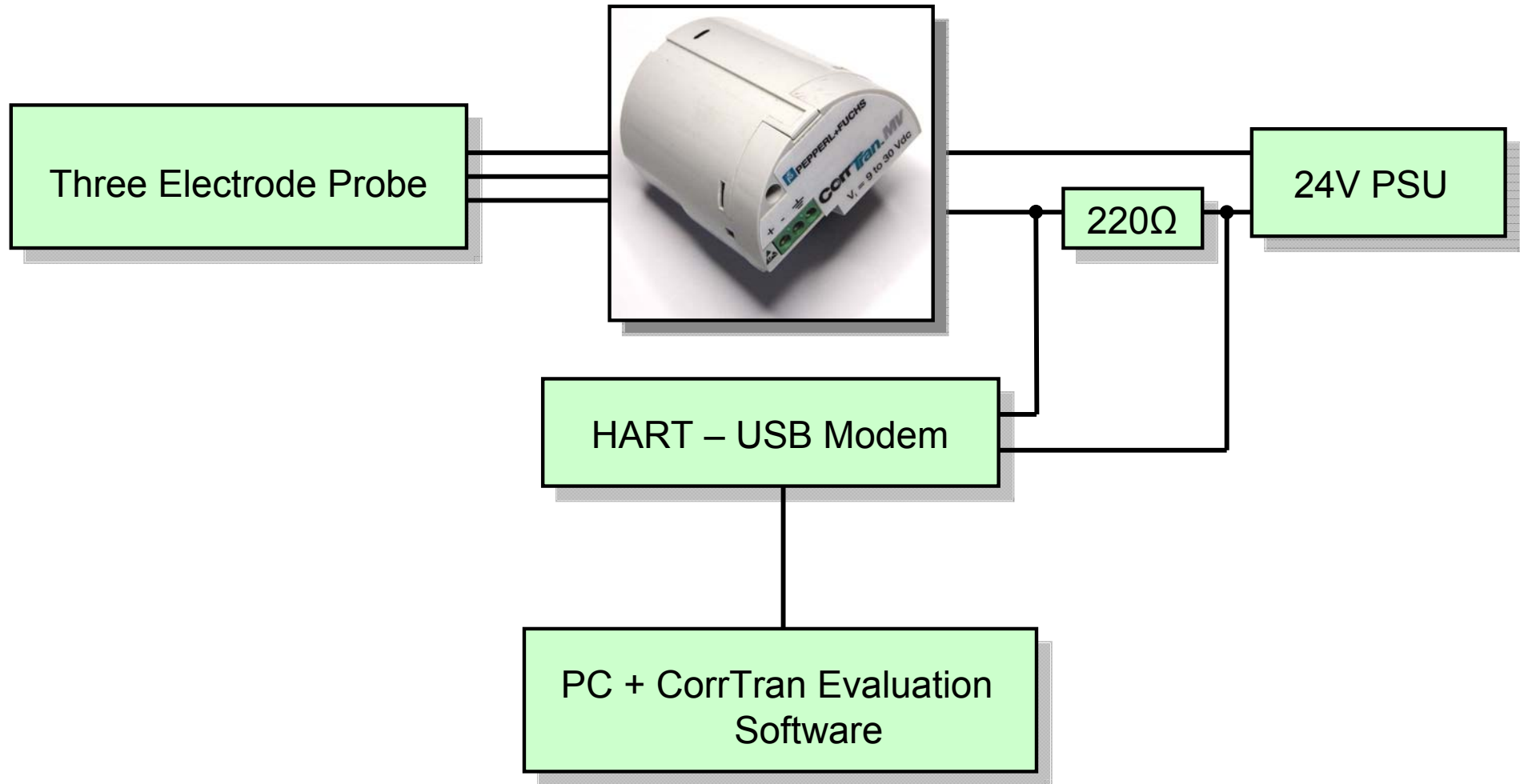
Problems with Plant Electrochemical Noise Measurements

- Electrode surface area is often too small to behave as the bulk plant surface
 - Available anode and cathode areas are limited
 - Small surface area exhibits more variation as a sample of a random process
- Probe electrode material may not be the same as the plant
 - Metallurgy and composition of the probe electrode material
 - Surface morphology
 - Film or scale composition
- Environmental conditions can differ
 - Flow regime can be different because of different geometry
 - Temperature and heat transfer are different
 - Mechanical stresses
 - Electrolyte composition

CorrTran MV ECN Measurement Trade-offs

- Time Record Length - Measurement Speed
 - Longer time record can give better accuracy and reproducibility, but measurement time increases unacceptably
- Sample Rate - Accuracy
 - Frequency range of interest is 0.001 to 1Hz
 - Not much to be gained by faster sample rate
- Localised Corrosion Factor Calculation
 - Present algorithm works satisfactorily in most cases
 - Development ongoing for a better algorithm
- Future Developments
 - Use potential electrochemical noise measurement when more appropriate
 - Improvements in data analysis techniques to speed up the measurement

CorrTran MV as a Laboratory Instrument



Pepperl+Fuchs CorrTran MV – Honeywell SmartCET

- CorrTran MV is a completely new hardware and firmware design
- CorrTran MV overcomes many of the shortcomings of the SmartCET
- Both use the same housing and probe
- Both are manufactured by Pepperl+Fuchs



Slides 10 and 15

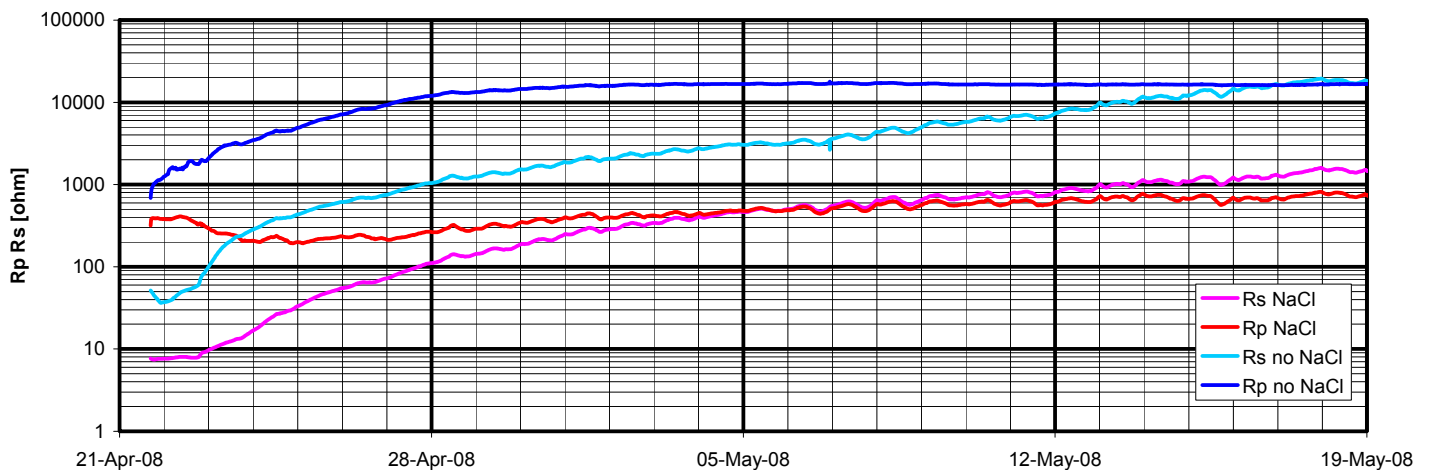
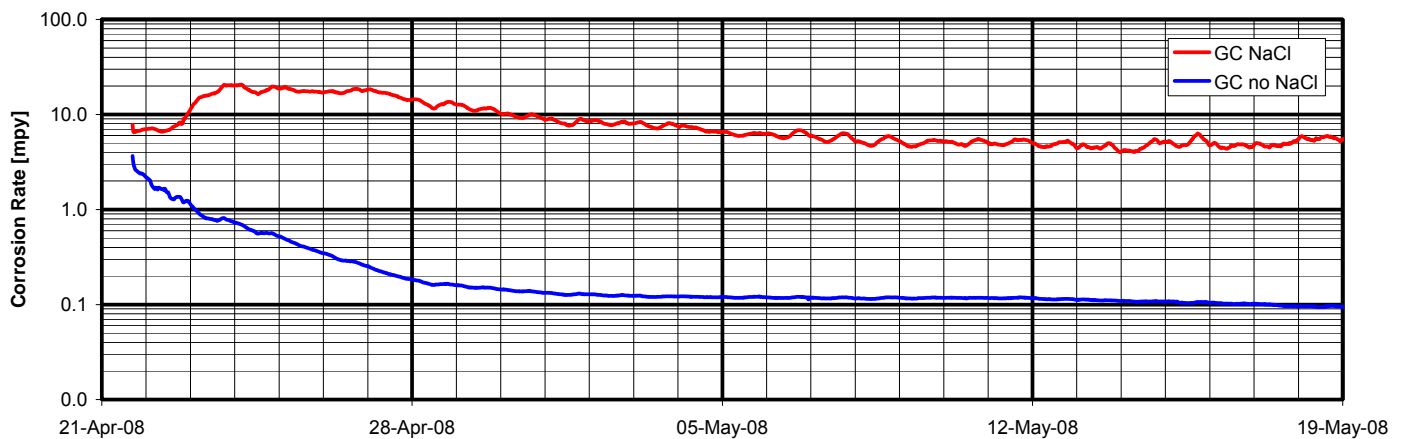
Carbon steel in concrete.

Two sand-cement mortar blocks were cast with embedded lengths of carbon steel bar as the test electrodes (3 electrodes, ca. 5 cm² surface area each). Approx. 3% NaCl (per weight of cement) was added to the mix for one of the blocks. Normally the high pH should cause the steel to passivate, presence of chloride leads to localised depassivation and hence corrosion.

The idea was to test the performance of the HDA technique in a low conductivity non-activation controlled system. As the mortar sets, cures and then dries the conductivity decreases considerably. In the block without chloride R_s changed from some 40 Ω over 20k Ω over the time of the test – a fairly severe test of the CorrTran device and of the technique.

Slide 10 shows the levels of the harmonic components (at 0.1 Hz). Slide 15 shows the calculated Stern-Geary B values.

For completeness, the plots below show the measured corrosion rates and the R_p and R_s values for the two samples. The data is the actual CorrTran output, no additional processing (smoothing etc. had been applied). The slight fluctuations are due to ambient temperature changes in the lab.



Slides 25 to 28

Typical electrochemical noise examples.

These are plots of some raw electrochemical current noise data captured using the CorrTran diagnostic software. Each trace covers one or two CorrTran measurement cycles, sample rate was the default 1 second. The abscissa scale is in minutes, the ordinate scale is in mV as seen by the circuit analog to digital converter, before any offset or scaling corrections.

Roughly, zero current corresponds to 625 mV and 1 mV equals 1 μA (per the 4.75 cm^2 electrode surface area).

Slide 25 is a passive system – Ti wire in tap water

Slide 26 is an example of general corrosion – carbon steel in 3% NaCl

Slide 27 is an example of pitting corrosion – Al in acidified 3% NaCl

Slide 28 is an example of crevice corrosion signal – carbon steel in 2% acetic acid, electrode masked with quick-set epoxy.