

Get the most out of your experiments

ZAHNER

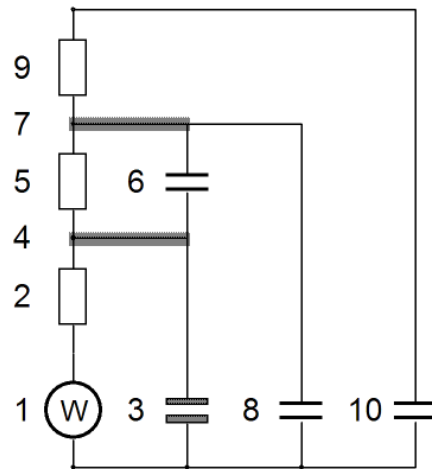
M E S S S Y S T E M E

News About Electrochemical Workstations

Zahner's Intention:

Enable the impedance user to perform a Consistent Uncertainty Estimation of his Physical Parameters Evaluated by EIS.

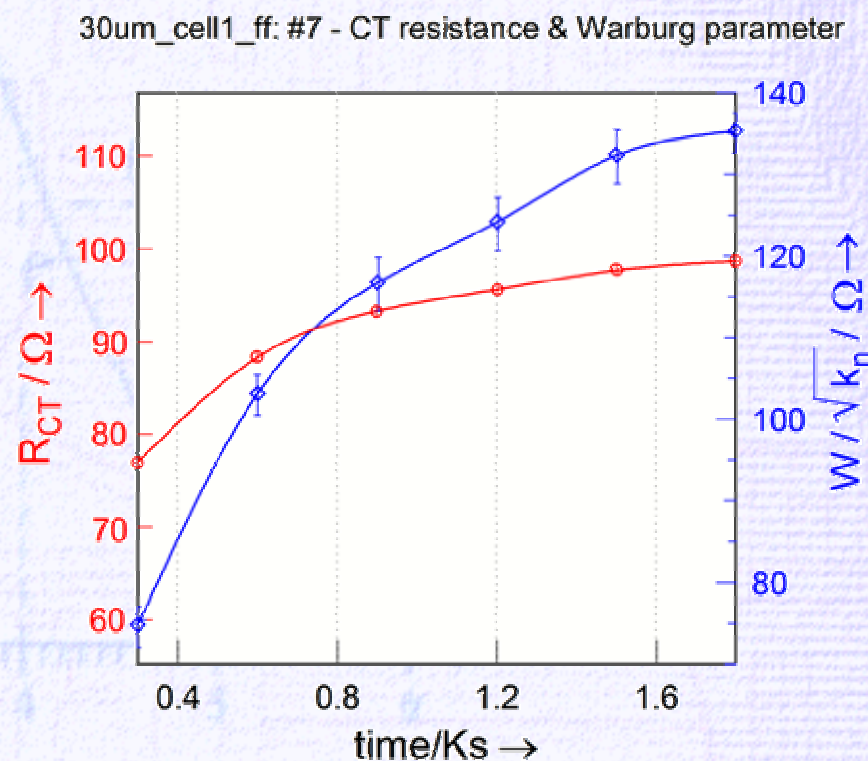
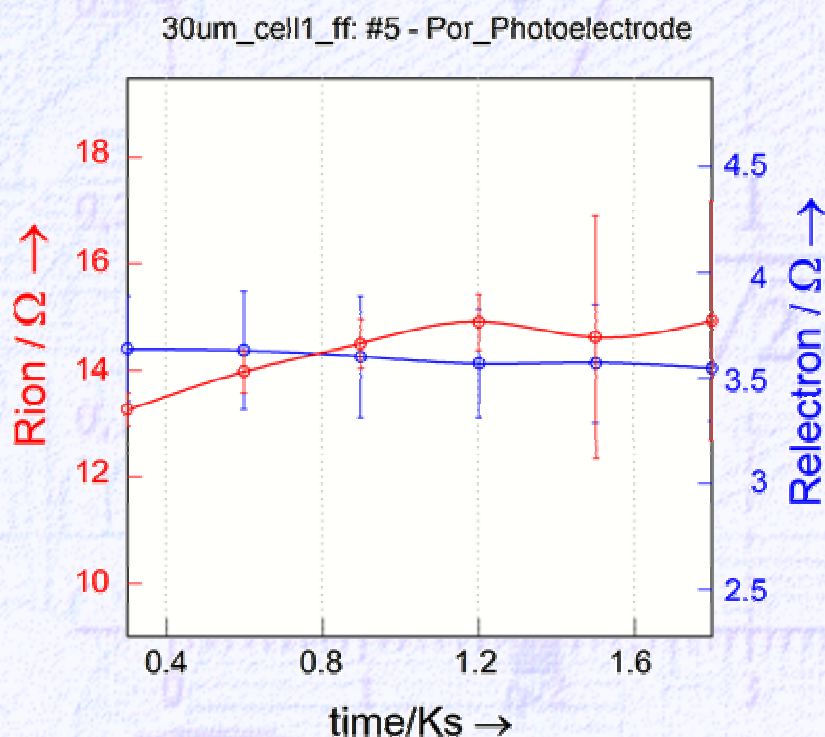
P3HT / Pedot:PSS



Nr.	Value	Unit	Significance	Error/%
1	79.17	$\text{K}\Omega \cdot \text{s}^{-1/2}$	0.33	0.78
2	10.11	$\text{K}\Omega$	0.16	1.58
3	214.8	nF^α	0.32	3.38
4	660.9	m	1.71	0.63
5	1			
6	10.29	$\text{K}\Omega$	0.30	2.66
7	0	Ω		
8	32.55	$\text{K}\Omega$	0.04	5.53
9	78.51	μF	0.11	2.69
10	1			
11	1.319	$\text{K}\Omega$	0.02	17.40
12	0	Ω		
13	84.06	nF	0.77	2.08
14	23.93	Ω	0.62	2.89
15	14.47	nF	0.13	12.61

Zahner's Intention:

Enable the impedance user to perform a Consistent Uncertainty Estimation of his Physical Parameters Evaluated by EIS.



Zahner's Intention:

**Enable the impedance user to perform a
Consistent Uncertainty Estimation of his
Physical Parameters Evaluated by EIS.**

***The Prerequisite:
Automatic Measurement Error Determination***

**The appropriate Zahner Tool:
Weighted Harmonics Autocorrelation**

Uncertainty Estimation by Weighted Harmonics Autocorrelation:

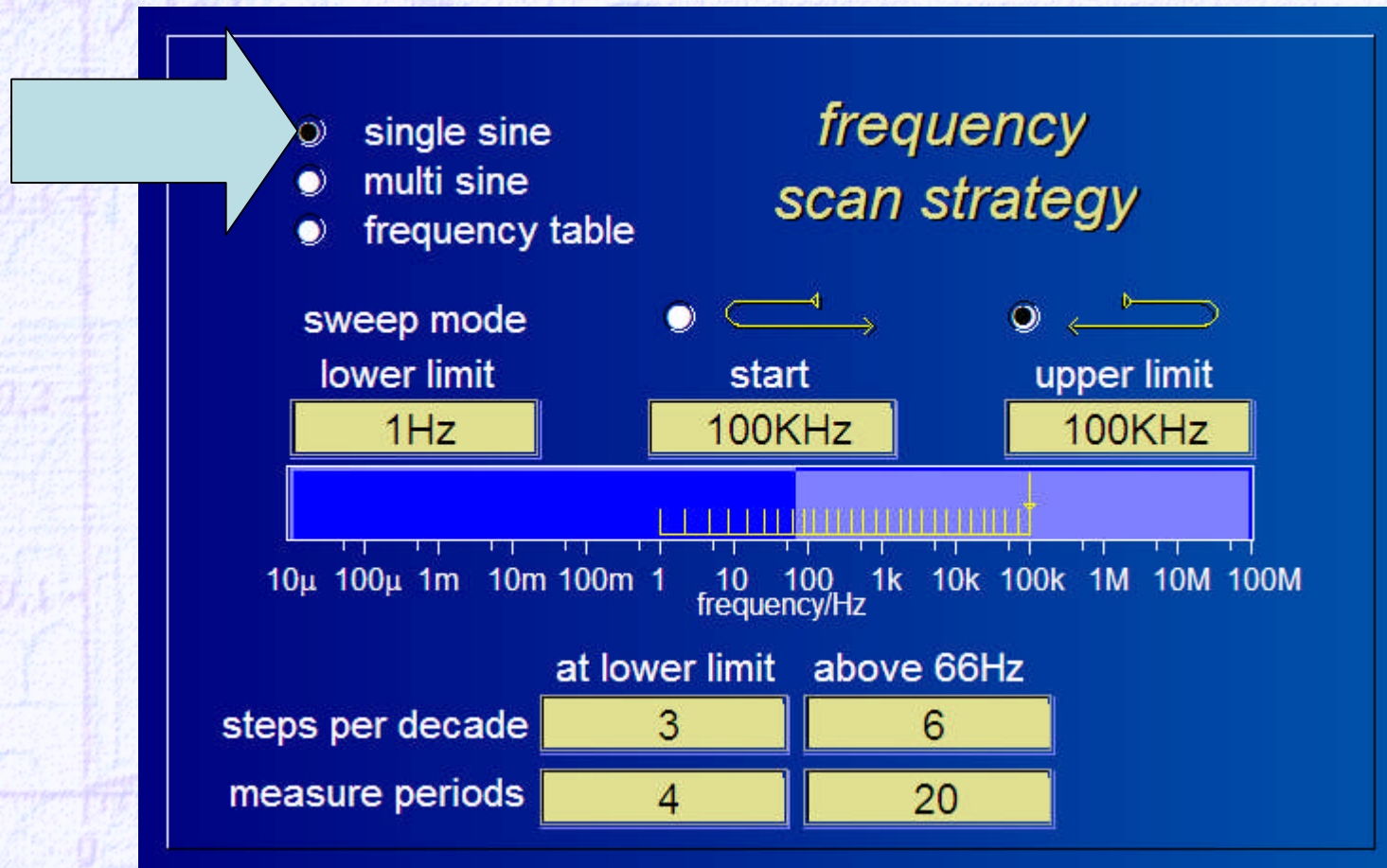
Under monochromatic (sinusoidal) excitation of a system, the harmonic distortion („noise“) content of the response signal may be used as a measure for the uncertainty!

Impedance Contributions Online 6 (2008) P4-1 – P4-13 <http://accessimpedance.iusi.bas.bg>

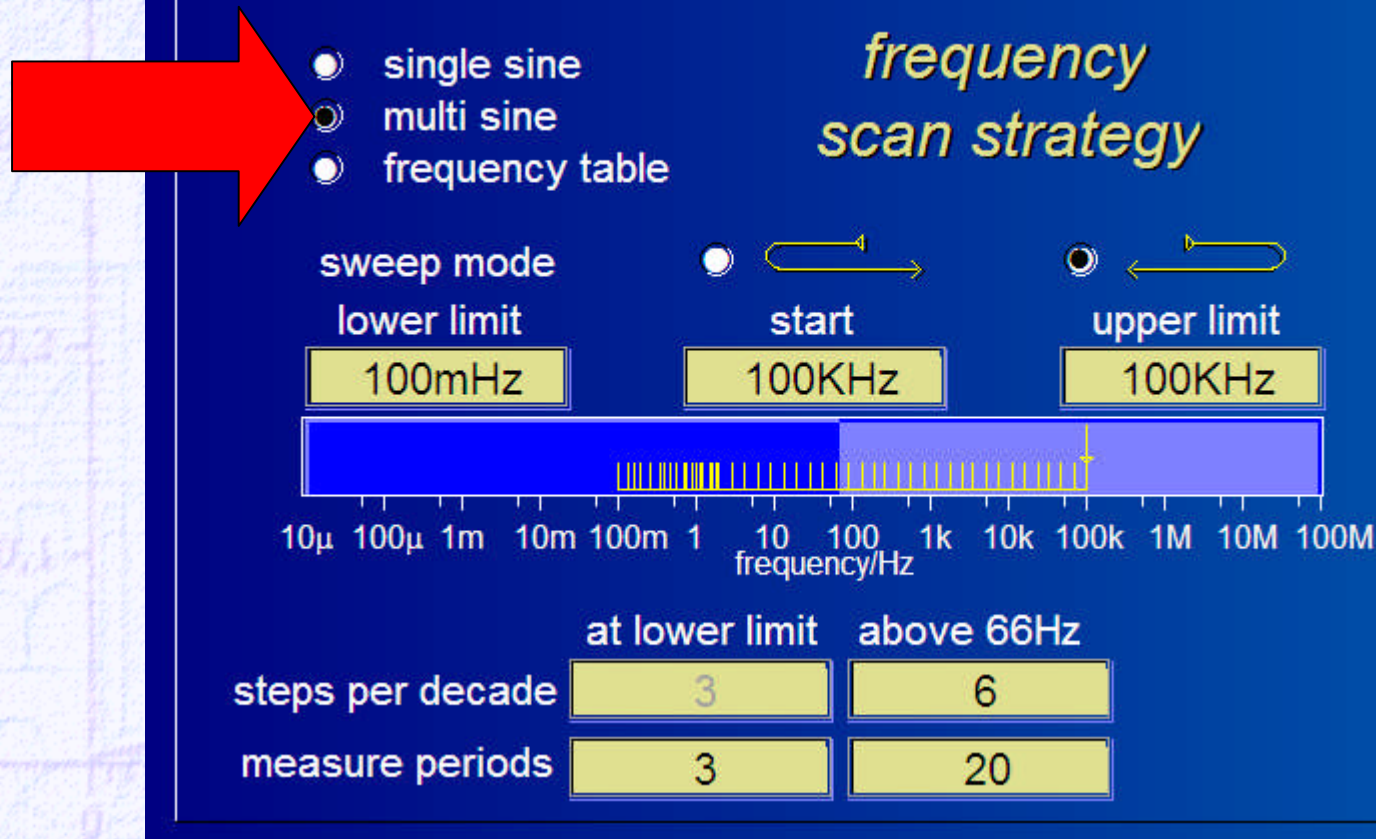
Prerequisite:
Single Sine!

the harmonic content must be unequivocally assigned to distortions:

New software release: Besides single sine and frequency table...



We now support multi sine excitation:



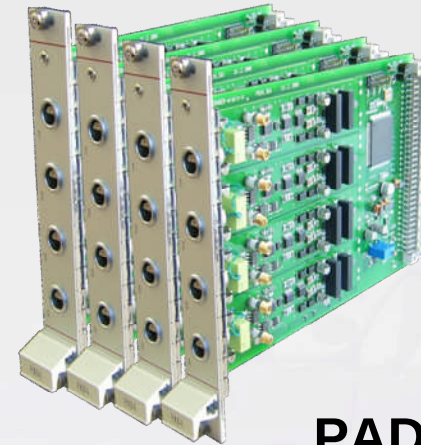
• News for Batteries • Fuel Cells • Stacks • Supercaps



3rd party load
> 1 KW

EL 1000

100V / 200A / 1KW



PAD4

4V/100 V



IM6/Zennium

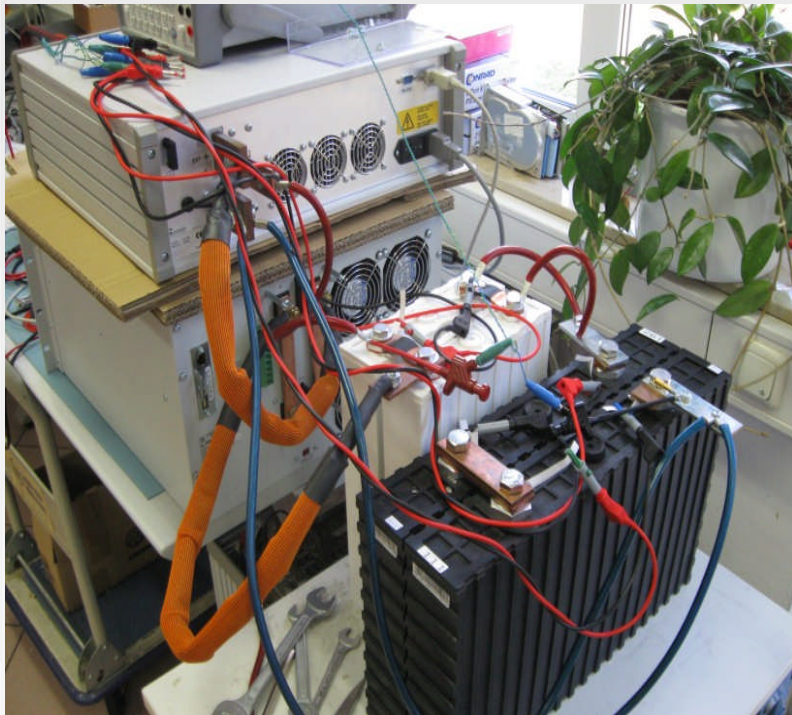


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Scientific Instrumentation

• Batteries • Fuel Cells • Supercaps STACKS



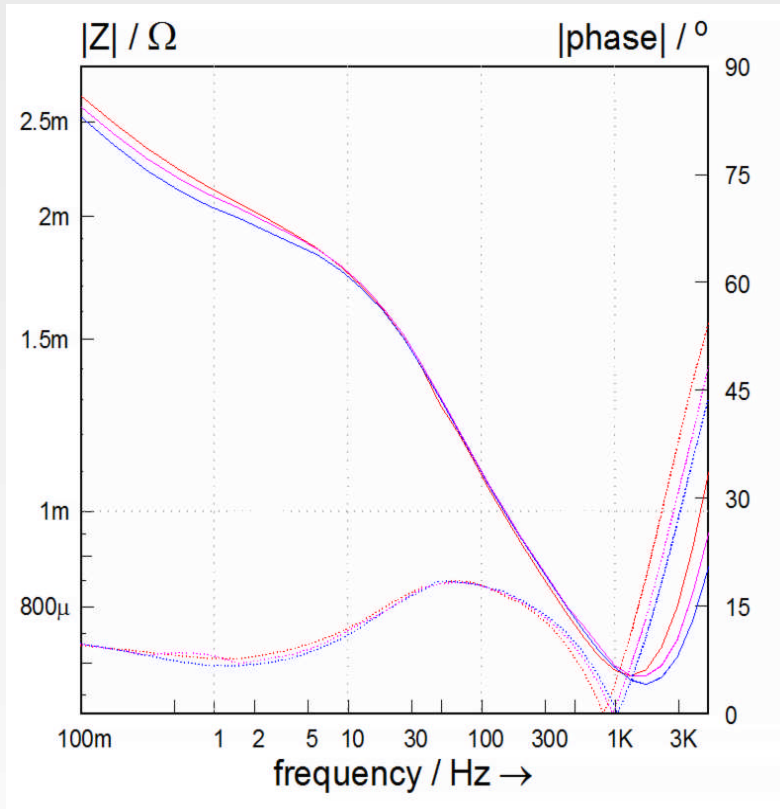
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LiFeP-
Accumulator
3Cell Stack

100Ah

Real time spectra of
individual cells:
true synchronous
parallel measurement

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Get the most out of your experiments

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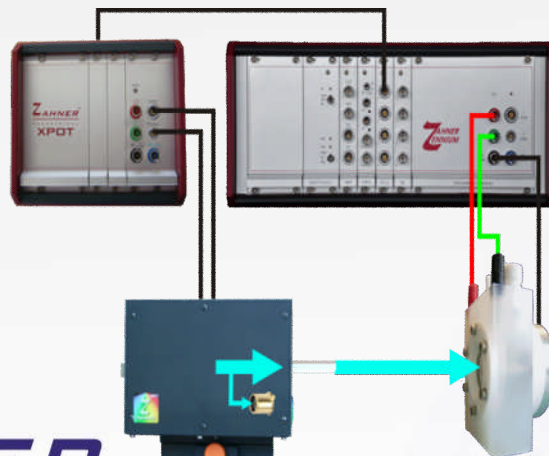
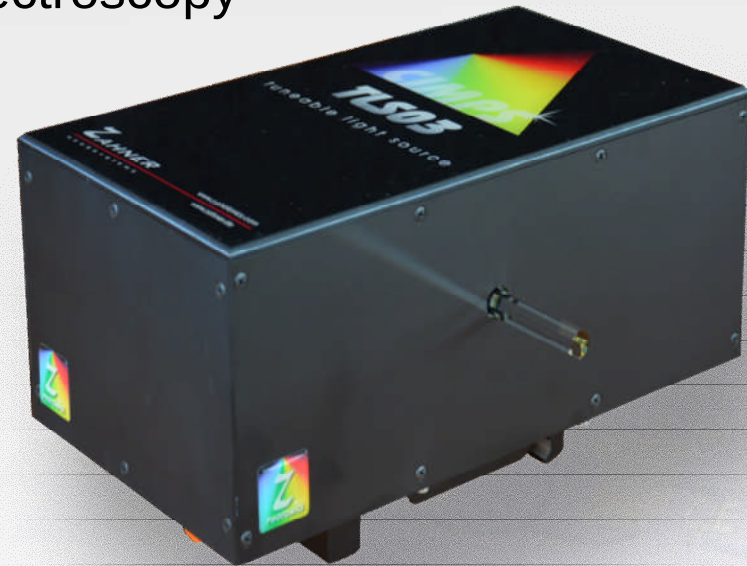
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Leader in Photo-Electrochemical Workstations

CIMPS-pcs2: Tunable Light Source

Wavelength resolved photocurrent spectroscopy
IPCE

- tunable light source TLS03
 - 365 – 1020 nm
 - Optional UVB-extension:
 - 290 – 1020 nm



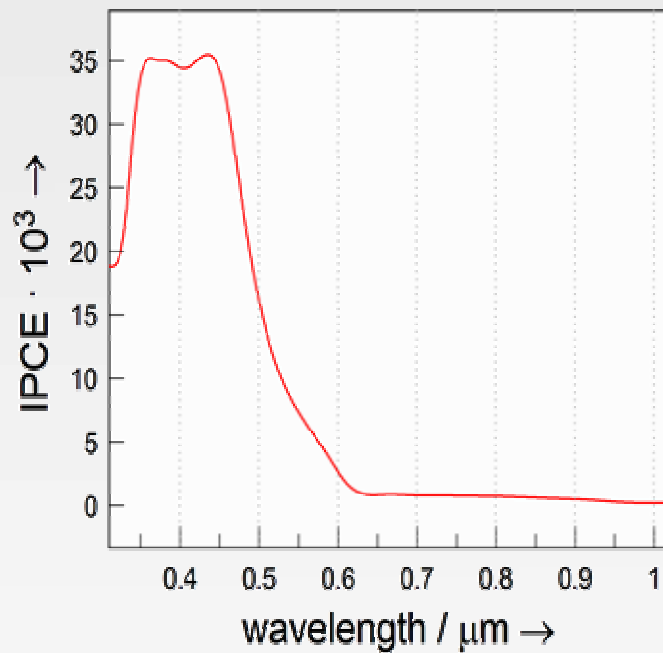
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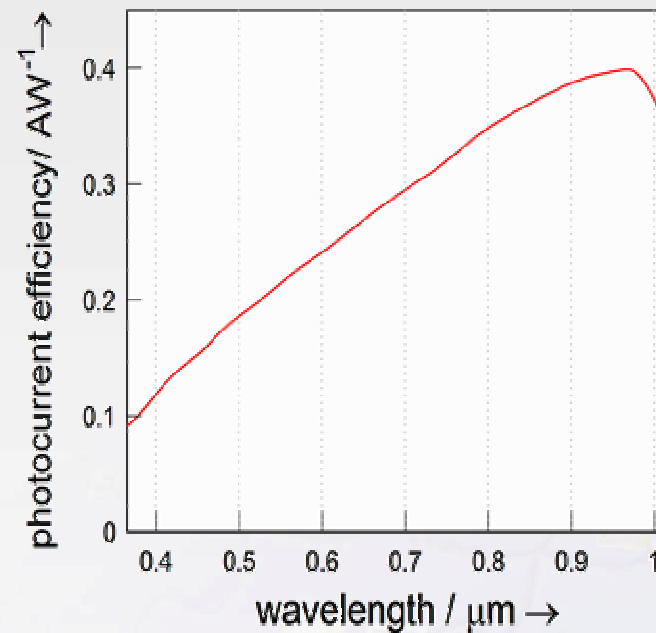


Scientific Instrumentation

CIMPS-pcs2 application



Copper in aq. sodium acetate
at pH 8.4



Backthinned silicon
photodiode

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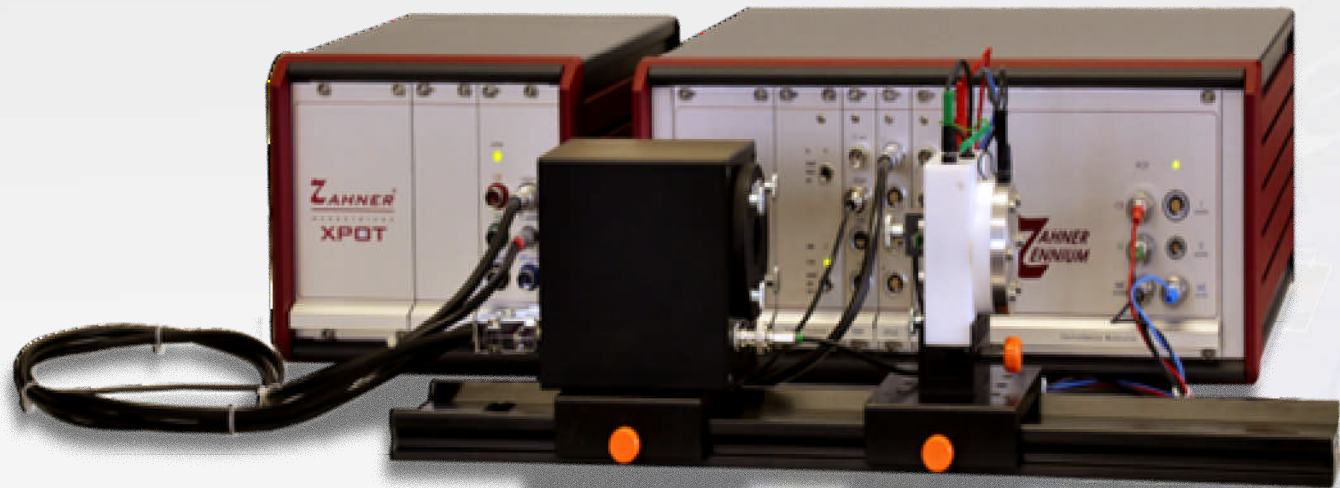
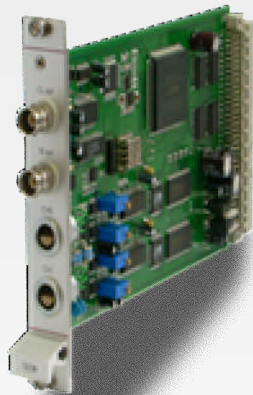


Scientific Instrumentation

CIMPS-fit

Photocurrent / photovoltage under light transients

- transient recorder TR8M



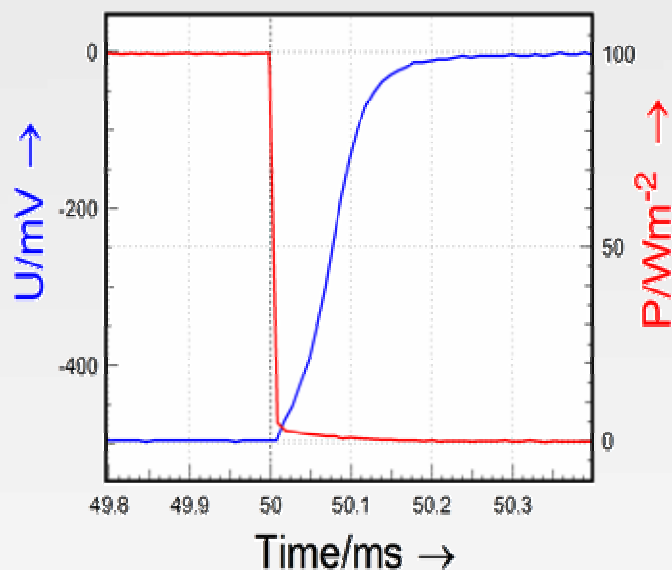
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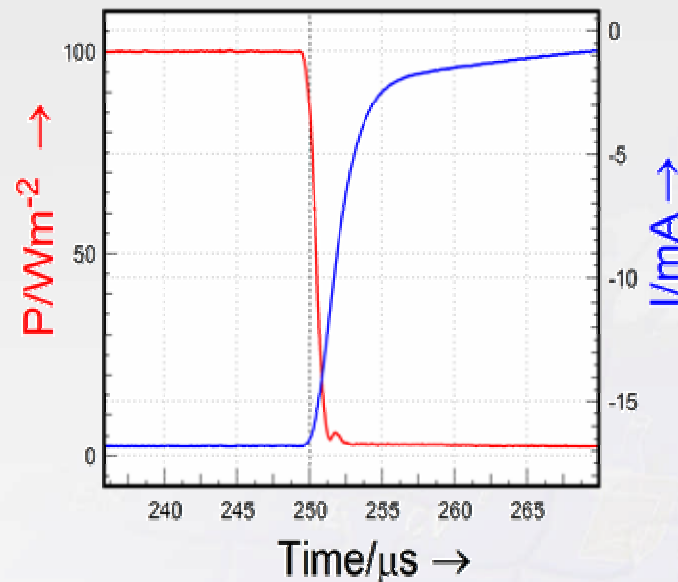


Scientific Instrumentation

CIMPS-fit application



Photovoltage transient
of an organic solar cell
*Cr-Al-Cr-P3HT-PCBM-PEDOT-Cr-
Au*



Photocurrent transient of a
monolithic silicon solar cell

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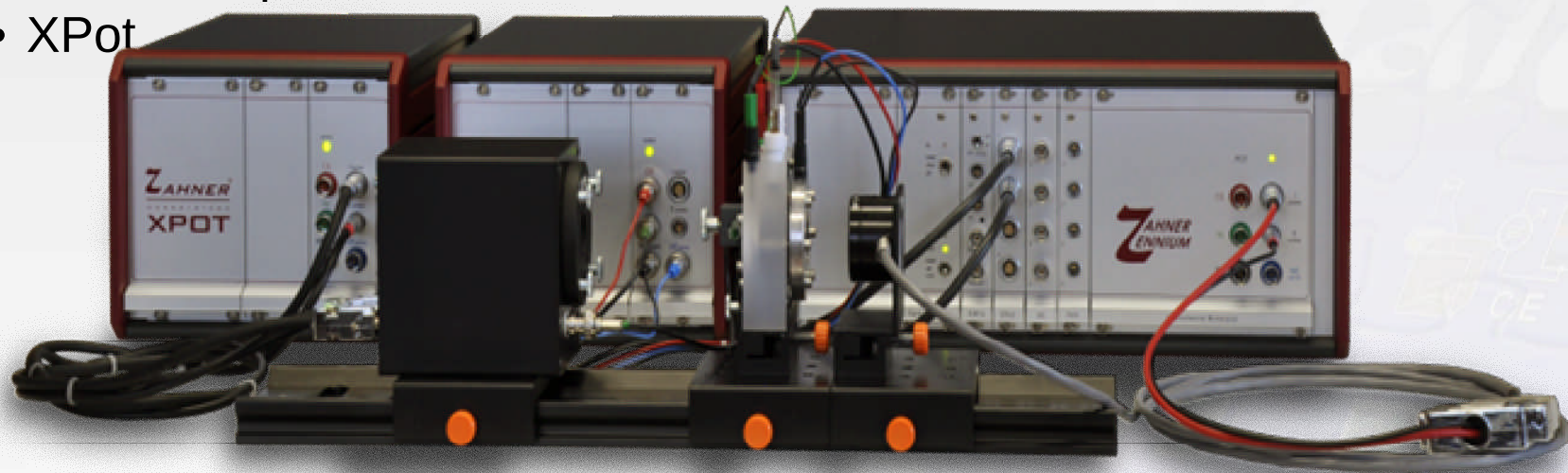


Scientific Instrumentation

CIMPS-dtr

OIS, dynamic transmittance / reflectance measurements

- calibrated photodiode
- XPot



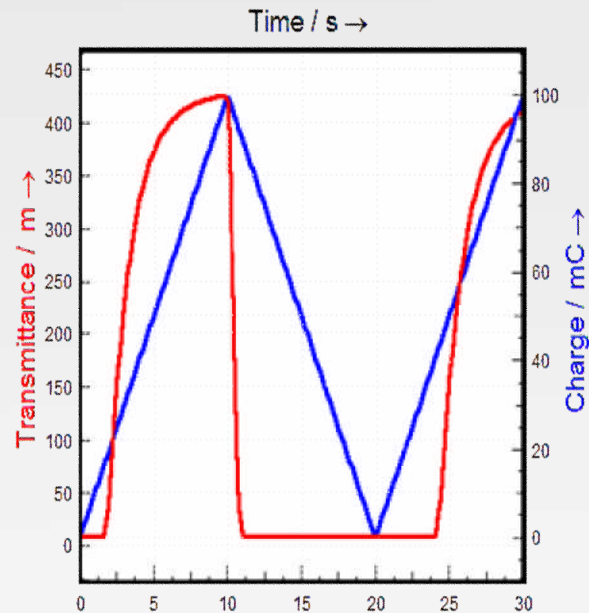
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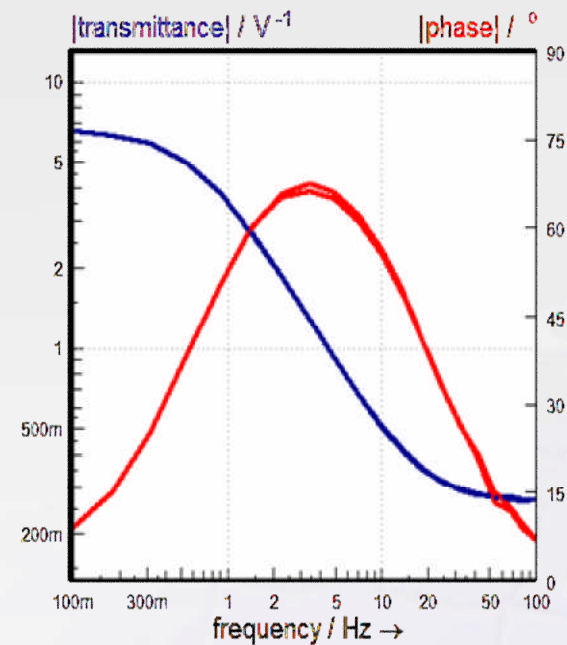


Scientific Instrumentation

CIMPS-dtr application



static transmission
vs. charge



dynamic transmission
vs. frequency

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LCD modulator at 2.3 V

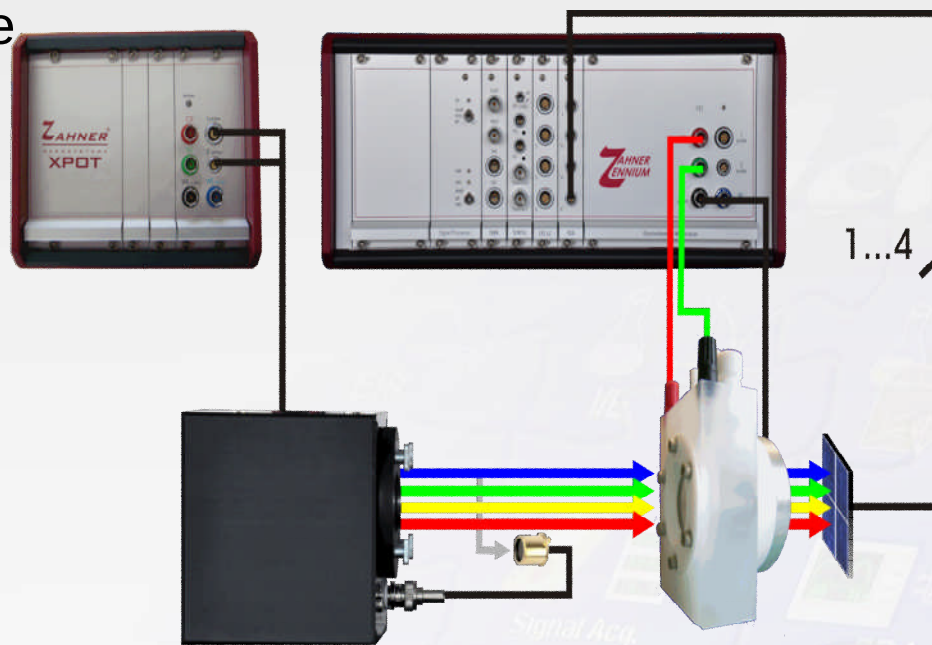
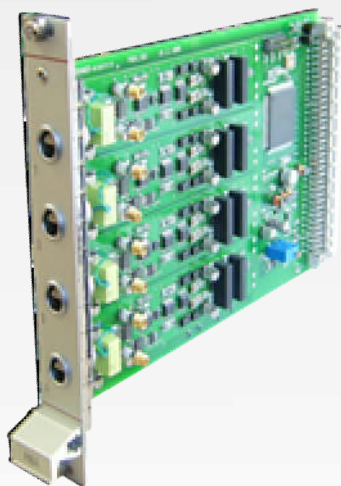


Scientific Instrumentation

CIMPS-mdtr

multi spectral OIS, dynamic transmittance / reflectance measurements

- multi spectral light source
- PAD4 card



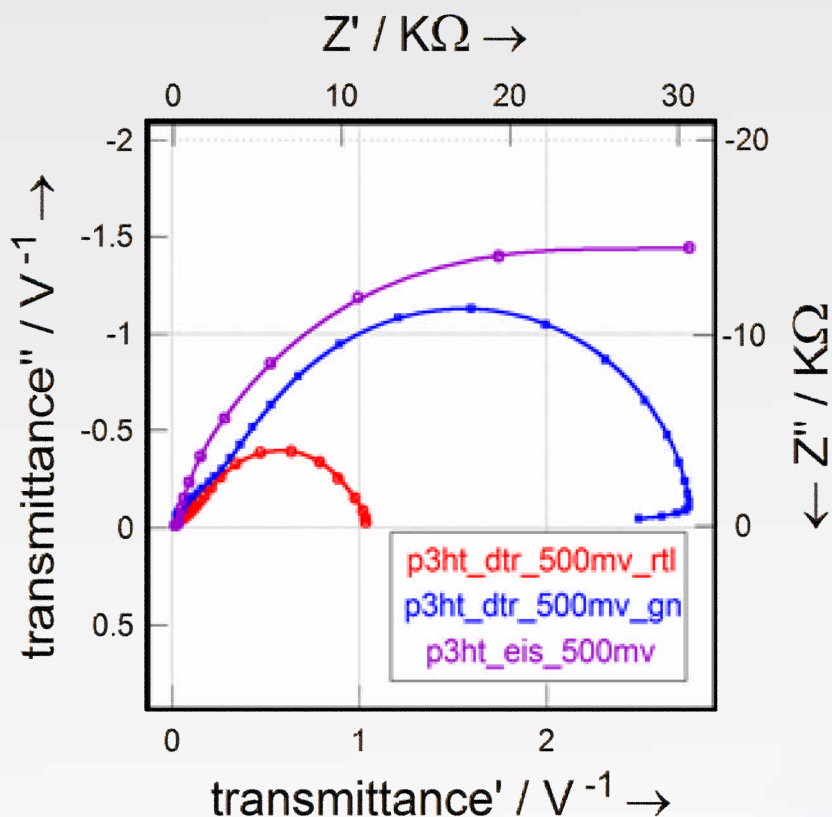
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Scientific Instrumentation

CIMPS-mdtr application



P3HT-PEDOT:PSS polymer multilayer

- EIS (violet curve)
- DTR at 535 nm (blue curve)
- DTR at 740 nm (red curve)

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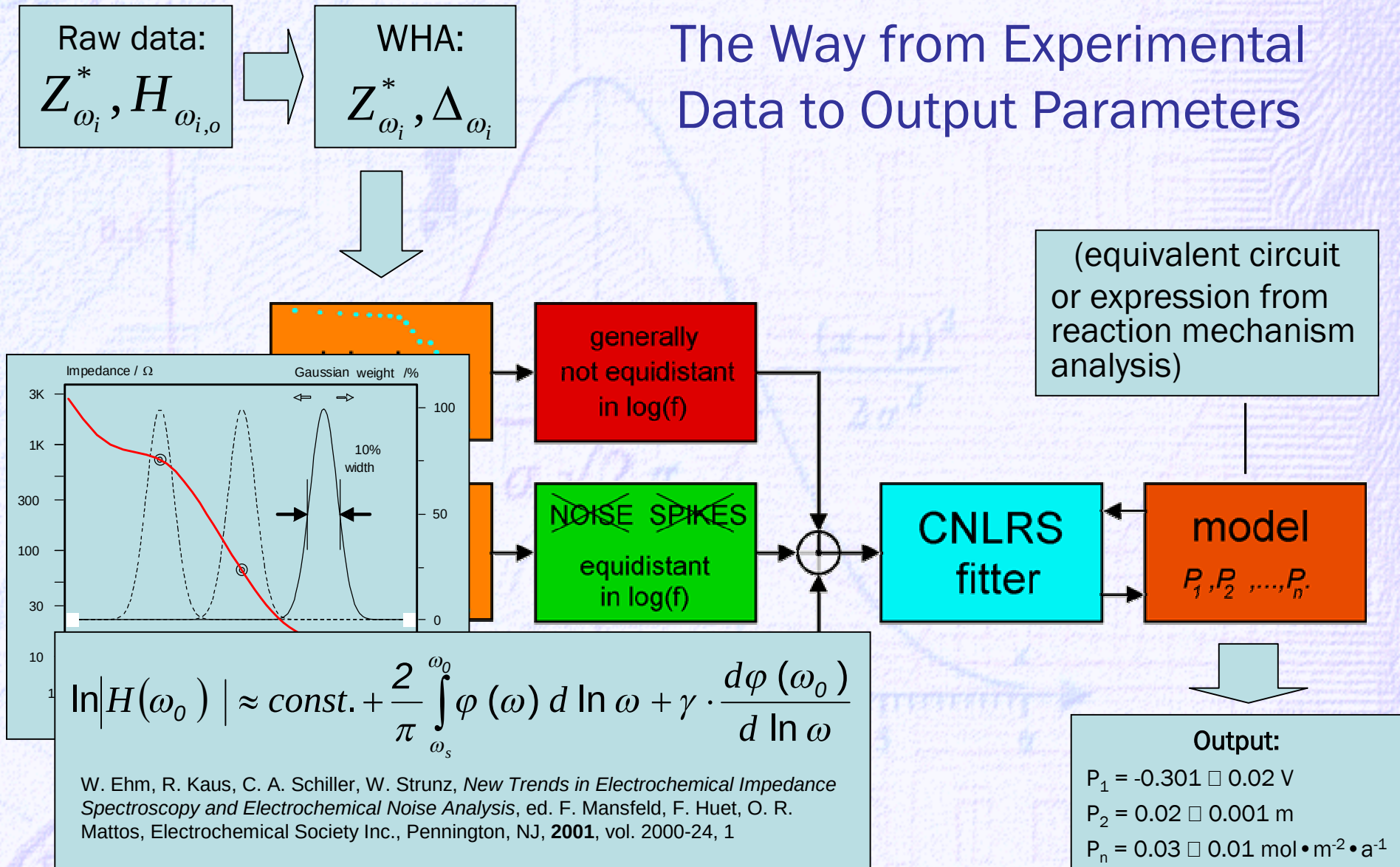
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Scientific Instrumentation

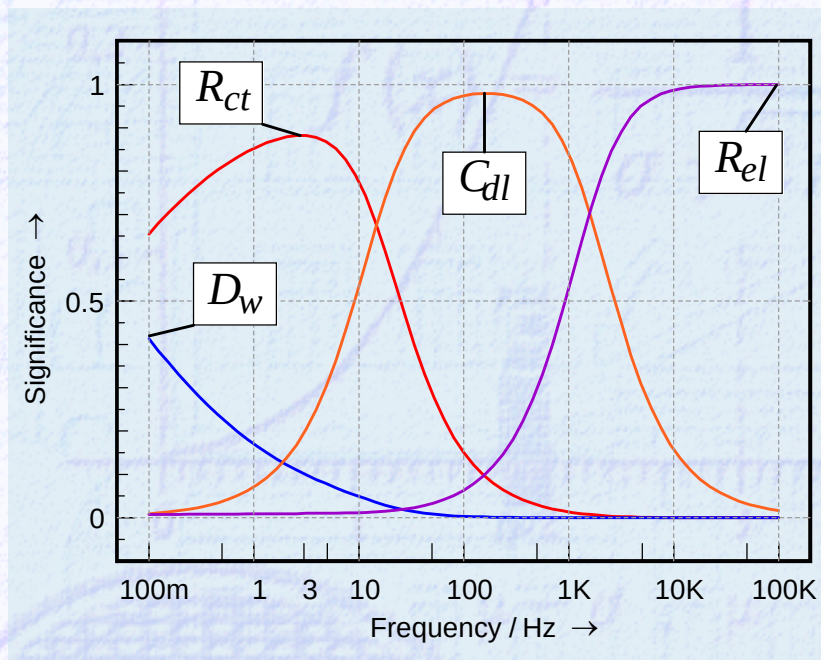
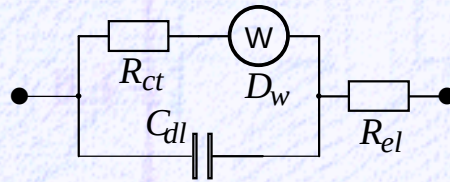
Flow of information in the Thales analysis procedure

The Way from Experimental Data to Output Parameters



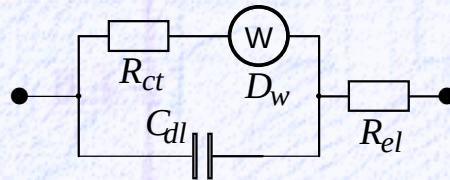
Considering the uncertainty caused by the analysis procedure: final deviation

$$S_i = \max \left(\frac{d|Z_n| \cdot P_i}{dP_i \cdot |Z_n|} \right)$$

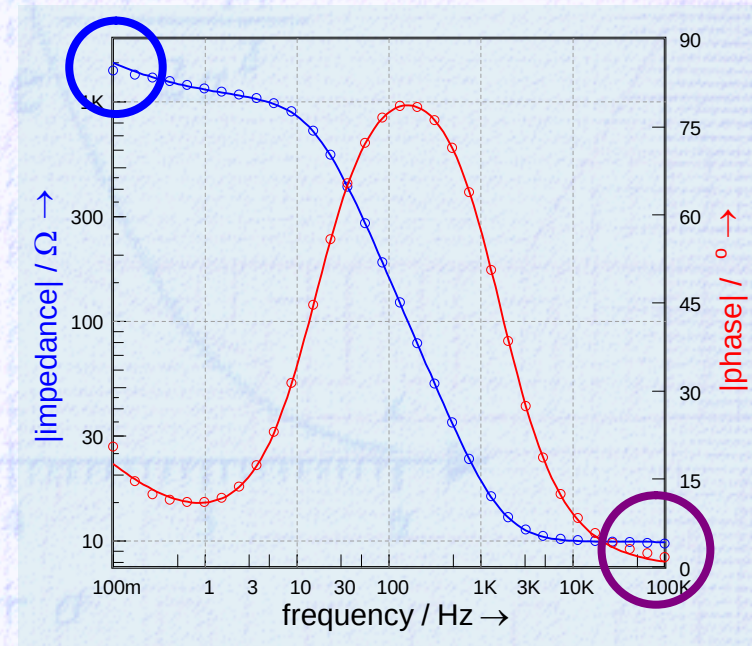
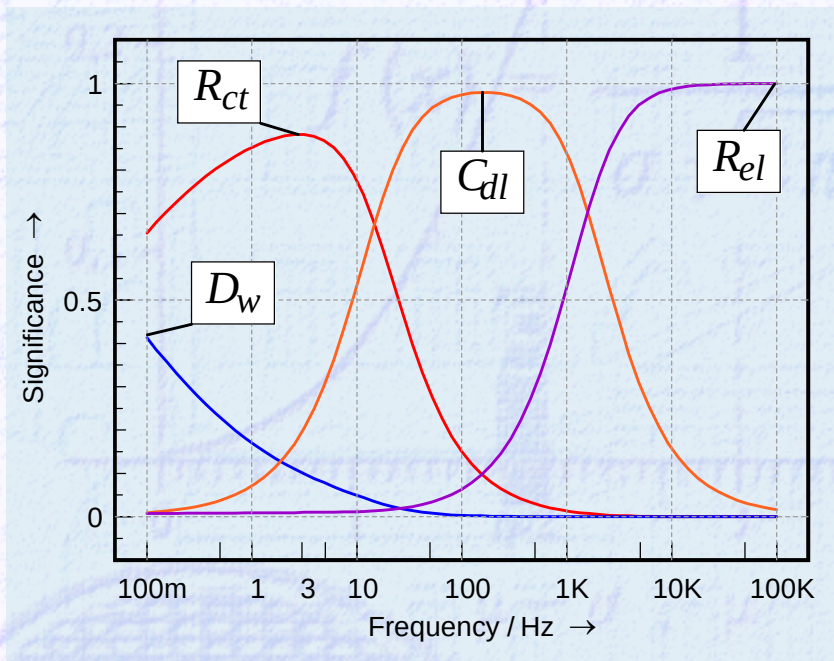
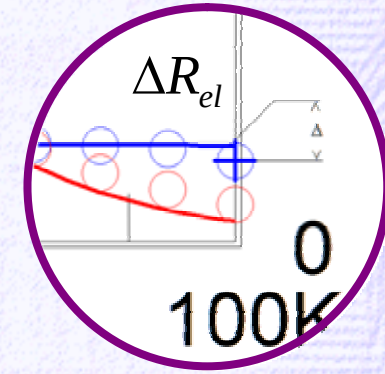
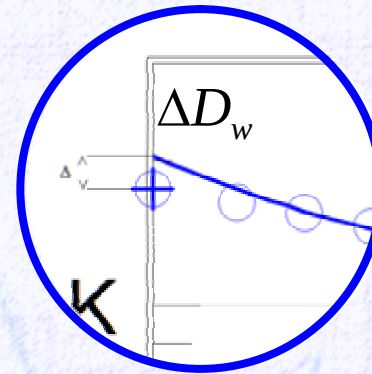


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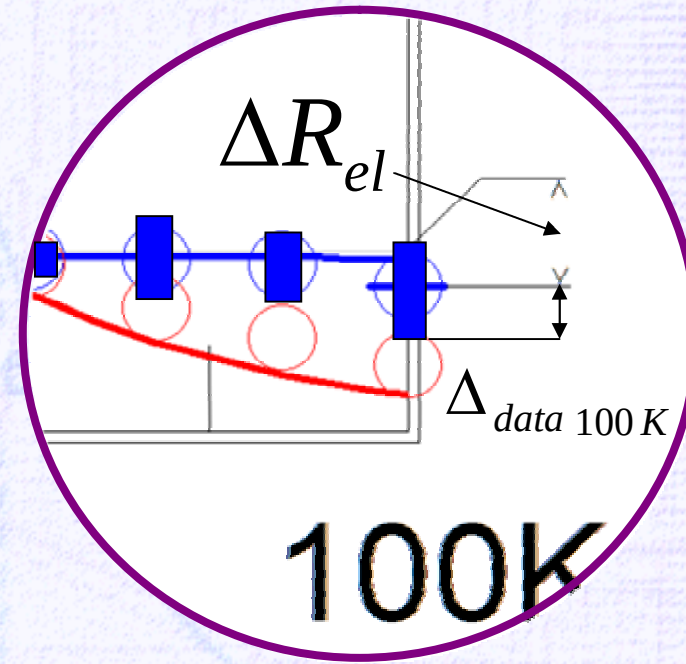
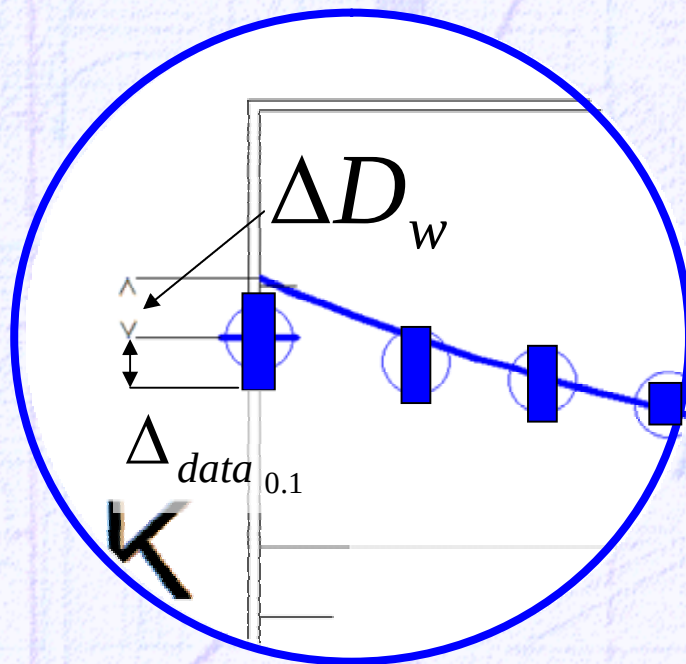


$$\Delta P_{i_{fit}} = \frac{\Delta_i}{S_i}$$

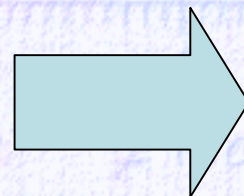


Considering the uncertainty caused by the analysis procedure: adding the measurement error

Introducing the measurement sample data error found by Weighted Harmonics Autocorrelation:



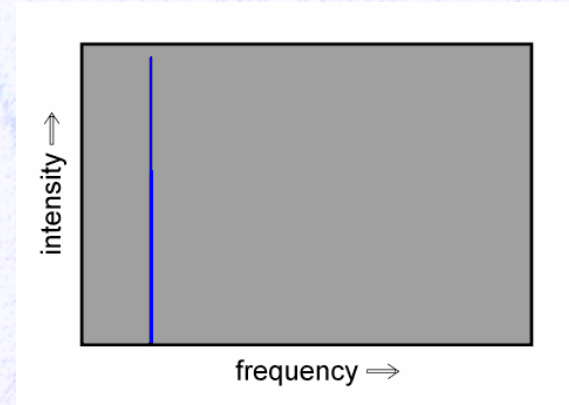
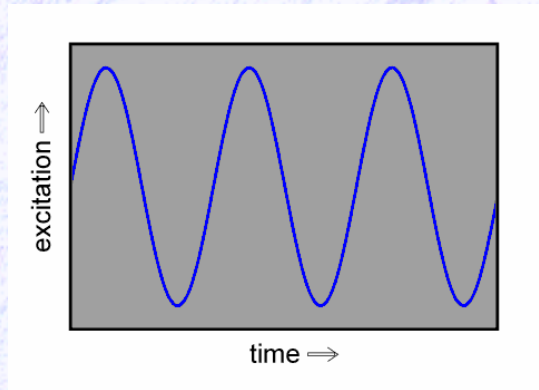
$$\Delta P_{i_{fit}} = \frac{\Delta_i}{S_i}$$



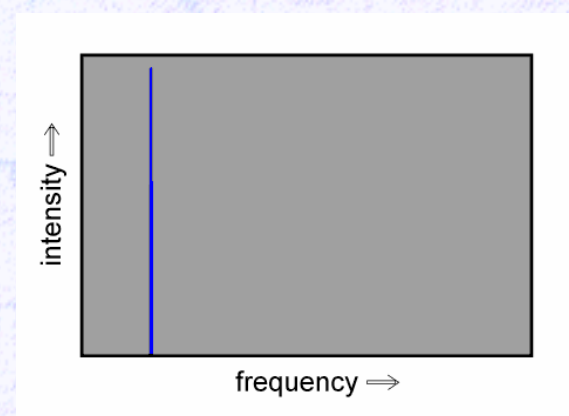
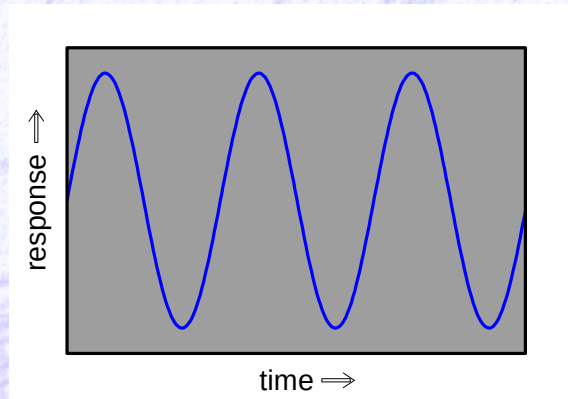
$$\Delta P_{i_{total}} = \frac{\Delta_i + \Delta_{data}}{S_i}$$

Monochromatic Oversampling

Excitation-signal: sinusoidal □ One sharp frequency line

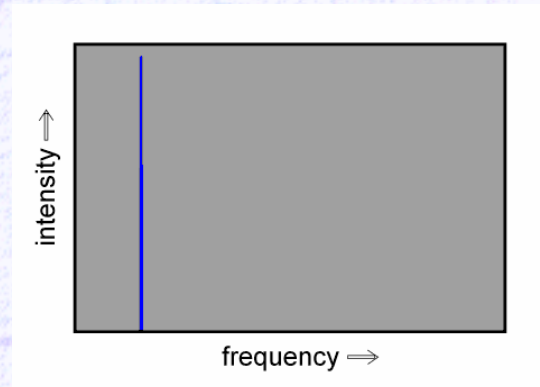
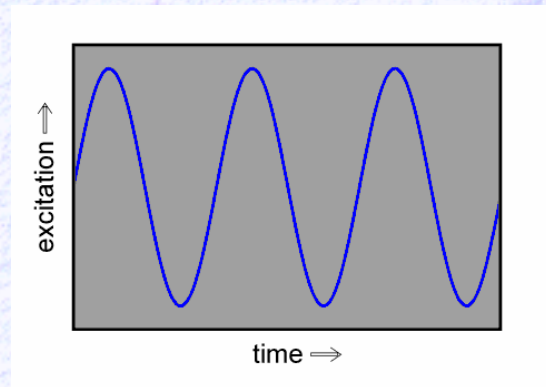


Response-signal under ideal conditions: as well exactly one line in the spectrum



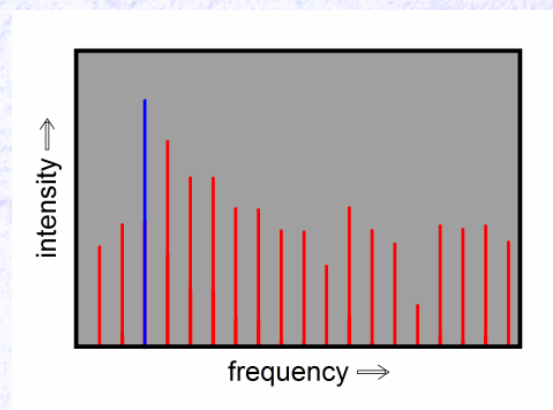
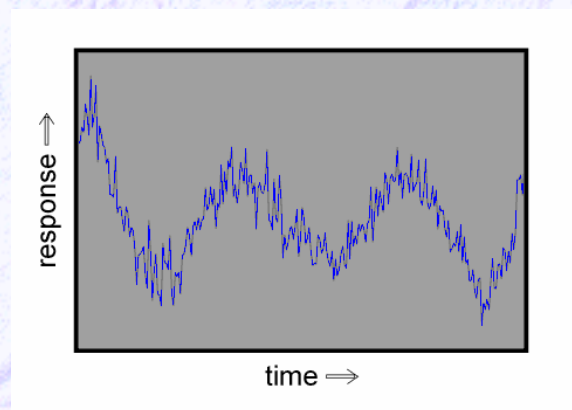
Monochromatic Oversampling

Under realistic conditions (in the presence of any disturbance) -



The inter-correlation of the additional lines carries the information on the uncertainty !

- the response signal contains „noise“!



Additional lines, appearing in the frequency spectrum can be unambiguously assigned to unwanted distortions !

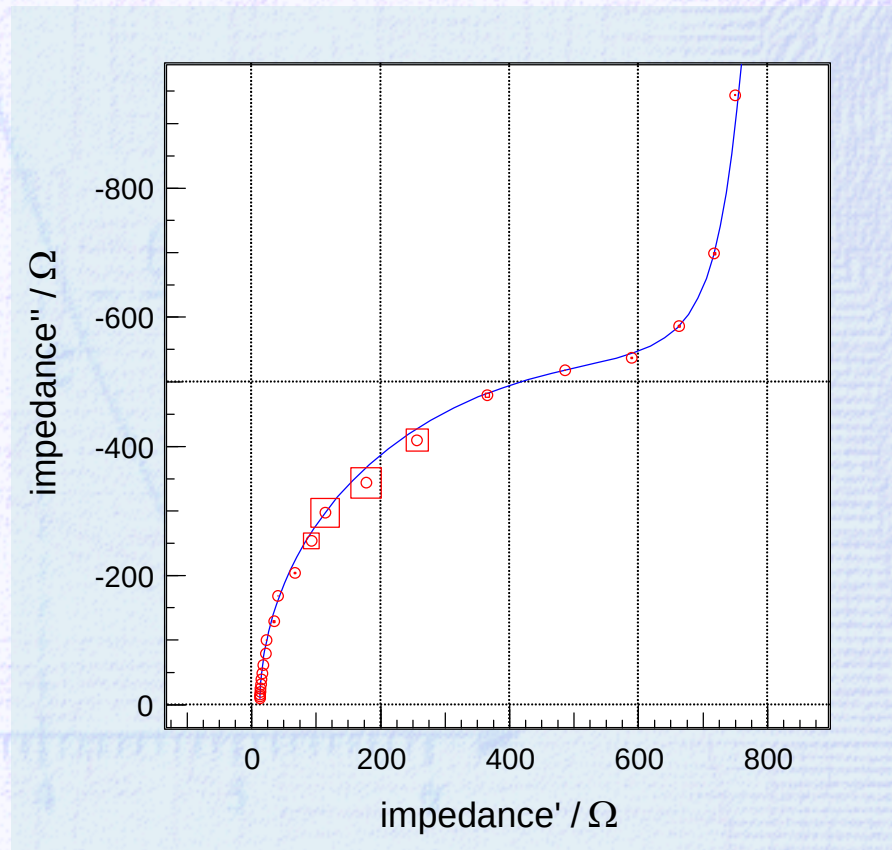
Control Experiments Under Sine Wave Interference

Interference signal: 100Hz sine wave

Complex plane diagram of the control circuit under single frequency disturbance.

Measurement from 1Hz to 1kHz.

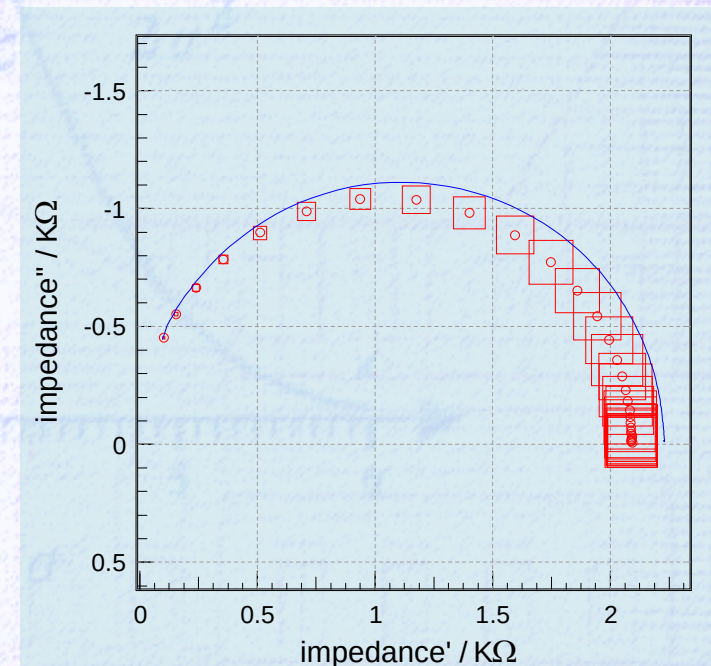
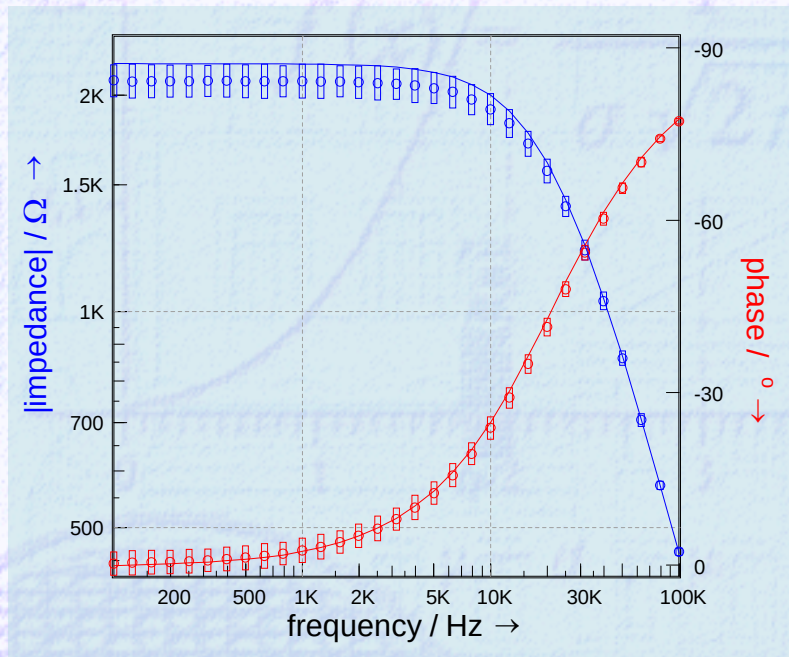
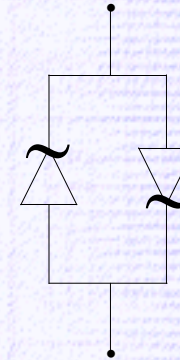
- Red circles: EIS values found under noise perturbation
- Solid line (blue): perfect undisturbed measurement
- Red squares: Error squares predicted by the Weighted Harmonic autocorrelation



Control Experiments with Non-Linear Objects

- Solid lines: perfect measurement at 1mV amplitude. The predicted uncertainty was close to zero (omitted in the diagram).
- Circles: values measured forcing non-linear conditions at 20mV amplitude.
- Error bars & squares: uncertainty predicted by the Weighted Harmonics Autocorrelation procedure at 20mV.

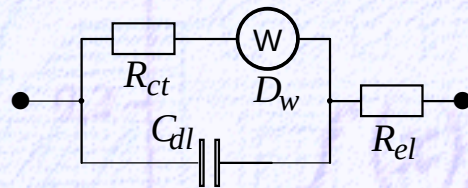
System under test:
2 anti-parallel
power-Schottky-
diodes with 10 μ A
bias-current.



Considering the uncertainty caused by the analysis procedure

Impedance model (equivalent circuit or from reaction mechanism analysis) $Z^*(\omega) = F(\omega, P_1, P_2, \dots, P_{n-1}, P_n)$

Z^* : complex impedance. F : transfer function. ω : frequency. P_i : parameters of interest



$$Z_{Randles}^*(\omega) = F(\omega, R_{ct}, D_W, C_{dl}, R_{el})$$

Significance S: measure for the ‘importance’ of a parameter within a model

$$S_i = \max \left(\frac{d|Z_n| \cdot P_i}{dP_i \cdot |Z_n|} \right)$$

relative impedance modulus variation $\frac{d|Z|}{|Z|}$

relative variation of a parameter $\frac{dP}{P}$

- Weighted Harmonics Autocorrelation method: realistic measurement error estimation for the common kinds of stochastic experimental distortions.
- „One shot“ method - needs only the data present in a single EIS-sample from Monochromatic Oversampling Method. Applicable on single-frequency characteristics like in Mott-Schottky analysis or Arrhenius plots.
- The error estimation found by Weighted Harmonics Autocorrelation: a base considering measurement error during fitting procedure.
- A Consistent Uncertainty Discussion of Physical Parameters Evaluated by EIS, starting from the measurement until the output parameters of the analysis procedure can be established:

Flat band potential = -0.301 ± 0.02 V

Effective gas diffusion length = 0.02 ± 0.001 m

Corrosion rate = 0.03 ± 0.01 mol • m⁻² • a⁻¹

Π

The background of the slide is a light blue grid with faint, semi-transparent mathematical content. A large, dark blue Gaussian distribution curve is centered on the grid. To the left of the curve, there is a vertical axis with tick marks and labels: 0.1, 0.3, 0.5, and 0.7. Above the curve, the formula $f(x) = \frac{1}{\sigma \sqrt{2\pi}}$ is visible. Below the curve, there are labels $\mu - \sigma$, μ , and $\mu + \sigma$ corresponding to points on the horizontal axis. The text "Thank you for your attention!" is centered over the curve in a large, black, sans-serif font.

Thank you for your attention!

The consequence for an accurate determination of “harmful” noise

1. Ignore isolated frequency components. Instead, weight frequency lines according to the presence of neighboring lines (autocorrelation), because neighboring lines may be caused by aliasing. Aliasing contributes directly to errors in the fundamental.
2. Weight harmonics with the inverse harmonic order, because the residual errors due to harmonics decrease with increasing frequency.



“Weighted Harmonics Autocorrelation”