



ECG-COMON



Electrochemical Noise Measurements with Dummy Cells: Evaluation of a Round-Robin Test Series

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ECG-COMON (European Cooperative Group on Corrosion
Monitoring of Nuclear Materials) www.ecg-comon.org

Introduction (1)

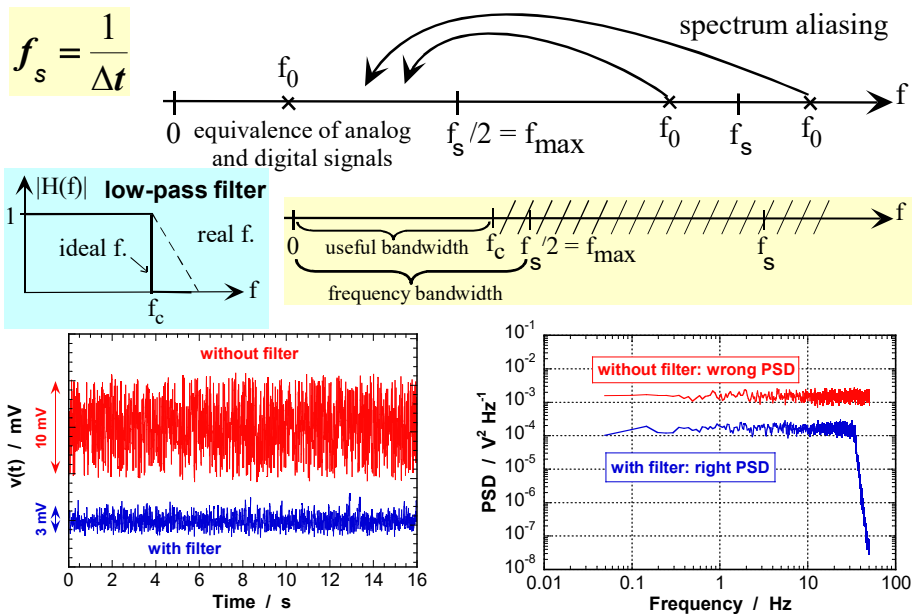
- **Electrochemical Noise (EN)**: widely used since Iverson's paper in 1968 to study corrosion processes
 - **EN**: promising technique to detect localized corrosion
 - In the eighties, EN (random signal) was **correctly measured with spectrum analyzers** (due to the presence of anti-aliasing filters)
 - Since the nineties, **personal computers with data acquisition cards** or digital voltmeters often lead to **improper EN measurements** due to aliasing occurring during the analog-to-digital conversion
 - Aliasing problem currently ignored in many commercial potentiostats
- ➔ **Round-Robin (RR) experiments** have been organized to improve the EN measurement procedure and evaluate the limitations of the technique

Introduction (2)

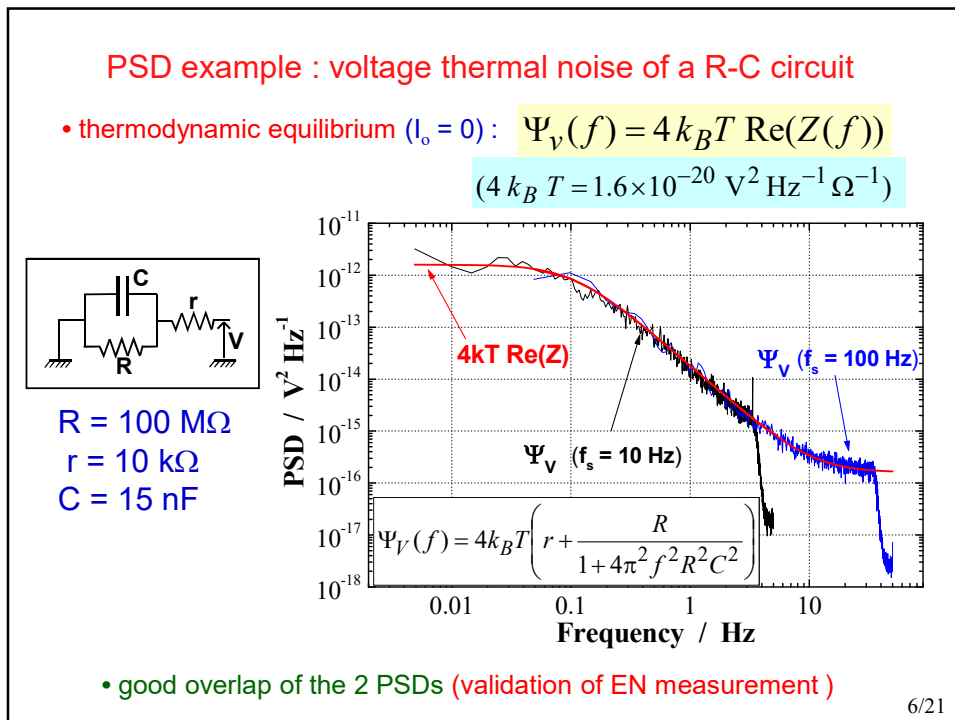
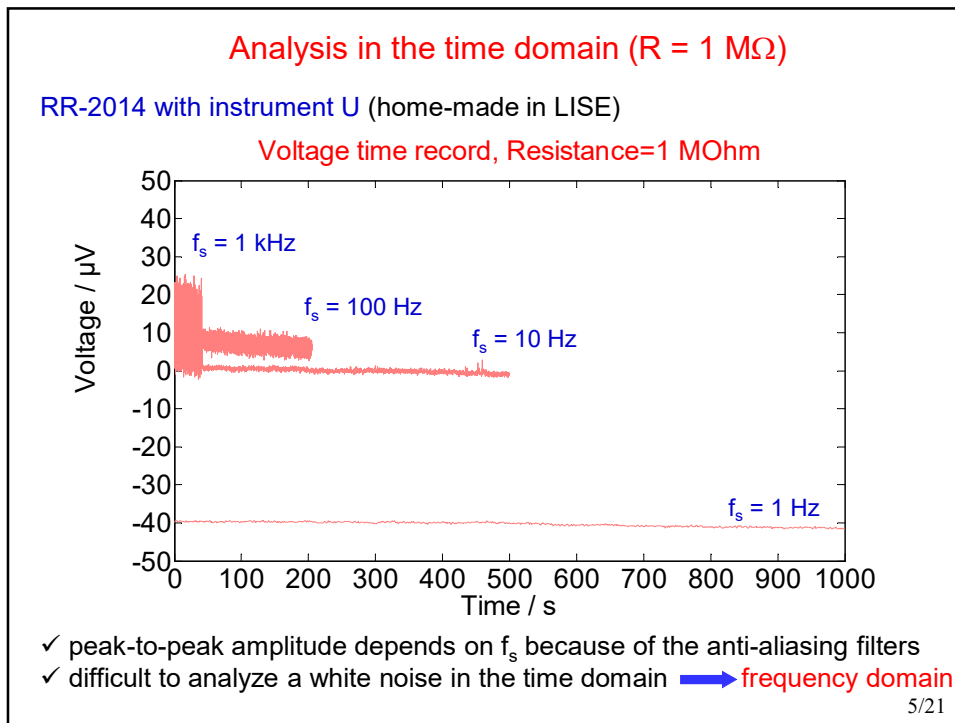
- First RR in Germany (1997) on aluminum (ΔV) and stainless steel (ΔI) in 3 different conditions: passive, pitting, and repassivating/passive
 - ➔ ✓ Almost all participants could detect **qualitative differences in EN** during the 3 stages
 - ✓ Differences in EN signal intensity **of two orders of magnitude** were obtained as a result of the different apparatus used.
- RR tests organized by ECG-COMON between 2006 and 2008: (ZRA mode, 3-electrode cell configuration, ΔV and ΔI)
 - ✓ Once with Al coupons in three different electrolytes (as in first RR)
 - ✓ Other tests used dummy cells composed of three identical pure resistors to obtain a well-defined noise level **in contrast to corroding electrodes**
- ➔ • **New RR tests organized in 2014-2016-2017** to check the EN measurement equipments with dummy cells
 - RR **opened to (non-) ECG members** and **most manufacturers**
 - Results of all these trials are **summarized in this paper**
 - It shows **strong imitations of most equipments**

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Analog to Digital Conversion: signal aliasing

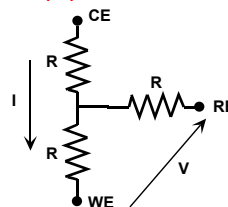


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Description of the Round-Robin test (1) ^{YKM5}

- 3 identical resistors in star arrangement (ZRA mode)
- $R = 1\text{ M}\Omega$ and $R = 100\text{ M}\Omega$
- thermal noise : low (as for passive electrodes)
but known ($\Psi_V = 6kTR$, $\Psi_I = 2kT/R$)



- dummy cells (1 and 100 M Ω) prepared in my laboratory
- procedure (see Appendix A in the paper) also sent:



- ✓ measurements have to be performed at different sampling frequencies (2 to 4 for all participants)
- ✓ reporting (ASCII files, 3 columns: time in s, voltage in V, current in A)

- analysis performed at LISE in the frequency domain (using FFT):
(only way to validate EN measurements)

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Description of the Round-Robin test (2)

- commercial, mostly general-purpose, potentiostats from 10 manufacturers
 - ACM Instruments (Gill AC)
 - Bio-Logic (SP-150, SP-200, SP-300, VMP3, software EC-Lab)
 - CH Instruments (CHI660E, CHI760E)
 - Gamry (PCI4/300, Ref600, Interface1000, soft. EN120, ESA400, ESA410)
 - Ivium Technologies (CompactStat, Vertex)
 - JPS Elektroniklabor GmbH & Co. KG (HRU/ZRA-FG-B, PGU-10V-1A)
 - Metrohm (Autolab PGSTAT)
 - Orignalys (OGS-100)
 - Princeton Applied Research (PARSTAT, software VersaSTAT)
 - Solartron (1287, Modulab, software Corrware, ECS)
- 1 custom-built EN system (U in my laboratory)
- 33 organizations, including 8 manufacturers who sent their own 17 data sets
- volume of data examined in the 3 RR tests

	total number of participants (manufacturers)	number of data sets received	number of data records received	number of PSDs calculated
RR - 2014	19 (7)	22	138	276
RR - 2016	19 (6)	27	201	402
RR - 2017	19 (3)	24	154	308

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YKM5 Consistency of title font format
Yap, Kwei Meng; 22/03/2018

Algorithm for PSD calculation with FFT

in this work: each time record divided in N sections of M = 512 data points

$N = \text{int}(\text{number of data in the file} / 512)$: from 8 to 350

loop N times

```
{
  acquisition of M data points of x(t)
  linear detrending
  remove the mean value of x (not informative since
                                corresponds to frequency 0)

  multiply by the Hann window
  FFT
  PSD calculation:
}
```

$$\Psi_x(m\Delta f) = \frac{2}{T} |X_T(m\Delta f)|^2 = \frac{2}{M} \Delta t \left| \sum_{n=0}^{M-1} x(n\Delta t) e^{-2i\pi m n / M} \right|^2$$

average the N PSDs

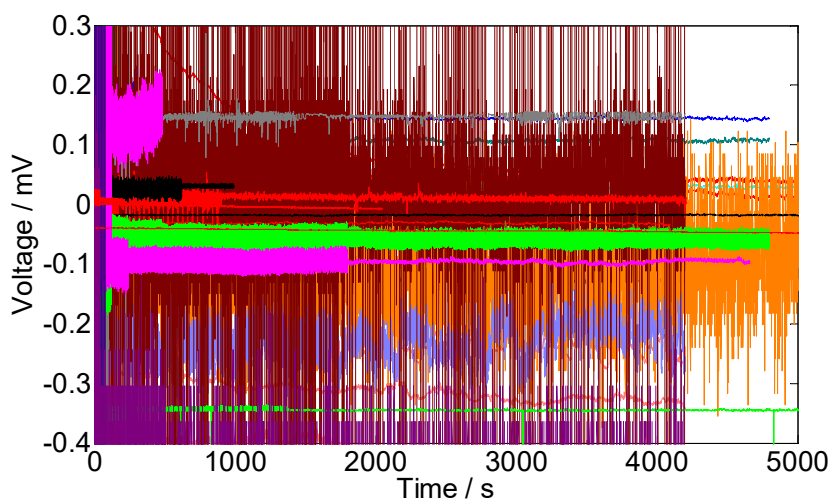
multiply the result by 8/3.

Periodogram (Welch) method: *pwelch* and *detrend* routines of Matlab

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Analysis in the time domain ($R = 1 \text{ M}\Omega$)

All potential time records (102) sampled in RR-2016

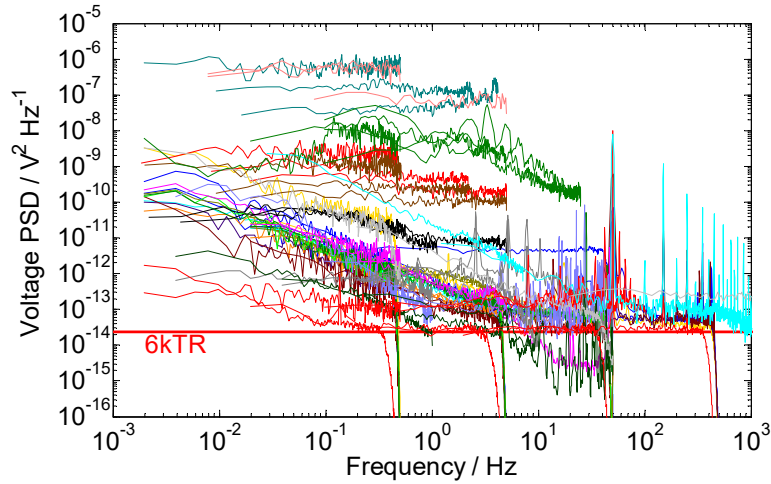


quite impossible to see all time records in the same plot

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Analysis of the voltage PSDs ($R = 1 \text{ M}\Omega$)

All results (77) in RR-2017

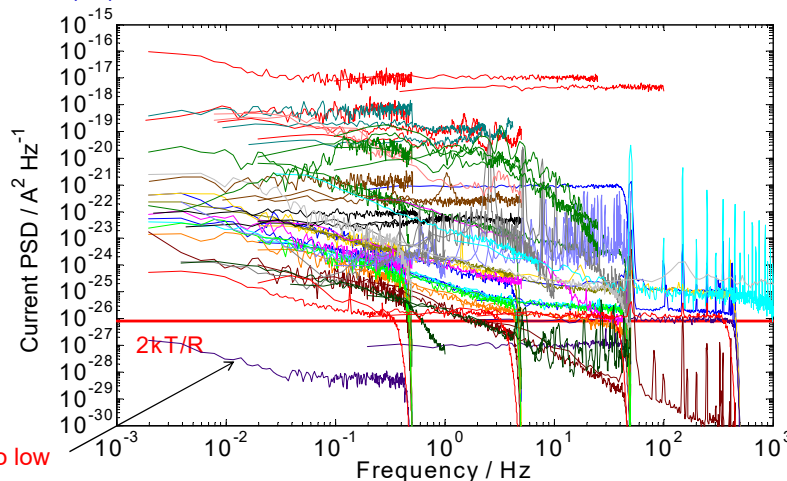


- ✓ Very large scatter : 8 decades in $\text{V}^2 \text{ Hz}^{-1}$, so 4 decades in Volt!!
- ✓ Evidence of aliasing for many equipments: no PSD decrease at frequency close to $f_s/2$ and bad overlap of the PSDs measured at different sampling frequencies f_s

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Analysis of the current PSDs ($R = 1 \text{ M}\Omega$)

All results (77) in RR-2017

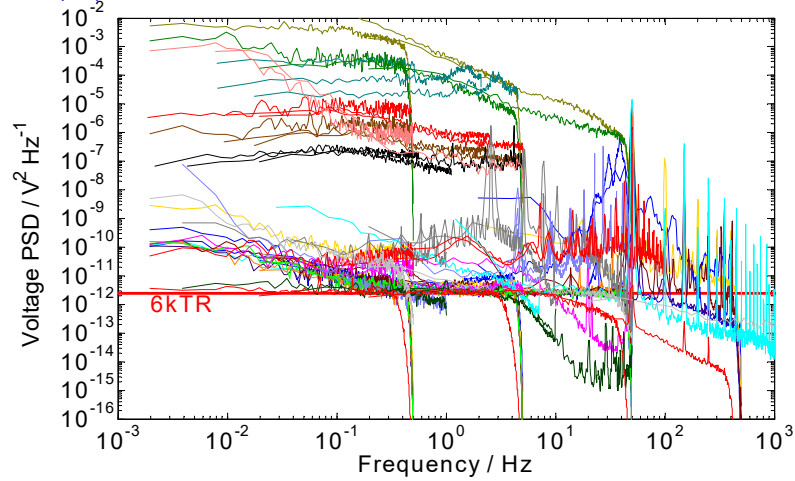


- ✓ Very large scatter : 10 decades in $\text{A}^2 \text{ Hz}^{-1}$, so 5 decades in Amp!!
- ✓ Evidence of aliasing for many equipments: no PSD decrease at frequency close to $f_s/2$ and bad overlap of the PSDs measured at different sampling frequencies f_s

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Analysis of the voltage PSDs ($R = 100 \text{ M}\Omega$)

All results (72) in RR-2017

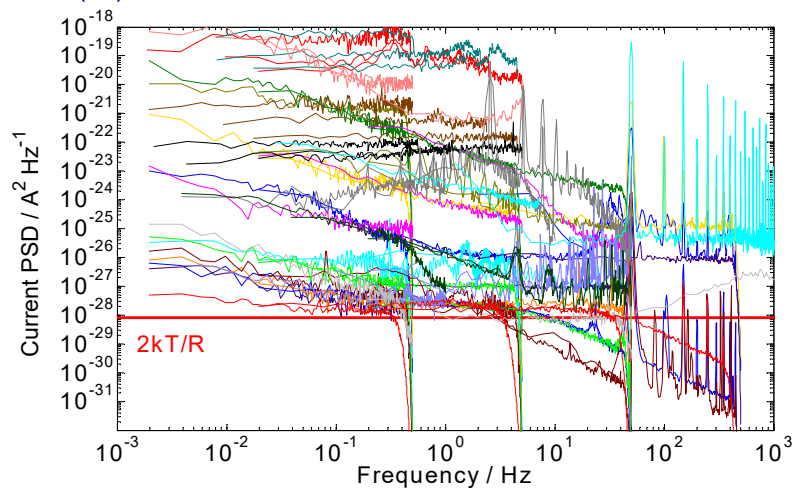


- ✓ Very large scatter : 10 decades in $\text{V}^2 \text{Hz}^{-1}$, so 5 decades in Volt!!
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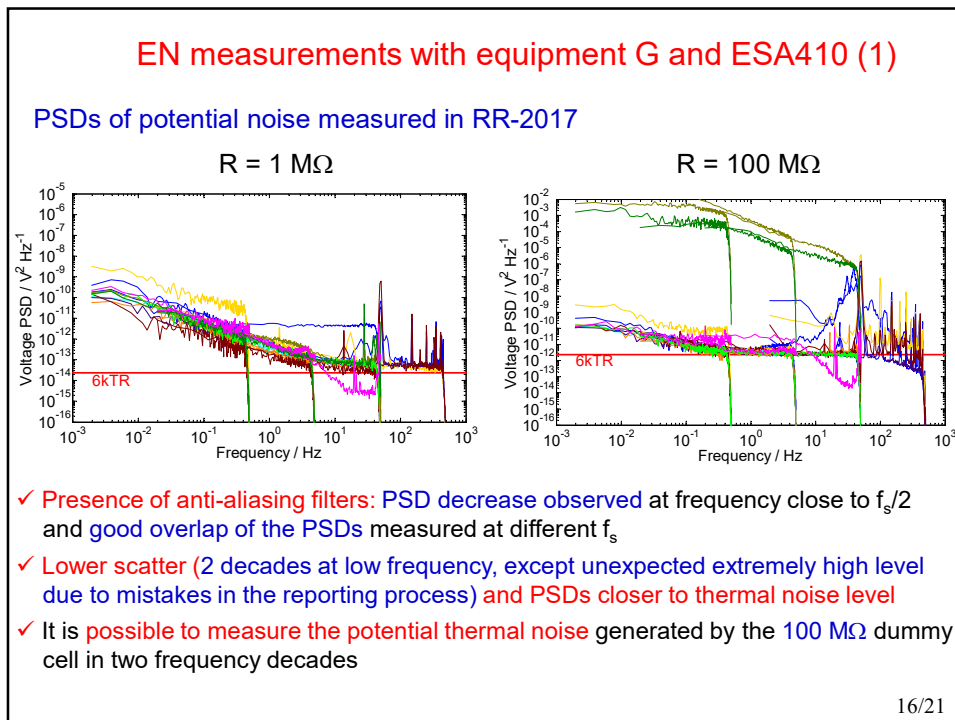
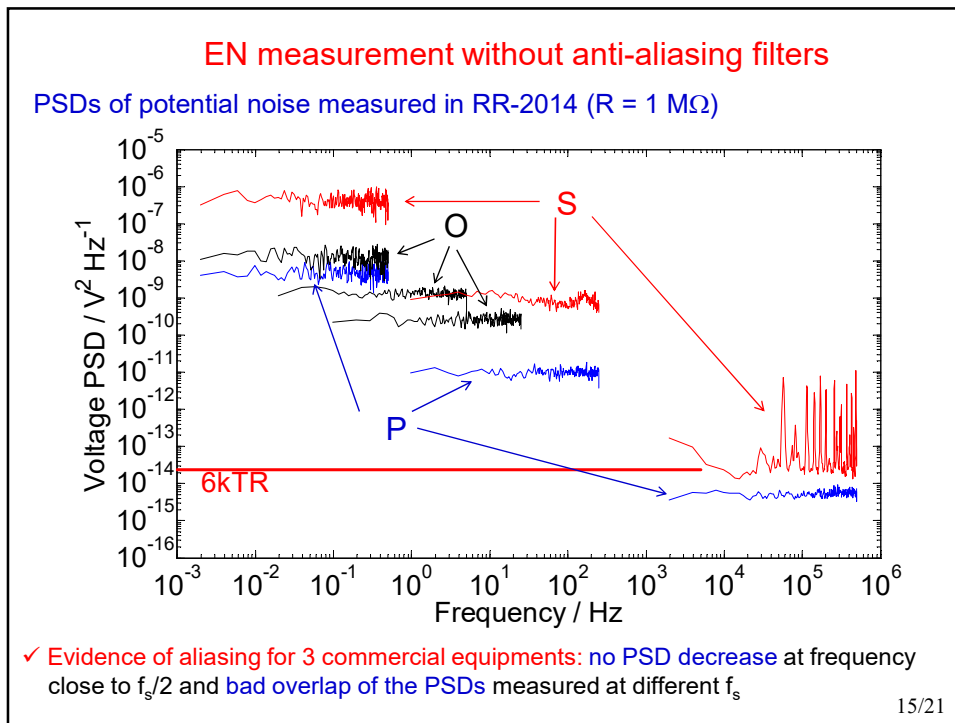
Analysis of the current PSDs ($R = 100 \text{ M}\Omega$)

All results (72) in RR-2017



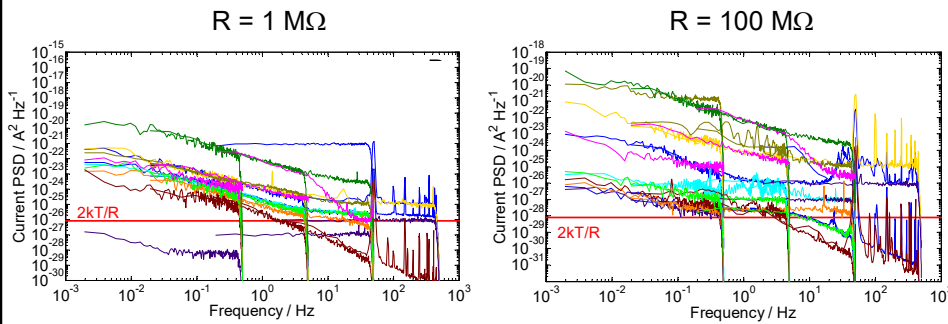
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EN measurements with equipment G and ESA410 (2)

PSDs of current noise measured in RR-2017



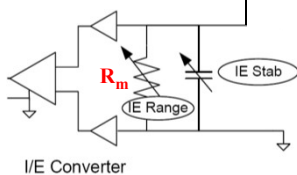
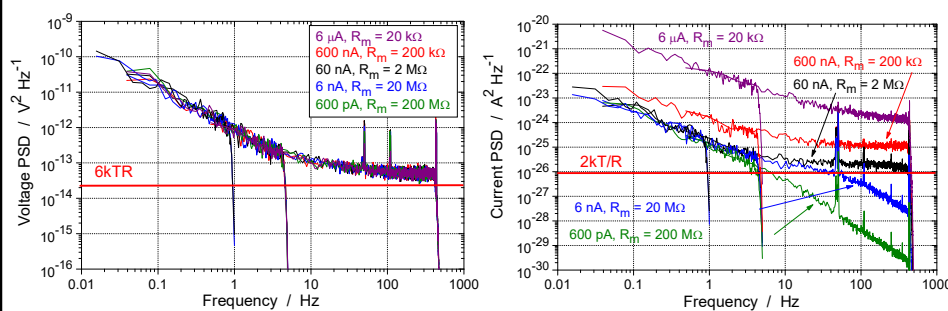
- ✓ Presence of anti-aliasing filters: PSD decrease observed at frequency close to $f_s/2$ and good overlap of the PSDs measured at different f_s
- ✓ Some current PSDs very close thermal noise level ($2kT/R$) for both dummy cells
- ✓ Larger scatter in the PSD amplitude than for the potential fluctuations

➔ Why a larger scatter in the current measurements?

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EN measurements with equipment G and ESA410 (3)

EN measurements at LISE on a 1 MΩ dummy cell



$$\Psi_{I_{meas}} = \frac{\Psi_{e_{ni}}}{R_m^2} + \frac{1}{1 + 4\pi^2 R_m^2 C^2 f^2} \left[4kT \frac{1}{R_m} + \frac{\Psi_{e_n}}{4R^2} + 2kT \frac{1}{R} \right]$$

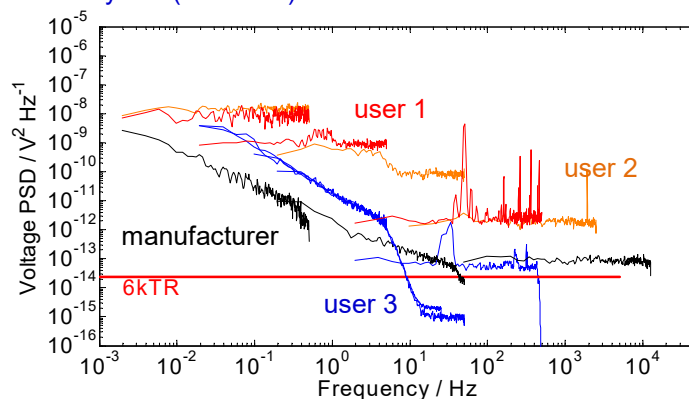
➔ a tutorial for EN measurements is needed

See C2018-11042: "Electrochemical Noise - Guidance for Improving Measurements and Data Analysis" (with equipment G), F. Huet, K. Ngo

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EN measurements with equipment B

EN measurements performed by the manufacturer and different users on a 1 M Ω dummy cell (RR-2016)



- ✓ Data from manufacturer give rather good overlap of the PSDs, indicating the presence of anti-aliasing filters in equipment B
 - ✓ Users of equipment B provided data showing no PSD overlap (orange and red) or PSDs unexpectedly low-pass filtered at about 5 Hz (blue)
- ➔ Manufacturers should provide guidelines to support users in adjusting correct settings of the filters and gains of the amplifiers

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Conclusions

- Validation of EN measurements can only be performed in the frequency domain by checking the overlap of PSDs measured at different sampling rates
- ECG website (free access): [psd_ECG-COMON.exe](#) for PSD calculation
- Good PSD measurements (= good PSD overlaps) for very few commercial potentiostats (Gamry with ESA-410, Bio-logic?, IPS?)
- Even with good equipments, data provided by common users are often wrong: they do not set the right parameters in the setup for ENM

➔ What can be done?

- The manufacturers should provide:
 - Improved software (no access to filters, no conflicting choice of f_s and I/E range limiting the frequency bandwidth...)
 - A tutorial for ENM with dummy cells for training users
- Read 2 papers:
 - Guideline for an assessment of EN measurement devices, S. Ritter, F. Huet, R. Cottis, *Materials and Corrosion*, 63 (2012) 297
 - Electrochemical Noise - Guidance for Improving Measurements and Data Analysis, (with equipment G), F. Huet, K. Ngo, C2018-11042

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