Guideline for an assessment of electrochemical noise measurement devices

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Abstract

Pro-active ageing management is becoming more and more important for the economical and safe operation of industrial plants. A key element for a pro-active ageing management approach is to apply in-situ corrosion monitoring. The electrochemical noise (EN) technique is an example of a promising method, especially for monitoring localised corrosion phenomena. Currently, research work on the EN technique is carried out in several labs worldwide for different kind of industrial applications but also for the investigation of corrosion mechanisms. A prerequisite for performing serious research on the EN measurement technique is a careful evaluation of the measuring system, even if commercially available EN measurement instruments are used. Therefore, testing on well-defined dummy cells should always be a preliminary step to assess the baseline noise of the EN measurement equipment and to ensure data validity. For this purpose a guideline has been developed by the European Cooperative Group on Corrosion Monitoring of Nuclear Materials (ECG-COMON, [1]) as an outcome from round-robin testing on EN. The current guideline describes a simple procedure for the performance and evaluation of EN measurement equipment using dummy cells.

Keywords: electrochemical noise; guideline; corrosion monitoring; dummy cell; measurement equipment

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1 Electrochemical noise measurements with a dummy cell

This procedure assumes the conventional three electrode EN measurement setup, in which the current noise between two identical working electrodes (WEs) is measured with a zero resistance ammeter (ZRA). The potential noise of this working electrode pair is then measured with respect to a third reference electrode (RE). For this guideline a series of dummy cells consisting of a “star”-arrangement of resistors is used, rather than an electrochemical cell. This provides a well-defined source impedance and noise level, thereby allowing the testing of the noise level and sensitivity of the measuring instruments. Note that, although the resistors used in the dummy cells will generate thermal noise, it is not expected that it will always be possible to measure this noise, and the primary objective of the experiment is to determine the instrument noise levels. The use of a range of resistor values in the dummy cells permits the assessment of the current and potential noise capabilities of the input amplifiers, which are expected to vary according to the source impedance.

1.1 Setup of the dummy cells

Each dummy cell is constructed of three resistors of equal value, connected in a “star”-arrangement (see Fig. 1). Three dummy cells will be used, with resistance values of 100 Ω , 10 k Ω , and 1 M Ω . If EN measurements are to be made on a very high resistance system, such as a highly passive alloy or intact paint coatings, a fourth dummy cell using 100 M Ω resistors can also be used.

Care should be taken in the construction of the dummy cells in order to avoid poor electrical contact, to minimise undue heating of the resistors (though normal soldering is acceptable) and to avoid the application of undue mechanical strain to the resistor terminals. The simplest

method of assembly involves soldering one end of each resistor together, then using clips to connect the other ends to the measuring instrument. Alternatively, if you plan on re-using the dummy cells, a rather more robust unit may be produced using matrix board (see Fig. 2). See [2] for a description of how to read the resistor values. If possible, it is always best to place the resistors in a metallic box and to connect this box to the ground (usually floating ground).

1.2 Measurements

Each dummy cell should be connected to the measuring system in exactly the same way as for a standard measurement. If a Faraday cage is used for normal measurements the dummy cell should be placed in the Faraday cage. Be careful to avoid contacting any part of the dummy cell with conducting surfaces. Switch the instrument on and allow the system temperature to stabilise for the greater of 15 minutes or the time you normally allow.

Measurements should be made at:

- a) the highest sampling rate that the instrument is capable of,
- b) one sample per second (or as close to that as possible), and
- c) another sampling rate between the two previous ones.

At least two different sampling rates (for example 1 and 10 Hz) must be used since it is impossible to validate EN measurements performed at a single sampling rate. Ideally each measurement should record at least 16384 (16K) samples to permit some spectrum averaging, but for slower sampling rates (such as 1 Hz) fewer samples are permitted, with a minimum of 2048.

All measurements should be made at the maximum sensitivity of the instrument (except in the unlikely event that this leads to overloading) and with other signal conditioning (anti-aliasing filters, etc.) as recommended by the manufacturer or at the values you consider most appropriate or would normally use. Avoid using the automatic setting of the measurement parameters (sensitivity, gain, offset correction, etc.), such as “autorange”, or use it once to know the range selected by the instrument, then deselect “autorange” and use this range for the EN measurements.

1.3 Reporting

The EN data obtained can be saved in any data format, e.g., ASCII. Another interesting possibility is to convert the data into XML files. In that way the EN data can be “standardised” including the most important information of the measurement and equipment. These files can then easily be exchanged with other laboratories or processed and evaluated automatically by EN analysis software (e.g., Matlab programmes). An introduction to XML is given in [3] and a template file can be found at [4]. A completed example file is available at [5]. The ASCII or XML files, but of course also other EN data formats, can then be used to calculate the power spectral densities (PSDs) of the EN data (see below).

2 Validation and analysis of the electrochemical noise data

Validation of the EN data cannot be performed in the time domain. This must be done in the frequency domain by calculating the PSD of the potential and current fluctuations for time records sampled at different sampling rates f_s , first to check whether an anti-aliasing filter was included in the data acquisition system before the analogue-to-digital converter, second to

check the good overlap of the different PSDs, and third to compare the experimental PSD to the theoretical PSD of the thermal noise, respectively $6 kTR$ for the potential thermal noise and $2 kT/R$ for the current thermal noise generated by the dummy cell with three resistors of resistance R in a “star”-arrangement (see Table 1 for the thermal noise PSD values). Indeed, according to Eqs. (15) and (16) in [6], if R_1 and R_2 denote the resistors connected through the ZRA and R_3 the resistor connected to the potential amplifier, the PSDs of the potential and current fluctuations are given, respectively, by:

$$\Psi_V(f) = \left| \frac{R_1 R_2}{R_1 + R_2} \right|^2 \left[\Psi_{i_1}(f) + \Psi_{i_2}(f) \right] + R_3^2 \Psi_{i_3}(f) \quad (1)$$

$$\Psi_I(f) = \left| \frac{R_1}{R_1 + R_2} \right|^2 \Psi_{i_1}(f) + \left| \frac{R_2}{R_1 + R_2} \right|^2 \Psi_{i_2}(f) \quad (2)$$

the term i_j ($j = 1$ to 3) being the current thermal noise generated by the resistor R_j . The PSDs of these uncorrelated noise sources i_j being equal to $4kT/R_j$, the values of $6 kT R$ and $2 kT/R$ are obtained for Ψ_V and Ψ_I , respectively, when all resistances are equal to R .

2.1 Calculation of the PSDs

The PSDs can be calculated according to the formulae presented in the Appendix. It is recommended to calculate the PSDs over a section of at least $M = 2048$ data points (although it is also possible to work with less data points). Less “noisy” PSDs can be gathered by calculating several sets of PSDs and averaging them (e.g., averaging over eight sequential or overlapping sections of 2048 data points each). The calculation and averaging of the PSDs can be performed by a small programme which can be downloaded from the web [7]. Instructions for using this programme are given in Section 6 of the Appendix.

2.2 Validation of the measured PSDs

The presence of anti-aliasing filters is revealed by a fall in the PSD at high frequency, close to the maximum frequency $f_{max} = f_s/2$ (also known as the Nyquist frequency). If the PSD is flat up to f_{max} , there is no anti-aliasing filter in the data acquisition system and the measured PSD is overestimated, since it contains the power of the signal at frequencies higher than f_{max} . Fig. 3 shows PSDs acquired without anti-aliasing filter (curves d, e, f), and PSDs acquired with an anti-aliasing filter (curves a, b, c) that show a decrease towards the highest frequencies, typical for PSDs of EN data generated by a device with anti-aliasing filter. Note for example the large difference in amplitude between curves c and f sampled at 10 Hz and the wide peak at 50 mHz in curve f, which comes from the aliasing of the 50 Hz noise of the power supply (see the peak at 50 Hz in curve a and d). Also note that curves a, b, and c, measured with a filter, overlap very well, while curves d, e, f measured without filter do not overlap.

Further disturbances at certain frequencies, coming from the measurement device or from external sources, can also be identified in the power spectra by the appearance of peaks at the corresponding frequencies.

2.3 Assessment of the baseline noise

The assessment of the baseline noise of the equipment can only be performed in the frequency domain by comparing the measured potential and current PSDs to the thermal noise PSDs of the resistors (see Table 1). The baseline noise of the equipment depends on the resistors used, so it should be measured for different resistors (e.g., 100 Ω , 10 k Ω , and 1 M Ω or 100 M Ω [†]).

[†] To simulate high resistive coatings; in that case if the current noise of the equipment is too high, this gives an important contribution on the measured EN.

See Fig. 4 for examples. Please note that it is not expected that it will always be possible to measure the thermal noise of the resistors. The objective of the experiment is to determine the instrument noise levels.

2.4 Verification of the time domain noise data

Once the PSD of the baseline noise has been determined, the time domain data of the EN measurements should also be plotted and checked. Problems such as quantisation can be identified that way (see Fig. 5). Finally the standard deviation or peak-to-peak amplitude of the potential and current fluctuations in the time domain can be determined with the absolute necessity of giving the frequency bandwidth $[\Delta f, f_c]$ analysed ($\Delta f = f_s/M$ is the minimum frequency analysed and f_c is the cut-off frequency of the anti-aliasing filter). Without the value of the frequency bandwidth, the peak-to-peak amplitude has no meaning.

3 Summarised procedure

- 1) Connect the dummy cell.
- 2) Warm up the system ($t > 15$ min).
- 3) Electrochemical noise measurements (preferably with all three dummy cells):
 - a) EN measurement with the highest possible sampling rate; duration of the measurement depends on the sampling rate: at least 16384 samples (e.g., at 100 Hz sampling rate $\rightarrow$ 170 s measurement time is sufficient);
 - b) EN measurement for (at least) 1 h 10 min with a sampling rate of 1 Hz (or as close as possible) to acquire 4096 samples;

- c) EN measurement with a sampling rate between the other two; duration of the measurement depends on the sampling rate: at least 16384 samples (e.g., at 10 Hz sampling rate $\rightarrow$ 28 min measurement time is sufficient).
- 4) Convert the data into any data format or into XML files according to the descriptions above (and in [3]) which can be used for calculation of the PSDs.
- 5) Calculate the PSDs of the EN data sets according to the descriptions above (and see Appendix), e.g., by using the PSD calculation programme (see Section 6 of the Appendix).
- 6) Analyse the PSDs to see whether a proper anti-aliasing filter is used, to control the overlap of the PSDs, and compare them to the thermal noise PSDs of the resistors. The time domain data of the EN measurements should be plotted and checked and finally the peak-to-peak amplitude of the potential and current fluctuations in the time domain and the frequency bandwidth $[\Delta f, f_c]$ analysed should be reported.

4 Acknowledgements

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5 References

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Appendix. Calculation of the PSDs

The calculation should always be performed with the fast Fourier transformation (FFT) method (periodogram algorithm) and not with the maximum entropy method (MEM) to validate the EN data.

1 Terminology for PSD calculation

- sampling frequency f_s
- sampling time interval $\Delta t = 1/f_s$
- number of points in the time record: M (for example $M = 1024, 2048, 4096, \dots$ data points)
- acquisition time $T = M/f_s = M \Delta t$.
- random signal $x(t)$ or, once sampled, $x(n\Delta t)$ with $n = 0$ to $M-1$

2 Definition of the analogue Fourier transformation and PSD

The most used definition is:

$$X(f) = \int_{-\infty}^{+\infty} x(t) e^{-2i\pi f t} dt \quad (3)$$

but you may find other definitions that are also correct; the idea is to choose one definition and to keep it forever in the calculations. Since the signal is known only between time 0 and time T , the Fourier transform depends in fact on T :

$$X_T(f) = \int_0^T x(t) e^{-2i\pi f t} dt \quad (4)$$

The corresponding PSD is:

$$\Psi_x(f) = \frac{2}{T} |X_T(f)|^2 \quad (5)$$

In fact, the PSD is the expected value of $\frac{2}{T} |X_T(f)|^2$ (and therefore, it is necessary to average to obtain sufficient accuracy). More precisely, it is given by the limit of this quantity when T tends to infinity when the signal can be supposed to be stationary, a necessary condition to define its PSD (and therefore, the PSD is defined for any real frequency). The factor two is for taking into account the negative frequencies, so here f is positive; this is called the “one-sided spectrum”.

3 Definition of the discrete Fourier transformation and PSD

The signal is now digitised, so t becomes $n\Delta t$ and f becomes $m\Delta f$ with $0 \leq m \leq M/2$. The maximum frequency is $f_{max} = f_s/2$ (Nyquist theorem); as a consequence, $\Delta f = f_s/M$ and, therefore, $\Delta t \Delta f = 1/M$.

The integral $X_T(f)$ becomes:

$$X_T(m\Delta f) = \sum_{n=0}^{M-1} x(n\Delta t) e^{-2i\pi m\Delta f n\Delta t} \Delta t = \Delta t \sum_{n=0}^{M-1} x(n\Delta t) e^{-2i\pi mn/M} \quad (6)$$

and the corresponding PSD:

$$\Psi_x(m\Delta f) = \frac{2}{T} |X_T(m\Delta f)|^2 = \frac{2}{M} \Delta t \left| \sum_{n=0}^{M-1} x(n\Delta t) e^{-2i\pi mn/M} \right|^2 \quad (7)$$

The last step is the calculation of the sum in Eq. 7: various FFT algorithms exist (the sum is sometimes multiplied by $1/M$ or $1/\sqrt{M}$). The best is to take an algorithm without scaling

factor. If you want to check your FFT algorithm, it is easy: you take $M = 8$ points and the signal $x(n\Delta t)$ defined by the 8 values: 1,0,0,0,0,0,0,0. The result of the FFT sum in Eq. 7 is equal to 1 for the first frequency $m = 0$.

4 Algorithm for PSD calculation

In practice, to improve the PSD accuracy, the PSD is averaged from the PSDs calculated with N time records of $x(t)$:

$$\Psi_x(m\Delta f) = \frac{2}{T} \frac{1}{N} \sum_{i=1}^N \left| X_{T,i}(m\Delta f) \right|^2 \quad (8)$$

The PSD is defined for $M/2$ frequencies linearly distributed between $\Delta f = f_s/M$ and

$f_{max} = \frac{M}{2} \Delta f = f_s/2$. But, because of the presence of the analogue low-pass anti-aliasing filter

before the analog-to-digital converter, the actual frequency bandwidth is $[\Delta f, f_c]$ if the cut-off frequency of the filter is set to f_c .

Finally, the basic PSD algorithm is:

loop N times

{

acquisition of $x(t)$

remove the mean value of x (not informative since corresponds to frequency 0)

FFT of x

PSD calculation (Eq. 7)

}

average of the N PSDs

5 Use of Hann window for PSD calculation

A Hann window can be used in the PSD calculation, first for reducing the width of spectral peaks (for example 50 Hz and harmonics), second to partially remove the influence of the signal drift, and third to obtain a better resolution of high-slope PSD at high frequency. The idea is to multiply the time record $x(t)$ by the following Hann window [9]:

$$w_n = 0.5 \left(1 - \cos \left[\frac{2\pi n}{M} \right] \right) \quad \text{for } n = 0, 1, 2, \dots, M - 1 \quad (9)$$

To take into account the energy loss in the Hann windowing, the final PSD must be multiplied by 8/3. The resulting algorithm for the PSD calculation with Hann windowing is then:

loop N times

{

acquisition of $x(t)$

remove the mean value of x

multiply by the Hann window

FFT

PSD calculation (Eq. 7)

}

average of the N PSDs

multiply the result by 8/3.

6 PSD calculation programme

The programme named “psd2_ECG-COMON.exe” [7] calculates the potential PSD, the current PSD, and the noise impedance Z_n (square root of the ratio PSD V/PSD I) of a EN time record saved in ASCII format, consisting of three columns (column 1: time in s; column 2: potential noise in V; column 3: current noise in A) which are separated by tabulators. The programme can also divide the time record in one or several sections over which it averages the PSDs. It uses the configuration file “config_psd2_ECG-COMON.txt” [7]. These two files must be in the directory where the data file is. Only the configuration file has to be modified according to your data. The structure of the configuration file is the following:

fichier_in hanning (0 = no, 1 = yes) nb_section nbpoint_section fichier_out

[*fichier_in*: name of the EN data file; *hanning*: Hann window will be used (1) or not (0); *nb_section*: number of sections in which the EN data file is divided; *nbpoint_section*: number of points/samples in each section; *fichier_out*: name of the file with the PSD and Z_n data].

For example:

Huet_RR1Mo_10Hz.asc 1 10 2048 Huet_RR1Mo_10HzPSD.txt

for a data file “Huet_RR1Mo_10Hz.asc” containing 20480 pairs of V and I values. In that case, the data file is divided in 10 sections of 2048 pairs of V and I values and the Hann window is used in each section. The result is stored in the file “Huet_RR1Mo_10HzPSD.txt” as follows:

data file = Huet_RR1Mo_10Hz.asc hanning = 1 nb_section = 10 nbpoint_section = 2048

frequency	PSD_v	PSD_i	Zn
4.882813e-003	1.901942e-011	2.974846e-024	2.528520e+006
9.765625e-003	1.913229e-012	9.364153e-025	1.429385e+006
1.464844e-002	5.789599e-013	5.085475e-025	1.066985e+006
...			

Please note:

- there must be no spaces in the names of *fichier_in* and *fichier_out*
- *nbpoint_section* must be a power of two
- in the EN data file the values of potential and current noise have to be in V and A (if not, ask F. Huet for a modified programme)

The programme(s) can be downloaded from the web [7]. For modifications of the programme, please feel free to ask F. Huet (francois.huet@upmc.fr). On the website also another version of the programme is available, which calculates PSDs from XML data files as described in Chapter 1.3 and in [3].

Figure captions

Fig. 1. Dummy cell configuration (all resistor values R are equal).

Fig. 2. Schematic of a dummy cell using a matrix board (the copper strips are shown at the front of the board for clarity, but they would normally be situated on the back of the board).

Fig. 3. Example of PSDs calculated from EN data measured with (curves a, b, c) and without (curves d, e, f) anti-aliasing filter (cut-off frequency set at $2/3 f_{\max}$) [8].

Fig. 4. Comparison of PSDs to the thermal noise PSDs of resistors ($= 6kTR$ and $2kT/R$) of $1\text{ M}\Omega$. Examples of PSDs measured by EN measurement devices with a rather high (system X) and low (system Y) baseline noise level.

Fig. 5. Example of electrochemical potential noise time domain data with a quantisation problem (note the distinct levels) due to inappropriate range and gain settings.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Tables

Table 1

Potential and current thermal noise PSD values for the resistors used in the dummy cells
($6 kTR$ and $2 kT/R$ with $k = 1.38 \cdot 10^{-23}$ J/K, $T = 298$ °K).

	Resistor values / Ω			
	R = 100	R = 10^4	R = 10^6	R = 10^8
Potential thermal noise PSDs / $V^2 \text{ Hz}^{-1}$	$2.47 \cdot 10^{-18}$	$2.47 \cdot 10^{-16}$	$2.47 \cdot 10^{-14}$	$2.47 \cdot 10^{-12}$
Current thermal noise PSDs / $A^2 \text{ Hz}^{-1}$	$8.23 \cdot 10^{-23}$	$8.23 \cdot 10^{-25}$	$8.23 \cdot 10^{-27}$	$8.23 \cdot 10^{-29}$