

Electrochemical Noise Measurements

Part III: Determination of the noise resistance R_n

I – INTRODUCTION

The objectives of the first and second parts of this note was to show that Bio-Logic instruments are able to perform reliable noise measurements, compared to ASTM requirements. This third part aims at comparing for a system its noise resistance R_n and its polarization resistance R_p , and using this example to describe the EC-Lab noise analysis tool.

There are several ways to analyze noise data, which are discussed in a review paper written by Cottis [1]. As seen earlier, one of them is to calculate a characteristic value of the corroding system called noise resistance R_n . R_n is defined as the standard deviation of the potential divided by the standard deviation of the current:

$$R_n = \frac{\sigma_E}{\sigma_I} \quad (1)$$

In certain conditions, R_n can be considered equivalent to the polarization resistance R_p . Various authors demonstrated this equivalence [2,3]. In EC-Lab® and EC-Lab® Express, an analysis tool called ENA (Electrochemical Noise Analysis) leads to the determination of R_n . If the impedance of the system is not a simple resistance i.e. if the impedance varies with the frequency, then the standard potential and current deviations need to be calculated using the PSD (Power Spectral Density) [2] and consequently:

$$R_n = \sqrt{\frac{\int_0^\infty \Psi_E(f) df}{\int_0^\infty \Psi_I(f) df}} \quad (2)$$

where Ψ_E and Ψ_I are the Power Spectral Densities (PSDs) of the potential and current noise, expressed in V^2/Hz and A^2/Hz , respectively. f is the frequency of the noise events. With the ENA tool, the PSDs can be calculated either by DFT (Discrete Fourier Transform) or by MEM (Maximum Entropy Method). This note will describe how to perform and analyze noise measurements using the ENA tool.

II – EXPERIMENTAL CONDITIONS

For all measurements, the electrolyte was a solution of $0.005 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and $0.495 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ prepared following ASTM procedure [4]. A Bio-Logic SP-200 potentiostat with EC-Lab® Express was used along with an Ultra Low Current option.

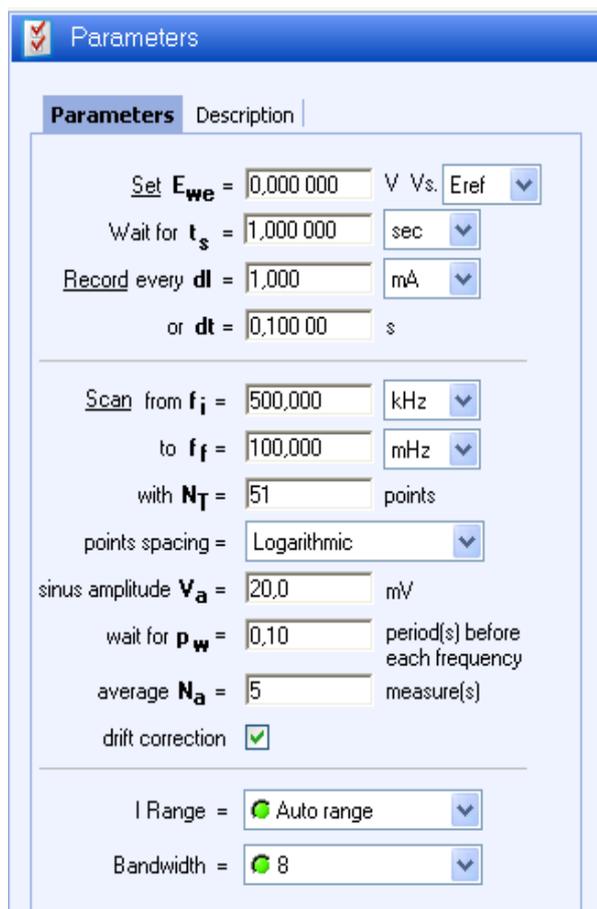
II - 1 IMPEDANCE MEASUREMENT

First of all, an impedance measurement was performed to determine R_p . The Working Electrode (WE) was a 1 cm^2 sample of AISI 430 stainless steel, the Counter Electrode (CE) was a graphite electrode and the Reference Electrode (Ref) a Saturated Calomel Electrode (SCE). The AISI sample was polished with 240 and 600-grit SiC paper, following the procedure described in ASTM G5 [5]. The technique used was PEIS and the conditions are listed in Fig. 1. Before performing the impedance measurement, the sample was left in the solution at OCV during 1 hour to make sure it reached steady-state.

II-2 NOISE MEASUREMENTS

Noise measurements were performed using as WE and CE, two 1 cm^2 AISI 430 stainless steel samples and as a reference electrode an SCE (Saturated Calomel Electrode). The samples were polished following the procedure described previously. The technique used was ZRA and the conditions are listed in Fig. 2. The potential range was $[-0.255V; -0.206 \text{ V}]$ such that the potential

measurement resolution is equal to 0.76 μV . The principle of the ZRA technique is to maintain 0 V between two samples: the working electrode (S1) and the counter electrode (S3). The resulting current flowing between the WE and the CE is the ECN (Electrochemical Current Noise). The potential evolution of the couple $E_{\text{we}}/E_{\text{ce}}$ (S1/S3) with respect to the reference electrode (S2) is the EPN (Electrochemical Potential Noise). It is advised to express noise amplitudes without trying to normalize by the area [1].



Parameters Description

Set E_{we} = 0,000 000 V Vs. Eref

Wait for t_s = 1,000 000 sec

Record every dI = 1,000 mA
or dt = 0,100 00 s

Scan from f_i = 500,000 kHz
to f_f = 100,000 mHz
with N_T = 51 points
points spacing = Logarithmic

sinus amplitude V_a = 20,0 mV

wait for p_w = 0,10 period(s) before each frequency

average N_a = 5 measure(s)

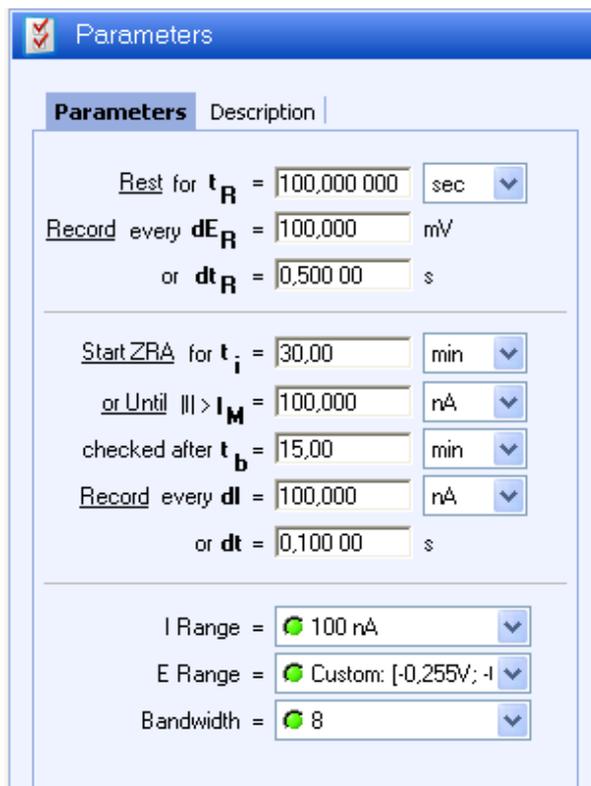
drift correction

I Range = Auto range

Bandwidth = 8

Figure 1 : PEIS conditions.

The sampling time depends on the frequency range of the events of interest. According to the Shannon theorem, if the phenomenon of interest has a frequency f then the sampling frequency must be equal to at least $2f$. The conditions used are shown in Fig. 2. E_{range} of +/- 2.5 V for the CE was set.



Parameters Description

Rest for t_R = 100,000 000 sec

Record every dE_R = 100,000 mV
or dt_R = 0,500 00 s

Start ZRA for t_i = 30,00 min
or Until $|I| > I_M$ = 100,000 nA

checked after t_b = 15,00 min

Record every dI = 100,000 nA
or dt = 0,100 00 s

I Range = 100 nA

E Range = Custom: [-0,255V; -1

Bandwidth = 8

Figure 2 : ZRA conditions.

The measurements were performed in a Faraday cage N-FAR600 provided by Bio-Logic SAS, earth-grounded to the potentiostat. The upper and lower frequency limits of the noise events are respectively:

$f_{\text{min}} = 1/(30 \times 60 \times 30 \times 60 \times 10) \approx 30 \text{ nHz}$ and
 $f_{\text{max}} = 1/(2 \times 0.1) = 5 \text{ Hz}$ (cf appendix of part I for more details). We also used a 5 Hz analog filter to remove the aliasing of frequencies higher than 5 Hz. This filter is available on SP-200, SP-240, SP-300 and VSP-300.

III – RESULTS

III - 1 IMPEDANCE MEASUREMENT

Figure 3 shows the Nyquist diagram of the impedance measurement described above.

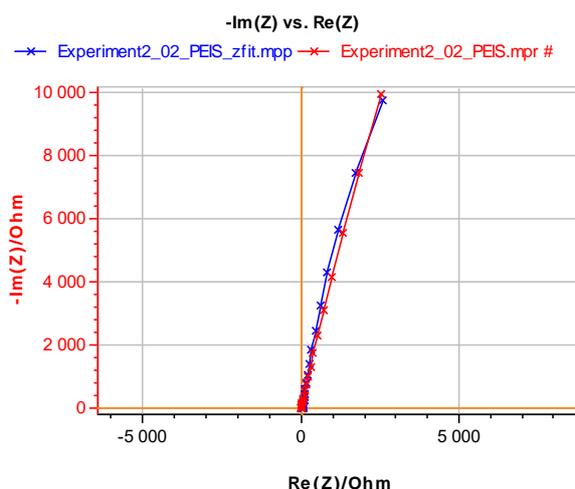


Figure 3 : Nyquist diagram of the impedance of an AISI 430 SS steel at E_{corr} in a solution of 0,005 mol L⁻¹ H₂SO₄ and 0.495 mol L⁻¹ Na₂SO₄ [5].

Using the Zfit analysis tool it can be seen that the electrical circuit equivalent to the impedance of this system is: R₁+Q₂/R₂. The parameters values obtained by using the minimization algorithm (Randomize+Simplex) are :

R₁ = R_Ω (electrolyte resistance) = 70 +/- 0.3Ω

R₂ = R_p (polarization resistance) = 76 000 +/- 500 Ω

C₂ (pseudo double layer capacitance obtained with Q₂) = 167 000 +/- 66 pF [6].

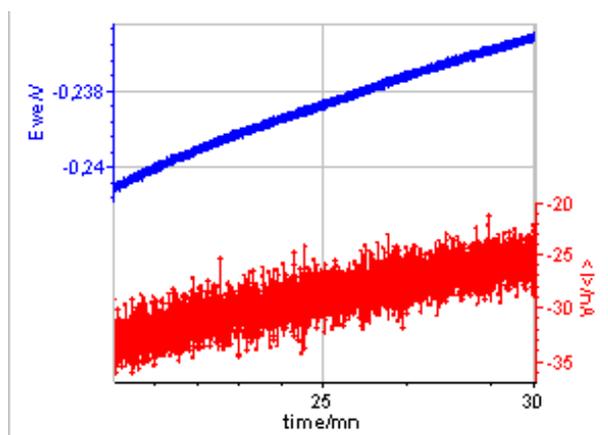


Figure 4 : EPN and ECN of AISI 430 in a solution of 0.005 mol L⁻¹ H₂SO₄ and 0.495 mol L⁻¹ Na₂SO₄

III - 2 NOISE MEASUREMENTS USING ZRA TECHNIQUE

In Fig. 4, the evolution of the EPN and the ECN can be seen. The total duration of the noise experiment was 30 min. The data that we chose to analyze were the data obtained after 20 min of immersion. The ENA tool is available in the Corrosion submenu of the analysis tools (cf. Fig. 5).

IV – NOISE ANALYSIS

IV - 1 R_n DETERMINATION

a. Description of the methods

A picture of the analysis window is shown in Fig. 6. The analysis tool offers the possibility to remove trends or drifts seen on the EPN or the ECN traces. The trend removal function actually subtracts from the original time trace a numerical curve obtained by either a linear or a 2nd order polynomial fit of the original trace. The traces resulting from trend removal are centered around 0 as can be seen for ECN in Fig. 7.

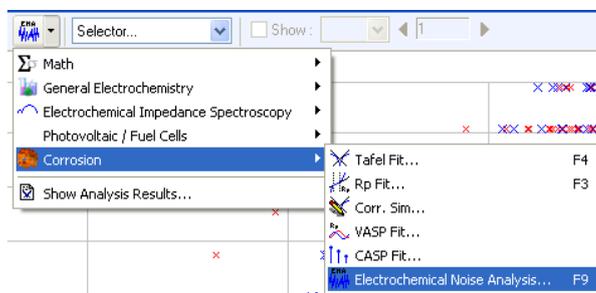


Figure 5 : The Electrochemical Noise Analysis tool

Figure 6 shows the ENA window and the available methods used to calculate R_n. The first method uses Eq. (1) for which the standard deviation is used. According to Eq. (2), R_n can also be calculated using PSDs obtained through the Fourier Transform of the signal. Two methods are proposed to calculate the Fourier transform: Amplitude spectrum (Discrete Fourier Transform) and MEM (Maximum Entropy Method).

The amplitude spectrum method uses a function to represent a time variable discrete input in the frequency domain. The analysis tool also allows to window the time traces of the ECN and EPN before calculating the amplitude spectrum. Windowing is used to remove the frequencies components of the signal created during the calculation of the amplitude spectrum by the discontinuities at the beginning and the end of the time record. More details on the effect of trend removals and windowing will be given in the appendix. Five different windowing processes are proposed in the ENA tool. The expressions for the calculation of the DFT and the windowing are shown in the Fourier transform section of the EC-Lab® and EC-Lab® Express user's manuals.

Table I : Rn calculated using the standard deviation with all available trend removal options

		ECN		
		None	Linear	2nd order
EPN	None	432 kΩ	831 kΩ	836 kΩ
	Linear	24,3 kΩ	46,7 kΩ	47 kΩ
	2nd order	9,5 kΩ	18,3 kΩ	18,4 kΩ

The MEM is based on the fact that any random time series $x(t)$ can be represented as the output of a filter (here called auto regressive) excited by a white noise (which is a signal with a constant amplitude for all its frequencies). White noise is considered to be the most random signal explaining the name of the method. In the ENA window (Fig. 6), it is possible to choose the order of the MEM. This order represents the poles of the transfer function of the filter. If the order is equal to n , the number of peaks of the resulting amplitude spectrum is $n/2$. More details on the MEM applied to the calculation of the Fourier transform of a noise signal can be found in the paper by Bertocci [7].

b. Results and comparison with R_p

Table I shows the noise resistance as defined by Eq. (1) with the various available conditions. We can see that trend removal can lead to huge variations.

According to Tab. II, the values of R_n calculated by the amplitude spectrum method are around the same values obtained with the standard deviation for the same trend removal conditions (2nd order polynom on both ECN and EPN).

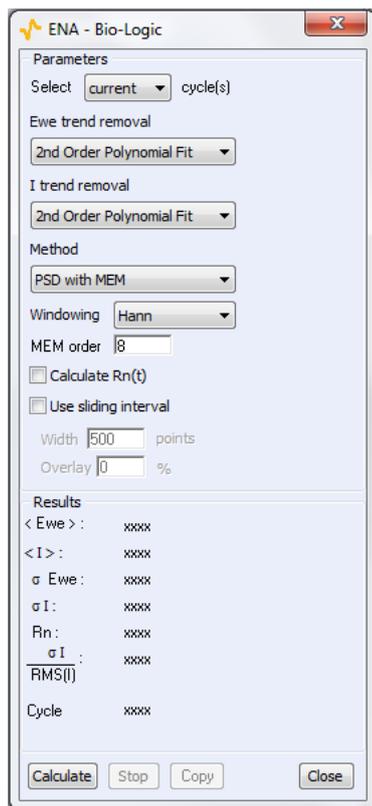


Figure 6 : The ENA window

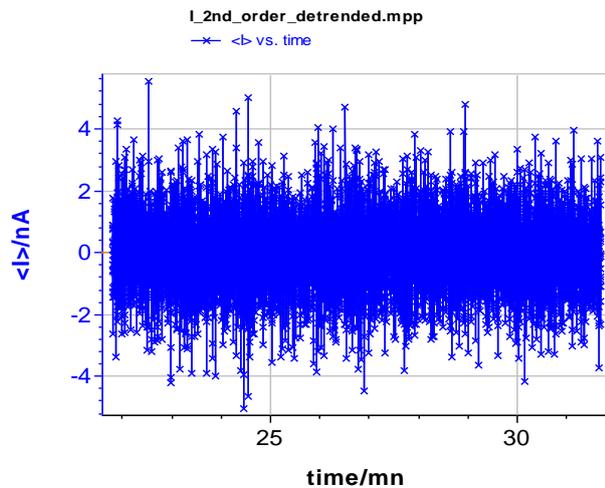


Figure 7: Detrended ECN resulting from 2nd order polynomial fit trend removal.

Table II: Rn calculated using 2nd order polynomial trend on potential and on current and amplitude spectrum method for the calculation of the PSD, using all available windows.

Window	Rn /k Ω
Rectangle	18,4
Barlett	17,9
Hann	18
Hamming	18
Blackman	17,7
Welch	18

Table III shows the values obtained by the ME Method using Barlett window and with an increasing order. With this method, the values obtained are close to the ones obtained by amplitude spectrum for the same trend removal and windowing conditions (2nd order polynom and Barlett windowing). It is interesting to note that Rn seems to reach a minimum after an order number of 6.

Table III: Rn values obtained with MEM for the calculation of the Fourier transform and using increasing orders, with Barlett windowing.

MEM order	Rn /k Ω
2	16,3
6	15,8
12	15,2
24	15

IV - 2 EFFECT OF THE TREND REMOVAL AND WINDOWING

Fig. 8a compares the amplitude spectrum of the original EPN (Fig. 8a, ■) and the detrended signals obtained by using either a linear (Fig. 8a, ▲) or a 2nd order polynomial fit (Fig. 8a, ●). At frequencies lower than 1 Hz, a straight component with a slope of -1 in the logarithmic plot can be seen on the original EPN. This very smooth component is related to the drift as it has also been shown in [8]. In Fig. 9a, it can be seen that the effect of detrending is to remove this smooth component from the amplitude spectrum.

Fig. 9b shows the amplitude spectrums of the windowed EPN : original EPN (Fig. 8b, ■), using Hamming window (Fig. 8b, ▲) and Barlett window (Fig. 8b, ●). It can be seen first that the Hamming window is not as good as the Barlett window to remove the smooth component. Finally, Fig. 8c shows the DFTs of EPN after : no detrending and Barlett windowing (Fig. 8b, ■), linear fit detrending and Barlett windowing (Fig. 8b, ▲), 2nd order polynom fit detrending and Barlett windowing (Fig. 8a, ●). It can be seen that 2nd order polynom fit detrending and Barlett windowing provides an amplitude spectrum with the lowest amplitude at the lowest frequencies. More detailed information about the effect of detrending and windowing are given in the appendix.

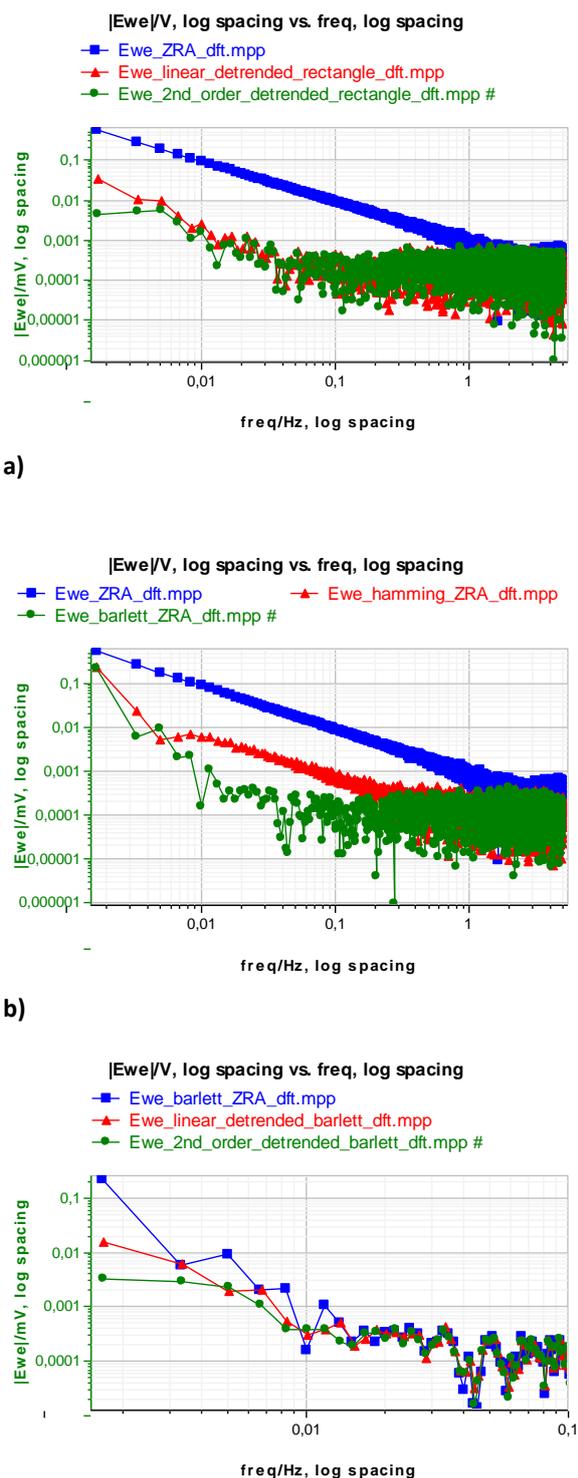


Figure 8: Effect of the windowing and the detrending on the amplitude spectrum of the EPN:
a) Detrending only, b) Windowing only, c) Detrending and windowing

V – CONCLUSION

The ZRA technique available in EC-Lab® and EC-Lab® Express can be used to perform noise measurements. This technique maintains 0 V between the working and the counter electrode. The associated analysis tools were also described. It was shown in this note that the calculated value R_n is very dependent on the type of data treatment (detrending and windowing). These two processes were shown to have similar effect and to remove the low frequency component. The different methods available in EC-Lab® and EC-Lab® Express must be used to cross-check the R_n value; for instance, in the example above, it seems that the R_n value is around 18 k Ω , because it has been found by all 3 methods (standard deviation, Amplitude spectrum and MEM). This value of R_n is around 3 times lower than the value of R_p determined by impedance spectroscopy.

Data files can be found in :

C:\Users\xxx\Documents\EC-Lab\Data\Samples\Corrosion\AN_39_ZRA_III_XXX

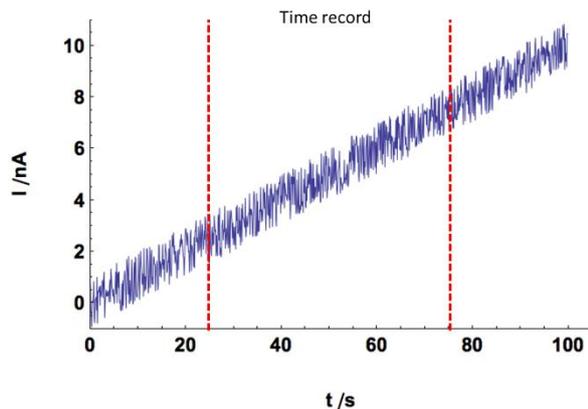
APPENDIX

The purpose of this appendix is to illustrate the effect of the windowing on the signal. Fig. 10a shows an actual input which was recorded by any device (in our case a potentiostat) between 25 and 75 s. If an amplitude spectrum is performed on this time record, the assumed input signal is shown in Fig. 10b, in which the time record is repeated throughout time.

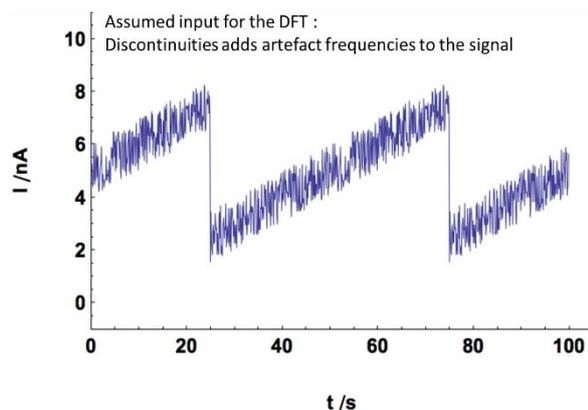
Discontinuities of the assumed input signal create additional artefact low frequencies to the signal. The main effect of the detrending and the windowing is to remove these artefact frequencies.

By using a linear detrending we remove the linear component of the signal in Fig. 9a. This gives a signal centered around 0, similar to what is shown in Fig. 7. The input assumed by

the amplitude spectrum for the same time record as above is shown in Fig. 10a. It can be seen that the discontinuities have disappeared. A window function is a function only defined over the time record that is equal to 0 at its boundaries and equal to one at the center at its definition domain. In Fig. 10b, it can be seen that the assumed input does not contain the discontinuities shown in Fig. 9b.

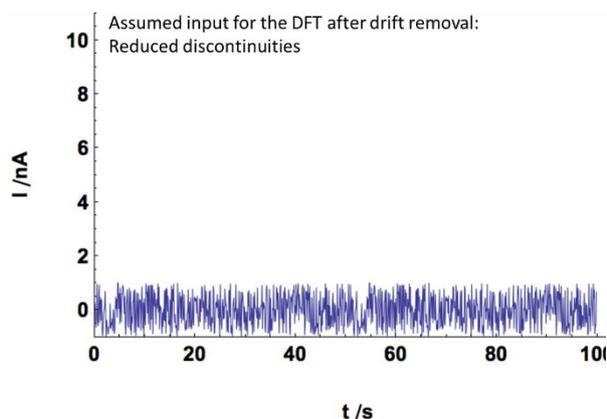


a)

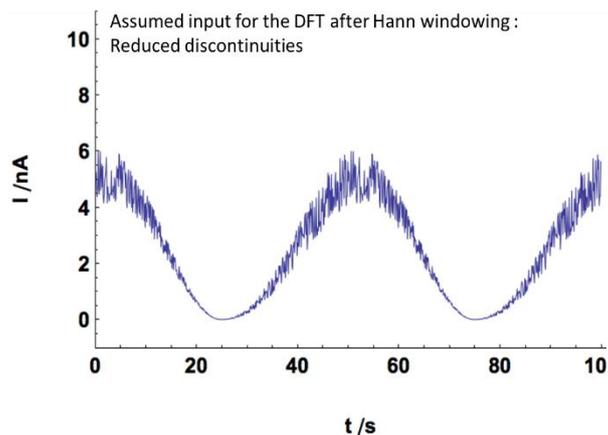


b)

Figure 9: a) Actual input with its time record b) Input assumed by the amplitude spectrum.



a)



b)

Figure 10: Effect of a) the detrending and b) the windowing on the time record of the actual input signal.

REFERENCES

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