

Electrochemical Noise Measurements

I - ASTM assessment and validation of the instrumental noise

I - INTRODUCTION

The aim of this application note is to show the ability of the Bio-logic equipment to perform reliable noise measurements that can be ultimately used to assess the corrosion characteristics of any corroding material. The procedures described below follow the ones given in the ASTM proceedings about noise measurement for corrosion applications [1]. Our results are compared with the requirements mentioned in the ASTM publication.

The Electrochemical Current Noise (ECN) is defined as the spontaneous current fluctuations occurring between two dissimilar or identical electrodes held at the same potential. These current fluctuations are due to a galvanic activity between either two dissimilar electrodes or two electrodes of the same material with microstructural differences. ECN is usually measured using a Zero Resistance Ammeter (ZRA), which connects the two working electrodes. A reference electrode or a pseudoreference electrode of the same material as the working electrodes can be used to measure the potential fluctuations, which are called Electrochemical Potential Noise (EPN). The first measurement of EPN for corrosion studies has been described by Iverson et al. [2] in 1968, followed 15 years later by Electrochemical Current Noise (ECN) measurements [3]. Noise measurements can be used to have information on the characteristics (noise resistance R_n) and the mechanisms (pitting, crevice, stress corrosion cracking, intergranular corrosion) of a corroding system [4].

II – ASTM REQUIREMENTS

Two procedures are described in the ASTM publication to assess and validate the instrumentation:

Procedure 1 consists in measuring the EPN and ECN when no electrochemical cell is connected to the potentiostat. The potential measurement terminals (S1, S2, S3) are

short-circuited to ground to record the EPN. The other leads (P1, P2) are left hanging. According to ASTM, “this should give a potential reading of 1 μ V or less” [1]. For the measurement of ECN, the leads are left open (“dangling leads”) : P1, S1, S2 on one side and P2, S3 on the other side are connected together. In the bandwidth from 0 to 10 Hz, the current noise levels should be lower than 10 pA.

Procedure 2 consists in analyzing a sine wave source considered to be a known source of noise. A 1 V_{pp}, 1 Hz sine wave is applied using a second channel of the VSP-300 feeding the first channel with which the measurement is made. This is explained in more details in the [Technical Note #25b](#). The test circuit that was used in the ASTM reference [1] is shown in Fig. 1.

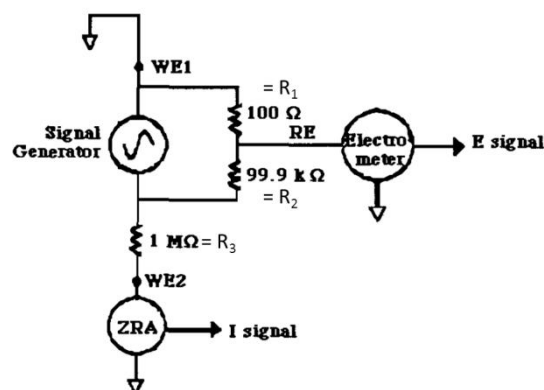


Fig.1 : Test circuit used in procedure 2.

A voltage divider is used to produce an output voltage that is a fraction of the input voltage, without affecting the dynamics of the wave signal. The peak to peak amplitude (E_{pp}) of the measured voltage (E signal) is obtained using the following formula:

$$E_{pp} = E_{inpp} (R_1 / (R_1 + R_2)) \quad (1)$$

Where E_{inpp} is the peak to peak voltage amplitude coming from the second channel of the VSP-300, R_1 and R_2 are the values of the resistances in the voltage divider. For R_1 and R_2 equal to 100 and 100 000 Ω , respectively, $E_{pp} = 1$ mV. The peak to peak amplitude (I_{pp}) of the current response (I signal) is obtained using the Ohm law :

$$I_{pp} = E_{inpp} / R_3 \quad (2)$$

where R_3 is the value of the resistance in the current measurement part of the circuit. For $R_3 = 1$ M Ω , $I_{pp} = 1$ μ A. The ASTM requirement for this measurement is that the instrumental noise should be two decades less than E_{pp} *i.e.* less than 0.01 mV.

III – EXPERIMENTAL SETUP

Noise measurements are performed with EC-Lab® and EC-Lab® Express using the ZRA technique that can be found in the Corrosion application section. In this technique, the potentiostat maintains a potential difference of 0 V between the Counter Electrode (CE) and the Working Electrode (WE) and measures the resulting current flowing between the CE and the WE. The potential difference between the CE/WE system and the Reference electrode (Ref) is also measured.

In this application note, a VSP-300 is used. For the procedure 1, an Ultra Low Current (ULC) option is used. The current range is 1 pA. The ZRA technique is used to record the ECN and the OCV Fast technique is used to record the EPN. For the procedure 2, no ULC option is used and the current range is 1 μ A. The CASP technique ([Application Note #37](#)) is used to generate the 1 Hz sine wave of 0.5 V amplitude (or 1 V peak to peak). The resulting potential is recorded using the ZRA technique. For both procedures, the smallest potential control range is used, allowing a control resolution of 1 μ V. A low pass 1 kHz analog filter is applied on the measured current and potential. This analog filter can be chosen in the Advanced Settings tab. The sampling rate is 100 Hz (*i.e.* one point every

0.01 s). The duration of the measurement is 300 s, which means that the lowest frequency that can be observed is $1/(300) \approx 3.3$ mHz (see Appendix).

IV – RESULTS

Procedure 1 : Fig. 2 shows the Discrete Fourier Transform (DFT) of the EPN. Following the expression of the Fourier Transform function of a sine wave [5], the values given are actually $\frac{1}{2}$ of the corresponding values in the time domain. In Fig. 2, it can be seen that the EPN is below 1 μ V at any frequency higher than around 30 mHz [1].

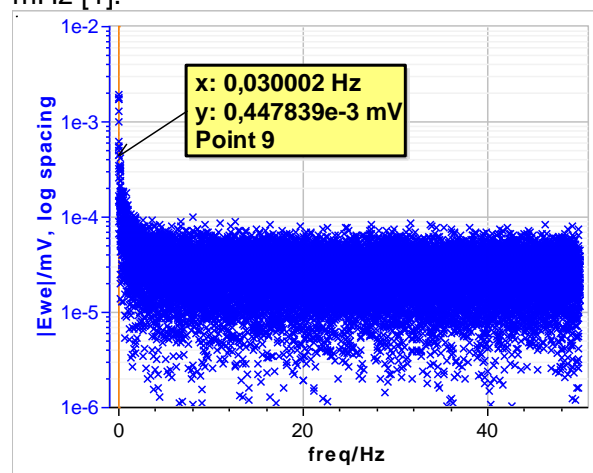


Fig. 2 : DFT of the EPN obtained following procedure 1.

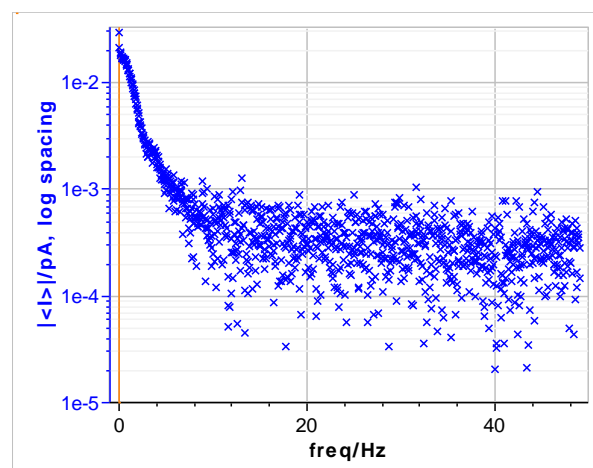


Fig. 3 : DFT of the ECN obtained following procedure 1.

The ECN obtained with the “dangling leads” is shown in Fig. 3. For every frequency up to 10 Hz, the current noise is below 0.1 pA, which is two decades below the threshold

current of 10 pA recommended in the ASTM reference [1].

Procedure 2 : Figs. 4 and 5 show the voltage trace resulting from the procedure 2 and its DFT, respectively. In Fig. 4, it can be seen that E_{pp} is $0.68 + 0.34 \approx 1$ mV as was theoretically expected. The DFT shows that almost all the potential noise of the instrument (i.e. all the signal except the 1 Hz applied “noise”) is lower than 5 μ V, which corresponds to 10 μ V in the time domain and is the value specified in the ASTM reference [1]. At 1 Hz, the value of the potential can be read. This potential is 250 μ V, which is around 1/2 of the amplitude of the measured potential (Fig. 4).

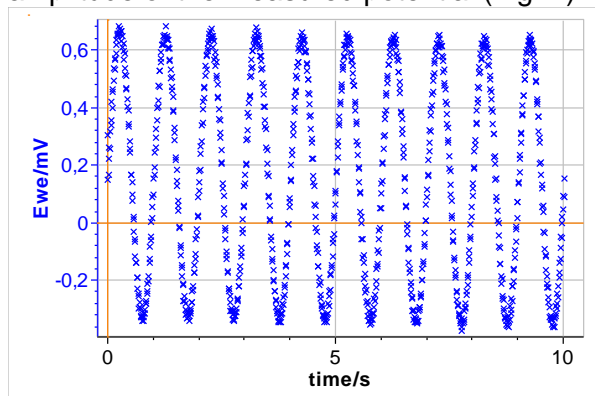


Fig. 4 : Voltage trace E resulting from the applied 1 Hz potential sine wave (Procedure 2).

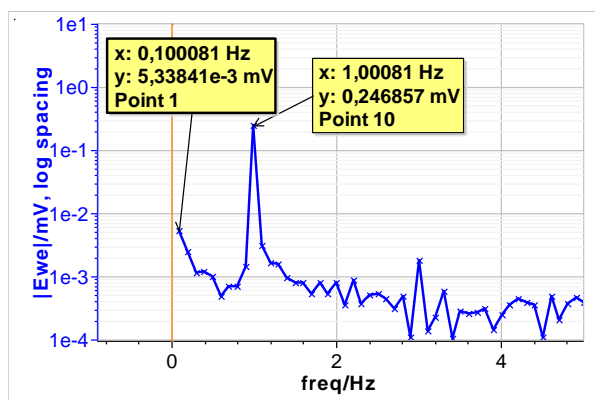


Fig. 5 : DFT of the Voltage trace E resulting from the applied 1 Hz potential sine wave (Procedure 2).

IV - CONCLUSIONS

This note shows that the intrinsic potential and current noise of the VSP-300 with an Ultra Low Current option complies with and is even better than what is required in the

ASTM publication for noise measurements. VSP-300 and associated technology SP-200, SP-240 and SP-300 potentiostats are fully suitable to perform reliable noise measurements on electrochemical systems. The second part of this note will show that Bio-Logic equipment can reliably perform noise measurements on a real electrochemical system in agreement with ASTM.

APPENDIX

The highest measurable frequency that can be resolved in the frequency domain is given by :

$$f_{\max} = 1/2\Delta t \quad (3)$$

where Δt = the sampling interval.

This frequency is known as the Nyquist frequency, cutoff or folding frequency. This is, in fact, the high-frequency limit in the spectra obtained. Thus, for a sampling rate of once every second (1 Hz), the highest frequency that can be resolved in the frequency domain is 0.5 Hz.

The low-frequency resolution of the spectrum of a discrete time record is given by :

$$f_{\min} = 1/N\Delta t \quad (4)$$

where N = the number of samples and Δt = the sampling interval.

REFERENCES

1. J. R. Kearns et al., ASTM STP 1277 (1996) 446.
2. W. P. Iverson, J. Electrochem. Soc. 115 (1968) 617.
3. J. L. Dawson, K. Hladky, D. A. Eden, “Electrochemical Noise – Some New developments in Corrosion Monitoring”, Proc. of the Conf. UK Corrosion '83, 99-108
4. R. A. Cottis, Corrosion 57, 3 (2001) 265.
5. R. Bracewell in: *The Fourier Transform and Its Applications, 3rd ed.* New York: McGraw-Hill, (1999) 79-90, 100-101.

Data files can be found in :

EC-Lab vxx.xx\Data\Samples\ZRA\Part I