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Application Note

1 The Measurement looks weird

Every now and then we get emails from customers, who have a “weird” result from a measurement. They are worried that the instrument might malfunction. Sometimes it is the cable and in rare cases the instrument causing the issue. The majority of these cases turn out to be issues with the electrochemical cell and its environment. We observed that such reports of “weird” results happen especially for Differential Pulse Voltammetry (DPV) and Square Wave Voltammetry (SWV). In this application note we will explain why that is and what measures can be taken to avoid the cause.

2 Environmental Noise

A well-known issue in all types of instrumental measurements is environmental noise: the dark noise from a photomultiplier tube, the stray light during photometry or electric fields during electrochemical measurements.
The majority of interferences are emitted randomly from multiple sources. This sounds like it is difficult to get rid of them, but fortunately multiple random interferences combined usually result in a Gauss curve or respectively a normal distribution around the true value of the measurement. Due to this property a common way to deal with noise is to measure multiple times the same value for a measurement, average all the results and use this average as a measurement point.
Measurements that are influenced by electrical fields or other electrical interferences show often sine wave shaped noise. Sources for electrical noise tend to have sine wave shapes. The cause is our power grid, which usually supplies ac power with a frequency of 50 or 60 Hz. In electrochemistry these interferences from the mains are the strongest interference (see Figure 2.1).
Often a waxing and waning of noise waves is observed. This is the interference pattern of multiple sine wave shaped signals.

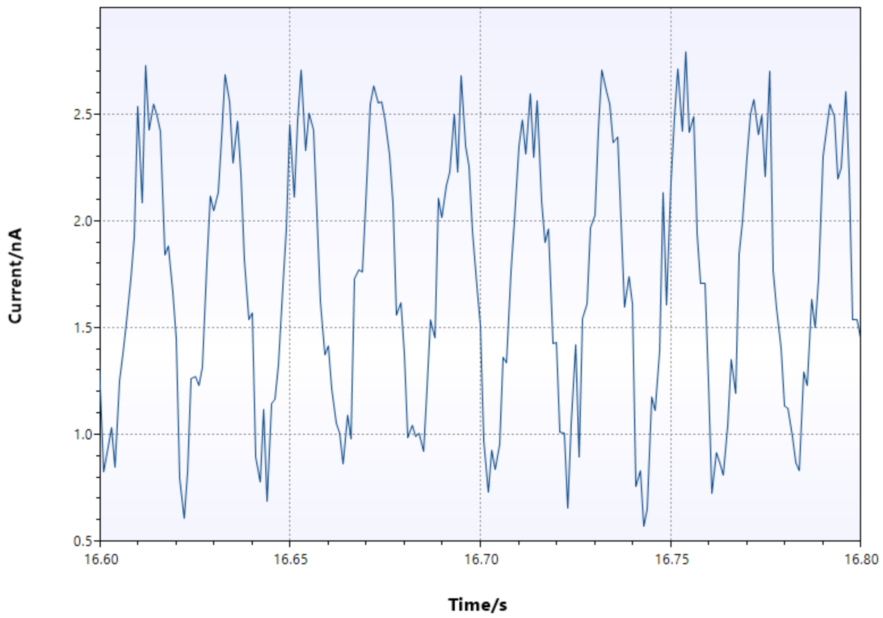

Figure 2.1 Cutout from a Chronoamperometry with visible 50 Hz noise

2.1 Noise impact on DPV and SWV

While the impact of noise on most curves is clearly visible as the normal distributed deviation from the true measurement value, it looks very different for differential methods like DPV and SWV. Despite the label at the axis during a DPV or SWV not the current I directly is plotted but the difference between the current of the forward and backward potential jump ΔI. As a result the curve is the differential of a Linear Sweep Voltammetry (LSV) without diffusion limitation.
The noise during your measurement will impact every measurement point two times: one time during the forward pulse and one time during the backward pulse. Your DPV or SWV have also a frequency for taking the measurement points and again this will create an interference pattern with the noise from the environment leading to a curve, which represents more the interference pattern than the measurement signal.
If the amplitude of your noise is low compared to you signal, the impact on the measurement will look similar to the noise you are used to, this means the curve is not smooth but the curve shows a few normal distributed deviations. If the amplitude of the noise is high, the DPV or SWV will show artifacts that look like additional peaks or the peak is missing, etc.

3 Demonstration with PalmSens Dummy Cell

A simple way of demonstrating the different impact of the noise is to use the PalmSens Dummy Cell in an environment with a lot of noise and little noise. The circuit connected to the WE A of the PalmSens Dummy Cell, which is delivered together with most of our potentiostats, is made to simulate a non-diffusion limited redox system. This means an LSV will result in a sigmoidal shape and a DPV or SWV should deliver a signal peak around 0 V. The dummy cell was connected to a PalmSens4 and placed onto an office desk without further protection for the low noise signal. The dummy cell was placed directly on top of a PC tower for the high noise environment. To make the noise easily visible first LSVs with special parameters were recorded. These parameters were chosen in a way that the PalmSens4 has very little time for averaging and thus the environmental noise is almost unfiltered recorded. In Figure 3.1 it is clearly visible how the high noise level creates an interference pattern in the measured current (red curve) and just small disturbances when exposed to the low noise environment (blue).

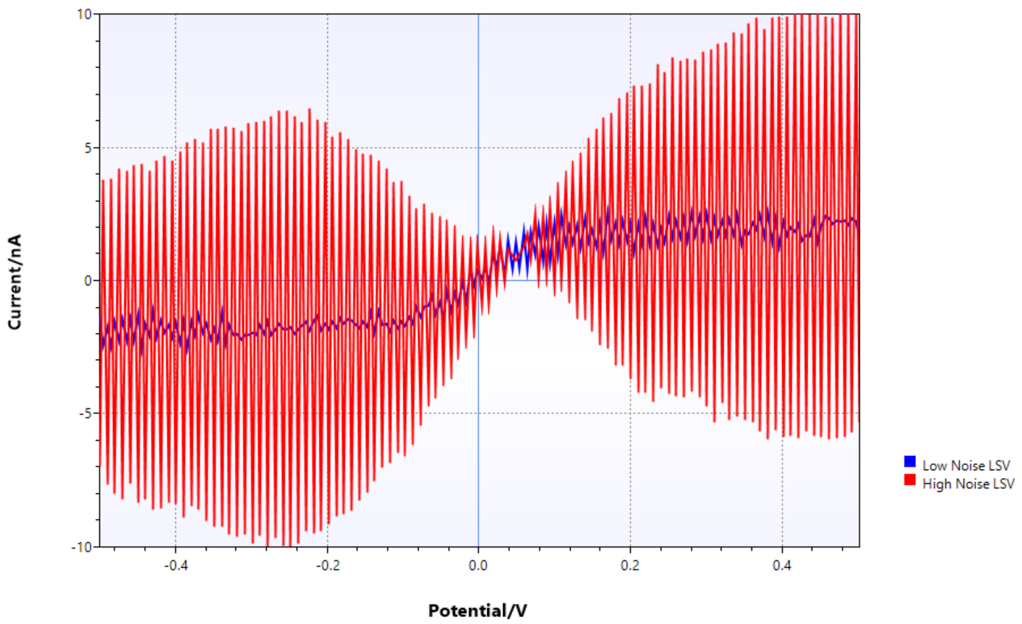

Figure 3.1 LSV with low averaging to investigate the noise level in a low noise environment (blue) and a high noise environment (red)

Under the same conditions DPVs are recorded. In Figure 3.2 it is clearly visible how the DPV recorded in the low noise environment shows the expected peak at 0 V (blue curve). The high noise environment lead to a DPV which does not show the expected results at all (red curve), but also it does not look like the usual normal distributed noise most people are used to. These measurements demonstrate that environmental noise has a very different impact on differential methods like DPV or SWV compared to measurements with a direct current measurement like LSV.

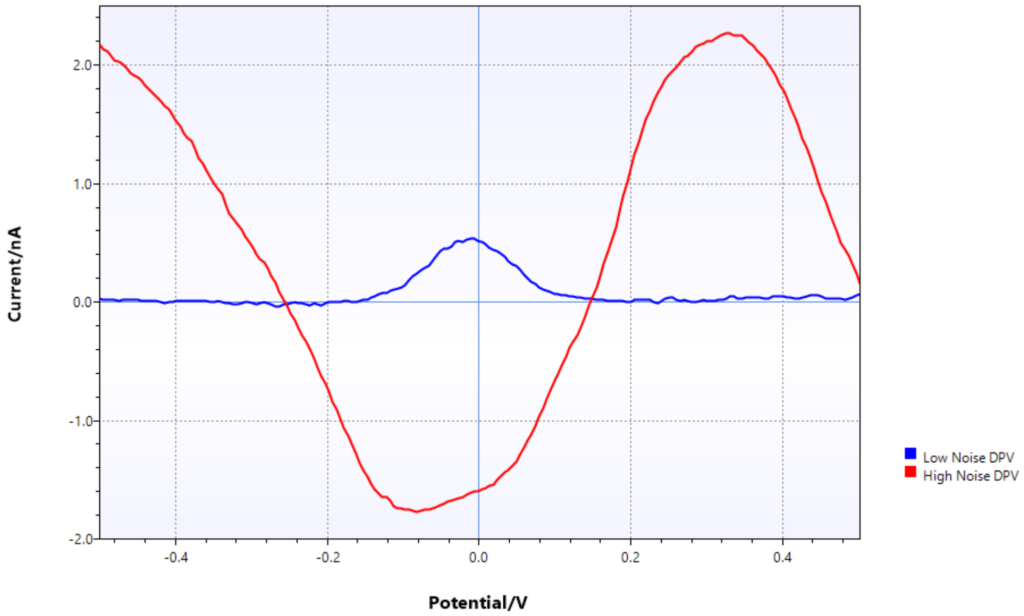

Figure 3.2 DPV in a low noise environment (blue) and a high noise environment (red)

4 Troubleshooting

Since it is clear that the "weird" results are caused by noise, the usual means to reduce noise will work to fix this issue. There are some standard methods to remove noise, but, unfortunately, identifying sources of noise and reducing the noise in your system is not always an exact science. Here are some tips to deal with the noise.

1. Check if it is really noise and check if measures you have taken improved the signal to noise ratio by recording LSVs. Choose parameters that allow you to record the noise unfiltered. A *Scan Rate* of 0.5 V and an *E step* of 5 mV should work fine for this purpose.
2. Check the mains frequency set in PSTrace. PalmSens potentiostats filter noise around 50 Hz or 60 Hz, because these are the two options for the power grid frequency. If you choose the *General settings* from the *Tools* menu at the top of the PSTrace window, you can see and change the settings for the mains frequency, for example in European countries this filter should be set to 50 Hz.
3. A Faraday cage is the best way to shield your measurement from noise. The sensor cable, which is included with every potentiostat delivery from PalmSens, is double shielded up to the point where the leads separate in the different connections. Usually it is sufficient to put your cable and cell up to this point into the Faraday cage. A Faraday cage is a metal box or a metal cage. All sides and the lid or door of the cage are electrical connected to each other. Additionally the Faraday cage is connected to the ground of the potentiostat (green plug). This way it forms a shield against environmental noise. This leads to a more than significant reduction of the noise.

4. Check your *Scan Rate, Frequency, t interval* etc. These are all parameters, which influence the time for the potentiostat to average values and thus the amount of values for each point of the measurement. Increasing the time for your potentiostat to collect more values will reduce the noise by a factor of $\sqrt{n}$, where n is the number of averaged values. This means decreasing the *Scan Rate, Frequency* or increasing the *t interval* will give your potentiostat more time to record values for the same data point and reduce the noise.
5. Remove sources of noise from your workstation. Many laboratories nowadays are full of measurement devices and computer, which are always switched on. All these instruments and devices create electrical fields and might interfere with your measurement.
6. Move to another location. Noise is emitted by so many sources and shielding a complex setup properly is not trivial. Sometimes just moving a cable a few centimeters can have an impact on the noise level. If you can move your setup to another bench or even room, there might be an improvement of your signal to noise ratio or it could get worse.