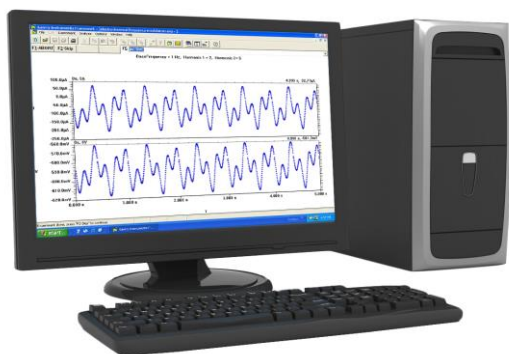# EFM140™ Electrochemical Frequency Modulation Software

The EFM140™ Electrochemical Frequency Modulation (EFM) Software is the first commercial implementation of this powerful corrosion measurement technique. Developed by corrosion scientists at the University of Leuven in Belgium with support from EPRI, EFM offers several advantages over other established corrosion techniques. EFM is suitable for systems where uniform corrosion is occurring. The EFM is a non-destructive technique that measures corrosion rate directly without knowledge of the Tafel constants. Even though the Tafel constants are not required, it measures them and a change in Tafel constant may indicate a change in corrosion mechanism.

The EFM140 is a complimentary software package to the standard corrosion techniques available in the DC105™ DC Corrosion Techniques software. Using these two packages in conjunction can give the corrosion scientist and corrosion engineer an extra level of confidence about the validity of his or her data. The theory behind the technique is the same Butler-Volmer kinetics that underpins all corrosion rate measurements.

*The **EFM140 Electrochemical Frequency Modulation Software** controls a Gamry Potentiostat to perform electrochemical corrosion measurements.*

Like most Gamry software, the EFM140 and a Gamry Potentiostat use the Gamry Framework™ Software for data acquisition and the Echem Analyst™ for data analysis. All of the electrochemical techniques, therefore, have a common look-and-feel, so moving from one

experiment to another is easy. Call us for the brochure entitled "Overview of Gamry Software", which describes the general features of the Gamry Framework and the Gamry Echem Analyst.

If a special application arises, Gamry's **Open Source Scripting** allows you to make the software changes to perform your custom experiment -- either in the data acquisition or the data analysis! If you like, Gamry can modify the software under your direction. You can even use our Sequence Wizard to combine different techniques into a single experiment.

Gamry has the widest range of electrochemical products for corrosion measurement on the market. Other Gamry software includes Electrochemical Impedance Spectroscopy, Electrochemical Noise, Critical Pitting Temperature, Cyclic Voltammetry, Pulse Voltammetry and Charge-Discharge. You can be confident that Gamry and your Gamry system will support you as your electrochemical needs evolve.

Theory

EFM is a complimentary technique to harmonic analysis from which similar information can be obtained. It has advantages over harmonic analysis in that it is not sensitive to harmonics in the applied signal and the responses are larger than in harmonic analysis. EFM is also analogous to impedance measurements except that in impedance the response in assumed to be linear whereas in EFM a non-linear response is required. Even though the responses are non-linear, it is still a non-destructive technique. In the EFM method a potential perturbation consisting of two sine waves at different frequencies is applied to a corroding metal sample. The current-voltage behavior of a corroding surface is typically non-linear so a perturbation at one frequency can result in responses at the same frequency and at harmonic and intermodulation frequencies. Intermodulation frequencies are frequencies which are sums or differences of the 2 fundamental frequencies and

their harmonics (see Table 1). The magnitude of these responses can be used to extract corrosion rate information as well as Tafel parameters. Let us take the example of a voltage perturbarion at two frequencies, ω_1 and ω_2, given as:

$\eta = V_0[\sin(\omega_1 t) + \sin(\omega_2 t)]$

where η = E-E_{corr} and V_0 is the magnitude of the applied voltage amplitude. Harmonic current response are observed at ω_1, $2\omega_1$, $3\omega_1$ and ω_2, $2\omega_2$, $3\omega_2$ as well as intermodulation frequencies like $2\omega_1 \pm \omega_2$ and $2\omega_2 \pm \omega_1$. The ratio of the amplitudes of the responses at different frequencies is used to extract corrosion rate information. Application of this method to a charge transfer controlled corrosion process leads to evaluation of the corrosion current density, i_{corr}, and the Tafel constants. Table 1 shows the amplitudes of the different harmonic and intermodulation frequencies.

	Frequency	Amplitude
ω_1	2	a
ω_2	5	a
ω_2-ω_1	3	b
ω_1+ω_2	7	b
ω_2-$2\omega_1$	1	c
$2\omega_2$-ω_1	8	c
ω_1+$2\omega_2$	12	c
$2\omega_1$+ω_2	9	c
$2\omega_1$	4	d
$2\omega_2$	10	d
$3\omega_1$	6	e
$3\omega_2$	15	e

Table 1. The intermodulation and harmonic frequencies with their corresponding amplitudes with the examples of 2 Hz and 5 Hz shown.
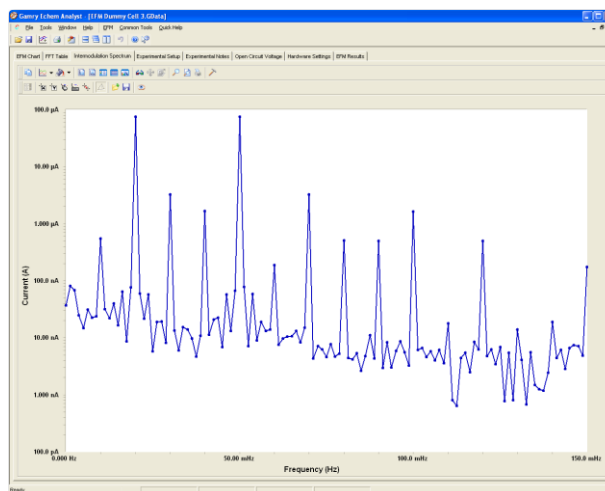

Figure 1. EFM data for a dummy cell showing the peaks at the different frequencies and their relative sizes

Gamry Potentiostats are available in models that can be installed inside a desktop computer or as fully portable systems that interface with a laptop to perform measurements in the field. Every Gamry Potentiostat is electrically floating, so you can perform experiments on grounded samples in the lab (autoclaves, strain rate testers) or in the field (pipelines, vessels). The data files from EFM140 are easily analyzed in the Echem Analyst, but the file format is tab-delimited ASCII text and can be easily imported into other software for further analysis.

The EFM140 performs the following experiments:

- **Electrochemical Frequency Modulation**
- **EFM Trend**

Electrochemical Frequency Modulation

Electrochemical Frequency Modulation is applied to a corroding system at the open circuit potential of that system. You can choose the frequencies at which to make the measurement. This frequency should typically be slow, in line with the slow scan rates used in polarization resistance experiments. Another identifier for the frequency would be the plateau region observed for a system in EIS. The number of cycles and amplitude of the signal can be chosen. The amplitude should be small enough not to significantly degrade the surface, but large enough to give you non-linear responses. The results from EFM can be different depending on the corrosion mechanism of the system. If the

corrosion scientist knows the mechanism before the start of the experiment she can choose from active, passive and diffusion. But not to worry, the selected options can be changed later date in the Echem Analyst. Figure 2 shows the setup dialog box for EFM.
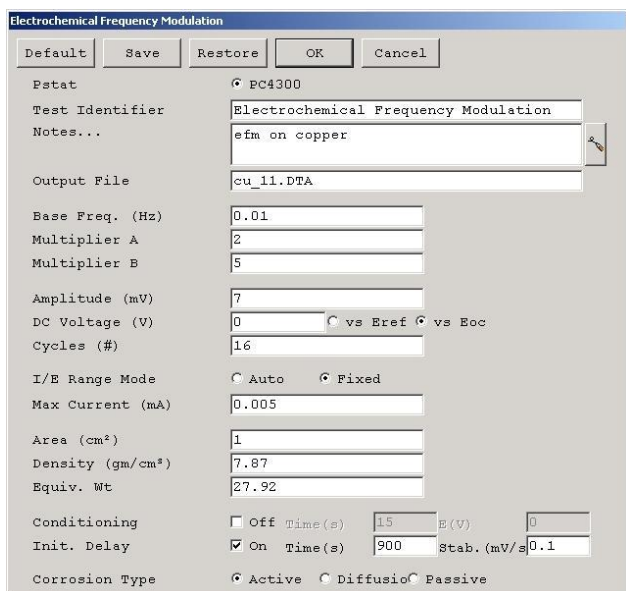

Figure 2. Setup Dialog box for EFM Experiment.

Once the data is collected, load it into the Echem Analyst and the intermodulation spectrum is calculated through a Fast Fourier Transform (FFT) of the data. An example of an intermodulation spectrum is shown in Figure 3 for a copper sample. i_{corr} and the Tafel constants are calculated using this intermodulation spectrum and are displayed on a separate page, along with the causality factors. It is possible to recalculate the corrosion rate depending on the corrosion mechanism chosen.
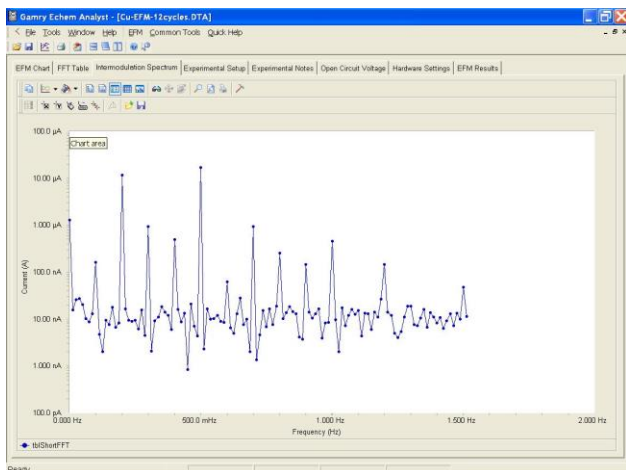

Figure 3. Intermodulation Spectrum of a Copper sample in 3.5% NaCl.

EFM Trend

The EFM140 also includes a "trend" experiment to monitor the corrosion of a sample over an extended time period. The parameters are set up like the single shot experiment except a repeat time is also specified. This experiment is analogous to the Rp/Ec experiment in the DC105 software. One of the features of this experiment is that you can monitor the Tafel constants as a function of time and hence identify when a corrosion mechanism changes.
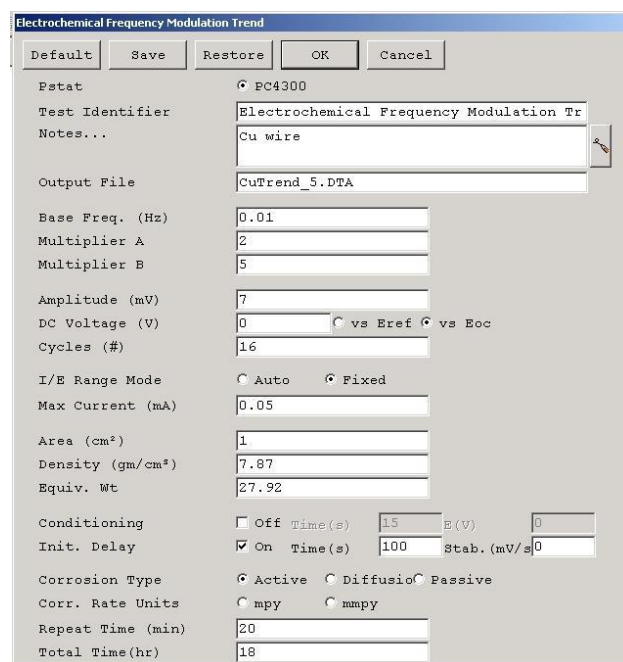

Figure 4. Setup Dialog Box for EFM Trend Experiment

Comparison to Recognized Corrosion Measurement Techniques

How does EFM compare to well established techniques? We ran an experiment to compare EFM with polarization resistance and electrochemical impedance spectroscopy. The test sample was mild steel in KCl solution.

We began with a simple LPR (Polarization Resistance) experiment. The results are shown in Figure 5. Analysis of the data within 5 mV of Eoc gave the line shown in red. It corresponds to an Rp value of 687 ohm-cm^2. Using the default beta values of 120 mV/decade yields a corrosion rate of 5.8. mpy in this electrolyte. This estimate can be refined if better estimates of the beta values are known.
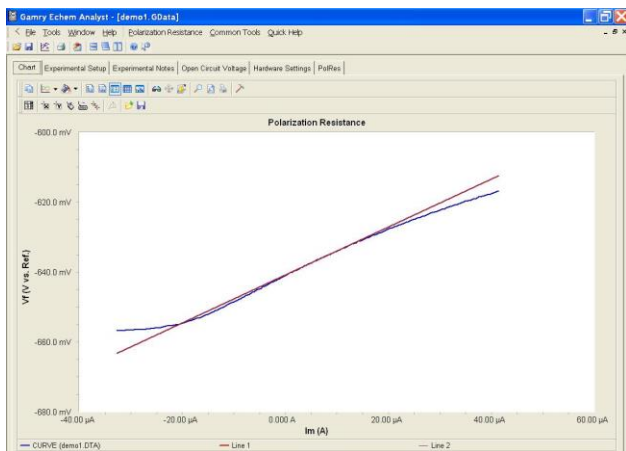
Figure 5. Linear Polarization Resistance data for mild steel in KCl solution.

One way to check for the validity of a simple LPR experiment is to make an EIS measurement. The EIS measurement can also give an estimate of the solution resistance. A routine EIS measurement was performed at the Open Circuit Potential. The results of the EIS measurement are shown in Figure 6. The red lines are the fit to the fairly simple model. As in many systems, the double layer capacitance is best modeled by a constant phase element. The value of the polarization resistance, 674 +/- 13 ohm-cm² , agrees quite well with that from the LPR experiment!
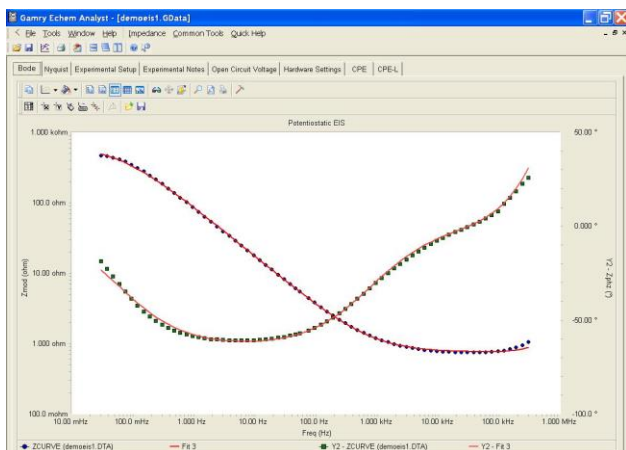

Figure 6. Electrochemical Impedance Spectroscopy data for mild steel in KCl solution.

Finally, we ran the same sample using the EFM technique using frequencies of 20 mHz and 50 mHz. Both of these frequencies are on the low frequency plateau on the EIS plot, in Figure 6. This is required by the EFM theory.
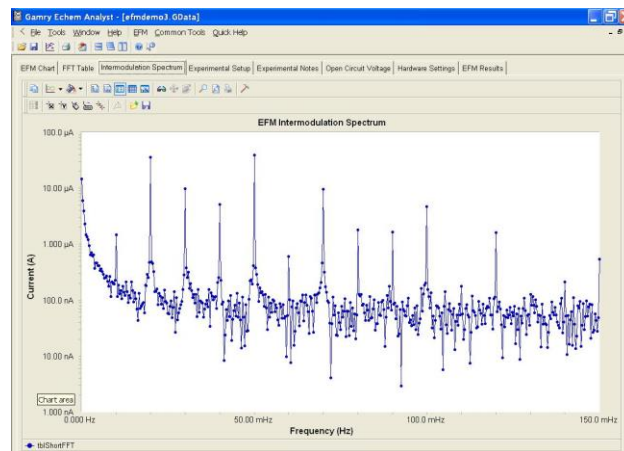

Figure 7. Electrochemical Frequency Modulation data for mild steel in KCl solution.

The results of the EFM analysis are shown in Figure 7. The EFM technique has the advantage that the corrosion rate can be calculated without prior knowledge of the Tafel constants. The corrosion rate calculated from the EFM measurement is 7.4 mpy. The EFM measurement also gives an internal self-check in the form of the two "Causality Factors". These two factors should have the values 2.0 and 3.0 if all of the conditions of EFM theory have been met. We see that our experiment meets the criteria!

The EFM corrosion rate (7.4 mpy) agrees well with the rate calculated from the LPR measurement (5.8 mpy). However, the LPR calculation assumed that both betas were 120 mV/decade. Now that we have estimates for the Tafel constants from the EFM measurement, we can recalculate the LPR corrosion rate. Table 2 summarizes the data from all three experiments. The agreement between the three non-destructive techniques is excellent!

Applications Assistance
If you're in the early stages of using electrochemical corrosion techniques, we can help. Pay a visit to **www.gamry.com**, go to the App Note section, and take a look at "Getting Started with Electrochemical Corrosion Measurement." There's an excellent list of references at the end of the Application Note. For specific questions, you'll always find a friendly technical advisor at our factory or your local Gamry sales office.

System Information
The EFM140 Electrochemical Frequency Modulation Software requires a Gamry Potentiostat to conduct experiments. Microsoft® Windows® XP/Vista/7 is required for operation of the EFM140. Gamry recommends a computer with the minimum

specifications recommended by Microsoft® for the operating system used.

Gamry Instruments can supply complete systems including the above items and system software installed in a desktop or laptop. Custom computer configurations, software, training, and installation are available by special order. Contact the factory or your local Gamry Distributor for further details on these systems.

	LPR	EIS	EFM
Corr. Rate (milliinches per year)	6.03	6.2	7.4
ßa	From EFM	From EFM	75.7
ßc	From EFM	From EFM	377
Rp (Ohms)	687	674	562

Table 2. Comparison of LPR, EIS, and EFM techniques

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