

Calibration of an Au-coated Quartz Crystal

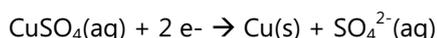
Introduction

This Application Note is the second in a series relating to the eQCM 10M™ and assumes that you have read and understand the material covered in the Application Note, *Basics of a Quartz Crystal Microbalance*.

The purpose of this Application Note is to show the reader a simple experiment where we reduce Cu²⁺ onto an Au electrode and then oxidize Cu back off. We will then use the result to calculate a calibration factor for the crystal. Conversely, we will show you how to calculate the molar mass of the species deposited using a calibration factor.

Each crystal has a theoretical calibration factor, however, under typical experimental conditions, these calibration factors will vary slightly. We will use Cu²⁺ to calculate a calibration factor which could then be used in subsequent experiments on the same crystal.

Cu²⁺ is reduced in a two electron reaction as shown below:



Our goal is to reduce Cu²⁺ onto an Au electrode, then use the frequency decrease and the charge passed to calculate a calibration factor.

Experiment Setup

A solution of CuSO₄ (5-10 mM) in 1 M H₂SO₄ was prepared and placed into the Teflon cell containing a 10 MHz Au-coated quartz crystal. No air/solution interface was present in the cell. The crystal's electroactive area was 0.209 cm² and the area of overlap was 0.205 cm².

Next, the eQCM 10M was interfaced to the cell using the supplied cell cable. A Series G 300 was connected to the working face of the crystal using a stacking banana plug to stacking pin cable. Cell setup was completed with a Pt counter electrode and an Ag/AgCl reference electrode.

Upon starting Resonator™, the nominal frequency of the crystal, 10 MHz, was entered in Center Freq along with a Freq. Width of 50 kHz and a Freq. Step of 0.2 Hz. Pressing **Single Scan** resulted in the spectrum shown in Figure 1. Next, the green cursors that appeared on the spectrum were moved closer to the resonant frequencies and **Start** was pressed to trigger continuous data acquisition.



Figure 1. Resonator screenshot after entering initial parameters and pressing Single Scan.

Next, the potentiostat was set up by selecting **Cyclic Voltammetry** from the Technique drop-down box and pressing **Setup**. A setup screen for cyclic voltammetry appeared and parameters were entered as shown below.

Initial E (V): 0.050

Scan Limit 1 (V): -0.250

Scan Limit 2 (V): 0.300

Final E (V): 0.050

Scan Rate (mV/s): 50

Step Size (mV): 2

Cycles (#): 5

I/E Range Mode: Fixed

Max Current (mA): 30

Sampling Mode: Fast

Once the potentiostat was set up, **OK** was clicked which closed the setup window, followed by **Run**. A screenshot of the potentiostat panel in Resonator during acquisition is shown in Figure 2. Note that the top plot shows both resonant frequencies for the entire time that the QCM has been acquiring data while the bottom plot shows current/voltage data. It is also possible to show current and voltage versus time by selecting **Time** in the Display Graph drop-down box.

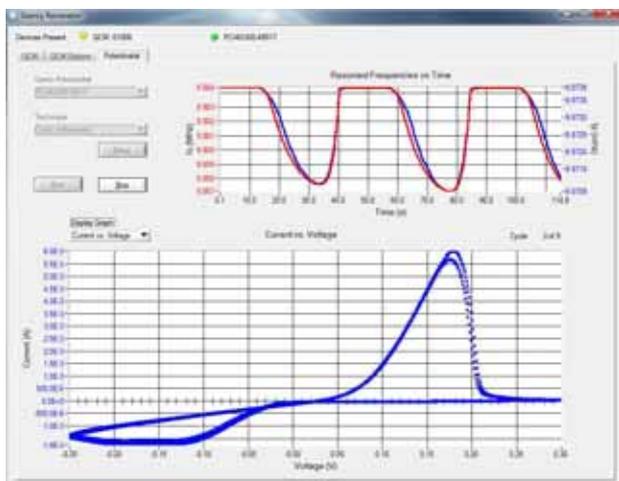


Figure 2. Screenshot of Resonator during acquisition.

After the acquisition was finished, the data file was then opened in Echem Analyst™.

Data Analysis

The first plot in Echem Analyst is a plot of current and frequency change versus voltage as shown in Figure 3 and the second plot is frequency change versus charge as shown in Figure 4.

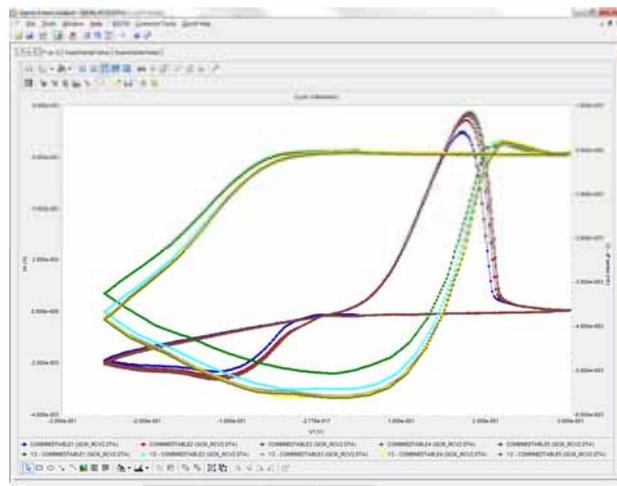


Figure 3. Echem Analyst showing current and frequency change versus voltage for the five cycles.

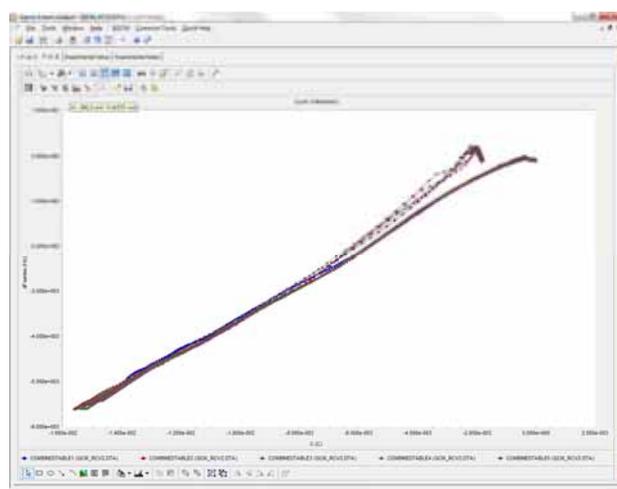


Figure 4. Echem Analyst showing frequency change versus charge for the five cycles.

The Curve Selector  can be used to plot data a variety of ways and also allows you to show or hide specific curves. The deposition portion of the curve was selected by clicking on the **Select Portion of the Curve** using the Mouse  tool. A linear fit was then calculated by choosing the **Linear Fit** option under the **Common Tools** menu. The Quick View pane at the bottom of the window in Figure 5 gives the slope of the linear fit as 376 kHz/C.

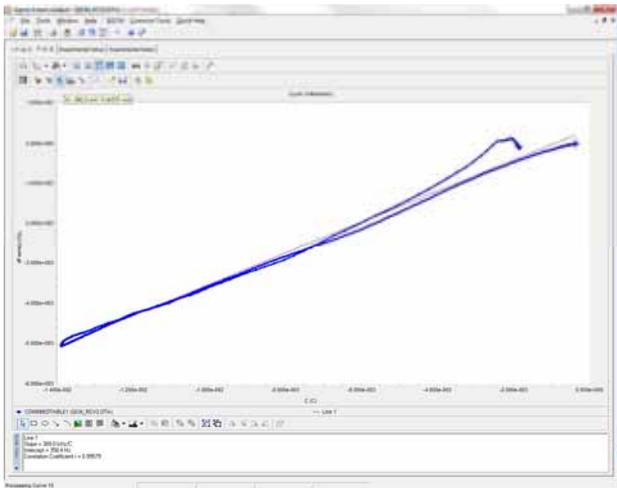


Figure 5. Echem Analyst showing the linear fit of change in frequency versus charge in the Quick View pane at the bottom of the window.

The calibration factor for the crystal is then calculated according to the equation

$$C_f = \frac{\text{Slope} * F * EA * n}{MM_{Cu} * 10^6}$$

where F is the Faraday Constant, EA is the electroactive area, MM_{Cu} is the molar mass of Cu, and n is the number of electrons. The 10^6 is used to convert from grams to micrograms. C_f is calculated to be 232 Hz cm²/μg. This is approximately 3% different than the theoretical value of 226 Hz cm²/μg.

If you already know your calibration factor accurately you can determine the molar mass of the mobile species (deposited in this instance) during your experiment using the following procedure.

Use the Curve Selector to plot change in mass (deltaM) versus charge as shown in Figure 6.

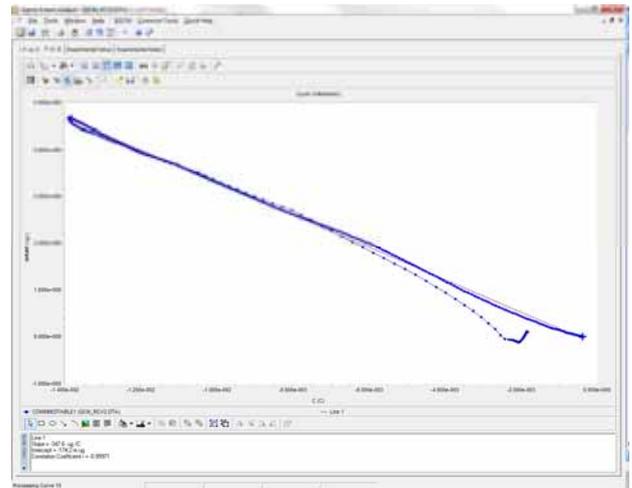


Figure 6. Echem Analyst showing the linear fit for change in mass versus charge in the Quick View pane at the bottom of the window.

Echem Analyst uses the calibration factor entered into Resonator along with the electroactive area to calculate the mass. The slope of the line, after performing a second linear fit, for the deposition is -347.6 μg/C. The molar mass of the Cu²⁺ can be calculated using the equation

$$MM = \frac{|\text{Slope}| * F * n}{10^6}$$

where F and n are as described previously. In this instance the molar mass was calculated to be 67.1 g/mol.

The purpose of this application note was to show how a calibration factor can be calculated for any given crystal. This application note also showed how to calculate the molar mass of a mobile species if the calibration factor of the crystal is known.

eQCM 10M



System Information

The eQCM 10M is shipped with the Gamry Resonator Software, Gamry Echem Analyst Software, a Quick Start Guide, a Hardware Operator's Manual (CD), a Software Operator's Manual (CD), one EQCM cell, one AC Power Adapter, one USB interface cable, one BNC cable, one potentiostat interface cable, and 5 Au-coated quartz crystals (10 MHz).

The eQCM 10M is protected by a two-year factory service warranty.

The eQCM 10M must be interfaced to a computer with a Gamry Potentiostat (models include the Reference 3000™, Reference 600™, Series G 750™, Series G 300™) and a PHE200™ license for incorporation and combination of QCM and potentiostat data into Echem Analyst. Microsoft® Windows XP SP3, Windows Vista®, or 7 is required.

SYSTEM	
Frequency Range	1 - 10 MHz
Frequency Resolution	0.02 Hz
Interface	USB
Operating Temperature Range	0 to 45 °C
Relative Humidity	Max 90% Non-condensing
Storage and Shipping Temperature	-25 to 75 °C
WEIGHT	
	1 kg
DIMENSIONS	
	175 x 115 x 80 mm
AC Power Adapter	100-264 V AC, 47-63 Hz
Quartz Crystal Microbalance	12V DC, 25 W



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