Technology Note

Tracking Recovery

Summary

Use of the AWSensors X1 Platform Tracking Recover feature to monitor overtones frequency and dissipation shifts of air-to-liquid medium exchanges onto 5 MHz QCM sensors.

Introduction

The Tracking Recovery feature included in AWSensors X1 platform allows the user to monitor large and fast frequency shifts in QCM (Quartz Crystal Microbalance) admittance spectrum. These sudden modifications in the sensor response are common is some applications where dramatical changes in the viscoelastic properties of the sensor surrounding medium take place.

This technical note illustrates the utility of tracking recovery feature to characterize an air-to-liquid medium exchange. According to Kanazawa and Gordon theory predictions [1], a complex frequency shift is expected in the sensor electromechanical response when the semi-infinite medium placed over the QCM's top electrode is replaced by other semi-infinite medium. This shift will depend on the viscosity and density properties of the final medium. Following, Kanazawa-Gordon equation is presented for both the frequency (Eq. 1) and the half-bandwidth (Eq. 2) shifts.

$$\Delta f = -f_0^{\frac{3}{2}}\left(\frac{n\eta_l\rho_l}{\pi\eta_q\rho_q}\right)^{\frac{1}{2}} \qquad Eq. 1$$

$$\Delta\Gamma = f_0^{\frac{3}{2}}\left(\frac{n\eta_l\rho_l}{\pi\eta_q\rho_q}\right)^{\frac{1}{2}} \qquad Eq. 2$$

Where η_l is the liquid viscosity, ρ_l is the liquid density, η_q represents quartz viscosity, ρ_q is the quartz density and f_0 the sensor resonant frequency. Variable *n* represents the odd overtone index *n*=1,3,5,…. Therefore, the same change in magnitude for both frequency and half-bandwidth is expected but with opposite sign.

Materials and Methods

We monitored the response of the different overtones of a 5 MHz 14 mm QCM sensor while the initial semi-infinite medium in contact with the sensor, air, is replaced by bi-distilled water. Results obtained have been compared with theoretical values predicted by Kanazawa-Gordon equation.

Instrumentation. An X1 Platform, operating in Tracking mode, was used to real-time monitor the complex frequency shifts (both resonator frequency and half-bandwidth) of a 5 MHz QCM sensor during an air-to-water medium exchange experiment. Overtones 1^{st} ,3^{rd} ,5^{th} ,7^{th} ,9^{th} ,11^{th} and 13^{th} were measured. X1 Thermal Control Unit was used to control the temperature during the experiment which was kept at 23 ºC. In addition, the X1 Flow Control Unit was used to create a continuous pulseless flow of 25 microliter/min of bi-distilled water through the sensor surface.

Sensor preparation. The 5 MHz sensor cleaned using AWSensors sensor cleaning protocol prior to the measurement and then immediately placed in an AWSensors flow cell designed for flow experiments.

Tracking Recovery feature setup. Before the experiment started, the tracking recovery option was activated in AWS Suite Mirage software, as shown in the **Figure 1**. The Peak Threshold parameter indicates the minimum conductance peak value that is considered valid to proceed with an experiment. **Figure 2a** shows an explicative diagram about the meaning of this parameter. Peak Threshold default value is 0.01 mS. If the conductance peak drops below the peak threshold, the sensor resonance is considered lost and the tracking recovery procedure is launched (if activated).

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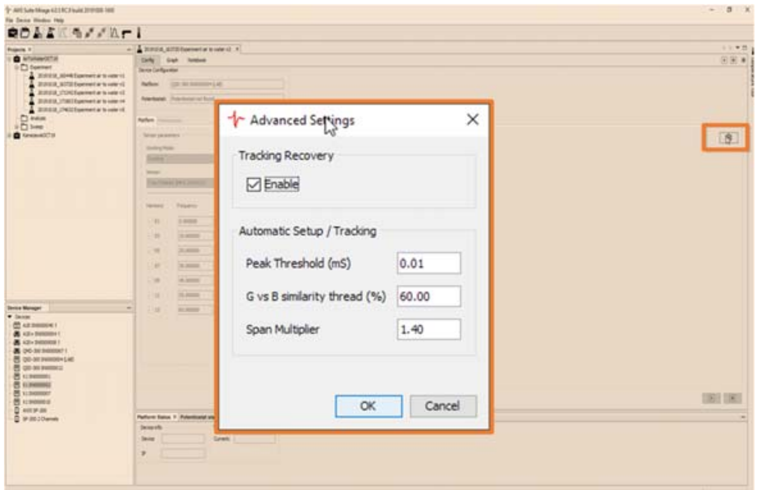
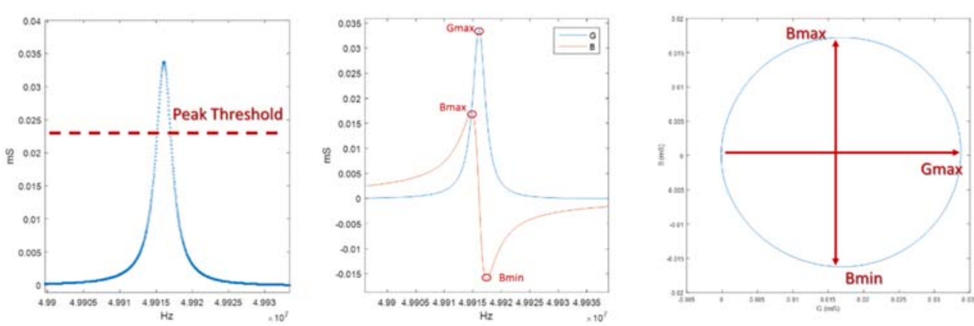


Figure 2. Tracking recovery setup panel included in AWSSuite software GUI.

G vs. B similarity threshold parameter indicates how similar sensor conductance and susceptance must be to consider that the sensor response is valid. Tracking mode is based on the fitting of the experimental sensor frequency response to a Lorentzian mathematical model. According to this model, a circle is obtained when susceptance is represented versus conductance as it is shown in **Figure 2b** and **Figure 2c.** When experimental data does not meet this condition, it could mean that the sensor resonance is distorted or out of range. G vs. B similarity threshold default value is 60%. If the similarity between experimental conductance and susceptance is lower than this threshold, the sensor resonance is



a) b) c)

Figure 1. a) Diagram showing conductance spectrum and peak threshold. b) Diagram showing both conductance and susceptance spectra. Conductance maximum (Gmax), Susceptance maximum (Bmax) and susceptance minimum (Bmin) have been marked. c) Diagram showing Susceptance versus Conductance similarity relation.

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considered lost and tracking recovery procedure is launched (if activated).

Materials and Methods

Figure 3 shows AWS Suite user interface software during an air-to-water medium exchange experiment. Blue lines represent normalized frequency shifts ($\Delta f/n$) for all the overtones, while red lines represent Dissipation (D) values. Half-bandwidth (Γ) values can be directly extracted from Dissipation by using the expression (Eq. 3):

$$D = \frac{2\Gamma}{f_0} \qquad Eq.\ 3$$

Although the QCM sensor response changed dramatically when water went through the measurement cell, the Tracking Recovery feature was used to monitor the resonance peak over the complete experiment.

Acquired normalized frequency and half-bandwidth shifts ($\Delta f/n$, $\Delta\Gamma/n$) have been compared with Kanazawa-Gordon equation theoretical predictions considering bi-distilled water density and viscosity respectively as 0.997 g/cm^3 and 0.000933 kg/(m·s). Both values have been extracted from the literature [2]. The comparison is shown in **Figure 4**, where both frequency and half-bandwidth have been represented vs. penetration depth, δ. Penetration depth accounts for the QCM shear wave energy entering the semi-infinite medium and its equation is presented below (Eq. 4). The higher the overtone mode, the lower the penetration depth is.

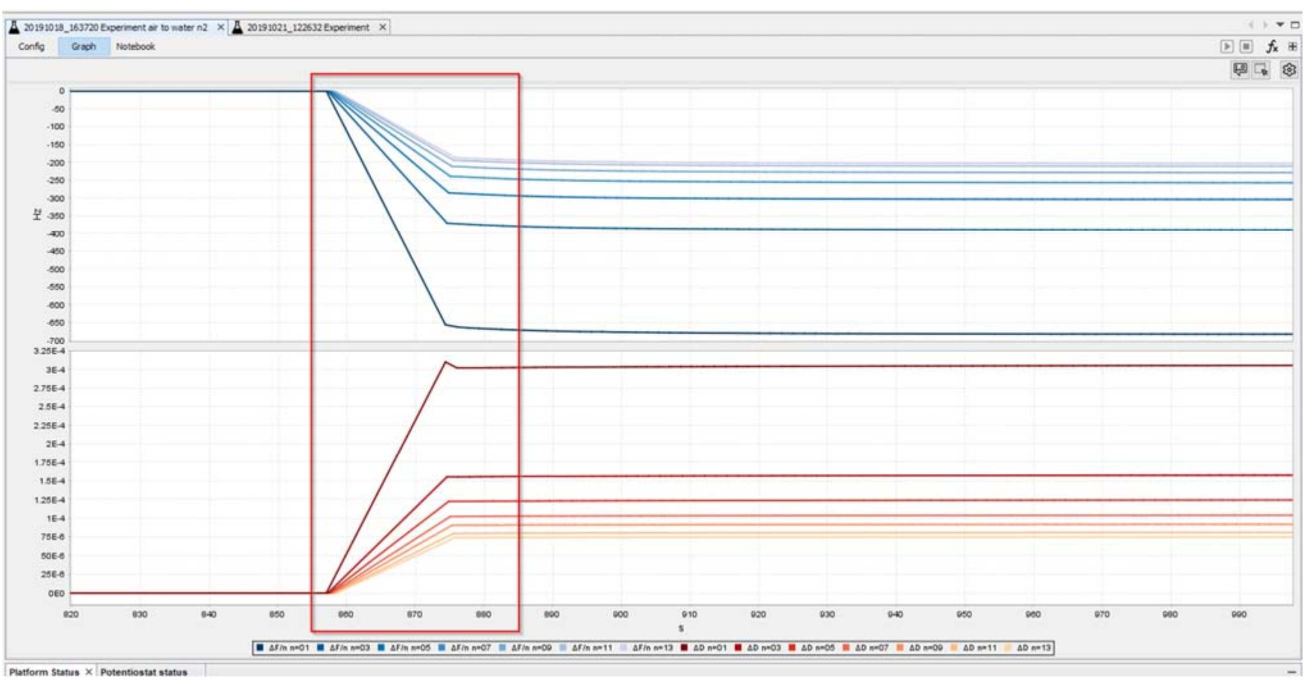

Figure 3. AWSSuite software GUI showing data gathered during one of the air-to-water medium exchange experiments. Blue curves represent the resonant frequency while red curves represent Dissipation. The red box shows the experiment part where the Tracking Recovery feature is run.

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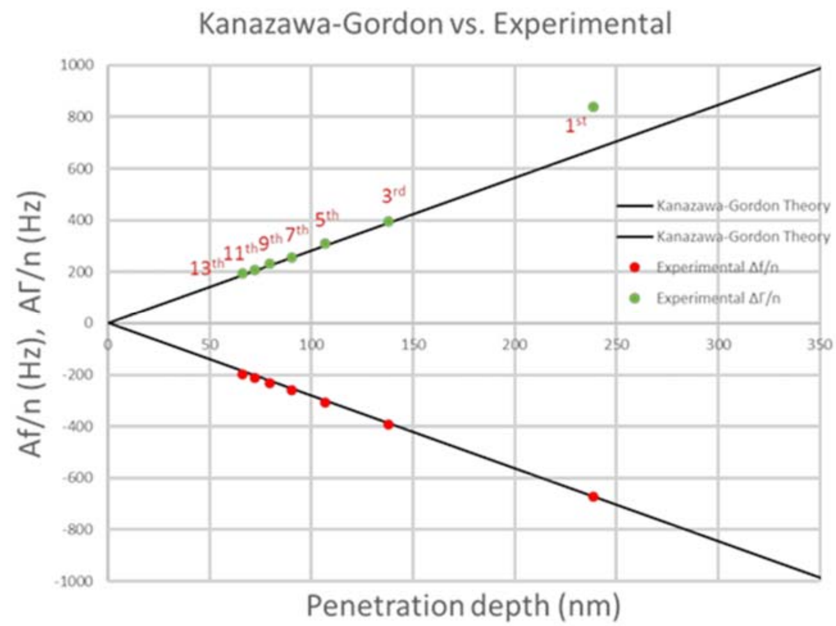

Figure 4. Kanazawa-Gordon equation prediction vs. experimental results.

$$\delta = \sqrt{\frac{\eta_l}{n\Pi f_0 \rho_l}} \qquad Eq.4$$

As it can be observed in **Figure 4**, experimental results are in good agreement with Kanazawa -Gordon theoretical predictions. It is worth mentioning the systematic discrepancy found in the bandwidth shift predicted by Kanazawa-Gordon and the one measured for the fundamental mode. Several authors in the QCM community have previously reported that the fundamental mode can exhibit anomalous behaviour [3].

References

1. Frequency of a quartz microbalance in contact with liquid. K. Keiji. Kanazawa and Joseph G. Gordon. Analytical Chemistry 1985 57 (8), 1770-1771. DOI: 10.1021/ac00285a062
2. Handbook of Chemistry and Physics, 53rd Edition, p. F4
3. The Quartz Crystal Microbalance in Soft Matter Research. D. Johannsmann. Springer International Publishing Switzerland 2015. DOI https://doi.org/10.1007/978-3-319-07836-6

Order Information

Product	Quantity	Reference
AWS X1	1	AWS X1 000031 A
AWS X1 Temperature Control Unit	1	AWS X1 000032 A
AWS X1 Flow Control Unit	1	AWS X1 000033 A
QCM flow cell for AWS platform	1	AWS CLS+ 000021 Q
AWS 14mm sensor, 5 MHz, Ti/Au, Polished	10	AWS SNS 000043 A

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