Quartz Crystal Microbalance References

Books and Review Articles

6. Daniel A. Buttry and Michael Ward, “Measurement of Interfacial Processes at Electrode Surfaces with the electrochemical Quartz Crystal Microbalance”, Chem. Reviews 92(6) (1922) 1355-1379. Note: This is one of the best review articles written on the subject of EQCMs. The theory is clearly explained, and the limitations of the technique and the current understanding are presented. Everybody in the field must read this paper!
7. Stephen Martin, “Closing Remarks”, Faraday Discuss 107(1997)463. Note: This is an excellent review of the QCM technology and theory as of 1997. It includes sections on: measurement techniques, modern devices, models and unsolved problems. The surface roughness issue is also discussed. S. Martin is one of the leaders in the field- read everything he writes.

Theoretical Models

5. T. W. Schneider and S. J. Martin, “Influence of compressional wave generation on a thickness shear mode resonator response in a fluid”, Anal. Chem. 67 (1995) 3324. Note: Acoustic interferometry was performed with TSM resonators to investigate the effect of compressional wave generation on the response (frequency and damping). The results indicate that even in semi-infinite liquids, compressional wave generation contributes significantly to device damping (motional resistance) but not to frequency shift.


11. R.A. Etchenique & E.J. Calvo, “Gravimetric measurement in redox polymer electrodes with the EQCM beyond the Sauerbrey limit [Short Communication]” Electrochemistry Communications, 1:5 (1999) 167-170. Note: The mass of non-rigid films is calculated based on electroacoustic impedance data and interpreted with Martin’s viscoelastic model.


**Tips, Tricks and Instrumentation**


Thin Film Deposition

1. G. Sauerbrey, Z. Phys. 155 (1959) 206. Note: The original paper proposing QCMs as a viable tool for micro mass determination. This is the first report on the use of quartz oscillators as microbalances, and where the proportionality between mass load and frequency shift was first proposed.


3. A. P. M. Glassford, “Analysis of the accuracy of a commercial quartz crystal microbalance”, in Progress in Astronautics and Aeronautics, edited by Allie M. Smith (American institute of Aeronautics and Astronautics, NY, 1977), vol 56, p. 175-196. Note: The Rayleigh energy method is used again to derive the change in frequency of a harmonically oscillating system when subjected to a small perturbation.


6. C. Lu and O. Lewis, “Investigation of film-thickness determination by oscillating quartz resonators with large mass load”, J. Appl. Phys. 43 (1972) 4385. Note: This paper includes the original derivation of the “Lu-Lewis” equation used by all modern thin-film monitors and controllers to calculate film thickness while properly accounting for the acoustic properties of the film deposited. A one-dimensional acoustical composite resonator model is used to study the behavior of a quartz crystal resonator with large mass load. It is found that the exact relationship between the frequency shift and the added mass depends on the acoustic impedance of the deposited material. This is also known as the Z-match model.


8. E. Benes, “Improved quartz crystal microbalance technique”, 56 (1984) 608. Note: Sequential measurement of the change in resonant frequency at the fundamental and its harmonic provides a method for real-time calculation of the acoustic impedance of the film during the deposition.


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**QCM with Liquid Deposit**

2. Zuxuan Lin and Michael Ward, “Determination of contact angles and surface tensions with the quartz crystal microbalance”, Anal. Chem. 68(1996) 1285. Note: A method based on the QCM for measuring the sessile contact angles and surface energies of liquid-air and liquid-liquid interfaces is described. The method involves measurement of the frequency change accompanying the introduction of a small liquid droplet to the center of a vibrating quartz resonator.

**QCM Immersed in Liquid**

5. K. K. Kanazawa and J. G. Gordon II, “Frequency of a Quartz Microbalance in contact with Liquid”, Anal. Chem. 57 (1985) 1770. Note: The dependence of frequency shift on density and viscosity of the liquid is derived by examining the coupling of the elastic shear waves in the crystal to the viscous shear waves in the liquid. This is the currently accepted formula used to explain the frequency shift in a quartz crystal oscillator when it is immersed in liquid.
oscillation frequency of a quartz crystal in contact with a fluid in terms of material parameters of the fluid and the quartz.

7. Muramatsu, H. et al., “Computation of Equivalent Circuit Parameters of Quartz Crystals in Contact with Liquids and Study of Liquid Properties”, Anal. Chem. 60(1988) 2142. **Note:** The dependence of the frequency shift and deficit resistance on the viscosity and density of the liquid is derived and tested experimentally. An Equivalent-Circuit description of the QCM is used to derive an equation relating the resistance to the viscosity and the density. This formula is currently used to calculate in-situ viscosities of liquids.


10. M. Yang and M. Thompson, “Multiple Chemical Information from the Thickness Shear Mode Acoustic Wave Sensor in the Liquid Phase”, Anal Chem. 65(1993) 1158. **Note:** The effects of viscosity, density and dielectric constant of a liquid on the response of a TSM bulk acoustic wave sensor are examined with respect to frequency response and the electrical properties of the equivalent circuit representation.

11. S. J. Martin et al., “Effect of Surface Roughness on the Response of Thickness-Shear Mode Resonators in Liquids”, Anal. Chem. 65(1993)2910. **Note:** The effect of surface microstructure on the response of the TSM resonator in contact with liquids was examined. Results show that, for roughness features much less than the liquid decay length, the surface may be considered hydrodynamically smooth and the response depends only on the density-viscosity product.


14. M. Rodahl, B. Kasemo et al., “Quartz Crystal microbalance setup for frequency and Q-factor measurements in gaseous and liquid environments”, Rev. Sci. Instrum. 66(7) (1995) 3924. **Note:** An experimental setup is reported that allows simultaneous measurement of frequency, Q-factor and amplitude of oscillation of a QCM.

15. Zuxuan Lin and Michael Ward, “The role of longitudinal waves in quartz crystal microbalance applications in liquids”, Anal. Chem. 67(1995) 685. **Note:** Important recommendations are presented to avoid the contributions of longitudinal waves to QCMs operated in liquids.


19. S. J. Martin, R. J. Huber et. al., “Resonator/Oscillator Response to Liquid Loading”, Anal. Chem. 69 (1997) 2050. Note: the effect of viscous liquid loading on a crystal is described based on the equivalent-circuit model. The model is carefully optimized to measure higher viscosity and higher density liquids with greater accuracy.

**Electrochemical QCM**

1. Bruckenstein S. and Shay M., “Experimental aspects of use of the quartz crystal microbalance in solution”, Electrochim. Acta 30(1985) 1295. Note: Includes a derivation of the “Boundary-Layer” derivation of frequency shifts in liquid solution which yields a result similar to that provided by Kanazawa and Gordon. A functional relationship between the frequency shift and the density and viscosity of the solution is derived. The mass sensitivity calibration of the QCM is verified experimentally.
10. S. J. Martin et. al. “Characterization of a Quartz Crystal Microbalance with Simultaneous Mass and Liquid Loading”, Anal. Chem. 63 (1991) 2272. Note: The electrical admittance of an AT-cut crystal QCM simultaneously loaded by a surface mass layer and a contacting Newtonian liquid is derived. With this model, changes in surface mass can be differentiated from changes in solution properties.
12. Buttry Daniel and Michael D. Ward, “Measurement of Interfacial Processes at Electrode Surfaces with the Electrochemical Quartz Crystal Microbalance”, Chem. Rev. 92(6)(1992) 1355-1379. Note: Excellent review article, with perhaps one of the most straightforward explanations of the piezoelectric effect and the equivalent electrical representation of AT-cut quartz crystal resonators. Everybody in the field must read this paper!
13. Wei-Wei Lee, Henry S. White and Michael Ward, “Depletion Layer Effects on the Response of the EQCM”, Anal. Chem. 65 (1993)3232. Note: This paper demonstrates the power of EQCM, showing the response of the EQCM to changes in density and viscosity at the depletion layer of a Fe(CN) reaction couple.
14. C. Wei et. al., “A combined Voltammetry and electrochemical quartz crystal microgravimetry study of the reduction of aqueous Se(IV) at gold”, J. Electroanal Chem. 375(1994) 109. Note: The EQCM is used to study a reaction mechanism.


25. Bund *, G. Schwitzgebel, “Investigations on metal depositions and dissolutions with an improved EQCMB based on quartz crystal impedance measurements” Electrochimica Acta 45 (2000) 3703–3710. Note: The frequency and damping changes of resonating quartz crystals in electrochemical experiments are measured at a time resolution of about 500 ms. The damping effects accompanying metal depositions and dissolutions (Ag and Cu) on polycrystalline Au electrodes of 6 and 10 MHz AT quartzes are studied and discussed in terms of roughness and sliding effects. Resistance measurement is not just useful for viscoelastic films.


**Calibration**


**Conductive Polymer Films**
1. D. Orata and Daniel Buttry, “Determination of Ion Populations and Solvent Content as Functions of Redox State and pH in Polyaniline”, J. Am. Chem. Soc. 109(1987) 3574. Note: The EQCM is used to investigate ion populations and solvent content of thin films of polyaniline on electrode surfaces as functions of redox state and pH. The ability to measure both electrochemical and gravimetric data simultaneously greatly simplifies modeling of this redox system.


3. Adrian W. Bott, “Characterization of Films Immobilized on an Electrode Surface Using the Electrochemical Quartz Crystal Microbalance” Current Separations, 18(3) (1999) 79. Note: The principles of the EQCM are discussed, together with some examples of its application in the study of electrodeposition and ion and solvent transport in redox active films.


11. A. L. Brisen, et. al.,”Quantification of dopant ions in polypyrrole films with electrochemical ICP-atomic emission spectrometry and comparison to electrochemical quartz crystal microbalance studies”, Analytica Chimica Acta 21292(2001) 1-12. Note: Anion ejection out of polypyrrole films was performed with electrochemistry combined with on-line ICP-AES and EQCM. The techniques all show to be complimentary for the understanding of the transport processes.

Chemical Sensors

2. W. H. King, “Piezoelectric Sorption Detector”, Anal. Chem. 36(1964) 1735. Note: this is the first report of an analytical application of QCM.
6. M. Tersea Gomes, et. al.,"Determination of Sulfur Dioxide in Wine Using a Quartz Crystal Microbalance”, Anal. Chem. 68(9) (1996) 1561. Note: A new method of analysis of both total and bound SO2 in wine is proposed, based on the QCM. Sulfur dioxide reduces Hg(II) ions in solution and the Hg(0) formed amalgams with the Au electrodes producing a frequency shift. The Hg(0) is easily driven off the crystals by heating.

**Biological/Biochemical Research**


**Phage detection**
3. Hengerer et. al., “Determination of Phage Antibody Affinities to Antigen by a Microbalance Sensor System”, BioTechniques 26 (1999) 956-964. Note: Antigen is immobilized on the QCM electrode and binding of the antibody is detected as a decrease in frequency. The technique is compared against SPR results.


Cell Adhesion


Adsorption

11. Makoto Muratsugu, et. al.,”Quartz Crystal Microbalance for the Detection of microgram quantities of Human Serum Albumin: Relationship between the frequency change and the mass of protein adsorbed”, Anal. Chem. 65 (1993) 2933. Note: This is a nice paper that shows the strict relationship between frequency shift and the amount of BSA or HAS adsorbed on a polished gold-coated QCM crystal.


14. F. Höök, M. Rodahl, P. Brzezinski and B. Kasemo, “Measurements Using the Quartz Crystal Microbalance Technique of Ferritin Monolayers on Methyl-Thiolated Gold:
17. Mjörn, K., Keller, C., Kasemo, B., and Elwing, H. "Protein repellent phospholipid bilayers at SiO2 surfaces for biosensor applications with Quartz Crystal Micro balance (QCM-D®) and surface plasmon resonance"(SPR)" Poster at Non-toxic control of marine biofouling, MASTEC-symposium Tjärnö 1998

**BioSensors**

4. Spangler, B.D., Wilkinson, E. A., and Murphy, J.,"Comparison of the Spreeta® surface plasmon resonance sensor and a quartz crystal microbalance for detection of Escherichia coli Heat-Labile Enterotoxin," J. Anal. Chim. Acta 444 , 149-161 (2001). Note: QCM and SPR technologies are compared against each other and also against ELISA testing. QCM is demonstrated to be more sensitive than SPR in this application.

**Immunosensors**


15. Yung-Chuan Liu, Chih-Ming Wang, Kuang-Pin Hsiung and Chienjin Huang, “Evaluation and application of conducting polymer entrapment on quartz crystal microbalance in flow injection immunoassay “, Biosensors and Bioelectronics, 18 (2003) 937. Note: this is also a great paper showing an example of a QCM interfaced to a sequential injection analysis system.

16. Ilaria Mannelli, Maria Minunni, Sara Tombelli and Marco Mascini, “Quartz crystal microbalance (QCM) affinity biosensor for genetically modified organisms (GMOs) detection “, Biosensors and Biotechnology, 18 (2003)129.


**DNA Sensors**


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**Self-Assembled Monolayers**


10. George M. Whitesides et. al., “Palladium as a substrate for SAMs used in Biotechnology”, Anal. Chem. 76 (2004) 6116-6121. Notes: No QCM was used here, but Whitesides is the father of SAMs and this is certainly an interesting alternative to Au as a substrate.

Thermal Analysis


Laser Ablation Studies


QCM/SPR Combination

1. Hengerer et. al., “Determination of Phage Antibody Affinities to Antigen by a Microbalance Sensor System”, BioTechniques 26 (1999) 956-964. Note: Antigen is immobilized on the QCM electrode and binding of the antibody is detected as a decrease in frequency. The technique is compared against SPR results.

2. Mjörn, K., Keller, C., Kasemo, B., and Elwing, H. "Protein repellent phospholipid bilayers at SiO2 surfaces for biosensor applications with Quartz Crystal Microbalance (QCM-D®) and surface plasmon resonance"(SPR)" Poster at Non-toxic control of marine biofouling, MASTEC-symposium Tjärnö 1998

3. Spangler, B.D., Wilkinson, E. A., and Murphy, J.,"Comparison of the Spreeta® surface plasmon resonance sensor and a quartz crystal microbalance for detection of Escherichia coli Heat-Labile Enterotoxin," J. Anal. Chim. Acta 444, 149-161 (2001). Note: QCM and SPR technologies are compared against each other and also against ELISA testing. QCM is demonstrated to be more sensitive than SPR in this application.
