

Welcome to the Spring 2009 QCM-D Training Workshop at The University of Kentucky

0

Quantifying Changes at Material Interfaces Using Dissipative Quartz Crystal Microbalance (QCM-D)

Mark Poggi, Ph.D., Archana Jaiswal, Ph.D., and Matthew Dixon, Ph.D.



Outline

- Brief Q-Sense History
- The QCM with the **Dissipation** monitoring principle.
- Applications
- Discussions
- Lunch! (Approx. Noon)
- Demonstration

Note: Quartz Crystal Microbalance = QCM

Who, What and Where?







Brief Q-Sense History

- **1995:** QCM-D patented
- **1996:** Q-Sense AB founded
- **1999:** Product development, prototype sales
- **2000:** Commercial focus, 1st generation product launched (D300)
- **2001:** US Subsidiary, Newport Beach, CA
- **2005:** Application Research Labs Established in MD.
- **2005:** 2nd Generation product launch, Q-Sense E4
- **2007:** E1 Product Launch, Module Launches (4)
- 2008: >500 Technical publications using QCM-D
- **2009:** Systems in 28 countries (~150 in North America)



Who uses QCM-D?

Academic/Government

- University of Illinois
- MIT
- EPA
- University of Kentucky
- USDA / EPA
- Georgia Tech
- Purdue University
- Lawrence Berkeley National Labs
- Virginia Tech (2)
- Max-Planck Institute

Industrial

- 3M
- Genentech
- BASF
- Kimberly Clark
- Medtronic
- Procter and Gamble (4)
- Rohm and Haas (2)
- Boston Scientific
- Amgen
- Unilever
- SC Johnson



Quartz is the only material known that possesses the following combination of properties:

- Piezoelectric ("pressure-electric"; piezein = to press, in Greek)
- Zero temperature coefficient cuts exist
- Stress compensated cut exists
- Low loss (i.e., high Q)
- Easy to process; low solubility in everything, under "normal" conditions, except the fluoride etchants; hard but not brittle
- Abundant in nature; easy to grow in large quantities, at low cost, and with relatively high purity and perfection. Of the man-grown single crystals, quartz, at ~3,000 tons per year, is second only to silicon in quantity grown (3 to 4 times as much Si is grown annually, as of 1997).







- Detection range in viscoelastic films: nm - μm

• Temperature Range 15-65° C; long term stability +/- 0.02° C

The QCM-D Sensor

Quartz

Gold Electrode





diam. 14mm

5MHz



Why is There a Notch in the Quartz Crystal?



Surfaces supplied by Q-Sense

Hard Model Surfaces available from Q-Sense:

- •Glass, ceramics (SiO2)
- •Plastics (PE, PP, PS and PVC)
- Stainless steel

On-Request Model Surfaces can be supplied by Q-Sense: Such as starch, grease/fat and many polymers



metals, oxides

SiO₂, Al₂O₃, Ti, Pt, Ag, W, Cu, Cr, Ir, Ta, FeC₃, TaN, CeO₂, Fe, Zn, ZnO₂, Fe₂O₃, ZnS, FeS, Stainless steel, ..., and custom made

polymers

PS, PC, PMMA, Fluoropolymer, PE, PP Users can coat with own polymers

hydroxyapatite

nanocrystalline, RMS ~2 nm

QCM-D ping principle: Teaching an Old Dog New Tricks



Instrument operation: Frequency and **Dissipation**

Features

•Sequential multi frequency measurement

•Freely oscillating crystal=true crystal frequency

•Enables multiple frequencies & viscoelastic modeling



The Quartz Crystal Microbalance with Dissipation monitoring (QCM-D) technique



Mathematical representation of the decay curve

 $A(t) = A_0 \cdot \exp(-t/\tau) \cdot \sin(2\pi f t + \phi)$

 $D=1/\pi f\tau$

Frequency change (Δf) : \Rightarrow adsorbed amount: $\Delta m = -C \cdot \Delta f$ (Sauerbrey equation)

Energy Dissipation (ΔD): \Rightarrow rigidity

Multiple frequency modeling: ⇒ shear viscosity and elasticity

Voinova et al., Physica Scripta 59 (1999) 391

The Q-Sense E4 System

www.q-sense.com



NSE

- 4 Sensors (simultaneous studies)
- Peltier Thermal Control
- 2 Weeks Learning time
- Flow / stagnant mode
- Wide range of chip coatings
- Parallel Modules

The E4 Measurement Chamber



QSENS

Examples of Experimental Design







4 Removable Flow Modules



- Volume above sensor 40 μL
- Minimum sample volume 200 μL
- Temperature 15-65 °C (± 0.02 °C)
- Programmable temperature ramping
- Easy access for cleaning

NSA



Cross section of flow module

The Q-Sense E-Series Modules

- •Standard Flow Module
- •Electrochemistry Cell
- •Window Module
- •Humidity Module
- •Open Module

OSE



QCM-D Technology Overview



Application Areas





Interactions

Molecule-molecule and molecule-surface •Small molecule-surface interactions

- Polyelectrolyte multilayer buildup
- Biomolecular interactions (Biofilm growth)
- •Protein deposition or fouling

Reactions or Structural Changes

- •Crosslinking events (polymers)
- Structural properties of materials/thin films
- Detergent activity
- •Conformation changes (receptor conformation)
- •Hydration/Swelling (polymers and other thin films)
- Degradation/Dissolution kinetics

Bulk Characterisation

•Viscoelastic properties of fluids (protein solutions, surfactants etc...)

Combined QCM-D and microscopy

New window module fits
under microscope

OSE

• Examples of applications: fluorescence, light or irradiation sensitive processes



QCM-D Technology Overview



So, What can QCM-D Measure?

Materials



Polyelectrolyte Multilayers



Caruso et al. Chem. Mater. 2005, 17, 171-175





Anti-fouling Development

Developing tailored materials 700 Cu²⁺-PVM_{21nm} - controlled uptake 600 - controlled release 500 **Medetomidine Medetomidine** Uptake Release ∆m (ng/cm²) 400 Water 300 200 Polymer (w/ Nanoparticles) 100 Crystal 0 Medetomidine 15 20 25 -5 0 10 30 5 Time (min)

Fant et al. J. Phys. Chem B. (2006).

Cooperative Adsorption of Functionalized Nanoparticles onto Silica



- Single functionalized particle-type will NOT assemble.

- When functionalized NPs are mixed with oppositely charged functionalized NPs... assembly DOES occur!

S. Smoukov et al., J. AM. CHEM. SOC. 2007, 129, 15623-15630 (2007)

Adsorption of Functionalized Nanoparticles onto Silica (cont)



Coating density impacted by immersion?

Using QCM-D to Follow the Adsorption of Functionalized Nanoparticles onto Silica



Adsorption Rate of Deposition as Determined with QCM-D

Concentratio n of 1:1 AuAg nanoparticles	Adsorption rate (Hz/min) (ng cm ⁻² min ⁻¹)			
	Initial flow mode	Stagnant mode	Average rate for first saturation	Flow over the adsorbed layer
50 µg/ml	(14.2) <mark>(251)</mark>	(1.4) <mark>(25)</mark>	(2.57) <mark>(45.5)</mark>	(3.7) <mark>(62)</mark>
150 µg/ml	(23.5) <mark>(416)</mark>	(2.1) <mark>(37)</mark>	(3.7) <mark>(65)</mark>	(0.4) <mark>(7.1)</mark>
400 µg/ml	(23) <mark>(407)</mark>	(2.2) <mark>(39)</mark>	(3.7) <mark>(65)</mark>	(0.3) <mark>(5.3)</mark>



M.A. Poggi et. al, J. Phys. Chem. C. submitted (2008)

So, What can QCM-D Measure?

Biological



Single Mismatch Detection During PNA (15-mer) and DNA (15-mer) Hybridization



Adsorption and Cross-linking of Polymers



	Measured	Prior to	After cross-
	parameter	cross-linking	linking
QCM-D	∆m, sauerbrey, n=3 (ng / cm²)	1168	730
	Thickness, sauerbrey n=3 (nm)	11.3	6.9
	Thickness, modelling (nm)	22.4	7.3
	Viscosity (e-3 N s m ⁻²)	1.8	6
	Elasticity (e4 N m ⁻²)	6.6	30
ELM	∆m (ng / cm²)	135	130
	Thickness (nm)	21	5
	Refractive index	1.35	1.40

Fant, C & Höök, F; Anal. Chem. (2001), 73, 5796-5804

Fibrinogen Adsorbed to the Surface of Biopolymers





Water

Weber et al. Langmuir 2007, 23, 3298-3304
Fibrinogen adsorption (cont.)



Weber et al. Langmuir 2007, 23, 3298-3304

Rapid Screening of Protein Adsorption onto Different Surface Chemistries



gsense



Surface mass density quantified at different stages of fibrillation.

Hovgaard et al. *Biophysical Journal*, 93, 2162-2169, **2007** T.P.J. Knowles et al. *PNAS*, 104, 10016-10021, **2007**





Bone Stem Cells on Ta & Cr Surfaces



Cell attachment stronger and more spread on Ta surface then Cr

Modin et al. Biomaterials 27 (2006) 1346–1354

Monitoring/Quantifying the Formation of Biofilms (cont.)

Fluorescence Microscopy





Bacteria: Leuconostoc mesenteroides Surface: Steel

H. Green Q-Sense AB. 2004.

Monitoring/Quantifying the Formation of Biofilms (cont.)



Monitoring/Quantifying the Formation of Biofilms (cont.)





Outline

- Measurement requirements
- Surfaces
- Cleaning protocols
- Sample preparation
- Tech Tips



QCM-D Experiment Planning S.S.I

Surface

What type of surface? How will I clean/prepare the surface?

Samples

What buffer (solvent)? Which concentration(s)? What Temperature? Do I need to degas my samples?

Instrument

How do I cleaning/prepare the instrument? What liquid path am I going to use? What about solvent compatibility? Flow rate/Batch mode?





Methods & Protocols



Collection of preparation and cleaning methods for surfaces and instrument



Wide Range of Crystal Surfaces

Metals & Metal Oxides

>Au, SiO₂, Al₂O₃, Ti, Stainless steel, Pt

>Ag, W, Cu, Cr, Ir, Ta, FeC_{3} , TaN, CeO_{2} , Fe, Zn, ZrO_{2} , SiOC, Iron oxide, $Si_{3}N_{4}$ etc

>Other coatings can be made on request

Unique Inorganic Coating

Hydroxyapatite (nanocrystalline, RMS roughness ~2-3 nm)

Spin Coated Polymers

>In stock: Polystyrene

Other polymers on request Examples: PC, PMMA, PP, PE, PVC

Users can coat sensors with their own polymers/materials

> Polymer Gold

Quartz Sensor crystal



Surfaces - Polymeric



Other methods •Surface attached polymerization



Surfaces – Specific Chemistry



•SLB NTA modified surface for His linkeage Protocol



•Biotin immobilization surface Protocol





Chemical Treatment, APM, TL1



Surface: gold

Deposits: lipids, thiols, proteins in molecular layers

Method:

- UVO-treatment (10 min)
- Heat 5:1:1-mixture of mQ-water, ammonia (25%) and hydrogen peroxide (30%) to 75°C
- •Immerse sensors in solution using a cleaning holder (5 min)
- •Clean tweezer in the same beaker
- Rinse in mQ-water, dry with N₂
- UVO-treatment (10 min)

W. Kern et al., RCA Review 31 (1970) 187

Cleaning Surfaces – UVO-Treatment



Sensors Dry and Dust Free

Rinse washing solution off



Keep tweezer below sensor

Dry with a clean gas





Never use compressed air!



QCM-D Experiment Planning S.S.I Surface

What type of surface? How will I clean it?



Pure Samples

<u>Water:</u> 18,3 MΩ MilliQ

Buffers: Prepare your own buffers, do not trust the "kitchen"!



? - Water, PBS, HEPES, MES, ACETAT,

sterile≠clean



Concentrations



Bulk effects – "Buffer step"



Effect:

offset in baseline of *f* and *D* when changing solution

Cause:

bulk properties - *density* & *viscosity* influence *f* and *D*



T Response of Our QCM-D



- E4 has T control +/- 0.02 °C
- D300 has T control +/- 0.03 °C

Zelenka, J. Piezoelectric Resonators and their Applications; Elsevier: Amsterdam-Oxford-New York-Tokyo, **1986;** Chapter 6.

P Response of Our QCM-D

 $\Delta f = -C_P \Delta P$ $C_P = \text{ constant independent of nature of gas in torr}$ $= 1 \times 10^{-9} * f_0$ $f_0 = \text{ fundamental frequency}$

For a 5 MHz crystal with ΔP = 760 torr Δf = - 3.8 Hz

Stockbridge, C. D. In *Vacuum Microbalance Techniques;* Behmdt, K. H., ~ Ed.; Plenum Press: New York, **1966**; Vol. 5, p 147.

Degas Samples



Origin • Buffer

Hydrophobic surfaces more problematic!

Degassing samples

Sonicator

OSE

• Heat (T_{sample}>T_{instrument})

QCM-D Experiment Planning S.S.I



PBS



What type of surface? How will I clean it?



What buffer (solvent)? Which concentration(s)? Temperature? Degassing



Instrument Cleaning

<u>Cleaning solutions:</u> Hellmanex II SDS 2% Roche cleaner

Always end with a water rinse and store chamber dry!

Replace rubber parts when worn out or every year.



Cross section of flow module

Clean the instrument before and after every experiment !!

Liquid Path (E4)



 \bigcirc

serial

gsei

2 by 2 serial

Solvent Combatibility



Check Appendix – Chemical Compatibility Chart!

Mass Transport Limitations



qsense

Summary





What type of surface? How will I clean it?

Samples >

What buffer (solvent)? Which concentration(s)? Temperature? Degassing



Cleaning Liquid path Solvent compatibility Flow rate

Measurement Time Line



Tech Tips

- Always start in blank (buffer, water etc)
- Avoid difference in bulk properties
- Bubble = trouble
- Do your own sample preparation!



Thank you for your attention!

Software Primer


Raw Data of Demo experiments

Modules 1 and 2: lard removal by two different commercially available surfactants Modules 3 and 4: surfactant adsorption from Millipore (3) and tap (4) water



Example Modeled Data of Module 1

Blue lines = frequency Red lines = dissipation Black symbols are the fits



Module 1 Modeled Thickness (red) and Viscosity (green)







QTools Software

Q-Sense Adapted Graphics and Plots

Fully exportable and customizable

- Sauerbrey thickness δ
- Models (Voight & Maxwell) thickness δ , shear viscosity η , and a shear elasticity μ
- Kinetics K_{off} , K_A , and K_{on}

QTools Software

Theoretical Modeling of the QCM-D Response (Viscoelastic Modeling)

 $\Delta f = f_1(n, \eta_f, \rho_f, \mu_f, \delta_f)$ $\Delta D = f_2(n, \eta_f, \rho_f, \mu_f, \delta_f)$

 ρ : density, (kg/m3)

 η : viscosity (G''/ ω), (kg/ms)

 μ : elasticity (G'), (Pa)

 δ : thickness, (m)





Voinova et al., Physica Scripta 59 (1999) 391

Information extracted from modeling (15 & 25 MHz)



Concluding Remarks

- QCM-D provides <u>not only</u> mass changes but also viscoelastic properties of chemical systems.
- Real-time, sensitive technique
- Surface interaction/reaction
- QCM-D provides the ability to <u>quantify</u>



The Q-Sense QCM-D Solution





Education & Training

	E E
Barren are	
	Strength Color

Turn key QCM-D system

Q-Sense E4

Advanced Modeling software



Data evaluation support



Annual User Meetings

User's 28 Countries

qsense

Thank You!

Mark A. Poggi, Ph.D. Territory Manager **Q-Sense, Inc** 808 Landmark Drive, Suite 124 Glen Burnie, MD 21061

Direct #: 404-863-4257 Office #: 877-773-6730 E-mail: Mark.Poggi@q-sense.com

Demo experiment polymeric adsorption on metallic surfaces

Objective

To demonstrate adsorption of a water soluble polymer: Diethylaminoethyl-Dextran to different surfaces.

Materials

- •Au, SiO₂, PS and Al₂O₃ crystals
- •PBS Buffer pH 7.4 150 mM NaCl (Sigma)
- •DEAE Dextran (50 µg/ml in PBS)