



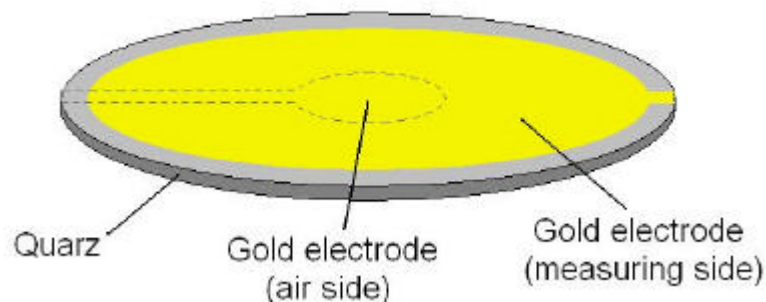
WHAT IS A QUARTZ CRYSTAL MICROBALANCE – QCM

Pierre and Marie Curie showed in 1880 that crystals of Rochelle salt could produce electricity when pressure was applied in certain crystallographic directions. Later they also showed the converse effect i.e. production of strain by application of electricity. These findings were the discovery of the piezoelectric effect. Piezoelectricity did not receive lot of interest in the beginning and a more detailed study of piezoelectricity was not started until 1917 when it was showed that quartz crystals could be used as transducers and receivers of ultrasound in water. In 1919 several devices of everyday interest based on the piezoelectricity of Rochelle salt was described i.e. loudspeakers, microphones and sound pick-ups. In 1921 the first quartz crystal controlled oscillator was described. These first quartz crystal controlled oscillators were based on X-cut crystals, which have the drawback of being very temperature sensitive. Therefore, the X-cut crystals are nowadays used in applications where the large temperature coefficient is of little importance, such as transducers in space sonars.

The dominance of the quartz crystal for all kind of frequency control applications started in 1934 when the AT-cut quartz crystal was introduced. The advantage with the AT-cut quartz crystal is that it has nearly zero frequency drift with temperature around room temperature. From the very beginning of using quartz crystal resonators as frequency control elements it was common to increase the frequency of the resonator by drawing pencil marks on the electrodes, or decreasing the frequency by rubbing of some electrode material with an eraser. The understanding of this mass induced frequency shift was only known on a qualitative basis. However, in 1959 Sauerbrey published a paper that showed that the frequency shift of a quartz crystal resonator is directly proportional to the added mass. Sauerbrey's work is generally taken as the breakthrough and the first step towards a new quantitative tool to measure very small masses i.e. the quartz crystal microbalance.

Hence, one can describe the QCM to be an ultra-sensitive mass sensor. The heart of the QCM is the piezoelectric AT-cut quartz crystal sandwiched between a pair of electrodes. When the electrodes are connected to an oscillator and an AC voltage is applied over the electrodes the quartz crystal starts to oscillate at its resonance frequency due to the piezoelectric effect (see figure below). This oscillation is generally very stable due to the high quality of the oscillation (high Q factor).

Quartz crystal - The heart of the QCM





If a rigid layer is evenly deposited on one or both of the electrodes the resonant frequency will decrease proportionally to the mass of the adsorbed layer according to the Sauerbrey equation:

$$\Delta f = -[2 \times f_0^2 \times \Delta m] / [A \times (\rho_q \mu_q)^{1/2}], \text{ where}$$

Δf = measured frequency shift,

f_0 = resonant frequency of the fundamental mode of the crystal,

Δm = mass change per unit area (g/cm^2),

A = piezo-electrically active area,

ρ_q = density of quartz, $2.648 \text{ g}/\text{cm}^3$,

μ_q = shear modulus of quartz, $2.947 \times 10^{11} \text{ g}/\text{cm} \times \text{s}^2$.

There are situations where the Sauerbrey equation does not hold, for example, when the added mass is a) not rigidly deposited on the electrode surface(s), b) slips on the surface or c) not deposited evenly on the electrode(s). Therefore, the Sauerbrey equation is only strictly applicable to uniform, rigid, thin-film deposits. Due to this the QCM was for many years just regarded as a gas-phase mass detector. Not until the beginning of 1980's scientists realized that a quartz crystal can be excited to a stable oscillation when it was completely immersed in a liquid. Much of the pioneering work in liquid phase QCM measurements have been done by Kanazawa and co-workers, who showed that the change in resonant frequency of a QCM taken from air into a liquid is proportional to the square root of the liquid's density-viscosity product:

$$\Delta f = -f_u^{2/3} [(\rho_L \eta_L) / (\pi \times (\rho_q \mu_q))]^{1/2}, \text{ where}$$

Δf = measured frequency shift,

f_u = resonant frequency of the unloaded crystal,

ρ_L = density of liquid in contact with the crystal,

η_L = viscosity of liquid in contact with the crystal,

ρ_q = density of quartz, $2.648 \text{ g}/\text{cm}^3$,

μ_q = shear modulus of quartz, $2.947 \times 10^{11} \text{ g}/\text{cm} \times \text{s}^2$.

After it was found out that an excessive viscous loading would not prohibit use of the QCM in liquids and that the response of the QCM is still extremely sensitive to mass changes at the solid-liquid QCMs have been used in direct contact with liquids and/or visco-elastic films to assess changes in mass and visco-elastic properties. Even in air or vacuum, where the damping of layers has been considered to be negligible or small the QCM has been used to probe dissipative processes on the quartz crystal. This is especially true for soft condensed matters such as thick polymer layers deposited on the quartz surface.



APPLICATIONS OF QCM

The QCM is basically a mass sensing device with the ability to measure very small mass changes on a quartz crystal resonator in real-time. The sensitivity of the QCM is approximately 100 times higher than an electronic fine balance with a sensitivity of 0.1 μg . This means that QCM's are capable of measuring mass changes as small as a fraction of a monolayer or single layer of atoms. The high sensitivity and the real-time monitoring of mass changes on the sensor crystal make QCM a very attractive technique for a large range of applications. Especially, the development of QCM systems for use in fluids or with visco-elastic deposits has dramatically increased the interest towards this technique. Major advantages of the QCM technique used for liquid systems are that it allows a label-free detection of molecules. A partial list of the application areas of the QCM is shown below, and it seems that the application areas are only limited by your imagination.

- Thin Film thickness monitoring in thermal, e-beam, sputtering, magnetron, ion and laser deposition.
- Electrochemistry of interfacial processes at electrode surfaces
- Biotechnology
 - Interactions of DNA and RNA with complementary strands
 - Specific recognition of protein ligands by immobilized receptors, immunological reactions
 - Detection of virus capsids, bacteria, mammalian cells
 - Adhesion of cells, liposomes and proteins
 - Biocompatibility of surfaces
 - Formation and prevention of formation of biofilms
- Functionalized surfaces
 - Creation of selective surfaces
 - Lipid membranes
 - Polymer coatings
 - Reactive surfaces
 - Gas sensors
 - Immunosensors
- Thin film formation
 - Langmuir and Langmuir-Blodgett films
 - Self-assembled monolayers
 - Polyelectrolyte adsorption
 - Spin coating
 - Bilayer formation
 - Adsorbed monolayers
- Surfactant research
 - Surfactant interactions with surfaces
 - Effectiveness of surfactants



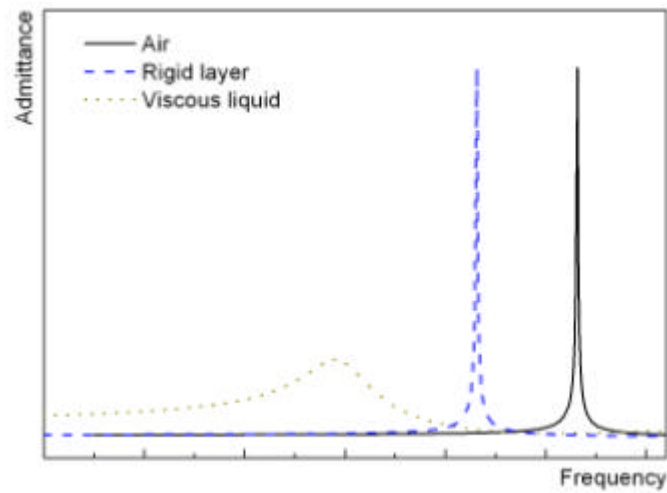
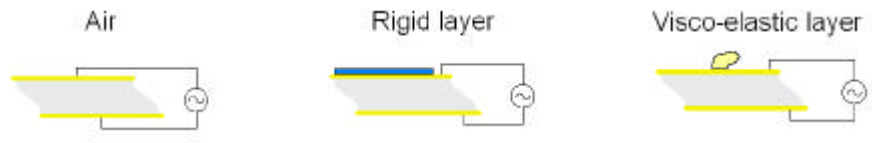
- Drug Research
 - Dissolution of polymer coatings
 - Molecular interaction of drugs
 - Cell response to pharmacological substances
 - Drug delivery
- Liquid Plating & Etching
- In situ monitoring of lubricant and petroleum properties

WORKING PRINCIPLE OF KSV-QCM500

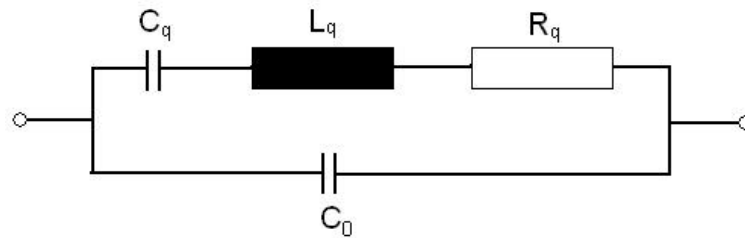
The KSV-QCM500 measuring principle is based on impedance analysis of the quartz crystal. In this measuring principle the quartz crystal is not resonating all the time, but the crystal is swept with potential perturbations with different frequencies close to the quartz crystals resonant frequency and the potential (U) over the crystal and the electricity (I) flowing through the crystal are recorded. The ratio of U and I then gives the Impedance (Z), and the result of the sweep is the so-called Impedance curve (the inverse curve is called Admittance). The Impedance or Admittance curve holds all the information concerning the properties of the quartz crystal and the layer deposited on the crystal (see figure 2 a). This sweep can be done as a function of time, which enables either the measurement of mass changes happening at the quartz crystal electrode surface or only once in steady state case studies. Normally an equivalent circuit model shown in figure 2b is fitted to this curve and the obtained parameters can be used for calculating the resonant frequency and quality factor (Q) or dissipation (D) of the quartz crystal i.e. masses and visco-elastic properties of the deposited layers. Shortly, one can say that the frequency of the crystal is where the admittance peak has its maximum, whereas the broader and lower the admittance peak is the lower the Q -value and more dissipation is taking place. Figure 2a also shows how the Admittance curve is affected by a rigidly deposited layer or a viscous liquid. Furthermore, the KSV-QCM500 can measure different harmonics of the quartz crystal, which gives additional value for determining visco-elastic coefficients of the coating.

In most cases quartz resonators are integrated to oscillator circuits to form a QCM for microweighing applications. While this is a cheap and convenient way of determining only resonance frequencies of quartz crystals, it will not give any information about the quality of the resonance (Q value) which on the other hand would help for visco-elastic analysis. The advantages of determining the Impedance or Admittance curve are:

- Both Frequency (f) and quality of resonance (Q factor) or dissipation are accessible
- Different harmonics can be sequentially be measured
- Undesired anomalies including scewed resonance curves or distorted resonances due to the interference of anharmonic sidebands are directly detected



a)



b)

Figure 2. a) Admittance curve for different overlayers on the quartz crystal electrodes, b) Equivalent circuit model for determining f and Q of the quartz crystal.

KSV-QCM500 FEATURES AND SPECIFICATIONS



- Impedance analysis, high sensitivity
- Gas and liquid phase measurements
- Direct measurements at air/water interfaces
- Continuous flow measurements
- Crystals easily mounted in measuring chamber or crystal holder
- Flexible choice of surfaces
- Not fixed to any resonant frequency, crystals in the range
- 3-50 MHz can be used
- Multi-frequency and temperature controlled measurements
- Mass and viscoelastic parameters simultaneously
- Real time measurements (seconds)
- Easy to use Windows based software
- Straightforward operation
- Mass sensitivity (5 MHz crystal)
 - $\sim 1 \text{ ng/cm}^2$ in air/gas
 - $\sim 5 \text{ ng/cm}^2$ in liquid
- D-factor sensitivity
 - $\sim 2 \times 10^{-8}$ in air
 - $\sim 3 \times 10^{-8}$ in liquid
- Max film thickness $\sim 5 \mu\text{m}$
- Active sensor area $\sim 20 \text{ mm}^2$
- Frequency range 3-50 MHz



EXAMPLE MEASUREMENTS MADE WITH THE QCM-Z500

Response of the QCM-Z500 to solutions containing different w-% of glycerol

As the QCM-Z500 uses impedance analysis it is highly suitable for operation under heavy viscous loading. The standard Measuring chamber supports operation in gas and liquid environments, and provides single-electrode exposure to liquids, which also is a prerequisite for compatibility with electrochemical QCM measurements. Figure 3 shows the frequency change of polished, gold coated 5 and 10 MHz crystals in contact with different glycerol solutions measured with the QCM-Z500. The tight correspondence between theory and experiment is clearly illustrated. Figure 4 on the other hand shows the Admittance Phase and Admittance Magnitude of a polished, gold coated 10 MHz crystal from which the data in Figure 3 was calculated. The results prove that the QCM-Z500 is an excellent tool for the evaluation of fluid properties.

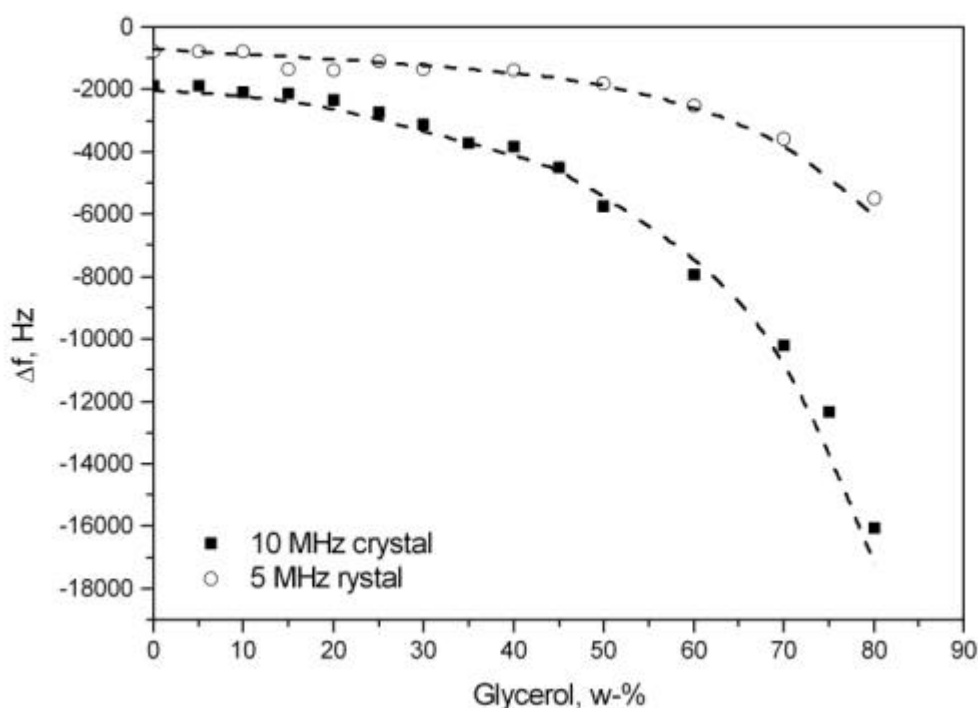


Figure 3. Δf versus glycerol weight percentage (in water) as measured with the QCM-Z500 (circles and squares) and predicted by theory (dashed lines) for two different quartz crystals with different fundamental resonance frequency.

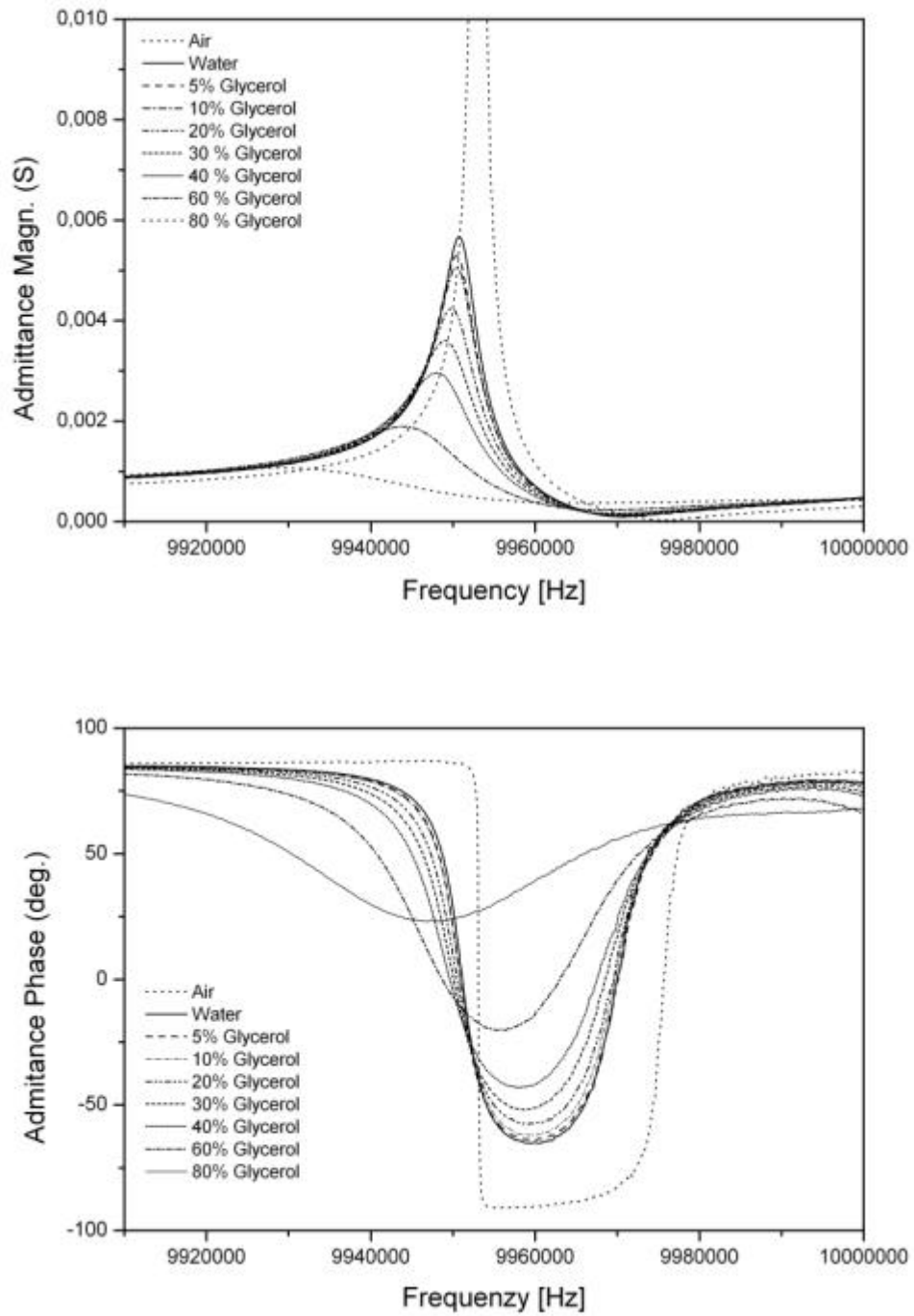


Figure 4. Admittance Magnitude and Admittance Phase of a polished, gold coated 10 MHz crystal in contact with different glycerol solutions measured with the QCM-Z500.

Protein adsorption studied with the QCM-Z500

Anything that has mass can generate a response from a QCM sensor. The universal response of the device is the reason for the wide range of application of the technology. The use of QCM has dramatically increased in recent years in the field of biotechnology. The QCM is routinely used to obtain information about for example protein adsorption/desorption, cell adhesion, protein-protein interaction, Degradation of polymers, biofouling and biofilm formation, drug analysis and DNA Biosensors.

Figure 5 show measurements adsorption of the protein Human Serum Albumin (HSA) to 5 MHz quartz crystals treated to have different properties. Measurements were performed with the QCM-Z500 standard measuring chamber. The frequency changes of 83, 39 and 36 Hz for the Hydrofobic Au, Hydrofilic Au and LB layer surfaces is in good agreement with a protein adsorption study to differently treated silica made with an in situ ellipsometer (reference 17). Table 1 shows the comparison between our results with the QCM-Z500 and the ellipsometer study. The tight correspondence between the results is clearly illustrated by table 1.

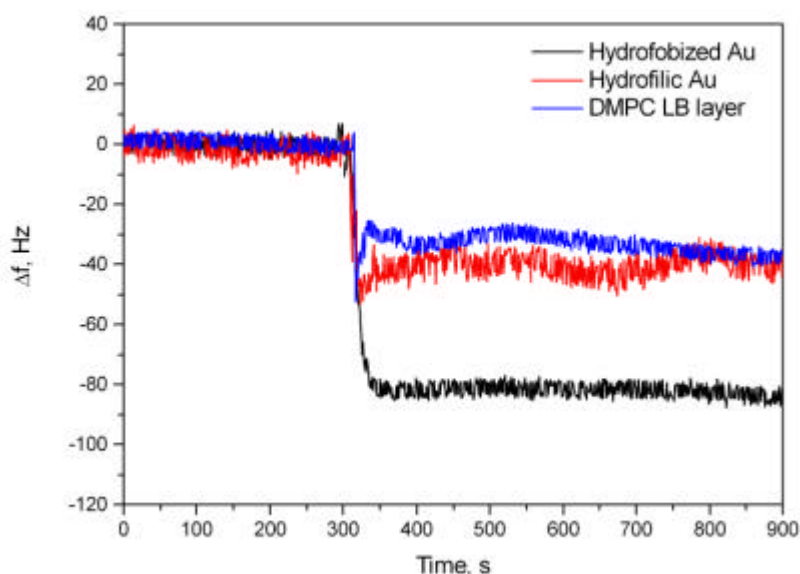


Figure 5. Frequency changes during adsorption of HSA to 5 MHz crystals with different properties.

Table 1. Adsorbed amounts of HSA at different surfaces.

Surface	Adsorbed amounts of HSA determined with QCM-Z500	Adsorbed amounts of HSA from reference 17
Hydrofobic	0.73 mg/m ²	0.80 mg/m ²
Hydrofilic	0.34 mg/m ²	0.35 mg/m ²
PC LB layer	0.32 mg/m ²	0.30 mg/m ²



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