

Mathematical Modeling of Mass Change in Biosensor Quartz Crystal Microbalance Using Matlab

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Abstract: The usage of quartz crystal resonators in different fields has developed remarkably. Even though the usage of a quartz crystal microbalance (QCM) dating back to fifties, the current attention is focusing on the liquid state applications. Broadly-based on Kanazawa's paradigmatic treatment, this investigation confers an emulation model to the hypothesis of the loaded QCM utilizing dissimilar bulk films on its superficies and submerged in a solution.

The correlation between the variation in sonorous frequency and the mass of particles adhesive on the surface of the QCM is the heart of the transferal procedure of genetic material from one organism to another in piezoelectric biosensors.

Particularly, electrical characteristics, such as phase angle, admittance and the sonorous frequency of loaded and unloaded QCM, are imitated by Matlab program. This data-package calculates the admittance band of a fluctuating QCM layered with a superlattice mass and that of a fluctuating QCM layered with a film of a specified solid to reach at a modification factor as a function of layer height. Accordingly, the loaded QCM can be utilized as a biosensor, and the modification to the Sauerbrey equation is not as much of ~3% for the polystyrene layer up to a height of ~15 μm . The simulation results are in excellent agreement with available experimental data.

Keywords: AT-Cut Quartz Crystals, QCM, Sauerbrey Equation, Mass Change, Matlab Program

1. Introduction

In general, a quartz crystal microbalance (QCM) is a mass detecting apparatus, able to calculate mass variations analogues to the formation of a monolayer. The QCM is relying upon the converse piezoelectric influence, originally invented by brothers Curie, where a mechanical stress in a quartz crystal is persuaded by the request of a potential difference (Cerda, 2014). The QCM is comprised of a tinny quartz wafer squeezed between two identical metal disks, attached to an oscillator circuit. AT-cut quartz crystals are commonly utilized due to their frequency steadiness as a function of temperature. Once an alternating potential is utilized perpendicularly on the crystal surface, a shear stress is induced in the crystal, and the atomic dislocation of quartz happens in the direction parallel to its surface. The shear vibration results in acoustic waves travelling perpendicular to the surface. After the extra mass is uniformly added on top of the QCM, the width of the QCM changes and a

variation in the resonance frequency is noticed. If the added mass is beneath ~2 % of the mass of the QCM, there is a direct correspondence amongst the change in frequency (Δf) and change in mass (Δm), and this is known as Sauerbrey equation (Sauerbrey, 1959).

Owing to its high sensitivity, the usage of QCM is progressively increasing, finding usages in physics, chemistry, engineering, medicine and others fields (Arnau, 2008). The history and initial applications of QCM can be found in the exceptional book by Lu and Czanderna (2012).

Initially, it was understood that the QCM could not be utilized in liquids since the energy loss would be noticeably large and the quartz crystal would stop to oscillate (Janata, 2010). Initial work by Konash and Bastiaans demonstrated that the oscillations of the quartz crystal will be stable only when one face of the QCM is in touch with the solution (Konash & Bastiaans, 1980). Nomura et al. were the first to effectively utilize the QCM to measure mass changes, accompanying with the electrodeposition of Ag (Nomura & Iijima, 1981).

Bruckenstein *et al.* also described the use of QCM to study mass changes due to the electrodeposition of Pb and Ag in acetonitrile solution (Bruckenstein & Swathirajan, 1985). Later, Schumacher *et al.* indicated that electrochemical oxidation/reduction cycles of a metal electrode caused in a rougher surface, and extra mass change between cycles was detected due to oxygen and trapped liquid on the rough surface (Schumacher, Borges & Kanazawa, 1985). Barzinjy and Zankana (2016) showed that the QCM micro-viscometer has the advantage over most other techniques of viscometry not in its accuracy of absolute viscosity measurement but in the very tiny quantity of sample liquid required for assessment. Meanwhile, these pioneering works, the use of QCM, as a working electrode, provides mass information in addition to electrochemical data, allowing scientists to study more complex systems. For instance, when there are two types of reactions: faradaic and non-faradaic. The former is a charge-transfer reaction; an electron is transferred across the solution-electrode interface. The latter happens without electrons being transferred but may involve the adsorption of electrolyte on an electrode. The consequences can be understood given knowledge of all electro-active species involved (Otero, 2015).

In most of these processes, there is a heat producing or absorbing, the thin film earns or mislay mass, the viscoelastic possessions of the compact film vary, and the characteristics preferred might be improved or damaged. QCM was settled to study these processes in thin films (Johannsmann, 2014). Rheological calculations of shear and injury modulus are typically prepared at small frequency on bulky samples with active automatic investigation arrangement. The QCM calorimeter concurrently calculate heat generating, mass adding or releasing, and viscoelastic feature alters in the similar, sub milligram compact film example once gases act together through the film in an isothermal environment. Additionally, the QCM is a novel technique adept of computing mass alteration at a surface concurrently through extraordinary accuracy. The quartz crystal microbalance possess an identical oversensitive sensor: for instance a 5MHz AT-cut quartz crystal microbalance, which computes mass changing in the Nano-gram ranges (Smith & Shirazi, 2005).

A biosensor, on the other hand, is well-defined as an extraordinary amalgamation of a receiver for identifying molecular and an adapter for assigning the transactions data keen on an electrical pointer (Nikolelis et al., 2013). Sequentially, an adapter is more accurately known as a tool for altering energy from one pattern to additional one for the aim of determining of a physical amount or for data transference. Theoretically, there are numerous devices that can be utilized in bio-sensing: thermal capability and heat transmission, acoustic waves, neutrons, photons, ions, radio-emitting particles, electrons, electric fields and magnetic fields. Practically, greatest investigative stages, in the frequent

usage, nowadays utilize optics, with only insufficient of the additional original adaptor modalities possessing conversion starting from theoretical tool examples to healthy profitable medium.

QCMs have been utilized widely for protein identifying (Whitcombe et al., 2011). Adaptation of quartz crystal microbalance face with numerous polymers similar to polyurethane (PU), polyethylene-amine (PEA), and polystyrene (PS) have been formerly investigated (Rodoplu, Sen & Mutlu, 2013). Polystyrene (Figure 1) is an actual communal polymer with a great treating aptitude as a result of its solubility in the maximum number of the carbon-based diluents. The Young's parameter, for example, of Polystyrene is $\sim 3\text{GPa}$ equally associated with $\sim 3\text{MPa}$ of polyurethane(PU) (LeSar, 2013). Because of this extraordinary mechanical strong point, no substantial viscoelastic combination possessions are detected amongst Polystyrene (PS) and the QCM.

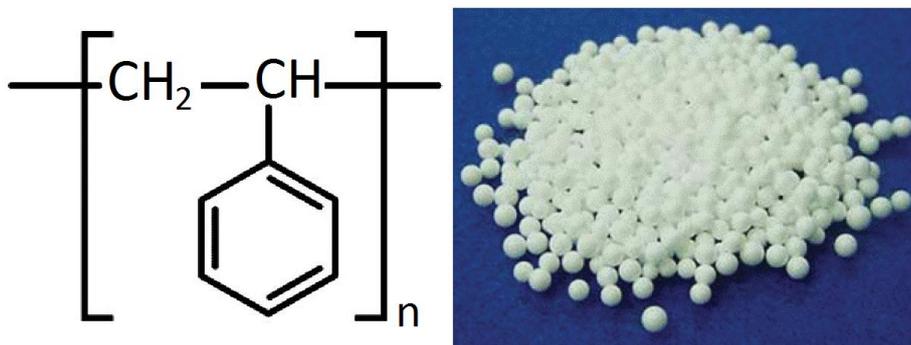


Figure 1: Repeat unit for polystyrene

In this study, the QCM surface is theoretically adjusted with polystyrene, which can be fundamentally preserved with a UV/O₃ procedure to reduce it hydrophilic. This investigation also sensibly examines the essential state of affairs to form a thickly filled film layer entirely covering the QCM upper gold surface. This biosensor then can be utilized to compute antibody binding that is precise to the immobilized credit peptide. Antibody categorized with bovine serum albumin (BSA), enzyme can bound to the polystyrene surface through physical adsorption, thus polystyrene is used as QCM biosensor. The superior of this biosensor among other biosensors is it could be regenerated after usage. For this reason, a process in the arrangement of a Matlab program developed in order to regulate the modification to the Sauerbrey correlation based on Kanazawa's exemplary case (Kanazawa & Gordon, 1985). The multifaceted shear modulus of a solvent, described by Katz and Ward (1996) utilized for one illustration of this exemplary case.

2. Theory

The QCM comprise a tinny AT-cut quartz-crystal flanked by two vacuum deposited electrodes (Figure 2) (Rodriguez-Pardo et al., 2007). Numerous diverse electrode materials such as Au, Pt, Cu and Ni could be utilized on upper side of the quartz disc. The utmost widely used is Au because of its comfort of producing and extensive applications. As a result of the piezoelectric characteristics and crystalline alignment of the quartz, a potential utilized for these probes causes a crystal shear disfigurement.

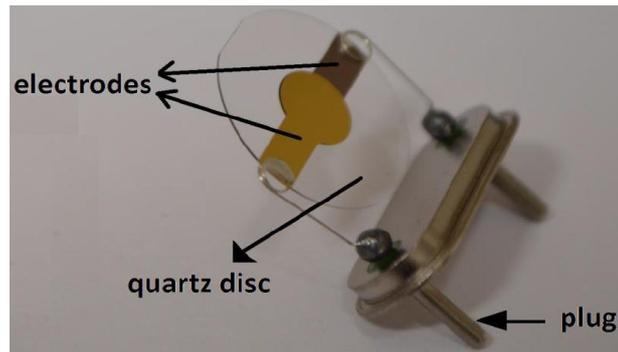


Figure 2: AT-cut QCM, upper and lower faces of the quartz possess Au electrodes

The original resonant frequency f_o of the bare QCM is specified by:

$$f_o = \frac{v_q}{2d} \quad (1)$$

where the thickness of the quartz crystal is d and the speed of the aural wave prevalence in quartz is v_q . Principally, Sauerbrey (1959) indicated that the variation of frequency produced via an adding mass on that resonator is offered by:

$$\frac{\Delta f_o}{\Delta m} = - \frac{2f_o^2}{A\sqrt{\rho_q\mu_q}} \quad (2)$$

which points toward that the resonant frequency change, *i.e.* Δf_o , regarding the mass change (Δm) is related to the f_o^2 and contrariwise related to the area of electrode, *i.e.* A . Meaning that, greater resonant frequency and minor electrode area, will produce a greater sensibility. Sauerbrey's equation is protracted for usage with adaptable films by Miller and Bolef (1968) and streamlined by Lu and Lewis (1972). Till now, extreme dense loading was thought to forbid the usage of the quartz crystal in solutions. This is more likely, and the reply of the quartz crystal is serviceable to changes in mass at the solid-solution crossing point. Once the quartz crystals microbalance runs inside a liquid, the viscosity and the density of the liquid both affects the resonance frequency of the QCM, hence it will be reduced. This issue originally investigated by Kanazawa and Gordon in 1985. They indicated that the crystal resonance frequency is affected by the liquid characteristics and hence the resonance frequency shift is represented by:

$$\Delta f_o = -f_o^{3/2} \sqrt{\frac{\eta_l \rho_l}{\pi \eta_q \mu_q}} \quad (3)$$

where η_l , is the viscosity and ρ_l is the density of liquid that the QCM electrode immersed in it and η_q , μ_q are the viscosity and density of the quartz respectively. Thus, one can state that the frequency shift can be calculated and it can be changed by changing the viscosity and the density of the investigated liquid. Moreover, once the quartz crystal runs in a liquid-phase media, the extreme shift change can happens on the QCM surface. Thus, these increase the sensitivity of the QCM and can respond to very small additional mass efficiently. This response makes quartz crystal to be a good candidate for biosensor applications, since the QCM can be coated with a tinny layer antigen, and QCM can be utilized for antibodies detection purpose. The QCM resonators can oscillate at a, relatively, greater harmonic-frequency to rise the precision and despondence (Equation 1). Consequently, the thickness

of the crystal needs to be reduced in order to achieve this greater resonant-frequency of a crystal. Nevertheless, the decreasing of thickness makes the crystal more brittle. Equation 1 can be rewritten in the following way to include the harmonics of the crystal.

$$f_N = \frac{N v_q}{2d_q} \quad (4)$$

Here f_N point to the resonant-frequency; N is the number of harmonics, must be integer number. It can be stated that, because of the attendance of anti-nodes at the surface of the crystal (Figure 3) the electrodes on the surface can only excite odd harmonics. The best representation of the loaded QCM via a surface mass layer and immersed inside liquid can be shown in Figure 3.

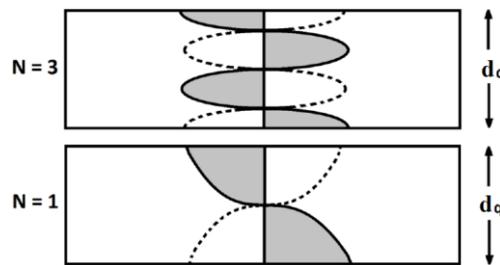


Figure 3: Shift sketches crossways QCM thickness for the 1st and the 3rd harmonics

The suggested geometry (Figure 4) of the amalgamated QCM/thin film oscillator by (áKeiji Kanazawa, 1997) is utilized in this investigation. The theory behind this geometry is not difficult.

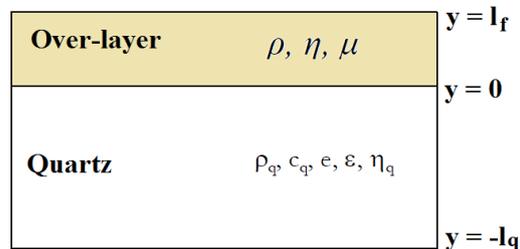


Figure 4: Geometry of a composite resonator

The starting point is at the crossing point between the QCM and the over-layer. The over-layer is described through the density ρ , shear modulus μ and viscosity η . The QCM factors comprise the density ρ_q , shear modulus c_q , appropriate piezoelectric constant e , relative permittivity ε and viscosity η_q . For the aim of production, the sequence resonances of unloaded-quartz have been chosen at precisely 5 MHz. The shear-waves in both the QCM and the over-layer are the addition of a wave traveling in the positive direction of y and another in the negative direction of y and have the form $e^{(i\omega t)}$.

Also, for the QCM, the amplitude of the wave traveling in the positive direction of y is A and in the negative direction of y is B . Likewise, the wave amplitudes in the over-layer are C and D . The wave-vector for the shear wave in the QCM is k_q and the over-layer is k . Moreover, the current-density consequential from applying of this potential is j . After knowing of j , the electrical action of the loaded and unloaded crystal, such as admittances, phase-angles, and the rest can be computed. The

shear-wave diffusion in the QCM and the over-layer possess the resulting arrangements:

$$U_{(y,t)} = Ae^{ik_q y} + B[e^{-ik_q y} e^{i\omega t}] \quad (5)$$

$$U_{(y,t)} = Ce^{iky} + D[e^{-iky} e^{i\omega t}] \quad (6)$$

The ultimate point AC voltage crossways the QCM is Φ_0 , so as to $-\Phi_0/2$ is functionalized at the top QCM surface (wherever $y=0$) and $\Phi_0/2$ at the lowest surface of the QCM ($y=-l_q$). The shear-wave relationship for the oscillating QCM and the over-layer are indicated in equations (7) and (8) correspondingly.

$$\left(c_q + \frac{e}{\varepsilon} + i\omega\eta_q\right) \frac{d^2 U}{dy^2} = -\omega\rho_q U \quad (7)$$

$$(\mu + i\omega\eta) \frac{d^2 U}{dy^2} = -\omega^2 \rho U \quad (8)$$

Equation (9) might be found from a couple sequential integrations of equation (7) through y . E and F are unsettled integration-constants.

$$\Phi = \frac{e}{\varepsilon} U + Ey + F \quad (9)$$

Now, these six undetermined constants, *i.e.* A, B, C, D, E and F , can be found from the boundary-conditions. At $y=-l_q$ the tension is zero. Latter, evaluation these constants, A, B, C, D, E and F , will offer the essential data that can be utilized to attain the current-density, j .

$$\Phi = \frac{e}{\varepsilon} U + Ey + F \quad (10)$$

The current-density in equation (10) can be utilized to rebuild the admittance against frequency-plot for the oscillating quartz crystal microbalance. The ratio of the current over the voltage vectors is basically gives the admittance, *i.e.* $Y=I/V$, which is correspondingly the opposite of the electrical impedance, *i.e.* $Z=V/I$. Hence, at the sequence resonance-frequency the admittance, Y , reaches its maximum value.

3. Results and Discussion

Audio wave-sensors have been extensively utilized for recognition of different chemical and biological-species in liquid phases. In this investigation, in order to investigate the admittance and its phase angle the authors settled a simulation program using Matlab. Utilizing the Kanazawa's model, the authors similarly highlighted the requisite modification to the Sauerbrey's correlation. This study utilized polystyrene since polystyrene is an insulator, inert, durable and resist water damaging. Polystyrene is prepared through styrene polymerization process, which is a building-block chemical utilized in the production of numerous products (Hu et al., 2010). As a result of its clearness and simplicity of purification, polystyrene is utilized for an extensive range of medical applications, comprising tissue-culture trays, analytical tubes, Petri plates, diagnostic apparatuses, covers for test tools and medical instruments (Rengier et al., 2010). The complicated shear-modulus of polystyrene-polymer with a solvent containing ~15% 2-chlorotoluene that has been described by Katz and Ward

(1996) previously were utilized for this theoretical-model. The input data (Katz & Ward, 1996) for the Matlab program are listed in Table 1:

Table 1: The input data for the Matlab program used in this study (Katz & Ward, 1996)

Item	Value
Thickness of AT-cut crystal quartz	345.8×10^{-6} m
Quartz density	2.648 g/cc
Shear-storage modulus of QCM	2.947×10^{10} Pa
Viscosity of QCM (η)	9.2475×10^{-3} kg m ⁻¹ sec ⁻¹
Dielectric constant	3.982×10^{-11} S ⁴ /kg.m ³
Piezoelectric constant	9.53×10^{-2} S/m ²
Film density	1.063 g/cc
Shear storage modulus	1.58×10^8 Pa
Shear loss modulus	1.66×10^9 Pa
Viscosity (η)	52.83 kg m ⁻¹ sec ⁻¹

A. Unloaded-QCM

The easiest instance is the unloaded-QCM resonator. Certain convinced computing is found by means of studying the admittance, *i.e.* 1/impedance, of the quartz crystal since the computing of the current-density relies upon the computing of the shear-wave amplitudes. The inverse of the impedance of the resonator was considered once the applied peak-voltage was ~1.0 V. The resultant admittance with its phase is presented in Figure 5.

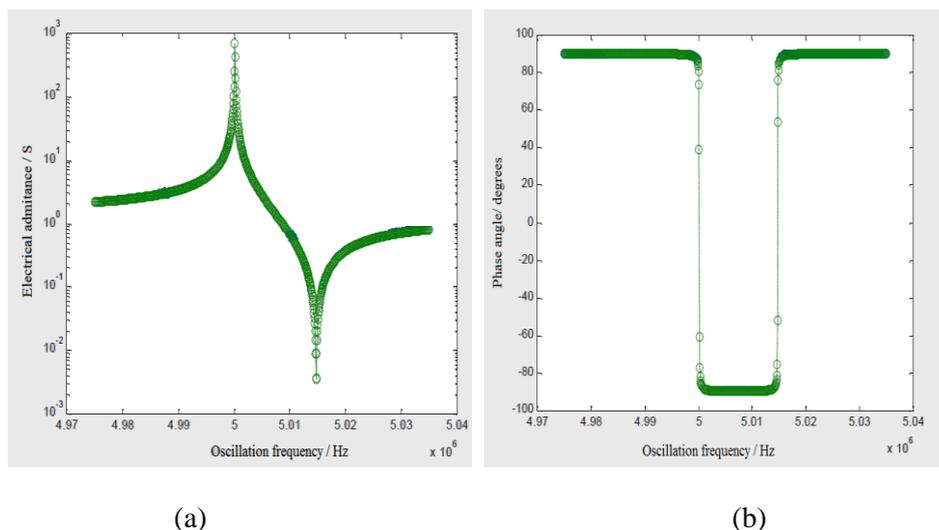


Figure 5: (a) Electrical admittance, (b) Admittance phase angle for an uncoated QCM

The admittance, as seen in Figure 5a, displays a highest point at the sequence resonant-frequency of ~ 5 MHz and a hill point at the corresponding resonant-frequency. The phase-behavior, likewise, reproduces the highest Q -factor of the quartz crystal resonator. The Matlab program, besides, plots the admittance-illustration in polar-coordinates system, a loop signifying the performance of the sequence resonance circuit. As presented in Figure 6, the loop diameter with regard to the extreme conductance, *i.e.* the real part of the admittance, and the center of the loop is related to the relative-permittivity of the QCM (Kanazawa & Cho, 2009). The frequency upon which the conductance displays an extreme is the sequence resonant-frequency.

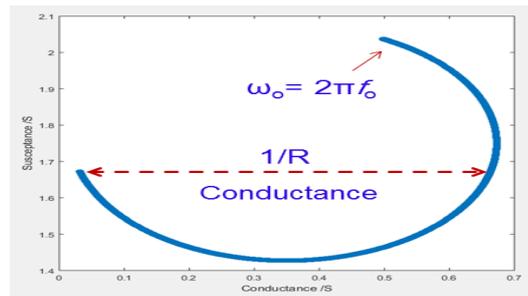


Figure 6: Susceptance (imaginary part of the admittance) vs. Conductance (real part of the admittance) curve for a ~ 5 MHz AT-cut QCM, as computed with an impedance-analyzer

B. Loaded QCM

To study the performance of quartz crystal once this implement runs in liquid-phase system, this study has selected a polymer as polystyrene for simulation. Polystyrene selection is due to the great mechanical strength that has been mentioned previously. The authors report an enhanced connection of A-Protein on quartz crystal biosensor through adjusting the Au outward of the QCM using an optimum polystyrene-polymer film thickness after that an acidic-treatment has been applied.

The physical characteristics of this polymer have been displayed previously. The spectrum of the admittance (Figure 7) with an extreme point nearby ~ 5 MHz is for a $1.881 \mu\text{m}$ (green) dense film of the polystyrene-polymer. The additional films of i^{th} thickness are $4.703 \mu\text{m}$ (red), $9.407 \mu\text{m}$ (blue), $18.814 \mu\text{m}$ (pink) and $32.926 \mu\text{m}$ (blue-green) in that order. Moreover, the admittance and the correspondence phase-angle for the tinniest film ($1.881 \mu\text{m}$) are indistinguishable in profile with the equivalent mass in place of the one prepared in SiO_2 . The similar trend observed by Dahlin *et al.* (2008) using different polymers. Nevertheless, once the film-thickness rises the oscillation-frequency and the admittance are hindered. Rocha and the coworkers presented a comprehensive and insight review regarding the QCM-surface produced acoustic wave skill for bio-sensing uses (Rocha-Gaso *et al.*, 2009). They emphasize the admittance damping is due to film thickness increasing. The admittances and the correspondence phase-angles with five diverse thickness values are presented in Figure 7. A shear-wave in a solution is intensely hindered in the propagation way. It can be stated that, films using thickness value of $1.881 \mu\text{m}$ can be counted as thin for the polystyrene-polymer. For the unloaded-QCM, the admittance extreme value comes about at precisely 5 MHz. This will move down the frequency due to an added mass. The spectrum of admittance with an extreme point nearby ~ 5 MHz is for a $1.881 \mu\text{m}$ thick film of the polystyrene-polymer.

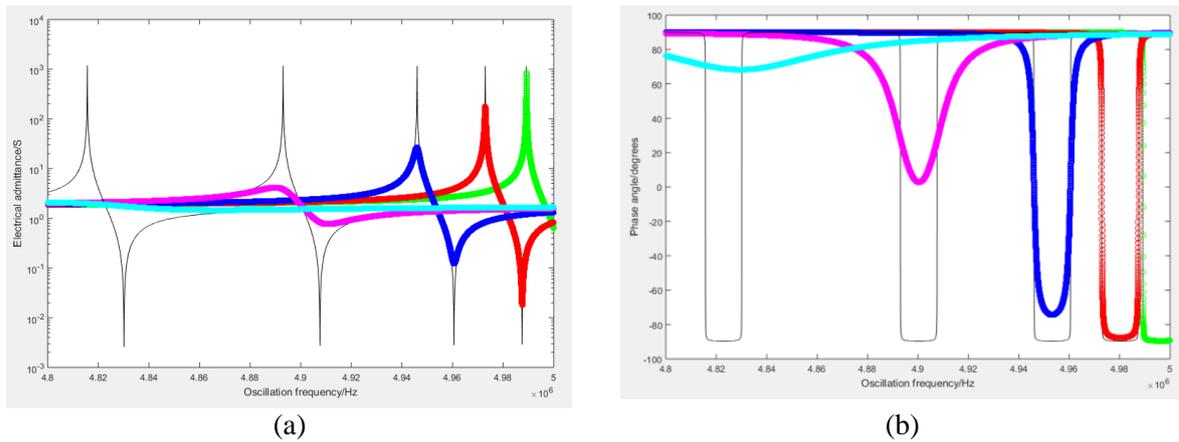


Figure 7: (a) Electrical admittance, (b) Admittance phase-angle for a quartz crystal covered with tinny films of the polystyrene-polymer close to its resonance transition-state and anti-resonance with five value thickness; 1.881 μm (green), 4.703 μm (red), 9.407 μm (blue), 18.814 μm (pink) and 32.926 μm (blue-green) respectively

It can be understood that, Sauerbrey's equation can only be utilized for a tinny solid film in air (Beers, 2012). But in a liquid-phase medium, the frequency-shift will increase as a result of Kanazawa's model due to the increasing of both viscosity and the density of the medium. This investigation also investigate the spectrum of admittance for the quartz crystal covered with the similar mass of SiO_2 or offers a modification factor for a diverse material coating as a function of film thickness, *i.e.*, supplementary mass, in the arrangement of k ($k \geq 1$) in this manner:

$$k = \frac{f_o - f_{liquid}}{f_o - f_{SiO_2}} = \frac{\Delta f_{liquid}}{\Delta f_{SiO_2}} \quad (11)$$

As illustrated in Figure 8 the modification to the Sauerbrey equation is less than $\sim 3\%$ for the polystyrene-polymer film until a 15 μm thickness. Using poly (4-ammonium styrene-sulfonic acid) films Vogt et al. showed that the Sauerbrey equation could be successfully applied up to 205nm. This limitation is much smaller than the obtained results $\sim 15 \mu\text{m}$ in our investigation. This also possibly has a consequence in utilizing quartz resonators as a biosensor using the polystyrene-polymer film until a 15 μm thickness.

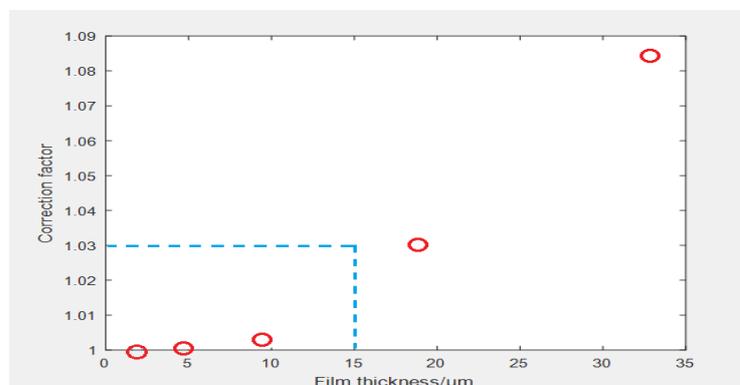


Figure 8: Correction to Sauerbrey's equation

4. Conclusion

Because of the growing requests in user, health and army fields progress of the extremely sensitive bio-sensors has delivered highest significance. In this study, the relations amongst the shear-wave and the empirical electrical-behavior of loaded-QCM have been explained extensively. The substantial hindering of the shear-wave in liquids permits the usage of the quartz crystal in a liquid media by controlling the sufferers. The phase-behavior of the shear-wave in a solution is appropriate to the arrangement of the shear-wave relationship. Information about the covering film physical performance is extremely helpful in explanation the outcome of electrical measurements. To sum up, the achieved outcome will support selecting appropriate polymers in the quartz crystal construction and use as a biosensor. It was our aim to calculate modification factors of denser films in Kanazawa's model based on Sauerbrey's relation. Thus the modification to the Sauerbrey relation is below ~3% for the polystyrene-polymer film until a thickness of 15 μm . The imitation outcomes are in magnificent acceptance with the existing experimental data.

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