

**Development of a Quartz Crystal Microbalance for the Detection
and Quantification of Real-Time Volatile Compound Production
in the Headspace of Wine Glasses**

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Abstract

A Quartz Crystal Microbalance (QCM) system was designed to measure the real-time development of volatile organic compound (VOC) production in the headspace of wine glasses and to identify whether glass shape imparts an influence on wine characteristics. The test system was assembled using a piezoelectric quartz crystal, a standard clock oscillator, a frequency counter and a data acquisition hardware and software package. Adsorption of standard volatile components water, ethanol, butanol and mixtures thereof on hydrophilically-coated, hydrophobically-coated and uncoated quartz crystal surfaces was measured as a function of time. Results indicated that nature of the coating greatly influences total adsorbed masses, which was attributed to the binding specificity between coatings and volatile compounds. Measurement of total adsorbed masses as a function of immersion depth of the sensor in a wine glass containing a 50:50 water/ethanol mixture showed a decrease in volatile concentration as the distance from the liquid interface increased. The research confirms that the QCM prototype is capable of accurately measuring production of small concentrations of VOC's in real-time and that the instrument may be capable of evaluating the influence of glass shape on wine characteristics

Introduction

It is widely known that the shape of a wine glass can have a large impact on the perception of wine (Hummel and others 2003). For example, wine tastings are often performed using the a standard glass with a predefined glass shape for all wine samples so as to balance the impact of different glass shapes on sensory perception. Many wine connoisseurs assert that the shape of a glass may influence intensity, quality, and hedonic tone of wine (Hummel and others 2003); however, the complexity and rapid kinetics of VOC concentration changes as a function of sampling conditions that is swirling, sample temperature and time between pouring and sampling make it difficult to validate this claim.

Traditional methods of monitoring VOC compositional changes in products have focused on classical chemical analysis, instrumental analysis and sensory evaluation (Ampuero and Bosset 2003, Fu and Finklea 2003). While these methods are accurate they lack the sensitivity and ability to measure VOC development in real-time. The major disadvantages of sensory analysis are firstly that sample exposure between pouring and sampling may vary and change the composition of wine, and secondly that the influence of a panelist's senses such as smell and taste, the panelist's mood, and the physical state of the panelist may positively or negatively influence the final results (Duffy and others 1999). Previous studies have used sensory analysis in order to validate the claim of the effect of glass shape on the characteristics of wine but have had little success due to the above mentioned reasons. Hummel and others (2003) indicate that a difference is detectable in wine that was stored and sampled in

glasses with different shapes. Authors noted though that panelists were not blind folded and were untrained which may have influenced the results.

The use of instrumental analysis to analyze the volatile composition in the headspace of a wine glass has been shown to require complex analytical techniques such as GC-MS or HPLC and all these techniques lack real-time capabilities (Ampuero and Bosset 2003). Furthermore, Ampuero and Bosset (2003) mention for many of the testing methods samples must be purified or fractionated to ensure accuracy of results. For example, direct injection of wine in HPLC columns has shown to rapidly lead to a failure of the separation column due to irreversible absorption of complex compounds on the column. Finally, data collected by these methods does not directly correlate to the consumer's preference of the wine.

QCM systems are typically constructed from piezoelectric materials (quartz in this application) that are incorporated into an oscillation circuit. When a current is applied to the piezoelectric material, the material expands or contracts depending on the magnitude and sign of the electric current. Application of an oscillating current will subsequently result in a mechanical oscillation of the quartz crystal (O'Sullivan and Guilbault 1999). The structure of this system allows for resonance of the mechanical and electrical oscillation at specific frequencies. These frequencies can be measured by a frequency counter and depend on the properties of the crystal, one of which is the mass of the crystal. Consequently, the mass of the crystal or any absorbed matter can be determined by recording alterations in the resonance frequencies. Sauerbrey

developed in 1959 the base equation that describes the relationship between the change in frequency (Δf) and the mass absorbed or desorbed (Δm) on the piezoelectric material.

$$\Delta f \propto K\Delta m \quad (1)$$

Sensitivity for QCM systems have been reported to be in the ppb levels and the use of selective coating membranes has introduced specificity to the adsorption (Gardner and Barlett 1994). Because of this, there is a growing trend to use QCM systems as microbalances in a wide variety of fields of study. Combined with the emerging technology of molecular selective membranes, a QCM system can become highly specific analytical mass sensors exceeding the capability of microbalances (O'Sullivan and Guilbault 1999, Wu 1999, Fu and Finklea 2003).

Materials and Methods

Materials

Volatile standards ethanol, butanol and crystal coating hexadecane (the hydrophobic crystal coating) were purchased from Sigma Chemical Co. (St. Louis, MO). Double distilled and deionized water was used for dilutions. Rain-X (hydrophilic crystal coating) was obtained from a local auto-parts store. Baleau Vineyard Coastal Merlot (2000 vintage) was obtained locally (Knoxville, TN). Glasses were purchased locally (Wal-Mart, Knoxville, TN)

QCM Setup

A prototype QCM system was constructed from AT-cut, gold-plated quartz crystals with a 10-MHz base frequency driven by a 5V standard clock oscillator at the base resonance frequency of the crystal. Mechanical oscillation of the crystal was measured by an external frequency counter, Universal Counter 3820, purchased from Sense-ations®, (Oak Ridge, TN). Measured frequencies were recorded by a personal computer with Labview 7.0™, purchased from National Instruments®, (Austin, TX) and data analysis was conducted on a standard spreadsheet program.

VOC Measurement

Crystal preparation. QCM experiments were conducted in a self-assembled controlled environmental chamber to minimize variations in moisture, temperature and help to prevent superimposed convection. Crystals were stored prior to and after measurements (minimum 1 hr) under vacuum in a dessicator to ensure complete desorption of volatiles. In regular intervals, crystals were additionally cleaned by sonication in an ethanol bath for a minimum of 1 hr and then dried in a vacuum oven. Hydrophilic and hydrophobic coatings were reapplied and crystals were dried in a vacuum oven. The crystals were then transferred and stored under vacuum in a dessicator until use.

Absorption measurement. A quartz crystal sensor, with or without a selective coating, was connected to the oscillation circuit. The crystal was equilibrated prior to immersion (pre-immersion phase) in the environmental chamber that contained the covered sample container (beaker or wine glass).

The sample cover was removed and the crystal was rapidly lowered into the uncovered sample container to a specific height above the sample surface (immersion phase), and then allowed to come to equilibrium in the headspace of the sample (post-immersion phase).

Data analysis. Absolute absorbed masses were calculated using equation (1). All experiments were conducted in quadruples. Results were reported in means and standard deviations.

Results and Discussion

Frequency changes during the pre-immersion, immersion and post-immersion phase. Fig 1 shows typical changes in the measured frequency as a function of time during pre-immersion, immersion and post-immersion phase. During the pre-immersion time, the frequency remained constant indicating that the crystal had been fully equilibrated with the atmosphere in the environmental chamber. Upon immersion, the frequency rapidly decreased to reach a minimum which can be attributed to the rapid absorption of volatile compounds in the headspace of the glass to the quartz crystal surface. In the post-immersion phase, the frequency again increased to reach equilibrium. Results in the post-immersion phase may be attributed to (1) desorption of compounds that were previously absorbed on the crystal in the pre-immersion phase that is gases that were present in the controlled environment changes (surface absorption and desorption processes) and (2) migration of absorbed gas molecules into the interior of the quartz crystal matrix (volume based adsorption) causing alterations in the base frequency of the crystal.

Volatile Concentrations of Ethanol:Water Mixtures. Equilibrium absorbed masses of standard ethanol:water mixtures with ethanol in water concentrations of 0, 25, 50 , 75 and 100% were calculated using equation (1) from recorded frequency changes during pre-immersion, immersion and post immersion phase of hydrophilic coated quartz crystals using standard 100ml beakers with a distance between liquid surface and sensor of 8 cm (**Fig. 2**). Results correlate to theoretical predictions that total vapor pressure of binary mixtures is a sum of the partial vapor pressure of each component which is determined by the concentration of each component in the mixture (Van Ness and Abbott 1983). It should be noted though that theoretical predictions are based on constant temperature and humidity but that slight variations in temperature ($\pm 5^{\circ}\text{F}$) and slight variations in humidity ($\pm 5\%$) may have occurred in the environmental chamber to insufficient control. Nevertheless, results a good correlation between measurements and theoretical predictions demonstrating the accuracy of the methodology.

Influence of Crystal Coating Selectivity on Absorbed Equilibrium Mass. Equilibrium absorbed masses of ethanol:water mixtures and 100% butanol on hydrophilic-coated, hydrophobic-coated, and uncoated crystals were calculated from measured frequency – time data (see Fig. 1) to demonstrate selectivity of coatings. The total absorbed mass measurements using the hydrophilic coated crystals were 7.6, 2.2 and 1.5 μg for ethanol, butanol and water (**Fig. 3**). The total absorbed masses using the hydrophobic coated crystals were significantly lower for the ethanol/water mixtures than for the hydrophilic

coating, e.g. 0.5 μg for water and 2.2 μg for ethanol. Interestingly, absorbed mass of butanol was higher using the hydrophobic coating than using hexadecane as a coating. Absorbed masses using uncoated crystals were extremely low and ranged from 0.5 to 0.05 μg . In the case of uncoated crystals, the absorbed mass was highest for butanol (0.5 μg). Results can be attributed to specific interaction between volatiles and the coating. Hexadecane is a non-polar alkane and will interact more strongly with other non-polar compounds. Butanol is more non-polar compared to ethanol or water and hence the interaction and absorption on a hexadecane-coated crystal is larger. The results suggest that the choice of coating introduces selectivity into the VOC measurement. Finally, results indicated that the quartz crystal surface itself is slightly hydrophobic and thus more specific to hydrophobic VOC's.

Measurement of VOC development in a Bordeaux glass. Fig. 4 shows the change in frequency with time of a hydrophilic-coated quartz crystal immersed in a Bordeaux glass that contained a Merlot red wine. Change in frequency was much more pronounced the smaller the immersion depth (that is the distance between liquid surface and sensor) was. In a sensory study conducted by Delwiche and Pelchat (2000) authors mentioned that wine was presented in a Bordeaux glass and that the volatiles were possibly the most dilute compared to other glasses due to the large cuppa. The measurements however indicate that the VOC concentration is a function of height from the wine surface may vary between different glass shapes. A direct comparison between different glasses using the QCM will allow this question to be answered.

Fig. 5 shows calculated masses from frequency-time experiments using two hydrophilic crystals and a 50% ethanol solution to measure height versus mass absorbed VOCs. The 50% ethanol solution was chosen because of its reasonably strong signal at even high immersion depths. It should be noted though that as the measurements were taken closer to the volatile liquid surface the concentration of volatiles almost overloaded the crystal oscillation. Generally, as the immersion depth increased, VOC absorbed masses increased. The results clearly indicate that VOC concentrations are a function of glass geometry. Interestingly, at immersion depths larger than 4 cm, absorbed masses changed little with increased distance from the surface.

Influence of Swirling on VOC Development in Bordeaux Glasses.

Finally, volatile concentrations were measured in Bordeaux glasses that were at rest and that were agitated (swirled) data now shown. Kinetics of volatile adsorption was significantly faster and absorbed masses were much higher upon swirling *e.g.*, equilibration occurred in 15s compared to 452s for pure ethanol and decrease in frequency was approximately twice as large compared to the static glass. This is the first confirmation of the important effect of swirling prior to determining the bouquet and aroma of a wine, which is a common practice of wine connoisseurs.

Conclusions

Results of this study demonstrate that QCM measurements are reproducible with acceptable standard deviations and that QCM is able to detect the development of VOC's in the headspace of glasses of wine in real time. The

surface chemistry of the QCM sensors may be tailored to induce specificity in the sensor for classes of components or single components and expand the functionality of QCMs beyond that of a microbalance. While a comparison between different glass shapes has not yet been conducted, the results show that this will be a feasible course of action with a QCM system.

The results may offer additional applications beyond the ones proposed in this study. For example, with the application of specific crystal coatings a QCM may be used for the real-time detection of pathogenic organisms; detection of allergens during production; detection of pollutants due to production; and quantification of sensory perceptions such as astringency in real-time (Kim and Park 2003, Liu and others 2003, Kaneda and others 2002, 2001, Boeker and others 2000). As such, this study has important implications for the advancement of analytical methods in food quality and safety.

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- Figure 1. General measurement curve for QCM measurements conducted in this experiment. Pre-immersion relates to the time period in the environmental chamber with the covered sample; Immersion relates to the time period of removal of the sample cover and insertion of the crystal to a specific height above sample; Post-immersion relates to time period of equilibrium of the crystal in the headspace of the sample
- Figure 2. Comparison of theoretical predictions of ethanol/water solution vapor pressures vs. measured vapor pressures using QCM system.
- Figure 3. Selectivity of hydrophilic, hydrophobic, and uncoated crystal coatings based on mass of VOC absorption in various VOC systems.
- Figure 4. Frequency differences in immersion height of crystal above the surface of Merlot wine in a standard Bordeaux (red wine) glass at room temperature.
- Figure 5. Immersion of a hydrophilic coated crystal sensor vs. mass absorbed to the crystals in a 50% mixture of ethanol contained within a standard Bordeaux glass.

Figure 1

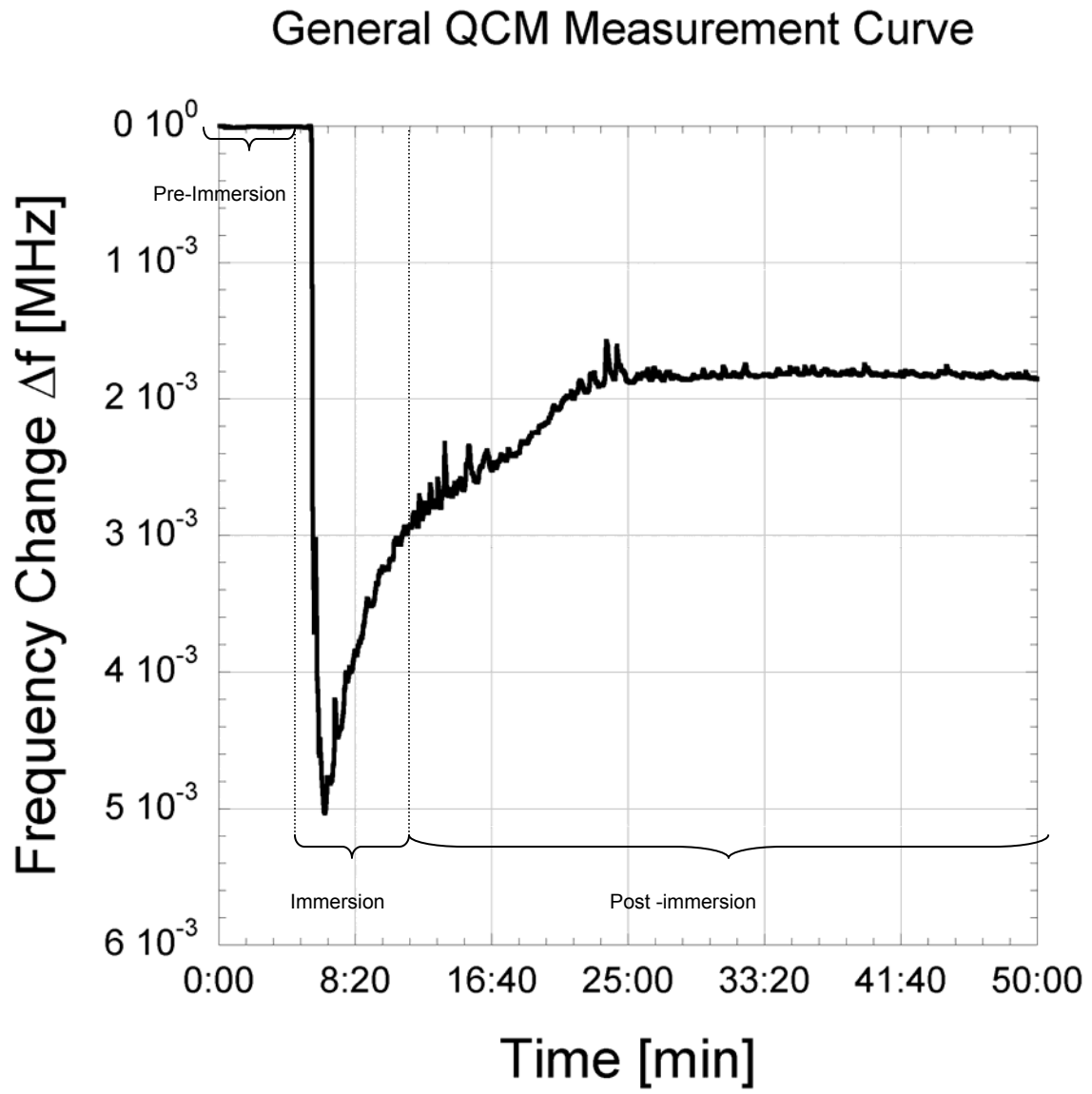


Figure 2

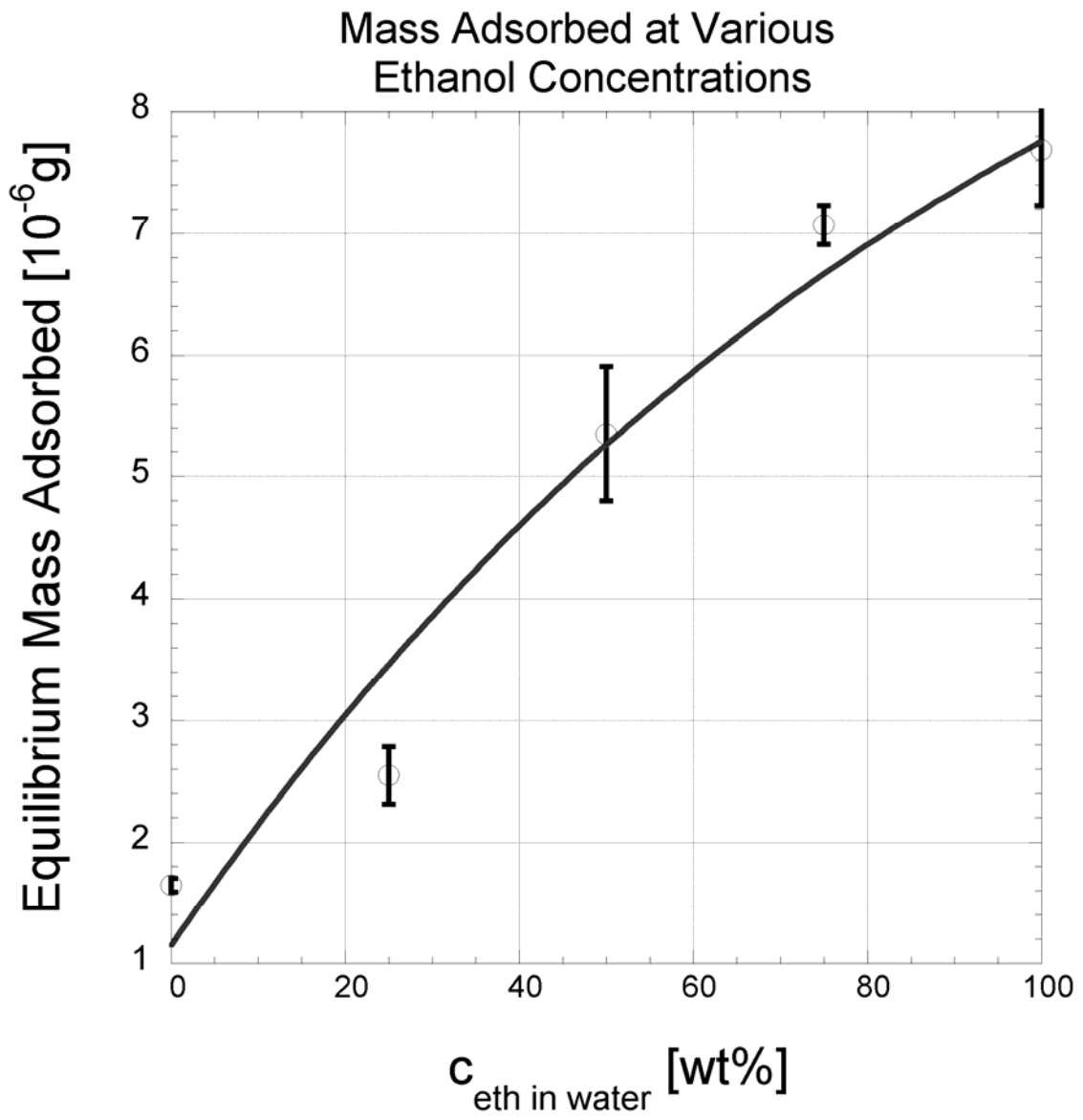


Figure 3

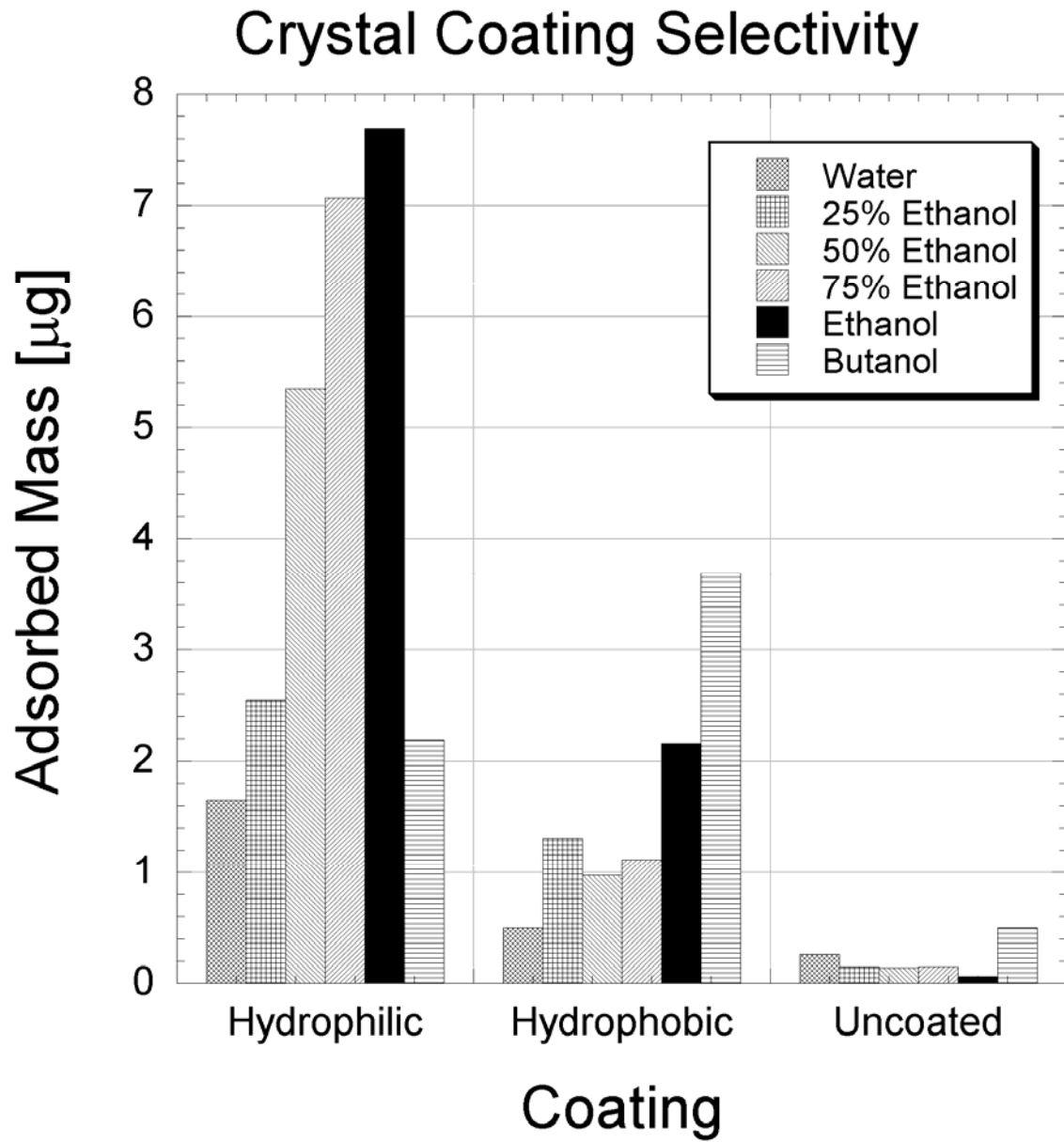


Figure 4

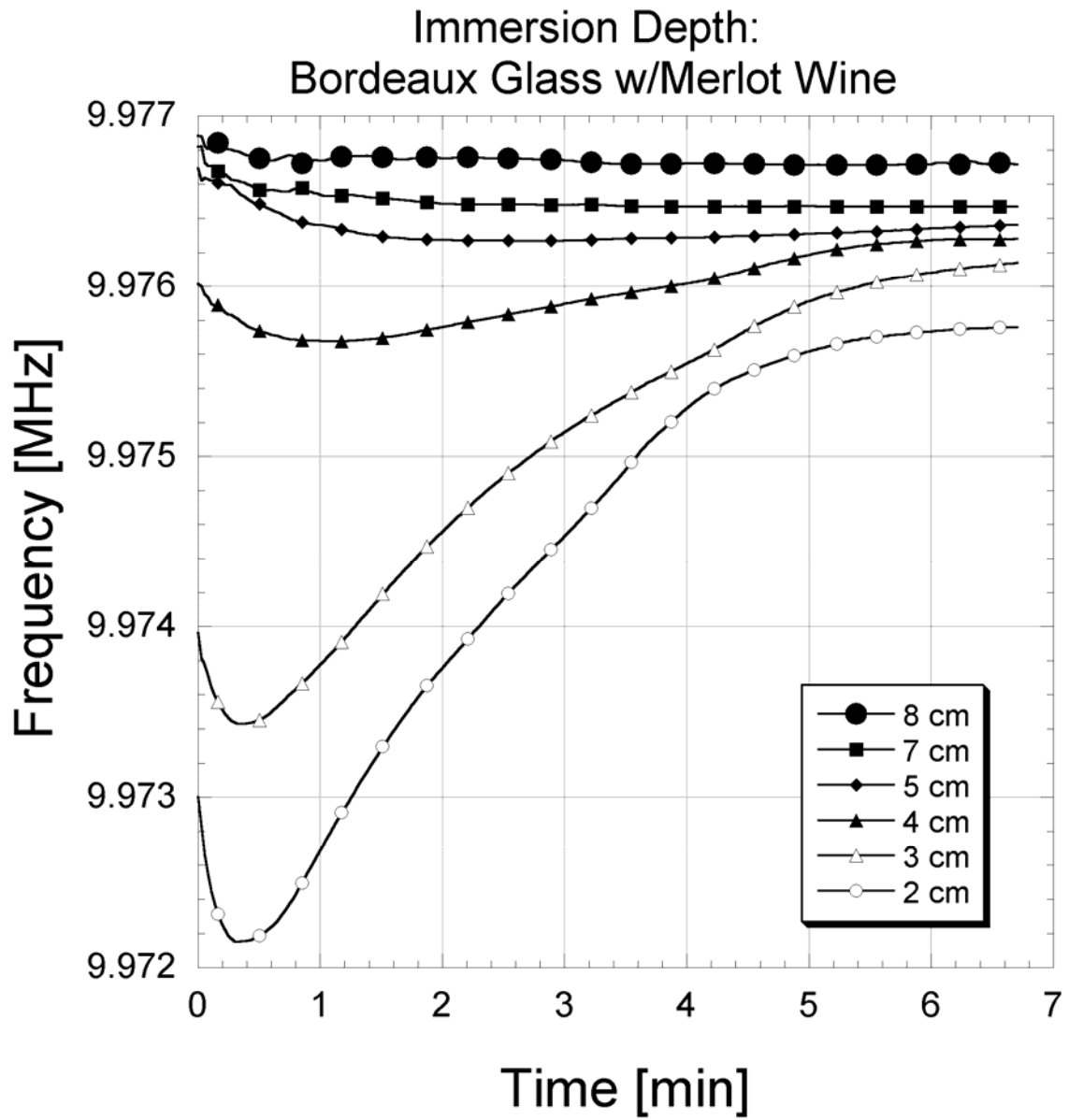


Figure 5

Immersion depth vs. mass adsorbed:
50% Ethanol in Bordeaux Glass

