

Laboratory 4

Absorption and humidity sensing

Objective

The objective of this laboratory is for you to explore how a piezoelectric resonator coated by a thin polymer film can be used as a highly sensitive sensor for water vapor. It also will help you understand how materials such as polymers adsorb and absorb water as a function of relative humidity.

Preparation

- Read pages 6-12; 16-19; 27-28 of the operating manual for the quartz crystal monitor (posted on Compass site)
- [Read: "The Relationship Between the Glass Transition Temperature and Water Vapor Absorption by Poly\(vinylpyrrolidone\)"](#), also on Compass
- It is suggested that you also look at the Wikipedia pages for Henry's Law and the Langmuir Isotherm/equation.
- As of this writing there is a good description of spin coating at: [Stanford spin coating](#)

Equipment and sample

- Quartz crystal monitor (QCM) and control electronics; flow cell for the QCM; quartz crystals.
- Solutions of PVP (poly(vinylpyrrolidone)) and PEO (poly(ethylene oxide)); spin coater.
- Apparatus for creating flows of dry air mixed with moist air that is saturated with water vapor; nitrogen tank.

Laboratory Safety: Absorption and humidity sensing

Required Personal Protective Equipment

- Safety glasses with side shields
- Long pants
- Closed foot shoes
- Chemical resistant gloves - (will be provided in the lab)

Safety Concerns

- Chemicals - potential for chemical exposure.
 - Chemical solutions of PVP [poly(vinylpyrrolidone)] and PEO [poly(ethylene oxide)] in acetonitrile will be used for this experiment. Acetone and Isopropyl alcohol will be used as cleaning solvents. Please read the safety data sheet for each of these chemicals

(found on Compass). Chemically resistant gloves must be worn when handling chemicals.

- [PVP](#)
 - [PEO](#)
 - [Acetonitrile](#)
 - [Acetone](#)
 - [Isopropyl alcohol](#)
- Spin Coater - potential for injury from sample chuck rotating at a high speed.
 - The center of this machine spins at a high rate of speed. Keep hands clear of the center chuck (sample holder) while the machine is on. This will reduce the risk of injury to the hands.
 - Compressed Gas - potential for injury from high-pressure gas.
 - All compressed gases are potentially hazardous because of the high pressure stored inside the cylinder. A sudden release of pressure can cause injuries and property damage by propelling a cylinder or whipping a line.
 - Use caution when opening the main regulator and pressure valves.

Waste Considerations

- PVP, PEO, acetonitrile, isopropyl alcohol, and acetone may not be dumped down the lab sink for any reason. Please place all used pipettes in the appropriate waste container.
- Kim wipes with minor amounts of solvents may be disposed of in the regular trash. For large spills, please inform teaching assistants or the lab manager.
- PVP and PEO solutions that are no longer used must be disposed of via the Division of Research Safety Waste collection program. The lab manager will handle the disposal.

Introduction

Gas sensing is an important technology for environmental and personal safety; it so versatile that it is used in a variety of applications ranging from control of combustion processes, to food storage and energy efficiency. Many of you probably have a CO sensor made from SnO in your apartment or home; essentially every car has an O₂ sensor made from ZrO₂:Y₂O₃ mounted in the exhaust manifold; and most modern clothes dryers incorporate a humidity sensor made from a conducting polymer that detects when the clothes are dry enough to turn off the heat. In this lab, you will use the equilibrium adsorption of water in a polymer film as a humidity sensor.

Experimental Procedures:

First steps: Determine the reliability of the quartz crystal monitor

- Observe the resonance frequency of the quartz crystal monitor (QCM) over a time period that you select. *In your lab report explain how you chose that time and why you feel it is*

adequate. Record the frequency of the QCM often over your measurement time. Determine the average and standard deviation of the frequency over the measurements made. Explain in your lab report how the average and standard deviation changed as you add additional measurements and use this to demonstrate that you made enough measurements to obtain good values for these two quantities (average and standard deviation). Be sure to list the final values obtained with a \pm value indicating the expected error in the values. This should be consistent with the standard deviation you obtained.

- Adjust C_0
 - The QCM200 System incorporates a method of a nulling C_0 capacitance to insure that the frequency and resistance values correspond to the true series resonance parameters of the quartz oscillator. The front panel of the controller includes a turn dial to control the bias voltage required by the varactor C_v and a switch to choose between Adjust and Hold modes for the controller. To set the null capacitance, put the controller into Adjust Mode. The unit will modulate the varactor bias with a 75 Hz sine wave and indicate if the C_0 compensation is High, Low, or Nulled. Start with the ten-turn dial set to 8.0 (an LED should indicate that the crystal is oscillating) and adjust according to the High/Low/Null status given by the controller. Lock the dial in when the two Null LEDs glow with equal intensity. Flip the switch on the controller back to the Hold mode.

Second steps: Determine the mass of a thin layer of spin-coated PVP and PEO

- Measure the mass of the clean quartz crystal (record this value in your lab notebook)
- Deposit enough PVP solution onto the surface of the crystal so that nearly the entire surface is covered (approximately 7-12 drops).
- Use the available spin coater pre-programmed recipes to spin the crystal at speeds of 1000-4000 rpm. This will result in a uniform thin layer of PVP on the surface of the crystal.
- Carefully remove the crystal from the spin coater and use a cotton swab or kim wipe and solvent to clean the bottom side. Be careful not to disturb the coating on the top side.
- Measure the mass of the crystal with the coating
- Calculate the PVP layer thickness, h
 - $h = \frac{m}{s\rho}$
 - where m is the measured mass of PVP, s is the area of the crystal, and ρ is the density of PVP (1.2 g/cm^3).
- Install the coated crystal in the QCM. Run dry air over the crystal until the frequency is stable. Record this value.
- You may want to remove the crystal and reweigh it on the balance.
- Use the QCM to measure the mass per unit area of the polymer film from the change in the resonance frequency of the crystal. *Include this value in your lab report and be sure to indicate the accuracy with a plus/minus error value.*
 - $f_{\text{coated}} - f_{\text{uncoated}} = -C_f \times \Delta m$
- Confirm that this value agrees with the value obtained by weighing the sample. *What might account for any differences observed?*
- Determine the thickness of the PVP layer as a function of spin speed for the spin coating

process. Three spin speeds should be investigated, time permitting. (Note that you can use solvents to remove the PVP layer from the quartz crystal. You may want to re-measure the quartz crystal prior to spinning on a new PVP layer to determine if you got the entire previous layer of PVP off.) *In your lab report, plot the layer thickness as a function of spin speed. Determine what the mathematical relationship is by fitting the data and include that in the report. Explain how accurately you can obtain a given PVP thickness. Compare the functional form from your data fit with expectations from spin-coater theory.*

- Repeat the above steps for PEO, which has a density of 1.45 g/cm³ for a MW of 100,000. *How does the PEO film thickness compare to that of the PVP at comparable speeds?*
- If you have time, repeat the coating process with a different concentration of PVP or PEO solution, or borrow data from another group if they chose a different concentration. *If you do this part, note in your report how the thickness of the polymer film changes with the concentration of the solution for a given spin speed.*

Third steps: determine water uptake by PVP as a function of humidity

- Select one spin speed, and measure the mass of the PVP and PEO films as a function of the partial pressure of water in the gas flow - do this by changing the ratio of wet gas to dry gas flowing over the cell. The frequency measured via the QCM is a function of partial pressure and the mass of material deposited on the crystal:

$$\Delta f = -C_f \cdot \Delta m$$

where Δf is the change in observed frequency in Hz, Δm is the change in mass per unit area in g/cm², and C_f is the sensitivity factor for the crystal. *For our 5 MHz AT-cut quartz crystal at room temperature, $C_f = 56.6 \text{ Hz} \cdot \text{cm}^2 / \mu\text{g}$*

$$mC = \frac{\alpha p}{1 + \alpha p}$$

Where α is a constant, p is the partial pressure, C is the bulk concentration of water, which after equilibrating time is approximately equal to the concentration at the surface.

- Partial Pressures are determined as follows:
 - Percentage of wet air flow to total air flow is given by

$$\phi = \frac{I_{wet}}{I_{total}} \times 100$$

- The relative humidity is related with partial pressure p via the relation:

$$\phi = \frac{p}{p^*} \times 100,$$

Where p^* is the vapor pressure of water, which can be found at https://en.wikipedia.org/wiki/Vapour_pressure_of_water for a given temperature.

- Repeat with 4-5 different relative humidity levels
- *In your report, make a plot of mass fraction of water in the PVP (PEO) as a function of water partial pressure. Fit the data and provide an equation relating the two variables.*
- *In your report, discuss how your results relate to Henry's Law, the Langmuir equation for surface coverage or the Flory-Huggins equation (described below). Are the results the same for PVP and PEO? What may account for any differences observed?*
- Time permitting: Using data from other lab groups for different spin speeds, determine how the time necessary to reach equilibrium depends upon PVP (PEO) thickness. Recommendation: change thicknesses by factors of two or more to obtain good data. From the time dependence vs. film thickness estimate the diffusion constant for water in PVP from $x = \sqrt{Dt}$ where you may take x as "effective film thickness" and "t" as the time to reach a selected fraction of the equilibrium mass fraction. You may need to develop your own model based on the data to justify your selection of times. *In your report, include the plot of time to reach a selected level of completion as a function of film thickness, a fit to the data showing the functional form, and an estimate of the water diffusivity in PVP (PEO).*

Gas Absorption Relationships

It is possible to derive several relationships using thermodynamics that may explain the absorption behavior of gases (in this case, water vapor). Some useful theories for comparison to your data are described below.

Henry's Law was developed by William Henry in 1803. It states that at constant temperature the amount of gas (or concentration, c) that dissolves in a given type and volume of liquid is directly proportional to its partial pressure, p :

$$p = k_h c$$

where k_h is a constant. This ignores any question of how well the gas adsorbs on the surface and assumes an equilibrium that is gas pressure-independent, connecting the bulk concentration of water in the polymer with the bulk concentration of water in the gas. All very simple. If the concentrations are very low then you might expect this to be accurate.

In the experiment conducted here the "liquid" is the polymer film. Because the gas molecules move

rapidly through solid PVP, the behavior is very similar to a liquid. The situation would be different if the diffusivity was very small. However, the assumption of high transport rate is something you will test in the lab. Note that k_h is generally temperature dependent.

A second important concept is the Langmuir Equation. This equation describes adsorption of a species on a surface where there are limited surface sites available. When you cover the surface very heavily there are no more sites available and so no more adsorption can occur. This would be the behavior where the surface coverage is high, which occurs at very high pressures. The Langmuir equation describes specifically how the surface coverage, θ , is related to the partial pressure, p , of the adsorbate (water in this case) in the gas phase.

The equation is as follows:

$$\theta = \frac{\alpha p}{1 + \alpha p}$$

where α is a constant. One then might assume that the surface coverage θ would take the place of p in the equation for Henry's Law, suggesting that one might observe:

$$k_h c = \frac{\alpha p}{1 + \alpha p}$$

which is a correction to Henry's law for large pressures.

The Flory-Huggins equation, on the other hand, takes into account the interaction between the water and the polymer film. This equation also adapts the entropy of mixing since the traditional model is no longer applicable given the large size difference between the water and polymer molecules. The Gibbs free energy of mixing (ΔG_{mix}) can thus be written as:

$$\Delta G_{mix} = \Delta H - T\Delta S$$

$$\Delta G_{mix} = RT[\chi_1 n_1 \phi_2 + n_1 \ln \phi_1 + n_2 \ln \phi_2]$$

Where 1 denotes the solvent (in this case, water) and 2 denotes the polymer, R is the gas constant, T is the absolute temperature, n is the number of moles, and ϕ is the volume fraction. χ in this case is the "interaction parameter" between the two molecules.

The activity of water in the polymer, a_1 , can thus be written as:

$$\ln a_1 = [\ln(1 - \phi_2) + \left(1 - \frac{1}{x}\right) \phi_2 + \chi_1 \phi_2^2]$$