

UNIVERSITY OF
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University of Waterloo
4B Nanotechnology Engineering
Group 7

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Lab 4 Gas Phase Self-Assembled Monolayer Formation

Introduction and Objective

The objective of this laboratory experiment is to self-assemble a monolayer of volatile octanethiol on to a quartz crystal microbalance (QCM) in the gas phase and to observe the shift in resonant frequency. This experiment will not only aid in understanding the requirements for stable measurement but also understanding the limit of detection and quantification of the QCM. This experiment is also intended to demonstrate the advantage of gas phase quantification over the liquid-phase.

Experimental Procedure

The procedure for this laboratory was obtained from the NE 455L/461L Nano Instruments Week 1 part of the Nanotechnology Engineering Program 4B Lab Manuals, 2010. No deviations were observed.

Observations

Initially, before the experiment had begun, we were able to obtain a stable frequency reading to within a 1 Hz variation. Waving our hand, tapping the table and apparatus did not seem to affect the resonant frequency visibly.

Discussion and Analysis of Data

Frequency data as a function of time for the formation of octanethiol monolayer can be seen in Figure 1.

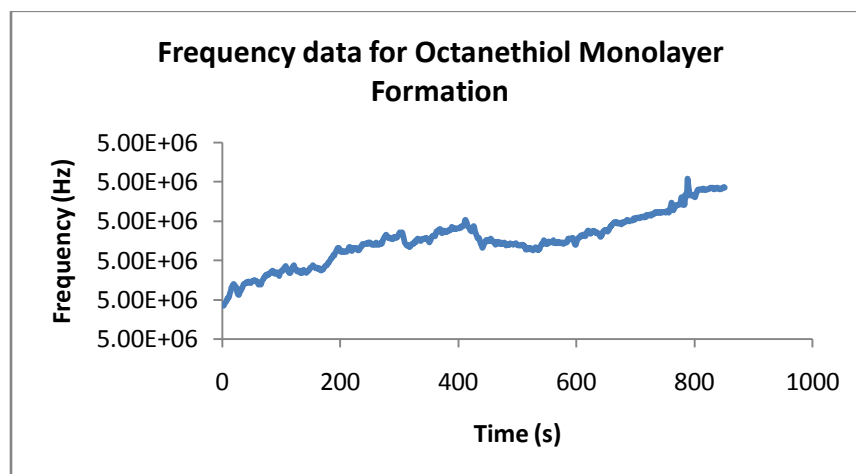


Figure 1

This plot was then normalized to correct for thermal drift and re-plotted in Figure 2.

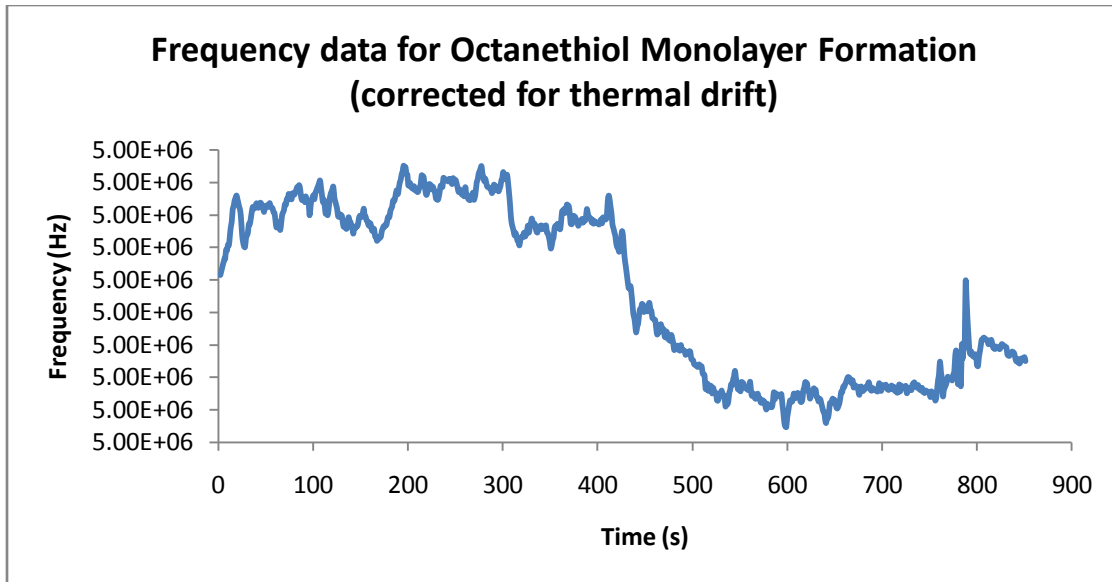


Figure 2

The frequency shift upon formation of octanethiol monolayer was calculated to be **-5.69 Hz**.

Using the Sauerbrey equation, we can calculate the mass adsorbed onto the surface:

$$\Delta m = -\frac{\Delta f}{C_f} = \frac{5.69 \text{ Hz}}{5.86 \times 10^7 \text{ Hz cm}^2 / \text{g}} = 97.1 \text{ ng/cm}^2. \text{ Assuming a surface area of } 1.33 \text{ cm}^2, \text{ the total mass adsorbed would be } 97.1 \text{ ng/cm}^2 * 1.33 \text{ cm}^2 = \mathbf{129 \text{ ng}}.$$

The packing density is simply the number of moles of octanethiol (molar mass = 146.3 g/mol)

per cm^2 area, i.e. $\frac{97.1 \text{ ng/cm}^2}{146.3 \text{ g/mol}} = 6.64 \times 10^{-10} \text{ mol/cm}^2$. The average footprint area for a *single*

surface bound octanethiol would be

$$\frac{1 \text{ cm}^2}{6.64 \times 10^{-10} \text{ mol} \times 6.022 \times 10^{23} \text{ octanethiols/mol}} = 2.5 \times 10^{-15} \text{ cm}^2 = 0.25 \text{ nm}^2 \text{ per octanethiol}.$$

Assuming a (111) crystal structure for gold provide an estimate for how many gold atoms are involved in the footprint in the monolayer formed and compare to the value estimated in the prelaboratory questions. (3 marks)

From above, we calculated 0.25 nm^2 per octanethiol. For a 1 cm^2 surface area, we expect to have $1 \text{ cm}^2 / 0.25 \text{ nm}^2 = 1 \text{ cm}^2 / 2.5 \times 10^{-15} \text{ cm}^2 = 4 \times 10^{14}$ octanethiol atoms in total. Assuming (111) crystal structure for gold, we estimate that each thiol molecule is associated with 3 gold atoms. Thus the total number of gold atoms involved in the footprint in the monolayer formed will be $4 \times 10^{14} * 3 = \mathbf{1.2 \times 10^{15}}$ gold atoms.

Compare the monolayer density to the value determined in the prelaboratory exercise and the optimal value determined in reference 1 and provide reasons for any discrepancies. (3 marks) (remove paragraph)

The monolayer density for a generic alkanethiol on an Au (111) surface stated in the prelaboratory exercise was $1.37 \times 10^{-10} \text{ mol/cm}^2$. The monolayer density obtained with octanethiol above was $6.06 \times 10^{-10} \text{ mol/cm}^2$. This difference arises from the fact that one footprint value was obtained for any generic alkanethiol while the value we obtained above was specifically for octanethiol. The latter value is therefore more correct.

The optimal value determined in reference 1 is $21.4 \text{ \AA}^2/\text{molecule}$ which is $2.14 \times 10^{-15} \text{ cm}^2/\text{molecule}$. Inverting and dividing by Avagadro's number gives us $7.76 \times 10^{-10} \text{ mol/cm}^2$. The percentage difference between this density and our obtained density is 21.9% which is fairly reasonable given the constraints of this laboratory and the non-idealities of our QCM.

Determine the noise of the experiment and the signal to noise ratio for the measurement. Provide a value for the frequency drop with its error range. (2 marks)

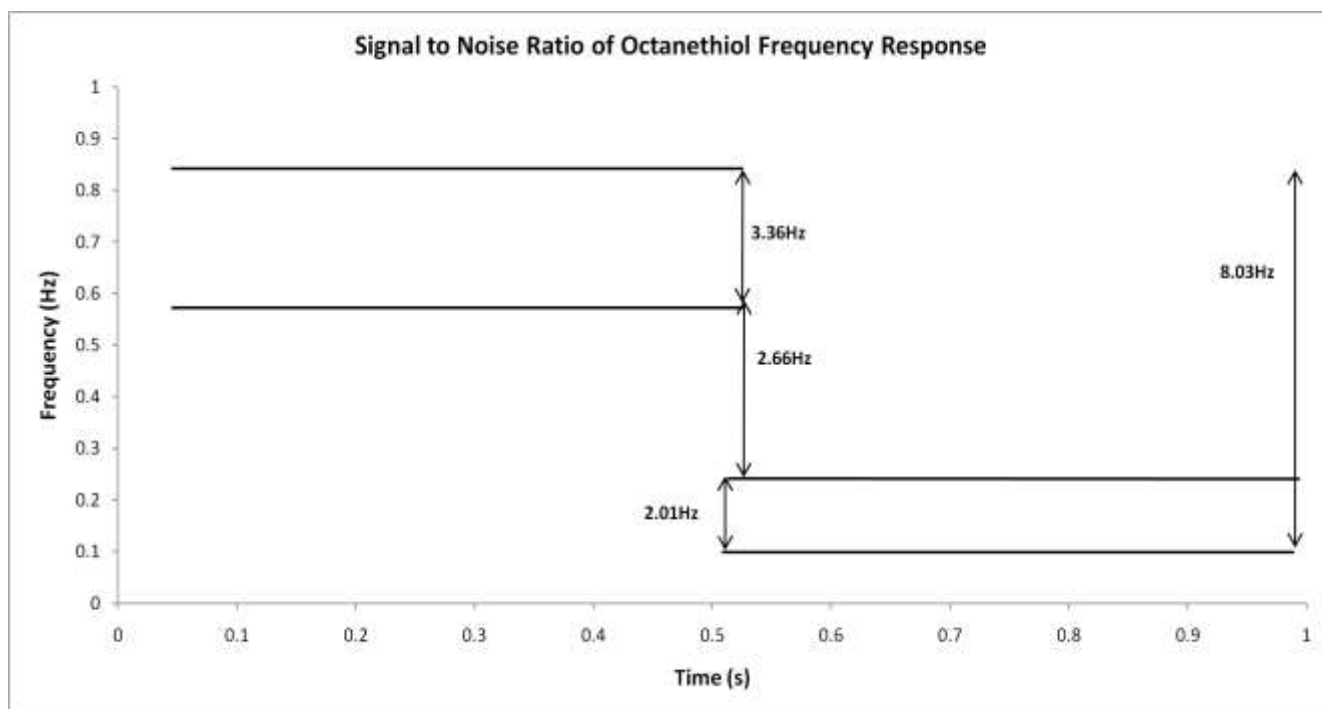


Figure 3

The frequency drop upon formation of octanethiol monolayer was calculated to be **5.69 Hz**. The noise in measurement before the octanethiol monolayer deposition was 3.36 Hz. The noise in monolayer deposition after the octanethiol layer formation was 2.01 Hz. Thus the total noise is $3.36 + 2.01 = \mathbf{5.37 \text{ Hz}}$. The signal to noise ratio is therefore $5.69 / 5.37 = \mathbf{1.06}$. Since this ratio is greater than 1, we conclude that our measurements are meaningful.

Due to the noise levels involved in the signal measurement as described in the previous paragraph, the frequency drop was calculated to be anywhere from 2.66 Hz and 8.03 Hz. This

implies an error range of [-3.03, 2.34]. The error range is non-symmetric since the noise levels were non-symmetric before and after the octanethiol monolayer formation. The average error in both directions is therefore $(3.03 + 2.34) / 2 = 2.69$. Thus the final frequency drop with error range is 5.69 ± 2.69 Hz. The relative error is $2.69 / 5.69 * 100\% = 47\%$.

Compare the crystals affinity for water before and after the monolayer reaction and discuss the reasons for this. (2 marks)

Immediately after washing the QCM with piranha solution, the QCM was hydrophilic when a droplet of water was added. The droplet spread itself evenly throughout the QCM's gold surface. This is because the unmodified gold surface is clean (i.e. does not contain any film) and naturally hydrophilic.

After the surface was modified with the octanethiol, the gold surface became hydrophobic. Each drop of water added would break up into individual droplets and would rush towards the outer circumference of the hydrophobic gold surface to minimize contact. This is because the octanethiol layer just deposited on the gold surface is very largely hydrophobic due to its long alkane chain.

Lab 5a Determining the Frequency Response of an Unmodified QCM in the Presence of Solvent Vapours

Introduction and Objective

The objective of this laboratory experiment is to deposit three different kinds of solvents, namely ethanol, acetone and water, and to determine the shift in resonant frequency upon addition of these volatile solvent vapours in the gas phase. The data from this lab will be used as blanks in the second part of this lab (Lab 5b) for vapour sensing applications.

Experimental Procedure

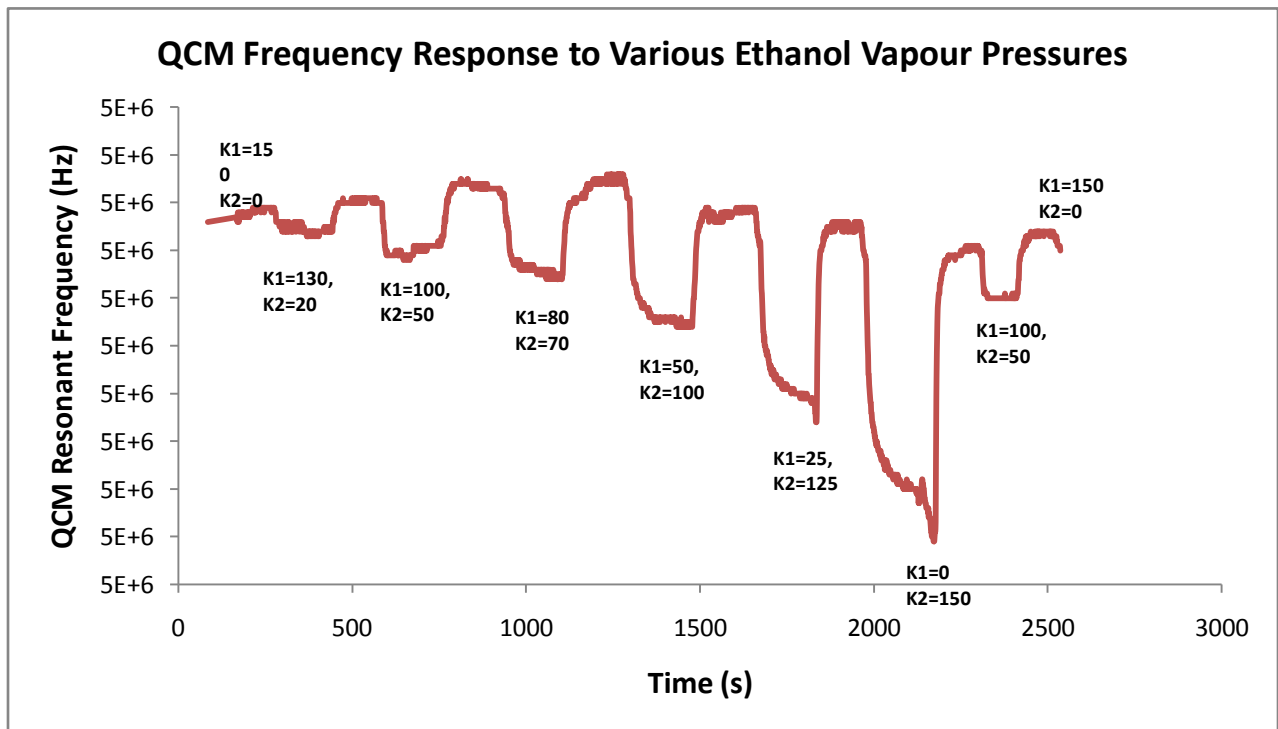
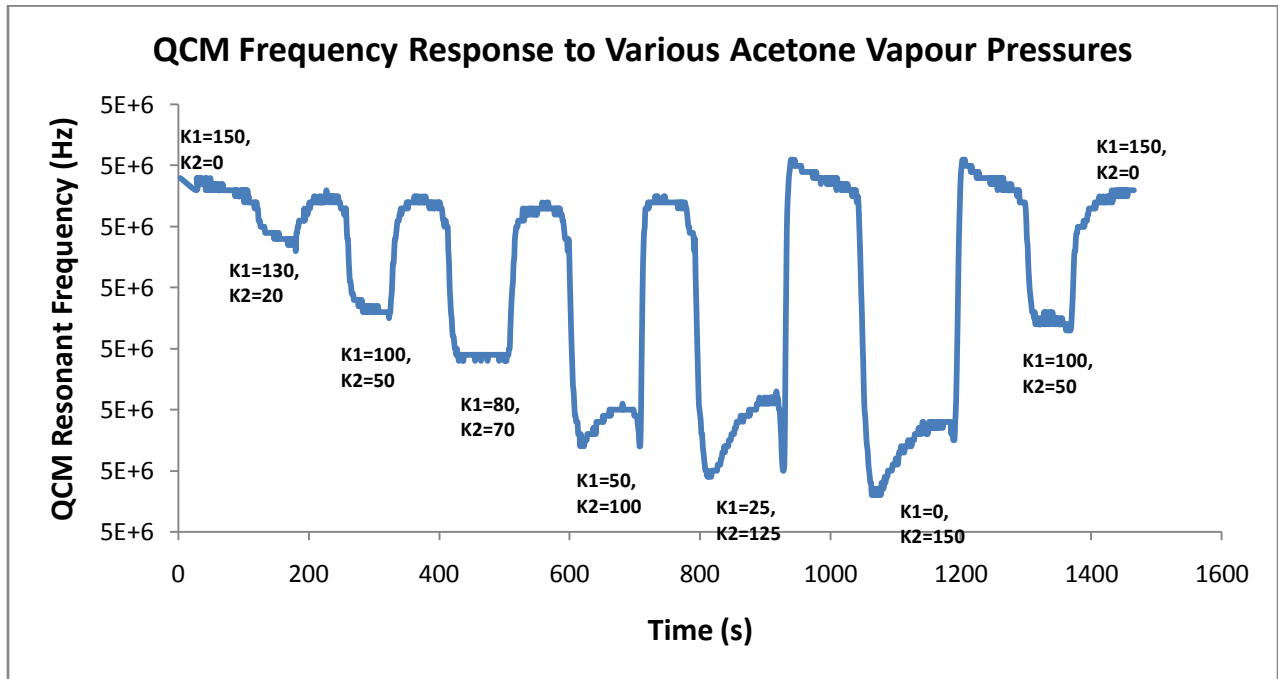
The procedure for this laboratory was obtained from the NE 455L/461L Nano Instruments Week 1 part of the Nanotechnology Engineering Program 4B Lab Manuals, 2010. No deviations were observed.

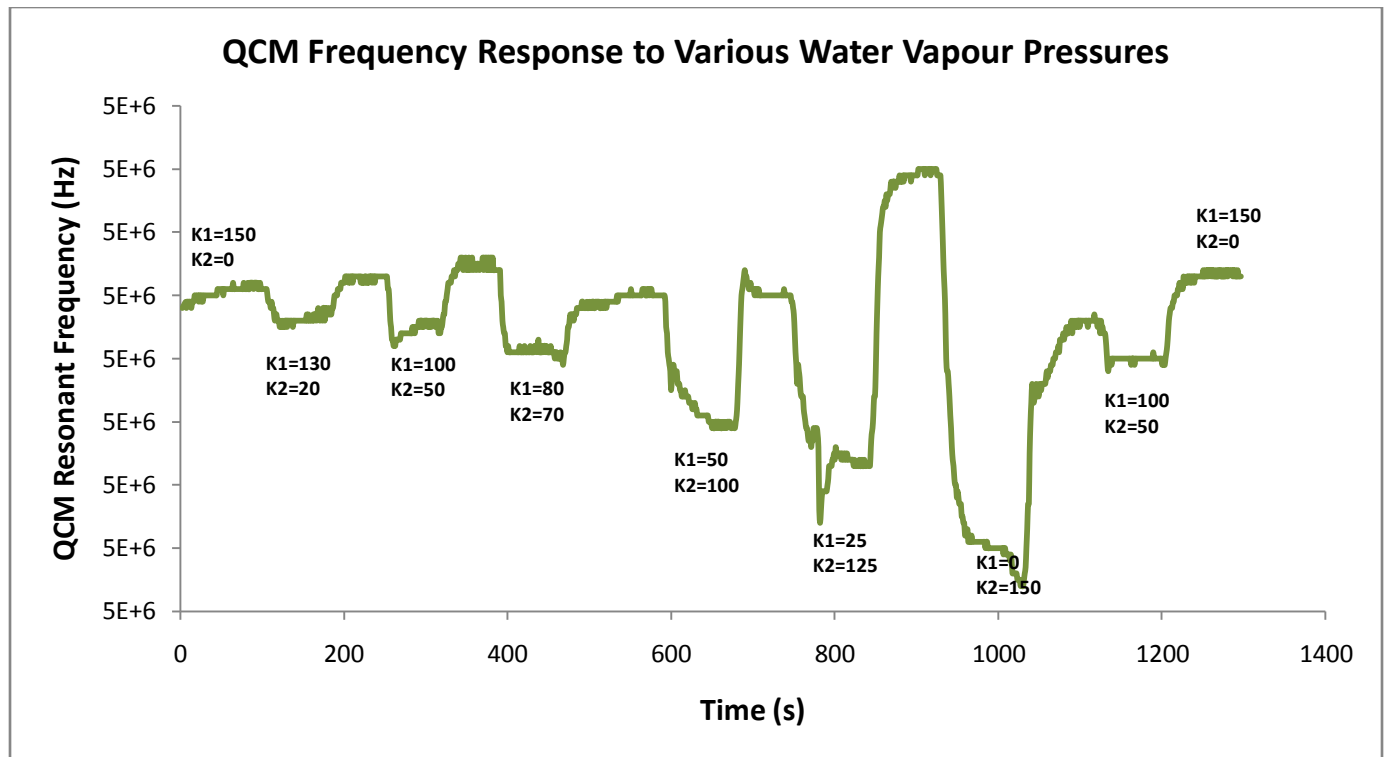
Discussion and Analysis of Data

The blank values of the vapour response are used for the laboratory in week two. In the final report discuss how much the background signals contribute to the signals. What phenomena is occurring to create background signals?

The frequency response to the 3 vapours studied is shown below in the following figures. K1 is the pressure of pure nitrogen in mL/min, while K2 is the pressure of the vapour (ethanol, acetone, water, etc.) also in mL/min. The total pressure of the system was always kept constant at 150 mL/min except momentarily when the pressures were being adjusted to new values.

These blank values of the vapour response are the background signals. The contribution of the background signals and the phenomenon occurring to cause them is discussed in Lab 5b.





Lab 5b Vapour Sensing with Nanoparticle Films

Introduction and Objective

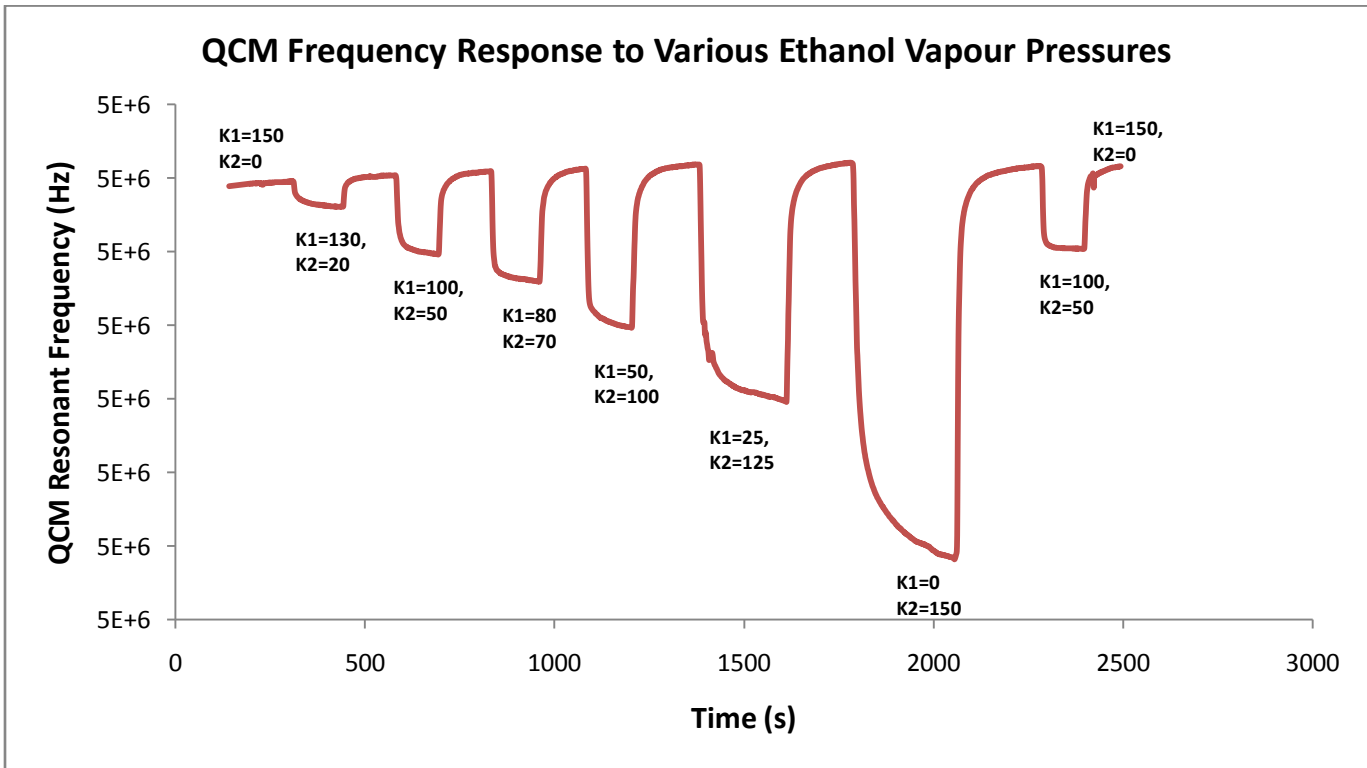
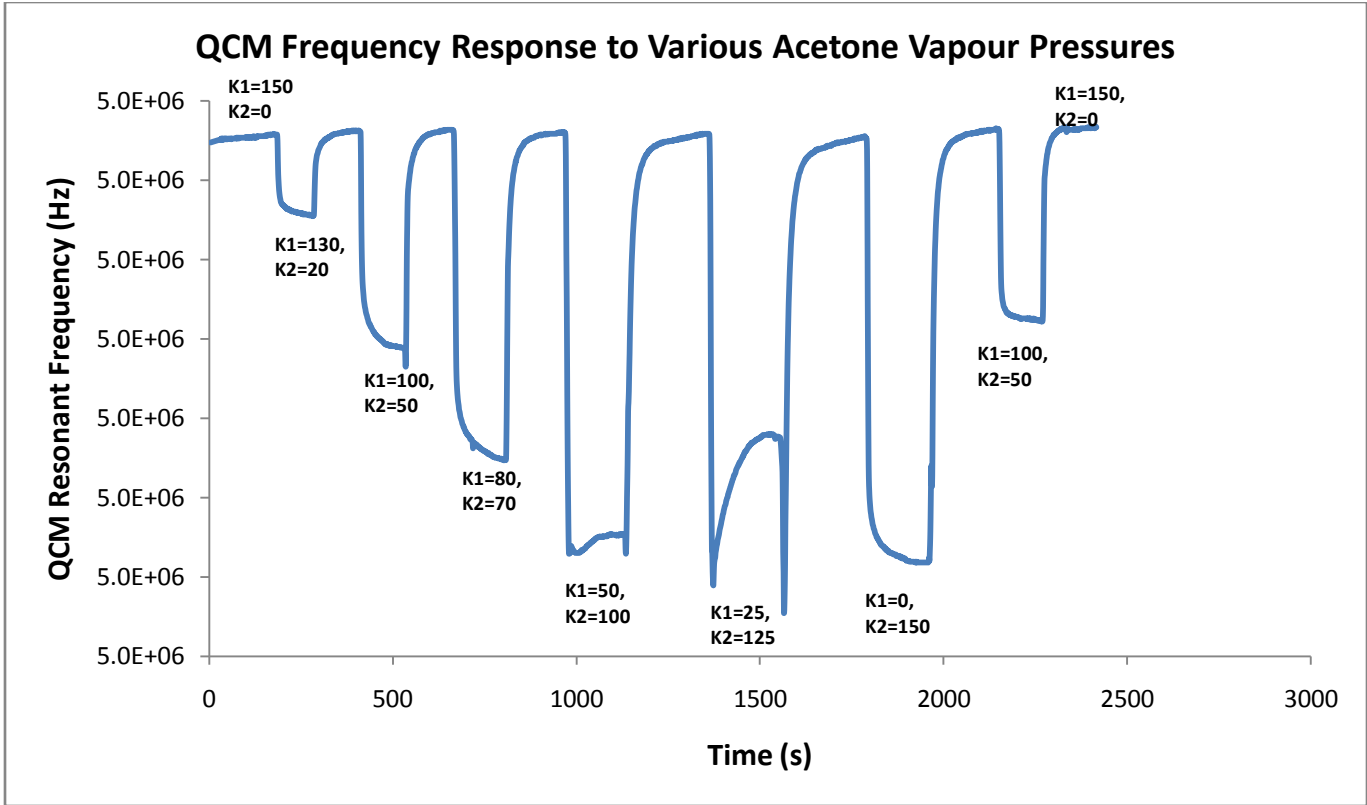
The objective of this laboratory experiment is to coat a thin layer of 100nm thick Au-MPC solution on top of the octanethiol modified QCM crystal and to then use this QCM for vapour sensing of acetone, ethanol and water vapours.

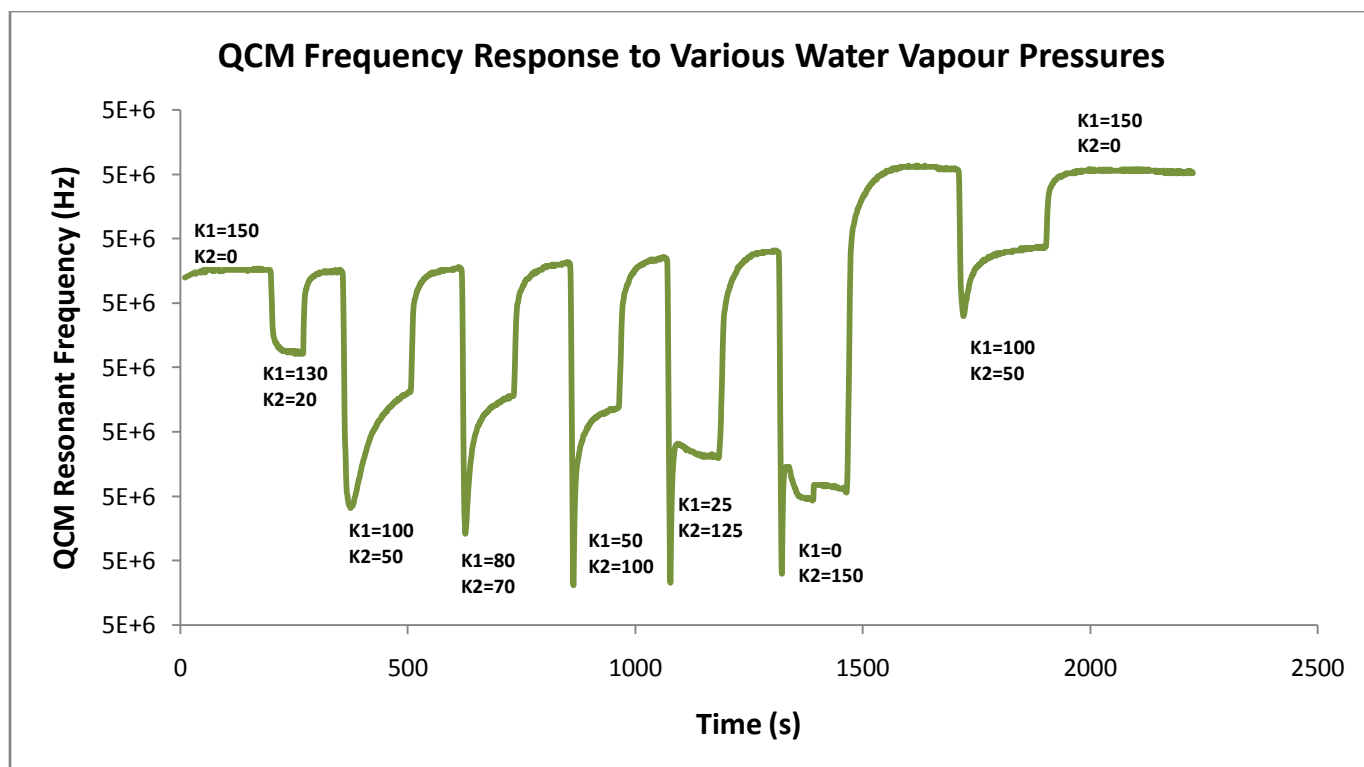
Experimental Procedure

The procedure for this laboratory was obtained from the NE 455L/461L Nano Instruments Week 1 part of the Nanotechnology Engineering Program 4B Lab Manuals, 2010. No deviations were observed.

Discussion and Analysis of Data

Plot the frequency data collected and label all events that occur. (2 marks)





First use the film thickness and the active surface area of the crystal to determine the volume of the MPC film. Determine the mass of solvent vapour that partitions into the film from the frequency shift data for each vapour at each concentration. Make sure to subtract the blank frequency from week 1 to obtain true frequency shifts from absorption into the nanoparticle film.

Volume of MPC film = Thickness * Area = 100 nm * 1.33 cm² = 1.33E-5 cm³ = 1.33E-8 dm³ = 1.33E-8 L.

The mass of solvent vapour that partitions into the film can be calculated from the normalized (i.e. blank data from Week 1 subtracted) frequency shift data using the Sauerbrey equation. Sample calculation for acetone at K1=130 mL/min:

$$\Delta m = \frac{\Delta f}{C_f} \times \text{Area} = \frac{9.1}{5.86 \times 10^7} \times 1.33 = 2.065 \times 10^{-7} \text{ g} = 206.5 \text{ ng}$$

Solvent	K1 (mL/min)	K2 (mL/min)	Frequency Shift (Hz)	BLANK Frequency Shift (Hz)	Combined Shift (Hz)	Mass into Film (ng)
Acetone	130	20	10.1	1.0	9.1	206.5
	100	50	27.3	1.7	25.6	581.0
	80	70	41.5	2.6	38.9	882.9
	50	100	53.1	3.9	49.2	1116.7
	25	125	55.2	4.4	50.8	1153.0

	0	150	53.6	5.5	48.1	1091.7
<i>Ethanol</i>	130	20	6.6	0.3	6.3	143.0
	100	50	21.0	1.0	20.0	453.9
	80	70	29.4	1.9	27.5	624.1
	50	100	42.6	2.9	39.7	901.0
	25	125	63.4	3.9	59.5	1350.4
	0	150	106.8	5.6	101.2	2296.9
<i>Water</i>	130	20	6.4	0.5	5.9	133.9
	100	50	17.8	0.9	16.9	383.6
	80	70	20.5	1.2	19.3	438.0
	50	100	24.5	2.0	22.5	510.7
	25	125	25.2	3.6	21.6	490.2
	0	150	25.0	6.5	18.5	419.9

As can be seen from the table above, the blank values do not contribute all that much to the overall signal. They roughly constitute only 6%-10% of the actual signal. The phenomenon occurring to create these background signals is the fact that the QCM is now immersed in a different medium than air which causes its resonant frequency to dampen a bit. This happens even if no vapour is actually adsorbed on the surface of the QCM to change its mass.

Determination of Cs for all vapours at all concentrations.

From the mass of vapour that was partitioned into the film, we can calculate Cs using the molar mass of the vapour (58.1 g/mol for acetone) and the volume of the film ($1.33\text{E-}5\text{ cm}^3$)

Sample calculation for acetone:

$$Cs = \# \text{ of moles} / \text{volume} = (\text{mass of vapour} / \text{molar mass}) / \text{volume} = 206.5\text{E-}9 \text{ g} / 58.1 \text{ g/mol} / 1.33\text{E-}8 \text{ L} = 0.267 \text{ mol/L.}$$

Vapour	Mass of Vapour in Film (ng)	Molar Mass (g/mol)	Cs (mol/L)
Acetone	206.5	58.1	0.267373
	581.0		0.75217
	882.9		1.142945
	1116.7		1.445576
	1153.0		1.492586
	1091.7		1.413256
Ethanol	143.0	46.1	0.233369
	453.9		0.740855
	624.1		1.018675
	901.0		1.470597
	1350.4		2.204043
	2296.9		3.748725
Water	133.9	18.0	0.558727
	383.6		1.600421
	438.0		1.8277

	510.7		2.130738
	490.2		2.045509
	419.9		1.75194

The C_s values can be calculated the same as that in the pre-lab using the formulas

$$P = p \left(\frac{r_v}{r_v + r_{N_2}} \right), C_v = \frac{P}{RT}, \text{ and from the NE 461L lab introduction manual.}$$

Sample calculation:

Acetone at 50/150 saturation:

$$C_v = 30.8 \text{ kPa} * (50 / 150) / (8.31447 \text{ L kPa} / \text{K} / \text{mol} * 298 \text{ K}) = 4.14\text{E-}3 \text{ mol/L.}$$

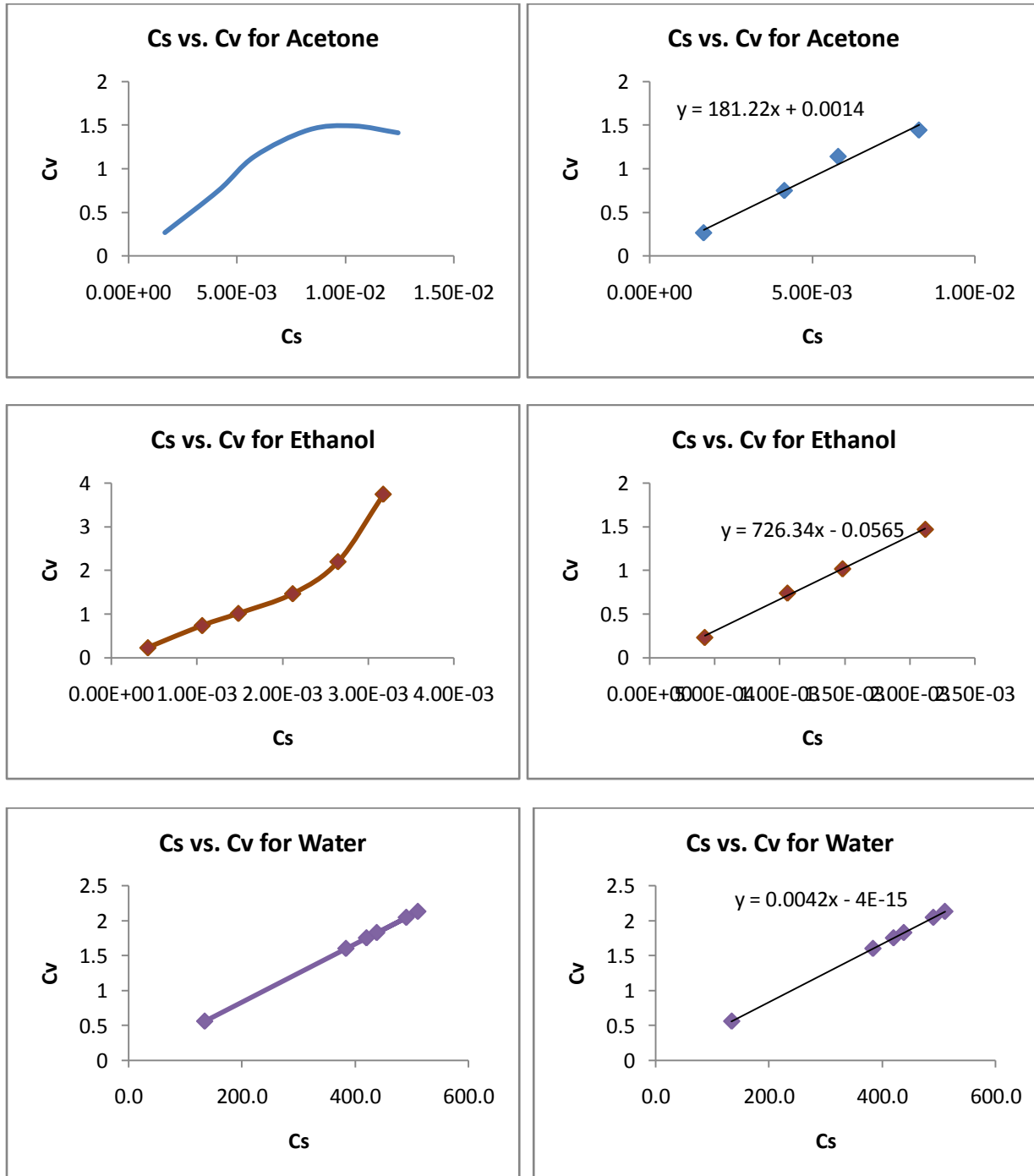
$$C_s = K * C_v = 500 * 4.14\text{E-}3 \text{ mol/L} = 2.07 \text{ mol/L}$$

The rest of the C_v and C_s values are tabulated below for each concentration and each vapour.

Vapour	p (Vapour pressure, kPa)	Flow of Vapour	Dilution Ratio	P (Pressure, kPa)	C_v (mol/L)	C_s (mol/L)
Acetone	30.80	20	0.133	4.107	0.001657	0.267373
		50	0.333	10.267	0.004142	0.75217
		70	0.467	14.373	0.005798	1.142945
		100	0.667	20.533	0.008283	1.445576
		125	0.833	25.667	0.010354	1.492586
		150	1.000	30.800	0.012425	1.413256
Ethanol	7.87	20	0.133	1.049	0.000423	0.233369
		50	0.333	2.623	0.001058	0.740855
		70	0.467	3.673	0.001482	1.018675
		100	0.667	5.247	0.002116	1.470597
		125	0.833	6.558	0.002646	2.204043
		150	1.000	7.870	0.003175	3.748725
Water	3.17	20	0.133	0.423	0.000171	0.558727
		50	0.333	1.057	0.000426	1.600421
		70	0.467	1.479	0.000597	1.8277
		100	0.667	2.113	0.000853	2.130738
		125	0.833	2.642	0.001066	2.045509
		150	1.000	3.170	0.001279	1.75194

Plot C_s versus C_v and determine the partition coefficient for each vapour. Note – in some cases saturation may occur and the plot will become ‘flat’ at high vapour concentrations. Do not use data from the flat portion of the curve but make note of the concentration where saturation occurred. (2 marks)

This is what we get when we plot C_s vs C_v for each vapour. The left side plots show the original data with flattening, and the right sides show the data after the 'flat' portion has been removed to leave just the linear regime so we can calculate its slope and determine the partition coefficient K .



Thus the partition functions, as determined from the slopes of the linear regimes of the C_s vs. C_v curve are as follows: Acetone: **181.22**, Ethanol: **726.34**, and Water: **0.0042**. We see that

ethanol has the highest partition coefficient, followed by acetone and lastly followed by water. This makes sense the partition coefficient measures the affinity for the vapour to bind to the atoms of the film on the QCM. Since the Au-MPC film we deposited is highly hydrophobic, ethanol, being an alcohol, has the highest K value due to its highest hydrophobicity. Water being the most hydrophilic has the lowest K value. Acetone, a ketone, is somewhere in between and consequently has a medium K value.

Determine the signal to noise ratio for the lowest frequency shifts measured. (2 marks)

The lowest frequency shifts occurred for the smallest pressures of each vapour. The signal to noise ratios for these frequency shifts were calculated and tabulated below (SNR = Signal/Noise). The noise was calculated by summing the variation in data (i.e. the amount of fluctuation) observed before and after a drop in resonant frequency.

	Noise Above (Hz)	Noise Below (Hz)	Total Noise (Hz)	Signal (Hz)	SNR
Acetone	1.1	2.3	3.4	10.1	2.97
Ethanol	1.4	4.1	5.5	6.6	1.20
Water	1.8	0.6	2.4	6.4	2.67

Determine the minimum concentration vapour that can be detected for all the vapours. (2 marks)

The lowest minimum concentration vapour occurs when the signal-to-noise ratio (SNR) is exactly 1. In other words, the signal equals the noise level. For a noise level of 3.4 for acetone for example, the minimum mass that can be detected is $3.4 / 5.86E7 * 1.33 = 8E-8$ g, and the minimum C_s detectable is $8E-8g / 58.1 \text{ g/mol} / 1.33E-8 \text{ L} = 0.0999 \text{ mol/L}$. Similar calculations maybe performed for ethanol and water vapours. The results are tabulated below:

	Total Noise (Hz)	Lowest Mass Detectable (g)	Lowest C_s detectable (mol/L)
Acetone	3.4	7.72E-08	0.0999
Ethanol	5.5	1.25E-07	0.2037
Water	2.4	5.45E-08	0.2273

Discuss the significance of the partition coefficient and how it can be used to distinguish the solvents investigated. (2 marks)

The partition coefficient is defined as $K = \frac{C_s}{C_v}$. It is the ratio between C_s and C_v . In other words,

the partition coefficient is the ratio of the concentration of vapour in the material of interest (stationary phase, i.e. film) to the concentration in the applied vapour phase surrounding the film.

If $K > 1$, then there is more vapour in the film than outside. If $K < 1$, then there is more vapour in the phase surrounding the film than in the film itself. A high K implies that more vapour has been absorbed into the film.

The value of K is a function of the vapour used, its partial pressure, and the properties of the stationary phase (i.e. the film). So if we used the same film or multiple identical films, we would be able to distinguish between the solvents by subjecting the film to the unknown vapour at a known pressure and calculating the value of K using frequency shift data and comparing this K value against a list of standards for which the value of K is known.

Lab 6 Preparation and Performance Testing of a Gratzel Photocell

Introduction and Objective

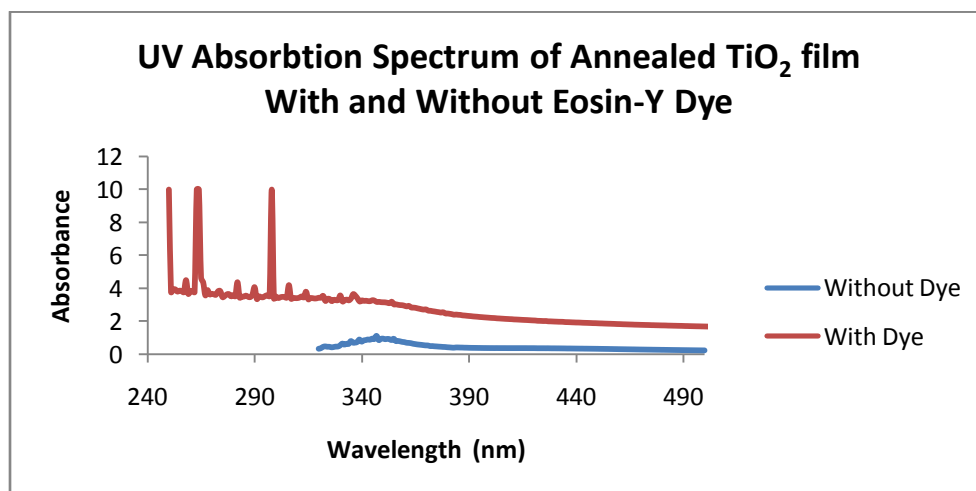
The objective of this laboratory experiment is to prepare a photocell comprising of TiO_2 nanoparticle film, and to characterize and test this photocell for its performance. Two different TiO_2 nanoparticle films will be prepared: one film will contain TiO_2 ordered directly from Sigma-Aldrich, and the other film will be prepared from a TiO_2 powder that was prepared in-house by Prof. Eric Prouzet.

Experimental Procedure

The procedure for this laboratory was obtained from the NE 455L/461L Nano Instruments Weeks 2 and 3 parts of the Nanotechnology Engineering Program 4B Lab Manuals, 2010. No deviations were observed.

Discussion and Analysis of Data

The following chart shows the absorbance data with and without the dyes loaded into the annealed anatase TiO_2 film.



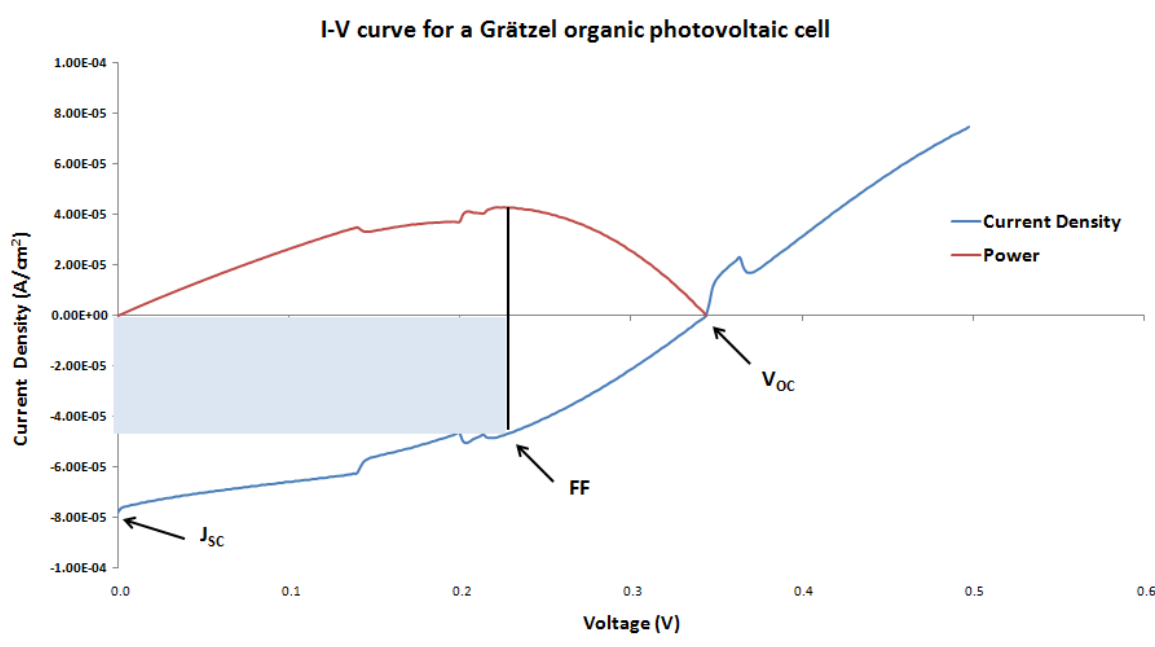
Note the sharp absorbance peaks at 250 nm, 264 nm, and 298 nm resulting from the Eosin-Y molecules. The TiO₂ on its own absorbs mostly only in the UV range from 330 nm to 370 nm.

1. Plot the *i-v* curve and label *J_{SC}*, *V_{OC}*, *FF* and maximum power (in watts/cm²). (8 marks)

Diameter of the hole punch = 6.45 mm = 0.645 cm

Radius = Diameter / 2 = 0.3225 cm

Area of hole punch = $\pi r^2 = \pi(0.3225 \text{ cm})^2 = 0.327 \text{ cm}^2$



From the above IV curve, we extract the key cell parameters:

$V_{oc} = 0.342 \text{ V}$, $J_{sc} = 7.83 \times 10^{-5} \text{ A/cm}^2$, Max power = $4.29 \times 10^{-5} \text{ W/cm}^2$. The fill factor can be

calculated as
$$FF = \frac{V \times J}{V_{oc} \times J_{sc}} = \frac{0.226 \times 4.75 \times 10^{-5} \text{ A}}{0.342 \times 7.83 \times 10^{-5} \text{ A}} = 0.19$$

2. Why is the annealing process done before treatment with Eosin Y? Would it be possible to mix the dye with the nanoparticles prior to the casting process? (2 marks)

The annealing process casts the TiO₂ film in place and significantly increases film strength and electrical conductivity between the film and the ITO. The annealing process is done *before* the Eosin-Y treatment so as to convert the film into two separate anatase and rutile (TiO₂) phases. This converts the film into a scaffold that can hold large numbers of dye molecules in a 3D matrix which increases the number of dye molecules that can be held by the film for any given surface area of the cell. This leads to significantly higher dye loading which increases the efficiency of the solar cell.

It would indeed be possible to mix the dye with the TiO₂ nanoparticles prior to the casting process but since the anatase-TiO₂ won't be formed into a matrix, the dye would have nothing

to hold onto resulting in very poor loading. The casting process is essential to fixing the thickness of the film and separating the anatase-rutile phases.

3. Why is the dye necessary for photocurrent instead of direct excitation of TiO_2 ? (2 marks)

Usually, the TiO_2 would act as both the source of photo-generated electrons as well as providing the electric field needed to separate the created excitons and produce a current. In a dye-sensitized Gratzel cell however, the bulk of the cell is used solely for charge transport while the dye becomes the primary source of photoelectrons. This way, we can engineer the dye and the TiO_2 separately to optimize for both exciton creation as well as charge transport.

Furthermore, TiO_2 only absorbs a small fraction of photons in the spectrum, namely only those in the UV range. The dye is necessary to absorb visible light above 300 nm wavelength.