

NAME _____

OREGON STATE UNIVERSITY

DEPARTMENT OF CHEMISTRY

Experiment 1

Integrated Laboratory Experiment

CHEMICAL INSTRUMENTATION

PART B. OPTICAL INSTRUMENTATION

| | | |
|-------|--|----|
| I. | Introduction | 2 |
| II. | Tungsten Light Source | 2 |
| III. | Monochromator | 4 |
| IV. | Sample Compartment | 6 |
| V. | Silicon Photodiode | 8 |
| VI. | Photomultiplier Tube | 11 |
| VII. | Wavelength Scan with Terminal | 14 |
| VIII. | CCD Spectrometer (finish day 1) | 16 |
| IX. | Noise, Frequency Response and Signal Averaging | 20 |
| X. | Optical Filters | 22 |
| XI. | Wavelength Calibration and Wavelength Resolution using a Mercury Line Source | 24 |
| XII. | Lab Report | 29 |
| | Data Sheet | 30 |

EXPERIMENT 1

PART B. OPTICAL INSTRUMENTATION

I. INTRODUCTION

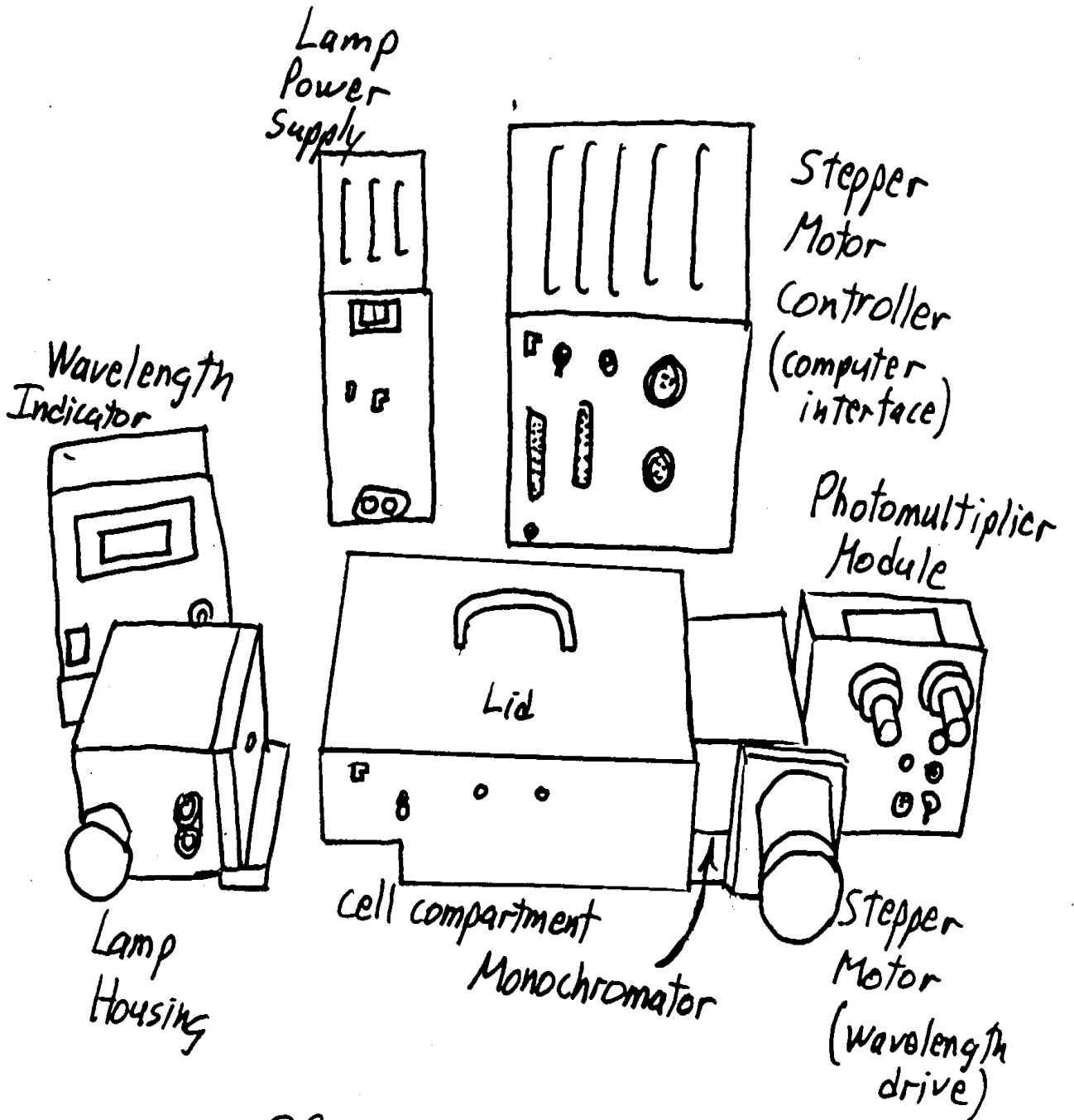
In this experiment, you will gain familiarity with the optical components at your instrument station. You will study the characteristics and operation of common wavelength selection devices, for example, the monochromator and glass filters; optical transducers, such as the photomultiplier tube, the silicon photodiode and the charge coupled device; and excitation sources, such as the tungsten light bulb and the mercury vapor lamp.

Objectives: Explain and determine experimentally: 1. the characteristics of light sources, monochromators and photodetectors commonly used in chemical laboratories; 2. the effect of slit width in a monochromator on the light throughput and wavelength resolution; 3. how the magnitude of signal fluctuations (noise) depends on the time constant or cutoff frequency of the signal processing electronics.

In the data sheet attached to the back, space is provided for the data, calculations and answers to questions. Be sure to attach the appropriate charts and print-outs of computer files at the end of the report.

II. TUNGSTEN LIGHT SOURCE

A **tungsten filament lamp** is commonly used as a radiation source for excitation in the near-ultraviolet (UV)-visible-near-infrared (IR) wavelength range (320 - 2500 nm). The spectral output for this lamp approaches that of a blackbody radiator. Find the PTR model 01 tungsten halogen light source and its 12-V dc power supply. If necessary, connect the power supply to the source with the black cable with double banana plugs at both ends. Turn the power supply on. Note that the manual shutter on the front port of the light source module can be used to block the exiting radiation. An f/2 lens mounted in the exit port focuses the radiation 2" beyond the front of the light source module. The knob on the side of the light source module facing you is used to adjust the position of the lamp and hence the position of the focused image of the lamp filament. This adjustment should be made only with the help of an instructor.



SPECTROMETER COMPONENTS

III. MONOCHROMATOR

A **monochromator** is a versatile wavelength selection device. It is used to select a particular narrow wavelength range from the total radiation range emitted by a source. The PTR Mini-Chrom scanning monochromator uses a Fastie-Ebert $f/4$ optical configuration. It contains an 1800 line/mm holographic diffraction grating and can be used to select wavelengths in the 220 nm to 1000 nm range. The monochromator has a **reciprocal linear dispersion (R_d)** of 6 nm/mm, a focal length of 74 mm, and a wavelength resolution of about 1 nm.

The basic design of the monochromator is shown in Figure 1. Ask a TA to show you a non-scanning demonstration model of the monochromator for your inspection. Locate the **entrance and exit slits** and the folding mirrors, the **collimating and focusing mirror**, and the **grating**. Light entering the entrance slit is reflected off the entrance folding mirror and collimated by the large spherical mirror and directed to the diffraction grating. The diffracted radiation from the grating strikes the spherical mirror again, reflects off the exit folding mirror and is focused in the focal plane containing the exit slit. The grating horizontally disperses the light so that the image for each wavelength, defined by the entrance slit, is focused at a different horizontal position in the focal plane. The image of one wavelength passes completely through the exit slit whereas nearby images are partially blocked. Most images are totally blocked. Therefore, the exit slit passes only a narrow band of wavelengths.

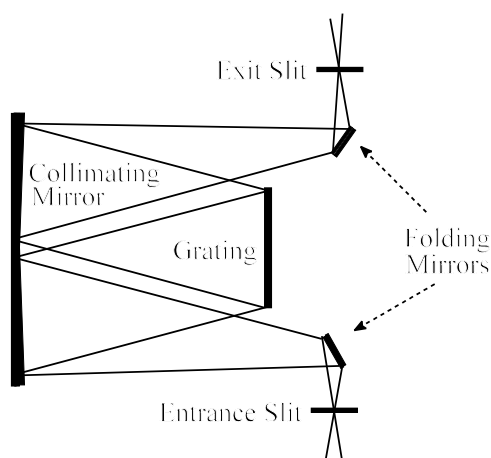


Figure 1. Monochromator

The central wavelength passed by the monochromator is changed by rotating the grating with a drive mechanism. In the non-scanning demonstration monochromator, the drive shaft of the grating is connected to a digital micrometer, which is calibrated to display the central wavelength passed by the monochromator in nanometers. In the scanning monochromator at your station, the

grating drive shaft is connected to a stepper motor, which can be rotated under control of software on the PC or rotated by hand (if the stepper motor is turned off.)

Hold the demonstration monochromator with one slit pointed towards the ceiling light and look into the monochromator through the other slit. Rotate the micrometer and note the color of light observed. Remove the cover. Rotate the wavelength control and note its effect on the position of the grating.

The wavelength range passed by the monochromator and the **wavelength resolution of the monochromator are determined by the slit widths (W)**. Three pairs of fixed slits with widths of 150, 300, and 600 μm plug interchangeably into the monochromator entrance and exit ports. **Locate these slits.** The size of the slit can be judged by eye by comparing the relative widths or by the colored dots on the slit discs, **150 μm (red), 300 μm (green) and 600 μm (yellow)**. The specified widths are nominal values and the actual values may differ by $\pm 15\%$.

The width of the **entrance slit** controls the amount of light entering the monochromator and affects the size of the optical image of each wavelength focused on the focal plane of the exit slit. The magnitude of the wavelength range that leaves the monochromator is determined by the width of the **exit slit** together with the width of the image of the entrance slit and the reciprocal linear dispersion (R_d) of the grating.

The **spectral bandpass, s, given in nm**, is defined as the **half-width** of the wavelength range passed by the exit slit (i.e., the value of s is such that the transmission of the monochromator at $\lambda_0 \pm s/2$ is $1/2$ that at λ_0 , where λ_0 is the central wavelength of the monochromator.) For moderate and larger slit widths, s is related to **W** by the equation,

$$s = R_d W \quad (1)$$

where R_d is the reciprocal linear dispersion of the grating in nm/mm and W is in mm.

For any monochromator or spectrometer, there is a practical limit to the smallest useful slit width because of optical aberrations of mirrors and lenses and diffraction effects blur the images in the focal plane. For the PTR monochromator the practical limit for W is about 100 to 150 μm or a wavelength range of 0.6 to 0.9 nm. For slit widths near this limit, the image of a line source in the focal plane is wider than the entrance slit, so $s > R_d W$, and Equation 1 is no longer valid. Thus **for very small slit widths, s is independent of W**.

For a **continuum source**, such as the tungsten lamp, **the radiant power Φ (exiting the exit slit) is proportional to W^2** provided that both the entrance and exit slits are the same width and the image of the source fully illuminates the entrance slit. Here the entrance slit width determines the amount of light entering the monochromator, while the exit slit width affects the range of

wavelengths exiting the monochromator. This **range of wavelengths is nominally $\lambda_0 \pm s$** where λ_0 is the central wavelength of the monochromator. The intensity pattern for this wavelength range is triangular with apex at the central wavelength, a half-width of s , and a nominal base width of $2s$. This function is often denoted the **slit function**.

For a **line source**, such as a Hg arc lamp, the emission lines are effectively distinct monochromatic lines. When a line source is scanned, the half-width of the recorded peak is equal to the spectral bandpass of the monochromator (and not the true width of the line). When the monochromator wavelength is set to one of these lines, the **radiant power Φ (exiting the exit slit) is proportional to W** provided that both the entrance and exit slits have the same width and the image of the source fully illuminates the entrance slit.

IV. SAMPLE COMPARTMENT

The light source, monochromator, and detector all connect to the ports of the PTR sample compartment. Locate the three ports. Remove the compartment lid and note that inside there are three lenses, a filter holder, and a sample cell holder.

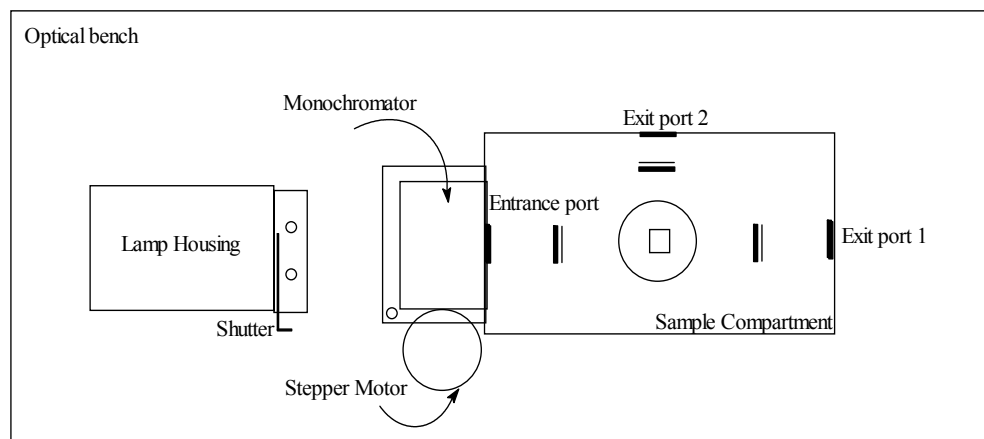


Figure 2. Initial configuration for the optical components.

The light source, monochromator (attached to its own base plate), and the sample compartment can be mounted in various configurations with $\frac{1}{4}$ -20 machine screws to a small optical bench to provide stability and light-tight connections. Insert one 150- μm slit into the entrance port of the monochromator and one 150- μm slit into the exit port of the monochromator. Mount the tungsten light source, monochromator and sample compartment to the bench in the configuration shown in Figure 2. Turn on the tungsten light source power supply and set the “Mini-Chrom” wavelength

display to battery position. **Now check that the stepper motor controller power is switched off** (red indicator light on front / switch on back) so that you can manually turn the monochromator wavelength drive shaft. Manually adjust the wavelength to 0.0 nm as shown on the wavelength display. **This wavelength setting is called the zero order setting because all wavelengths are diffracted from the grating at the same angle.** Since the tungsten source is a continuum light source, the monochromator passes white light at the zero order position of the grating.

Now use a small piece of white paper to follow the path of the light beam. First put the paper in front of the entrance slit of the monochromator. Do you see the image of the tungsten filament? Now place the paper by the entrance port inside the sample compartment. You should see the white slit image passed by the monochromator. The width of the image is equal to the entrance or exit slit width. If you had used the 300 μm slits, the image would be twice as wide. Now note how the light image gets bigger as you move the paper toward the first lens. This first lens focuses the radiation at the sample cell position. After the sample cell, the light spreads out again and is intercepted by the second lens, which refocuses it at the exit port of the sample compartment. Later one of the photodetectors will be placed at this position.

Check the alignment of all the components to make sure that the white image is centered in the middle of the exit port of the sample compartment. If it is not, first check that the side of the monochromator is **square against the sample compartment** and if necessary, gently move the monochromator to seat it better. If the alignment of the source image on the monochromator entrance slit is poor, adjust the lamp position with the knob on the lamp housing. **CAUTION: the lamp is hot.** The lamp can be adjusted horizontally (push/pull) and also twisted to make a slight vertical adjustment. If needed, obtain help from an instructor.

Now let's see some colors! Place the strip of paper at the sample cell position. Change the monochromator wavelength to 400 nm by manually **rotating the stepper motor shaft**. You should see a blue image. Slowly rotate the drive shaft to pass through wavelengths sequentially until you reach 600 nm. You should see green, yellow, and red light as you proceed with this manual wavelength scan. **Record in the data sheet** the values for the shortest and the longest wavelength for the colors of light that you experimentally detected with your eye (rough estimates are fine at this point).

V. SILICON PHOTODIODE

A. Introduction

A **silicon photodiode (PD)** is a common optical transducer for radiation in the NIR-VIS-

NUV regions. A photodiode is based on a semiconductor **pn junction** where the **p material** is Si doped to have a deficient number of electrons (or an excess of holes) while the **n material** is Si doped to an excess number of electrons. The pn junction is “reverse biased” so that the p-material is at a more negative potential than the n-material. This serves to increase the size of the “depletion region” which is the boundary region between the two materials that is free of both mobile electrons and holes. A certain fraction of the photons that strike the depletion region promote electrons in the valence band up to the conduction band thus producing electron-hole pairs. A wire is connected between the n-material and the circuitry designed to measure the number of charge carriers generated by the photon striking the detector. In this photoconductive mode, under proper conditions, the photocurrent is directly proportional to the radiant power impinging on the active surface of the detector as expressed in Equation 2:

$$i_p = \Phi R(\lambda) \quad (2)$$

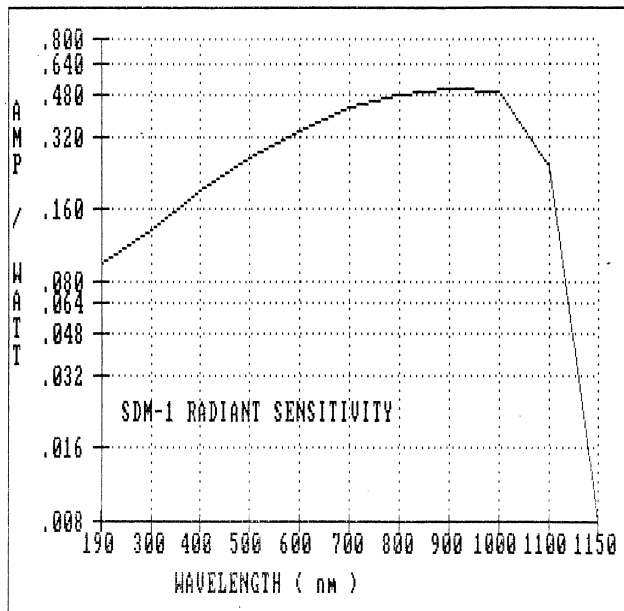


Figure 3. Responsivity curve for a photodiode ($R(\lambda)$ vs. λ).

where Φ is the radiant power in watts (related to the number of photons per second that strike the photodiode), i_p is the photocurrent in amperes, and $R(\lambda)$ is the **responsivity** of the photodiode in amperes per watt. $R(\lambda)$ is itself dependent on wavelength as shown in Fig. 3, but it is assumed that $R(\lambda)$ is effectively constant over the small wavelength range impinging on the photodiode at a single wavelength setting. Note that your photodiode can be effectively used in the wavelength range of 190-1150 nm.

When no radiation is impinging on the photodiode, a small current is observed due to thermally generated electron-hole pairs. This residual current is denoted as the **dark current** and is given the symbol i_d .

The photocurrent from the photodiode is most effectively measured by connecting it to an OA in the current-to-voltage converter configuration as shown in Figure 4. Note that the n-material of the photodiode is connected to the OA summing point. The OA output voltage is then measured with the ECR or DMM. The output voltage E_o is positive because the photocurrent flows away from the summing point.

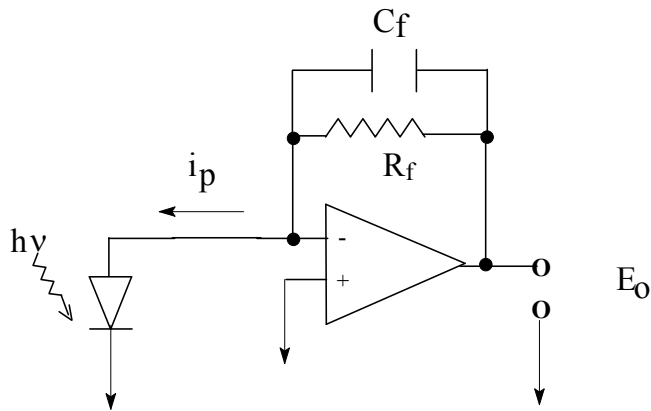


Figure 4. Configuration for the photodiode. Note that the PD and above circuitry are all contained in the PTR cylindrical module.

The PTR silicon photodiode detector module (the PD) consists of a silicon photodiode and just such an operational amplifier circuit for signal processing. For your PD - amplifier combination, the feedback resistor R_f is $1.00 \times 10^7 \Omega$ (**the transfer function G (defined below) is $1.00 \times 10^7 \text{ V/A or } \Omega$**) and the feedback capacitance C_f is $3 \times 10^{-6} \mu\text{F}$ yielding a time constant of 0.03 ms for the PD. The total voltage output of the OA is due to the photocurrent, the dark current, and the voltage offset of the OA. A balance control in the photodiode module has been adjusted so that the output is near zero when the photodetector is blocked from radiation. To determine the photocurrent voltage E_p you will measure the total signal E_t when the PD is exposed to light and then measure the dark signal voltage E_d when the light is blocked. Thus,

$$E_p = E_t - E_d \quad (3)$$

The photocurrent voltage is then related to the photocurrent itself and to the incident radiant power by

$$E_p = i_p G = \Phi R(\lambda) G \quad (4)$$

where **G is the transfer function of the OA circuit and equals R_f of the current-to-voltage converter in this device.** Note that the photocurrent voltage is directly proportional to the incident radiant power.

B. *Experimental*

You will use the photodiode detector to measure the radiant power of the tungsten lamp isolated by the monochromator.

Find the model SDM-1 photodiode module at your station. Light enters the 5-mm circular aperture and strikes the active surface of the PD inside. Mount the PD module to exit port 1 (opposite to the lamp module) of the right wall of the sample compartment with two 6-32 thumb screws and replace the lid of the sample compartment. Plug exit port 2 in the back of the sample compartment with the aperture blocker (black circular disc).

Check drift. Open the ECR program and set the range to the **10 V range or adjust to keep signal on scale.** (Be sure the 15-V power supply for the PD is not plugged into the detector yet.) The PD is connected to the ADC connector box using a special cable that has a gold-colored connector called an SMB connector on one end and a BNC on the other end. Attach the end with the SMB directly to the PD module and the BNC to channel 0 on the connector box using a BNC tee. On the other side of the tee, connect a double BNC cable to the BNC-to-banana-plug adapter to make a convenient connection to the DMM. Recall that the plug adapter has a tab on one side marked "GND" and this side of the banana plug goes to the COM plug on the DMM. To power the detector, first connect the 15 V power supply cable to the PD module and then plug the power supply into a wall or strip socket. **To prevent damage,** always connect the power cable to the module **before** the power supply is connected to the ac line. Also when removing the signal cable, pull gently on the connector (**not the wire**).

Turn the light source on and open the shutter. Manually set the monochromator wavelength to about **390 nm with both 150- μm slits** installed in the monochromator. Be sure the lamp image is still focused on the monochromator entrance slit (ask if you do not know what this means). Start the ECR program and monitor the signal. If the signal is less than 0.1 V, manually adjust the monochromator to a slightly longer wavelength; if the signal is off scale, manually adjust the monochromator to a slightly shorter wavelength. Stop the recorder program (do not worry about saving the data now). Clear the chart and restart the program and monitor the photocurrent voltage for 5 min and save the data file this time. The voltage should remain constant within about $\pm 20\text{-}40$ mV. Typical drift after warmup is $\sim 1\%$ **per minute** and is due to slow vaporization of the tungsten filament and temperature fluctuations. Open the file in Excel and calculate the relative drift for your system where relative drift = slope in V/min, divided by the initial voltage, X100%. Ask an instructor to confirm that your drift is acceptable and record on the Data Sheet.

Determine total current and dark current at 350 nm. **Change the monochromator wavelength to 350 nm.** Put the DMM on the 5-V dc range. With the light shutter open, **measure and record the total signal voltage from the PD on the Data Sheet.** **If the total signal voltage is less than 20 mV or greater than 500 mV,** check with a TA because there may be optical alignment

problems. Fix and re-measure if needed. Next, close the light shutter and **measure and record the dark signal on the most sensitive scale for the DMM. If the dark signal is larger than 10 mV**, there might be a light leak, fix it and re-measure. If you need help, check with a TA. If you ran at a different wavelength other than 350 nm, make sure and record the new wavelength. From these two measurements, you will determine the photocurrent voltage and Φ the incident radiant power from the source in watts.

VI. PHOTOMULTIPLIER TUBE

A. Introduction

A **photomultiplier tube (PMT)** is an optical transducer used in the same wavelength region as the PD and although its responsivity at longer wavelengths is poorer, it can measure lower light levels because it provides internal amplification. A PMT consists of a photosensitive cathode (**photocathode**), **dynodes**, and an **anode**. A fraction of the photons that strike the photocathode cause emission of electrons called **photoelectrons**. These photoelectrons strike the first dynode, which is biased at a more positive potential than the photocathode and is coated with a secondary emission material that gives off several electrons per incident electron. These secondary electrons strike a second dynode, then a third dynode, etc. After typically 6 to 11 dynodes, the original photoelectron is converted to a charge packet of $10^3 - 10^6$ electrons. The packet is then collected by the anode. The anode is typically connected to the summing point of an OA to convert the photocurrent to a voltage which is directly proportional to the radiant power impinging on the photocathode.

The following equations are used to describe the operation of a PMT:

$$i_{cp} = R(\lambda)\Phi \quad (5)$$

$$i_{ap} = mi_{cp} = mR(\lambda)\Phi \quad (6)$$

$$m = i_{ap}/i_{cp} \quad (7)$$

$$E_p = i_{ap}G = \Phi R(\lambda)mG \quad (8)$$

where Φ and $R(\lambda)$ have been defined previously (eq. 1), i_{cp} is the photocathodic current (the photoelectron current collected by the first dynode of the PMT), i_{ap} is the photoanodic current (the output current of the PMT), **m is the current gain** of the PMT, E_p is the photocurrent voltage (the output of the OA due to photons), and G is the transfer function of the OA circuit. The current gain is dependent on the bias voltage supplied to the PMT but is independent of the incident wavelength.

Note that equation 8 is similar to equation 4 except that the gain factor, m , has been added.

The dependence of $R(\lambda)$ on wavelength for your PMT is shown in Figure 5. For the equations above to apply to real situations with a finite wavelength range incident on the PMT, $R(\lambda)$ is assumed to be constant for all wavelengths in the range.

The PMT outputs a dark signal in the absence of radiation striking the detector. This anodic dark current (i_{ad}) is typically 10^{-9} to 10^{-12} A and results in a dark current voltage (E_d) given by

$$E_d = i_{ad}G \quad (9)$$

Thus, the photocurrent voltage is obtained from the difference between a total signal (E_t) and a dark signal (E_d) (see equation 3). The dark current voltage is obtained from the difference in the dark signals measured with the PMT bias voltage turned on and turned off. The signal with the

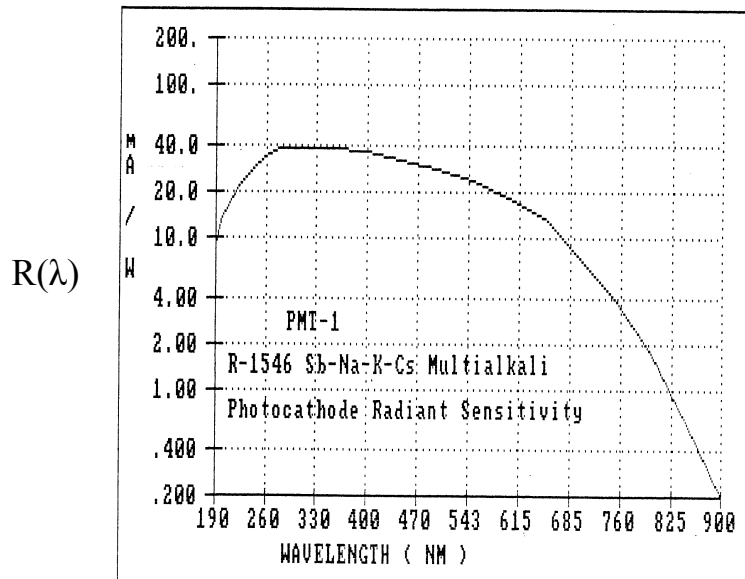


Figure 5. Responsivity curve for the PMT. Note that the units of $R(\lambda)$ are different from those in Figure 3.

PMT bias voltage off is due to voltage offsets from the amplifier circuits.

This offset voltage or the dark plus offset voltage is often adjusted to near zero with a balance control.

Find the PTR photomultiplier module which contains a Hamamatsu R-1546 side-on PMT, an adjustable high voltage (H.V.) power supply, and signal processing circuitry. As shown in Figure 6, the internal signal processing circuitry consists of an operational amplifier in the

current-to-voltage configuration plus an

additional operational amplifier wired in the follower-with-gain configuration to provide a variable gain of $\times 1$ to $\times 5$. Offset and dark current signals can be nulled out by a variable voltage connected to the non-inverting input of the first OA. The feedback resistance is $1.00 \times 10^6 \Omega$ when the amplifier gain is at $1\times$ yielding a signal processor transfer function G of 1.00×10^6 V/A or Ω (**note that this G is different for the PMT than it is for the PD**). The feedback capacitance is $1.0 \times 10^{-3} \mu\text{F}$ resulting in a 1-ms time constant for the PMT.

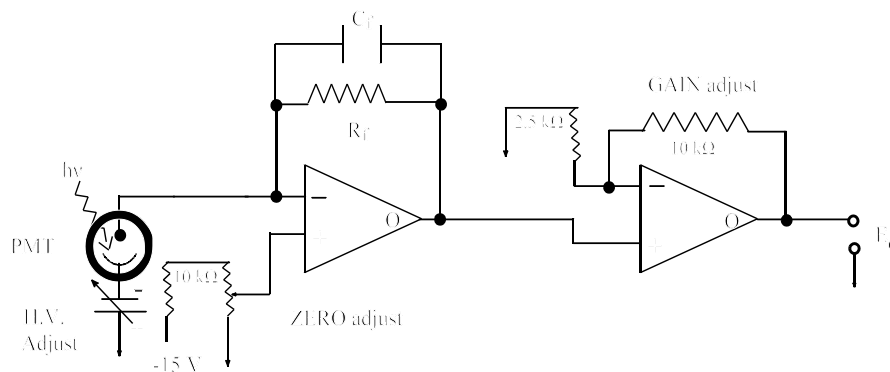


Figure 6. Signal processing circuit for PMT. The above circuitry is inside the PMT module.

Look at the PMT module. Locate the light input port. The ten-turn dial on the **upper left** labeled **GAIN** is used to vary the internal amplifier gain and **it is only operational when the GAIN switch is in the VAR position**. The ten-turn dial in the **upper right** labeled **H.V. stands for high voltage and is used to adjust the PMT bias voltage** from 0 to -1000 V. Each complete rotation of the dial is equivalent to -100 V. The knob below the HV dial is the **ZERO** offset adjustment for the PMT.

CAUTION:

The PMT is damaged by exposure to high light levels such as room light. Never connect power to the PMT until the module is connected to the sample compartment and the sample compartment lid is in place.

B. *Experimental*

Determine total current and dark current . Make sure and use the same wavelength you used in part VB, p 10-11 with 150 μm slits. Now we are ready to use the PMT module to measure light signals and to observe how the gain **m** varies with the bias voltage. Check that the light source is on. **Make sure that the PMT power supply is not yet connected to the wall socket. Check that the unused mounting holes in the PMT module are plugged with the small rounded screws or covered with black tape (check the bottom and the back of the PMT module).** Mount the PMT module to the right port of the sample compartment with two 6-32 thumb screws and replace the lid of the sample compartment. Open the ECR program. Install a BNC tee on the ADC channel 0 and

connect the BNC end of the cable from the PMT (gold SMB goes to the PMT) and the DMM into the tee and set the DMM to the 5-V dc range and the ECR to +/- 10 V range. Finally connect the PMT power supply to the +/-15 V socket on the front of the PMT module first and finally plug the power supply into a wall socket.

On the PMT module, set the gain switch to X1 and both the H.V. and GAIN dials to zero (fully counterclockwise). Turn the PMT module power switch on. Next, adjust the ZERO knob on the PMT to produce an output of 0 V (± 1 mV) as measured with the DMM. Start the ECR. Now set the PMT H.V. (i.e., bias voltage) to -390 V using the H.V. dial (note that this is ten turn dial from 0 to 1000V). With the shutter on the light source open, **measure and record on the Data Sheet** the total photocurrent signal voltage. **If the total signal is not between 0.3 V and 2 V, ask one of the instructors to help you check the optical alignment or change the wavelength to a slightly longer value and note this on the data sheet.** Next, close the shutter and measure and record the dark current signal. **Repeat these measurements two more times with PMT H.V. values of -420 V and -480 V.** Stop the ECR and save the data. From these data, the photocurrent voltage, photoanodic current, photocathodic current and PMT gain will be calculated at each H.V. Based on your observation of the ECR output, generally how does the PMT gain vary with the H.V.?

VII. WAVELENGTH SCAN WITH “TERMINAL” PROGRAM.

A. Introduction

Now you will learn how to scan the monochromator and to obtain spectra. A **spectrum** is a plot of the photocurrent signal (intensity) versus wavelength. The **shape of a spectrum** of a radiation source such as the tungsten lamp depends on several factors: 1) the spectral response of the lamp or radiant power emitted versus wavelength, 2) the spectral response of the PMT (recall that $R(\lambda)$ is wavelength dependent), and 3) the spectral characteristics of the monochromator. The overall optical efficiency of the monochromator varies with wavelength primarily due to variation of the diffraction efficiency of the grating with wavelength. The photocurrent voltage observed at a given wavelength is due to a convolution or composite of all these wavelength dependent quantities.

The scanning of the monochromator operates using a **stepper motor on the grating drive shaft and the stepper motor controller unit**, which is connected through an RS232 serial line to the COM1 port on a computer. The stepper motor performs different functions based on simple ASCII characters (e.g., letters, numbers) that it receives from the controller. In this course, you will use two different programs for communicating commands to the stepper motor controller and thus the

monochromator. First, you will learn about the primitive "TERMINAL" program. This type of application program allows the computer to emulate a standard keyboard -- thus, when the "a" key is struck, the ASCII code for an "a" is output on the serial port line which is used to communicate with the stepper motor controller. You have to do all of the calculations to relate steps of the motor to wavelength. However, because stepper motors are used in all kinds of chemical instrumentation, it is important to see how they work at a basic level. Later, you'll use the more sophisticated "MONOCHROMATOR" program, which calculates the number of steps for you and operates the monochromator as you would expect to see in a commercial instrument.

Here are the most important facts to remember about operating your stepper motor and the monochromator with the TERMINAL program:

For Stations 1-6:

- one revolution of the motor shaft takes 400 steps and changes the wavelength passed by the grating by 50 nm
- hence, turning the stepper motor 8 steps equals one nm change
- or one step corresponds to a change in wavelength of 1/8 nm or 0.125 nm

For Station 7:

- one revolution of the motor shaft takes 800 steps and changes the wavelength passed by the grating by 50 nm
- hence, turning the stepper motor 16 steps equals one nm change
- or one step corresponds to a change in wavelength of 1/16 nm or 0.0625 nm

B. Experimental

Adjust PMT bias voltage so the tungsten/halide source spectrum will remain on scale. Use the same experimental setup used in Section VI (e.g., 150- μ m slits) except connect the PMT module output to the DMM on the 5 V range. Close the light shutter. Manually set the monochromator wavelength to 575 nm (approximately the wavelength of greatest response). Set the PMT bias voltage at \approx -200 V. Record the dark current voltage. Open the light source shutter and adjust the PMT bias voltage until the signal output at the PMT is about 0.85 V and record the required PMT bias voltage value.

Obtain emission spectrum of tungsten lamp. If not already done, use a BNC tee connector on the ADC channel 0 to connect both the DMM and the PMT output. Open the ECR program and select the +/- 1 V scale. Record the rest of the ECR settings and add a comment in the comment box indicating the wavelength range for this scan.

Follow the instructions in the document entitled “**Scanning the Monochromator with Terminal**” on the CH 461 web pag. Ready the monochromator for a wavelength scan from 300 to 750 nm at a scan rate of 200 nm/min using the **Terminal program**. Before actually starting the scan calculate how long it will take to scan to 600 nm and record this in the comments box and also on the Data Sheet.

Begin the scan as described in Step C of the instructions by **simultaneously starting ECR and pressing Enter** on the keyboard. **As the scan progresses, record on the Data Sheet the approximate voltage and time at the 600 nm mark for reference later.** When finished scanning to 750 nm, save the chart to a file and record the total time elapsed for the scan. If your scan settings were correct, this scan should take 2.25 min. Open the file **and plot in Excel. Ask a TA to check your scan to see if it is reasonable.** Be sure to record all the parameters used in the scan (e.g., ECR chart scale and collection rate, slit width, monochromator scan rate, H.V. and GAIN settings for the PMT, wavelength range, etc.). Save the Excel chart. At this time, answer the questions in the Data Sheet on this part. Everyone in your group is required to gain experience working with the equipment, so everybody should take turns operating different parts of the equipment.

VIII. CCD SPECTROMETER

A. Introduction

A charge-coupled detector (CCD) is another type of photodetector. It consists of an array of miniature, solid state detectors on a chip. The active sensing regions are called pixels. The pixels are independent from each other such that the intensity of light striking each pixel can be determined. The primary use of a 2-dimensional CCD is obtaining digital images such as in a video camera.

Photons striking a pixel produce electron-hole pairs in proportion to the number of photons. The charge associated with each pixel is initially “zeroed” and then the light signal is “**integrated**” for a specified length of time. At end of the **integration period**, the signals associated with all the pixels are read and digitized in a sequential manner and stored in computer memory. The resulting data file with the signal intensity associated with each pixel can be displayed on the monitor. See the CH 461 web site for an animation about the operation of a CCD spectrometer.

For use in spectroscopy, the CCD detector is placed in the focal plane of a spectrograph (see

color diagram on CH 461 web page). A spectrograph is similar to a monochromator in that it includes an entrance slit and grating, but it is different in that there is no exit slit in the focal plane. Instead, a CCD is mounted in the focal plane. Light is brought into the spectrograph with a fiber optic cable connected to the SMA input. This light enters the entrance slit, passes through an optical filter, and is collimated by a spherical mirror. The collimated light is diffracted by a plane grating, and the resulting diffracted light is focused by a second spherical mirror. An image of the spectrum is projected onto a linear CCD array. Because a spectrum is dispersed across the photosensitive surface of the CCD, each pixel observes a small and different wavelength range. A plot of signal versus pixel number is also a plot of signal versus wavelength.

The Ocean Optics, Inc. (OOI) USB2000 CCD at your stations is $f/4$, contains a 600 line/mm holographic diffraction grating blazed at 400 nm, has a 25 μm slit width, and selects wavelengths in the 200 nm to 850 nm range. The CCD has 2048 pixels that are 14 μm wide and 200 μm high. Each pixel intercepts a wavelength range of 0.32 nm. The stated **wavelength resolution** is 4.1 pixels, which is approximately equivalent to 1.2 nm. For practical purposes in CH 461, the **wavelength resolution** of the spectrometer is equivalent to its **spectral bandpass, $\Delta\lambda$** . The output signal is displayed on the computer screen as counts from 0 to 4096. One count corresponds roughly to 100 photons striking the pixel during the integration time. If the signal count values are at or near 4096, the pixel is saturated and does not give a correct intensity. **In this case the integration time or source intensity should be reduced to bring the signal on scale and around 3000 to 3500 counts for the maximum signal. Avoid bumping the optical cables - put the detector and the cables off to the back so that it doesn't get moved during the measurements.**

B. Experimental

Close the light source shutter. Remove the PMT module from the sample compartment and install the fiber optic SMA adapter in its place. Exercise care when handling fiber optics -- they should not be bent sharply or crimped. Connect a blue 400- μm fiber optic cable (pink band and labeled P-400) between this adapter and the OOI spectrometer. Plug the special USB cable into the spectrometer and connect to the USB plug on the side of the monitor. Click on the OOI icon on the desktop to activate the software to run the spectrometer. If needed, you will find more detailed operating instructions for the OOI spectrometer on the course web page.

Observe range of wavelengths passed by PTR monochromator with CCD detector.

Setup CCD:

- Choose an integration time of 10 ms, average of 1, boxcar of 0 and all boxes unchecked.
- Select the S mode (scope for raw data).
- With the shutter closed, store a dark signal spectrum (dark bulb icon), and then obtain the dark spectrum corrected signal (- dark bulb icon). Because the shutter is still closed, the intensity should be approximately zero for the entire spectrum - is it?
- Adjust the wavelength scale to display 375 to 425 nm (red crossed arrows icon (set scale)) and manually adjust the PTR monochromator wavelength to 385 nm.
- Open the light source shutter enough to bring the signal on scale. You should see a triangular shape on the screen that represents the range of wavelengths passed by the PTR monochromator (i.e., the slit function).
- Zoom in on the triangle by changing the display range.
- **Notes:** (i) if the signal is not observed or is too small (less than 1000 counts), increase the integration time. (ii) if the signal is off scale, reduce the integration time (3 ms minimum) or partially close the light source shutter. (iii) if the spectrum is too noisy, first check the alignment, and if that is okay then increase the value for **average** above 1 to implement signal averaging. (iv) for the most accurate quantitative determination of the dark-current corrected signals later on, you should store the dark current with the same integration time used for the signal; this extra step is not necessary here.

Manual Scan of Slit Function:

Now manually scan from 375 to 400 nm (or the range you have selected) by turning the stepper motor drive shaft (make sure the stepper motor is de-energized first by sending either E0 (sta 1-6) or E3 (sta 7) or turn the power off) and note how the triangular slit function moves across the wavelength range. The center of the triangle moves corresponding to the monochromator wavelength setting; the width of the triangle remains constant (because it defines the wavelength range passed through both the entrance and the exit slits of the PTR monochromator). The height of the triangle varies with wavelength because the lamp intensity varies with wavelength.

Consider the contrast between a scanning spectrometer based on a monochromator with a "single-channel" detector such as a PMT and a multichannel spectrometer based on a spectrograph and CCD. The multichannel spectrometer has the advantage of displaying the entire spectrum

simultaneously. A disadvantage of the CCD is that the pixel area is very small so the pixel observes considerably fewer photons than a PMT which has a photodetector surface on the order of 1 cm². Thus, the minimum light levels that can be detected with a PMT are much lower than that with a CCD; this means that the PMT is a more sensitive detector at lower light levels than is the CCD.

At a wavelength of your choice, freeze and print an image of the triangular shape by selecting the camera icon (toggles on / off), then go to File - Print Preview and print one page showing the spectrum for each member of your team. Later you measure the half-width (“full width at half the maximum intensity”) of the triangle, which represents the spectral bandpass of the PTR monochromator coupled to the CCD spectrometer. Ideally, this observed spectral bandpass is

$$S_{\text{obs}}^2 = S_{\text{PTR}}^2 + S_{\text{CCD}}^2$$

Explore CCD settings:

Position the triangle in the middle of the screen and click on the apex to move the cursor on the screen:

- Change the integration time. What effect does a change in the integration time have on the intensity of the signal? Reset to 10 ms.
- Compare the wavelength displayed at the bottom of the screen to that on the PTR wavelength display. Are these the same? If not check with an instructor.
- Change the boxcar setting. What effect does this have on the display? Reset to 0.
- Change the number of averages. What effect does this have? Reset this to 1.

This point is a good point to stop if there are fewer than 20 min before the end of the first laboratory period. If you have at least 30 min, continue to Section IX. When you stop, be sure to turn the power off to all modules including the stepper motor controller and unplug the PMT power supply from the AC socket before you leave for the day.

IX. NOISE, FREQUENCY RESPONSE, AND SIGNAL AVERAGING

A. Introduction

Noise is unwanted fluctuations in signals and is often random. Noise can be observed if the resolution of the readout device or ADC is sufficiently good. Noise can limit the precision of measuring real signals. The magnitude of the noise is usually specified by a root-mean-square (**rms**) value. **The rms value is calculated as the standard deviation** from repetitive measurements of the signal. Noise can also be characterized by a peak-to-peak (p-p) value which is the difference between the maximum and minimum excursions of the observed signal.

Most chemical instruments such as spectrometers have circuitry or software to reduce the amount of noise in the observed signal. Noise is reduced by integrating the signal over a period of time, by averaging repetitive measurements (signal averaging), or with circuitry that controls the frequency response or the frequency bandpass using an electronic filtering networks. The factor that the user changes in filtering networks is usually the **response time**, the **time constant**, or the **cutoff frequency**. Noise corresponds to fluctuations at all electrical frequencies, whereas real signals are usually encoded at one frequency or over a small frequency range. Integration or signal averaging reduces noise for fluctuations that are much shorter than the integration or averaging time because many faster positive or negative excursions balance out over time. **Filtering networks** are often adjusted to pass the low frequencies at which the signal is encoded, but to attenuate other higher frequency fluctuations that contain no useful information. Remember that in experiment 1A you studied how a larger time constant in a circuit results in a longer response time ($\approx 5\tau$). This longer response time “averages out” the faster fluctuations or higher frequency noise.

In this experiment, you will observe how the noise in the dark signal for the CCD depends on the number of repetitions for a given data point. The averaging time and total time to acquire the signal information is the product of the integration time and the number of repetitions averaged. With a 10-ms integration time and averaging 10 repetitions, the effective averaging time is 100 ms. **For random noise, the standard deviation of the mean should theoretically decrease by the square root of 10 when the number of repetitions averaged per point is increased from 1 to 10.**

B. Experimental *Determine noise as a function of number of points averaged.*

Use the same set up used in Part VIII B(p.6). Turn the light source off. Adjust the OOI spectrometer parameters as follows:

- integration time: 10 ms
- average: 1
- boxcar: 0
- turn off the correction for electronic dark signal correction (toggles on/off)
- change the y scale from 0 to 200
- wavelength (cursor position): any value

From the top Menu, select Time Acquisition | Configure | Configure Acquisition to open the **Time Acquisition Configuration** screen and set the following parameters:

- check the boxes for “stream data to disk”, “show values in status bar”
- write to disk every ____ acquisitions: 20
- in the prompt for “stream” filename, enter a file name with the extension “.time”, for example, “C:\CH461\DATA>Noise_station_X_2019_01.time”. The OOI program looks for the extension “.time”, and Excel at your computer has been associated with the “.time” extension. Insert your station number for X and the number 01 is for number of averages taken.
- **do not** check the boxes for: “save every data acquisition”, “save full spectrum with each data acquisition”, and “continue until manually stopped”.
- initial delay: 1 ms
- frequency (minimum time between acquisitions): 40 ms
- duration (time over which to take data, 1-s minimum): 3 s

Next select from the top menu, open the **Channel Configuration screen** by going to Time Acquisition | Configure | Configure Time Channel.

Open Channel A and set the following:

- Enabled (checked)
- Plotted (not checked)
- Wavelength: 445 nm
- Factor: 1
- Bandwidth: 0
- Offset: 0

Disable the other channels (B-F, combination 1 and combination 2): Enable D/A (not checked)
The values above should result in enough points to calculate a reasonable estimate of the standard deviation or noise. You might think you should get 300 points in 3 s at this frequency, but there is considerable overhead time needed to store the data and write it to disk.

Click the Time Acquisition icon (the Clock) so that the Start Acquisition icon (Arrow) is green for go. Click the Green Arrow to Start data acquisition. The acquisition should stop automatically in a few seconds. When complete, **locate the file**, open in Excel, and make sure that at least 50 points were taken.

Repeat the experiment with the same integration time but set the value of “average” to 10; you will also need to open the **Time Acquisition Configuration screen** to set the value “duration” to 6 s and to change the file name to a different name. Acquire the data, open both of the files, and **calculate the standard deviation for each run**. Did the standard deviation for the noise change with the number of averages as you expected?

X. OPTICAL FILTERS

A. Introduction

Filters are wavelength selection devices that, in general, isolate a broader wavelength range than that of a monochromator or spectrograph. They are not as versatile because the wavelength range isolated is fixed for a given filter. In the following experiment, the transmission characteristics of both an absorption band and a cutoff filter are studied (plots of the spectral transmittance of the filters are available in the lab and are on the course web page). Absorption filters are essentially colored glass, plastic, or other transparent materials that work by transmitting certain wavelengths while absorbing or not transmitting other wavelengths. **Absorption band filters** transmit radiation within a specified wavelength range. **Cutoff filters** pass radiation above or below a specified wavelength.

B. Experimental

Use the same optical configuration of the CCD spectrometer used in Section IX except remove the PTR monochromator (remove bolts and gently slide backwards). Turn the light source on. Adjust the OOI spectrometer parameters as follows:

- integration time: 5 ms
- average: 10
- boxcar: 0
- y scale: 0 to 4100
- displayed wavelength range: 400 - 700 nm
- S mode at the start

1. *Set up for transmittance measurements.*

- Adjust the shutter on the light source (W lamp) so that the shutter is almost completely closed to bring the spectrum intensity on scale. **You should see about 3000-3500 counts at the peak maximum. Do not touch the shutter again during this part of the experiment.**
- Increase the average value to 50 to smooth out the spectrum.
- Acquire the **dark spectrum** by temporarily blocking the light entering the sample compartment by placing an opaque object in the slot in the lamp housing (e.g. yellow cardboard piece) and acquire a dark spectrum (the dark bulb icon).
- Remove the opaque object and you should see the light enter the sample compartment. Freeze the spectrum and print copies for each group member.
- Take a **reference spectrum** (the bright bulb icon) and then change from the “scope” mode (S) (i.e., raw data) to the “transmission” mode (T) (i.e., transmittance). In the transmittance mode, T is calculated in the software from the relation

$$T = \frac{\Phi_s(\lambda) - \Phi_d(\lambda)}{\Phi_r(\lambda) - \Phi_d(\lambda)} \quad (10)$$

where $\Phi_s(\lambda)$, $\Phi_r(\lambda)$ and $\Phi_d(\lambda)$ refer to the sample signal, reference signal and dark signal, respectively, that are recorded simultaneously for each pixel in the CCD detector array. You should see a transmittance of 100% for all wavelengths at this point. **If not, check with a TA.**

2. *Determine transmittance of a cutoff filter.* Obtain a **red** Kodak Wratten gelatin filter (1" square) which is mounted in a shiny paper holder with a circular aperture. Insert the filter into the clips on the filter holder in front of the input lens in the sample compartment. (The surface of these gelatin filters is delicate so do not touch the actual filter.) Be sure the light beam is not blocked by the paper holder but goes through the filter.

- Move the cursor on the screen to 650 nm where the transmittance plateaus and record the value for the transmittance in the Data Sheet.
 - Change the wavelength range from 575 to 600 nm and move the cursor to find the wavelength where the transmittance dips below 1% and is near zero T. The wavelength at this point is called **the cutoff**. Record this wavelength on the Data Sheet. Freeze the spectrum and print a copy for each team member.
3. *Determine transmittance of an absorption band filter. **Reset the wavelength scale to display 400 - 700 nm.*** Replace the red filter with a green plastic filter (1" x 1.25") which acts as a band filter. **Freeze the spectrum and print copies.** Move the cursor to the wavelength around 500 nm yielding the maximum transmittance and record this transmittance and wavelength in the Data Sheet. **When finished, remove the green filter from the sample compartment.** Compare the spectra of the green and red filters.

XI. WAVELENGTH CALIBRATION AND WAVELENGTH RESOLUTION USING A MERCURY LINE SOURCE

XIA. Introduction

There are two basic ways to check the **wavelength calibration** of a spectrometer or monochromator:

1. Use a radiation source that emits discrete lines at known wavelengths;
2. Use a filter or absorbing material that has sharp absorption bands and known wavelengths of maximum absorption.

You will use the first method and a mercury vapor lamp as the light source. This low-pressure arc lamp provides a number of discrete emission lines in the UV-visible wavelength range which include the following mercury wavelengths (all values are in nm):

| | | | | | | | | | | | | | |
|-------|-------|-------|-------|-------|-----|-------|-------|-------|-------|-------|-------|-----|-----|
| 253.7 | 296.5 | 302.2 | 312.6 | 313.2 | 365 | 365.5 | 366.3 | 404.7 | 407.8 | 435.8 | 546.1 | 577 | 579 |
|-------|-------|-------|-------|-------|-----|-------|-------|-------|-------|-------|-------|-----|-----|

When a line source is scanned with a scanning monochromator or viewed with a CCD spectrometer, the half-width of the observed peak in nanometers is equal to the **spectral bandpass**, s , of the monochromator or spectrometer. The magnitude of s determines the resolution or the

ability to separate the signals coming from two closely spaced monochromatic lines. **The condition for baseline separation, or baseline resolution, is that the wavelength difference between two consecutive lines must be greater than $2s$.** For a scanning monochromator, the slit width, W , can be decreased to improve resolution until the point is reached where s is independent of W .

XIB. Experimental for wavelength calibration for the OOI - CCD spectrometer

You will now observe the line spectrum of a mercury lamp and check the wavelength calibration and wavelength resolution of the OOI - CCD spectrometer.

1. *Set up instrument.* Use the same experimental setup as in Section X (e.g., CCD spectrometer), except replace the tungsten lamp with the MP-1020 mercury vapor lamp (gray) at the same position on the optical bench. The mounting base of the Hg lamp attaches with 1/4-20 bolts to the optical bench at stations 1-6. Turn the power supply on for the Hg lamp so it can warm up for about 5 minutes before using it. At Station 7 connect the Hg calibration source directly to the monochromator input at the compartment exit port using a 400 μm fiber optic and the SMA connector (also check that the red light comes on the source box - if not change the battery).

2. *Acquire line spectrum of the Hg lamp.*

Adjust the OOI spectrometer parameters at the start as follows:

displayed wavelength range: 200 - 800 nm;

integration time: 10 ms;

average: 1;

boxcar: 0;

S mode.

You should see a spectrum including the lines identified on the previous page. Adjust the integration time to keep most of the lines on scale. If you are using the MP-1020, reduce the fluctuations by using the averaging mode with a value of about 50. With a value of 50, the signals for 50 consecutive integrations are averaged and the mean is displayed as one point per pixel. This helps reduce random noise that has positive and negative excursions. **Note that the product of the two parameters, integration time and average, determine how long it takes to acquire data. In general you do not want to this total time to exceed 1 s or acquisition will be very slow!**

Next, block the light for a moment and acquire a dark signal spectrum. Then acquire a dark corrected spectrum and freeze and **print a copy of the Hg spectrum for each team member. Save a file of the spectrum.** Now move the cursor using the mouse, arrow keys, or the cursor peak right or left icons ($\Lambda<$ and $\Lambda>$) to the peak maximum of the 253.7 nm line listed in Table III in the Data Sheet (p. 33) and record the wavelength value displayed at the bottom of the screen in the table (note: check that the green filter has been removed!). It should be close to the expected value. Repeat for the second mercury line at 546.1 nm listed in Table III. Later you will calculate the wavelength correction in displayed reading for your system for these two lines and few others.

3. *Examine resolution of two different Hg doublets.* To learn more about **wavelength resolution** using the CCD you will look in detail at two different pairs of closely spaced Hg lines called doublets (see Table IV in Data Sheets p 33). For a doublet to be resolved down to the baseline, the wavelength difference between the lines must be greater than the spectrometer wavelength resolution or the spectral bandpass (recall this is 1.2 nm for your CCD with a boxcar setting of 0).

3a. For the first doublet, set the wavelength scale display from 401 to 411 nm and adjust the integration time to obtain a maximum signal of 2000 to 3000 counts for the more intense line. You should see nearly baseline resolution of the doublet. **Print a copy for each team member.**

3b. For the second doublet, set the wavelength scale from 574 to 584 nm and adjust the integration time to obtain a maximum signal of 2000 to 3000 counts for the doublet lines. **Print a copy for each team member.** These two lines are only about 2 nm apart. Notice the wavelength resolution of the spectrometer is not good enough to fully resolve these lines down to the baseline. Change the boxcar value to 1 and then to 2. The boxcar function averages the data across several pixels and effectively reduces wavelength resolution. It is more useful to use Boxcar to smooth the data for broad spectra. A box car value of 1 means that the data point for a given pixel represents the average of signals from the original pixel and the two adjacent pixels (one higher and one lower). **Unless otherwise required, use a boxcar of 0.**

XIC. Experimental for wavelength calibration **using the PTR spectrometer with the PMT detector** and the Monochromator scanning program.

1. *Setup instrument.*

At stations 1-6: With the Hg lamp still in place, replace the CCD detector and fiber optic adapter on the exit port of the sample compartment with the PMT module. Check that the slit widths for both entrance and exit slits on the monochromator are 150 μm . Slide the PTR monochromator back in place on the entrance port and fasten with one screw so it doesn't move around. Connect the PMT output to the +IN of channel A on the SCM module and use the switches to ground channel B and -IN. Set the Cut Off frequency on the SCM to 1 Hz and the SCM Gain to 1. Put the BNC tee on the ADC Channel 0 and connect both the output of the SCM and the DMM. Set the PMT bias voltage initially to about -550 V.

At station 7: With the Hg source still in place on the exit port, replace the CCD detector and fiber optic adapter on the exit port of the sample compartment with the PTR monochromator fixed with the PMT module. Before bolting down the PMT check that the slit widths for both entrance and exit slits on the monochromator are 150 μm . Use a BNC tee on the ADC Channel 0 and connect both the output of the PMT and the DMM. Set the PMT bias voltage initially to about -800 V.

2. *Set up Monochromator program and the stepper motor controller.*

Use the **Monochromator** program for wavelength scanning (shortcut on the desktop). This and several of the other programs used in this course were written in LabVIEW, an industry standard programming language used to communicate with the ADC interface card installed in your computer. Program options include, for example, selection of initial and final wavelengths in nm, scan rate in nm/min, and adjusting the zero offset. The program calculates how many stepper-motor steps are required to go to a selected wavelength based on the location of zero order for your system. Recall that you had to figure this out when the Terminal program was used previously to control the monochromator! During a scan the step counter values are displayed on the screen. These are the same commands that you used earlier to control the scan using Terminal.

First, turn ON the power switch of the stepper motor controller. Second open the Monochromator program (the order is important!). If communication between the computer and the controller is successful, you'll see several commands in the left panel of the Monochromator screen and the "Initial Wavelength" and "Final Wavelength" fields of the Monochromator screen at the top will read "0." If you do not see these results, close the program and reopen it. If all else fails, consult an instructor before proceeding. Select Dev1/ai0, +/- 5 V (lower right on screen) and use a scan rate of 5 nm/min throughout this part unless otherwise stated. **Note: because the PC and stepper motor controller communicate by serial RS232, patience is sometimes required when sending and receiving commands!**

Check that the "Zero Offset" value given in Monochromator is the same as that last used for the Terminal program (within 1 or 2 steps). If not, update the offset value by typing in the updated offset and then close Monochromator and then reopen the program. This should update the offset value stored in the program.

3. *Optimize the PMT HV voltage so that the Hg line intensity is on scale and record the Spectrum.*

- a. Set "Initial Wavelength" to 543 nm, "Final Wavelength" to 549 nm, and "Scan Rate" to 10 nm/min.
- b. Select "Begin Scan." The program will send commands to the stepper motor controller such as F0 and then will send the zero offset number to go to 0 nm plus the number of steps needed to go to Initial Wavelength, and the I and D values to perform a 10 nm/min scan, and then the scan will start. You should see a narrow peak with a triangular shape at about 546 nm. If not check with the instructor.
- c. Set the initial wavelength to 546 and press Go to Initial. Use the arrows next to the initial wavelength box to step up and/or down around 546 until you maximize the signal intensity on the DMM. **Note: when you make a change in wavelength you have to press Go to Initial to see the effect on signal.** You should now be on the peak! **Record the wavelength readout on the MiniChrom for the peak and record in Table V(p 34).** Next adjust the PMT HV bias voltage until the maximum signal is on scale between 1 and 3 V. Record the PMT bias voltage in Table V.
- d. With these settings, rerun the scan in **part a** and confirm that the 546 peak is on scale and **then save the scan and plot later in Excel.**

- e. Now change the scan rate to 200 nm/min and execute a full scan of the Hg source from 230 to 630 nm. **Save the plot and later open in Excel and plot.** Change the data series to line only, set the X axis from 230 to 630 nm and print a copy of **only the GRAPH (not all the data points)**.

- a. Later, open the full spectrum file in Excel and check the calibration of several lines from the Hg source against the list of known Hg lines (p. 24). Find the difference in wavelength between these and report correction. This is the wavelength calibration table.

XID. *Wavelength Resolution* with the PTR Monochromator system

Determine resolution of Hg doublet as a function of slit width.

1. Check that entrance and exits slit widths installed on the monochromator are 150 μm . Set "Initial Wavelength" to 570 nm, "Final Wavelength" to 585 nm, and "Scan Speed" to 5 nm/min. Run the scan. If the peak maximum is not 1-1.5 V (stations 1-6) or about 0.2 V (station 7), adjust the PMT bias voltage and repeat the scan. You should see that the 577.0 nm and 579.0 nm Hg doublet lines are close to being baseline resolved. **Save the spectrum** and open it in Excel.

2. Next change both the entrance and the exit slits from 150 to 300 μm . Check the optical alignment including having the monochromator wall snugly against the sample compartment wall. Run the scan as in 1 above. If the peaks are squared off at the top, the signal is too high so lower the PMT bias voltage to bring these on scale. **Save the spectrum** once you have a successful scan and open it in Excel to make sure the experiment worked. Did you observe the wavelength resolution of this Hg doublet to change as expected with a change in the slit widths?

XII. LAB REPORT

Complete the data sheet and answer all questions. Include labeled charts and graphs and table. Include any spectra printed from files of the raw data but not all the data points unless asked for.

Data Sheet for Experiment 1B (also posted on CH 461 Web Site).

Name _____ Date _____ Station # _____

IV. Sample Compartment-Colors! (bottom p. 7)

Shortest detectable wavelength: _____ nm; Color: _____

Longest detectable wavelength: _____ nm; Color: _____

VB. Using the Silicon Photodiode (the PD). (p. 10)

PD drift (V/min): _____ (Attach Excel Chart (graph only))

Dark current voltage (E_d): _____

Total output voltage (E_t): _____

Photocurrent voltage (E_p): _____

Show the calculation of

1) the photocurrent (i_p) from the photocurrent voltage from eq. 4 (p. 9)

2) the incident radiant power (Φ) with eq. 2 (p. 8)

VIB: Using the PMT as the Photodetector. (p. 11)

Check that the PMT optical alignment position is optimized for this experiment to get good results.

What is the wavelength monochromator set to? _____ nm

Was the PMT zero knob adjusted to output 0 V at the start of this experiment? _____

Table I. PMT Gain

| PMT Bias Voltage Settings (V) | E_t Total Voltage (measured) (mV) | E_d Dark Current Voltage (measured) (mV) | E_p Photocurrent Voltage (mV) | i_{cp} Photocathodic Current (nA) | i_{ap} Photoanodic Current (nA) | m Gain |
|-------------------------------|-------------------------------------|--|---------------------------------|-------------------------------------|-----------------------------------|----------|
| -390 | | | | | | |
| -420 | | | | | | |
| -480 | | | | | | |

Fill in the rest of table I as follows on the next page for each PMT bias voltage:

1) determine E_p and i_{ap} from eq. 3 (p. 9) and 8 (p.11), respectively,

2) calculate the photocathodic current from eq. 5 (p. 11) , the value of $R(\lambda)$ for the PMT at the wavelength used (note the units in fig. 5 are mA/W), and the incident radiant power measured with the PD in section V (Φ is the same because the source, the slit width, and wavelength are not altered), and

3) calculate the gain m from eq. 7 (p. 11).

Illustrate your approach by showing the calculation of E_p , i_{ap} , i_{cp} , and m for the -390 V setting of the PMT. (Use actual data in sample calculations with units and proper Sig. Figs.)

4) attach a plot from the ECR program showing the steps in gain for the output for this part.

VIIB: Wavelength Scanning using the tungsten/halide source. (p. 15)

PMT dark current voltage: _____

PMT voltage at 0.85 V: _____

ECR recorder program settings: _____

At 600 nm, approximate voltage observed: _____ and corresponding time: _____

Calculated time to scan from 300 to 750 nm at 200 nm/min: _____

Time measured to scan from 300 to 750 nm at 200 nm/min: _____

Open the scan file in Excel and plot signal vs. wavelength (you will have to convert time to wavelength). Attach a hardcopy of this labeled plot.

1. At what wavelength does the system begin to respond? _____ nm

2. At what wavelength is the response of the system at a maximum? _____ nm

VIIIB. CCD spectrometer (p. 16)

From the copy of the spectrum from 375-400 nm, measure and report the half-width of the triangle which represents the spectral bandpass of the combined PTR monochromator and OOI spectrometer. Indicate how you obtained this value directly on the hardcopy.

Calculate the expected half-width of the triangle. Show your calculation based on the bandpass for the PTR mono and the CCD coupled together.

IXB: Noise, Frequency Response and Signal Averaging (p. 20)**Table II. Effect of Signal Averaging**

| number of integrations per data point (Hz) | mean signal (counts) | standard deviation (counts) |
|--|----------------------|-----------------------------|
| 1 | | |
| 10 | | |

Does the magnitude of the noise depend upon the number of integrations averaged as expected? See lab manual for discussion (p.20). Explain your reasoning in a sentence or two with evidence. Attach a copy of the raw data in this case.

XB: Optical Filters (p. 22)

The transmittance, T , is the ratio of the radiation passed by the filter to the radiation passed when the filter is removed (first spectrum).

- Transmittance of the red Kodak filter at 650 nm. T at 650 nm = _____
 - Wavelength where transmittance crosses below 1% = _____ nm (also label on hardcopy). This is the "cutoff wavelength".
- For the green filter plastic filter, maximum T value = _____
 - Wavelength of maximum T = _____ nm
 - Half-width of transmittance band = _____ nm (also show this calculation on the hardcopy)

XIB: Wavelength Calibration and Wavelength Resolution with the Hybrid OOI - CCD Spectrometer using the Mercury Source

Table III. Wavelength Calibration for the OOI- CCD Spectrometer. Add three other lines of your choice for Hg spectrum to the list below. (p. 26)

| Wavelength of mercury line (nm) | Wavelength of peak maximum displayed on monitor or in file (nm) | Correction for displayed reading (nm) |
|---------------------------------|---|---------------------------------------|
| 253.7 | | |
| 546.1 | | |
| | | |
| | | |
| | | |

Table IV. Resolution for the Hybrid OOI- CCD Spectrometer for two different Hg doublets (p 26)

| Doublets (nm) | True separation of lines (nm) | Spectrometer Wavelength resolution* (nm) | Nearly Baseline Resolved? (Yes or No) |
|---------------|-------------------------------|--|---------------------------------------|
| 404 & 407 | | | |
| 577 & 579 | | | |

* See spectrometer specifications in Section VIIIA

XIC: Wavelength Calibration with PTR Monochromator System

3.b. Plot the spectrum of the 546.1 nm Hg line in Excel and calculate the half-width in nm and compare to the expected half-width. Show your work on the hardcopy of this peak. As mentioned in Section III, the reciprocal linear dispersion of the grating is 6 nm/mm.

3.c. Report value for MiniChrom readout at the peak for the 546.1 nm Hg line in Table V.

3.e. Complete Table V. on the next page using the plot of complete Hg spectrum using the Hybrid spectrometer. (p. 29)

Table V. Calibration of Readout Display and Monochromator Program. Add three other lines for Hg to the list here. Report only 546.1 for the MiniChrom Readout.

| | MiniChrom PTR Wavelength Readout Display | | Monochromator Program File for PTR | | |
|--------------------------------------|---|---|---|---------------------------------------|----------------------|
| True wavelength of mercury line (nm) | Wavelength reading at the peak maximum intensity (nm) | Wavelength correction in display reading (nm) | Wavelength used in program at the peak maximum intensity (nm) | Wavelength correction in program (nm) | PMT bias voltage (V) |
| 253.7 | NA | NA | | | |
| 546.1 | | | | | |
| | NA | NA | | | |
| | NA | NA | | | |
| | NA | NA | | | |

Answer this question in your report: Look at the scan of the Hg spectrum taken with the PTR monochromator system. A fairly intense signal is observed at 507.4 nm. This indicates that some source radiation is entering the monochromator and passing through the exit slit to the PMT detector. However, according to the reference list for true wavelengths for the Hg line spectrum, the mercury lamp does not emit at this wavelength! What is happening here and what emission line from Hg is really being observed in this case? Succinctly explain your reasoning.

XID: Wavelength Resolution with PTR Monochromator System for Mercury doublet.

From your saved data for the two scans with differing slit widths for the Hg doublet at 577nm & 579 nm, import the data into a spreadsheet and produce a proper graph of **both scans on the same chart** of signal versus wavelength (identify which graph is for the 150 slit and which is for the 300 μm slit).

- a. Make a statement about your success in baseline separating these Hg lines.

- b. Calculate what slit width value is really necessary to produce baseline resolution of these two lines.

- c. Do your results support the calculated slit value? Explain briefly.