Nanoparticle Optics: Light Scattering
Size Determination of Polystryene Nanospheres
by Light Scattering and Mie Theory

OUTLINE OF THE PROCEDURE
A) Observe Rayleigh scattering from silica nanoparticles.
B) Observe HOTS from monodisperse particles: sulfur and polystyrene nanoparticles.
C) Rank your unknown polystyrene samples using HOTS.
D) Measure the angles of the scattering minima for your unknown particles.
E) Use MiePlot to model the scattering of your unknown and determine their size.

TAKE NOTES IN YOUR LABORATORY NOTEBOOK. TURN IN THE YELLOW SHEETS WITH YOU LAB REPORT.

Laser Safety: NEVER LOOK INTO THE LASER BEAM OR A REFLECTION OF THE LASER BEAM. While the laser many not appear very powerful, its characteristic of spatial coherence allow your eye to focus it to a very small spot on your retina. Looking into the laser can permanently damage your eye. Play it safe. If you are unsure where the laser beam and its reflections are going, us a white card to trace its path.

## Lab Report Check List

Your lab report should include:

1. 25pts) Your preliminary ranking of the particles sizes of you unknowns using HOTS.

2. 70pts) A table summarizing the results of your measurements and modeling (see example table). The table should include your groups experimental measurements of the scattering angle minima for each unknown, the best fit angles, and the best fit radii. The laser wavelength you used and your unknowns should also be shown.

3. 30pts) A graph of the perpendicular scattering intensity versus angle for each of your unknowns calculated for each of your best fit sizes.

4. 10pts) The yellow pages from your notebook.

An additional 15pts is based on how close you got the actual particle sizes.

Total 150pts.

Assigned laser color _____

Assigned unknowns _____
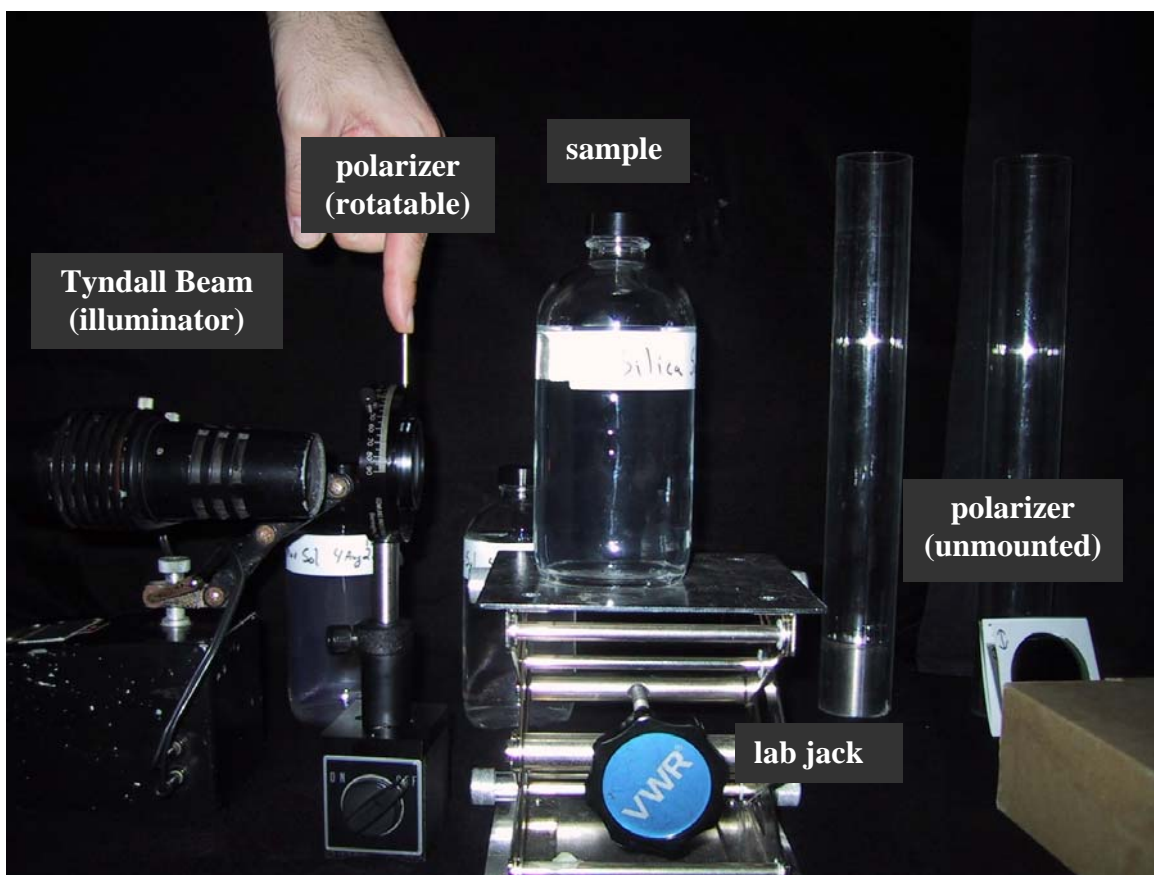
PART A) **Use the Tyndall beam to explore polarization in Rayleigh scattering.** Use the Tyndall Beam (collimated white light source) to view the light scattering from silica nanoparticles (20 nm diameter). You will also need the mounted rotatable polarizer and the unmounted polarizer.

Step 1)   Observe scattering of the unpolarized beam.   Set the bottle of silica nanoparticles on the lab jack and turn on the illuminator. The light beam should pass through the center of the bottle. Remove the rotatable polarizer from the beam. Pick up the unmounted polarizer. Turn off the lights and close the door. Allow your eyes to acclimate to the darkness. With you eye in the horizontal plane, 90° to the beam, observe the scattered light from the beam. Note that it is bluish.

Step 2) Observe the scattered light through the polarizer. Rotate the polarizer. Note that the scattering is polarized. What orientation of the polarizer extinguishes the light? With the polarizer in the orientation that extinguished the light, move your eye in the scattering plane. Note that the intensity of the light increases. What happens when you fix the scattering angle at 90° and move your eye out of the horizontal plane?

Step 3)   Insert the mounted polarizer into the illuminator beam. Turn off the lights and close the door. Allow your eyes to acclimate to the darkness. With you eye in the horizontal plane 90° to the beam, observe the scattered light from the beam. Rotate the polarizer. You should find a position where the scattered light is extinguished. Use the unmounted polarizer to establish which polarization this is. While the scattering is extinguished, what happens when you move your eye out of the horizontal plane?

PART B) **Use the vertically polarized Tyndall beam to observe higher order Tyndall spectra (HOTS).** Use the mounted rotatable polarizer from part A. Verify that it is vertically polarized using the unmounted polarizer. Place the bottle of sulfur nanoparticles on the lab jack. Unlike the very small silica nanoparticles, these sulfur nanoparticles are on the order of the wavelength of light. They are also monodisperse (all the same size). Place you eye in the horizontal plane (use one eye only). Move your eye through 0-180° in the horizontal plane. Note the bands of color. Also note that the color bands repeat. Each group of colors is referred to as and *order*. These colors are not the same as you see from prism (not ROYGBIV). For a prism each color is one wavelength. In HOTS each color is due to the absence of a narrow band of wavelengths.

How many orders can you see?

Normally you cannot see HOTS because monodisperse particles are relatively rare in nature. Polydisperse (many particle sizes) particles do not show HOTS. This is because the same structure in the scattering intensity versus angle that gives rise to "HOTS" is different for each particle size. These many scattering patterns add together to wash out the color and give white light (e.g. milk).

PART C) **Use HOTS to rank your unknowns from smallest to largest particle size.** Using the same apparatus as part B, observe HOTS for your unknown samples. Larger particles have more orders, while smaller particles have fewer. Write this result in your notebook and include it in your lab report.
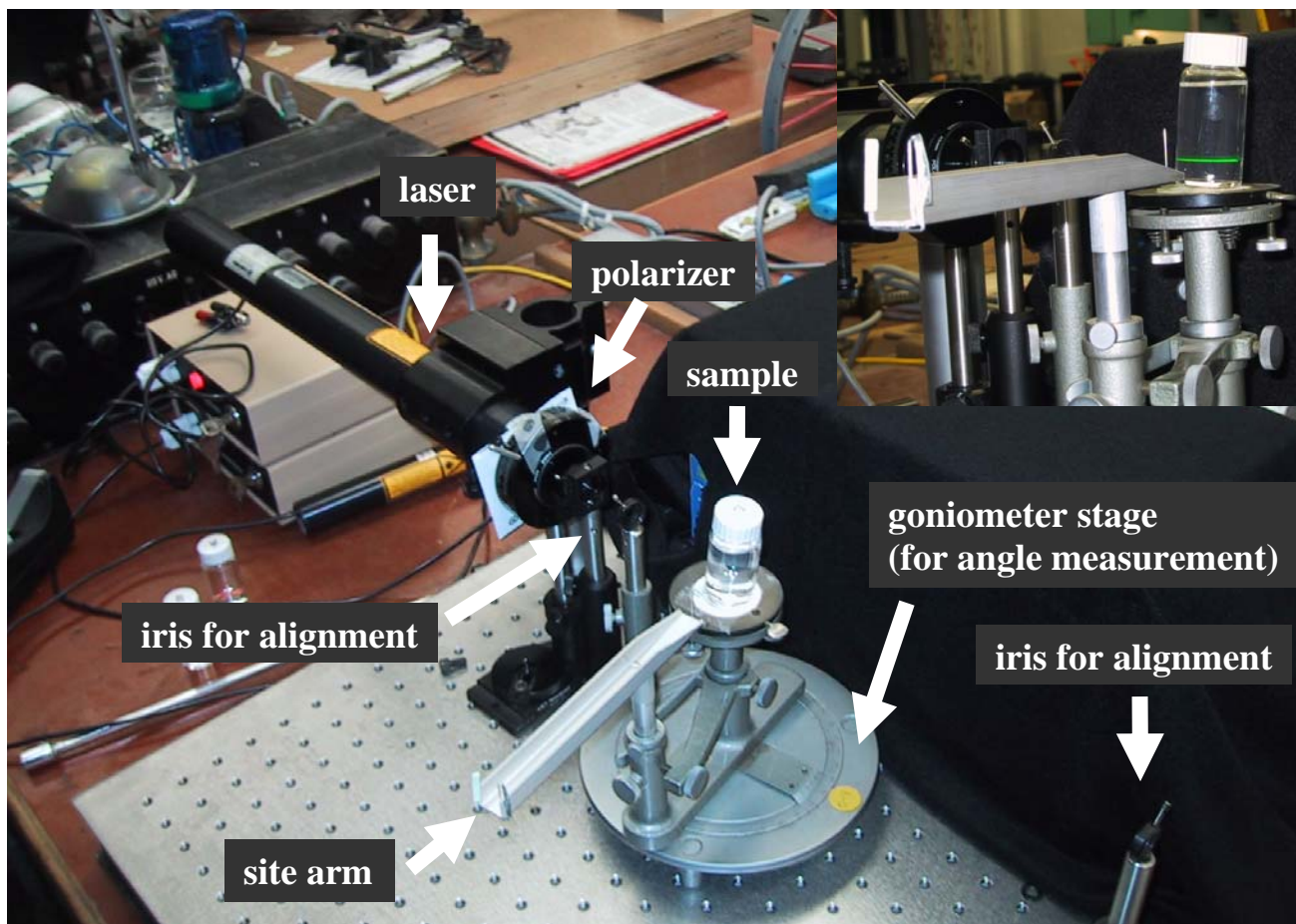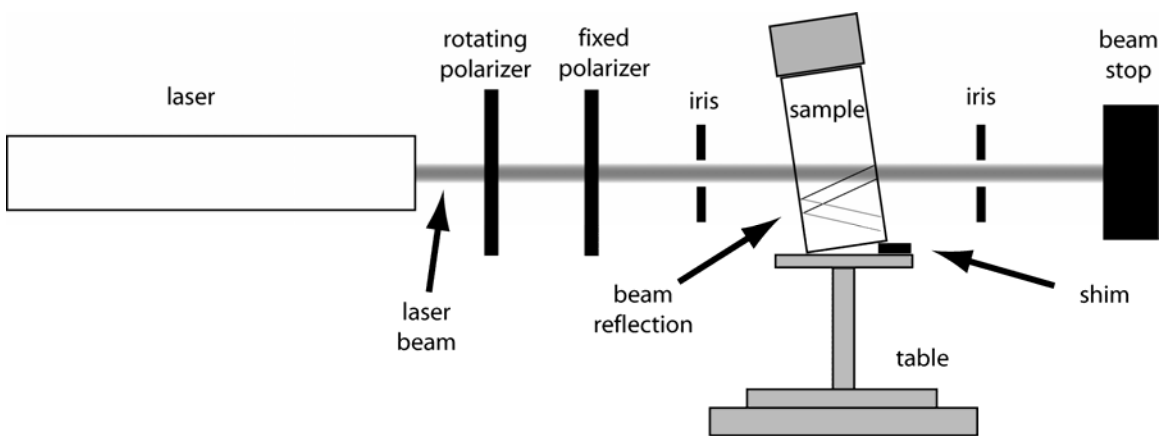
PART D Measure the angles for the scattering minima for your unknowns.

Step 0) Verify alignment of the optical system. Remove any sample from the table and turn on the laser. Rotate the adjustable (rotating) polarized to approximately maximize the intensity of the laser beam. a) Verify that it the beam is passing through both irises. b) Use a card to show that the beam is directly over the center of the table. c) Rotate the site so that the beam hits the center wire. The part of the beam that passes around the center wire should be in the middle of the two 'goal posts' at the outer end of the site arm.

Step 1) Check the polarization of the beam. Use one of the unmounted polarizers from your Tyndall beam experiments to verify that the laser is vertically polarized.   The polarization of the beam is controlled by the last polarizer and is fixed (clipped).   The first polarizer (rotatable) is used to attenuate the laser beam.

Step 2) Read zero angle from the goniometer. (See the scale at the base of the table). The scale has a vernier scale, you will not need the vernier scale for this experiment. Read the goniometer scale to the nearest degree. It happens that the way this particular goniometer is set up, there are no graduations at zero angle. Because zero angle is our reference, we have set the table so we can read the goniometer. With the site arm set as described in step 0, read the goniometer.   We will use this value to calculate our scattering angles from the goniometer readings. Be careful to note in your notebook which way the scattering angle increases. In particular, you need to know if the value on the scale increases or decreases as the scattering angle increases.

Step 3) Place your first unknown on the table with a shim as shown in the diagram. Be very careful of reflections when placing anything in the laser beam. Reflected laser beams are as dangerous as the primary beam. You must be cognizant of your lab partners positions to remain safe. Align the sample by observing the laser beam reflections so that the beam passes through the vial on its 'diameter.'   The reflections should be in the vertical plane if the beam passes through the vial on its diameter.

Step 4) Reduce the intensity of the beam. Turn off the lights in the room and close the door. Adjust the rotatable polarizer to reduce the intensity of the beam as far as you can but still have the beam path through you sample clearly visible. If the beam is too bright your eye is dazzled and you will not be able to see the scattering minima.

Step 5) Observe the scattering minima. With your eye in the horizontal plane, move through the scattering angle 30-150°.

> Do not attempt to measure angles outside this range. At the small angles this places your head dangerously close to the laser beam. The subtended angle of the beam path also decrease significantly, so it is difficult to view the minima outside these angles.

Use only one eye. You should see minima for most of your samples. You and each of your lab partners should measure the positions of the minima using the site arm. The site arm does not help you see the minimum, rather it allows you to measure the angle. While looking thought the goal posts with the site wire centered between them, the minimum should be centered on the site wire.
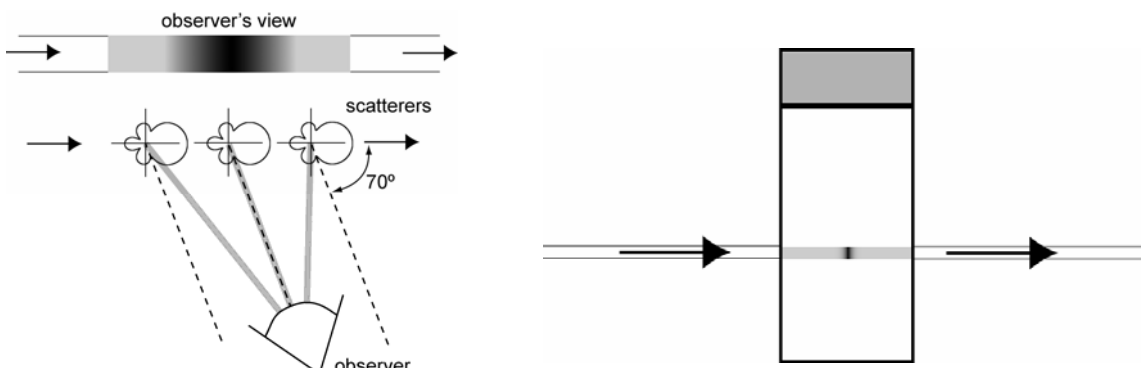
The minimum will appear as a dark band in the beam track because the beam track subtends a range of scattering angles. The figure to the left shows three scatters at different positions along the beam. Their shape is a polar plot of the scattering intensity versus angle. The dashed lines show the direction of the first scattering minimum (70° in this example). The observer's eye is positioned to be at the minimum for the middle particle. Because the observer is not infinitely far away, the scattering angle for the other two particles is different, thus not at the minimum and appear brighter. The result is that we observe a dark band. The width and darkness of the band varies, depending on details of the scattering. (If you use both eyes, each eye sees the position of the dark band at different positions.)

Step 6) Calculate the scattering angles. In your notebook, you have just recorded the raw values of the scattering angles (read from the goniometer scale). Convert these to the scattering angle in the same table. Convince your self that they are correct.

Step 7) Turn off the laser, return your unknowns to the box.

Part E) Model your results in MiePlot.

Step 0)   Download Mieplot from the NanoLab www site. Install this on your computer. It is a small program and should not present any difficulty.

Step 1) Start MiePlot and set it up to model the intensity versus scattering angle of polystyrene nanoparticles in water.

1a) Set up for polystyrene spheres in water. From the Advanced drop down menu select refractive index, sphere, data from file, choose polystyrene.rix. If you do not see this file, navigate to the directory where you unziped MiePlot. (Polystyrene.rix is provided with the MiePlot zip file from the NanoLab www site. It is not part of Philip Laven's MiePlot distribution.) Then again from the Advanced drop down menu select refractive index, surrounding medium, water, Segelstein, then a box will pop up, the complex box should be unchecked.

1b) Set up to calculate and to plot the intensity versus scattering angle. On the top right from the drop down box (initially: intensity v. scattering angle) select intensity v. scattering angle.

1c) Set up the wavelength to correspond to the laser you used. If you used the RED HeNe laser, enter 632.8 nm. If you used the GREEN HeNe laser, enter 543.5 nm.

1d)   Select the size of the sphere. NOTE MiePlot uses RADIUS in units of MICROMETERS. Start with a radius of 0.1 µm.

1e) Calculate the values and make the plot. Click New Plot. A progress bar will appear on the upper right. When it is finished your plot will be displayed. Note that by default two curves are displayed. These are the parallel and perpendicular polarization (with respect to the scattering plane). We are specifically interested in the perpendicular polarization, so you can have MiePlot display only the perpendicular polarization by selecting it from the polarization drop down menu.

Step 2) Perform the modeling. Mie theory calculations are a complex. They can be used to calculate the intensity versus scattering angle of nanoparticles given their size and refractive index. However the mathematics cannot be easily inverted. You cannot put in the intensity versus angle and get out the particle size! To determine the particle size, we perform several calculations and then compare them to our experimental data.   The particle size with calculated intensity minima at the positions you observed is the best-fit particle size determine from Mie Theory.

By default your calculations are performed 0-180°. Experimentally you can only get meaningful results from about 30-150°. Do not be concerned that the calculations show more minima than you observed if the calculated minima are outside the range of your measurements. However if your calculation shows many more minima in your range of observation than you observed, you are probably in the wrong size range. (How are the number of minima related to size?)

You will also note that not all minima are the same depth and sharpness. This effects how easily and accurately you can measure them. You can check how good your fit is by varying the particle size in you calculation
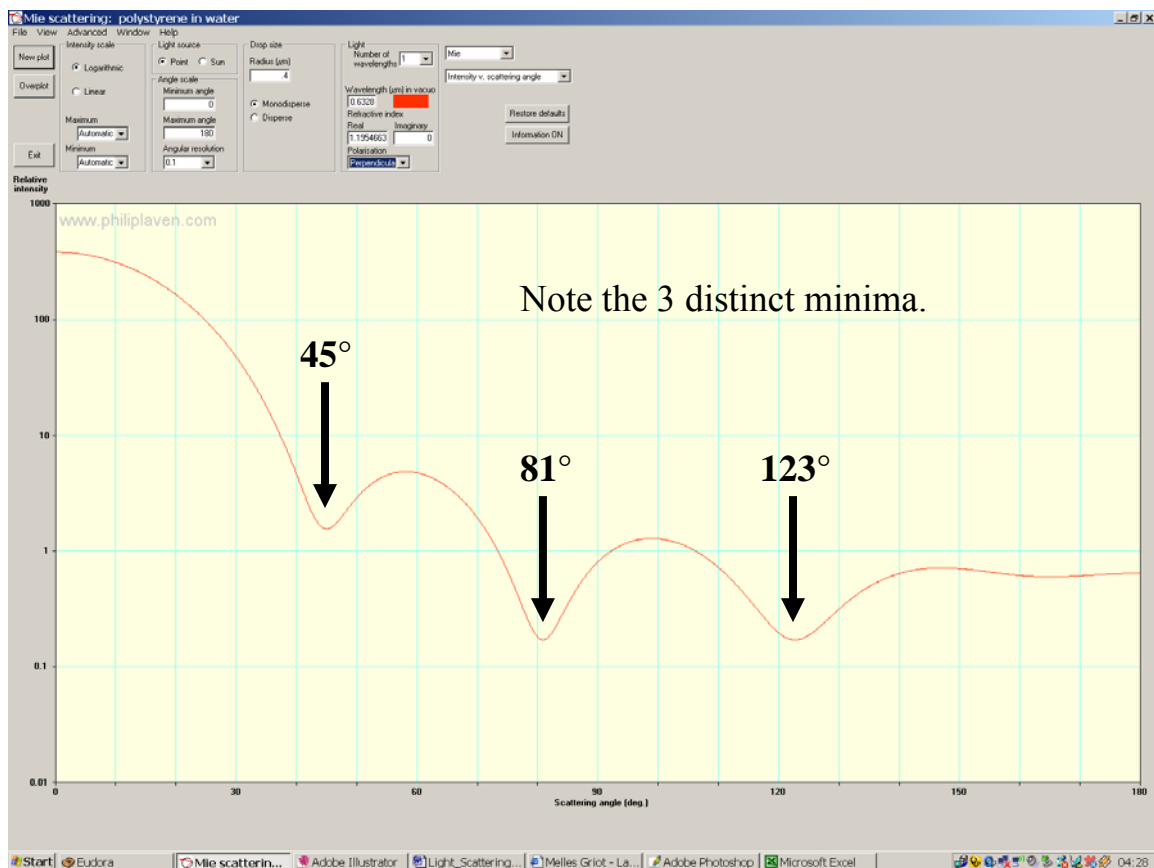
Exporting and working with data from Mieplot.

From the `file` menu, select `save numerical results as text file`.

This file can be imported into excel as a **TAB** delimited text file.

From the file drop down menu select open. From the open window, select files of type: text files (*.prn, *.txt, *.csv). Now navigate to your file and select open. The text import wizard will start. Note that tab delimited text is the default, so pressing finish on this screen often will give you the desired result.

In detail:

- step 1) under `delimited`, click `next`;

- step 2) in the `delimiters` box select `tab`, click `next`;

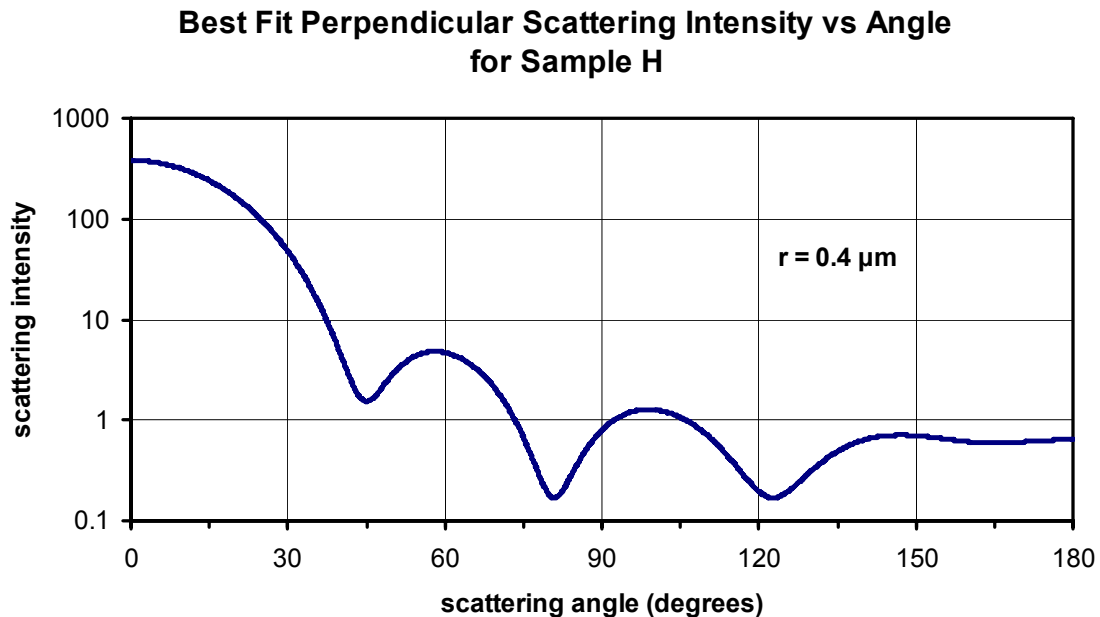- step 3) in the `column data format` box select `general`, now click `finish`.

MiePlot v3.4.10							
Date & Time: 2005-03-29 04:26:50							
Calculation Method: Mie (plane wave)							
Sphere:	polystyrene						
Medium:	water						
Refractive index	Real part:	1.19546638	Imaginary part:	0			
Wavelength:	0.6328	um					
Radius:	0.4	um	Effective radius:	5.2943			
Graph type:	Intensity v. scattering angle						
Angle	Perpendicular	Parallel	Unpolarised				
theta	[S1(theta)]^2	[S2(theta)]^2	[[S1(theta)]^2 + [S2(theta)]^2]/2				
0	380.4917203	380.4917203	380.4917203				
0.1	380.4841457	380.4836413	380.4838935				
0.2	380.4614228	380.4594053	380.460414				
0.3	380.4235538	380.4190151	380.4212845				
179.8	0.639011198	0.638992504	0.639001851				
179.9	0.639024821	0.639020148	0.639022484				
180	0.639029362	0.639029362	0.639029362				
Real and imaginary values of S1 (perpendicular polarisation) and S2 (parallel polarisation)							
Angle	S1 Real	S1 Imaginary	S1 Magnitude	S1 Phase	S2 Real	S2 Imaginary	S2 Magnitude	S2 Phase
0	13.15357644	-14.40399761	19.50619697	312.40199	13.153576	-14.403998	19.506197	312.40199
0.1	13.15346844	-14.4038333	19.50600281	312.40209	13.153471	-14.403813	19.50599	312.40213
0.2	13.15314444	-14.40334038	19.50542034	312.40236	13.153156	-14.40326	19.505369	312.40254
0.3	13.15260445	-14.40251888	19.50444959	312.40281	13.15263	-14.402338	19.504333	312.40323
0.4	13.15184849	-14.40136882	19.5030906	312.40345	13.151894	-14.401047	19.502884	312.40419

We are interested only in the first table, the intensities versus angle, and specifically in the column labeled: perpendicular [S1(theta)]^2, the intensity of the perpendicular polarization. The table contains these values from 0-180°. Below this table is the table of the complex scattering amplitude, S1 and S2. These are the actual quantities calculated by Mie theory from which the intensities are derived.

For each of your unknowns samples, find the best fit particle size using MiePlot. Report your results in a table. Include a graph of the calculated best-fit perpendicular scattering intensity versus scattering angle for each of your unknowns.

Example Graph: Use a logarithmic scale on the intensity axis. Include the best fit radius of your particle on the plot. Make one graph for each of your unknowns.

Example Table:

	Simon	Malcolm	Bruno	mean		
	measured angle	measured angle	measured angle	measured angle	best fit angle	best fit radius
	(degrees)	(degrees)	(degrees)	(degrees)	(degrees)	(um)
unknown # H	43	44	42	43.0	45	0.4
	80	83	78	80.3	81	
	123	120	121	121.3	123	
unknown # J	–				20	0.8
	38	38	37	37.7	37	
	55	53	55	54.3	56	
	72	73	72	72.3	73	
	93	91	94	92.7	92	
	114	115	113	114.0	113	
	–				135	
	–				154	
	–				170	
unknown # K	38	38	38	38.0	40	0.45
	72	74	72	72.7	71	
	118	119	117	118.0	117	
	–				165	

NanoLab Light Scattering Activity
perpendicular scattering minima
laser wavelength = 632.8 nm

TROUBLE SHOOTING TIPS

1) Polarization is not set properly. It should be vertical to the scattering plane in these experiments.

2) Your eye is not in the scattering plane. The scattering plane is defined by two paths, the path from the particle to the light source and the path between the particle and the observer. In the laboratory frame, we have set up the experiment so that the scattering plane is the horizontal plane. Observing the scattering from above or below the plane will give you different results—typically bad results.

3) The vial is not tilted. The laser beam reflects from the back surface of the vial. If the reflected beam folds back onto the main beam, the scattering from it will be observed on top of the scattering from the main beam. Because the effects you are measuring are NOT symmetric for forward (0-90°) and backward (90-180°) scattering, this will confound your measurements. Place a shim under the far edge of the vial. This will tip the vial, sending the reflections downward. As long as you can easily distinguish (and ignore) the reflected beam, the vial is tilted enough.

4) Laser beam too bright. If the beam is too bright, your eye is dazzled which makes seeing the minima difficult. Reduce the intensity and try again.