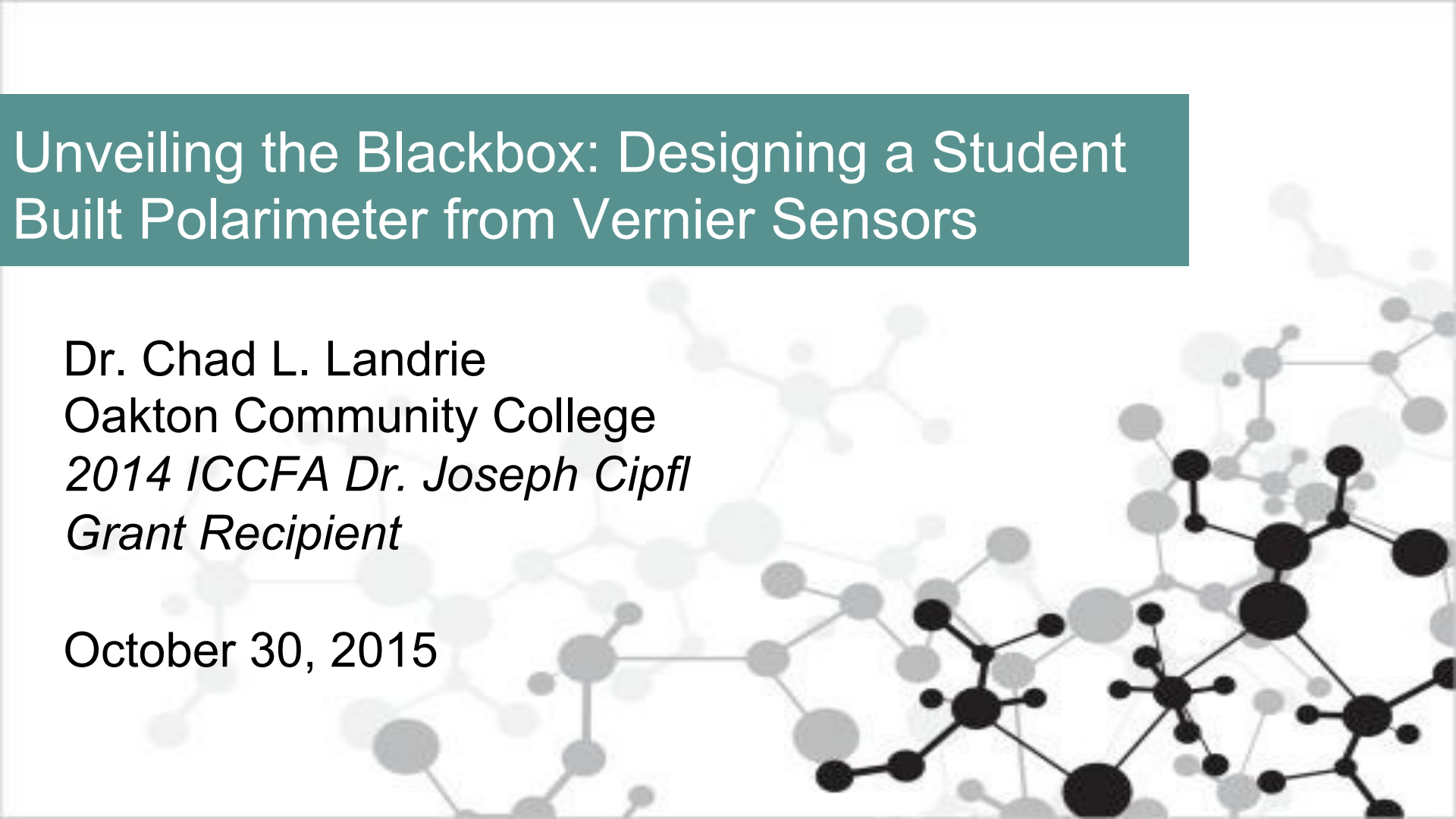


Unveiling the Blackbox: Designing a Student Built Polarimeter from Vernier Sensors

Dr. Chad L. Landrie
Oakton Community College
*2014 ICCFA Dr. Joseph Cipfl
Grant Recipient*

October 30, 2015



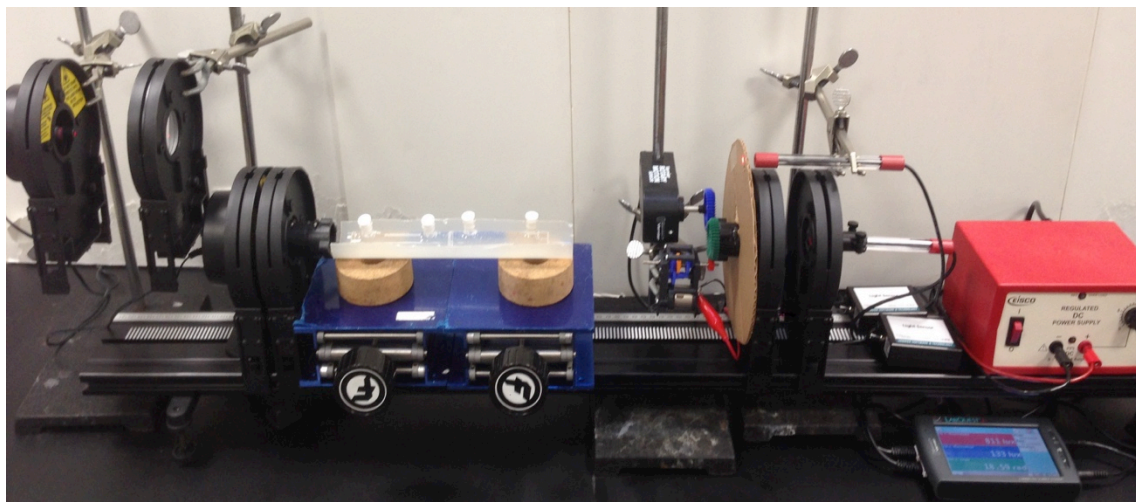
Our Goals

Some molecules are **chiral**.

Chiral molecules rotate **plane polarized light**.

A **polarimeter** measures the **magnitude** of this rotation.

We aimed to **design** a polarimeter that students could build.



Objectives

- recognize chirality and associated properties in molecules, especially biological
- describe the nature of light and its polarization
- apply Malus's Law (a $\cos^2$ function) to find optical rotation
- construct an analytical instrument
- investigate the measurement limits of an analytical instrument
- do something new!

Objects Can be Chiral

Achiral



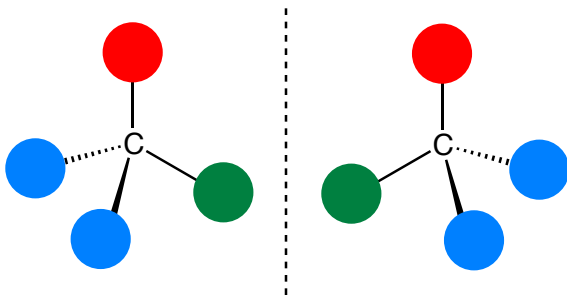
Chiral



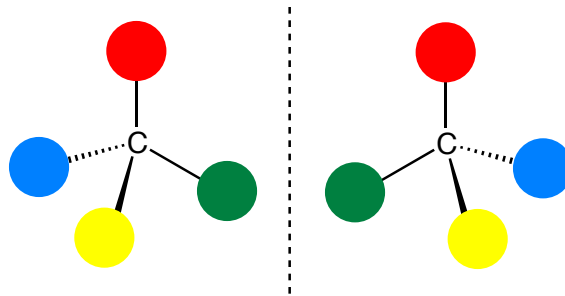
An object is **chiral** if its two mirror image forms are **not superimposable** on one another

Molecules Can be Chiral

Achiral

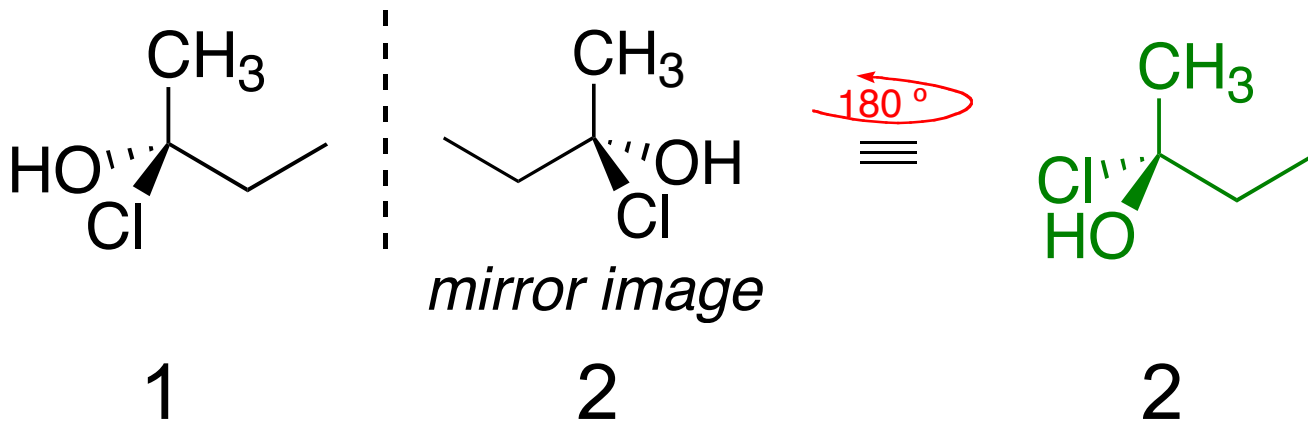


Chiral



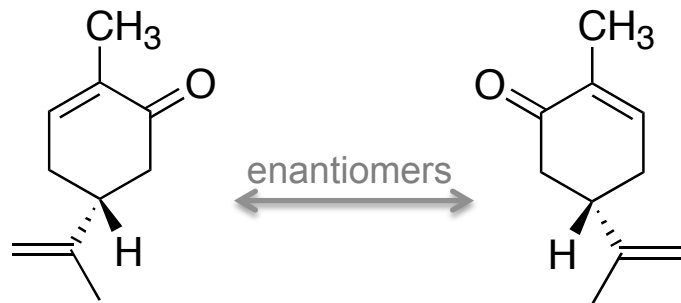
A molecule is **chiral** if its two mirror image forms are **not superimposable** on one another

Molecules Can be Chiral



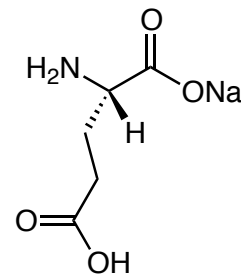
A molecule is **chiral** if its two mirror image forms are **not superimposable** on one another

Molecular Chirality in Nature

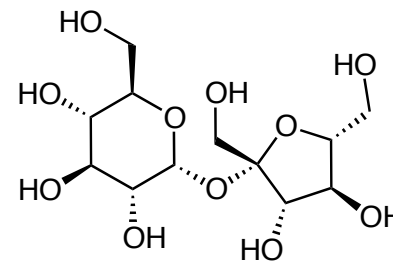


(R)-(-)-carvone

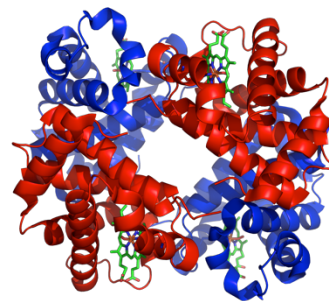
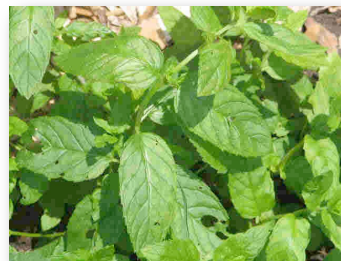
(S)-(+)-carvone



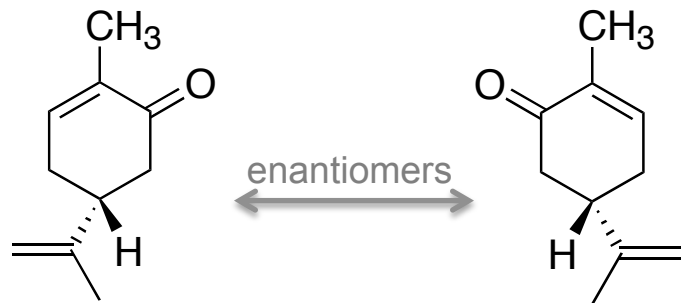
monosodium glutamate
(amino acid)



sucrose
(carbohydrate)



Chiral Molecules Rotate Plane Polarized Light

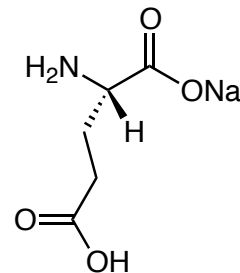


(R)-(-)-carvone

(S)-(+)-carvone

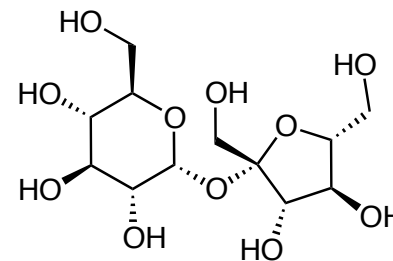
$[\alpha] = -61^\circ$

$[\alpha] = +61^\circ$



monosodium glutamate
(amino acid)

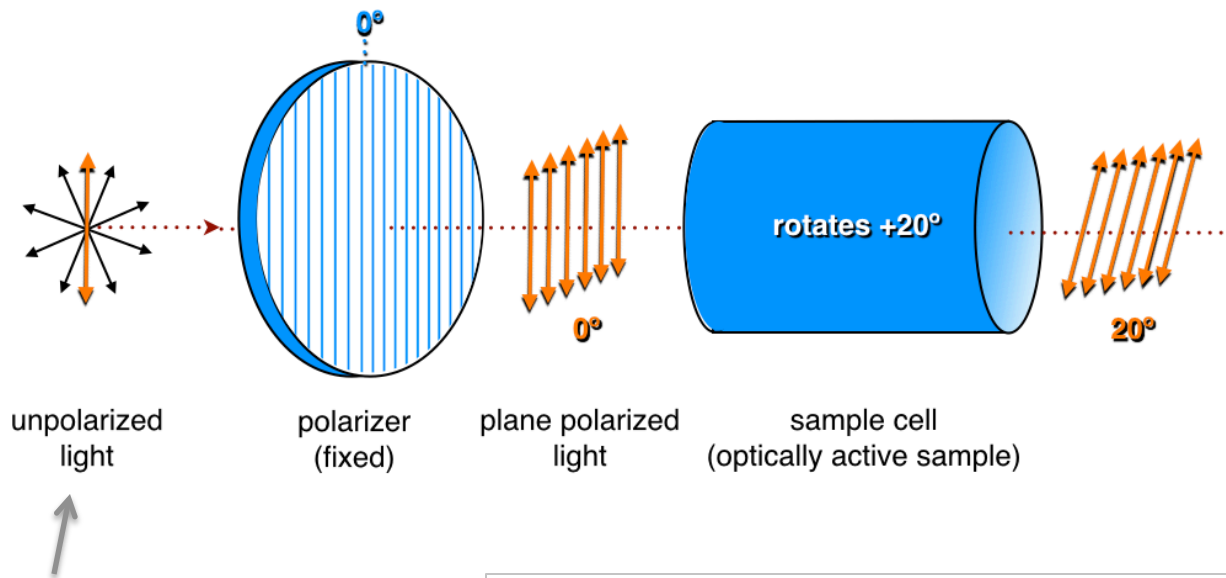
$[\alpha] = +24^\circ$ pH < 2
 $[\alpha] = -5^\circ$ pH = 7



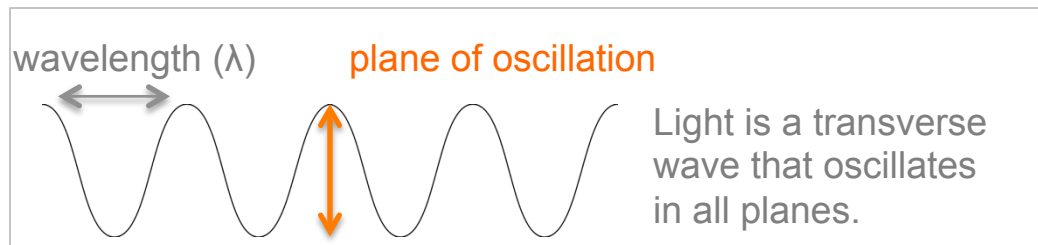
sucrose
(carbohydrate)

$[\alpha] = +67^\circ$

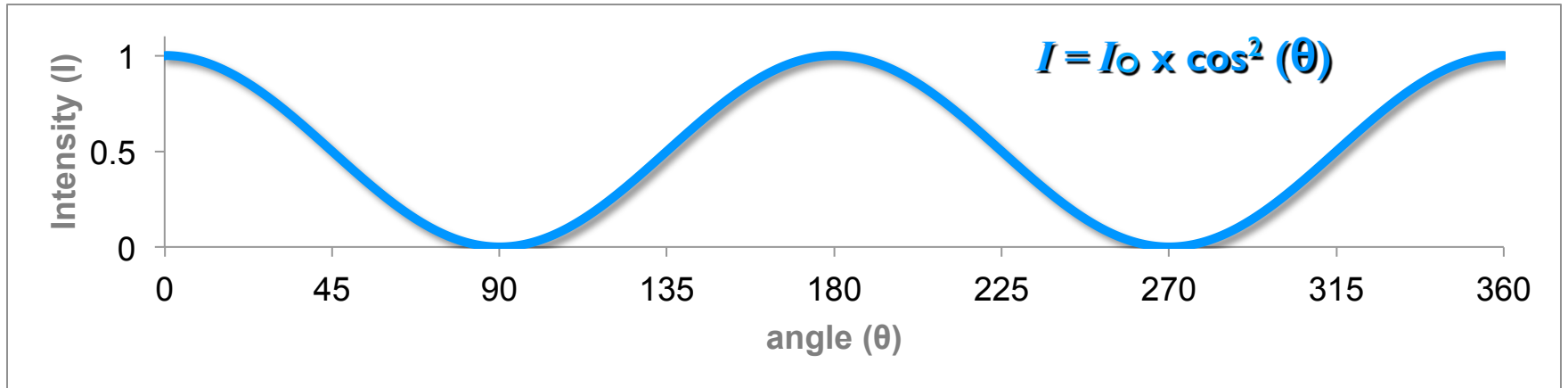
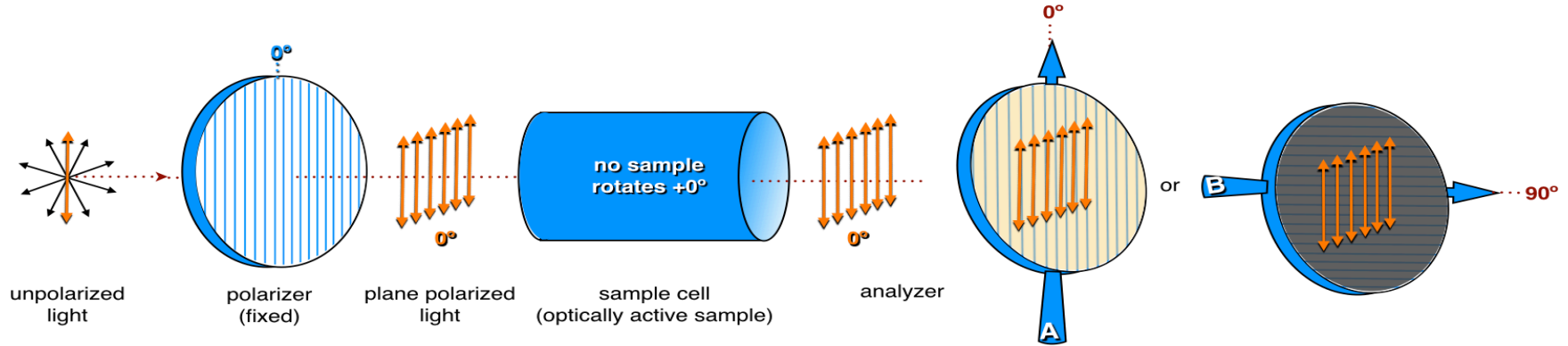
Chiral Molecules Rotate Plane Polarized Light



Light source must be monochromatic since chiral molecules rotate different wavelengths of light by different amounts (optical rotary dispersion)

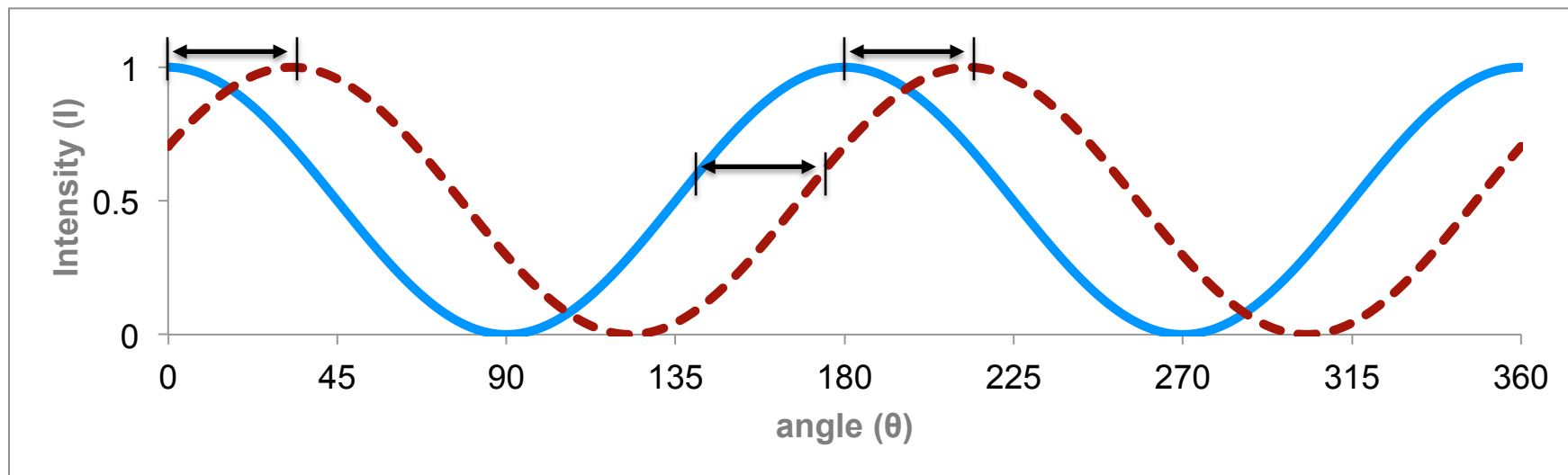


Malus's Law of Two Polarizers

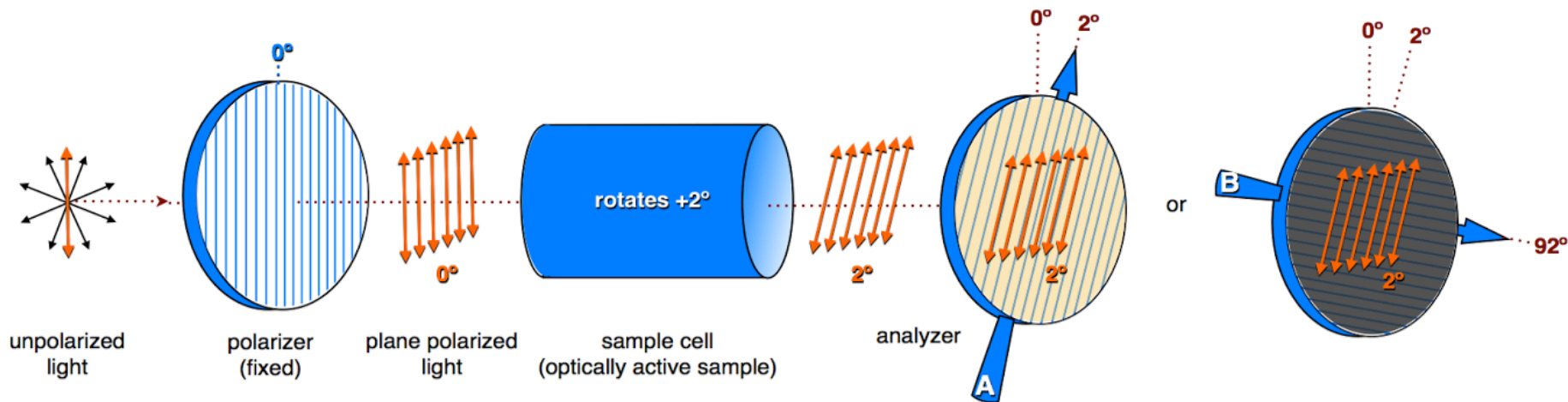


Measuring Optical Rotation

Optical Rotation = the difference between **reference** and **sample** at any congruent points in the curves

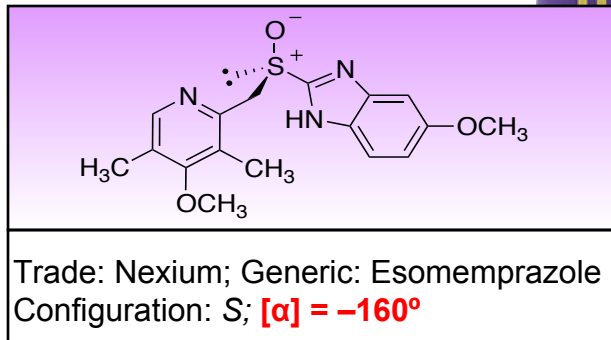
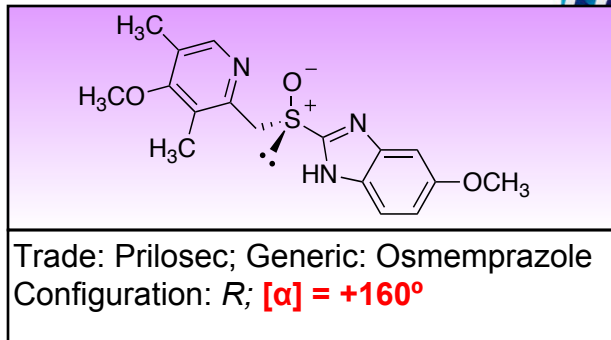


Optical Rotation is Concentration Dependent



$$\text{specific optical rotation, } [\alpha] = \frac{\alpha_{\text{observed}}}{\text{pathlength (dm)} * \text{concentration (g/mL)}}$$

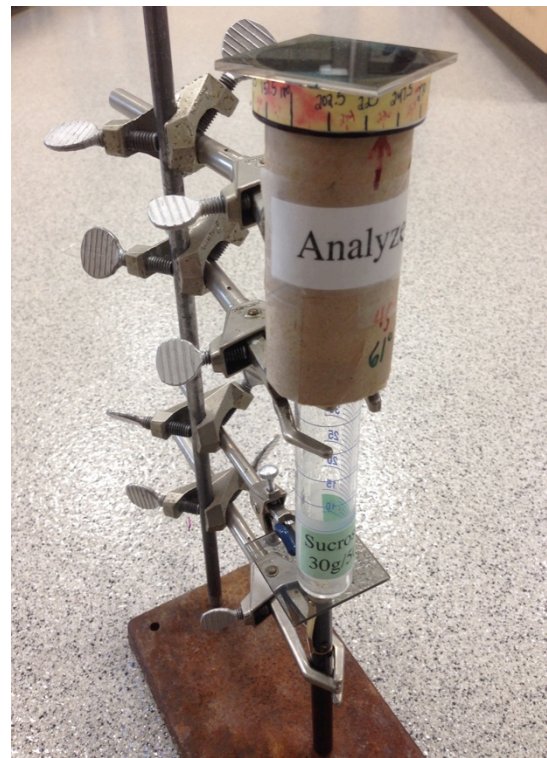
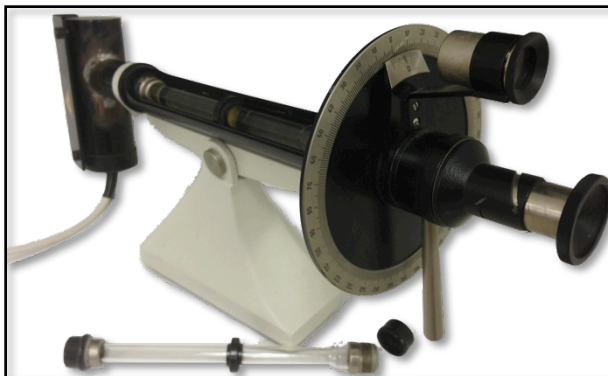
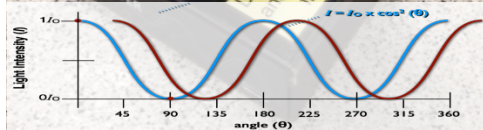
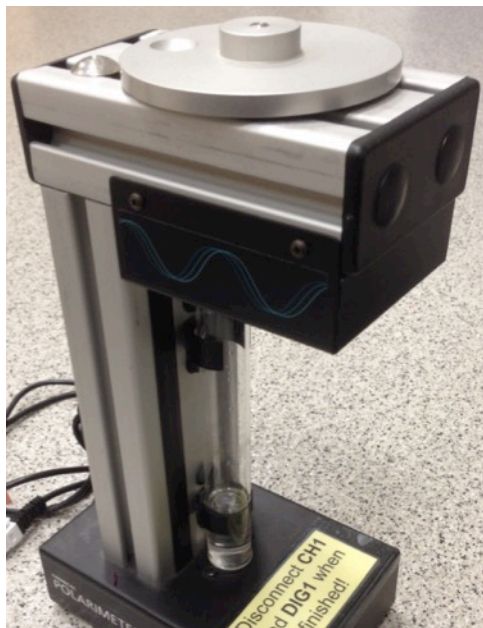
Specific Optical Rotations of Mixtures



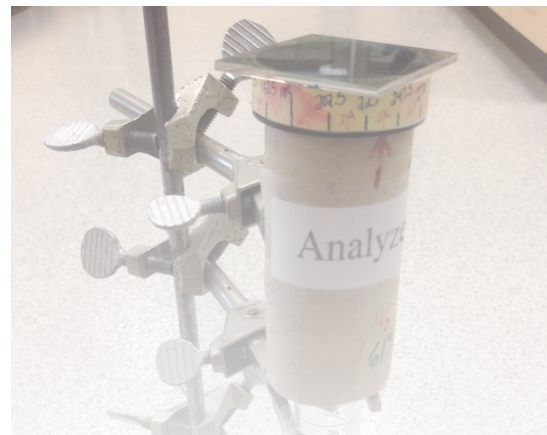
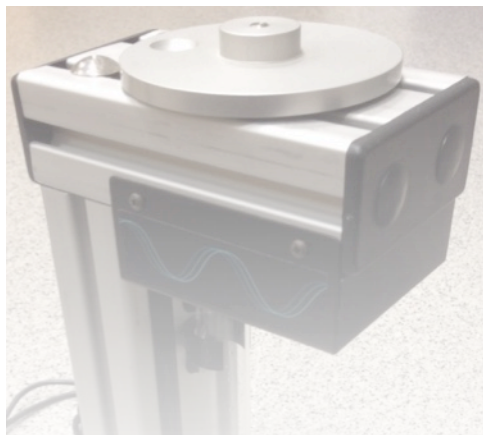
% Prilosec	% Nexium	ee	Optical Rotation of the Mixture $[\alpha]$
100	0	100	$+160^\circ$
75	25	50	$+80^\circ$
50	50	0	0
25	75	50	-80°
0	100	100	-160°

$$\text{optical purity (ee)} = \frac{[\alpha]_{\text{observed for mixture}}}{[\alpha]_{\text{pure major enantiomer}}}$$

Polarimeters in Our Organic Laboratory



Polarimeters in Our Organic Laboratory



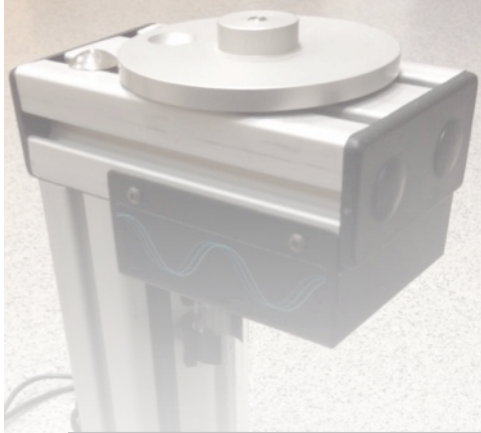
Advantages:

- fast measurement
- easy to use
- manual = affordable

Disadvantages:

- fast measurement
- easy to use
- Can become a black box

Polarimeters in Our Organic Laboratory



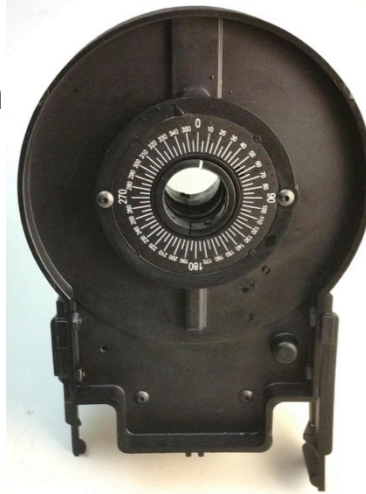
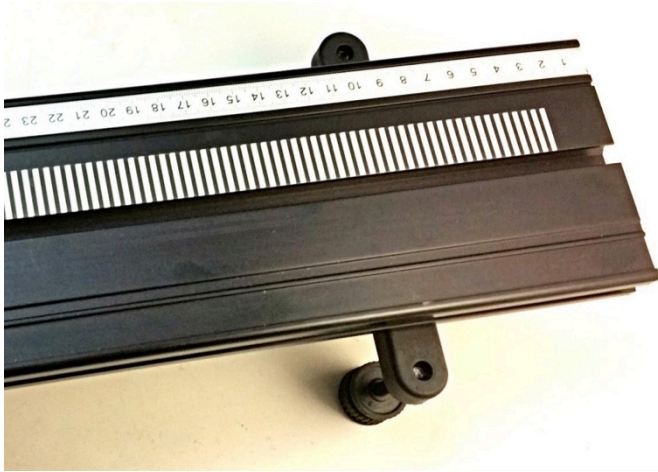
Our Goals:

- design polarimeter that could be built repeatedly
- plot Malus's Law for optical rotation determination
- perhaps do something new

Vernier Parts

Combination 1.2 m Track/Optics Bench

- foundation of polarimeter, 2 m
- polaroid filters, light source and light detectors snap onto track



Polarizer

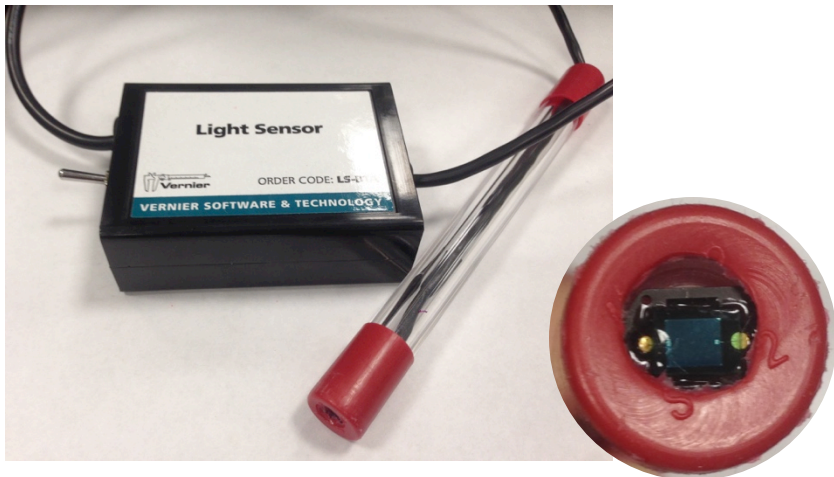
- rotate by hand
- may read angle on analog scale
- or connect to rotary motion sensor



Rotary Motion Sensor

- Connect to polarizer (rubber bands supplied)
- Resolution = 0.25°
- max speed = 7.5 rev/s
- Quadrature optical encoder

Vernier Parts



Light Detector

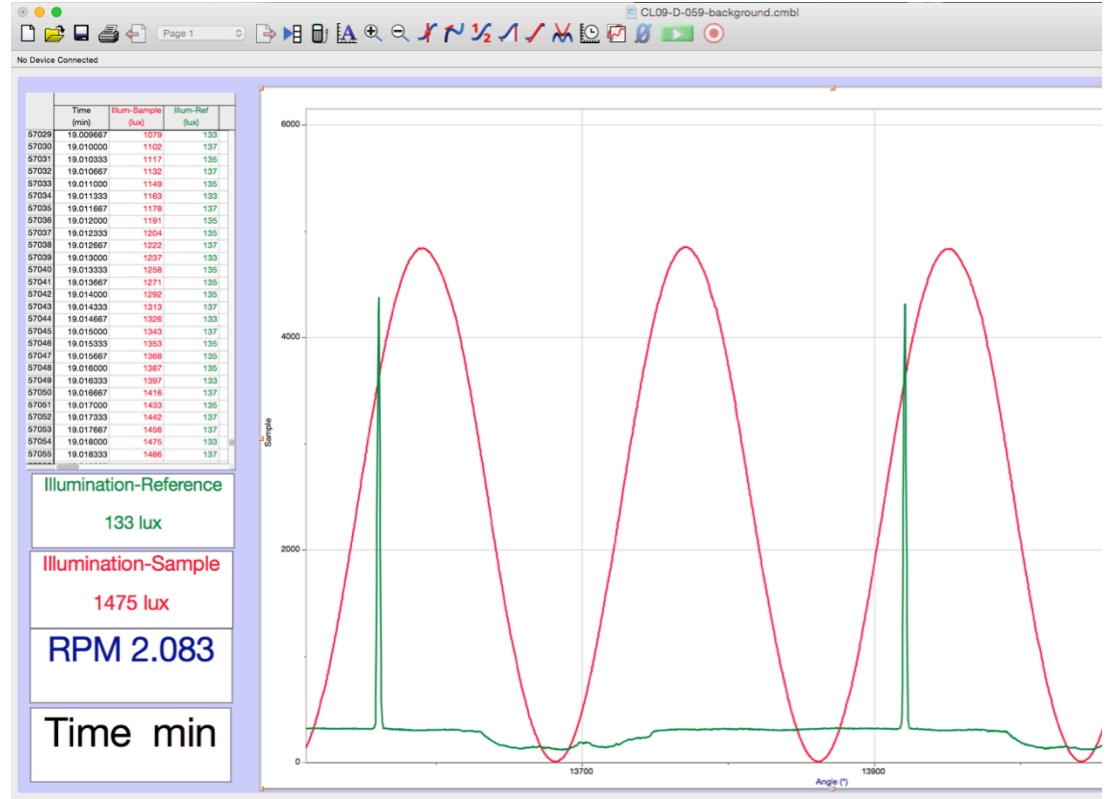
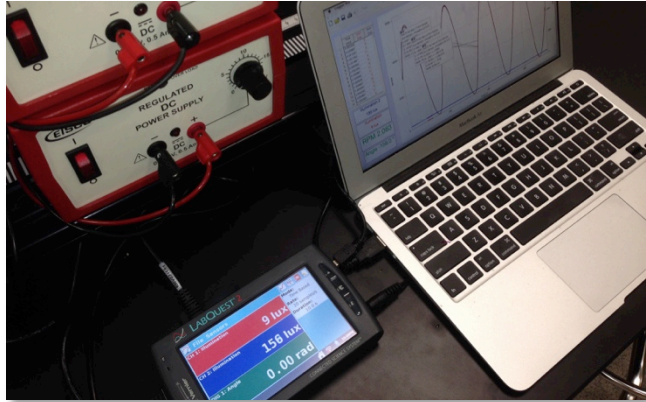
- Si-photodiode
- Produces voltage proportional to light intensity (lux)
- Spectral range of human eye
- 3 sensitivity ranges (0-600, 6000, 600,000)



Red Laser Light Source

- Wavelength: 633 nm
- not a common wavelength
- but cheap: \$120
- green available: \$250
- adjustable angle

Data Collection

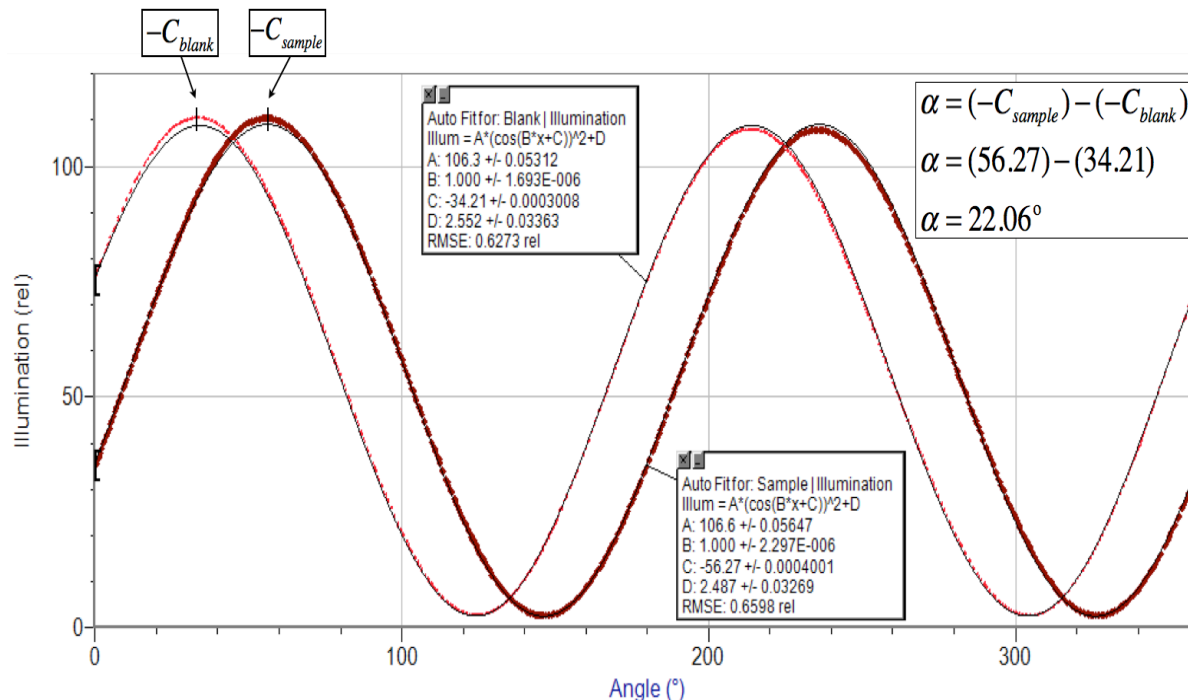


- Connect sensors to LabQuest2, \$329
- Collect and process data with LoggerPro
- Oakton has a site license so all students may download for offline data processing

Vernier LoggerPro Curve Fitting

$$\text{Illum} = A(\cos(Bx+C))^2+D$$

-C = phase shift parameter;
degrees offset from zero



LoggerPro will fit $\cos^2$ curves,
give coefficients:

A = amplitude

B = frequency

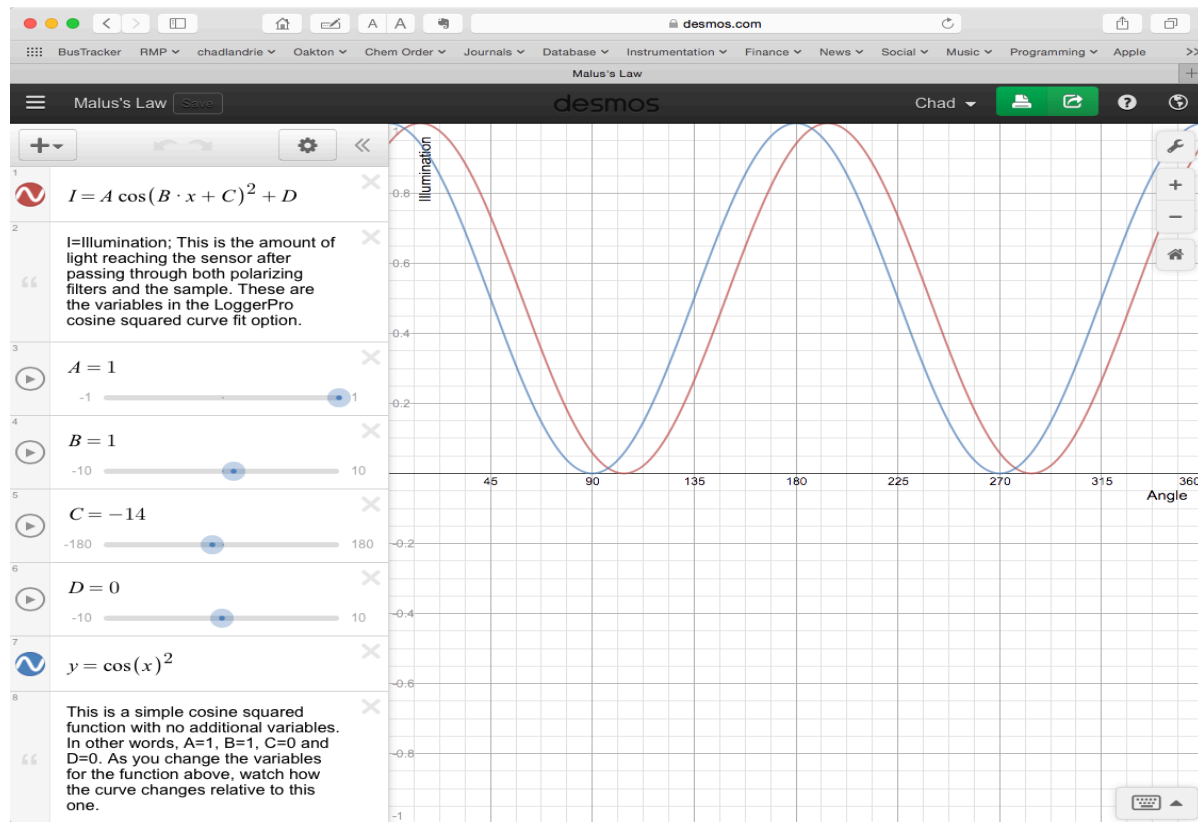
C = phase shift parameter

D = y-offset

Starting angle for background/
reference is irrelevant

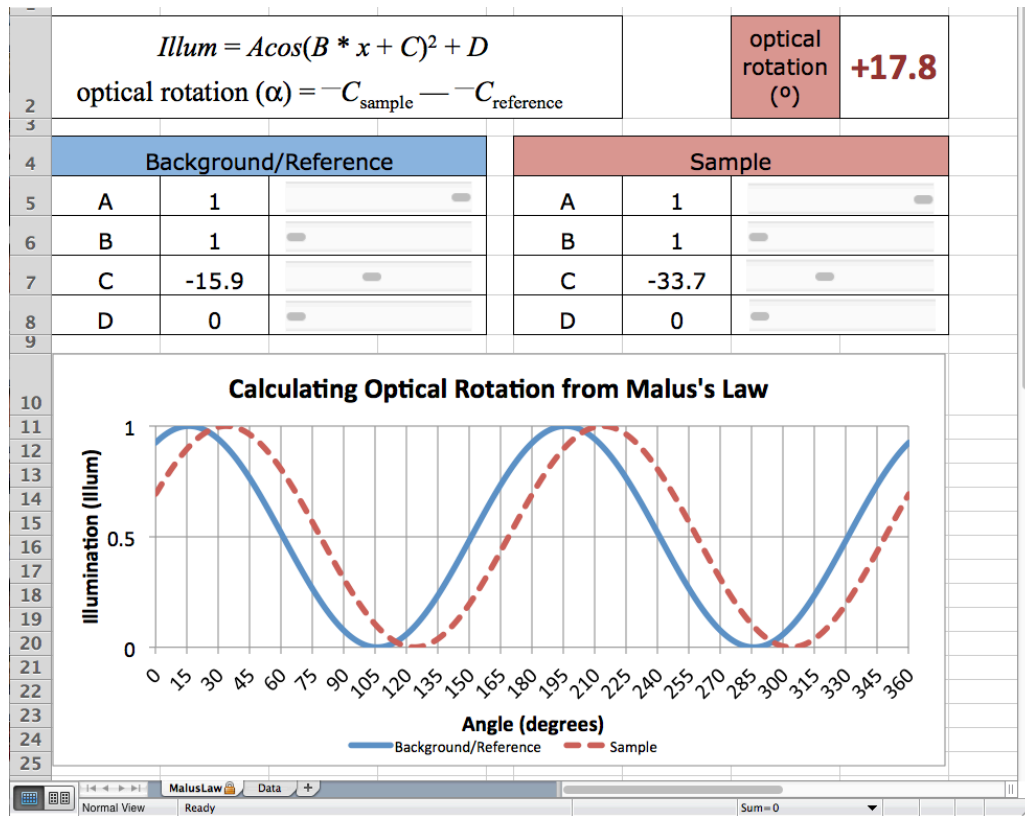
Optical rotation (a) is found by
difference

Investigating $\cos^2$ with Desmos



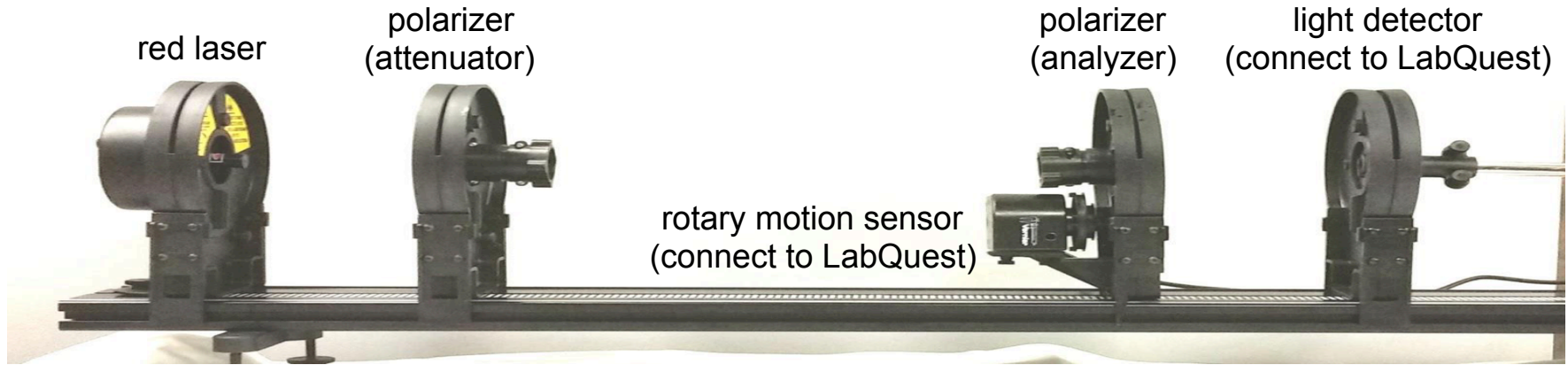
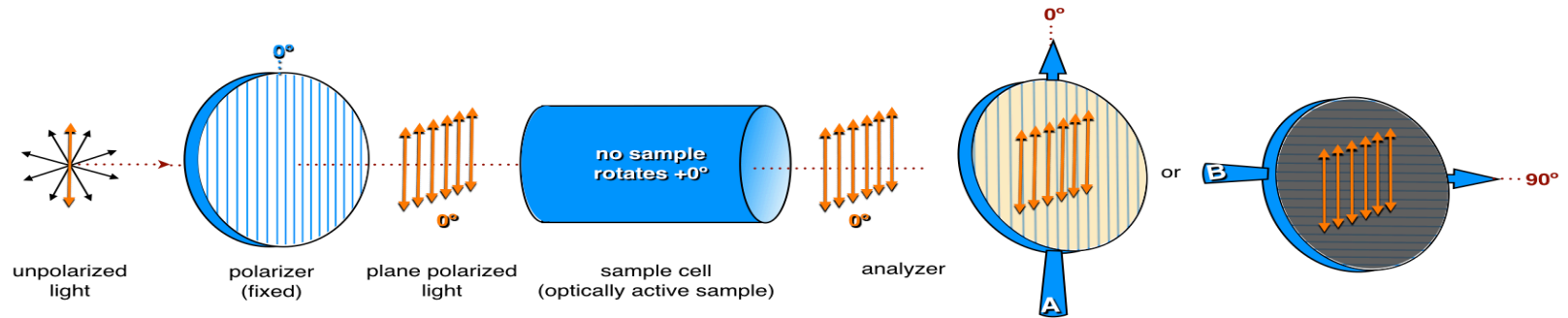
- developed a Google Desmos graphing calculator graph for $\cos^2$
- allows students to use sliders to investigate properties of coefficients given by LoggerPro curve fit
- blue stationary; red moves with sliders

Investigating $\cos^2$ with Excel

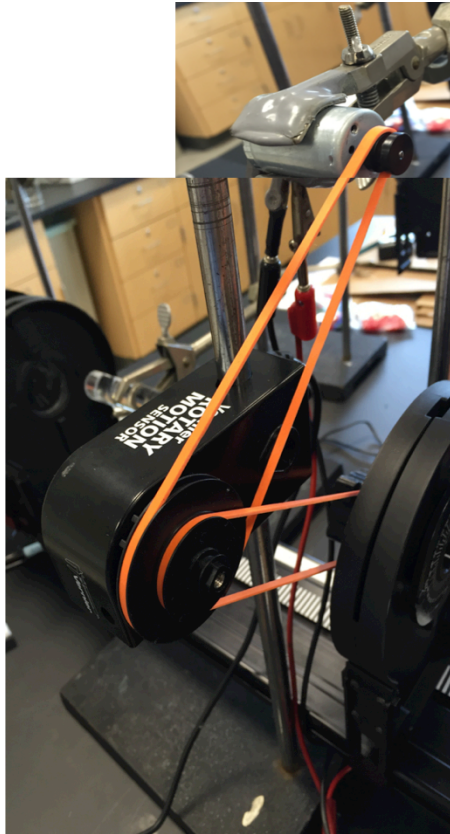


- sliders used to adjust coefficients for $\cos^2$ curve
- Both background and sample could be changed
- optical rotation is calculated

Polarimeter Assembly

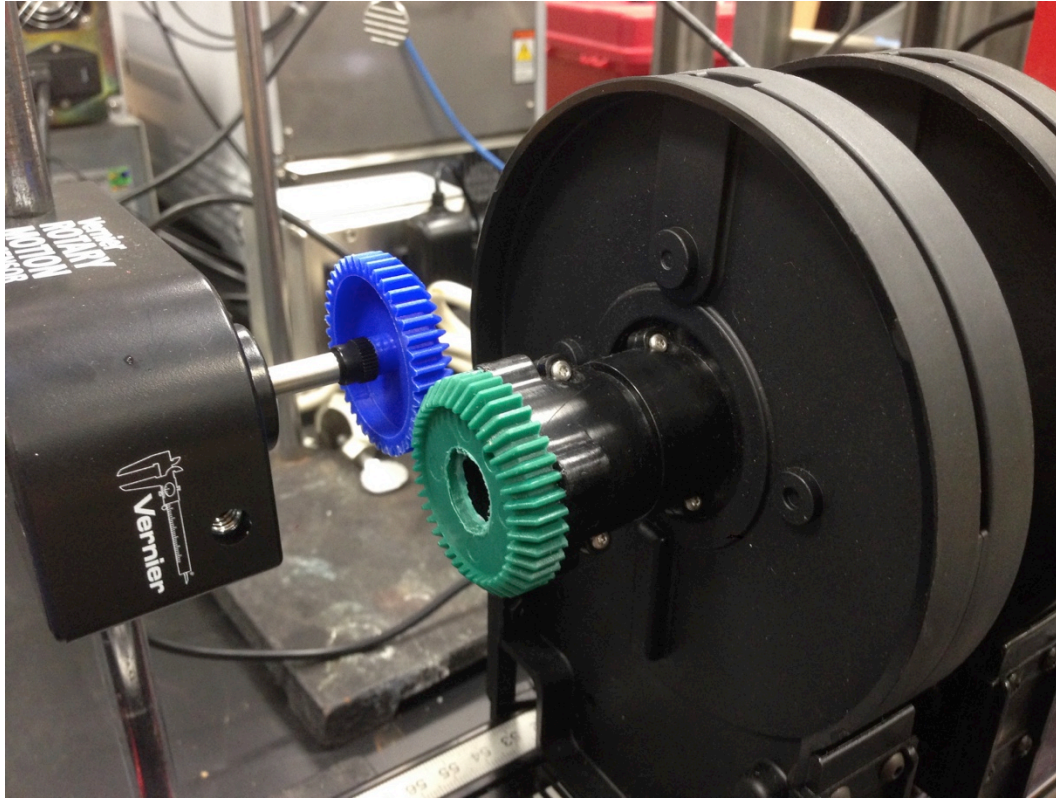


Measuring the Angle of Rotation



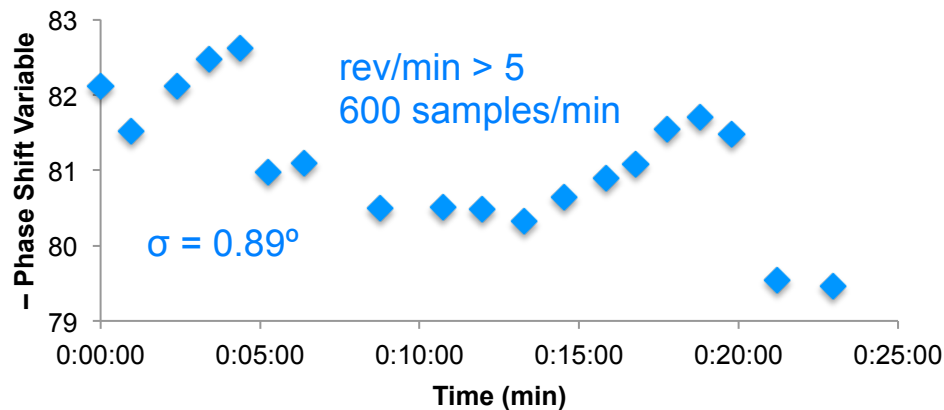
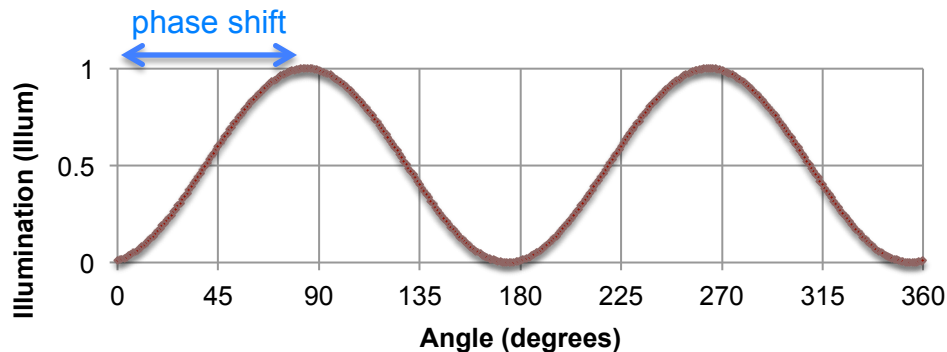
- connecting rotary motion sensor to polarizer with rubber bands was highly problematic
- rubber bands slipped with low tension leading to inaccurate angle measurements, especially when rotating by hand
- motor could not drive RMS when bands were under high tension
- Elasticity of rubber bands caused forward rotation to give different α than reverse rotation

Gears Are Better



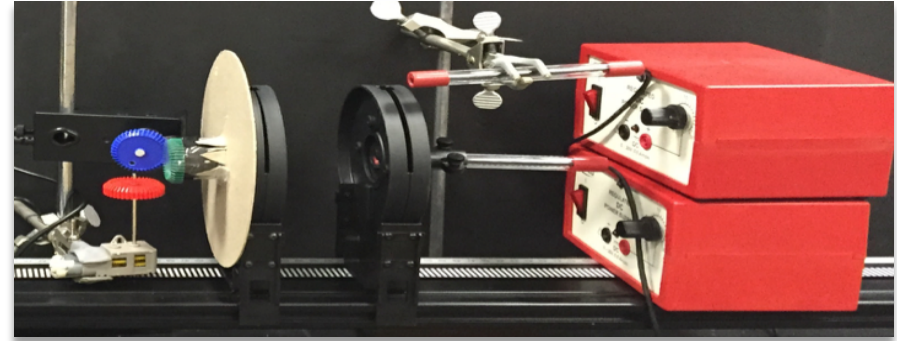
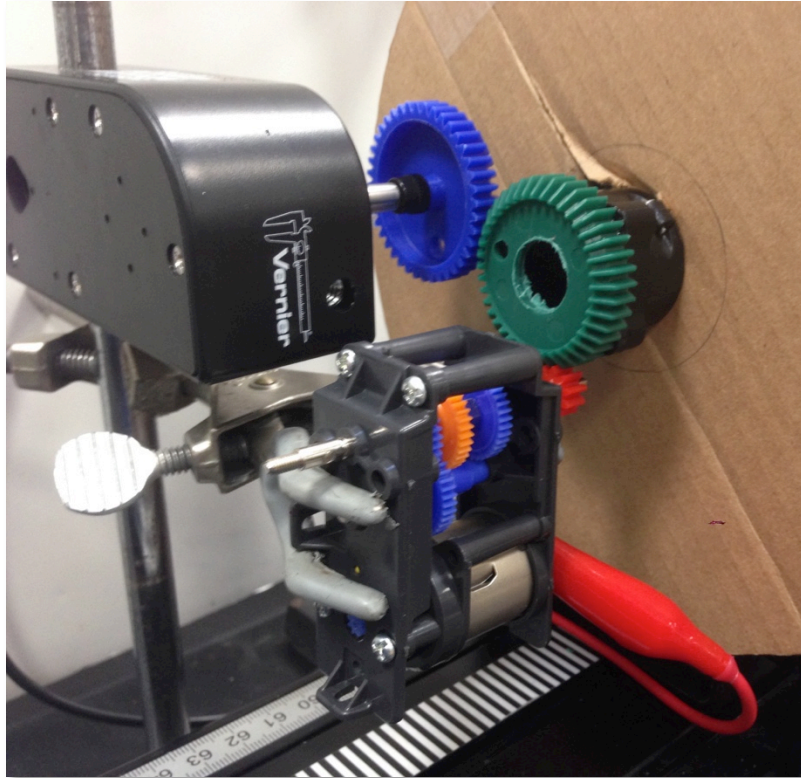
- **green gear** affixed to analyzer with superglue; hole drilled in center for light path
- **blue gear** screwed onto rotary motion sensor
- gear ratio 1:1
- precise measurement of rotation with no lag; 360° forward and back
- User rotates green gear/ analyzer by hand

Low Precision for Background Measurements



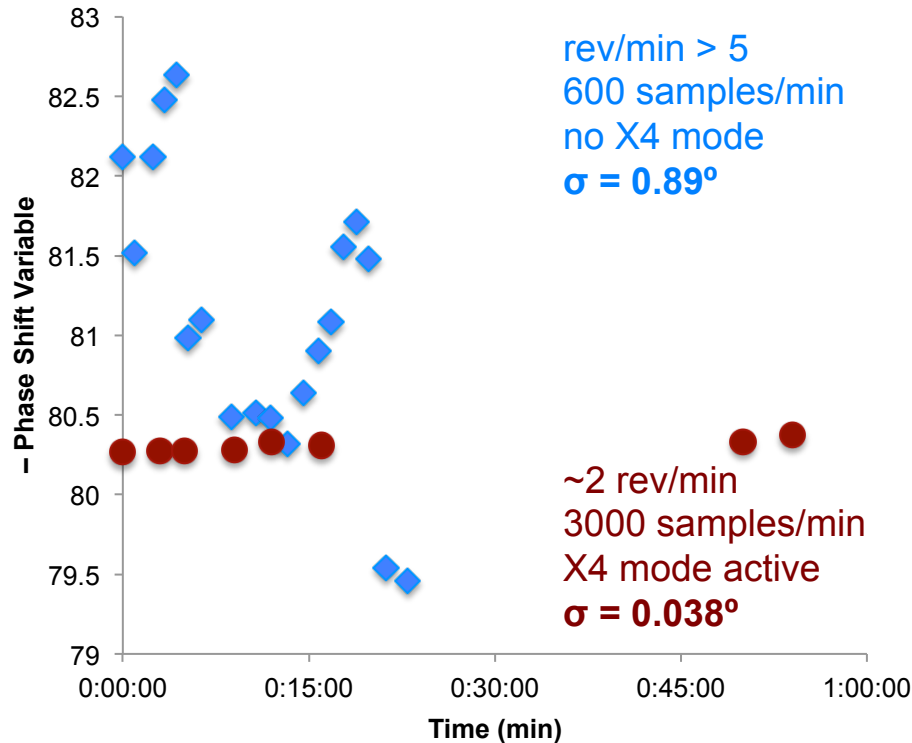
- measured background no sample
- turned analyzer forward 360° and backward 360° for each measurement
- analyzer turned by hand 5-10 rev/min?
- Used LoggerPro to fit $\cos^2$ curve and find phase shift parameter
- sampling = 600 samples/min

Further Modifications



- gears allowed us to precisely control rate of rotation of analyzer (rev/min) by connecting to a DC motor driven by a low voltage power supply
- Two power supplies = rotate both directions;
- 0-20 V; 0.5 amp limit
- a gear box was essential for rate below 10 rev/min; higher gear ratio allowed us to use higher voltage to overcome friction, while lowering rev/min

Significantly Improved Precision

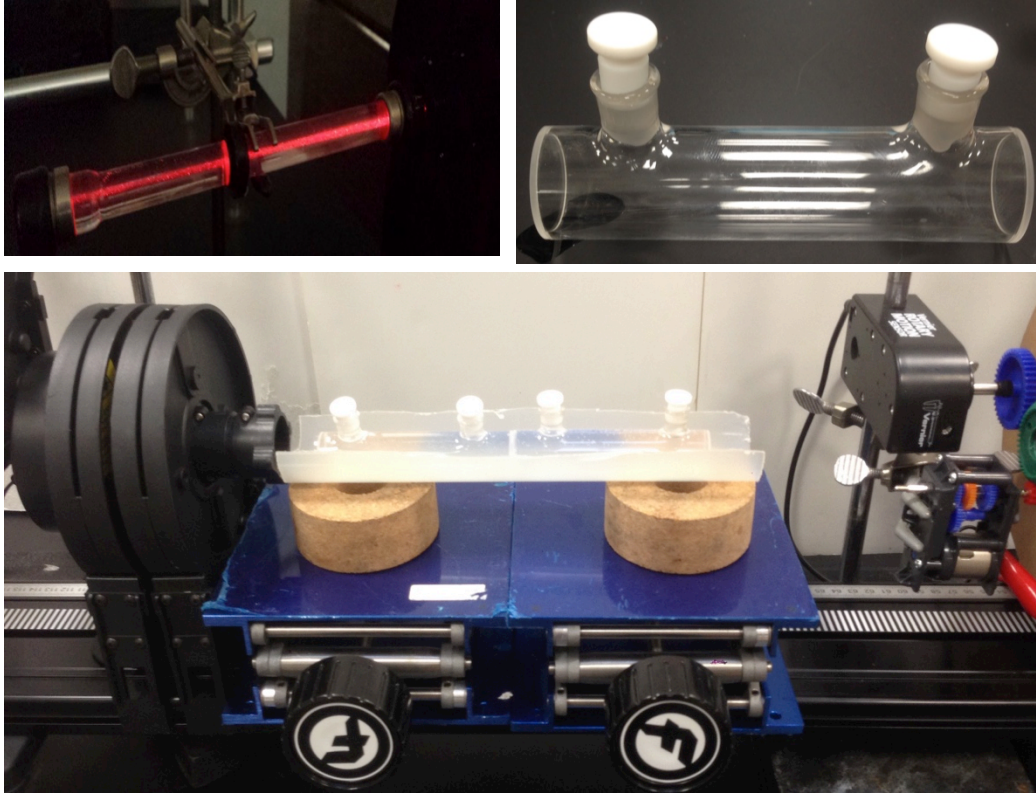


Discoveries:

- Rotary motion sensor default precision = 1°
- LoggerPro must be changed to X4 Mode which has precision = 0.25° (max)
- max sampling rate for RMS in LoggerPro = 6000 samples/sec
- lowering rev/min of analyzer decreases required sample rate, but increases sampling time
- lowest analyzer velocity without stalling ~ 2 rev/min; used motor to rotate analyzer
- **reproducible small drift in background**

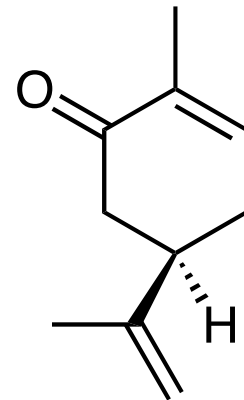
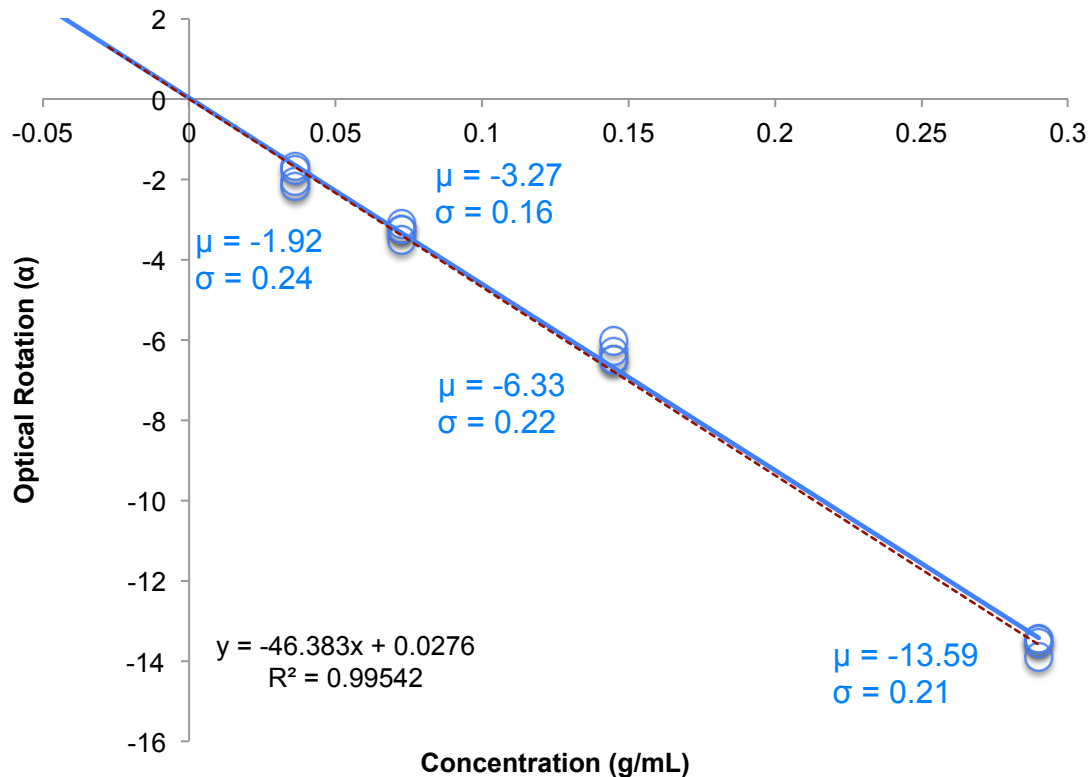
$$\frac{360\text{deg}}{1\text{rev}} \times \frac{2\text{rev}}{1\text{min}} \times \frac{1\text{min}}{3000\text{sample}} = 0.25\text{ deg/sample}$$

Sample Holder and Cells



- main challenge was aligning laser so that it illuminated the small Si-diode
- standard polarimeter tubes have small windows making alignment difficult, expensive
- found glass tubes with wide windows (\$100 from Precision Cells)
- constructed sample holder that kept tubes aligned, adjustments made with lab jacks

Serial Dilutions of Carvone at High Concentration

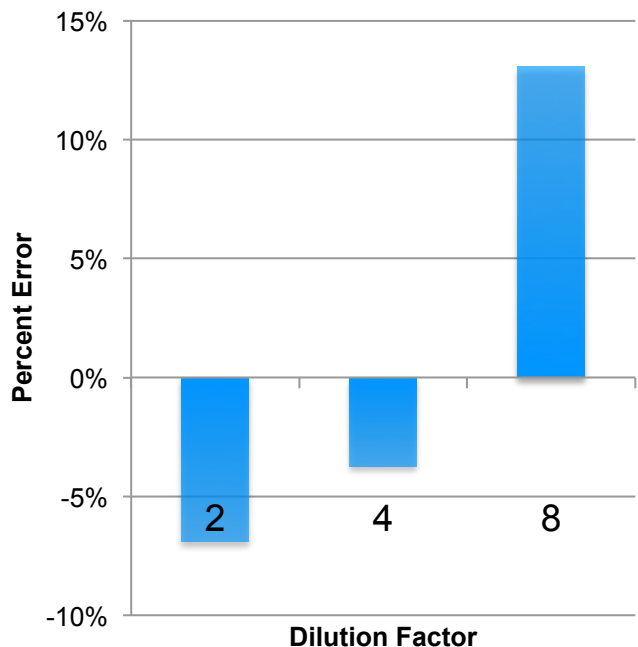


$$[\alpha]_{589}^{25} = -61^{\circ}$$

- cannot compare absolute measures of α since wavelength dependent
- Red laser = 636 nm
- α is linearly correlated with concentration
- we found excellent linearity for serial dilutions

Serial Dilutions of Carvone at High Concentration

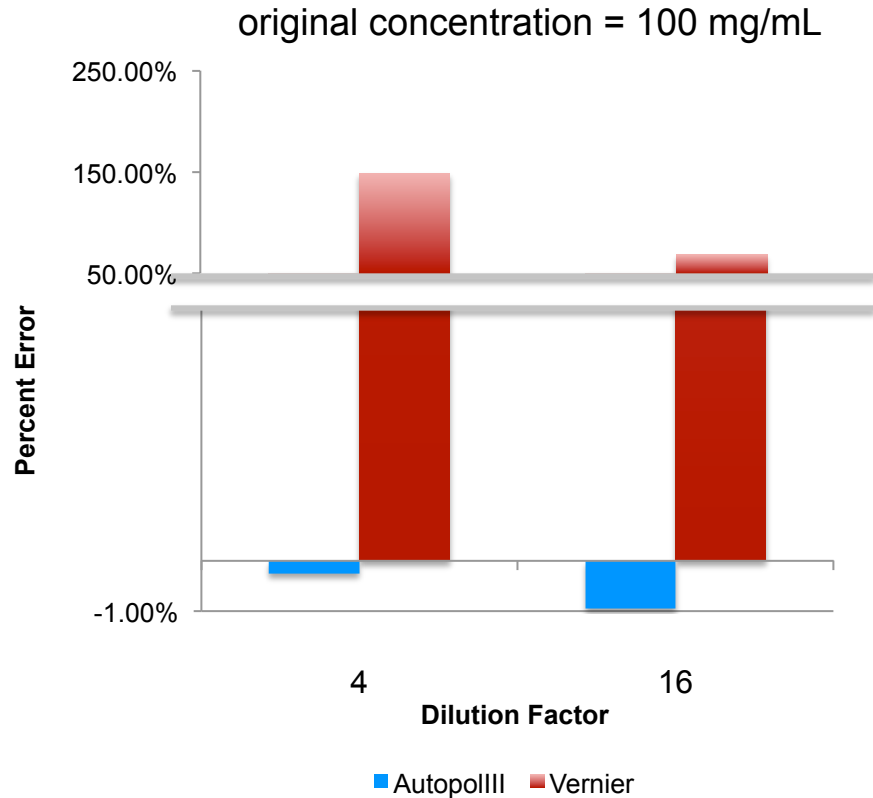
original concentration = 290 mg/mL



- Our precision is limited by rotary motion sensor
- We have found optical rotation standard deviation to be $\pm 0.25^\circ$ with our method
- At lower concentrations we expect higher percent errors reducing concentration by half increases percent error by factor of 2.

Dilution Factor	Conc. (mg/mL)	Optical rotation, α	Conc. STDEV (mg/mL)	Percent Error
1	290	-13.9	± 5	2%
2	145	-6.8	± 5	4%
4	72.5	-3.4	± 5	7%
8	36.25	-1.7	± 5	15%

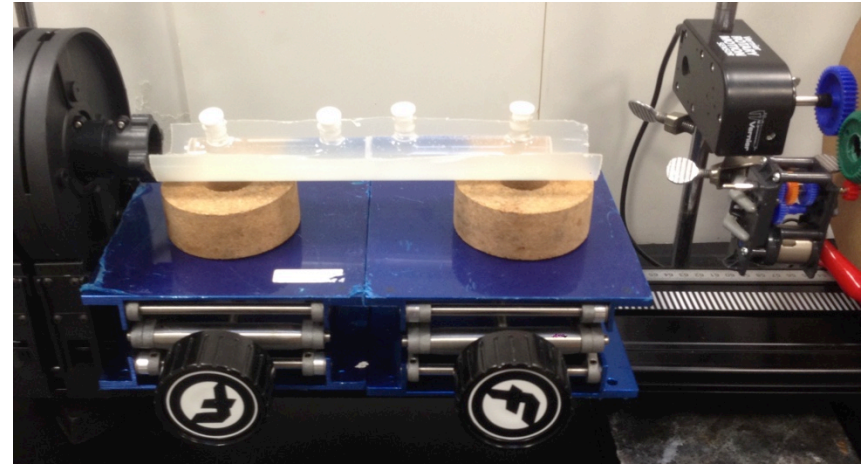
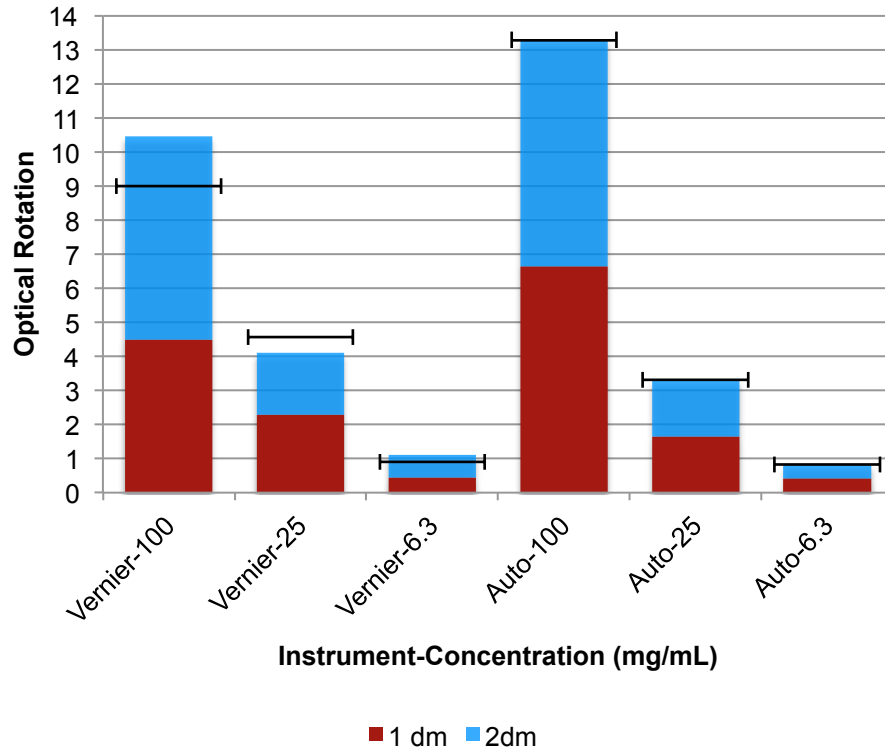
Serial Dilutions of Sucrose at Low Concentration



- Autopol III precision $\pm 0.002^\circ$
- Cannot measure optical rotations for sucrose at concentrations below 6 mg/mL
- Cannot distinguish measurement from noise below this threshold
- threshold could be lowered by increasing pathlength

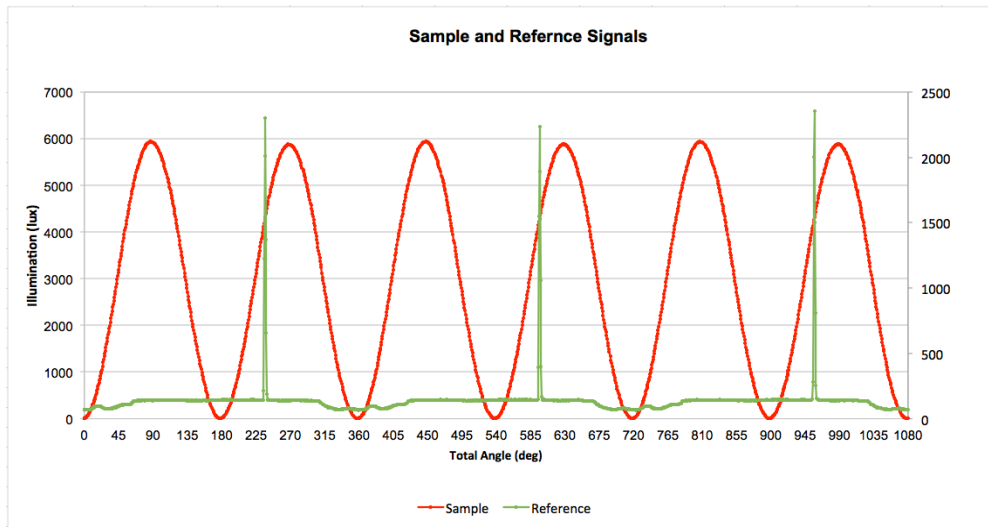
Dilution Factor	Conc. (mg/mL)	Conc. STDEV	Percent Error
1	100	± 5.6	5.6%
4	25	± 5.6	22%
16	6.25	± 5.6	89%

Increasing Pathlength

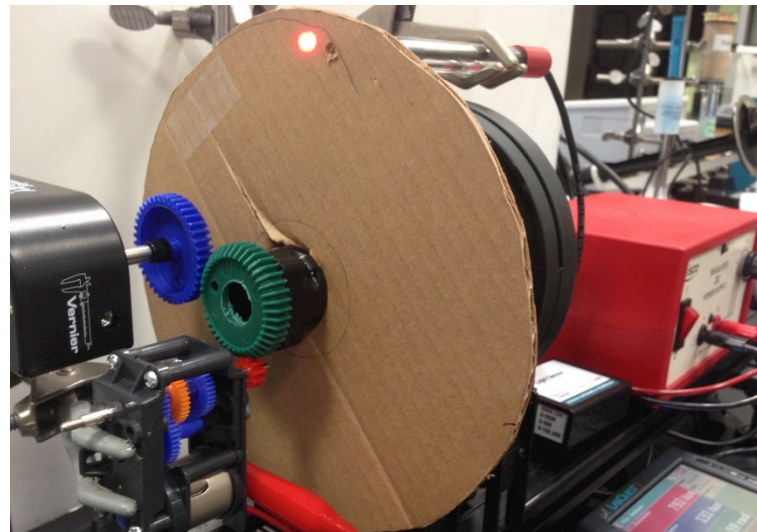


- pathlength and optical rotation are directly proportional
- could add more sample tubes with a longer track (2 m available)

A New Way to Reference the Sample



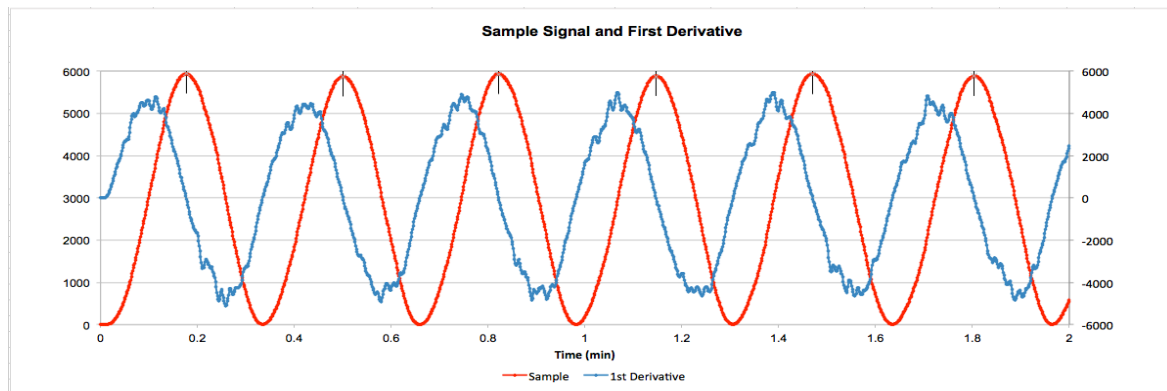
- could we measure the distance from reference spike to nearest sample peak
- how to accurately pick tops of peaks?
- sign of a derivative changes at peak; where is crosses zero?



- circular disc was attached to rotating analyzer arm with a hole
- laser widened with convex lens
- second light detector connected behind disc

Using Excel as Spectroscopic Software

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF
1	Detection Limits: Reference				Detection Limits: Sample				Change the smooth width by changing these 17 coefficients in row 5, columns J through Z.																							
2	Amplitude threshold		100	Amplitude threshold		3000	-8 -7 -6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6 7 8																									
3	Slope threshold		200	Slope threshold		20	0 0 0 0 0 -4 -3 -2 -1 0 1 2 3 4 0 0 0 0 0																									
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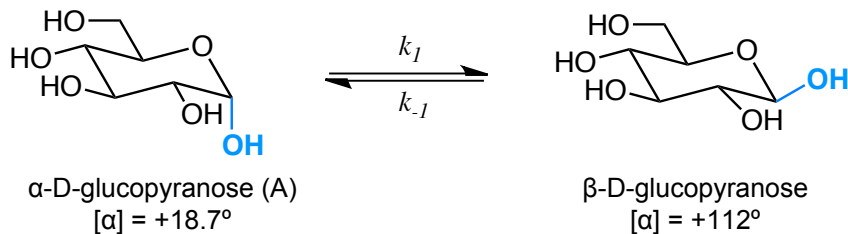


Features:

- Determines first derivative of sample and reference signals
- Derivative smoothing reduces noisy signal
- Amplitude and slope thresholds evaluated
- when all criteria are met, a peak is picked at downward heading derivative crossing zero

Why?

We can then measure optical rotation over time without manually collecting and recording numerous samples. We can then investigate kinetics of processes such as mutarotation.

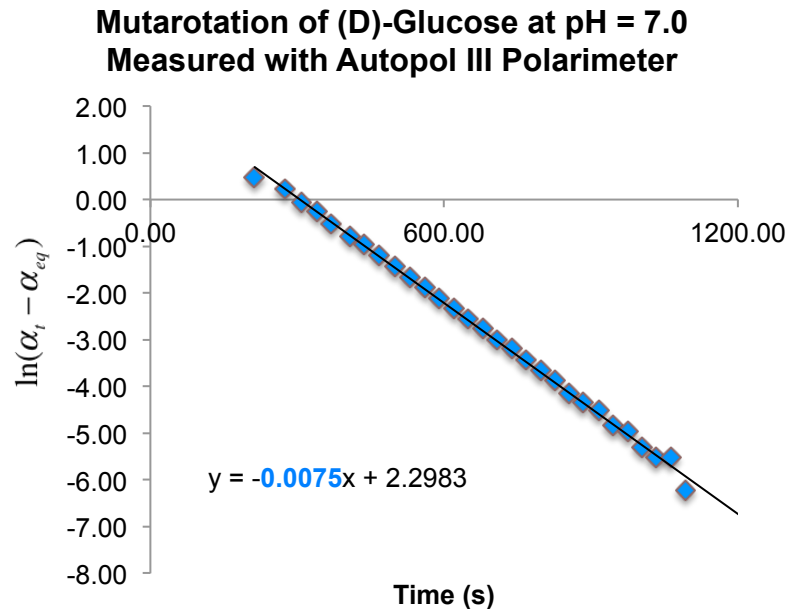


Integrated 1st Order Rate Law

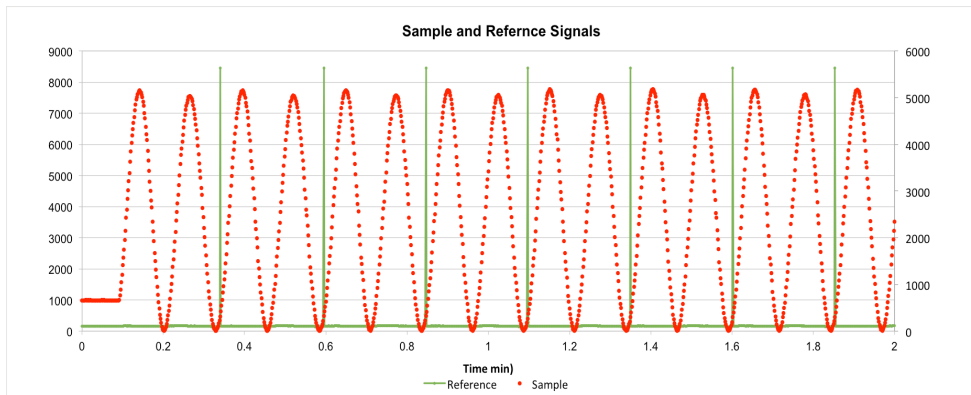
$$\ln[A] = -kt + \ln[A]_0$$

and since concentration is directly
proportional to optical rotation

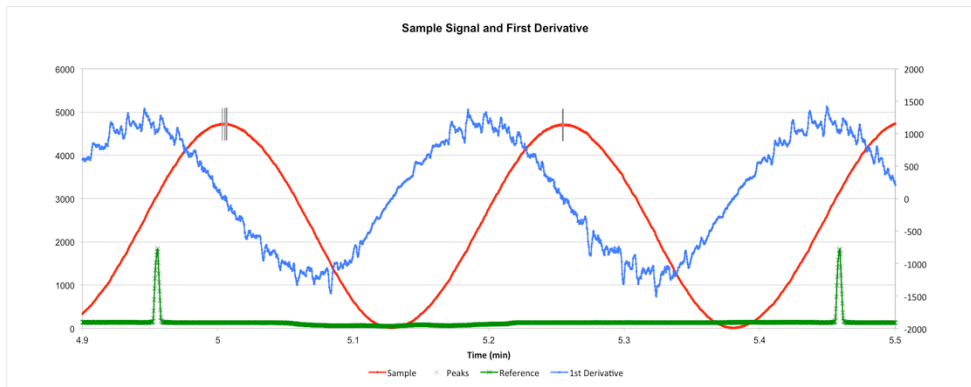
$$\ln(\alpha_t - \alpha_{eq}) = -kt + \ln(\alpha_0 - \alpha_{eq})$$



Roadblock

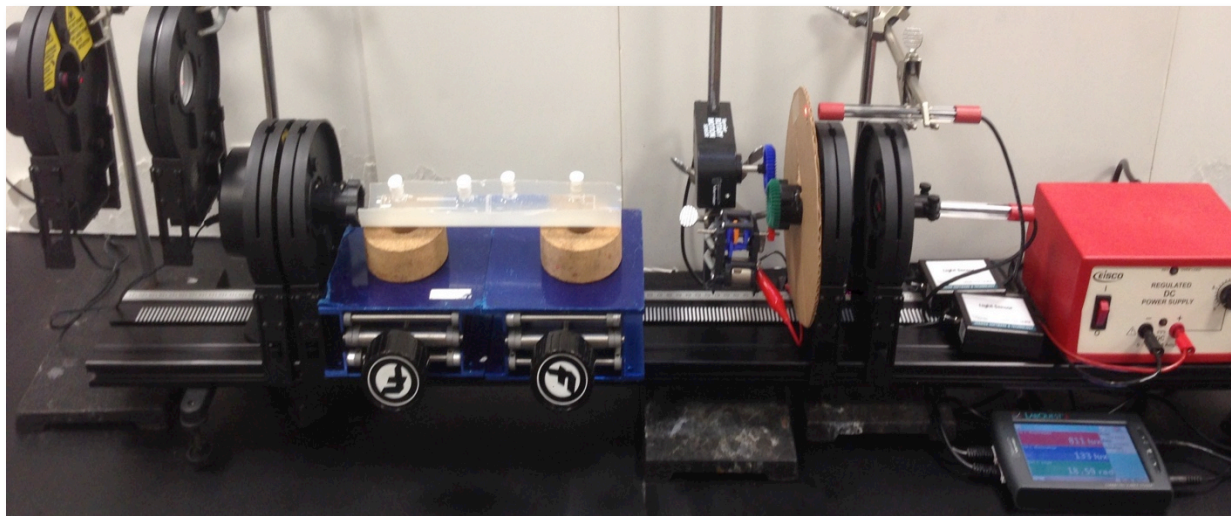


- 600 samples/min for 10 min at 2 rev/min
- consistent peak picking
- Precision: $\sigma = 0.40^\circ$
- **Seems low, but leads to large percent error if $\Delta\alpha \sim 1.5^\circ$**
- cause due to low sampling rate which gives **1.2 %/sample**



- 3000 samples/min for 10 min at 2 rev/min = **0.25 %/sample**
- difficulty finding peak maximum
- low precision; **s = 1.29°**
- our Excel file has difficulty handling >30,000 rows of data
- **our computer or the software?**

Thank You



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