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CEE 772: Instrumental Methods in Environmental Analysis

Lecture #3

Statistics: Detection Limits

Spectroscopy: Beer's Law & Electronic Transitions

(Skoog, Chapt. 6 & 13)

(pp.116-120, 134-140, 300-312)

(Harris, Chapt. 1)
(pp.1-20)

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Errors: Random or Indeterminate

- Causes of "Noise"
- Result of a large number of small errors which cannot be easily isolated from each other
- They occur over short time scales and may be nearly random
- Can use classical statistics with these, because of their nearly-independent and random nature

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Errors: Systematic or Determinant

- Instrumental Errors
 - Corrected by calibration
 - Changes in line voltage
 - Increases in resistances due to oxidation of electrical contacts
 - Changes in temperature
 - Vibration of optical elements
 - Induced currents from nearby power lines

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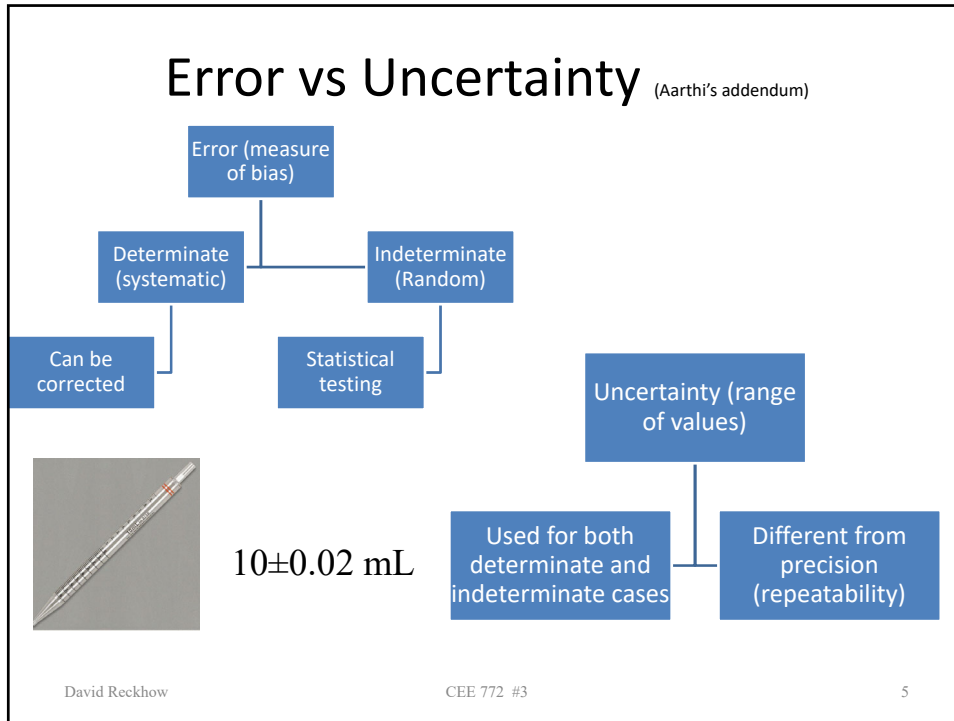
Errors: Systematic or Determinant

- Method Errors
 - Non-ideal chemical & physical behavior
 - Some may also be accounted for by calibration, standard addition, etc.
 - Incomplete reactions
 - Unwanted side reactions (interferences)
 - Contamination of reagents
- Personal errors
 - Lack of concentration on the part of the analyst
 - Sometimes creates outliers
 - Mis-reading instrument or apparatus
 - Transposing numbers, error in calculations
 - Addition of incorrect volume

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Detection Limit, Sensitivity & Resolution

- Detection Limit
 - The minimum concentration (or weight) of analyte that can be detected at a known confidence level
 - Minimum distinguishable signal (S_m)

$$S_m = \bar{S}_{b1} + k(SD_{b1})$$

Mean blank signal $\rightarrow \bar{S}_{b1}$ $\rightarrow k(SD_{b1})$ s.d. of blank signal

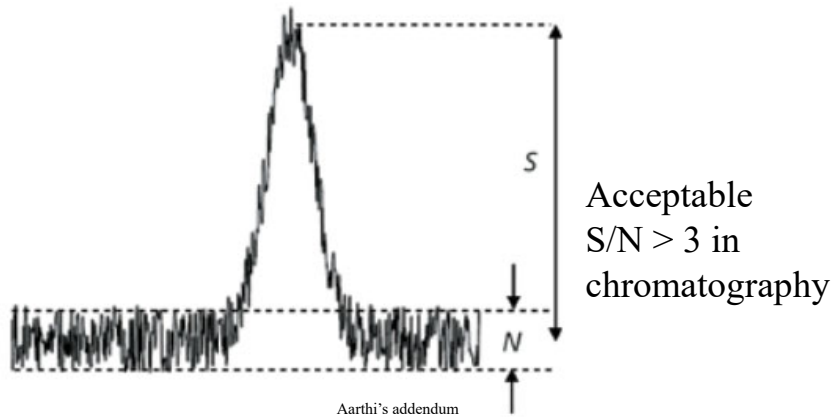
- Often, $k=3$ for 95% confidence interval (non-gaussian)
- Detection limit (C_m)

$$C_m = \frac{S_m - \bar{S}_{b1}}{m}$$

\leftarrow Slope of standard curve

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Detection Limit, Sensitivity & Resolution



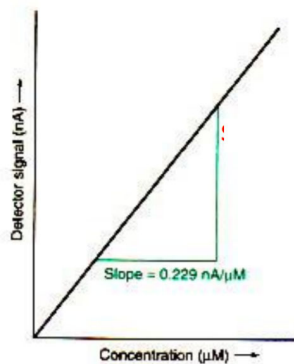
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Detection Limit, Sensitivity & Resolution

• Sensitivity



Ability to distinguish small differences in concentration

- Calibration Sensitivity: slope of a calibration curve at the concentration of interest
- Analytical Sensitivity: response to noise ratio (change in detector signal)

$$\gamma = \frac{m}{s_s}$$

slope \rightarrow m \leftarrow s.d. of signal s_s

<https://www2.chemistry.msu.edu/courses/cem434/Lecture%202.pdf>

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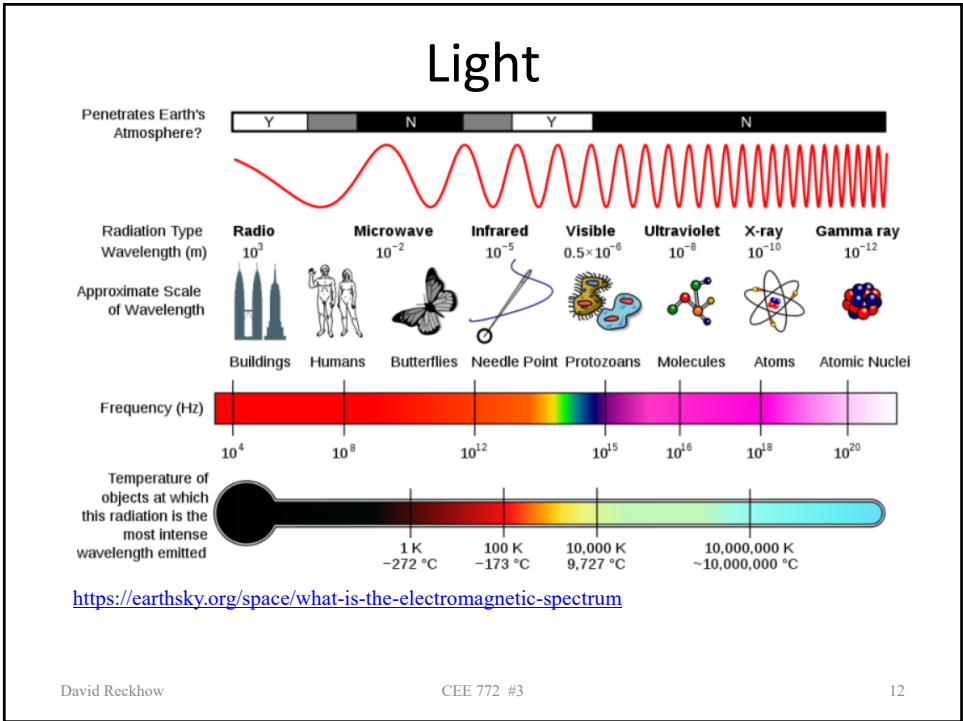
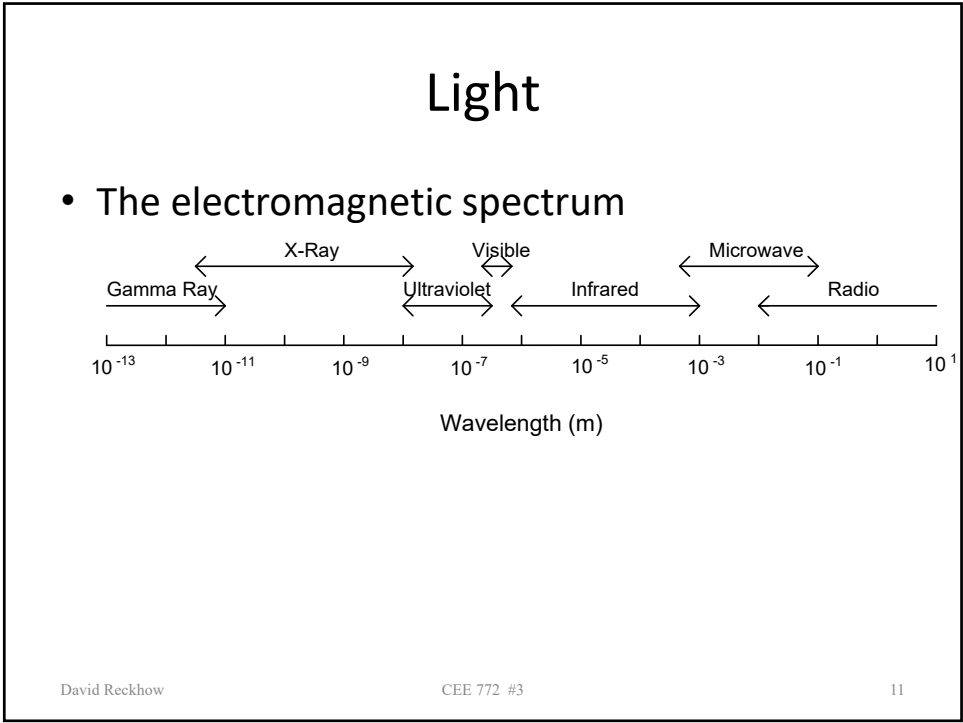
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Detection Limit, Sensitivity & Resolution

- Resolution (Arthi's addendum)
 - Closeness to true value; closer the value better the resolution
 - smallest unit of measurement that can be indicated by an instrument.
 - Different for different instruments
- Sensitivity** is the smallest amount of **difference** in quantity that will change an instrument's reading.

Topics Covered

- Beer's Law
- Spectra
- Structure and Absorbance
- Standard Curves



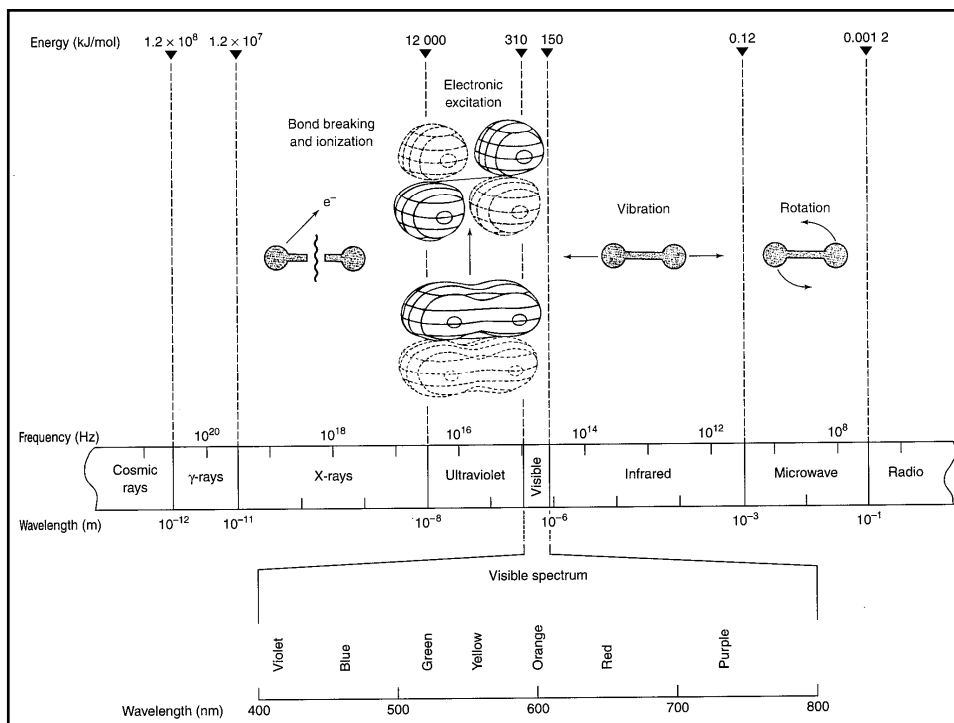
Light

$C = \lambda U$
 $C = \text{speed of light} = 3 \times 10^8 \text{ m/s}$

$E = h \lambda$
 $h = \text{Planck's constant} = 6.62607004 \times 10^{-34} \text{ m}^2 \text{ kg / s}$

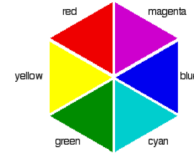
The diagram shows two waveforms. The top waveform is labeled 'High frequency' and has a 'short wavelength' indicated by a double-headed arrow between two peaks. The bottom waveform is labeled 'Low frequency' and has a 'long wavelength' indicated by a double-headed arrow between two peaks.

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Wavelength and Color

Also called “complementary color”



Wavelength of absorbance maximum (nm)	Color Absorbed	Color Remaining
380-420	Violet	Green-yellow
420-440	Violet-blue	Yellow
440-470	Blue	Orange
470-500	Blue-green	Red
500-520	Green	Purple
520-550	Yellow-green	Violet
550-580	Yellow	Violet-blue
580-620	Orange	Blue
620-680	Red	Blue-green
680-780	Purple	Green

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Transmittance

- Beer/Lambert's Law

$$I = I_0 e^{-\gamma x}$$

- Sum of scattering cross section and absorption coefficient

$$\gamma = \tau + \kappa$$

- Absorption coefficient

$$\kappa = \frac{ac}{2.303}$$

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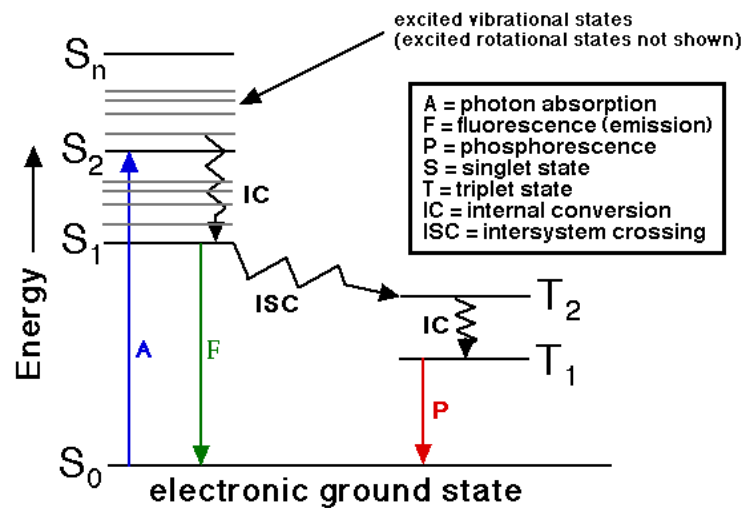
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Absorbance

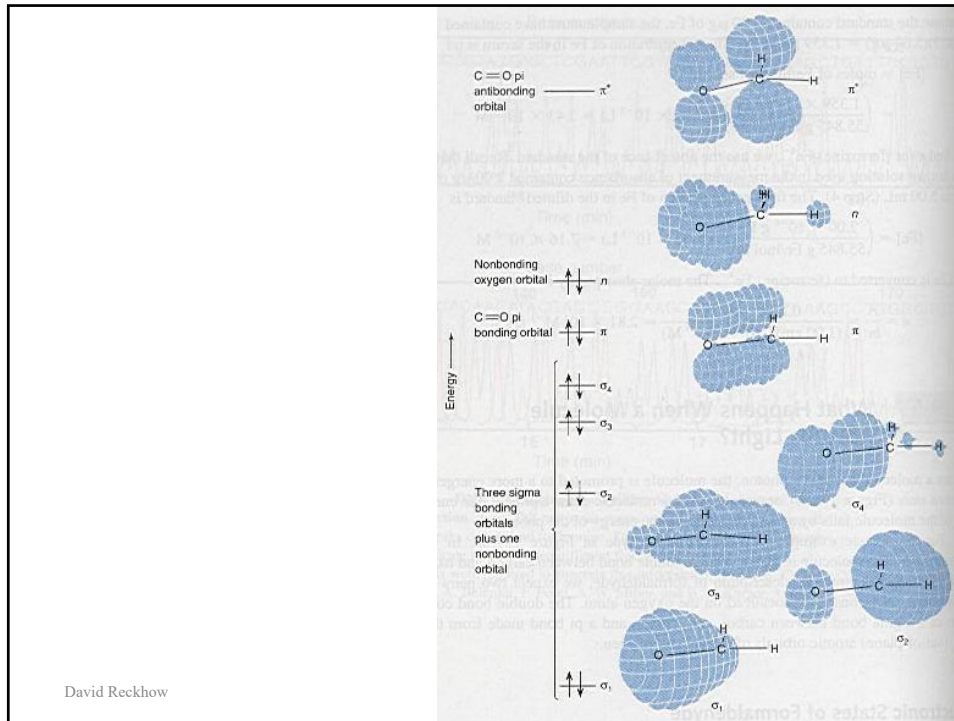
- Transmittance
- Absorbance
 - $A = -\log(T)$
 - $A = acx$
- Absorptivity
 - a : absorbance per mg/L concentration
 - ϵ : absorbance for 1 mole/L concentration
 - Molar absorptivity ($L\ cm^{-1}\ mol^{-1}$)

$$T \equiv \frac{I}{I_0} = e^{-acx/2.303}$$

Energy Absorption & Bonding



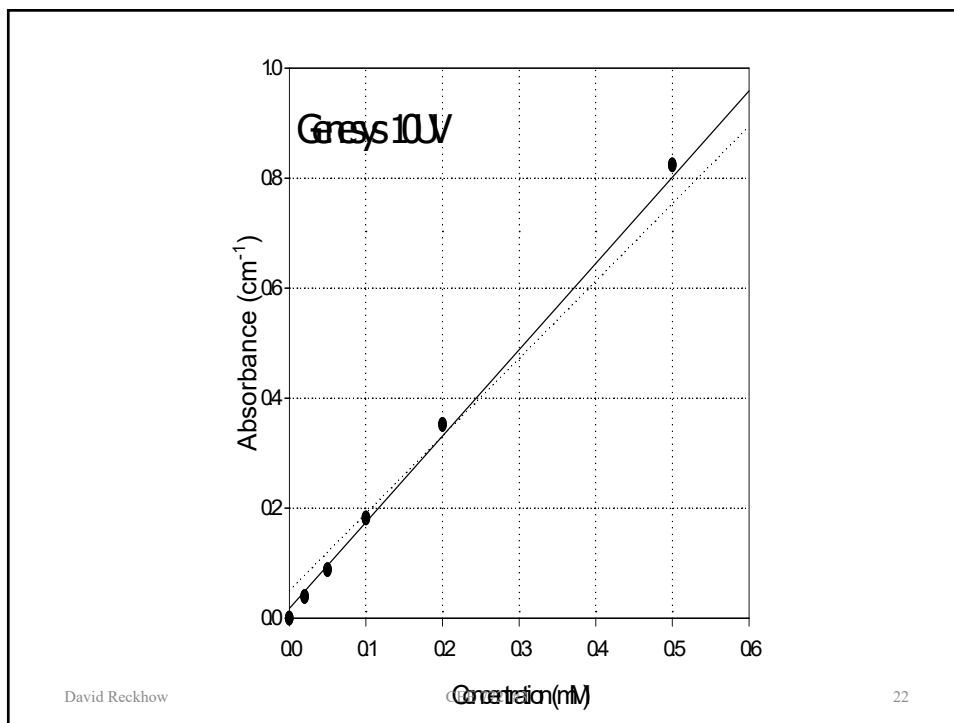
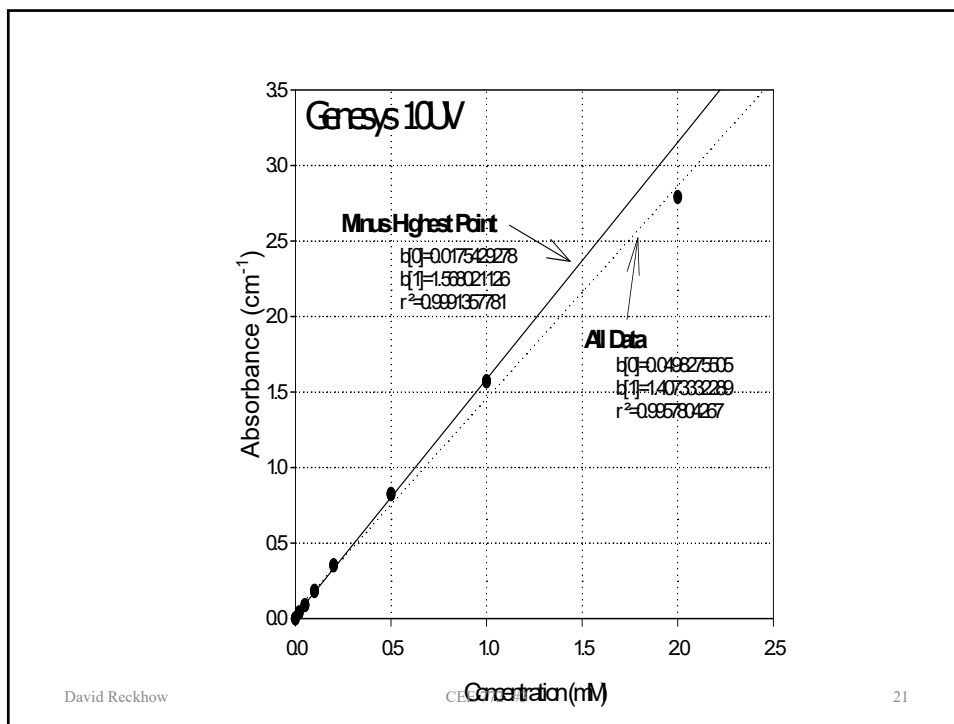
Partial energy diagram in a photoluminescence system

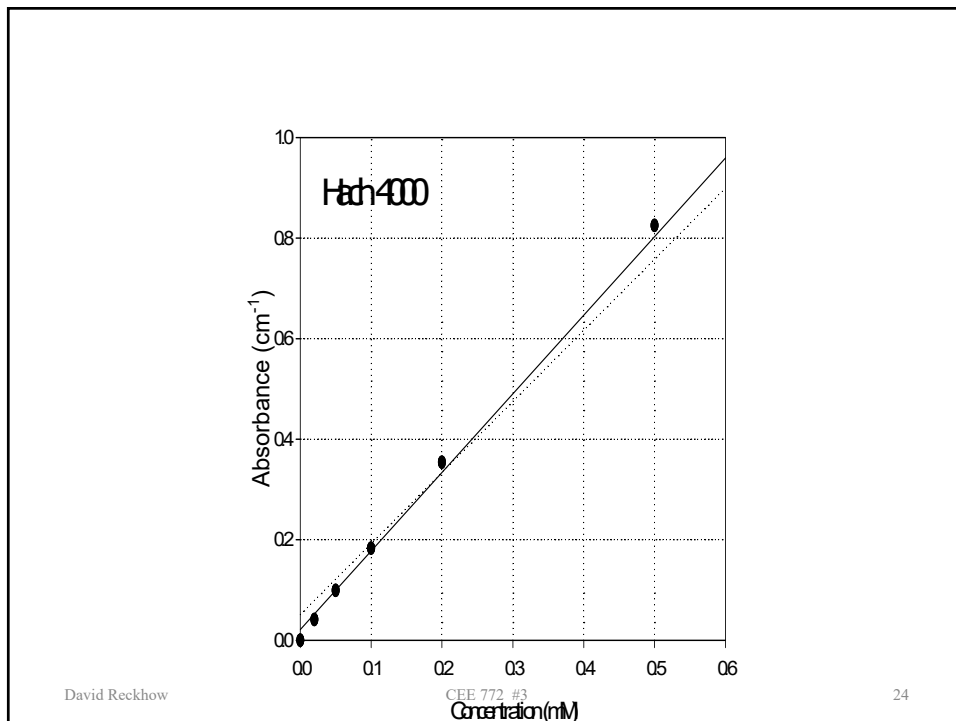
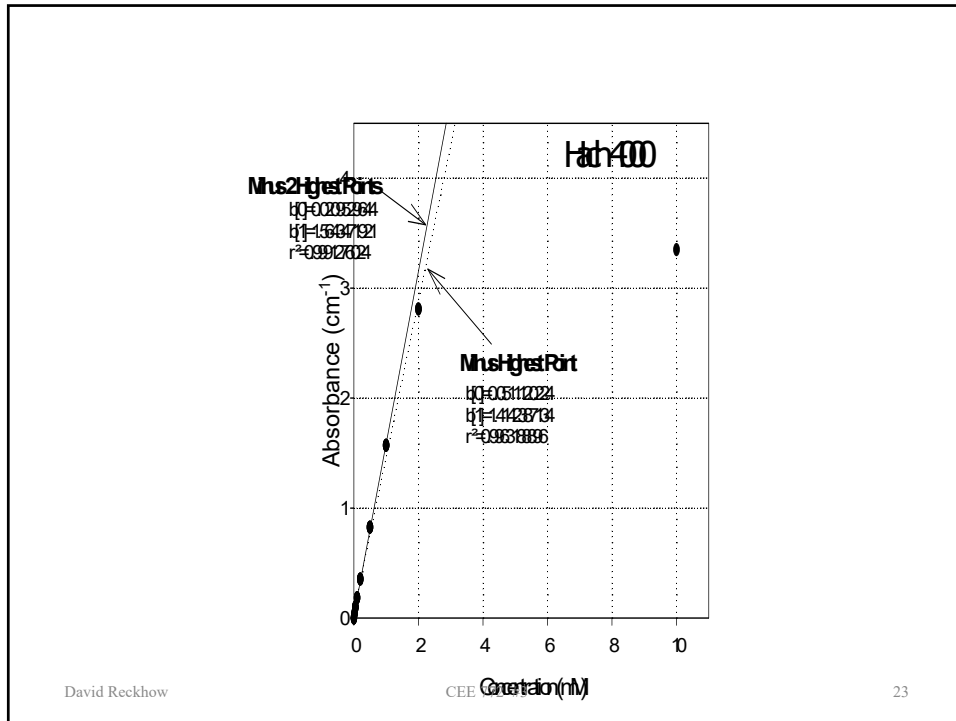


EVE Spectrophotometers

Characteristic	Bausch & Lomb to Milton Roy to:			ThermoSpectronic; ThermoElectron		Perkin-Elmer			Hewlett-Packard	Hach
	Spec 20	Spec 21D	Spec 70	Genesis 20	Genesis 10UV	Model 111	Lambda 3A	Lambda 3B	Diode Array	DR40001
Location & condition		Marst 24	3 rd fl storage	Marston 24	304 Elab II 213 Elab II	3 rd fl storage	308 Elab II 24 Marston	24 Marston	308 Elab II	304 Elab II
Optical system	Single beam	Single beam	Single beam	Single beam	Split beam	Single beam	DoubleBeam	Double Beam	Diode Array	Single Beam
Monochromator	Grating			Grating	Grating		Holographic Grating	Holographic Grating	Holographic Concave Grtn.	Seya-Namioka split-beam
Groove Density	600/mm			1200/mm	1200/mm		1440/mm	1440/mm		1200/mm
Detector	Phototube			Solid state			Photo-multiplier	Photo-multiplier	328 Photo-diodes	
Lamp(s)	Tungsten			Tungsten	Xenon		Tungsten-Br Deuterium	Tungsten-Br Deuterium	Deuterium ^b	Tungsten, Deuterium
Readout	Analog	Digital	Analog	Digital	Digital	Analog	Digital	Digital	Digital	Digital
Cell Holder	0.5-1" tube			1 cm & tubes		multi-position	0.1-10cm	0.1-10cm	0.1-10cm	1-10 cm
Wavelength Range	340-625 nm ^a	Vis	Vis	325-1100nm	190-1100nm	UV/Vis	190-900 nm	190-900nm	190-820nm	190-1100nm
Wavelength Accuracy	2.5 nm			2.0 nm	1 nm		0.5 nm	0.3 nm	2 nm	1 nm
Wavelength Precision	1.0 nm			0.5 nm	0.5 nm		0.2 nm	0.1 nm	0.05 nm	0.1 nm
Effective Bandwidth	20 nm			8 nm	5 nm		<2 nm	1 nm	2 nm	4 nm
Photometric Accuracy	2.5 %T			0.003 A; 1% (0.3A up)	0.5% T		0.3 %T ^d , 0.005 A	0.3 %T ^d , 0.005 A	0.3 %T ^d , 0.005 A	
Photometric Precision	1 %T						0.15 %T ^d , 0.002 A	0.15 %T ^d , 0.002 A		0.001 A
Stray Light	< 0.5% ^a			<0.1%T	<0.1%T		<0.05%	<0.02%	<0.05%	<0.05%T
Baseline Flatness							0.005 A	0.002 A	0.001 A	
Noise				<0.002 A	<0.002 A		<0.0003 A	<0.0003 A	<0.0002 A	
Zero Abs Stability				<0.003A/hr	<0.001A/hr		<0.0005A/hr	<0.0005A/hr	<0.001A/hr	

1 Green=good operating condition; blue=some operational problems; red=currenty not operating





Functional Groups

Compound Type	Formula	Example	λ_{\max} (nm)
Alkene	$\text{RCH}=\text{CHR}'$	Ethylene	193
Alkyne	$\text{RC}\equiv\text{CR}'$	Acetylene	173
Ketone	$\text{RR}'\text{C}=\text{O}$	Acetone	271
Aldehyde	$\text{RHC}=\text{O}$	Acetaldehyde	293
Carboxyl	RCOOH	Acetic Acid	208
Nitrile	$\text{RC}\equiv\text{N}$	Acetonitrile	<160
Nitro	RNO_2	Nitromethane	271
Amide	RCONH_2	Acetamide	208

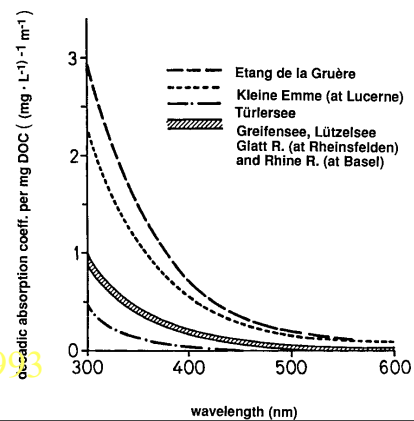
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Background NOM

- Specific Absorbance of water samples from several Swiss lakes and rivers

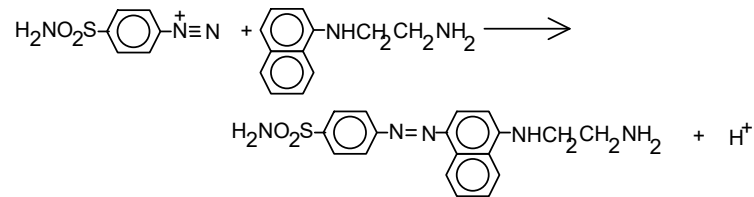
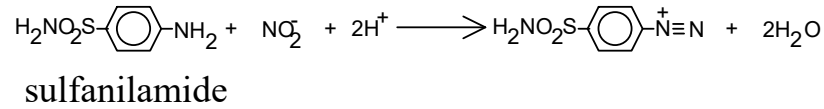


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Nitrite method

- diazotization



Aromatic amine to diazonium salt.

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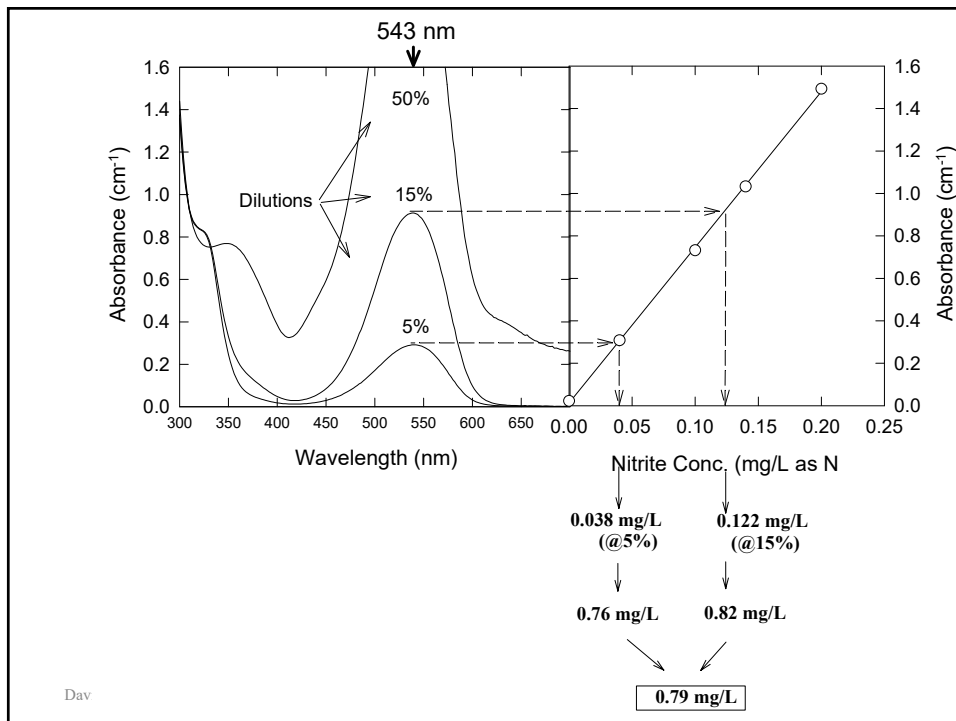
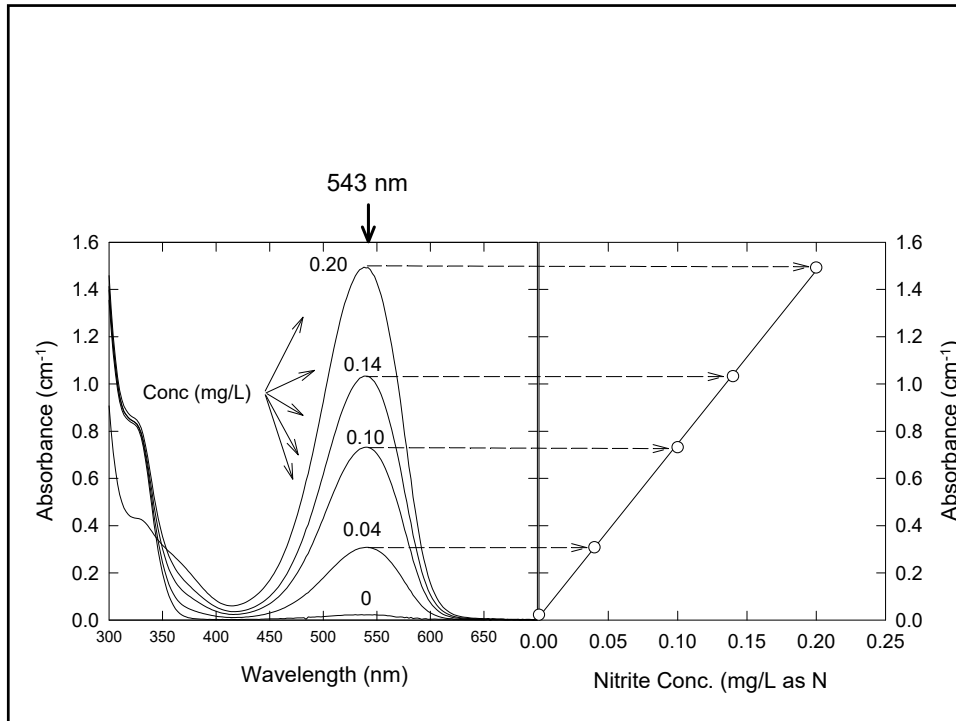
Nitrite method

- The $\text{NO}_2\text{-N}$ is measured colorimetrically following reaction with a diazotizing reagent (sulfanilamide) and a coupling reagent [N-(1-naphthyl)-ethylenediamine dihydrochloride]. A pinkish-purple color develops that is then measured between the wavelengths of 510 and 550 nm; maximum sensitivity is approximately 540 nm (Keeney and Nelson, 1982).

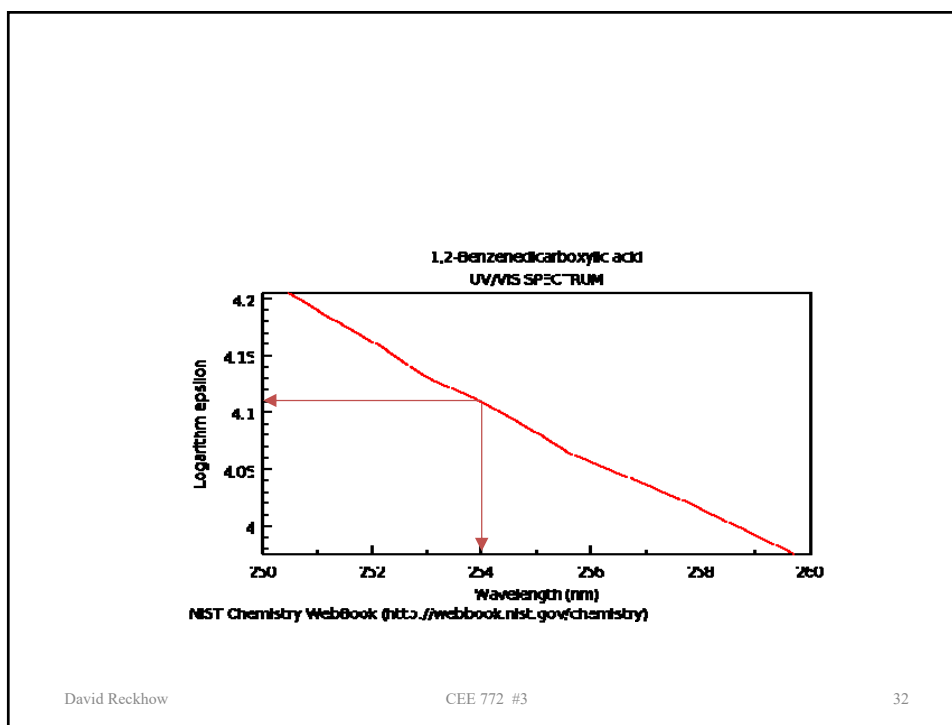
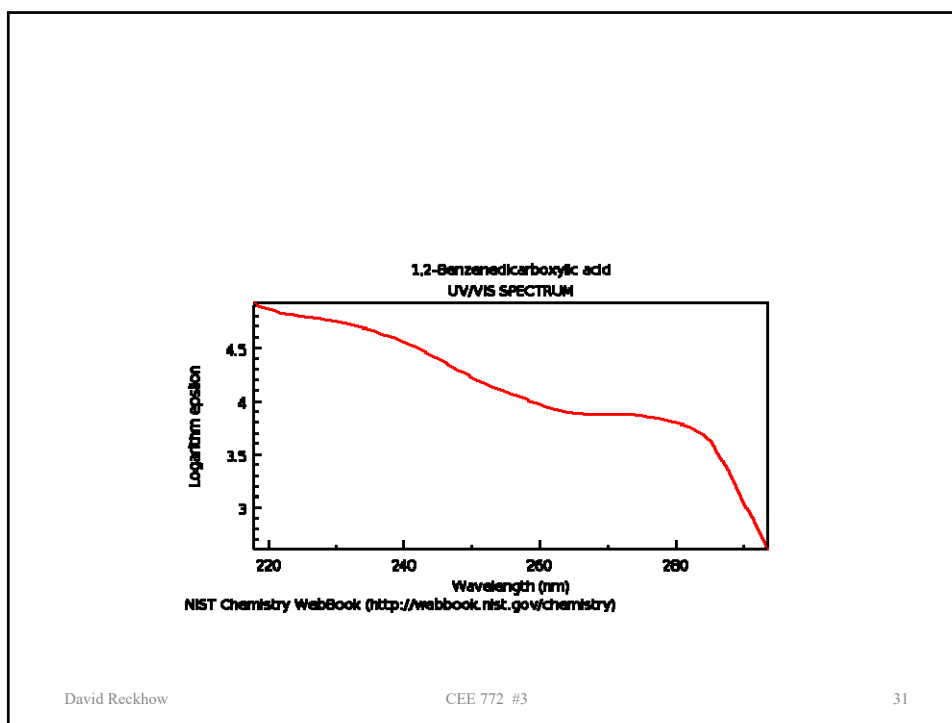
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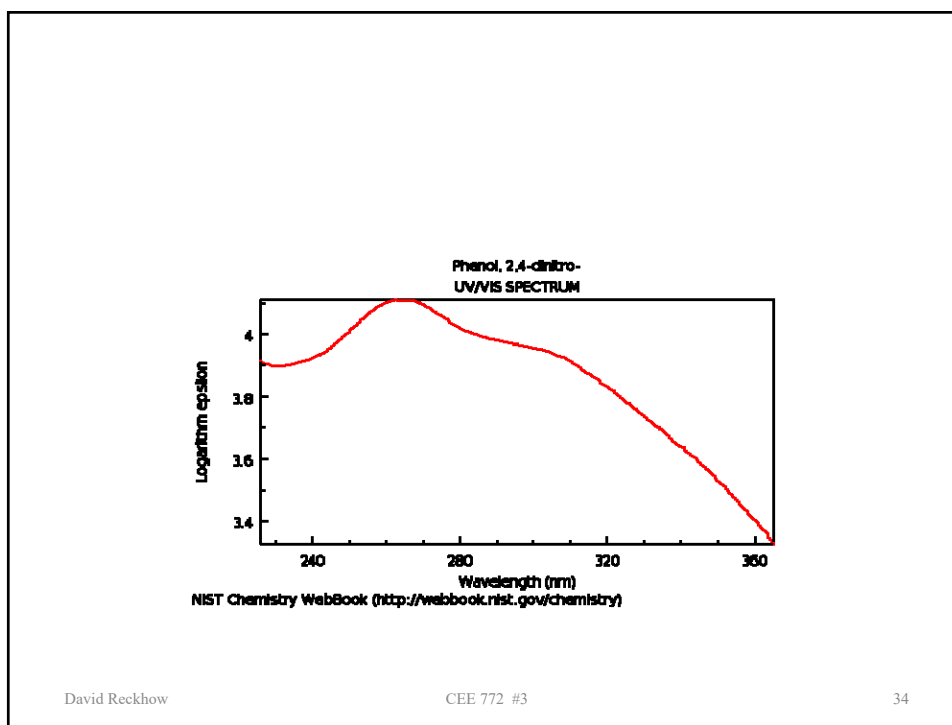
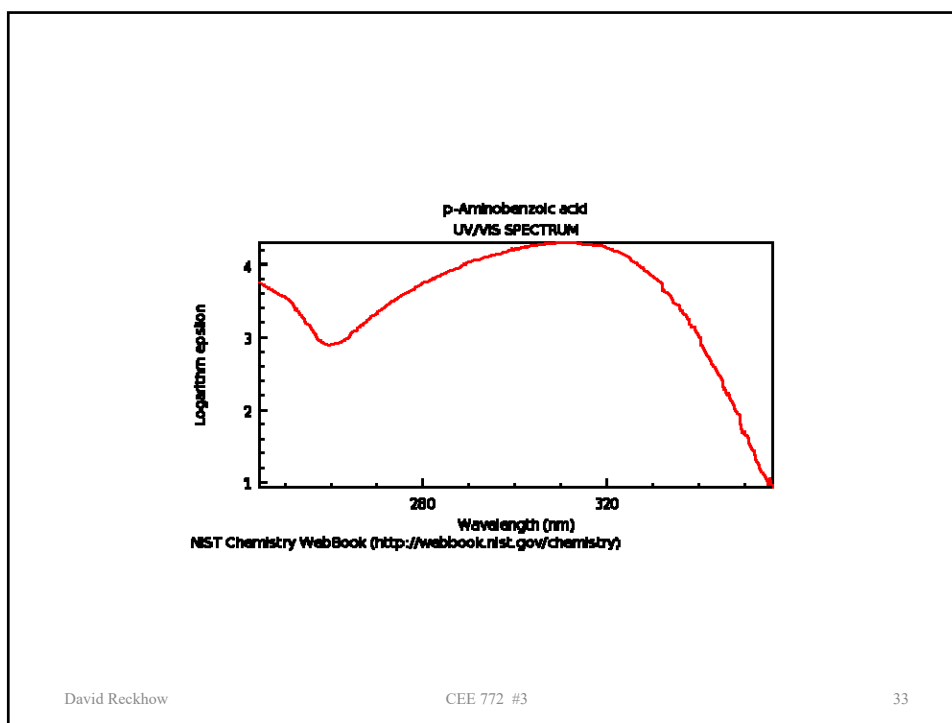
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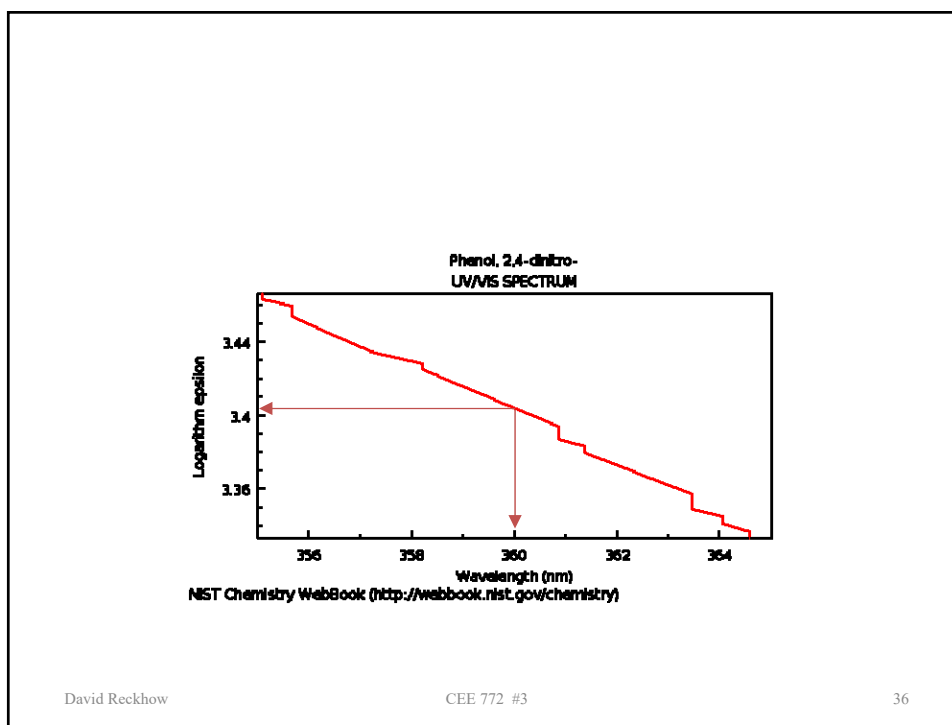
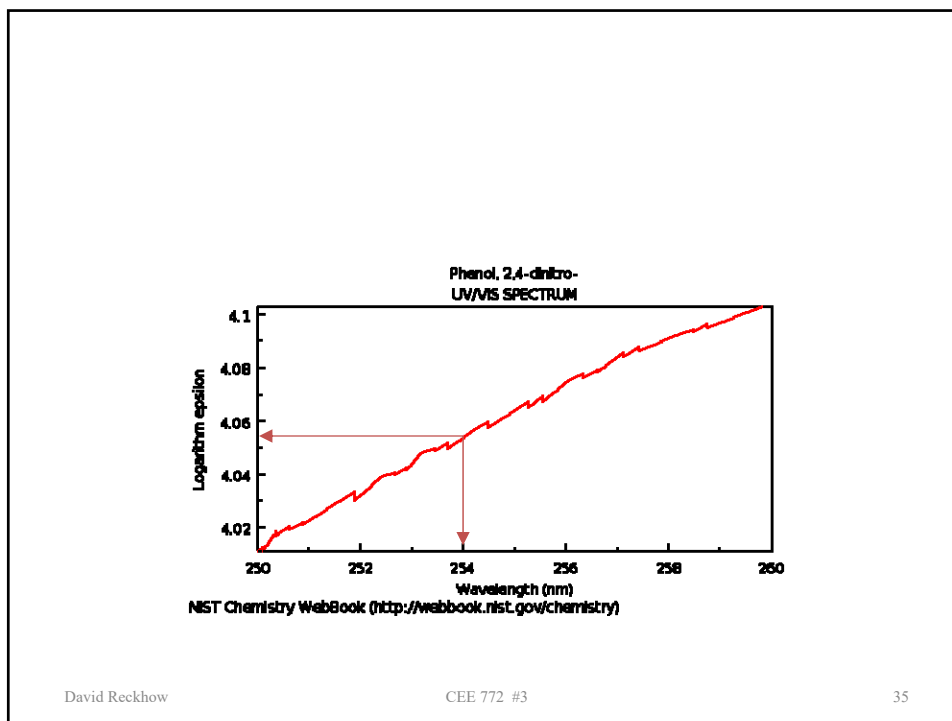
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