

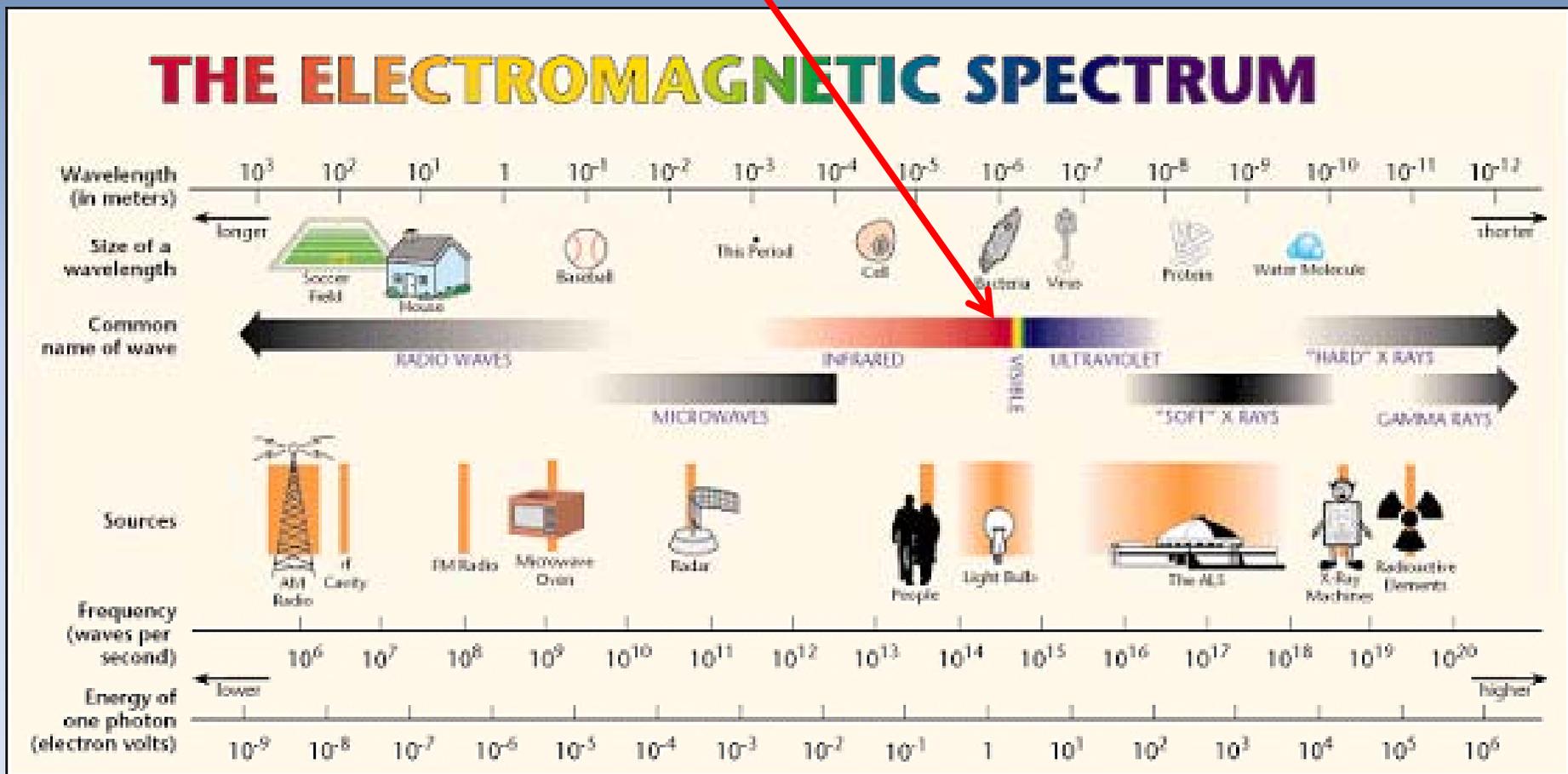
Thirty-Five Years and
Counting – Near-IR
Spectroscopy in
Wheat Quality
Analysis – What We
do Well and What
We'd Like to Do



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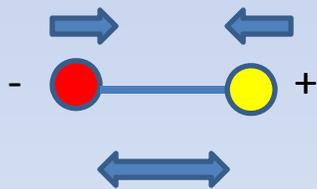
Near-Infrared Region (750-2500 nm)



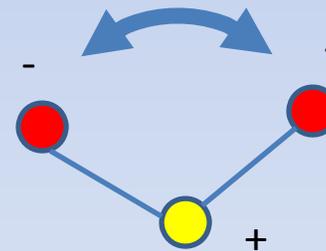
(source: <http://www.safetycenter.navy.mil>)

Common Absorption Bands

- C-H
- N-H
- O-H

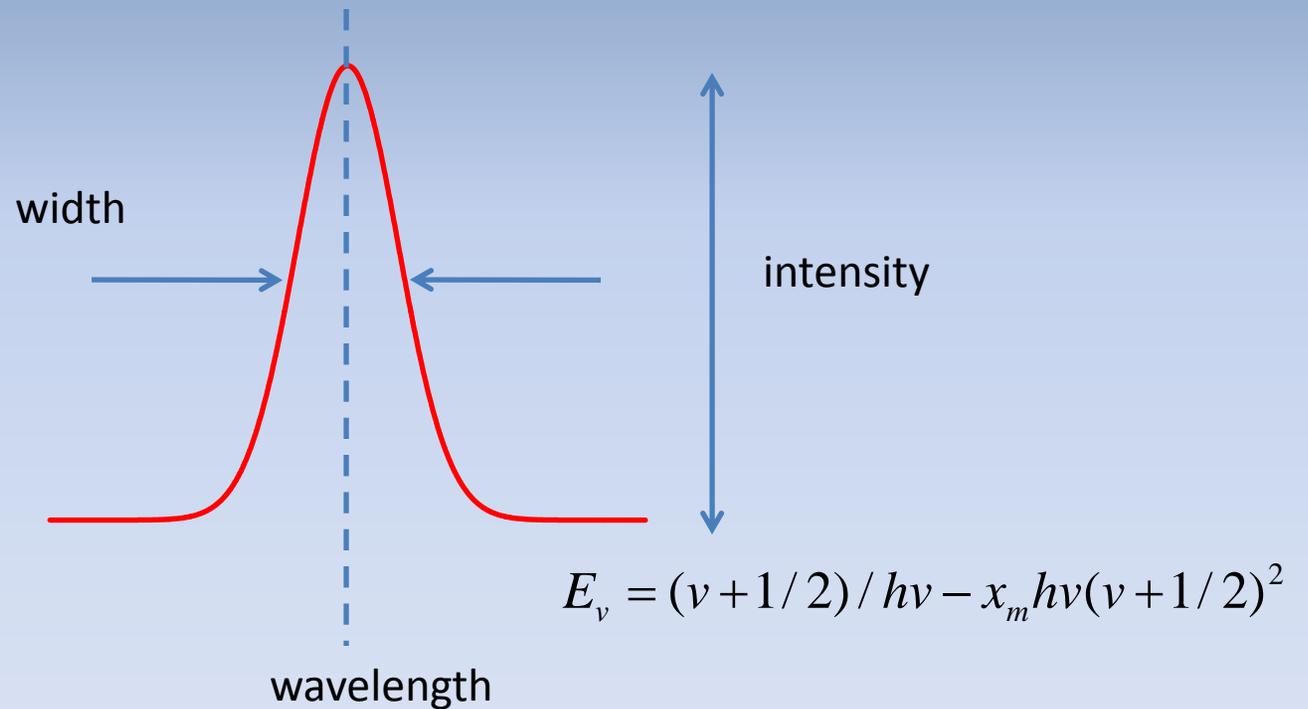


stretching



bending

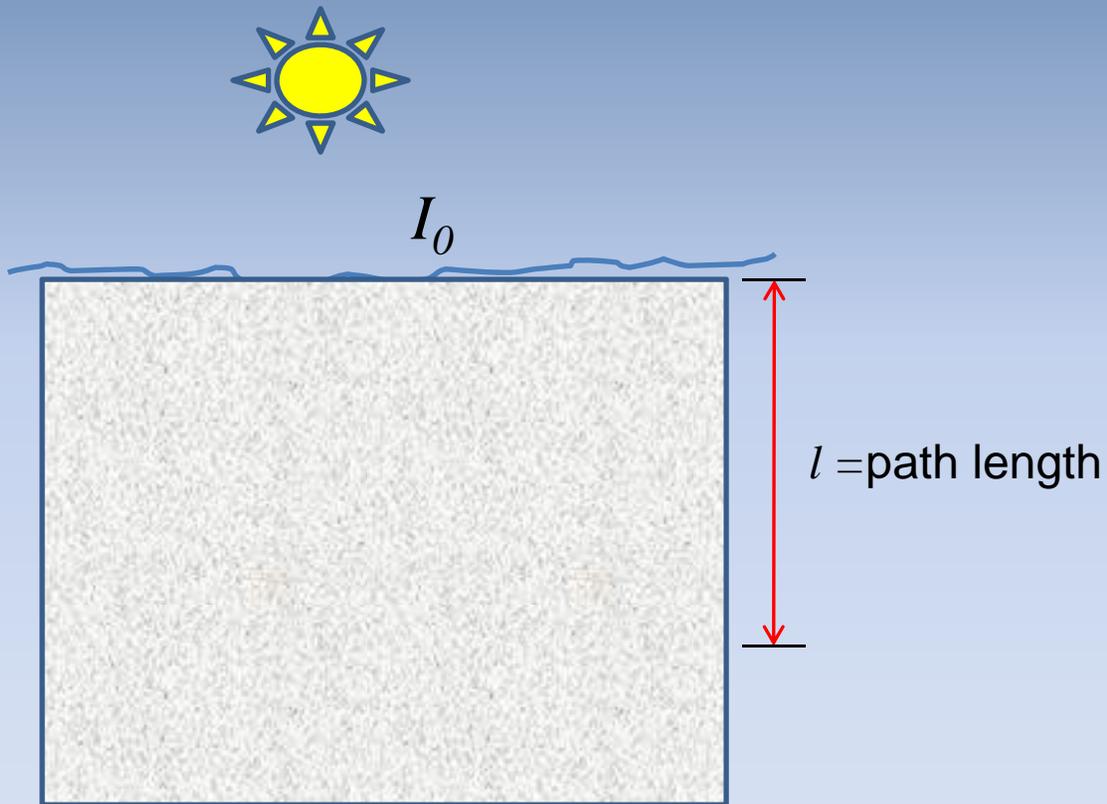
NIR absorption Band



Special Properties of Inter-atomic Bonds that Lead to the NIR Practicality

- Bonds involving hydrogen vibrate independently of other bonds within the molecule due to hydrogen's low mass.
- Adjacent bonds possessing similar strengths and reduced masses produced coupled responses.

Beer Lambert Law

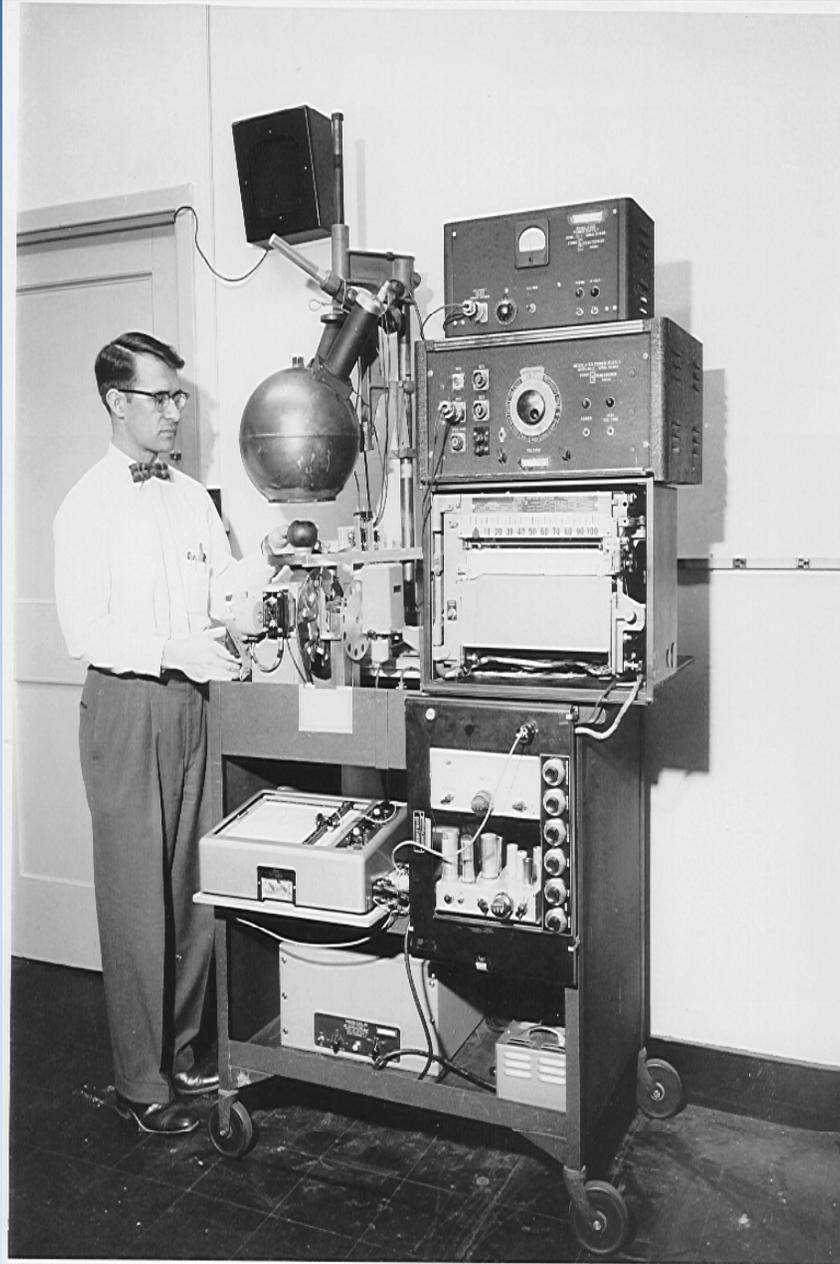


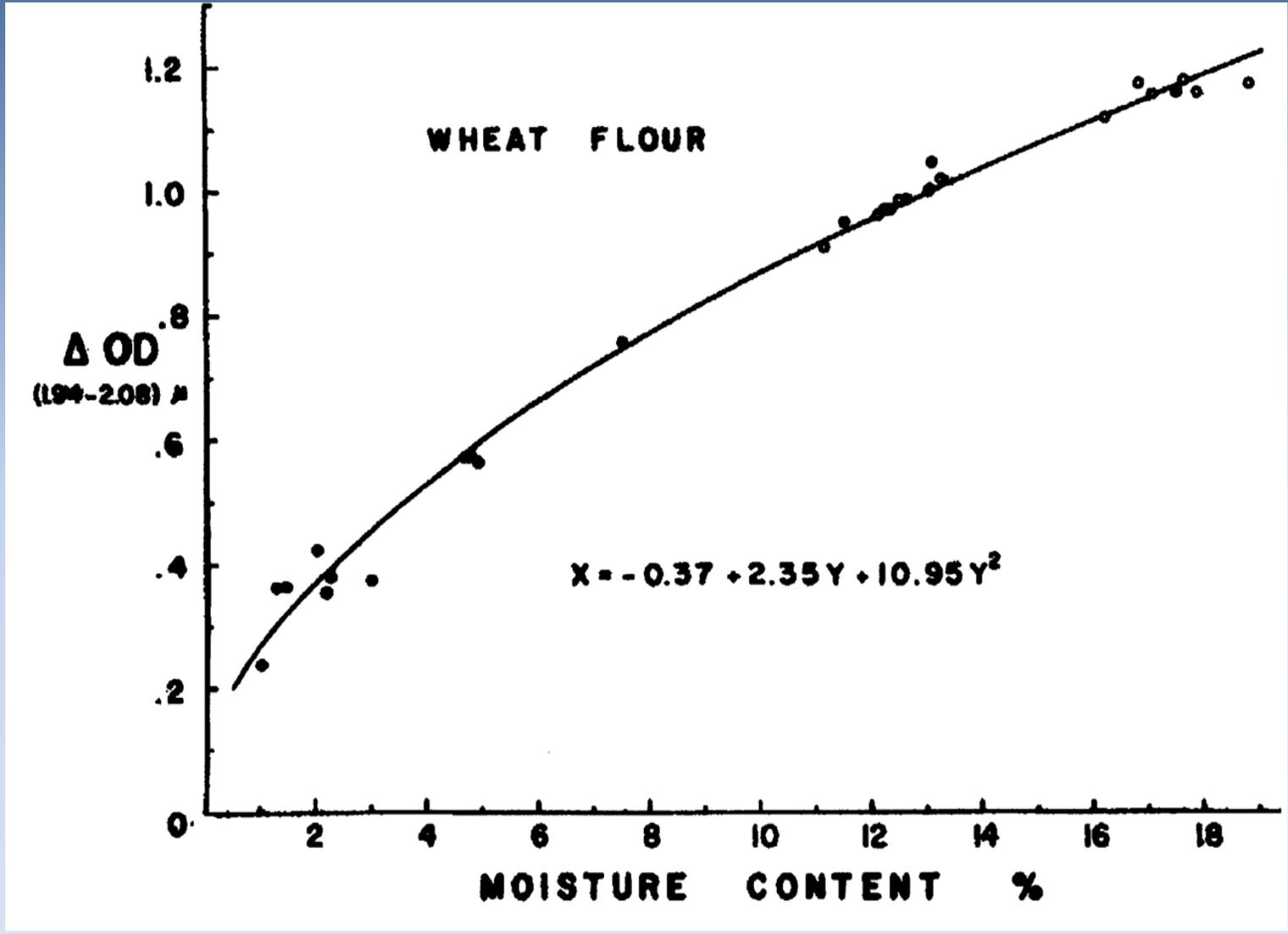
$$I = I_0 10^{-\epsilon Cl}$$

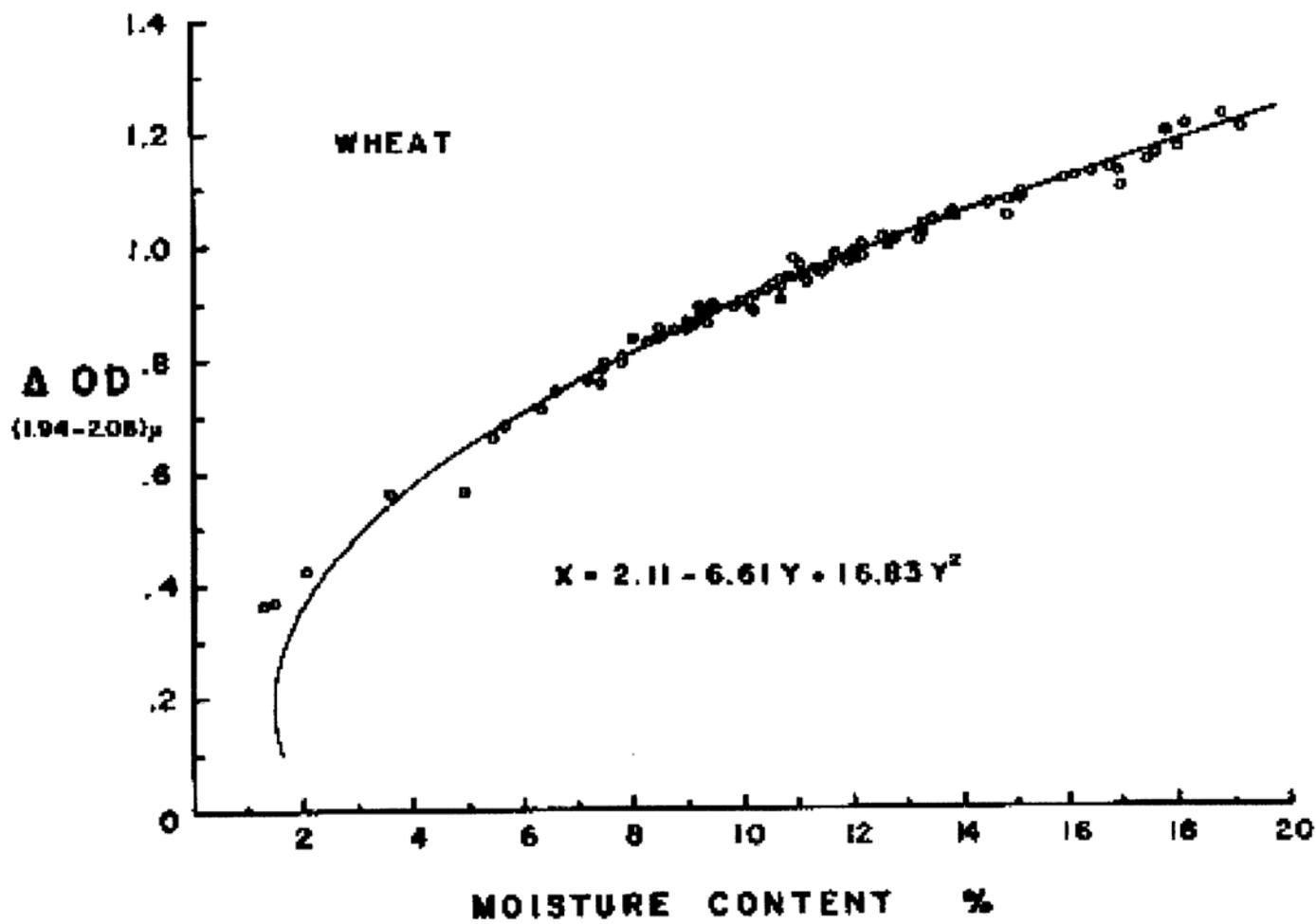
$$\frac{I}{I_0} = T = 10^{-\epsilon Cl}$$

$$\log\left(\frac{1}{T}\right) = A = \epsilon Cl$$

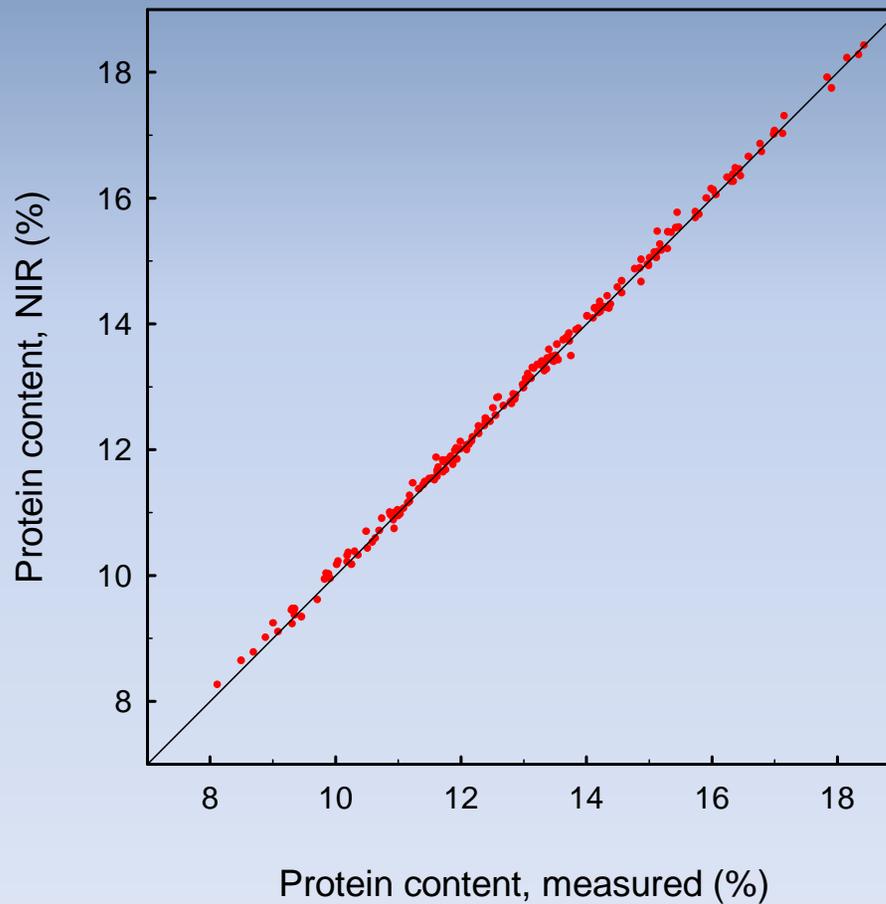
C = concentration
 ϵ = absorptivity







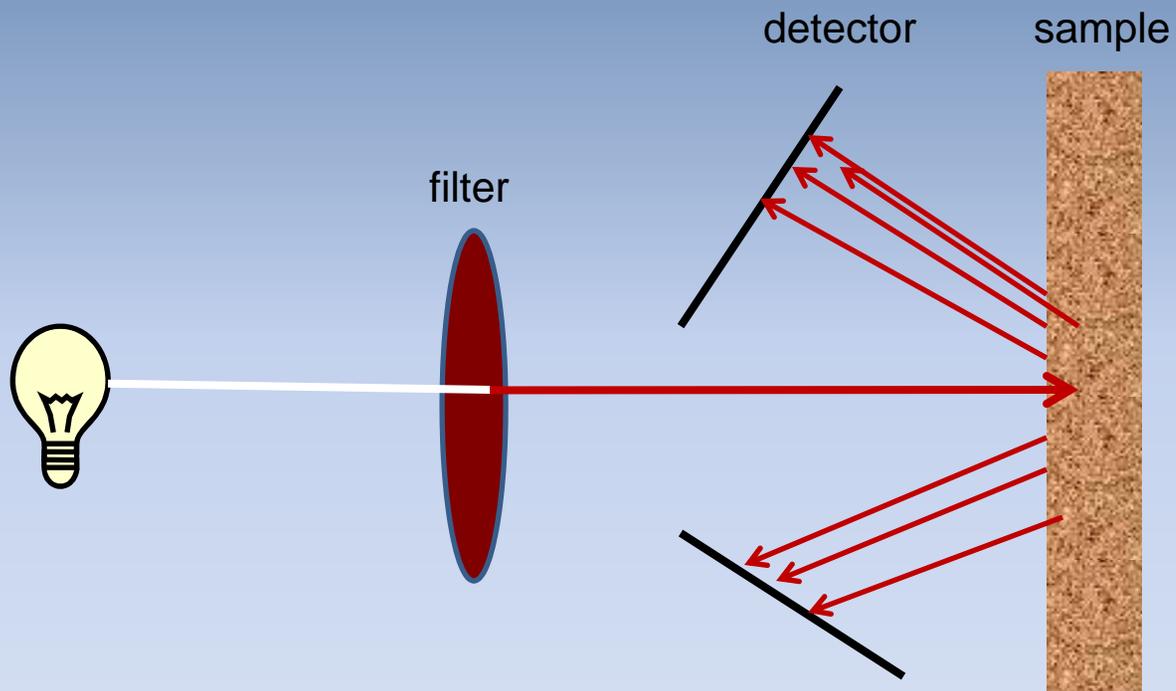
Success Story – Protein Content



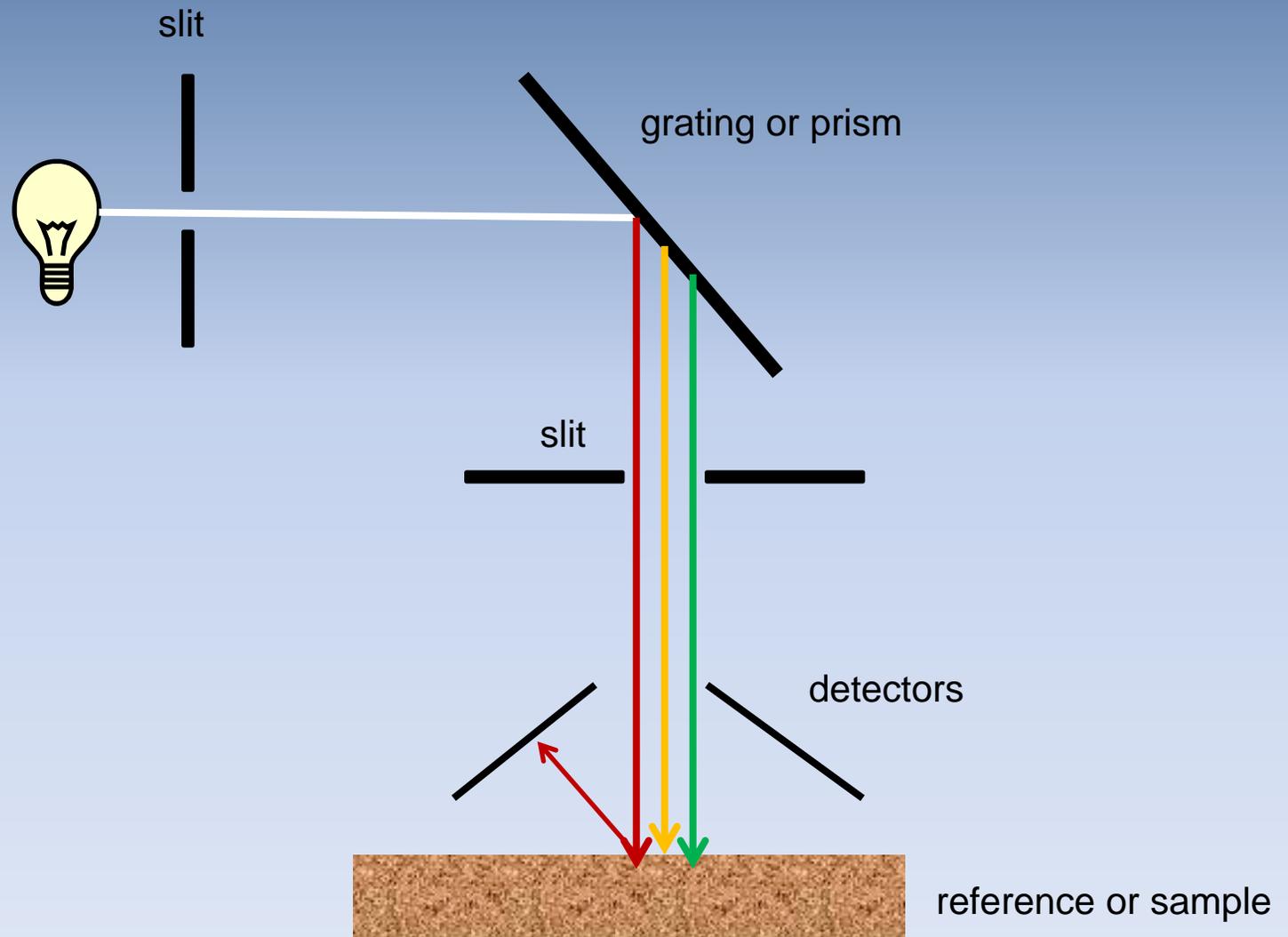
Instrument Types

- Interference Filter (3 to 20+) – simple, inexpensive
- Diode array – fast, but higher in noise
- Scanning monochromator (dispersive) – Very low noise, more expensive, slower, good for course material
- Fourier Transform (interferometer) – High wavelength accuracy, sharper bandpass)

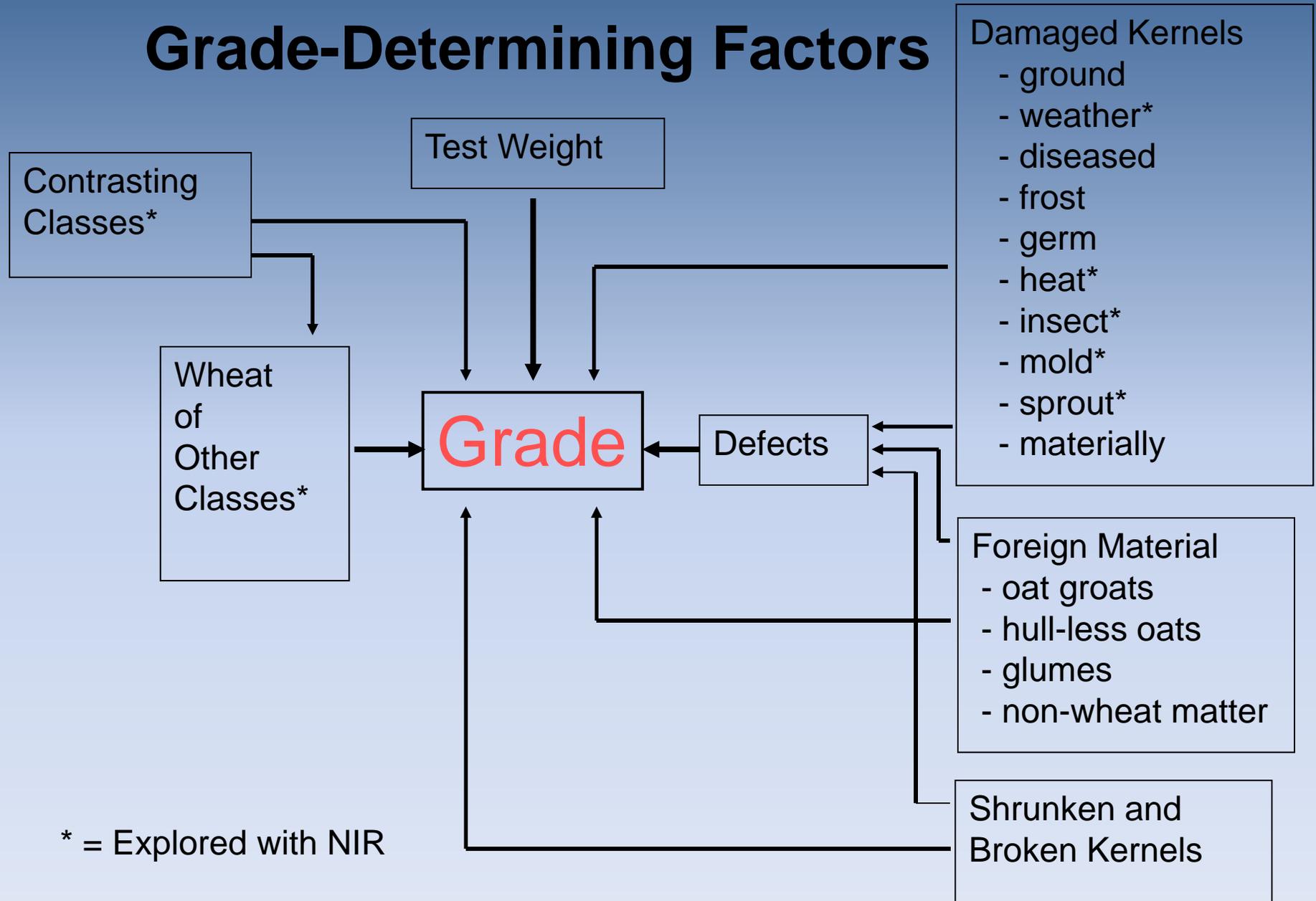
Basic Interference Filter Design



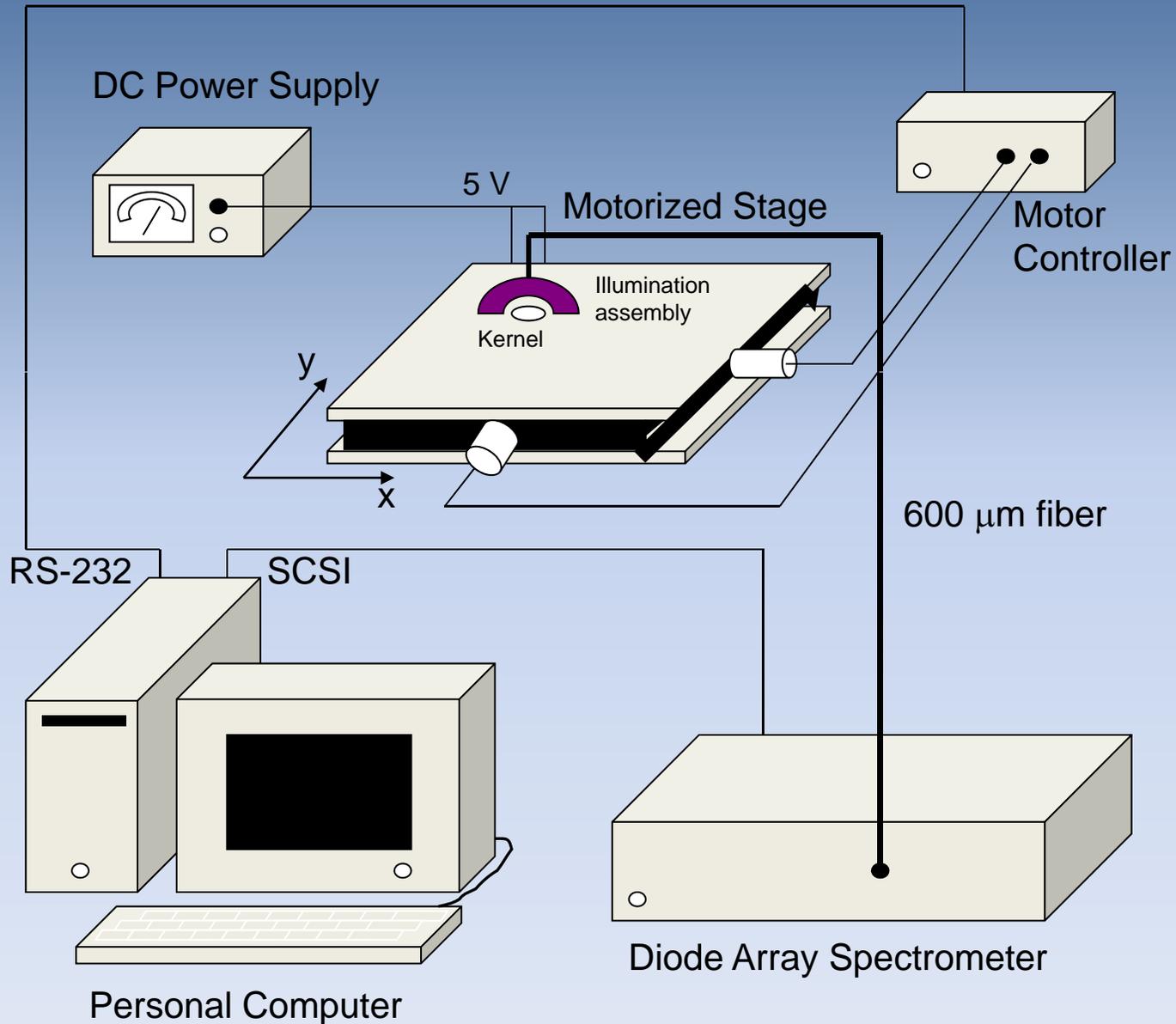
Single Beam Monochromator



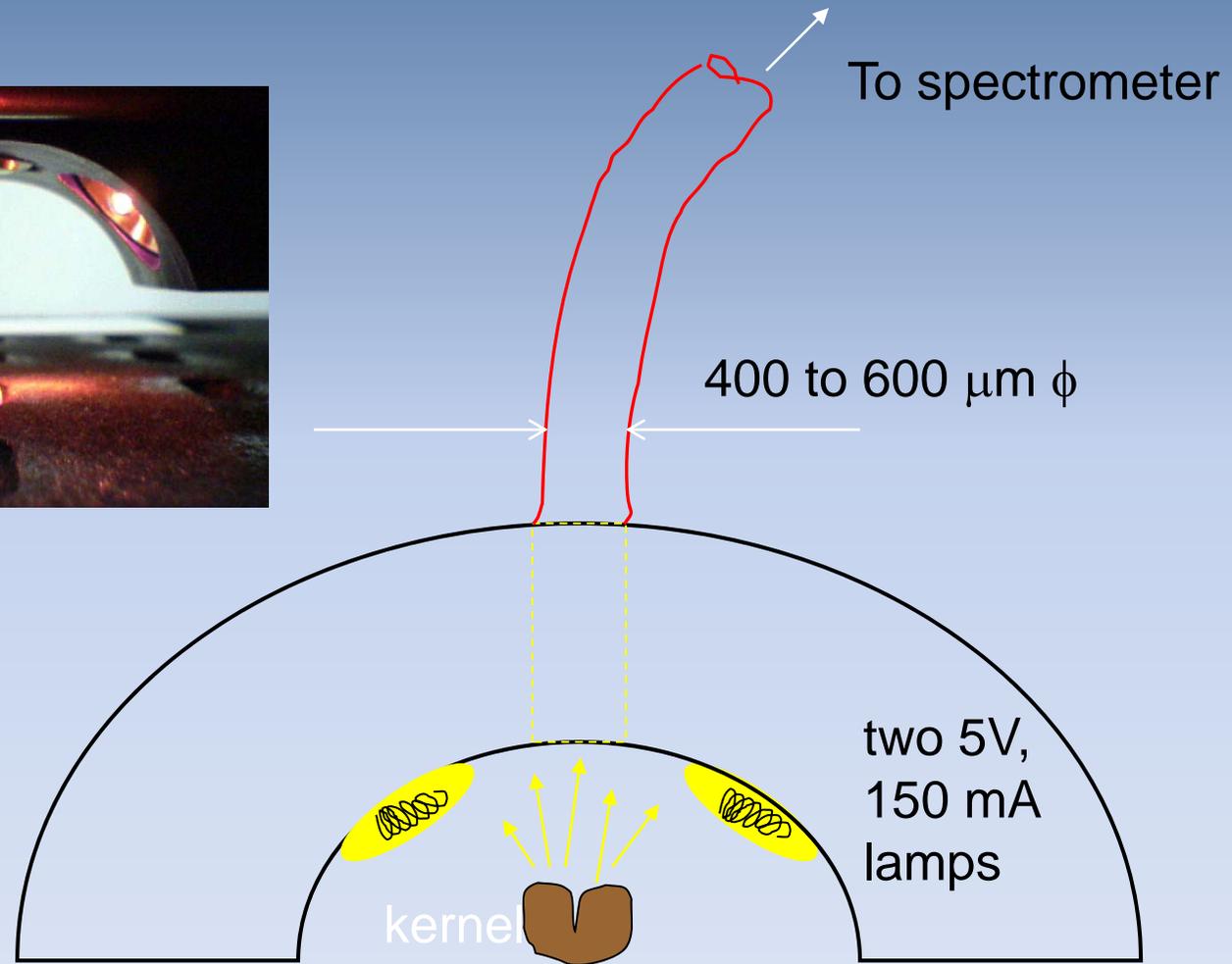
U.S. Wheat Grade-Determining Factors



Single Kernel Reflectance Apparatus



Diagnostic Reflectance Assembly



Difficulty of Task

Easy

Difficult

Impossible?



wheat vs nonwheat



wheat class



damaged wheat



variety identification



functionality

NIR Calibrations with Wheat

- Moisture
- Protein
- Ash (cellulose and fiber in bran)
- Hardness (proxy for particle size distribution, measurable at two wavelengths, 1680 & 2230 nm)
- Dough Development (monitoring changes in OH and CH bands in water, starch, and protein)
- Starch Damage
- Insects
- Starch Waxiness

Other NIR – Wheat Investigations

- Amino acids (lysine, threonine, tryptophan, methionine)
- Classification
- Ergosterol (fungi)
- History of environmental stress during seed development
- Rye translocation
- Glutenin and gliadin

Past Studies at USDA-Beltsville: NIR Wheat Quality

1. Detection of 1AL/1RS or 1BL/1RS Wheat/Rye Translocation.
2. Classification of Waxy, Partial Waxy, and Wild-type Wheat.
3. Detection of Wheat Scab by Hyperspectral Image Analysis.
4. Use of NIR for Assessment of Environmental Stress.

Popular Multivariate Modeling Techniques

- Multiple Linear Regression (MLR)
- Principal Components Regression (PCR)
- Partial Least Squares (PLS)
- Artificial Neural Networks (ANN)
- Locally Weighted Regression (LWR)

Multiple Linear Regression (MLR)

$$y = b_1x_1 + b_2x_2 + \dots + b_mx_m + e$$

Where,

y = Analyte

b_i = The i^{th} coefficient

x_i = The i^{th} wavelength

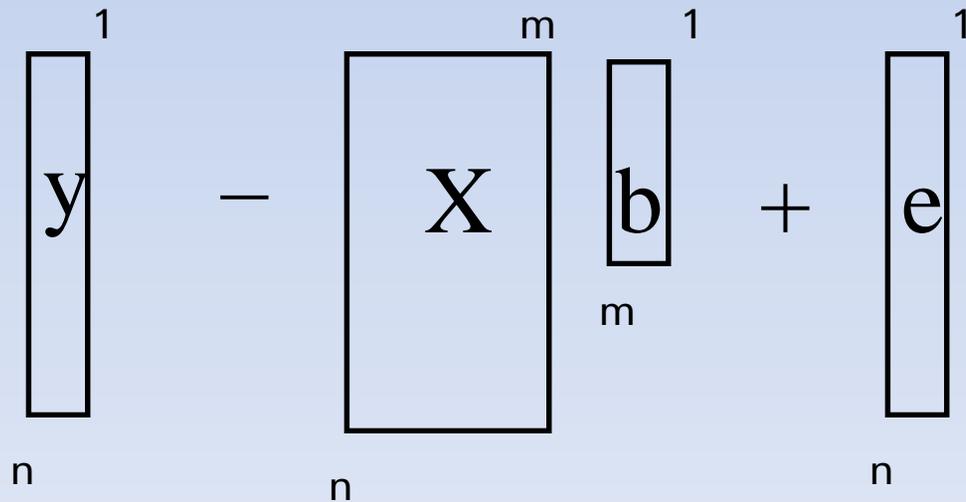
e = The residual

MLR

in matrix notation

$$\mathbf{y} = \mathbf{X}\mathbf{b} + \mathbf{e}$$

$n \times 1$ $n \times m$ $m \times 1$ $n \times 1$



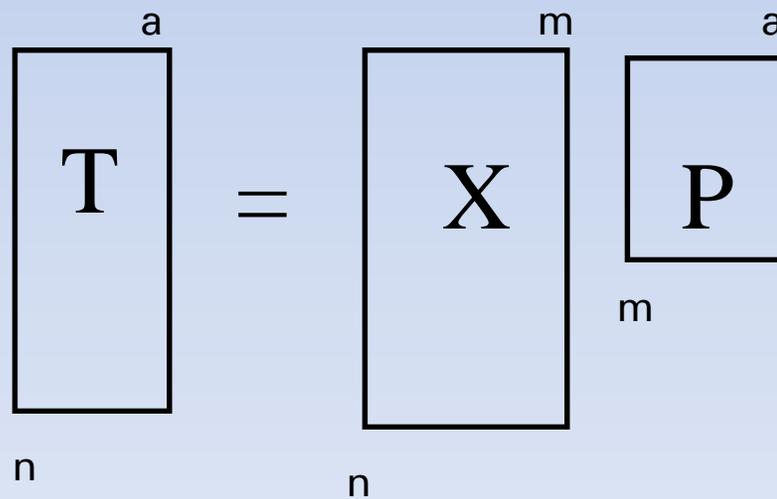
Principal Component Regression (PCR)

$$\mathbf{y} = \mathbf{T}\mathbf{b} + \mathbf{e}$$

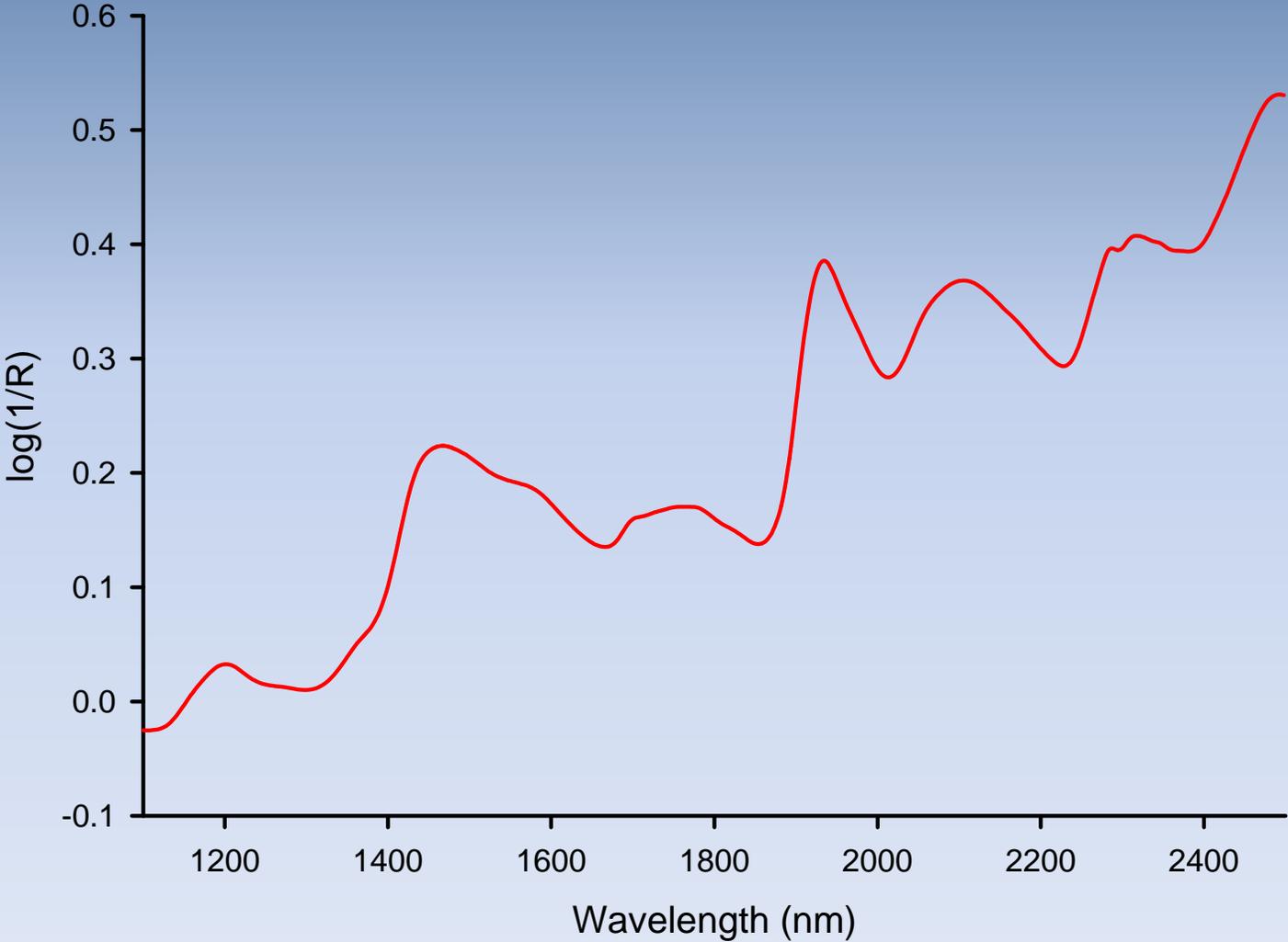
A diagram illustrating the dimensions of the variables in the equation $\mathbf{y} = \mathbf{T}\mathbf{b} + \mathbf{e}$. It shows four vertical rectangles representing vectors or matrices. The first rectangle is labeled \mathbf{y} and has a '1' above it and an 'n' below it. The second rectangle is labeled \mathbf{T} and has an 'a' above it and an 'n' below it. The third rectangle is labeled \mathbf{b} and has a '1' above it and an 'a' below it. The fourth rectangle is labeled \mathbf{e} and has a '1' above it and an 'n' below it. The rectangles are arranged in a sequence: \mathbf{y} , followed by an equals sign, \mathbf{T} , followed by \mathbf{b} , followed by a plus sign, and finally \mathbf{e} .

Decomposition of \mathbf{X}

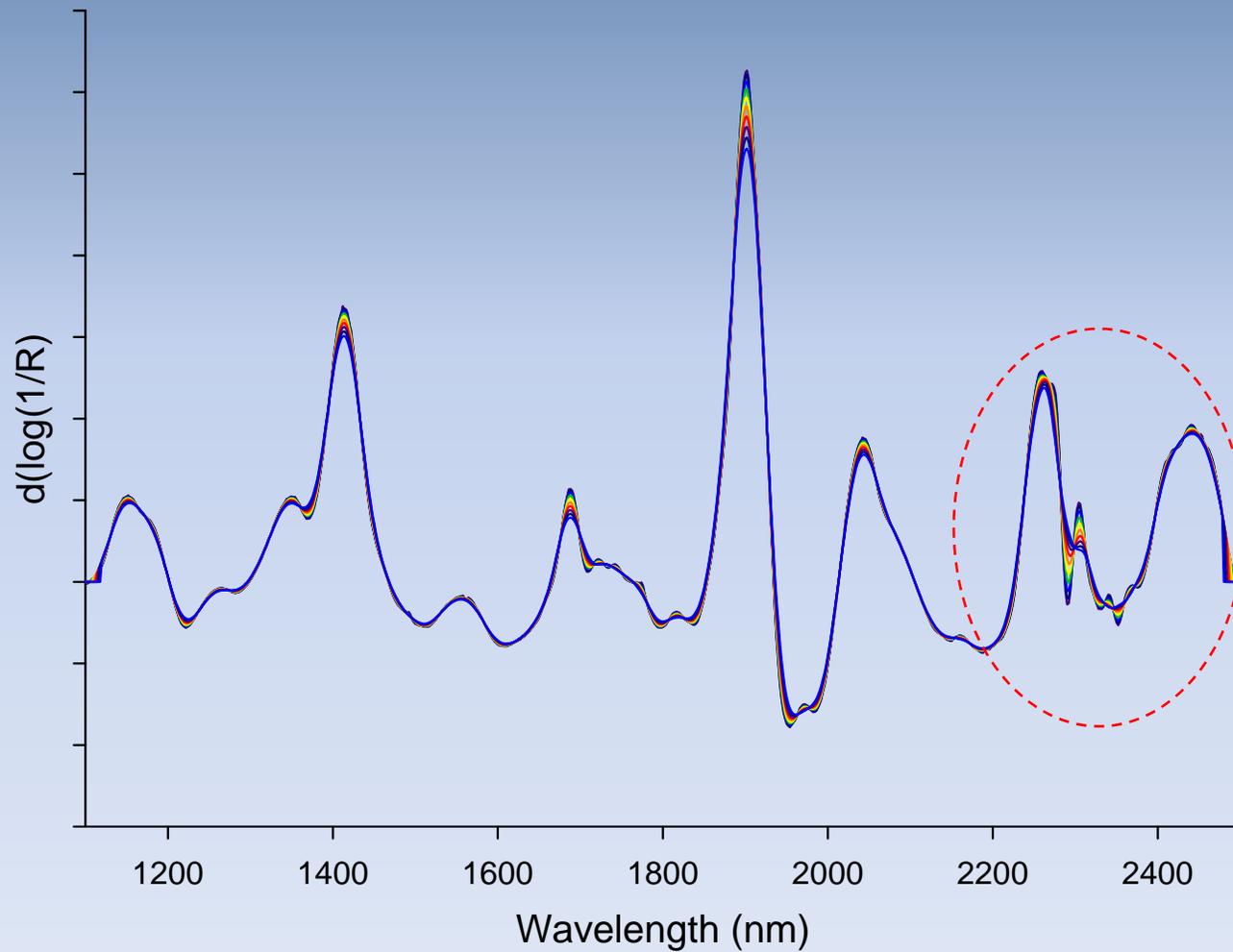
$$\mathbf{T} = \mathbf{X}\mathbf{P}$$



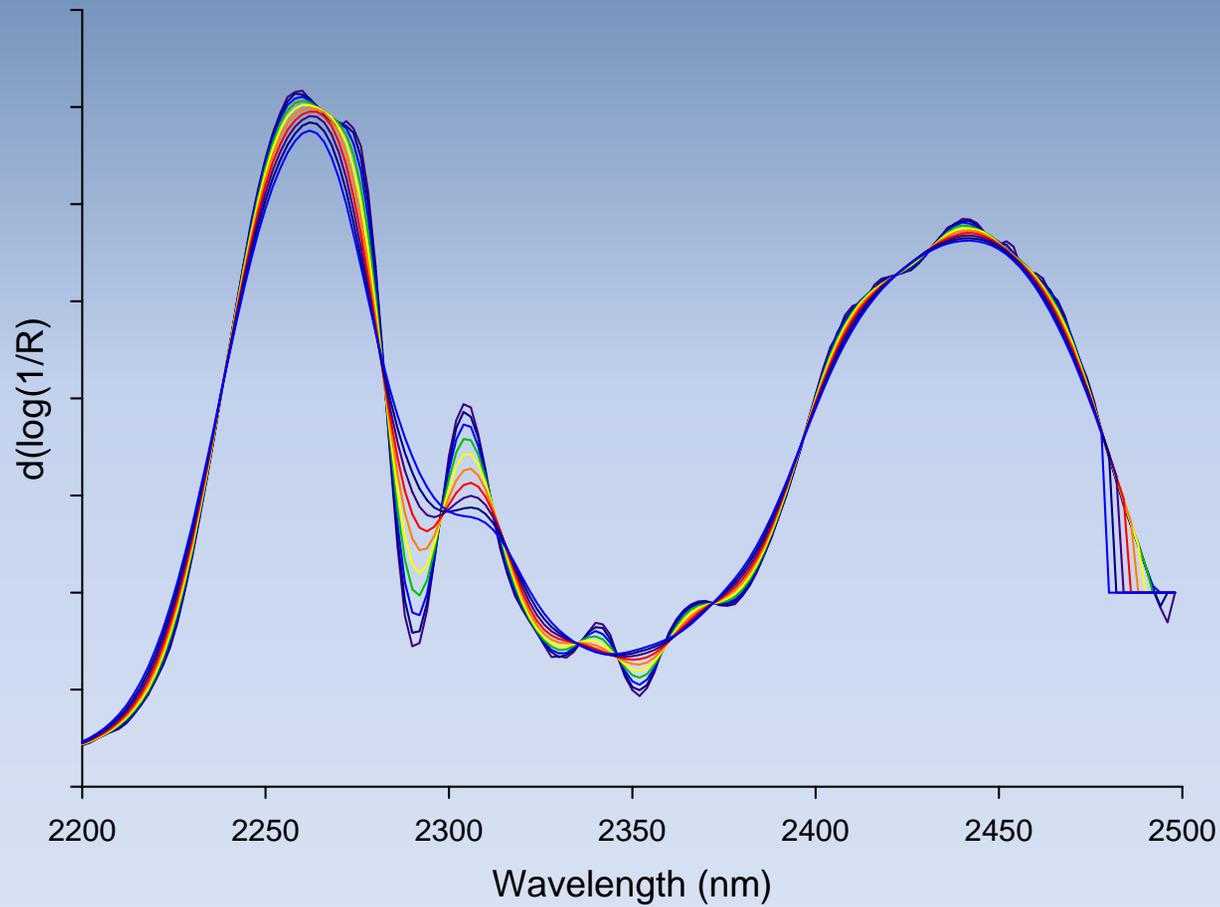
A Typical Spectrum of Ground Wheat



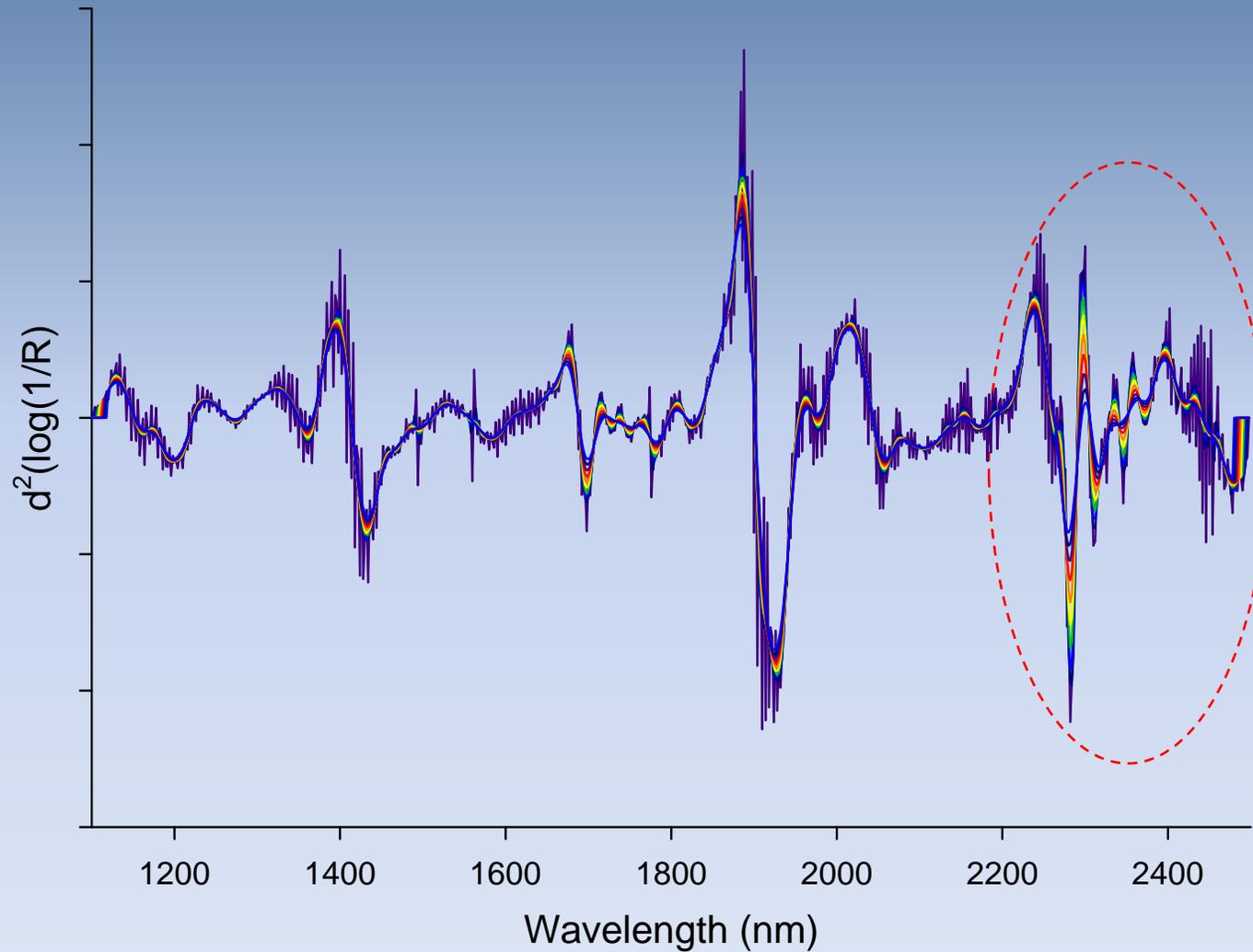
First Derivative, Savitzky-Golay (3,5,...,21 points)



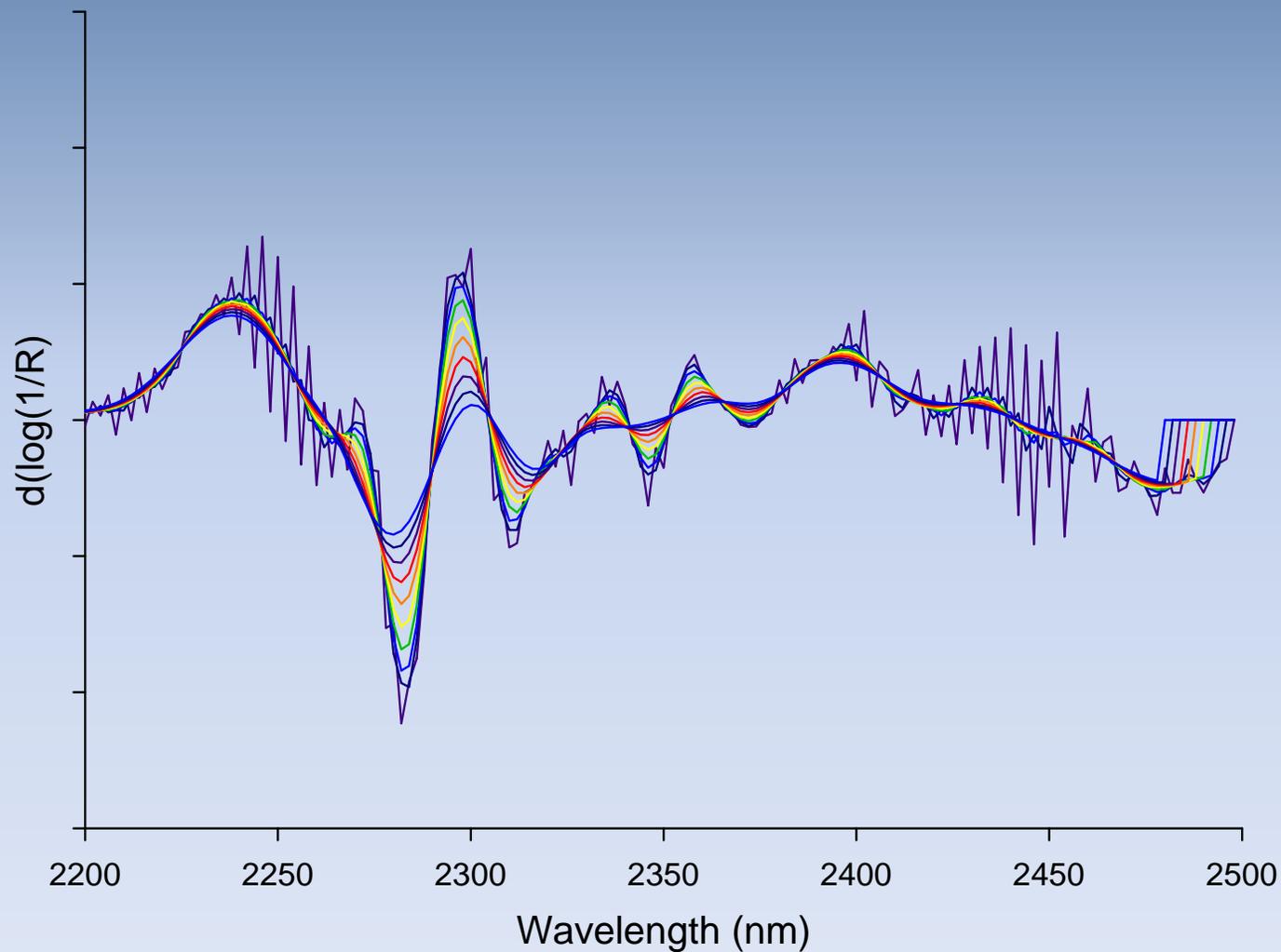
First Derivative, Savitzky-Golay (3,5,...,21 points) (2200-2500 nm)



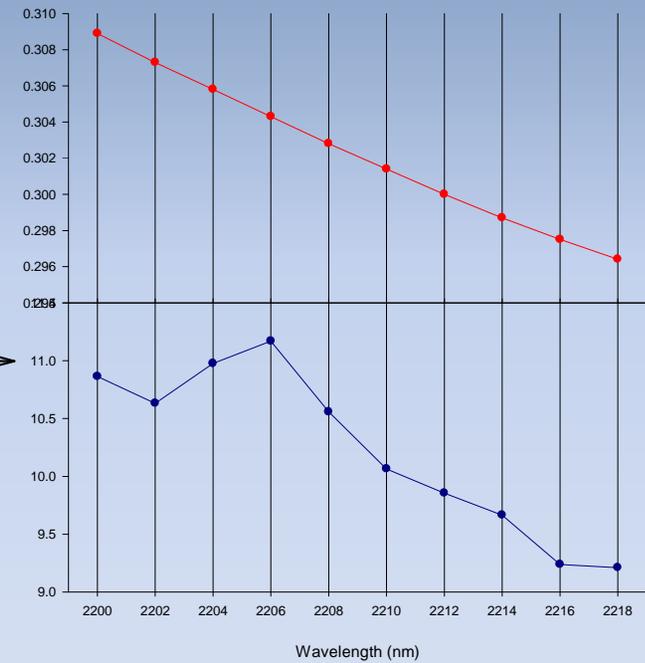
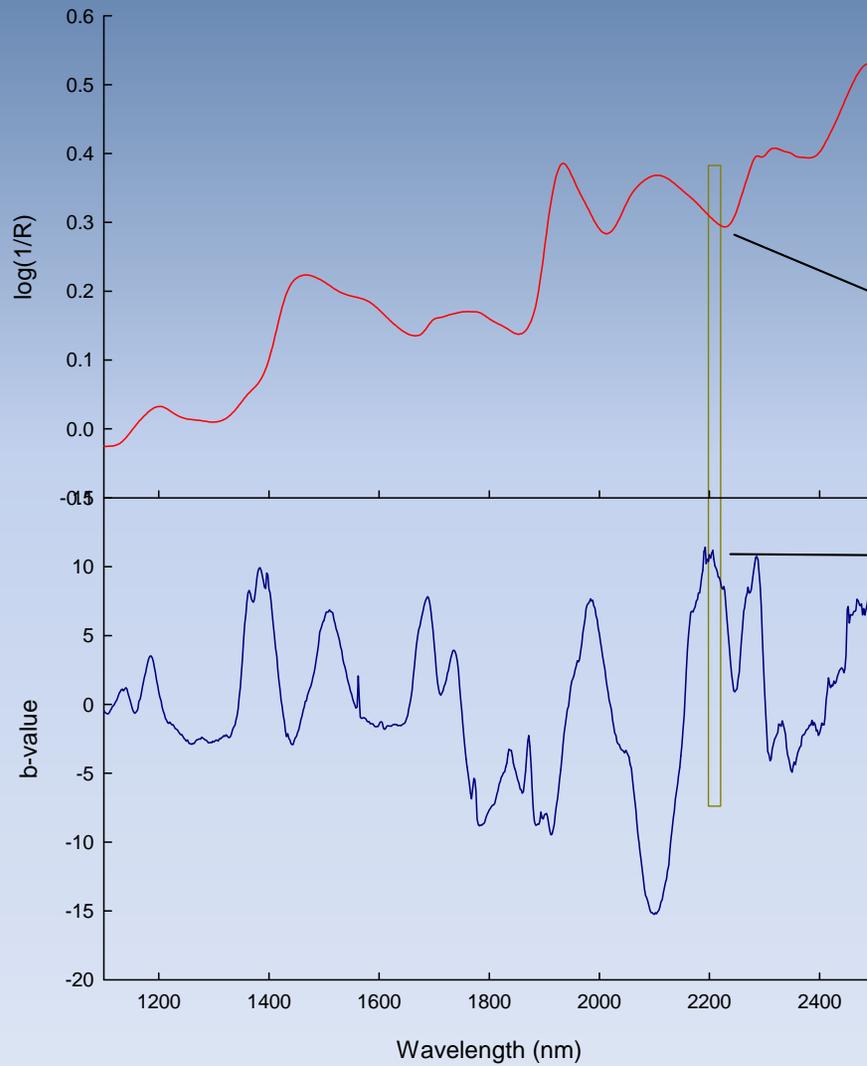
2nd Derivative, Savitzky-Golay (3,5,...,21 points)



2nd Derivative, Savitzky-Golay (3,5,...,21 points) (2200-2500 nm)

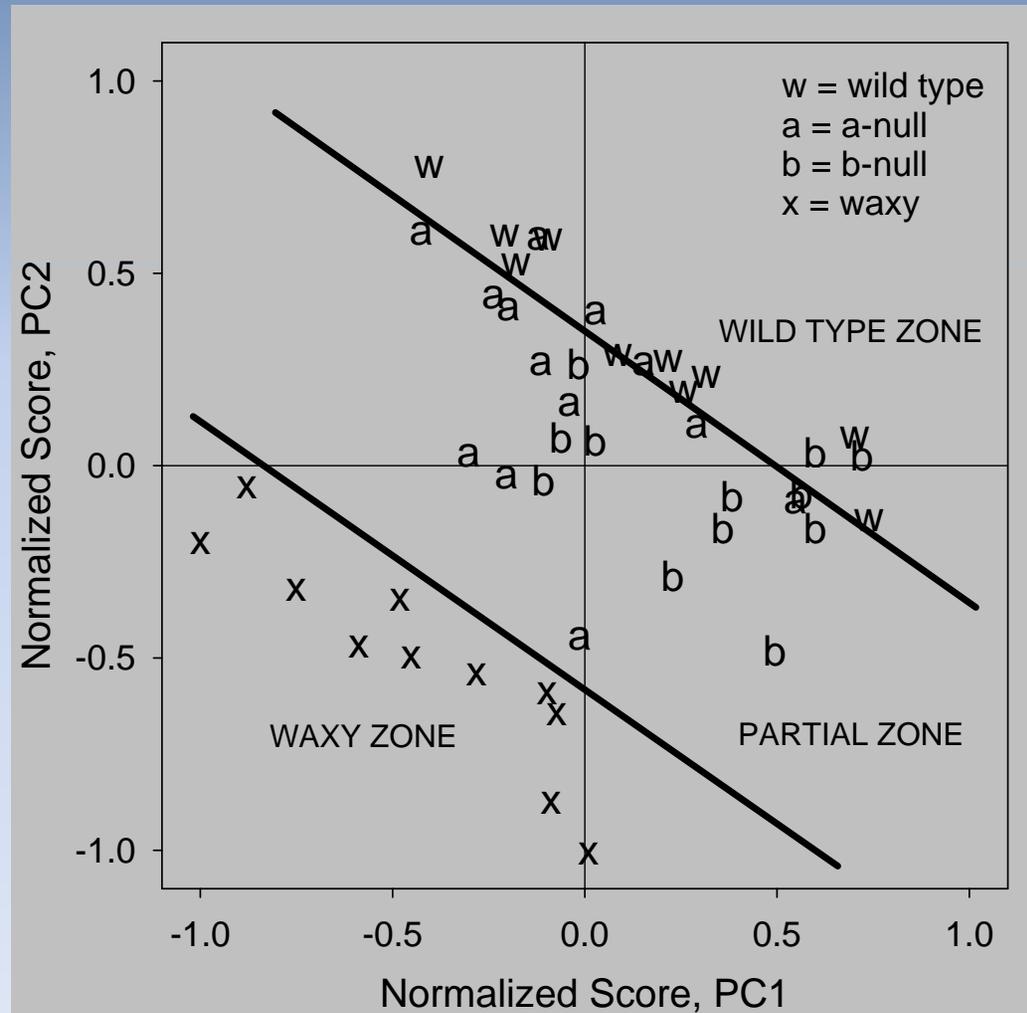


Applying the Multivariate Regression Equation



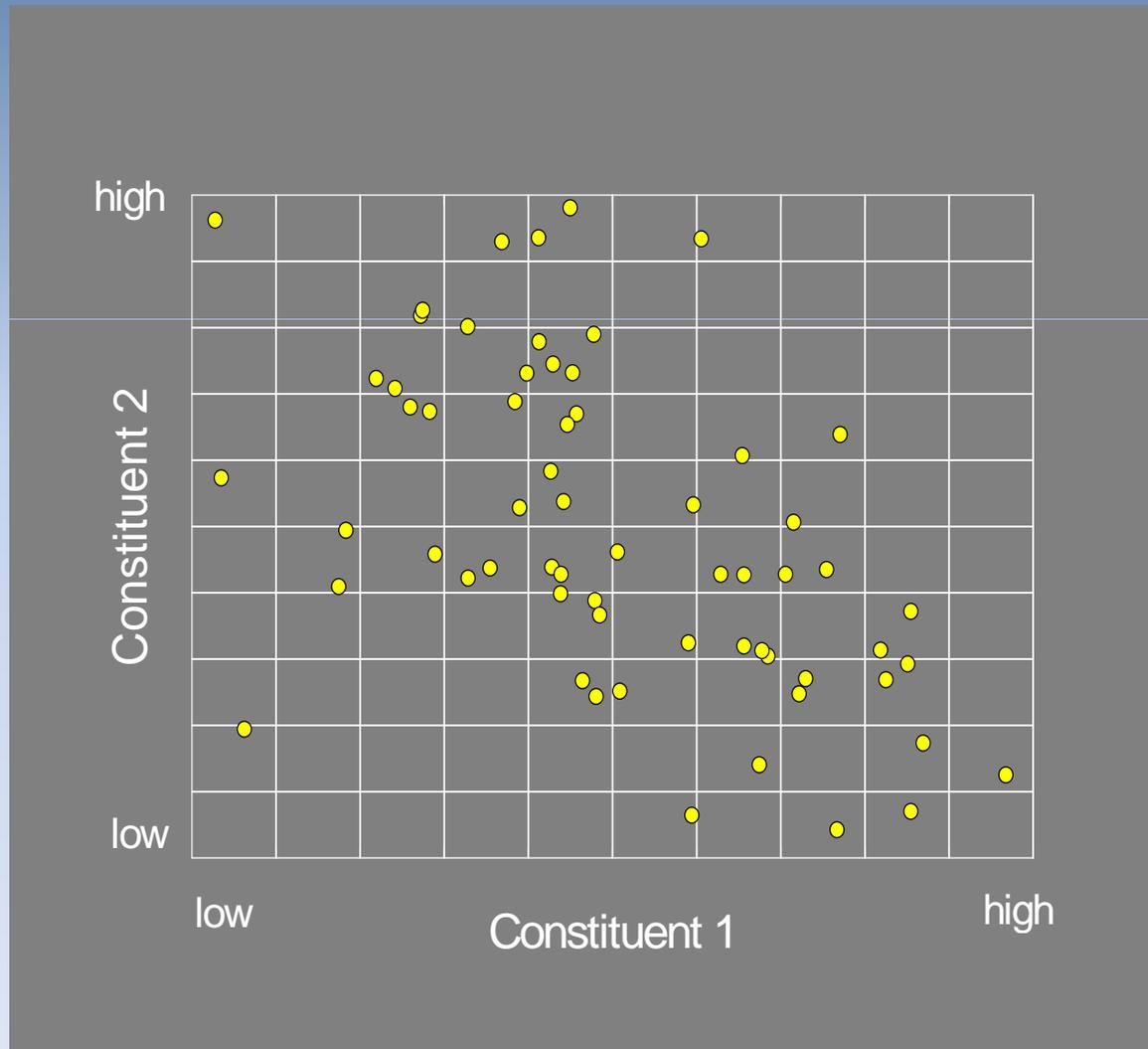
$$b_{2200}x_{2200} + b_{2202}x_{2202} + \dots + b_{2218}x_{2218}$$

First Two Principal Components Ground Durum Wheat Diffuse Reflectance (1100-2500 nm)

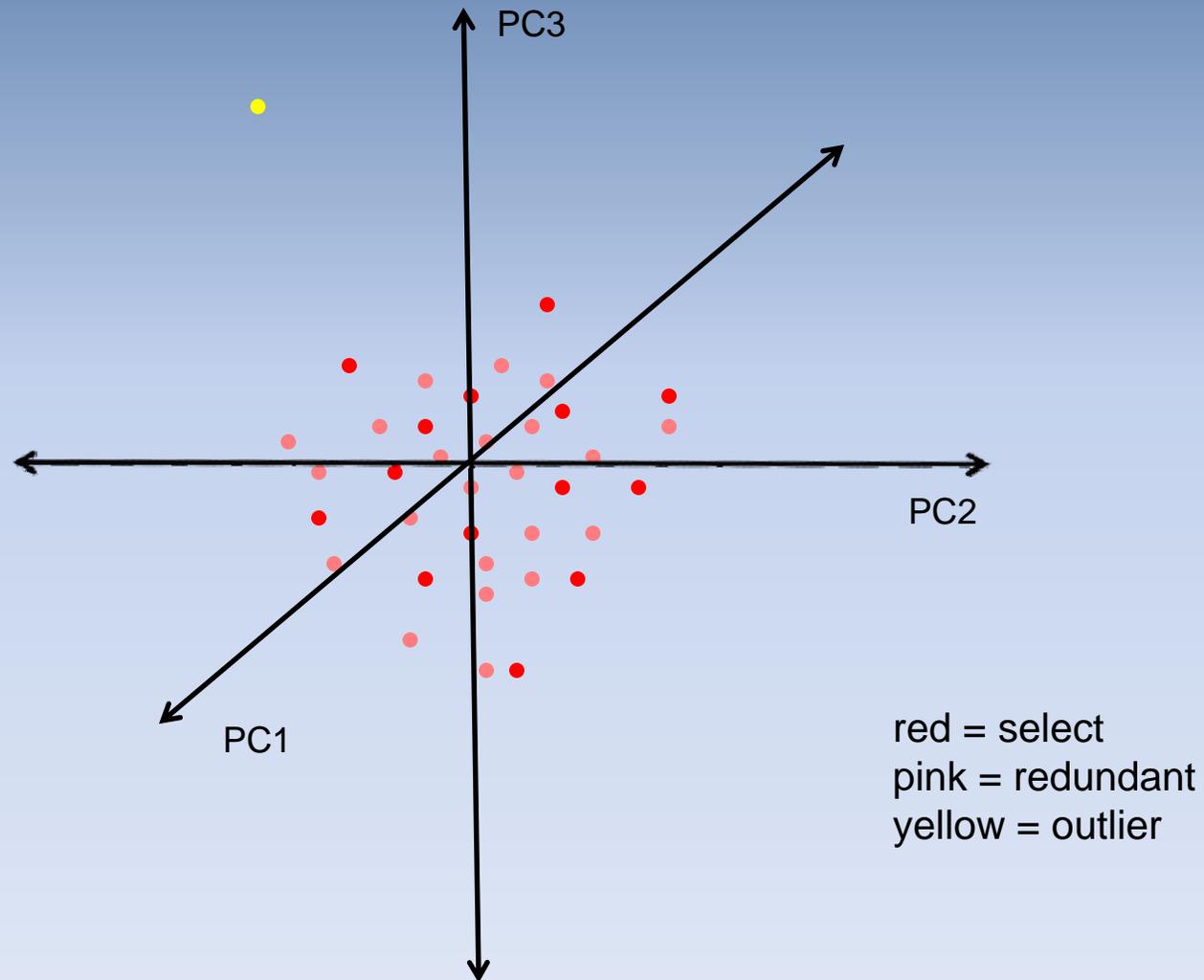


Selection of Samples for Calibration

by reference chemical analyses



Spectrally Based Sample Selection (Mahalanobis Distance)



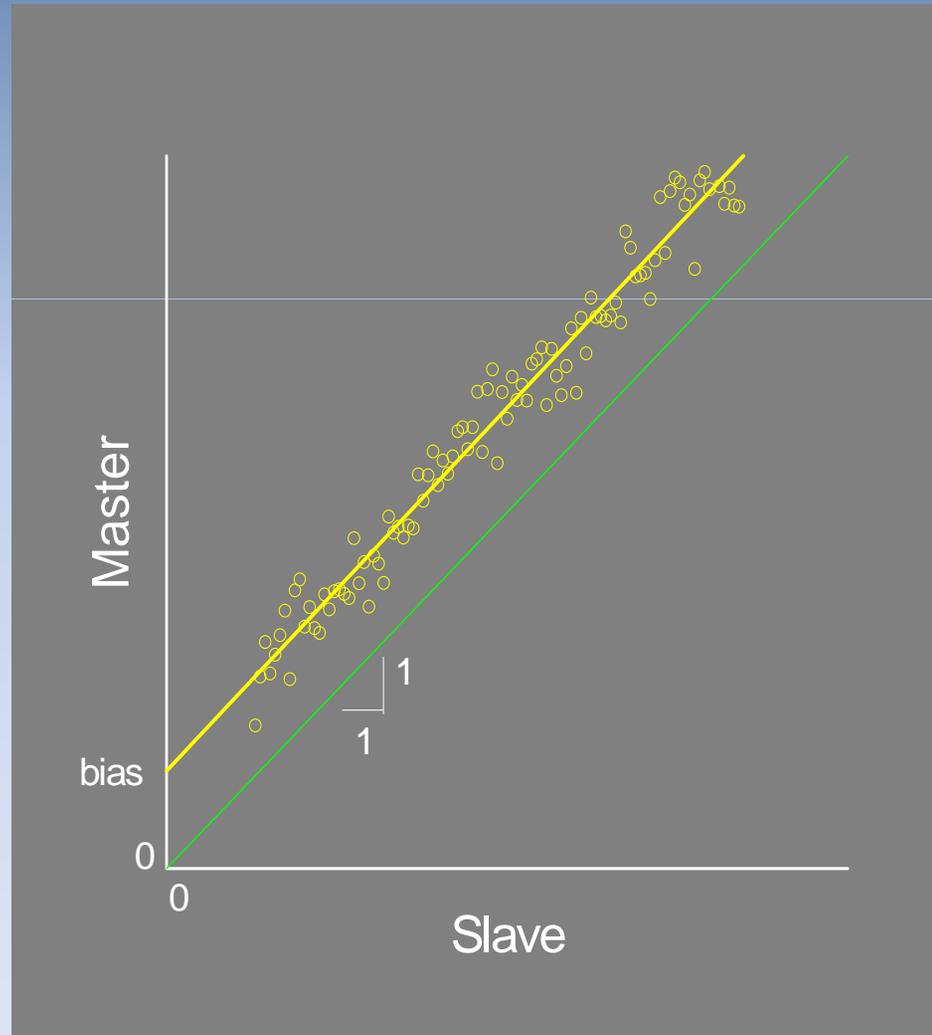
Error

$$\sigma^2_{overall_error} = \sigma^2_{sampling_error} + \sigma^2_{analytical_error}$$



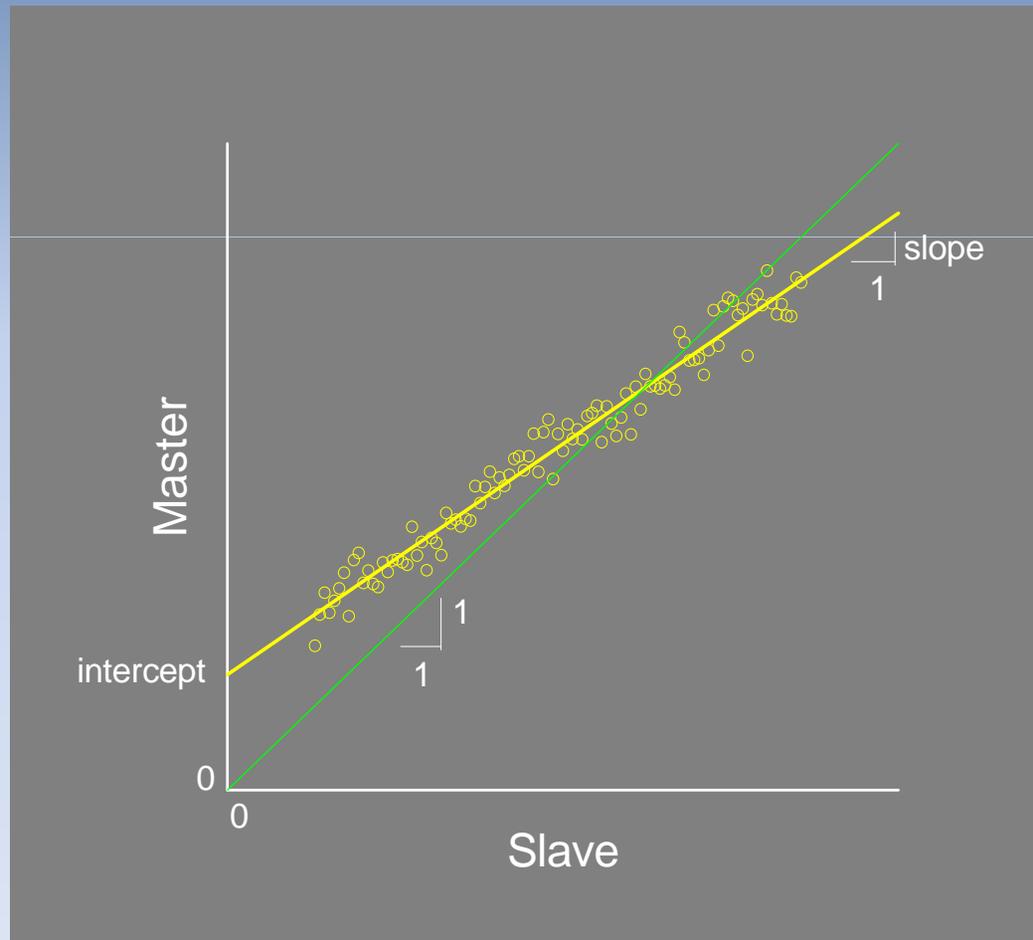
Standardization

bias adjustment



Standardization

slope and intercept adjustment



How Many Samples for Calibration?

(Murray and Cowe, 2004)

W = WIDE range in composition, especially regarding the analyte of interest.

E = EVEN distribution (as opposed to normal distribution), which ensures good representation at extremes.

P = PRECISE reference analytical procedure.

T = TYPICAL samples of those to be encountered in the future.

Misconceptions About Near-Infrared Analysis

(DiFoggio, Appl. Spectrosc. 1995)

- 1 “Near-infrared predictions can never be better than the primary reference method.”
- 2 “Regression models that only use terms that are linear in spectral absorbance cannot account for nonlinear effects.”
- 3 “Bias and skew adjustments to near-IR prediction equations are simply mathematical manipulations that make no physical assumptions.”

Parting Thoughts

- Advances in near-IR chemometric methodologies can be ascribed to the ever increasing improvements in personal computers.
- Highly sophisticated, easy to use, software packages make it much easier to develop calibrations.
- Research is active in nonlinear algorithms, pattern recognition, and discriminant analysis as well as in the traditional linear quantitative methodologies.

NIR Wish List for Wheat

(some ongoing studies)

- Gluten quality
- Degree of waxiness in partial waxy wheats
- DON (NIR?, Raman)
- Milling yield (NIR + imaging)
- Other _____ ?

Thank You

