



# NIR Application in Malting

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# Outline

1. What is NIR method?
2. Principles and instrument
3. What can NIR do for us?
4. Challenges and limitations
5. Discussion

# What is NIR Method?

- A spectroscopic method that uses the near-infrared region of the electromagnetic spectrum
- Based on a mathematical interpretation of the electromagnetic information collected from the sample that is tested
- It is a secondary method; the analytical results generated by a NIR instrument are a “prediction” not “direct measurement”

# What is NIR Method?

- It is fast and non-destructive
- It requires limited sample preparation
- It can produce multi-parameters from a single test
- It requires limited skill on operator
- Its accuracy depends on the reference methods used for calibration development, and the techniques used for calibration development

# History

- **1800:** The 1st NIR Spectrum recorded (Herschel)
- **1950-1960 :** Potential of NIR quantitative analysis was recognized (Kaye)
- **1960s:** Research program on NIR analysis of agriculture stuff at USDA (Norris)
- **1971-1987:** Development of the 1st to 5th generation of NIR Instrument
- **1980s:** Introduction of Principal Component calibration
- **1990s:** Development of Nonlinear calibration methods
- **Present:** More applications, better instrument & easier to use

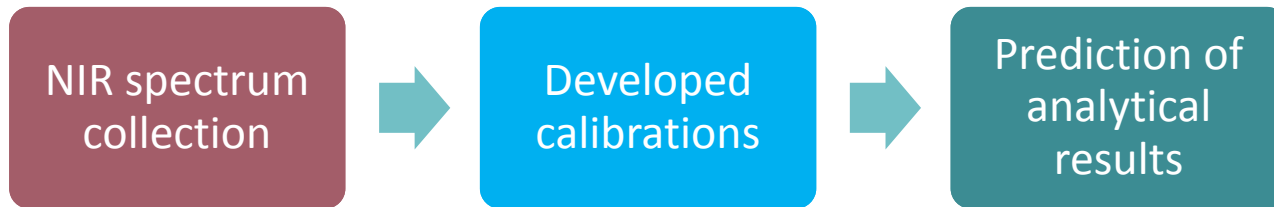
# Typical Application

- Astronomical spectroscopy
- Remote monitoring
- Materials science
- Medical uses
- Pharmaceutical
- Agriculture
- Food industry

# NIR Instrument Is not a Magic Box !!!

## Steps involved in NIR analysis:

1. Collect NIR spectrum data on test sample with a NIR Instrument
2. Plug NIR spectrum data into the calibrations (computer + mathematic models)
3. Predict analytical results (computer + mathematic models)



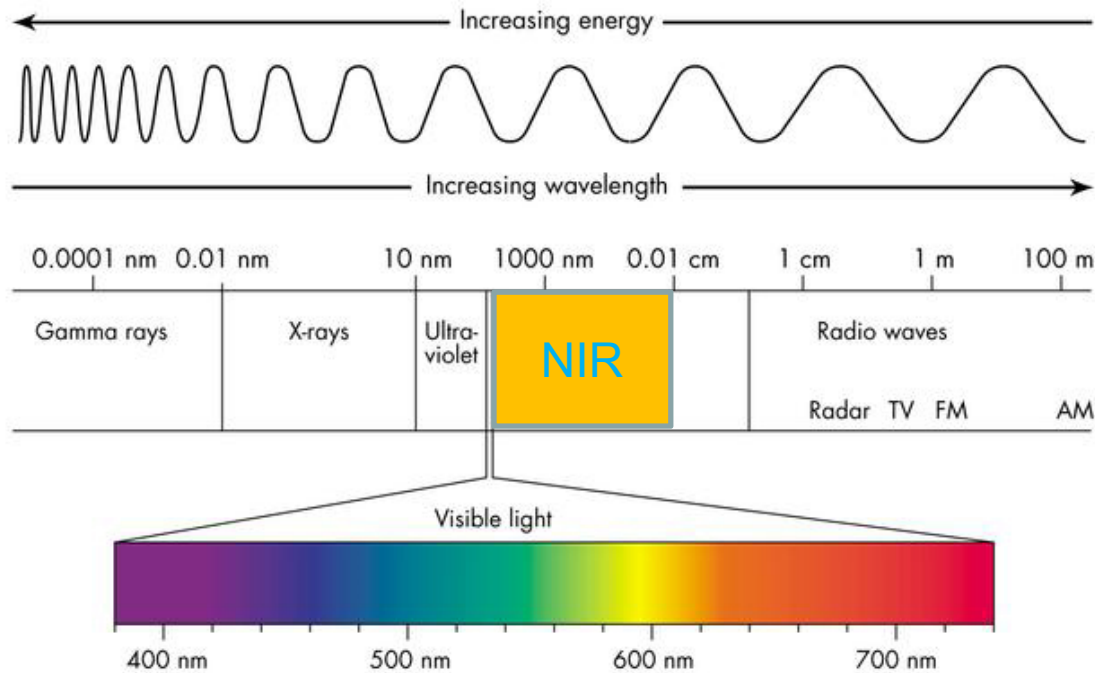
# Some Basics

## Terminology

- NIR = Near Infrared
- NIR= Near Infrared Reflectance
- NIT= Near Infrared Transmittance
- NIRS = Near Infrared Spectroscopy



# Some Basics

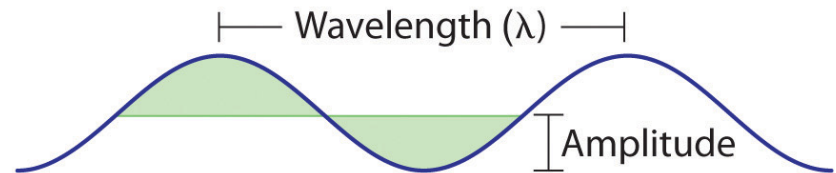


- The spectrum visible to the human eye: from 400 - 800nm
- **Near infrared spectrum covers: from about 750 - 2500nm**
- Infrared spectrum covers: from about 2500 - 25000nm

Image: <http://the-wombat.com/UVNIRphoto.htm>

# Some Basics

- NIR technology involves light interacting with matter where electromagnetic radiation occurs in the form of waves.
  - **Wavelength** of a light ( $\lambda$ ) is the distance between the two high points.
  - $\lambda$  is normally measured in nanometer (nm) in NIR spectrum (**1nm =  $10^{-9}\text{m}$** )
  - **Wave number ( $\text{cm}^{-1}$ ) =  $1/\lambda$**



**Wave number =  $10^7$  /wavelength (nanometer)**

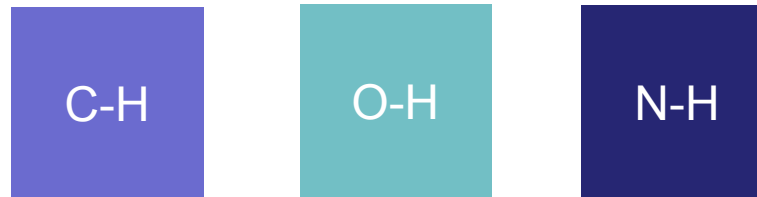
Image: [http://catalog.flatworldknowledge.com/bookhub/4309?e=averill\\_1.0-ch06\\_s01](http://catalog.flatworldknowledge.com/bookhub/4309?e=averill_1.0-ch06_s01)

# Some Basics

*Take a chemical fingerprint of a material using NIR light at a specific wavelength:*

- The test sample is radiated by NIR light for collecting absorption or reflectance signals
- Measure the wavelength and intensities of the absorption of NIR light by a sample
- The absorption or reflectance spectrum is directly proportional to the chemical compositions of the sample.

# Some Basics

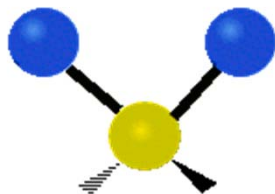


- NIR absorption is mainly due to hydrogen bonds
- Specific bonds between the atoms vibrate at a certain frequency and each type of these chemical bonds within a sample will absorb NIR light of a specific wavelength, while all other wavelengths are being reflected.
- NIR light is absorbed by molecules containing these functional groups such as: **fats, proteins, carbohydrates, organic acids, alcohol and water**

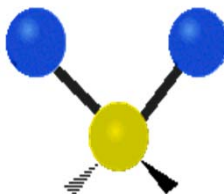
# Some Basics

The atoms in a CH<sub>2</sub> group, commonly found in organic compounds, can vibrate in six different ways:

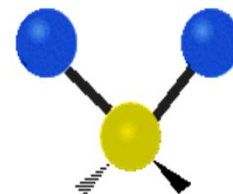
**Symmetrical Stretching**



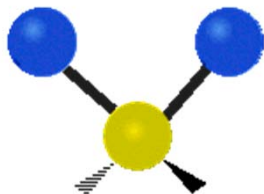
**Asymmetrical Stretching**



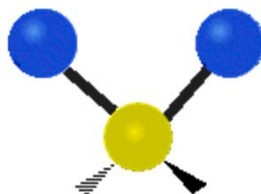
**Scissoring (Bending)**



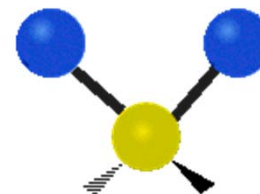
**Twisting**



**Rocking**



**Wagging**



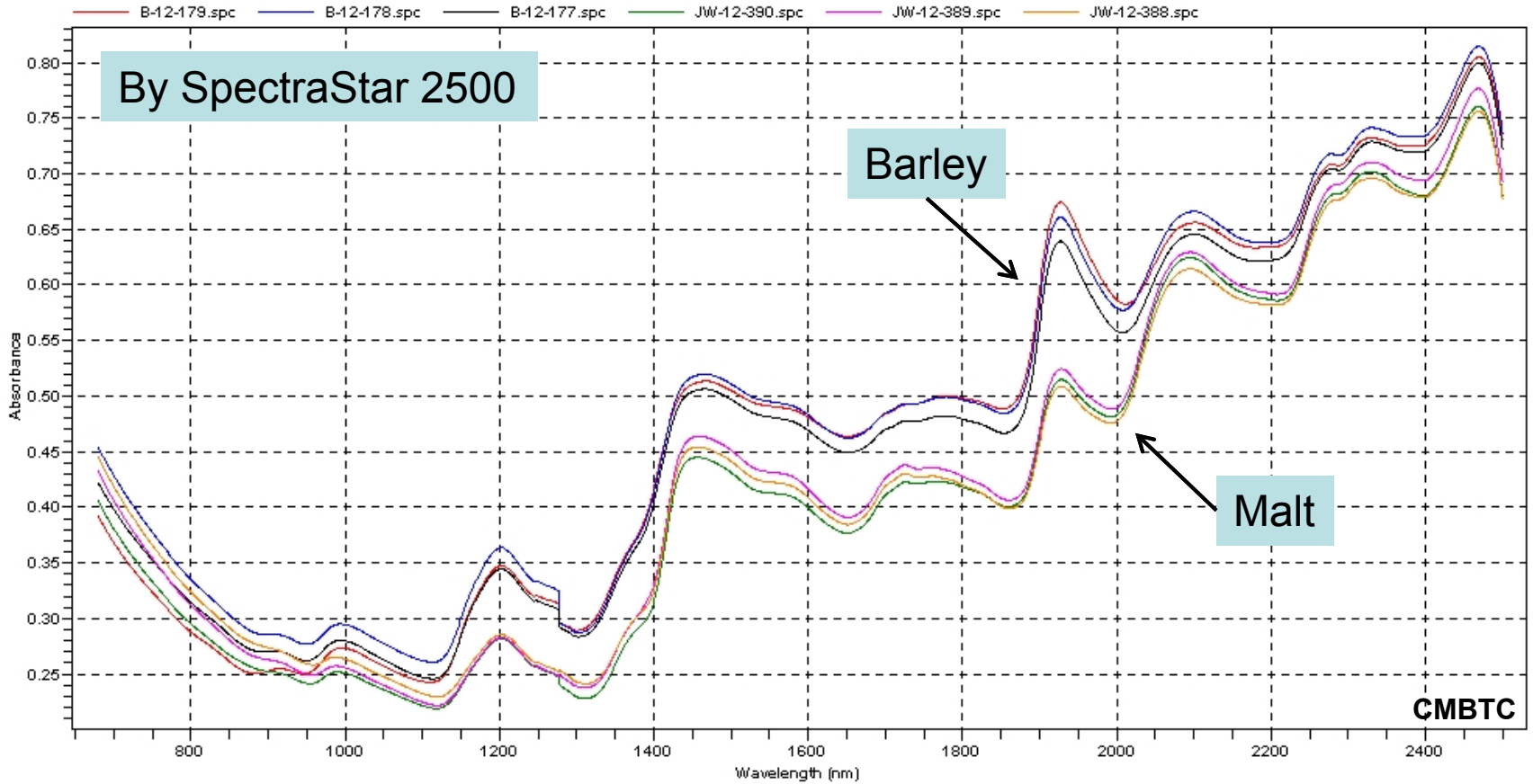
Images: [http://en.wikipedia.org/wiki/Molecular\\_vibration](http://en.wikipedia.org/wiki/Molecular_vibration)

# Some Basics

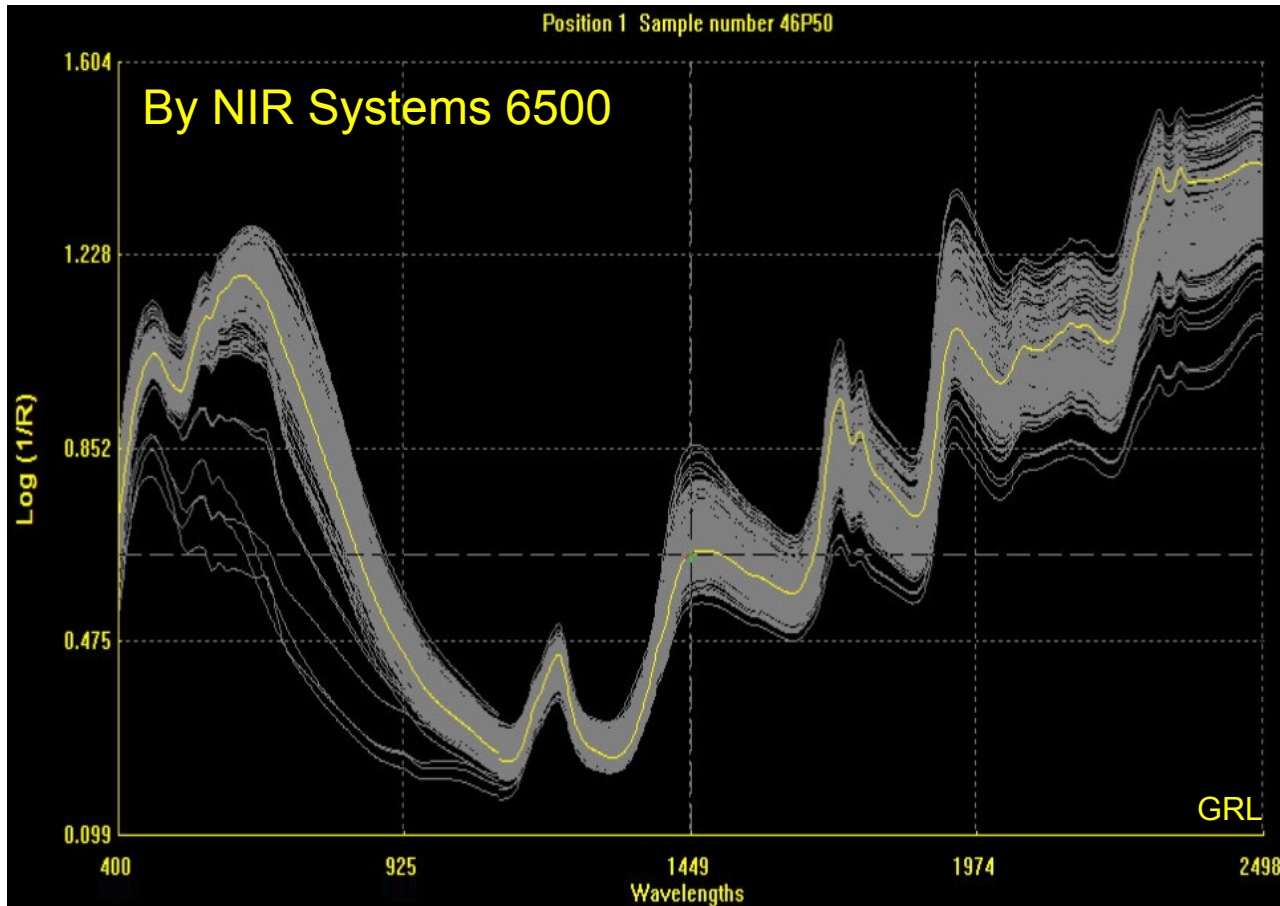
## NIR Reflectance analysis vs. NIR Transmission analysis

- In practice, the sample to be analysed is bombarded with NIR lights of different wavelengths.
- At each wavelength, some of the lights will be absorbed by specific chemical bonds. At the same time other lights will be scattered and reflected by other chemical bonds (NIR Reflectance ).
- In contrast, some of the lights may pass through the sample, which is described as NIR Transmittance (NIT).

# NIR Spectra



# NIR Spectra



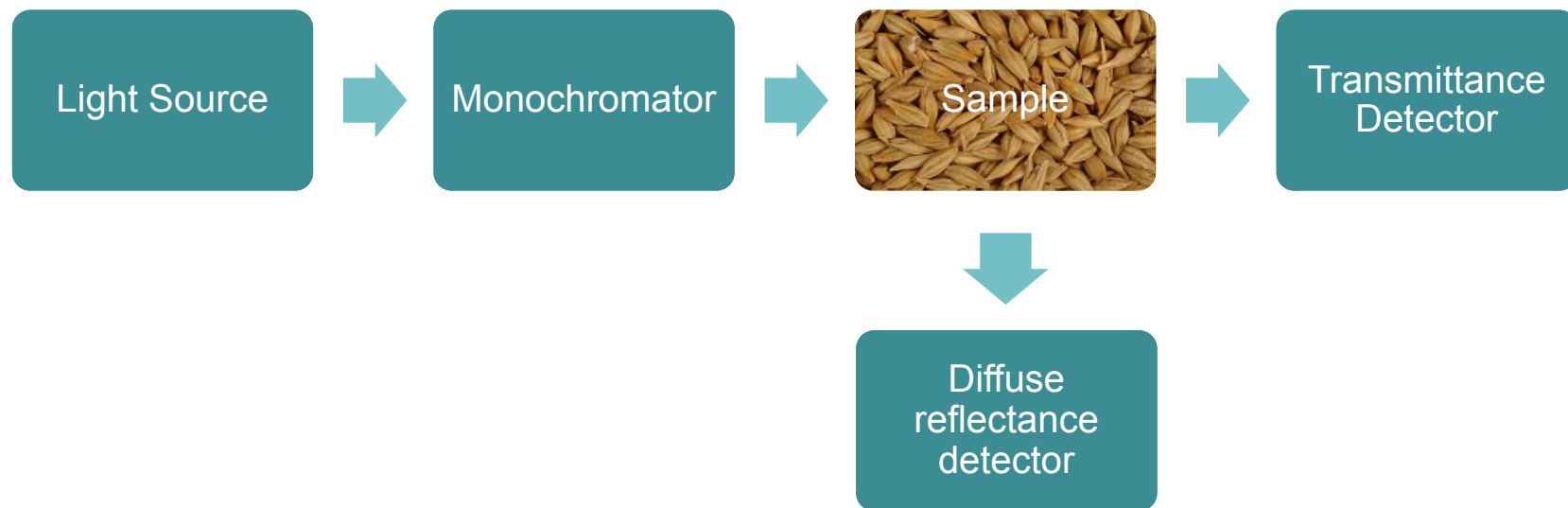


# Instrument

- A NIR spectrometer is generally composed of a light source
- Monochromator
- Sample holder or a sample presentation interface
- Detector, allowing for transmittance or reflectance measurements

# Instrument

## Basic configurations of NIR spectrometer



# Instrument

1. The light source; usually a tungsten halogen lamp
2. Detector types:
  - **Silicon** - fast, low noise, highly sensitive (visible to 1100 nm)
  - **Lead Sulfide (PbS)** - slower, sensitive from 1100 to 2500 nm
  - **Indium gallium arsenide (InGaAs)** – combines the speed and size characteristics of the silicon detector with the wavelength range of the PbS detector.
3. Sample presentation: unprepared, ground, & liquid etc.

# Some NIR Instruments

Unity's  
SpectraStar  
2500XL



Foss'  
Infratec™ 1241  
Grain Analyser



Perten's  
DA 7250  
(diode array based)



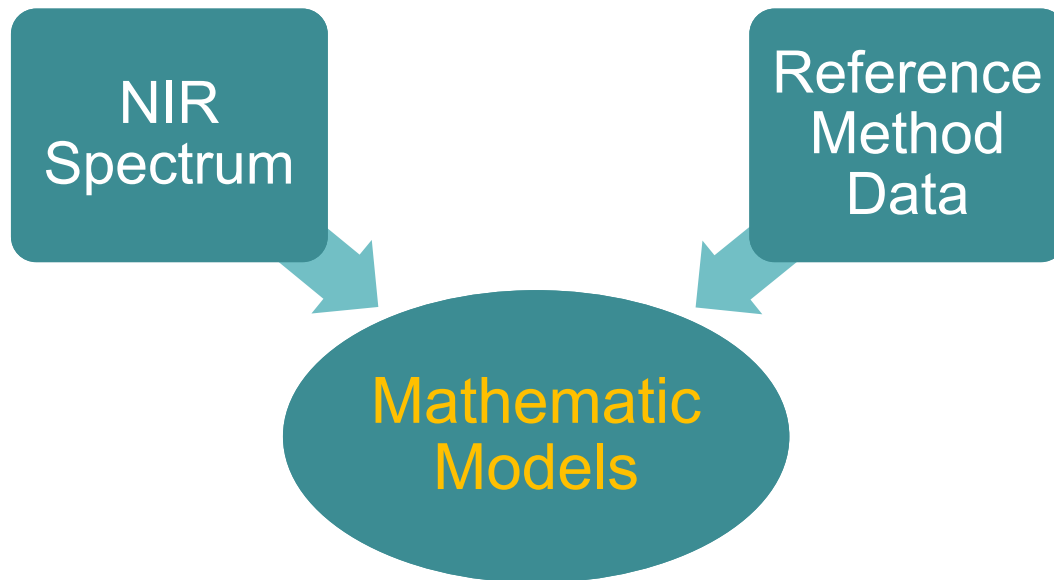
Foss  
NIRSystems  
6500



Images: [www.foss.dk](http://www.foss.dk), [www.unityscientific.com](http://www.unityscientific.com), [www.foodprocessing-technology.com](http://www.foodprocessing-technology.com), [www.wteservice.trustpass.alibaba.com](http://www.wteservice.trustpass.alibaba.com)

# What Is Calibration?

The established Mathematical Relationships between NIR spectrum & analytical results generated by reference methods



# Mathematical component of calibration model

- Single-term (one independent variable) regression equation:

$$Y = a + bX + e \text{ or } \hat{Y} = a + bX$$

- $Y$  is the reference and  $X$  is  $\log(1/R)$
  - $a$  and  $b$  are regression constants
  - $\hat{Y}$  is an approximation to  $Y$
  - $e = Y - \hat{Y}$
- Multi-term linear regression equation:
    - $Y = a + b_1x_1 + b_2x_2 + \dots + b_kx_k$ 
      - $x$ 's are  $\log(1/R)$ ; values at  $k$  different wavelengths

# The Calibration Process

1. Selection of a representative calibration sample set
2. NIR spectra acquisition and determination of reference values
3. Multivariate modeling to relate the “spectral variations” to the “reference values” of the analytical target property
4. Validation of the model by cross validation, set validation or external validation

# Techniques for Calibration Development

- Select/pre-treat spectrum data (Reduce data points & reduce noises)
- Select pre-treat reference data (Eliminate outliers & data transformation)
- Establish regressions between NIR data and the reference method data



# Techniques for Calibration Development

Mathematical or statistical methods for extracting information & relating measurements

- Simple regression analysis
- Multivariate regression analysis
- Principal components analysis (PCA)
- Discriminant analysis
- Artificial neural networks

# What NIR Can Do For Us?

- According to some researchers and NIR instrument providers, nearly all the quality parameters of interest to maltsters can be measured (predicted) by NIR .
- Up to date, only limited analysis measured by NIR have been accepted by maltsters and brewers such as moisture and protein, alcohol content etc. although NIR method shows lots of promise

# Using NIR Analysis

- Many grain and malting companies have successfully implemented NIR spectrometers in their quality control laboratories for routine use in raw material qualification
- This is based on the fact that the customers accept the results generated by NIR analysis

# Malt Analysis Expected by Brewers

<b>Criteria for “Ideal Malts”</b>		
	<b>2-R Barley</b>	<b>6-R Barley</b>
<b>Total protein,</b>	11.3-12.8	11.3-13.3
<b>On 7/64 screen, %</b>	>70	>60
<b>B-glucan, ppm</b>	<115	<140
<b>F/C, %</b>	<1.5	<1.5
<b>Soluble protein, %</b>	4.9-5.6	5.2-5.7
<b>Soluble protein/ Total protein, %</b>	42-47	42-47
<b>Turbidity, NTU</b>	<10	<10
<b>Viscosity, CP</b>	<1.50	<1.50
<b>F-Extract, %</b>	>81.1%	>79.0
<b>Color, ASBC</b>	1.6-2.0	1.8-2.2
<b>Diastatic power, <math>\alpha</math>L</b>	120-160	140-180
<b><math>\alpha</math>-Amylase, DU</b>	45-80	45-80
(American Malting Barley Association, 2003)		

# NIR Analysis Used by Malting & Brewing Industries

Barley	Status	Malt	Status	Beer	Status	Hops	Status
Moisture	Good accuracy	Moisture	Good accuracy	Alcohol	Very accurate	$\alpha$ - Acids	
Protein	Good accuracy	Protein	Good accuracy	Original gravity		B- Acids	
Extract		Extract		Apparent extract		Hop storage Index	
Enzymes		Enzymes		Real extract			
B-glucan		B-glucan					
Soluble protein/FAN		Soluble protein/FAN					
		Color					
		Friability					
		Color					
		Wort viscosity					

# Standard Error and Repeatability for Reference Method

	$S_r$	$r_{95}$
<b>Moisture</b>	0.12	0.3
<b>Friability</b>	1.7	4.8
<b>Extract</b>	0.16	0.4
<b><math>\beta</math> Glucan</b>	5	14
<b>Viscosity</b>	0.01	0
<b>Soluble Protein</b>	0.1	0.3
<b>Protein</b>	0.12	0.3
<b>FAN</b>	3.2	9
<b>Colour</b>	0.05	0.1
<b>DP</b>	4.2	12
<b>Alpha</b>	2.2	6.2

GRL, Canadian Grain Commission, Winnipeg

# Standard Error of NIR Calibrations Developed by Different Researchers

Using barley to predict potential malt quality			
	Helm SEC	Li SecV	GRL SEC
<b>Protein</b>	0.28	0.28	0.2
<b>Extract</b>	0.6	0.43	0.45
<b>DP</b>	6.7	13	14
<b>Alpha</b>	2.2	2.8	5
<b>SP</b>	0.15	0.19	0.16
<b>B- Glucan</b>	33		116
<b>Friability</b>	4.8	3.2	3.8

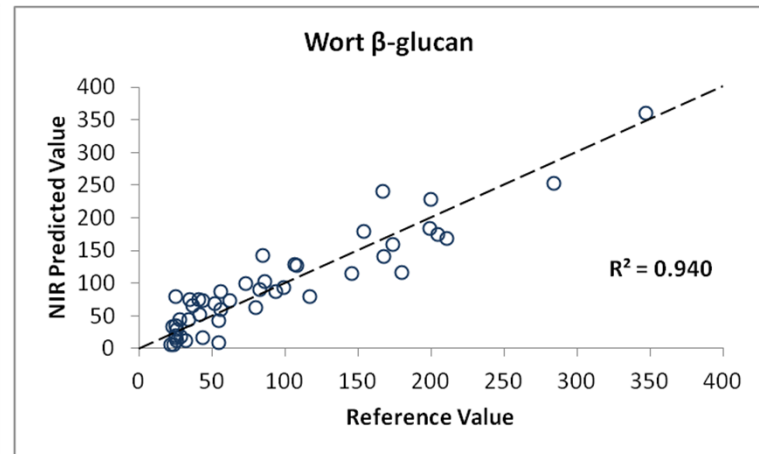
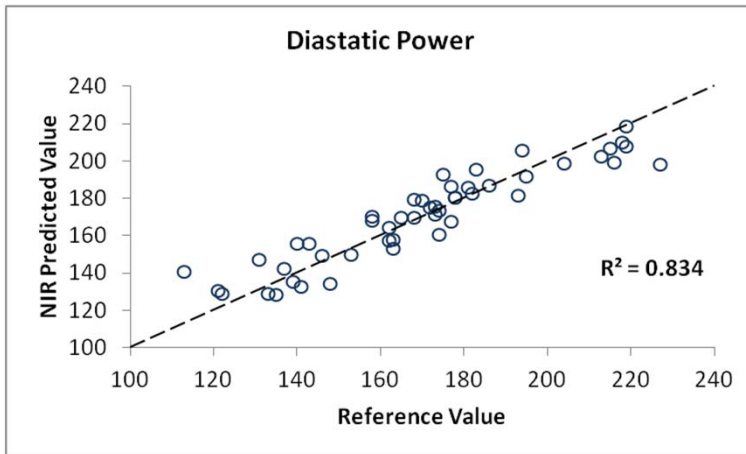
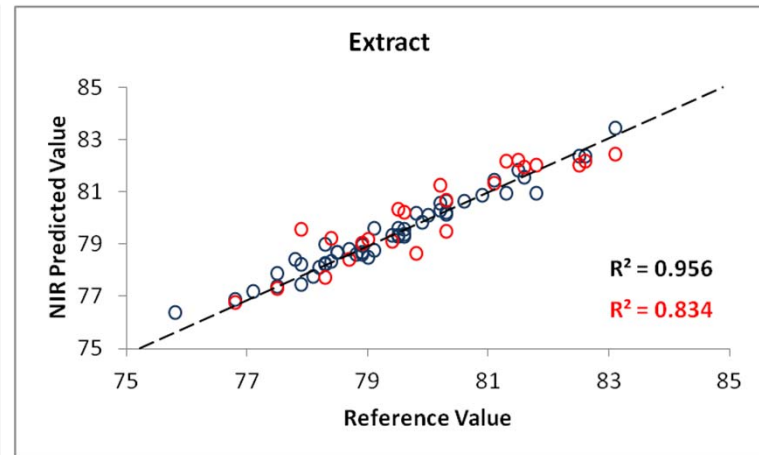
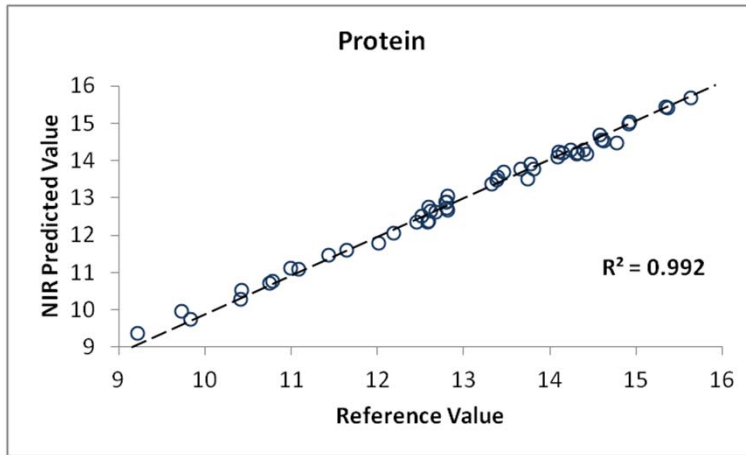
This approach has been used by barley breeders for screening breeding lines with different degree of success.

# Standard Error of NIR Calibrations Developed by Different Researchers

For Malt Analysis						
	Halsey England 1987	Munk Denmark 2000	Panozzo Australia 2001	Fantozzie Italy	MacLead GRL Canada 2011	Li CMBTC Canada 2013
<b>Protein,%</b>	0.3	0.31			0.29	0.43
<b>Extract,%</b>		0.6	0.9	0.58	0.59	0.52
<b>Friability,%</b>	5.7	5.6		2.2	5.6	5.0
<b>Soluble protein,%</b>			0.3	0.13	0.2	0.25
<b>FAN, ppm</b>			17	6	10	12
<b>β Glucan, ppm</b>		118	165		158	63
<b>Diastatic power, °L</b>			20		16	11
<b>A-amylase ,DU</b>					7.0	5.6



# NIR vs. Reference



# Factors That May Affect Accuracy of Predicted Results

- Sampling error & sample preparation
- Reference error
- Reference method error (lab, operator, procedure)
- Operating environment
- NIR instrument (Spectral measurement, choice of data treatment, calibration techniques)

# Challenges for NIR Methods

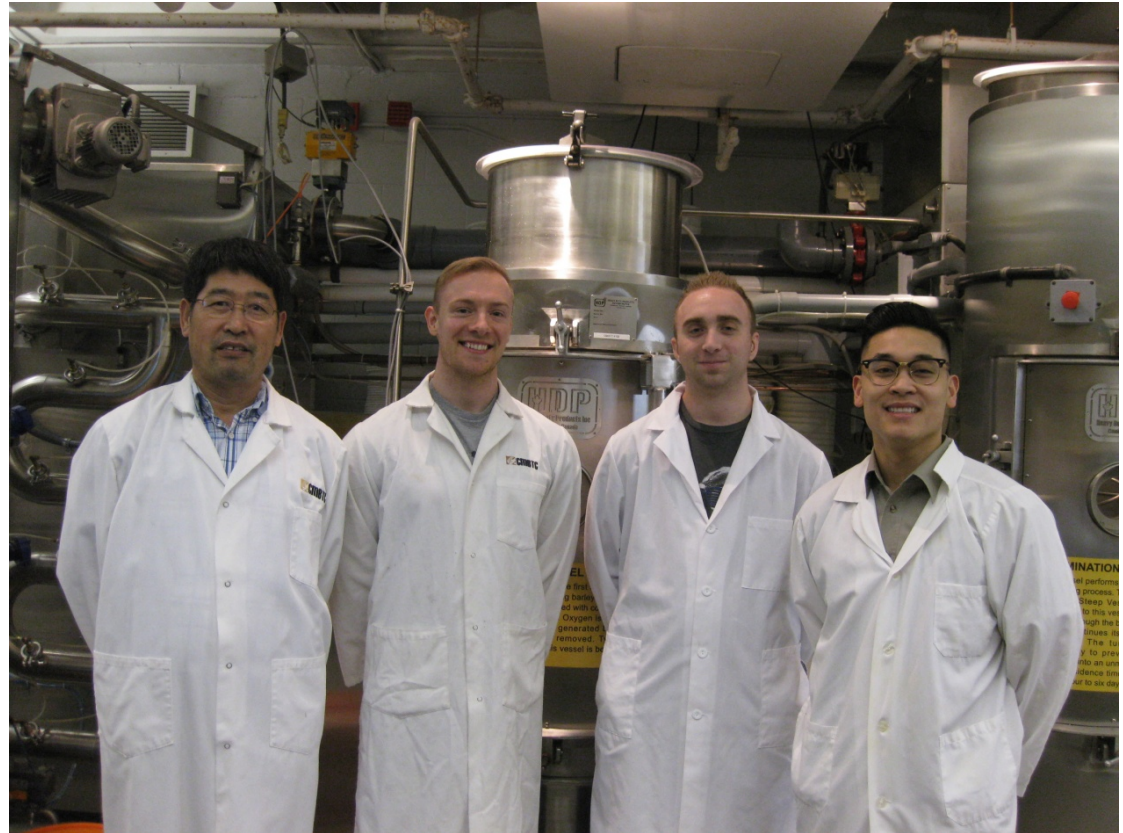
- Creating database (60-1000) & data sharing
- Developing accurate and robust calibrations
- Maintaining Calibration
- Uniformity across NIR units (different models and manufacturers)
- Standardized calibration evaluations
- Sharing calibrations (Legal roles and regulations)
- Agree in the reference methods
- **Acceptance by your customers**

# Discussion

- Will a NIR instrument be the solution to our production quality control and other analytical problems?
- Can NIR instruments provide maltsters with a complete malt analysis with an acceptable accuracy?
- Is it simple enough for someone without the technical skill to operate?

# Acknowledgements

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Yueshu Li, Adam Franczyk, Ian McCaig, Aaron Onio

# Malt Academy



Next 2-week Malting  
Program

Aug. 25th – Sept. 5<sup>th</sup>, 2014

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*The Science of Beer*