NIRS – Getting started

US Dairy Forage Research Center

2004 Consortium Annual Meeting

Terminology

NIR = Near Infrared

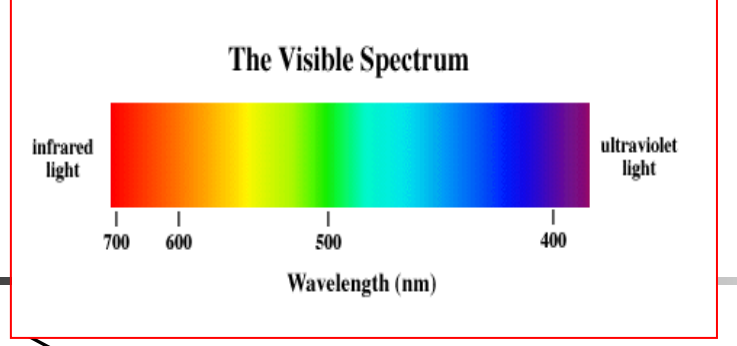
or

NIR = Near Infrared Reflectance

NIT = Near Infrared Transmittance

History

1800	The First NIR Spectrum recorded (Herschel)
1950-1960	Potential of NIR quantitative analysis was recognized (Kaye)
1960s	Research program at USDA (Norris) for NIR analysis of agricultural commodities
1971	First Generation of NIR Instruments - Reflectance
1975	Second Generation of NIR Instruments - More Stable Electronics and improved Optics
1977-1978	Third Generation of NIR Instruments - Microprocessors, Small Computers
1982-1983	Fourth Generation of NIR Instruments – Scanning Monochromators
1980s	Principal components calibration techniques introduced
1987	Fifth Generation of NIR Instruments - Transmittance
1990s	Nonlinear calibration methods (Local, ANN)



NIR MIR FIR

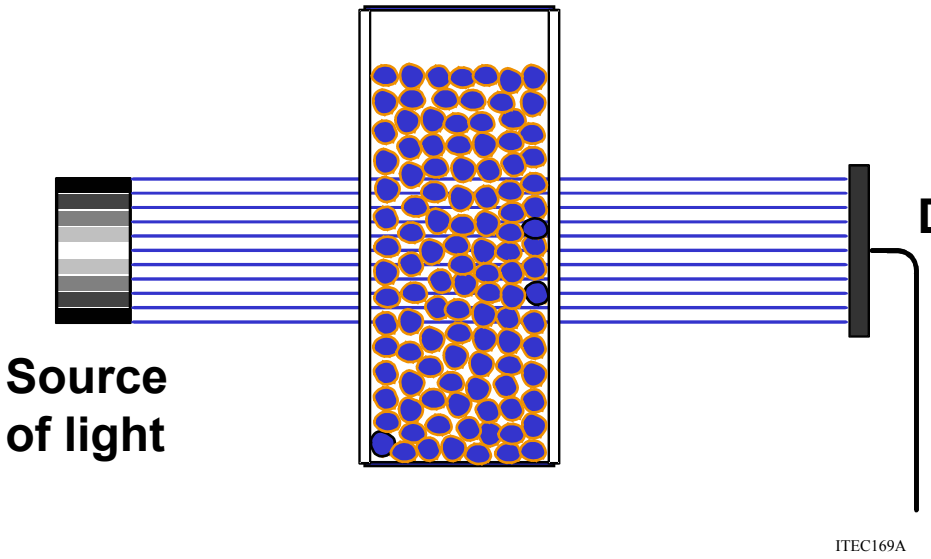
Gamma X-rays UV Visibile Infrared Microwave Radio

Region	Characteristic	wavelenght Range (nm)
Near Infrared (NIR)	Overtones, Combination	700-2500
Middle Infrared (MIR)	Fundamental vibration	2500-5x10^4
Far Infrared (FIR)	Rotation	5x10^4-10^6

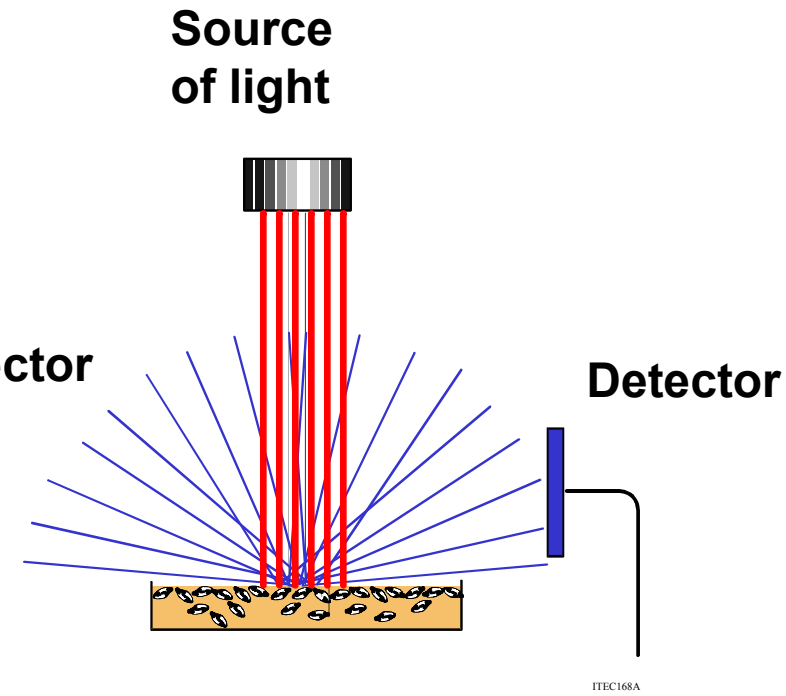
NIT NIR

700 1100 2500

Trnsmission/Reflectance

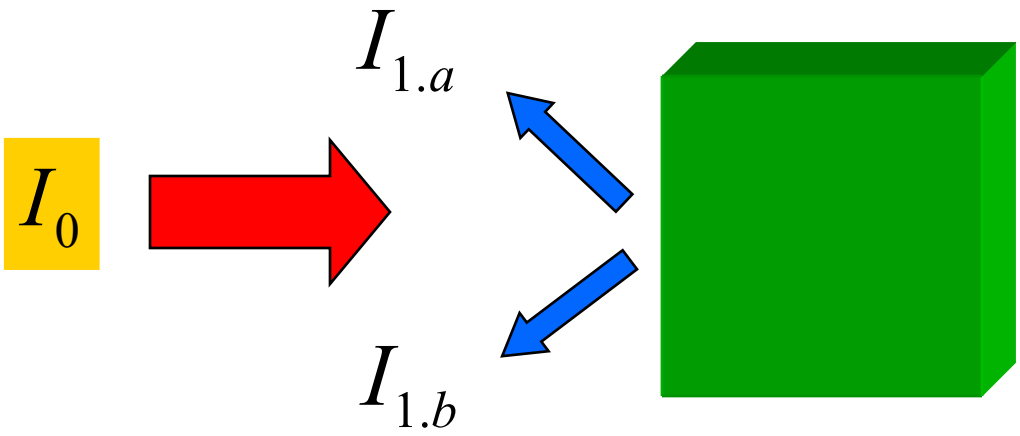


Trasmission (NIT)



Reflectance (NIR)

Absorption units



$$\text{Reflect\_(R)} = \frac{I_{1a} + I_{1b}}{I_0}$$

$$Absorption = 1 - R$$

$$Absorbance\_Units(AU) = \log\frac{1}{R}$$

$R = 0.01$

$AU = 2$

NIR absorption

Absorbance is mainly due to Hydrogen bonds

- CH

- OH

- NH

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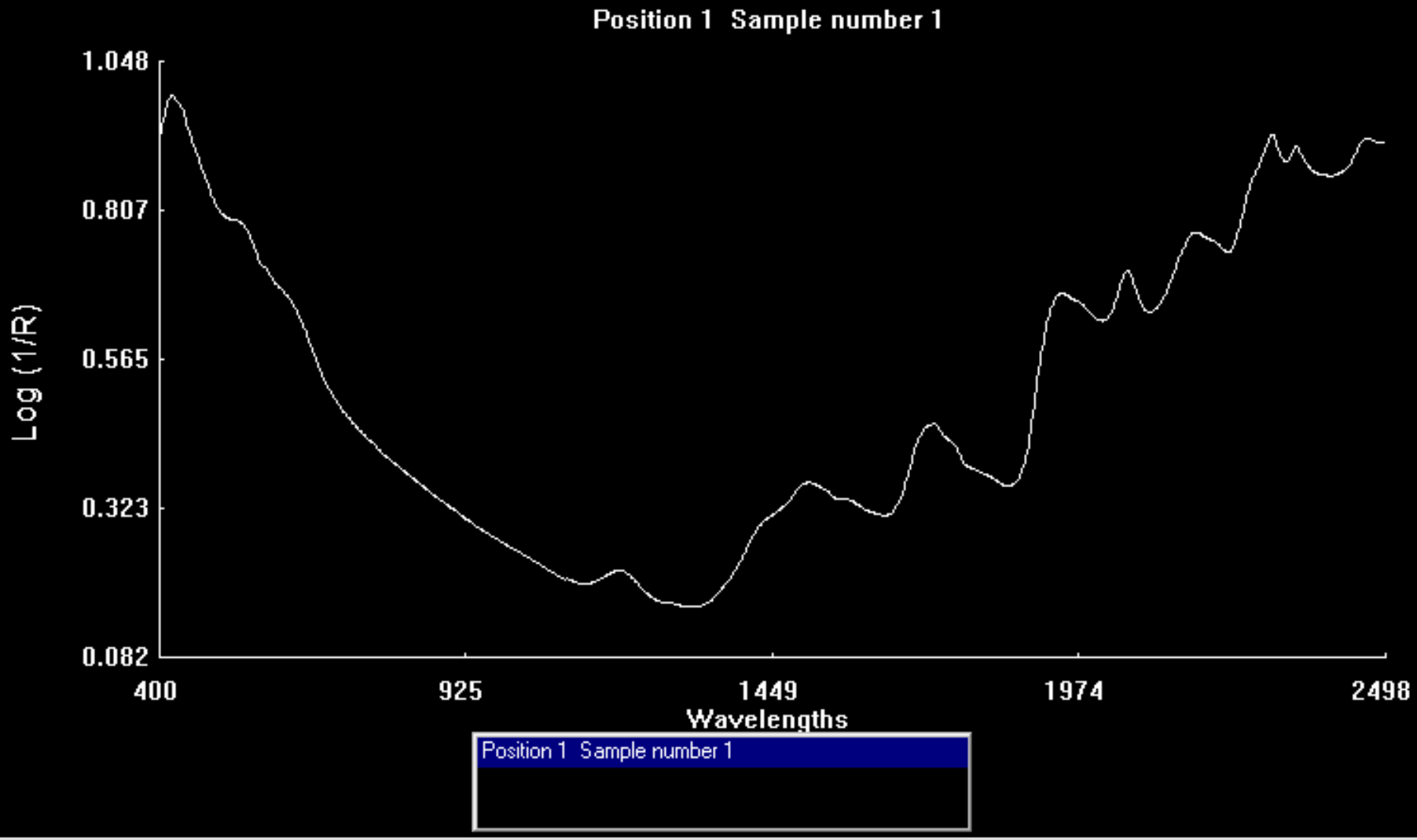
File Options Window Help

Percent Complete:

Cursor off | Zoom off | Plot All | Rewind | Clear | Next | Close | Exit



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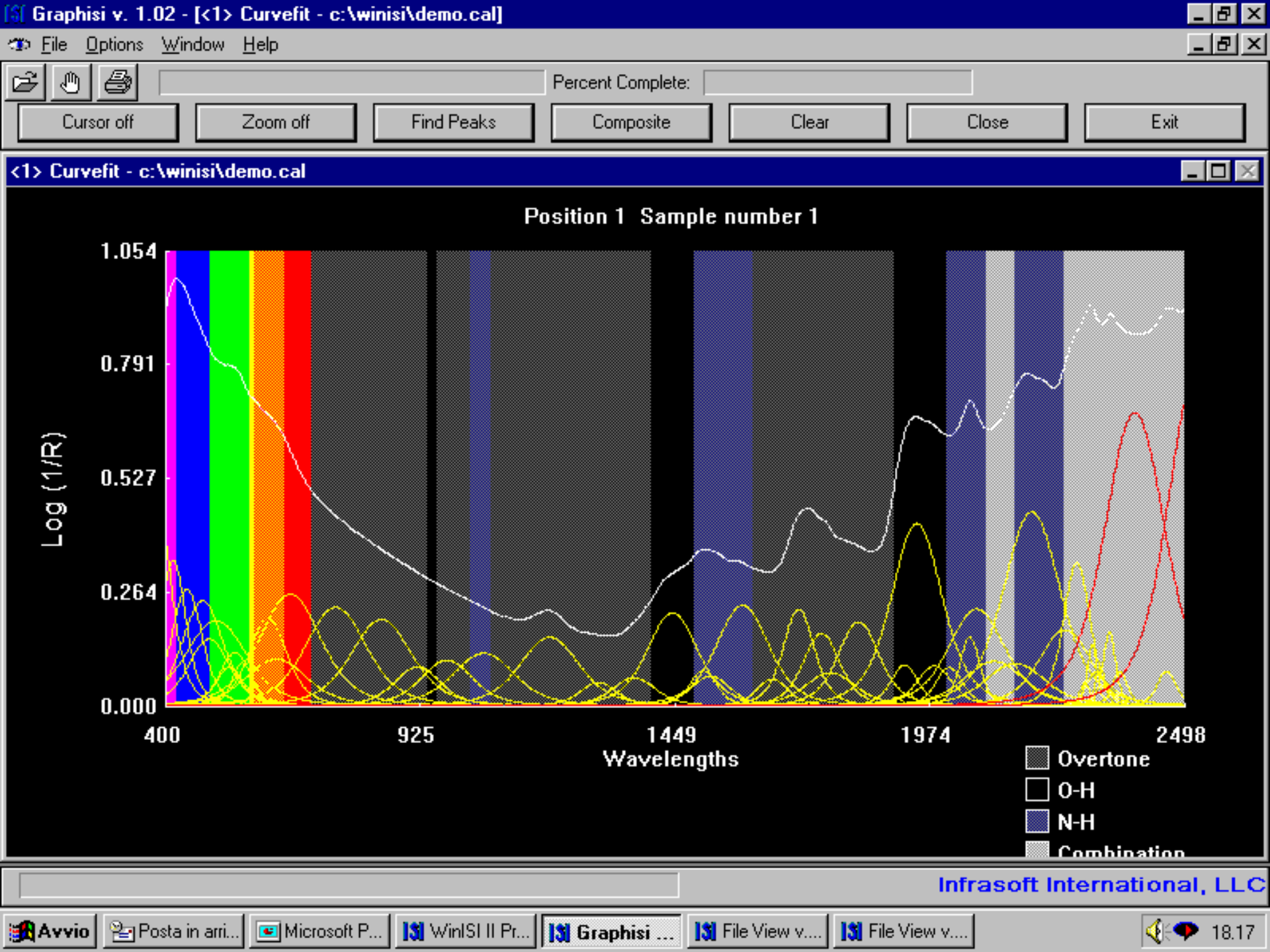
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Percent Complete:
Cursor off
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Composite
Clear
Close
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<1> Curvefit - c:\winisi\demo.cal
Position 1 Sample number 1
1.054
0.791
0.527
0.264
0.000
Log (1/R)
400
925
1449
1974
2498
Wavelengths
Overtone
O-H
N-H
Combination
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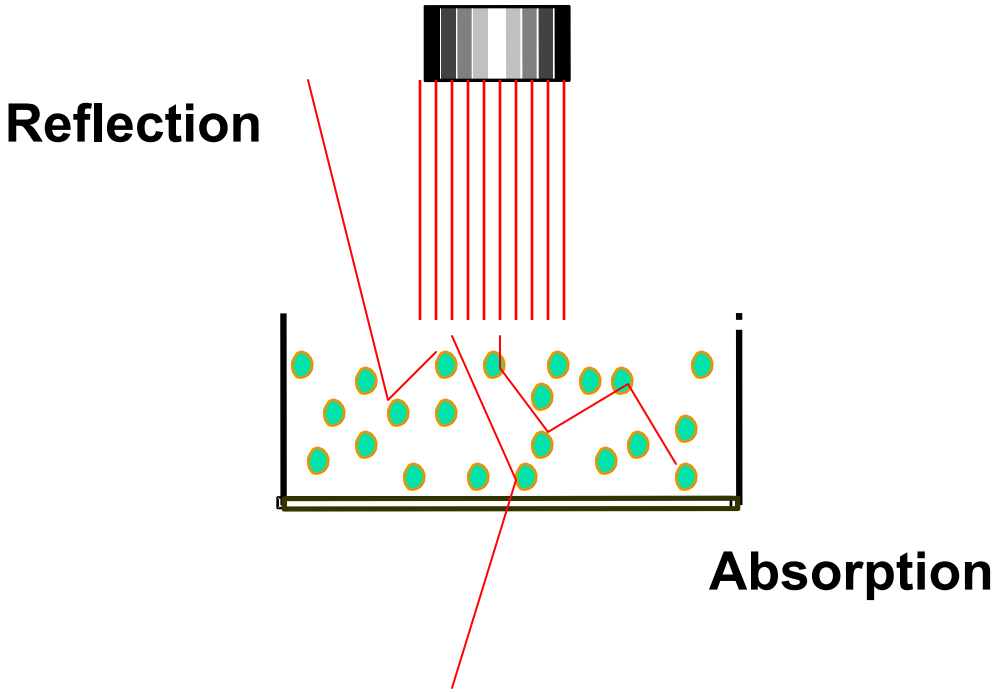
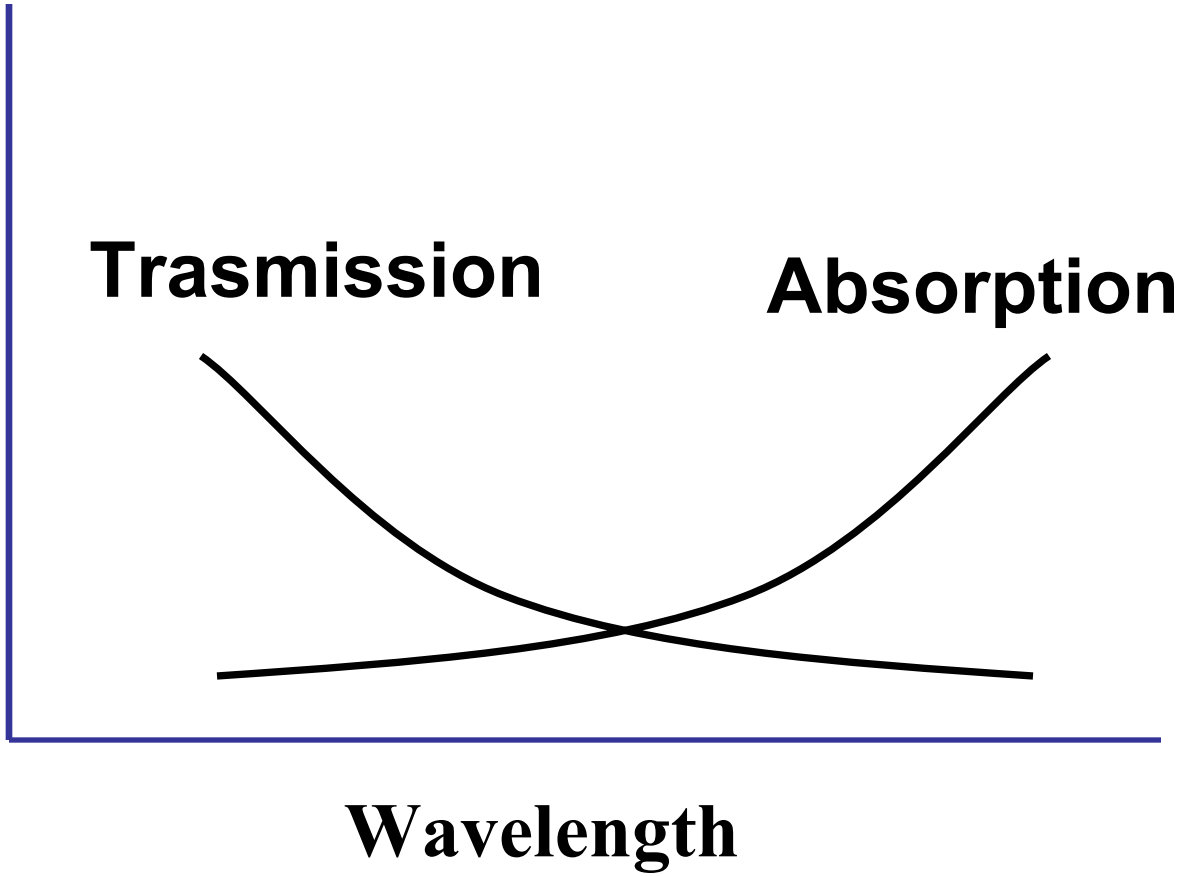
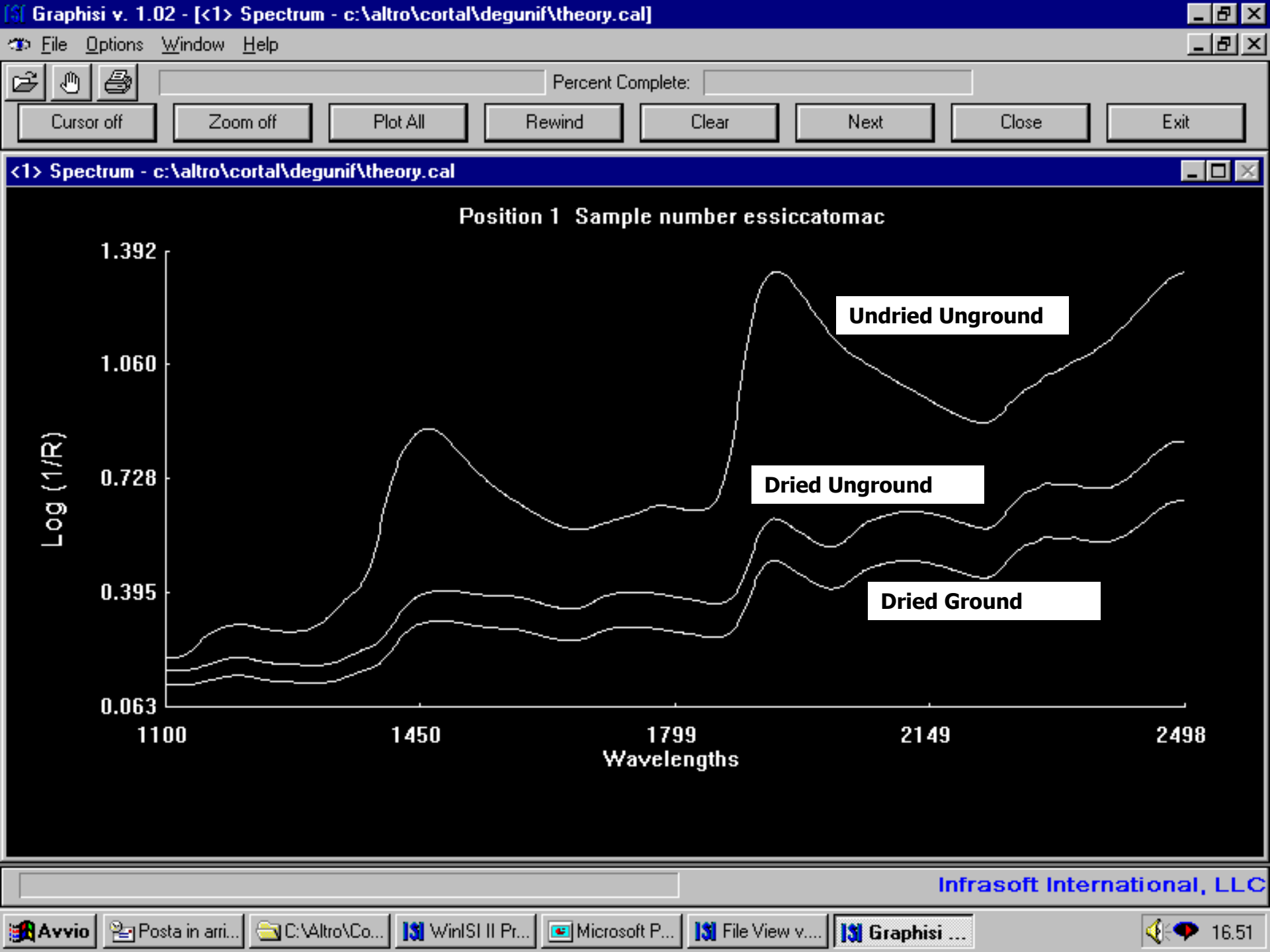
Light - Matter interaction



Light - Matter interaction




Graphisi v. 1.02 - [<1> Spectrum - c:\altro\cortal\degunif\theory.cal]
File
Options
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Position 1 Sample number essiccatomac
1.392
1.060
0.728
0.395
0.063
Log (1/R)
1100
1450
1799
2149
2498
Wavelengths
Undried Unground
Dried Unground
Dried Ground
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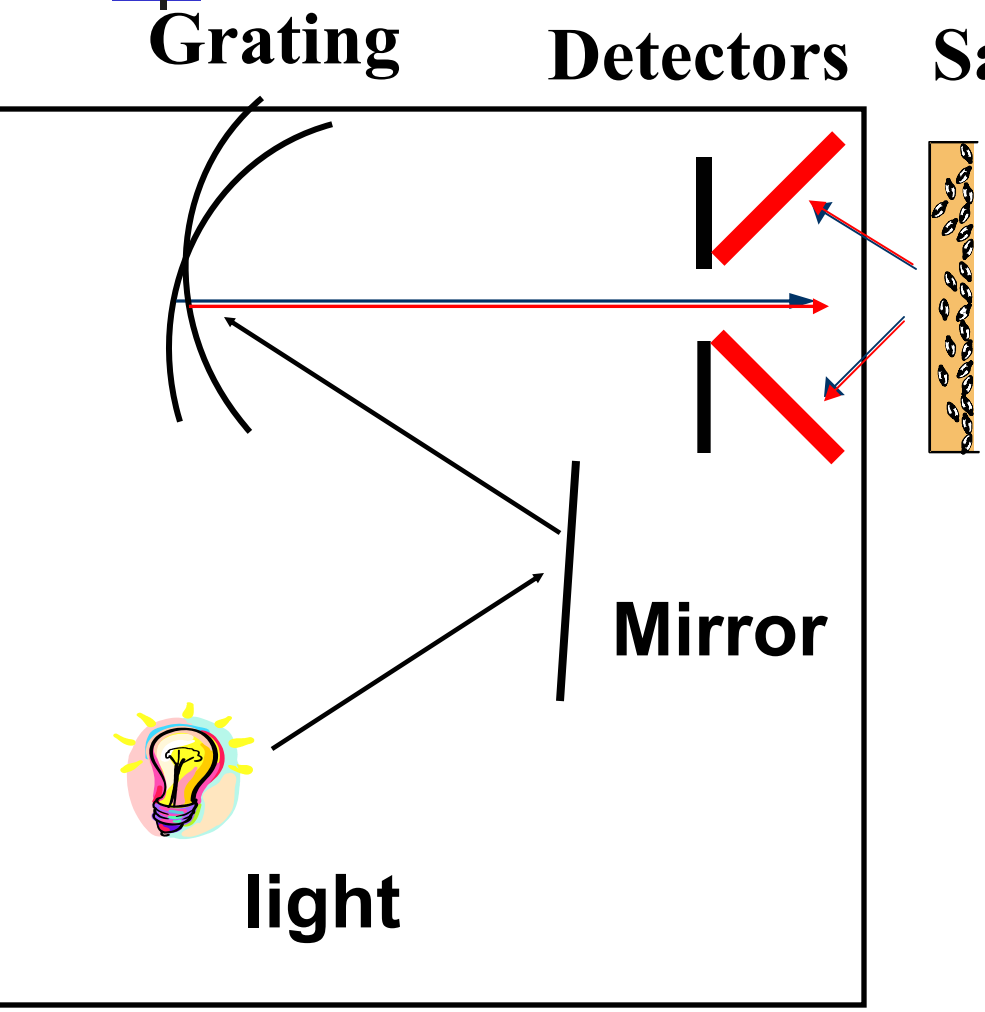
Foss NIRSystem 5000-6500

Lab instrument

The most used instrument in agriculture

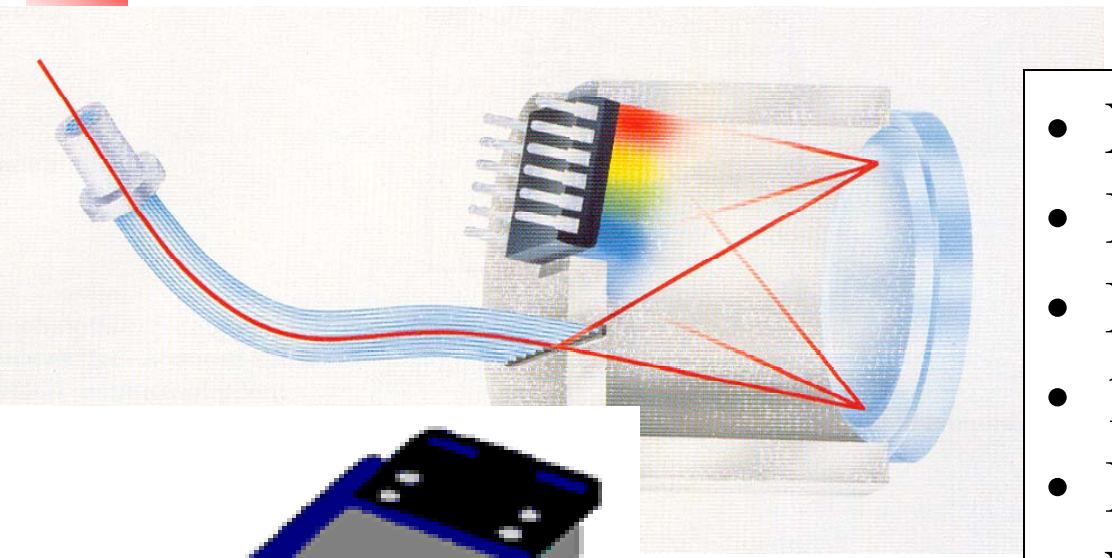
There are several Forage and /or Feed Network based on this instrument

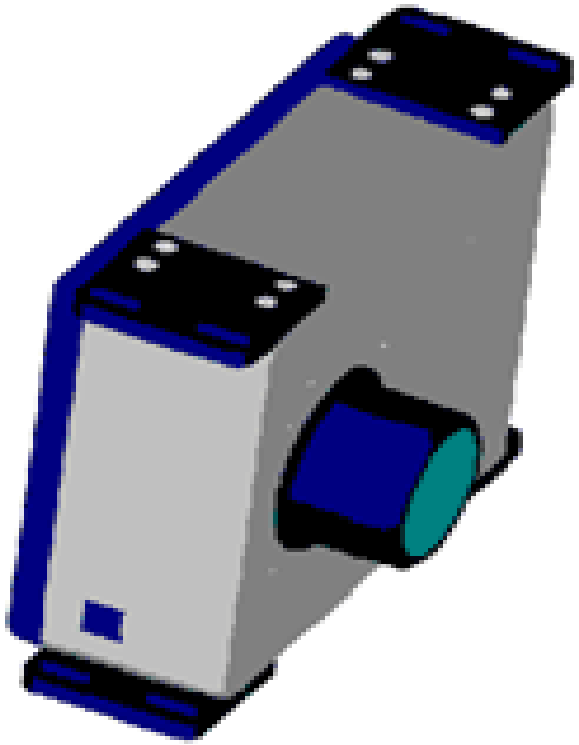
Foss NIRSystem 5000-6500



- Moving parts
- Pre-dispersive
- PbS detectors
- Slow scanning (1 sec)
- Highly accurate
- 400-1098; 1100-2498nm
- Every 2nm

Zeiss - Corona NIR 45





- **NO moving parts**
- **Post-dispersive**
- **InGaAs detector**
- **128 diodes**
- **Fast scanning (10 ms)**
- **Very accurate**
- **900-1700nm**
- **Every 6nm**

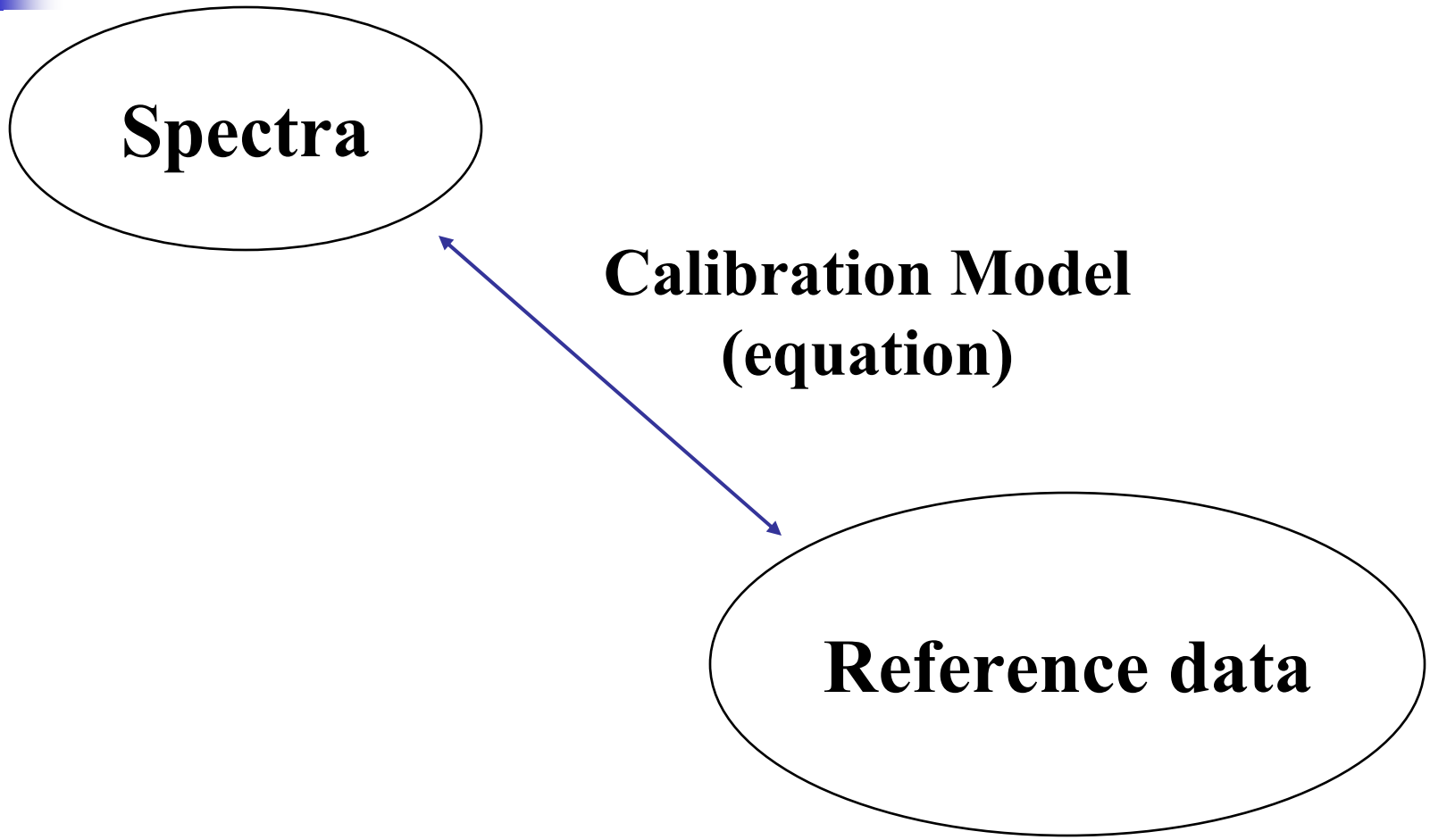
Foss NIRSystem 5000-6500

- **Diagnostics procedures:**
  They are required to make sure all of the parts are working properly
  - **Weekly diagnostics**
  - **Daily check cell**
- **Standardization procedures**
  - **Sealed cups with different products**
  - **Repeated periodically (once a year)**

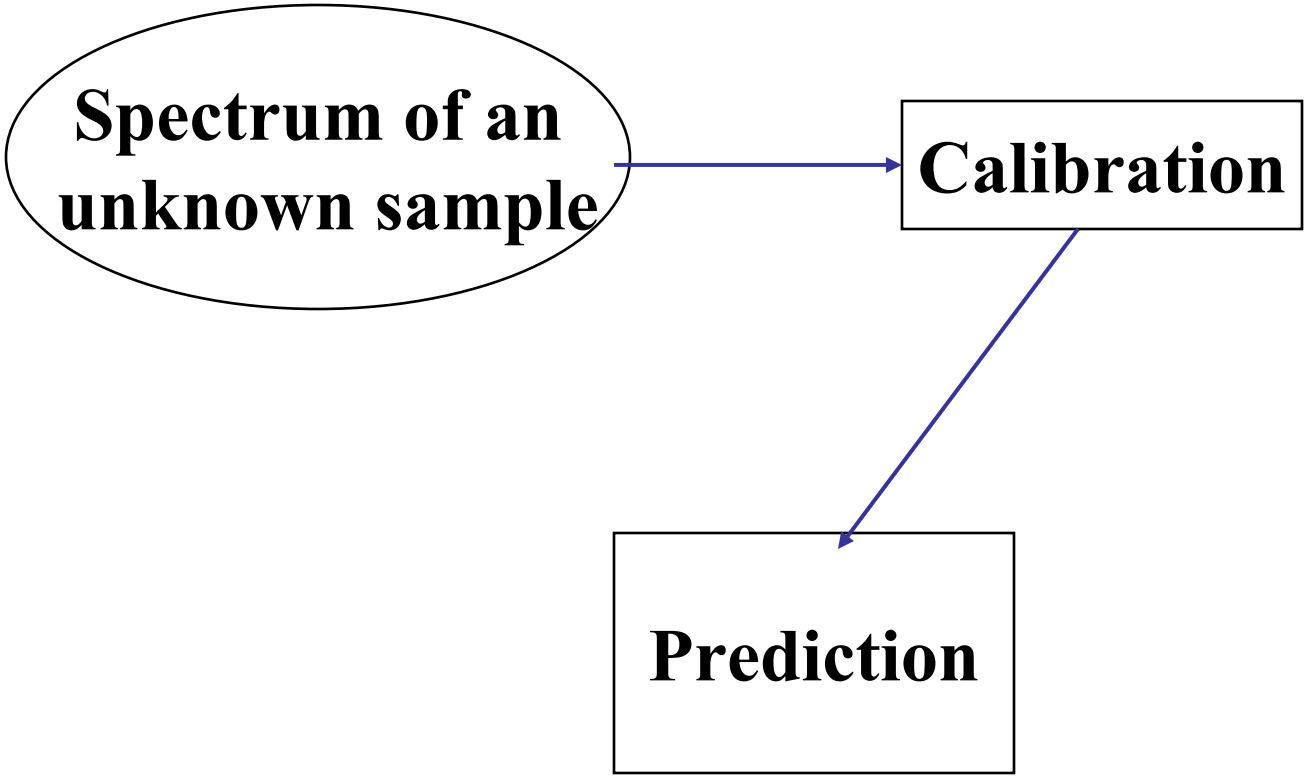
Zeiss - Corona NIR 45

- **Diagnostics procedures:**
  There are no diagnostics. No moving parts reduce variation in performances
  - **Daily check cell? We think it would be necessary to ensure the instrument is working properly**
- **Standardization procedures**
  - **There are no procedures**
  - **Solved by calibration**

What is a Calibration?



Use of a Calibration



Routine Analysis

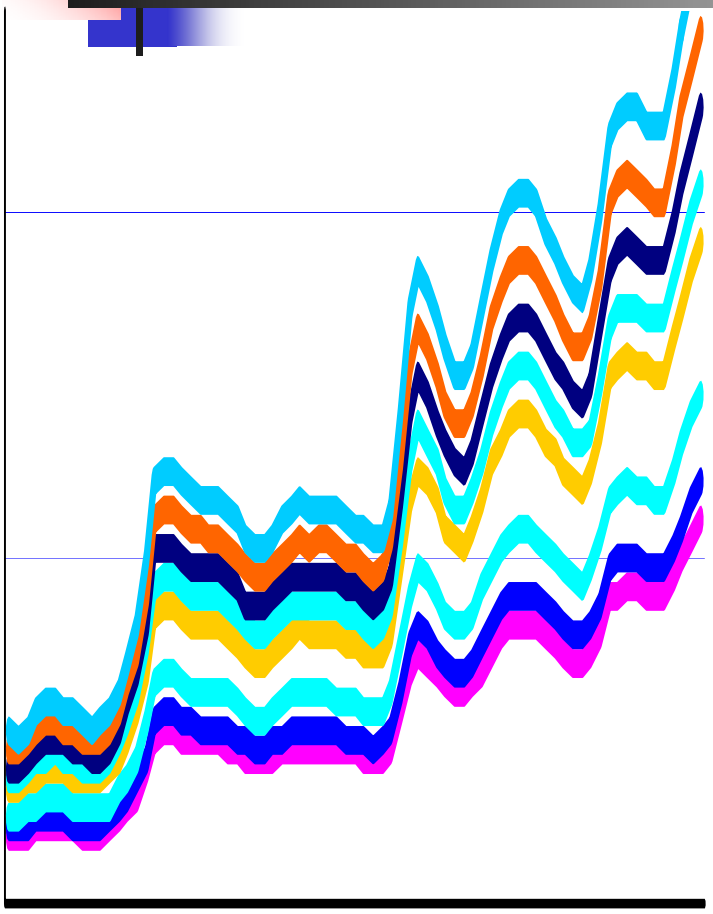
Sample

SPECTRUM

	DRY MATTER	AS IS	GH	T
PROTEIN	51.42	46.28	1.25	2.13
FAT	1.96	1.76	1.25	2.13
FIBER	5.4	4.86	1.25	2.13
DM	100.00	90.00	1.25	2.13
MOISTURE	0.0	10.00		

0.04 0.09 0.14 0.16 0.26 0.54 0.55 .059

What is Calibration?



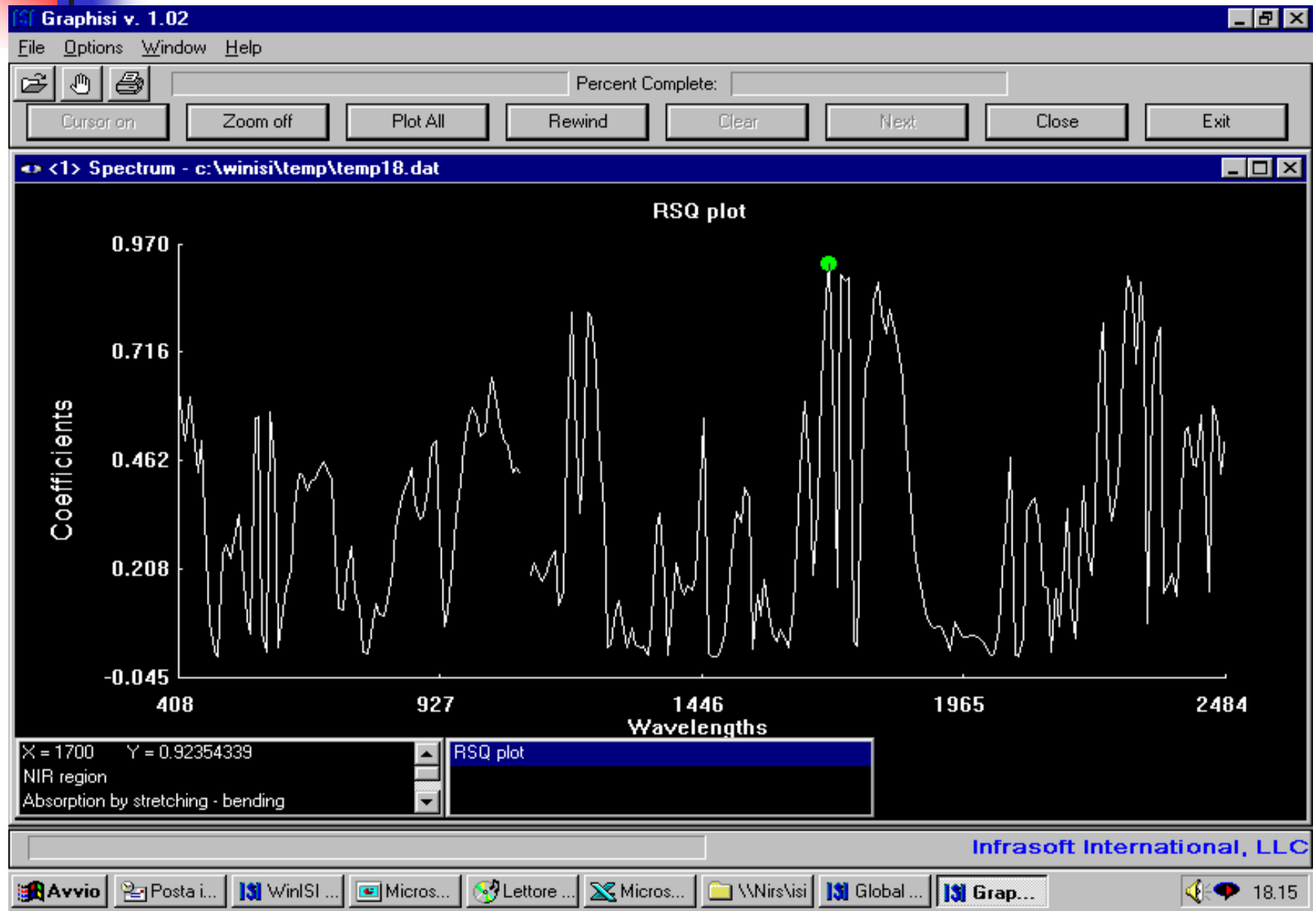
Y1	Y2	Y3…
12.8	97.4	43.2
11.5	96.2	45.6
10.7	94.3	48.0
10.5	96.7	45.2
9.7	98.3	47.9
8.4	96.5	44.1
7.5	95.0	46.7
7.2	93.2	41.4

Regression

$$Y=b0+b1x1+b2x2+\ldots+bnxn$$

Simple, multiple, multivariate, neural network

Simple and multiple Calibration



Simple and multiple Calibration

Step-up Regression Statistics

Input File	demo.cal	REP File	None
Validation File	None	Equation File	None
Math Treatment	1, 4, 4, 1	Number of variables	259
Scatter Corrected	SNV and Detrend	Downeight outliers	No
Constituent	FAT	Number of samples	65
Mean 10.487		Range 6.39 - 15.08	Standard deviation 1.587
Number of terms 1	SEC 0.442	R^2 0.922	

	Coefficient	Data Point	Wavelength	F
B(0) =	-0.382			
B(1) =	-291.073	648	1700	761.00

Stepwise Regression Statistics

Input File	demo.cal	REP File	None
Validation File	None	Equation File	None
Math Treatment	1, 4, 4, 1	Number of variables	259
Scatter Corrected	SNV and Detrend	Downeight outliers	No
Constituent	FAT	Number of samples	65
Mean 10.487		Range 6.39 - 15.08	Standard deviation 1.587
Number of terms 6	SEC 0.280	R^2 0.969	

	Coefficient	Data Point	Wavelength	F
B(0) =	3.439			
B(1) =	-45.387	832	2068	13.04
B(2) =	-149.161	944	2292	99.29
B(3) =	-134.486	142	688	23.70
B(4) =	-257.806	230	864	13.09
B(5) =	322.309	660	1724	52.40
B(6) =	-18.276	6	416	12.74

Population structure

Chemical variation

Botanical composition

Climatic areas

Years of production

Cultivars/hybrids

Harvesting methods

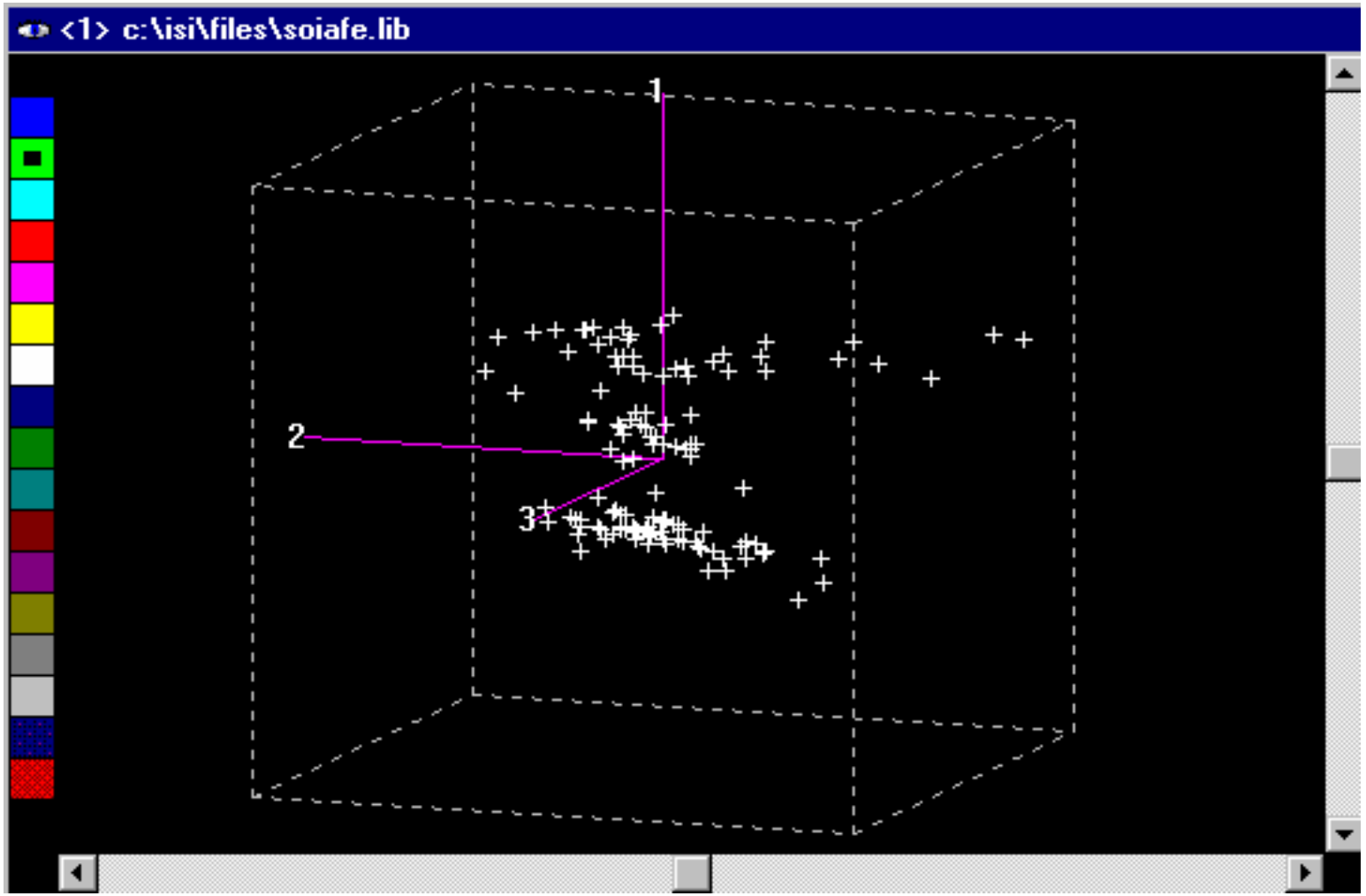
Population structure: How to built it

- **Our goal is to build an homogenueous distribution of samples which covers the variability of the product**

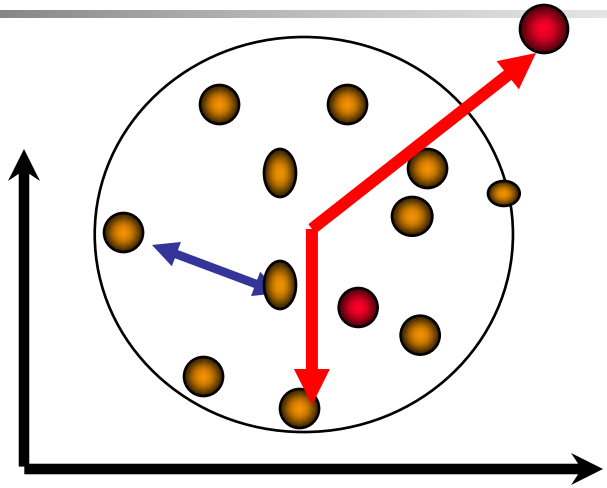
- **In commercial labs it is difficult to know the origin and history of samples analyzed.**

- **PCA and scores are the tools to use building a population based on NIR spectra.**

Principal components and population structure



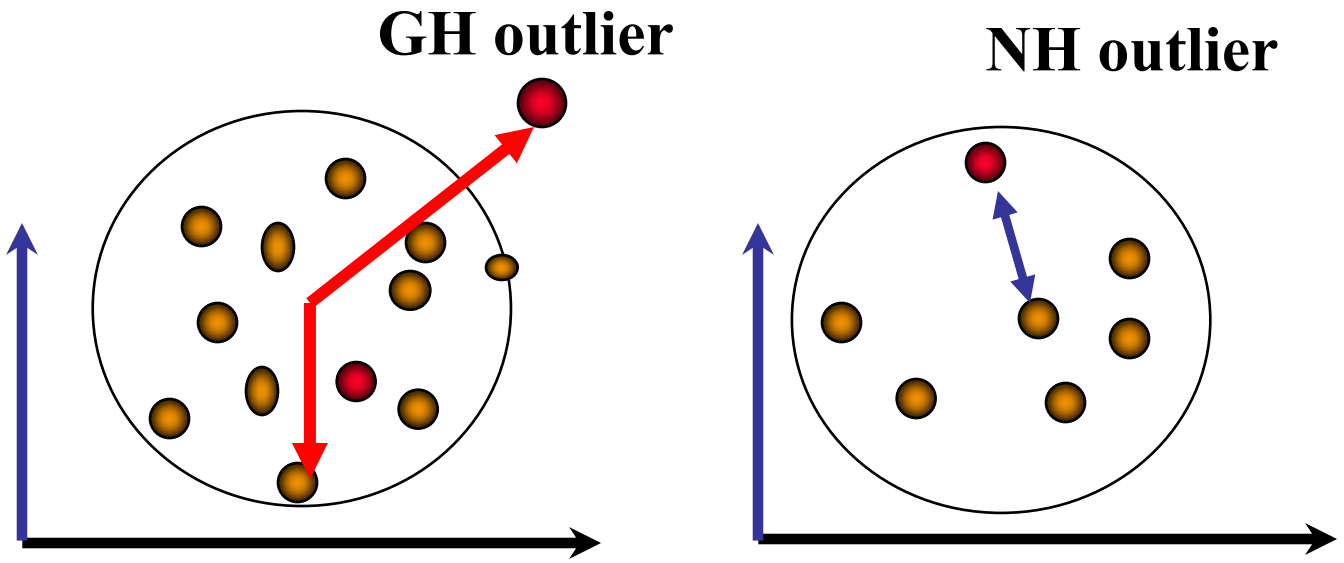
Population structure:How to built it



Global H number = distance from the population average (center) (maximum value=3.0)

Neighborhood H number = distance from the closest sample (value=0.6)

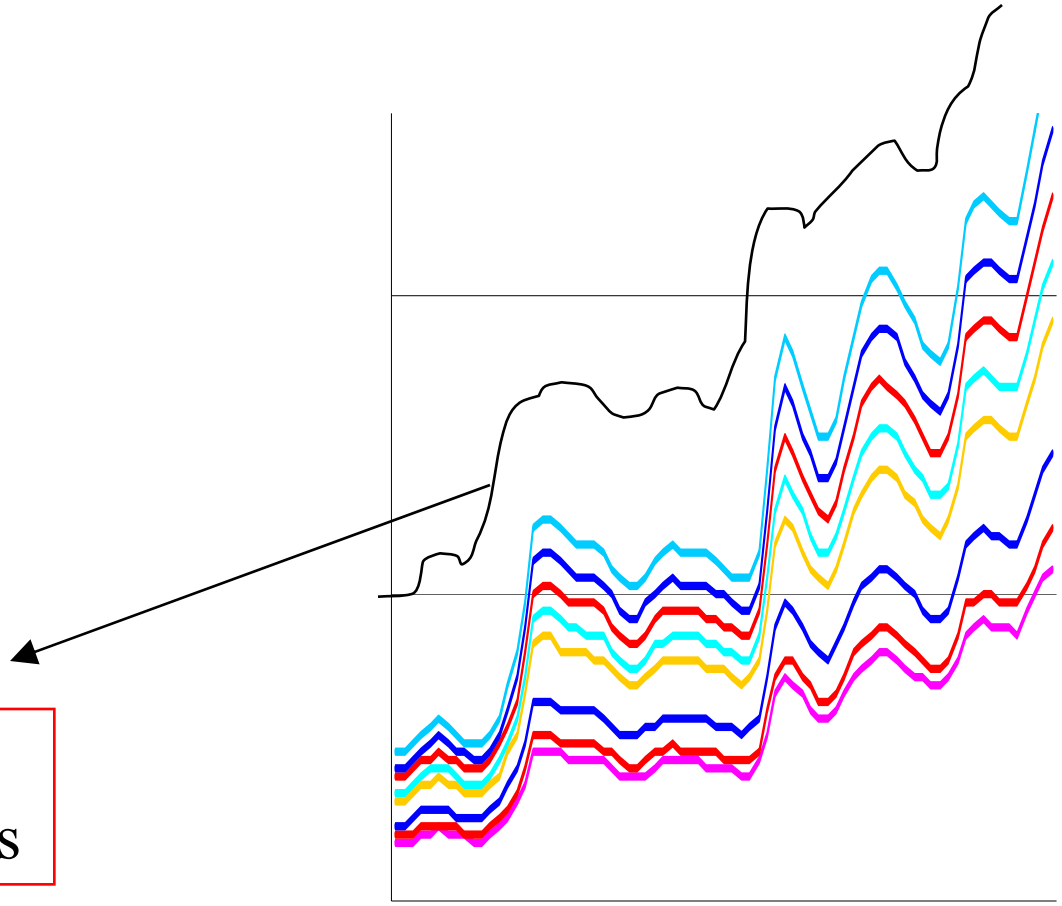
Determination of outliers samples



GH >3.0

NH >0.6

Building a Calibration



NH and GH **
Unrealiable predictions

Wha's next in NIRS

- New hardware
- New calibration procedures
- New standardization procedures
- Undried, unground feeds and forages

Undried unground analysis