

«*Un autre regard sur votre process* »

# La spectrométrie dans le proche infrarouge appliquée au suivi de processus de transformation

**CRA-W – Gembloux**

**Département Qualité des Productions agricoles**

*Laboratoire de Spectrométrie*

**Après-midi d'étude**

**Jeudi 16 mars 2006**



**Centre wallon de  
Recherches agronomiques**



*Ministère de la  
Région Wallonne.*



Centre wallon de Recherches agronomiques - **Département Qualité des productions agricoles**  
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dptqual@cra.wallonie.be - <http://cra.wallonie.be>



Centre wallon de Recherches agronomiques



RÉGION WALLONNE

- **PRESENTATION OF CRA-W**
- **NIR theory**
- **HISTORY & NIRS APPLICATIONS AT CRA-W**
- **NETWORKING**
- **CHEMOMETRICS**





# Walloon Agricultural Research Centre (Gembloux)

- **Founded in 1872**
- **Public Interest Organisation (OIP)**
- **Under the Regional Government of Wallonia.**

**<http://www.cra.wallonie.be/>**



# Walloon Agricultural Research Centre

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## 7 Departments:

1. Biotechnology
2. Crop production
3. Biological Control and Plant Genetic Resources
4. Pesticide research
5. Agricultural Engineering
6. Animal Production and Nutrition
- 7. Quality of Agricultural Products**

## + 2 units

1. Agricultural Systems (in Libramont)
2. Biometry, Data Management and Agrometeorology

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<b>Personnel: ~450, Scientists: ~120</b>
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## 3 laboratories :

- **Microbiology & Molecular biology**  
*Dr Gilbert Berben*
- **Analytical chemistry & Technology**  
*Dr Georges Sinnaeve*
- **Physical methods**  
*Dr Vincent Baeten*

---

**50 employees - 15 scientists**



## Physical methods

- Near Infrared Spectroscopy
  - Near Infrared Micro-spectroscopy
  - Hyperspectral Imaging Spectroscopy
- Mid Infrared Spectroscopy
- Raman Spectroscopy



# Near Infrared Spectroscopy

## Why NIR ?

- Fast
  - < 2 min/spl (→ sec)
  - multiple analyses (cheap)
- Simple to operate
  - short training
  - on-line
  - no sample prep. or reduced
- Simple to maintain
  - lamps, ...

## Drawbacks:

- Need of calibrations
- Lack of accuracy
- LOD >>



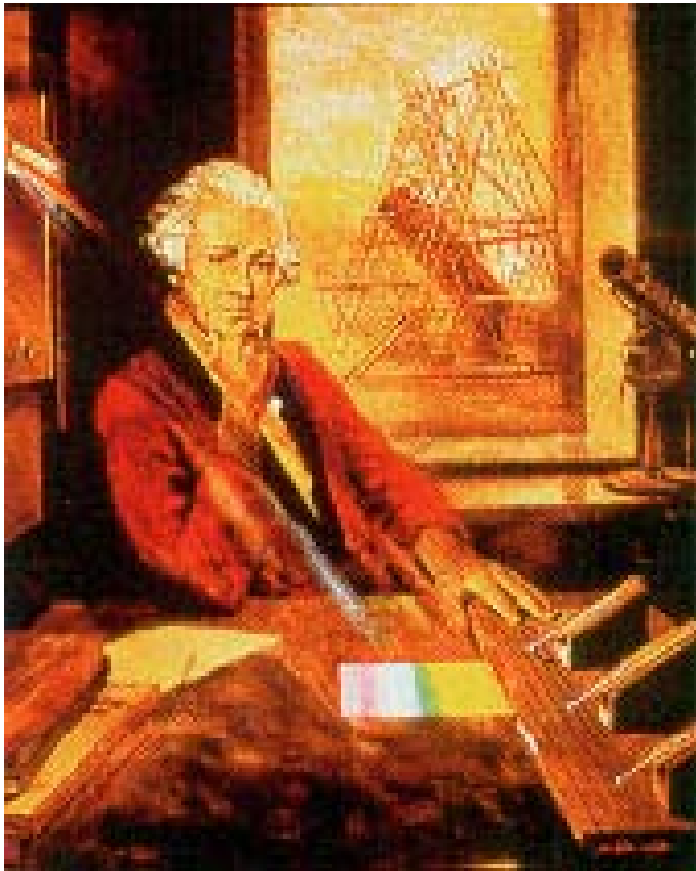
# Near Infrared Spectroscopy

## How does it work?



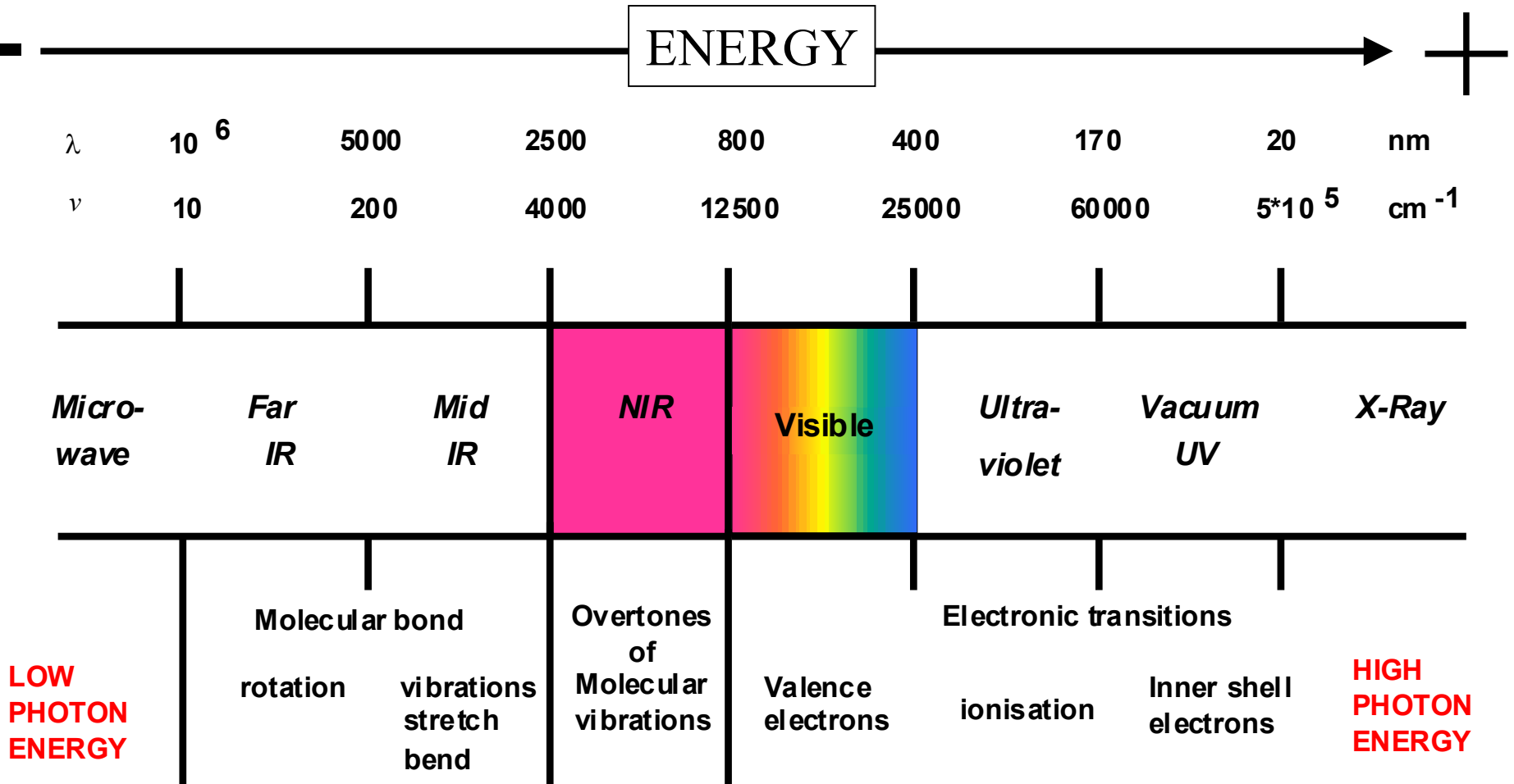


# Discovery of Near InfraRed Radiation




- 17 March 1800
- William Herschel, Astronomer Royal attempts to find out the spectral region responsible for heat formation in his telescope.
- The NIR is discovered.
- *Philosophical Transactions of the Royal Society* **90**:255-83

# The Electromagnetic Spectrum



$$\lambda \nu = c = 3 \times 10^8 \text{ m s}^{-1} \quad E_{\text{photon}} = h \nu \quad h = 6.6 \times 10^{-34} \text{ Js}$$


$$\lambda \nu = c$$

$$\text{WAVENUMBER (cm}^{-1}\text{)} = \text{FREQUENCY (Hz)}/100.C$$

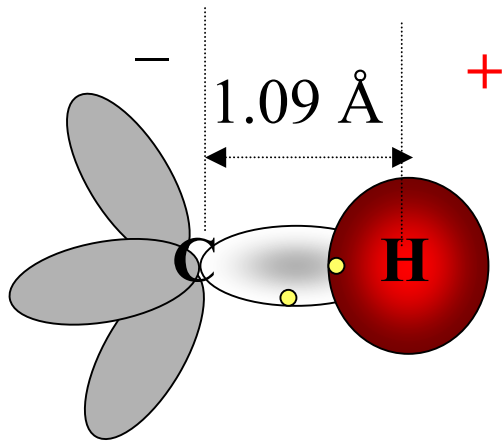
$$\text{Wavelength(nm)} = 10,000,000/\text{wavenumber(cm}^{-1}\text{)}$$

$$1\ 000\ \text{nm} = 10\ 000\ \text{cm}^{-1}$$

$$2\ 500\ \text{nm} = 4\ 000\ \text{cm}^{-1}$$



# NATURE OF THE COVALENT BOND

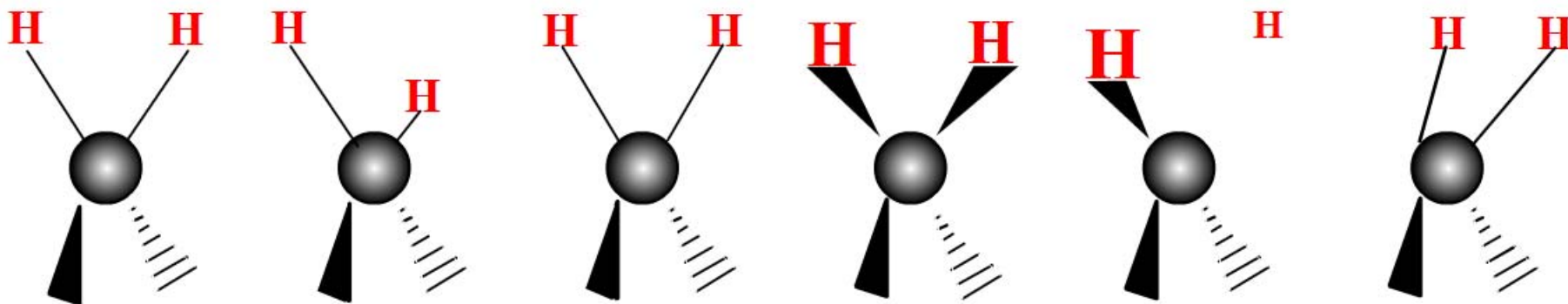


- Covalent bonds **SHARE** electrons between atoms in a molecule
- Bonds have **length, strength & direction unique to each pair of atoms**
- Bonds act like **springs** joining atoms
- Bonds **vibrate** at unique frequencies due to atomic **masses & ‘stiffness’**
- If vibration changes the **dipole moment** then bond can absorb **INFRARED photons**
- A **photon** of EXACTLY the right frequency is absorbed & excites the bond to a higher vibrational state

• Frequency = **qualitative** analysis: **IDENTITY**

• Amplitude = **quantitative** analysis: **AMOUNT**

# Vibrational Modes of the Methylene Group -CH<sub>2</sub> -



sym

stretching

antisym

⋮

scissoring

wagging

twisting

bending

rocking

2851

2919

1470

1176

inactive

725 cm<sup>-1</sup>

3.507

3.426

6.812

8.503

13.79 μm

1765 nm 1725 nm

1215 nm

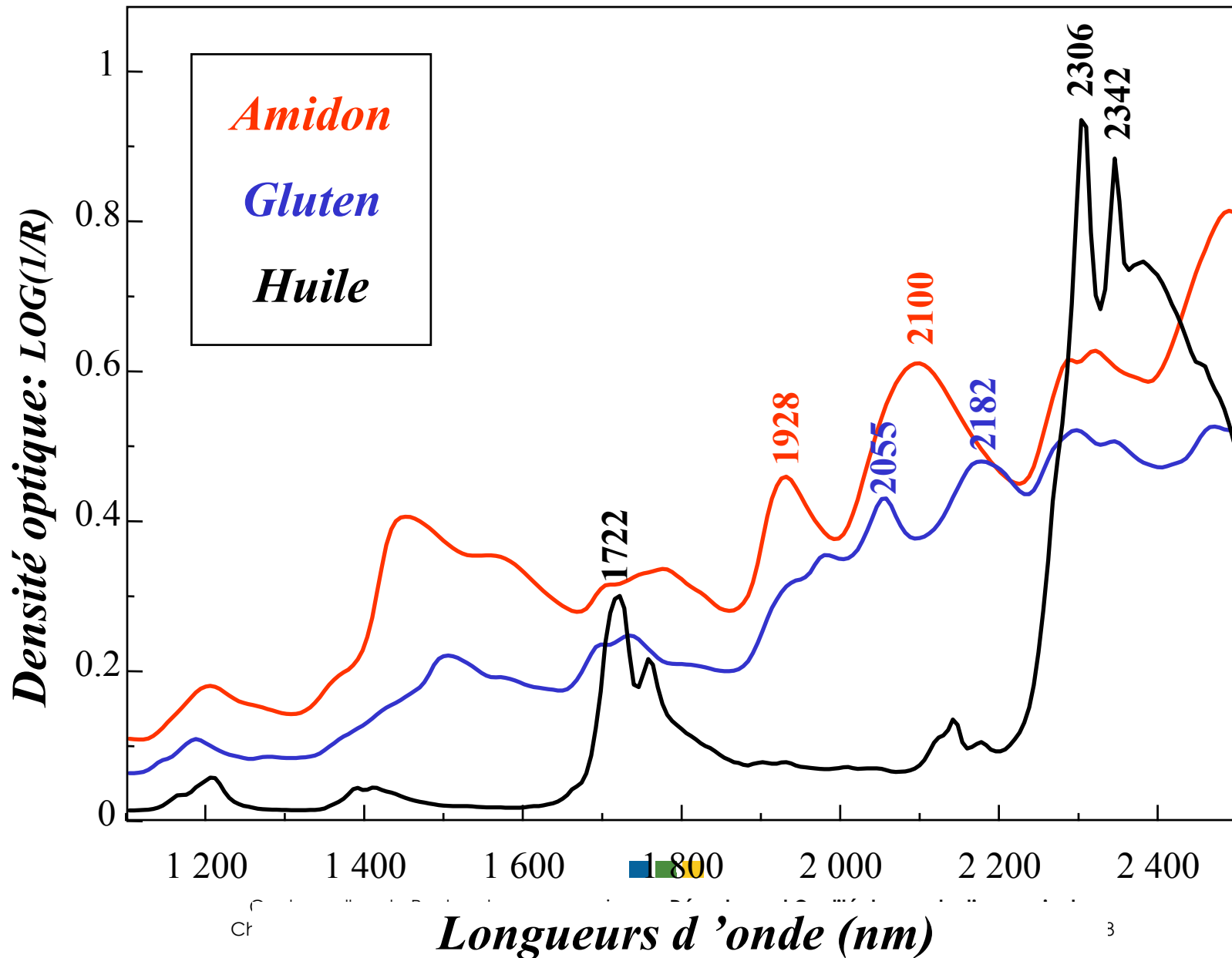
938 nm

913 nm

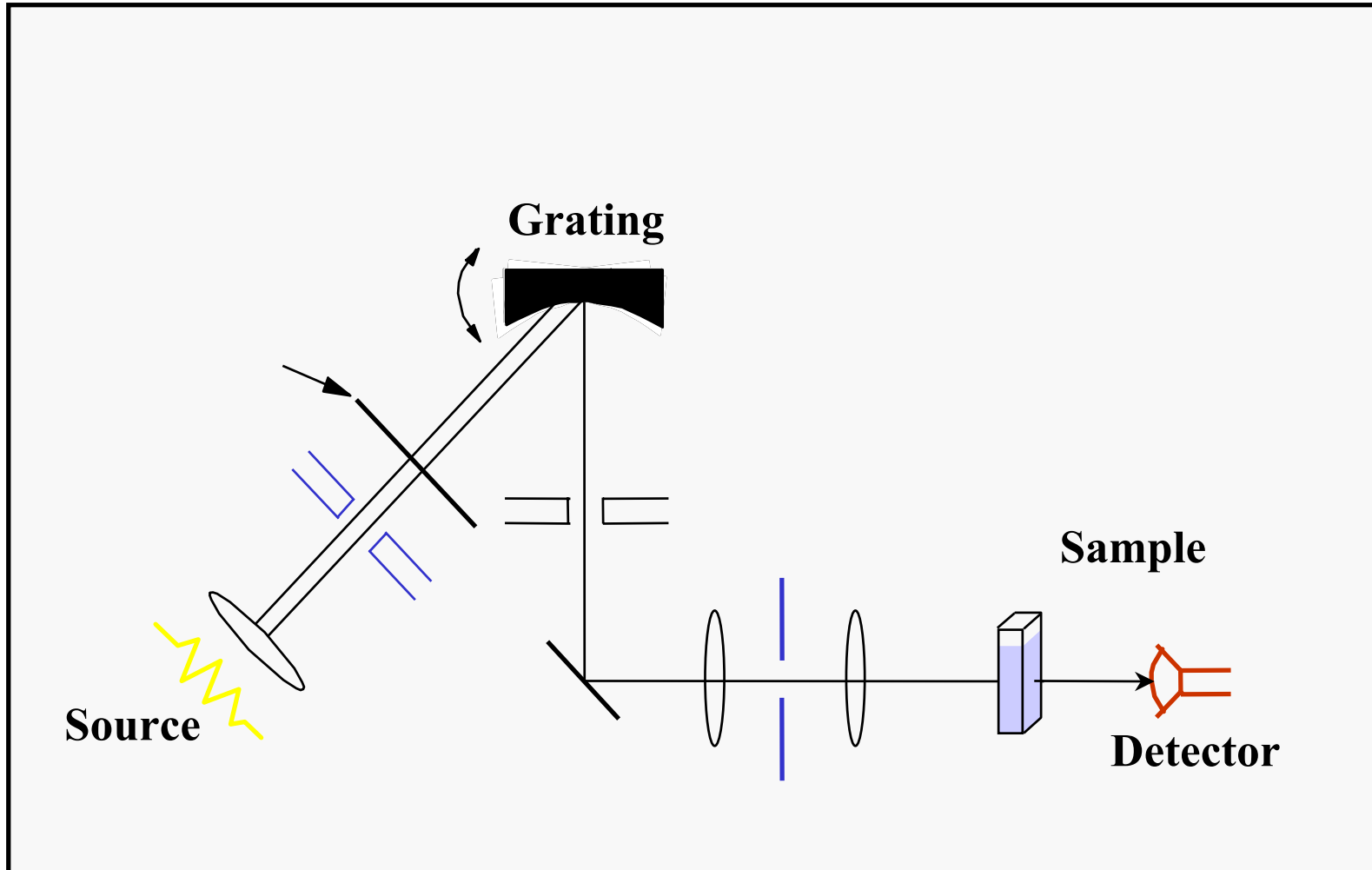
762 nm

746 nm

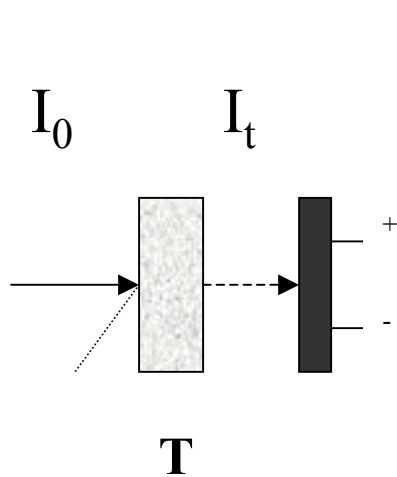
# Spectres de produits purs



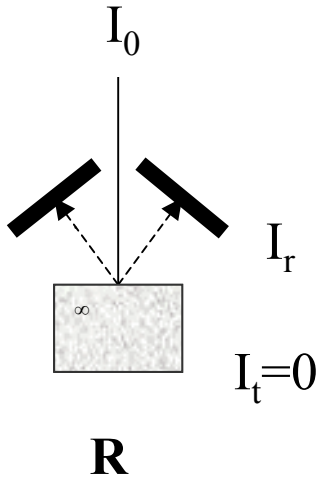
# Instruments



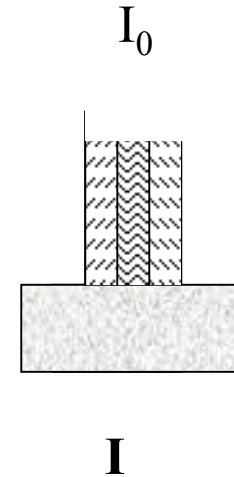
## SAMPLE PRESENTATION MODE



TRANSMISSION



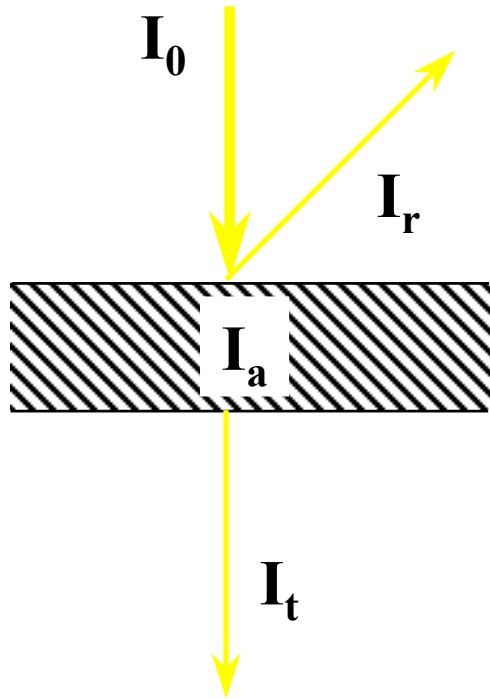
REFLECTANCE  
or transreflectance  
0-45° optics or  
integrating sphere



INTERACTANCE  
Fibre optic probe



# Instruments



***REFLECTION***

$$R = \frac{I_r}{I_0}$$

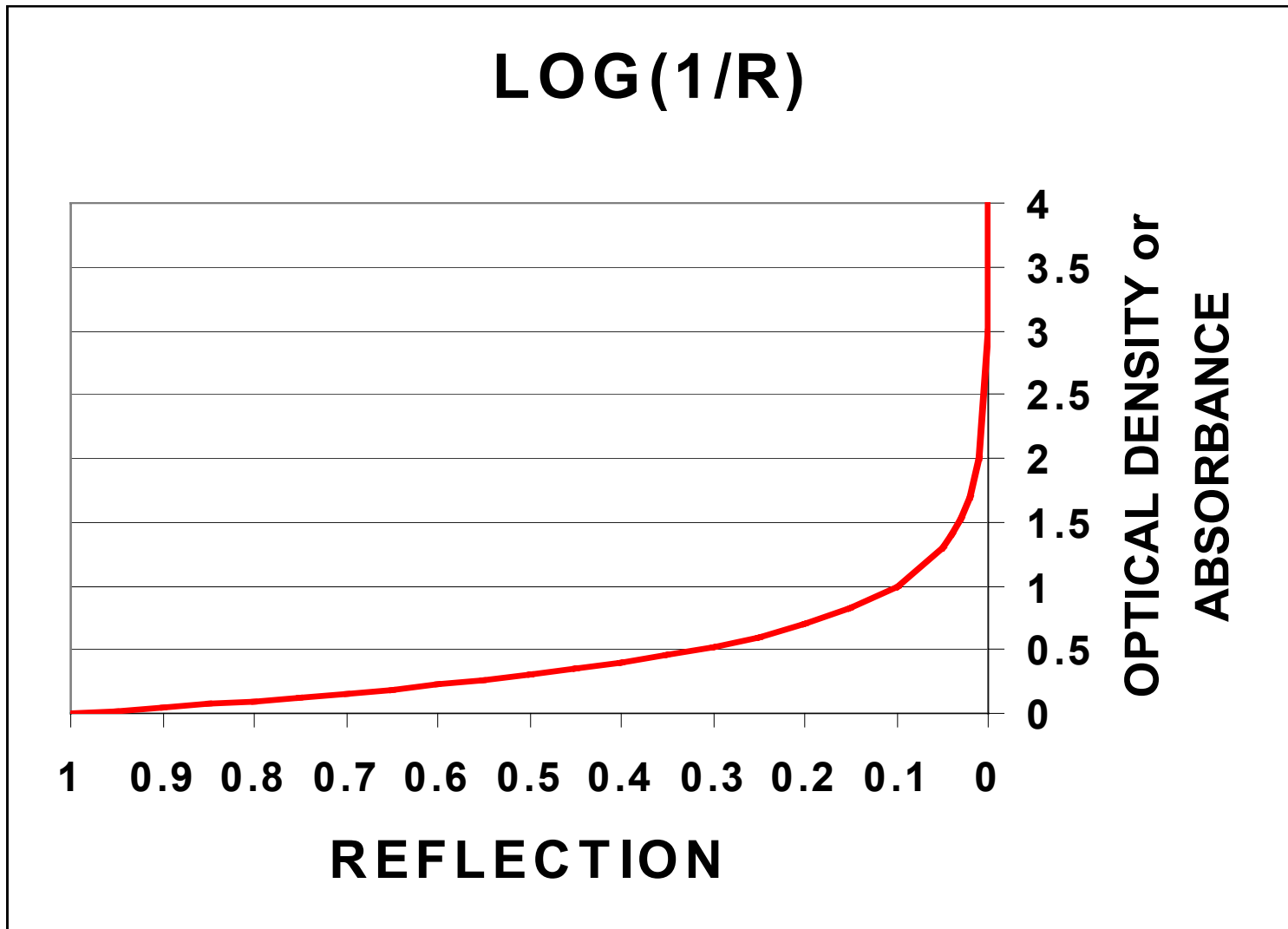
***TRANSMISSION***

$$T = \frac{I_t}{I_0}$$

***ABSORBANCE or OPTICAL DENSITY***

$$A = \text{Log}\left(\frac{1}{R}\right) = \text{Log}\left(\frac{1}{T}\right)$$





# Instruments

- **Filters (interferential filters)**
- **Monochromator : dispersive system (tilting grating)**
- **AOTF (Acoustic Optical Tunable Filter)**
- **LCTF (Liquid Crystal Tunable Filter)**
- **Interferometers (Michelson or polarization)**  
-----
- **Diode Array (fixed grating)**



# INSTRUMENT IMPROVEMENTS:

- Sources
- Optical components (laser)
- Detectors
- Electronics (communication)

## Sample presentation:

- large cups
- slurries
- liquids
- on-line (belts, pipes, ...)
  - fibre optics
  - remote scanning





# THE PAST



# NIR INSTRUMENTS – CRA-W

- 1976 R.Biston au CRA – Station de Haute Belgique
- 1979 Neotec FQA51 (*Feed Quality Analyser*)



# NIR INSTRUMENTS – CRA-W

- 1981 Neotec 6350 (*Research Analyser*) + Nova III

## New Instrumentations

>65 companies

Better noise,

More flexible,

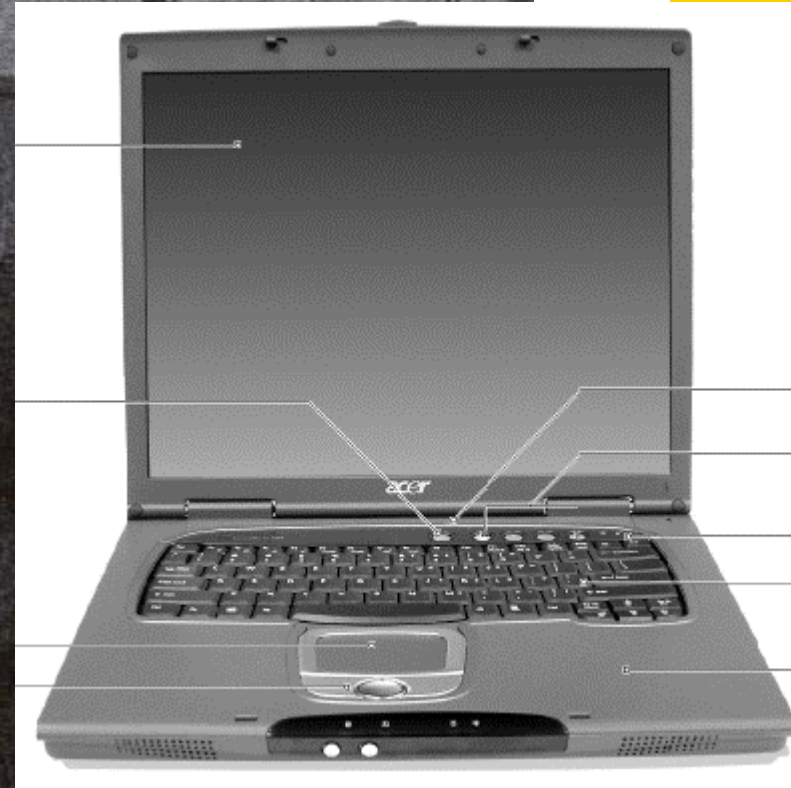
Better sample presentation

...

Portable (miniaturization)

But

Almost the same spectral  
information as 25 years ago



# APPLICATIONS





# APPLICATIONS developed at CRA-W



- Fertilizers (N, P, K, Humic acids)
- Soils (N, C, CEC, ...)
- Seeds & Phyto-sanitary Protection (seed/seed)
- Crop monitoring (N)
- Precision Agriculture
- Nutritive value (feed & forages)
- Technology (flour, baking quality,...)
- Authenticity (orange juice, wine, olive oil, meat, honey,...)
- Fruits
- Bio-fermentation monitoring



# •NUTRITIVE VALUE OF FEED

## CHEMICAL COMPOSITION & DIGESTIBILITY

- Moisture – DM**
- Ashes – OM**
  - + P, Ca, K, Mg
- Fat**
  - + FA profile
- Proteins (N)**
  - + AA profile
- Fibres**
  - (cellulose, NDF, ADF, ADL)
- Starch**
  - + amylose - amylopectin
- Total Sugar**
  - + sugar profile
- OMD**
  - in vivo, in vitro, enzymatic*

### Feed Ingredients

Cereals & by-products  
Wheat bran  
Soyameal  
Sugarbeet pulp  
Animal protein (MBM)  
.....

### Complete feed

Cattle  
Swine  
Poultry  
Pet food

# NIRS MICROSCOPY & IMAGING



# • NIR INFRARED MICROSCOPE

## Meat and Bone Meal DETECTION

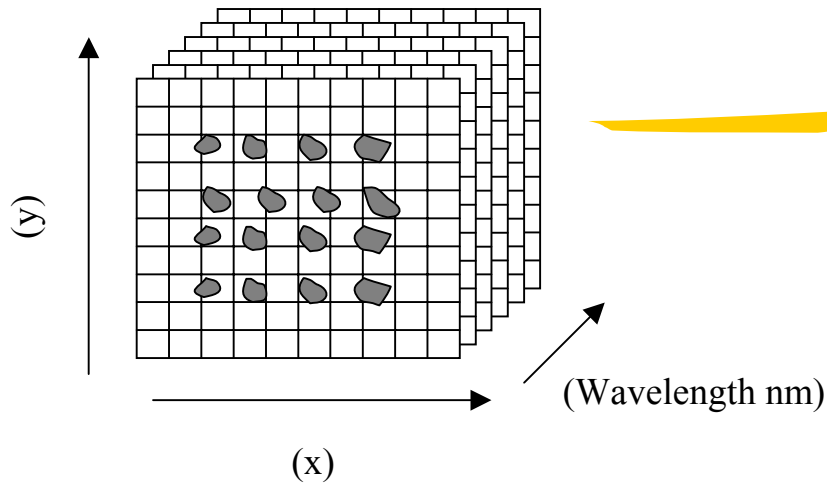
PerkinElmer FT-NIR



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# NIR Camera

Matrix NIR,  
Spectral Dimensions, Inc.



- Camera InGaAs
- 900 - 1700 / 10 nm
- 240 x 320 pixels
- Each pixel: 70  $\mu\text{m}$  \* 70  $\mu\text{m}$
- Analyzed surface : 5 cm
- 76 800 spectra 24 MB
- 300 - 350 particles
- Analysis time : +/- 5 min

ISO 17025

**CRA-W – DQPA 23-02-2006**  
**Community Reference Laboratory**  
**for Animal Proteins**

Recherches agronomiques  
CRA-W  
Gembloux  
dptqual@cra.wallonie.be

# NETWORKING

## STANDARDISATION OF INSTRUMENTS

**Same models on all the instruments**

**Make the instruments alike**



# 9 laboratoires interconnectés en région wallonne



**Asbl REQUASUD**  
**Cellule de coordination**  
**Chaussée de Namur, 24**  
**5030 GEMBLoux**

**081/62.03.71**  
**[requasud@cra.wallonie.be](mailto:requasud@cra.wallonie.be)**

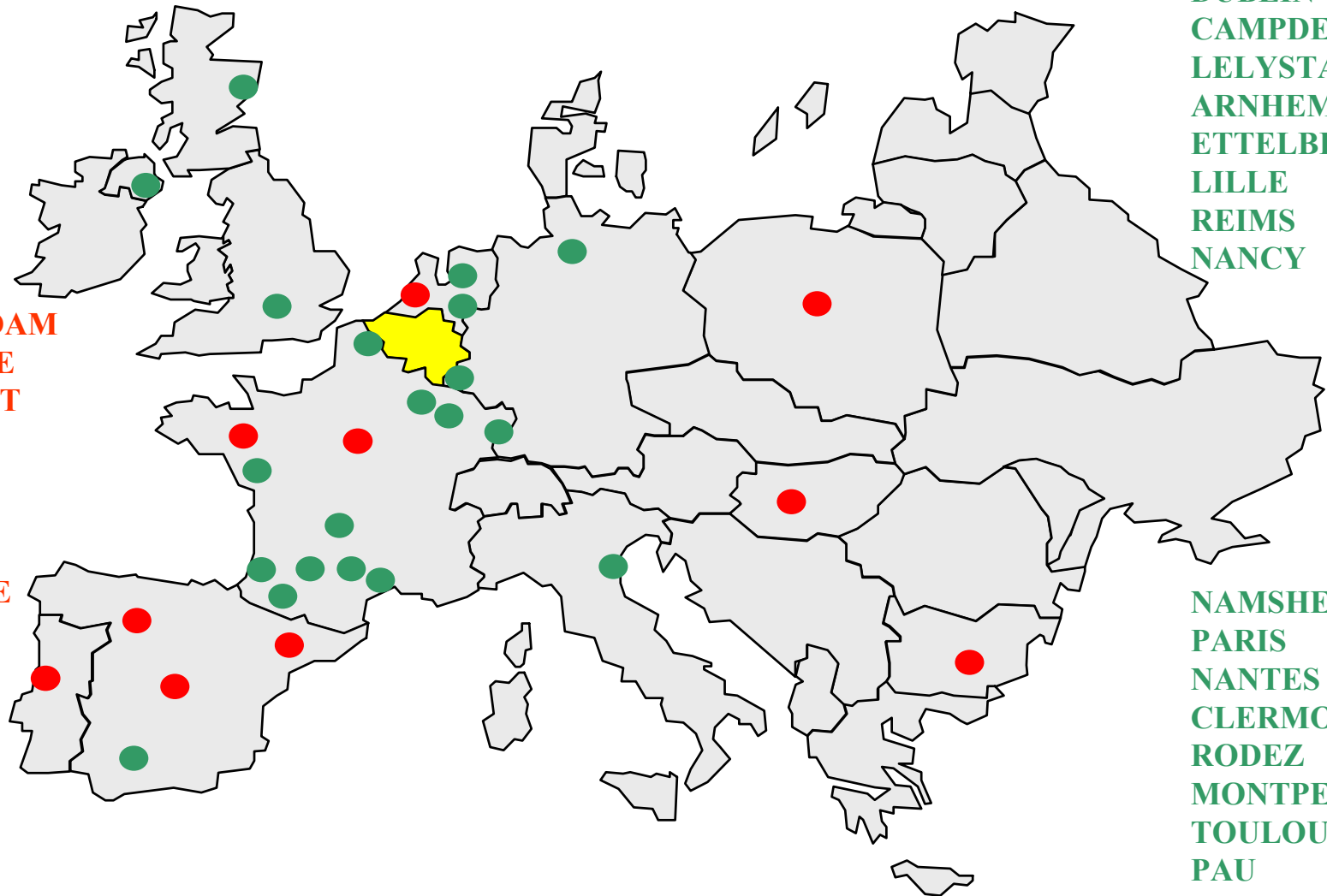


# EUROPEAN CRAG<sub>x</sub> CONTACTS



ABERDEEN  
DUBLIN  
CAMPDEN  
LELYSTAD  
ARNHEM  
ETTELBRUCK  
LILLE  
REIMS  
NANCY

ROTTERDAM  
VARSOVIE  
BUCAREST  
PARIS  
RENNES  
FRAGA  
MADRID  
LISBONNE



NAMSHEIM  
PARIS  
NANTES  
CLERMONT-F  
RODEZ  
MONTPELLIER  
TOULOUSE  
PAU  
PADOVA  
CORDOBA  
MADRID



# EUROPEAN PROVIMI NETWORK

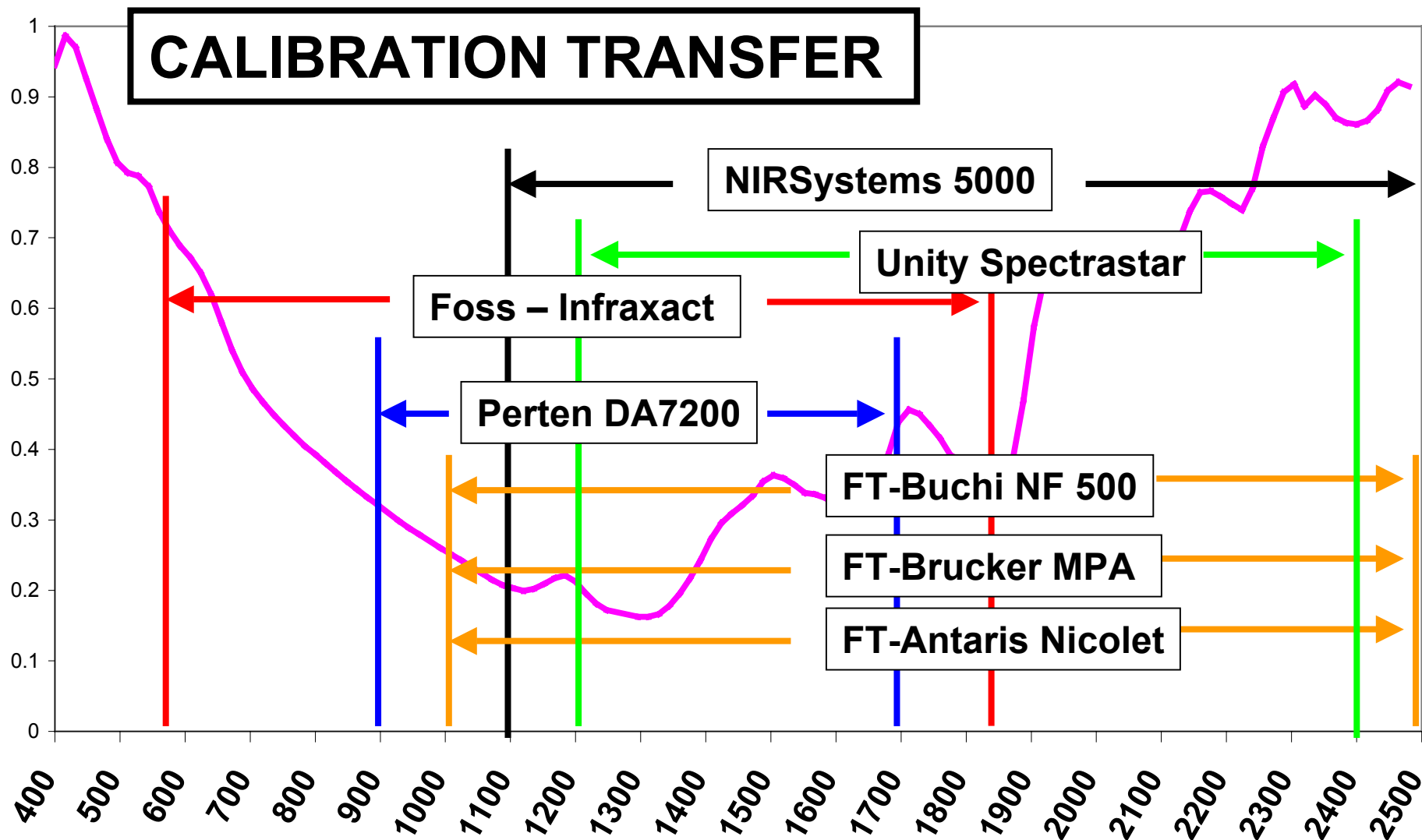




A-W  
oux

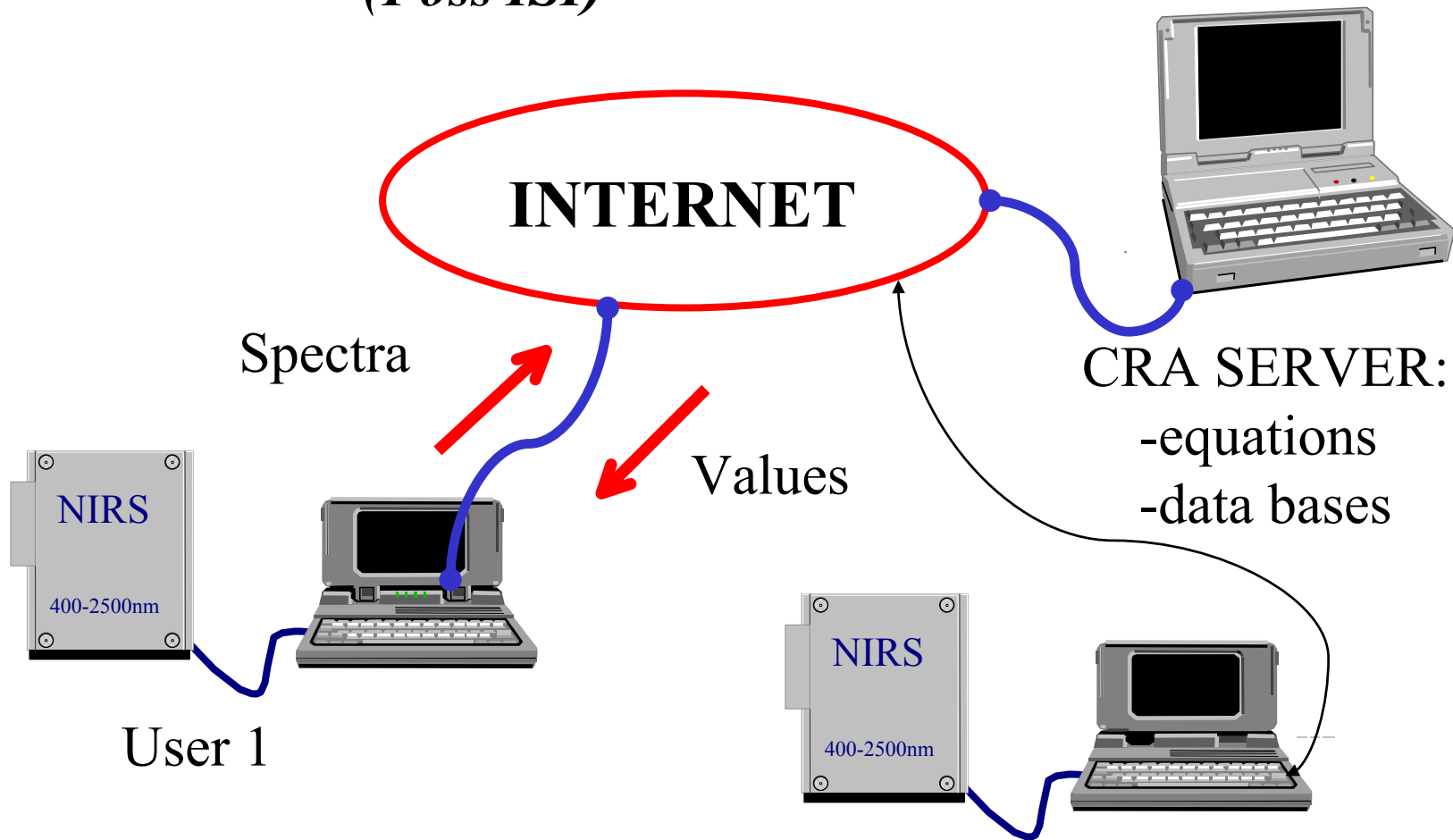
# WORLD NIRS CONTACTS





# • Networks of instruments (2000)

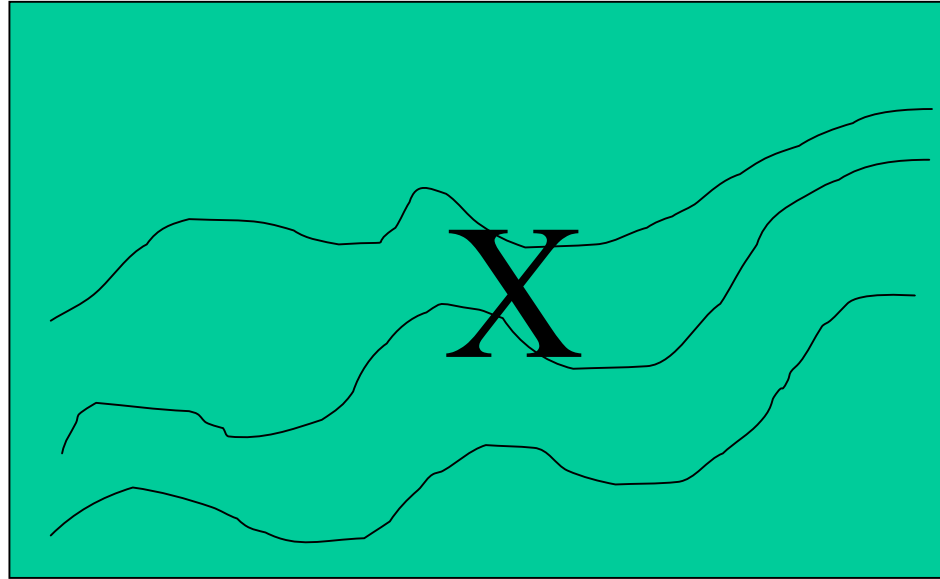
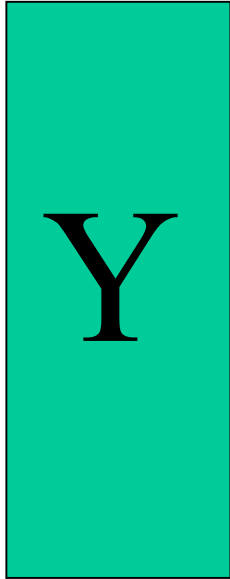
## **RINA<sup>®</sup>** : *Remote Instrument Near Analysis* (Foss ISI)



# CHEMOMETRICS

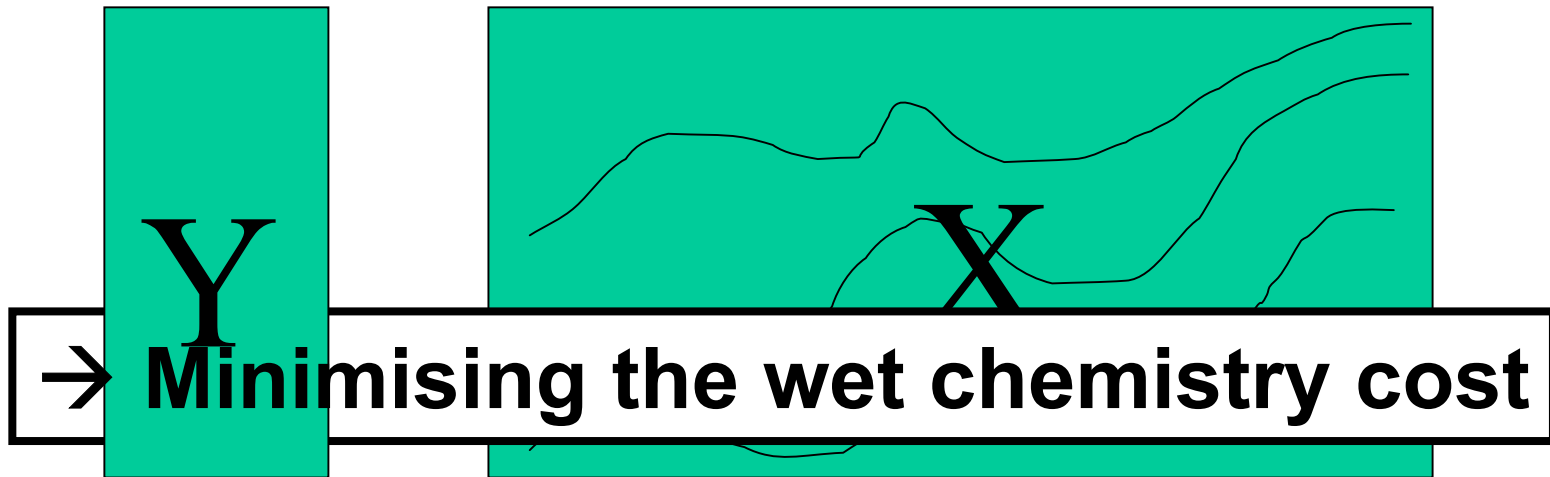


# Calibration : Multiple Linear Regression



$$\hat{Y} = b_0 + \sum b_i x_i$$





**Reference**  
**Wet Chemistry**  
**SEL ??**  
**r (repeatability)**

**R (reproducibility)**

**Spectral variability**  
**Varieties, Years, Locations,**  
**Origins, ....**  
**Samples prep., Grinders,**  
**Temperatures, Operators, ...**  
**Batches, ...**

**Experimental Designs**



## ➤ CHEMOMETRICS

Many Packages (manufacturers)  
+ MatLab

Quantitative  
MLR, PCR, PLS, ANN, SVM,....

Qualitative  
LDA, QDA, KNN, SVM, SIMCA,..





## Uncertainty of the NIR analyses

$$s(\hat{y}_i - y_i) = \left[ (1 + h_i) \cdot SEC^2 - S_{ref}^2 \right]^{1/2}$$

**Fernandez Pierna & al., Chemom., Intell. Lab. Syst. 65,281 (2003)**

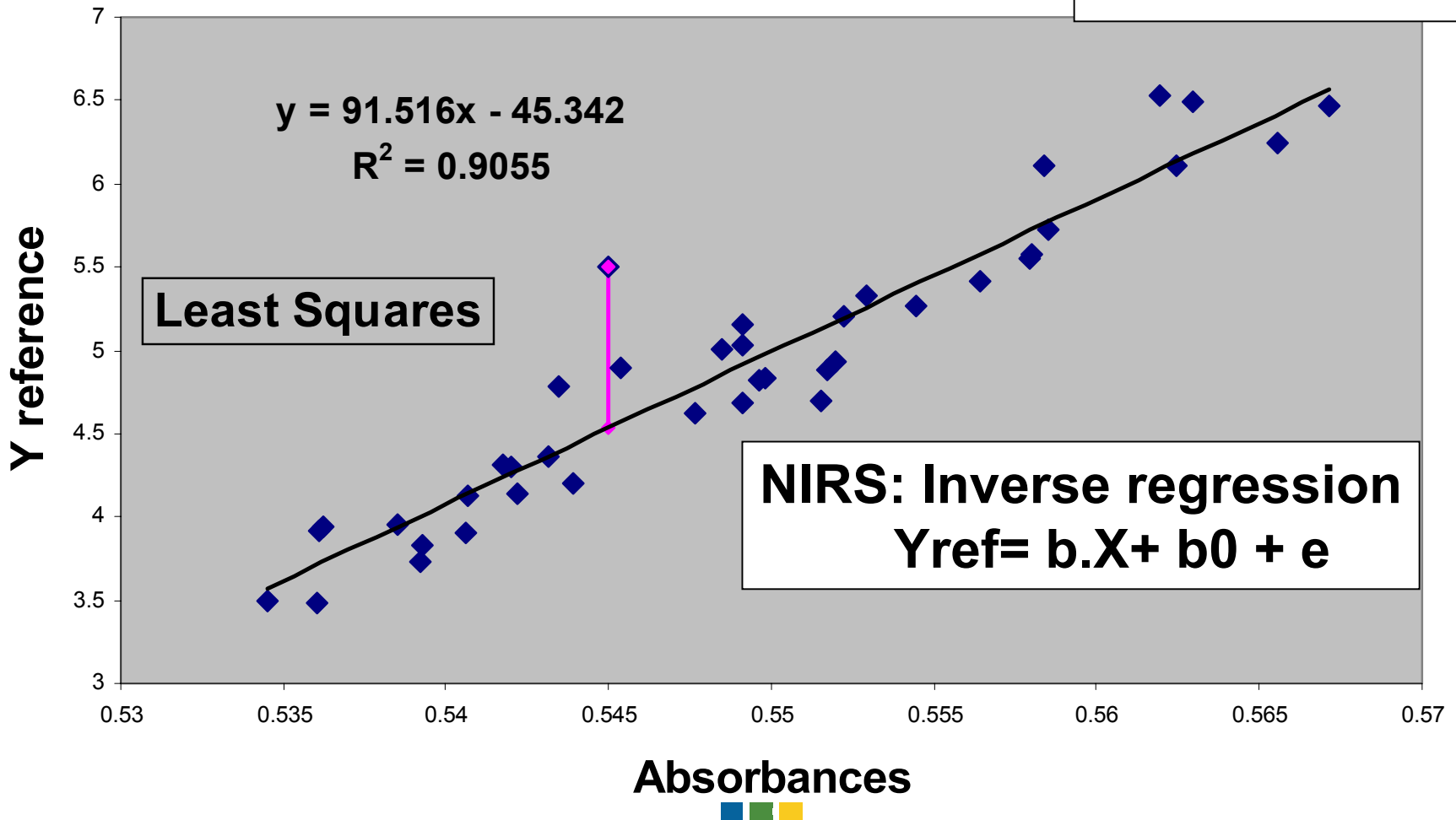




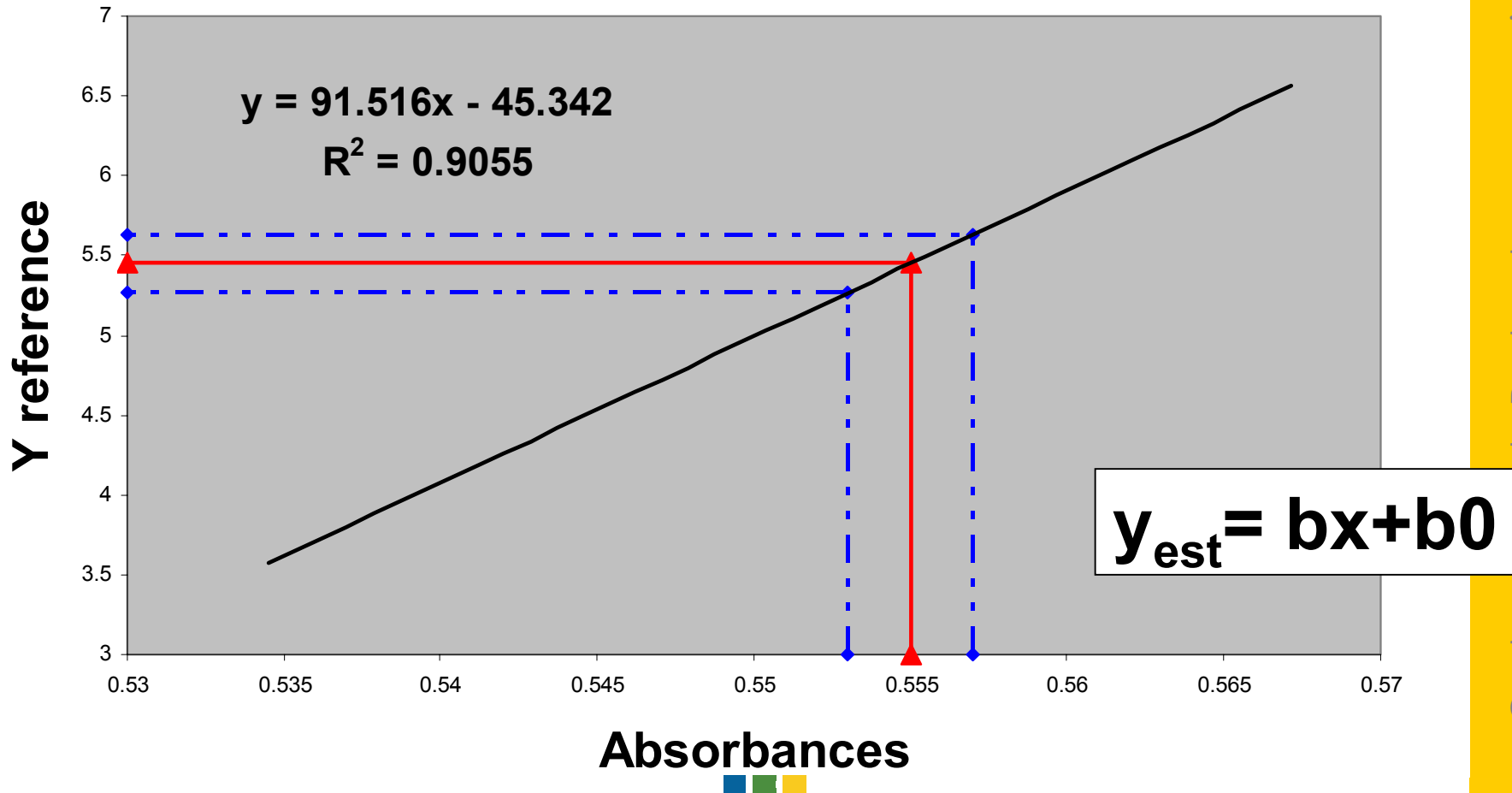
# Chemometrics : uncertainty

## CALIBRATION

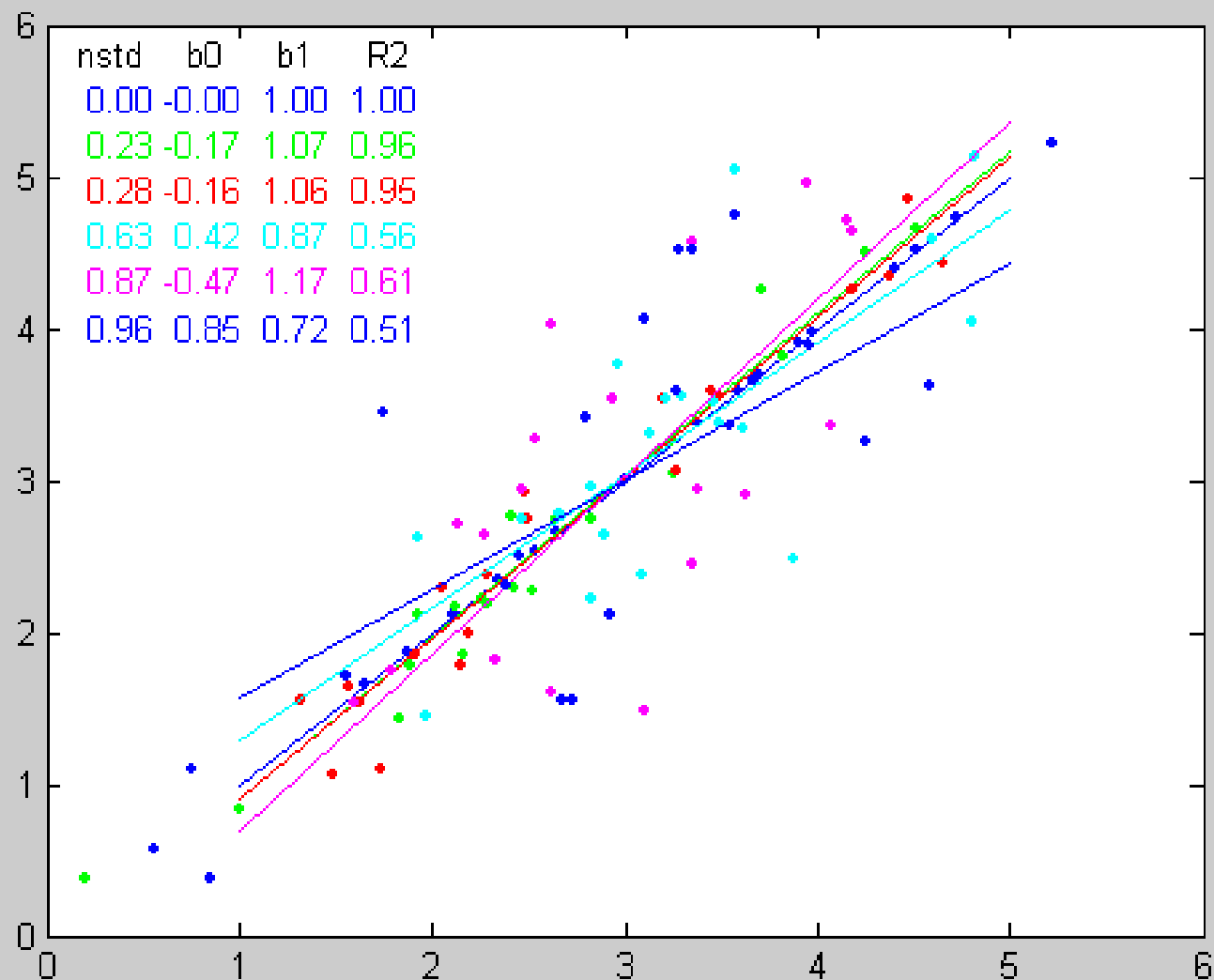
$$b = \frac{\text{COV}(x, y)}{s_X^2}$$



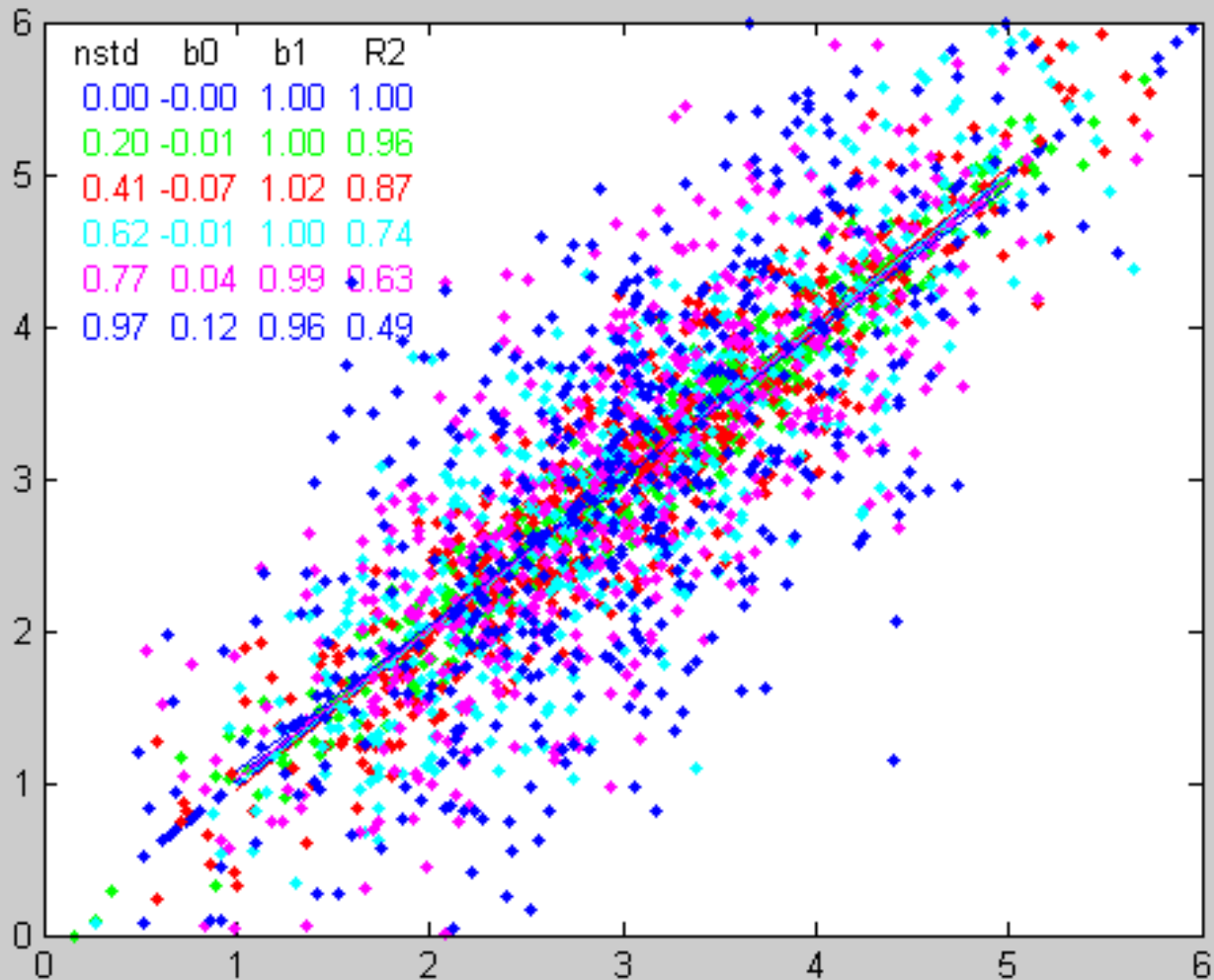
## PREDICTION



# N=20



# N=500





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Results 1 - 10 of about 2,270 for NIRS [on-line](#). (0.03 seconds)



Near infrared on-line measurement of degree of cook in extrusion processing of wheat flour

On-line monitoring of rumen fluid in milking cows by fibre optics in transmittance mode using the longer NIR region

Non-invasive fermentation analysis using an artificial neural network algorithm for processing near infrared spectra (*ethanol*)

Monitoring carotenoid and chlorophyll pigments in virgin olive oil by visible-near infrared transmittance spectroscopy. On-line application

On-line monitoring of melt-extrusion transesterification of ethylene vinylacetate copolymers by near infrared spectroscopy and chemometrics

On-line monitoring of kinetic and sensory parameters in acetic fermentation by near infrared spectroscopy





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- ◆ Guidance for Industry PAT — A Framework for Innovative Pharmaceutical Development, Manufacturing, and Quality Assurance [[HTML](#)] or [[PDF](#)]
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# **Guidance for Industry**

## **PAT — A Framework for Innovative Pharmaceutical Development, Manufacturing, and Quality Assurance**

### **Controls on line**

- all the process parameters**

- ingredients, intermediate products and final products**

**→ full traceability and immediate release of the products**







17:30 Visite du laboratoire de spectrométrie

*That's all folks !*

*Merci bramin p'o m'awès choutè*

