Use of a NIR mini spectrometer for polyamides discrimination on a production unit

Hebert Perrine [1], Montagnier Safia [1], Guilment Jean [1]
Lallemand Jordane [2] et Roussel Sylvie [2]

[1] ARKEMA - CERDATO / Laboratoire d'Étude des Matériaux (LEM) - Route du Rilsan, 27470 Serquigny – **France** - perrine.hebert@arkema.com

[2] Ondalys - 4 rue Georges Besse, 34830 Clapiers, **France** - sroussel@ondalys.fr

LOCATION IDRC
NAME Perrine Hebert
DATE 2018/08/01

- WHO ARE WE ?
  WHAT ARE OUR NEEDS?
- WHAT TECHNOLOGY CHOICE FOR OUR NEEDS ?
- WHAT RESULTS DID WE OBTAIN ?

ARKEMA
INNOVATIVE CHEMISTRY

WHO ARE WE ?

ARKEMA
INNOVATIVE CHEMISTRY

ARKEMA TODAY

€7.7 bn sales

19,000 employees worldwide

Worldwide presence in **50** countries

136 industrial sites

3 R&D and innovation geographical hubs



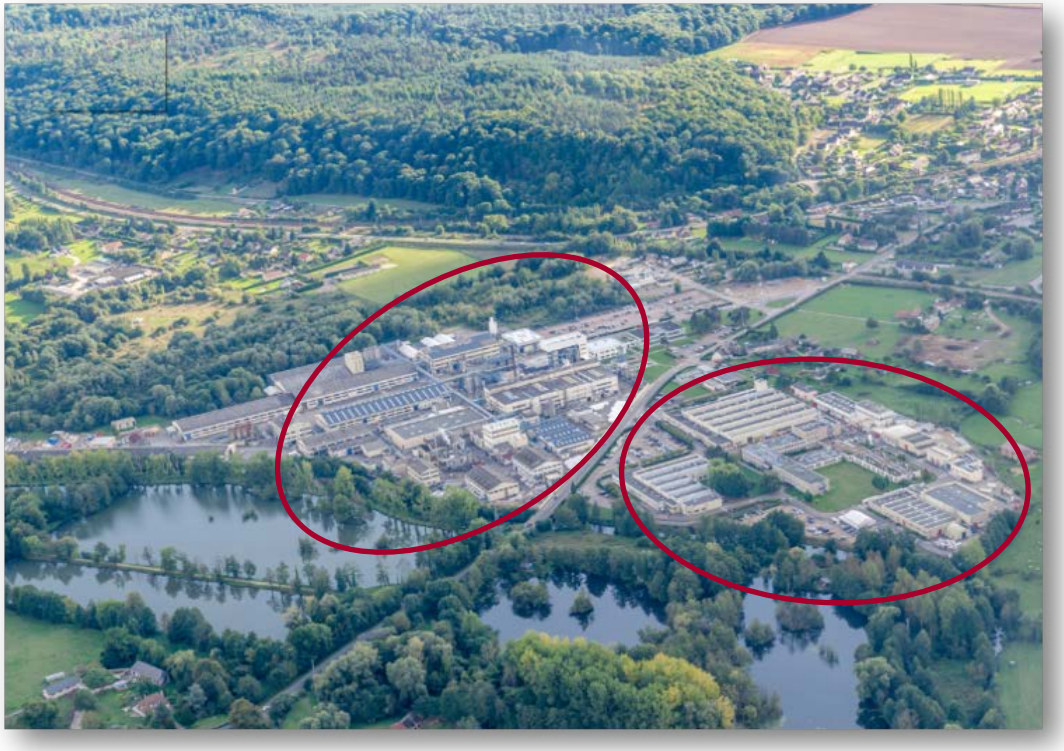


North America
38 production sites
3,600 employees

Europe
59 production sites
10,400 employees

Asia and rest of the world
39 production sites
5,000 employees

SERQUIGNY'S PLATFORM : A PLANT + A RESEARCH AND DEVELOPMENT CENTER



→ **Manufacturing, research and development of high performance polymers**

- **Long chain alliphatic Polyamides Rilsan®, Rilsamid®**
- **High temperature Polyamides**
- **Transparent Polyamides**
- **Pebax®**

WHAT ARE OUR NEEDS?

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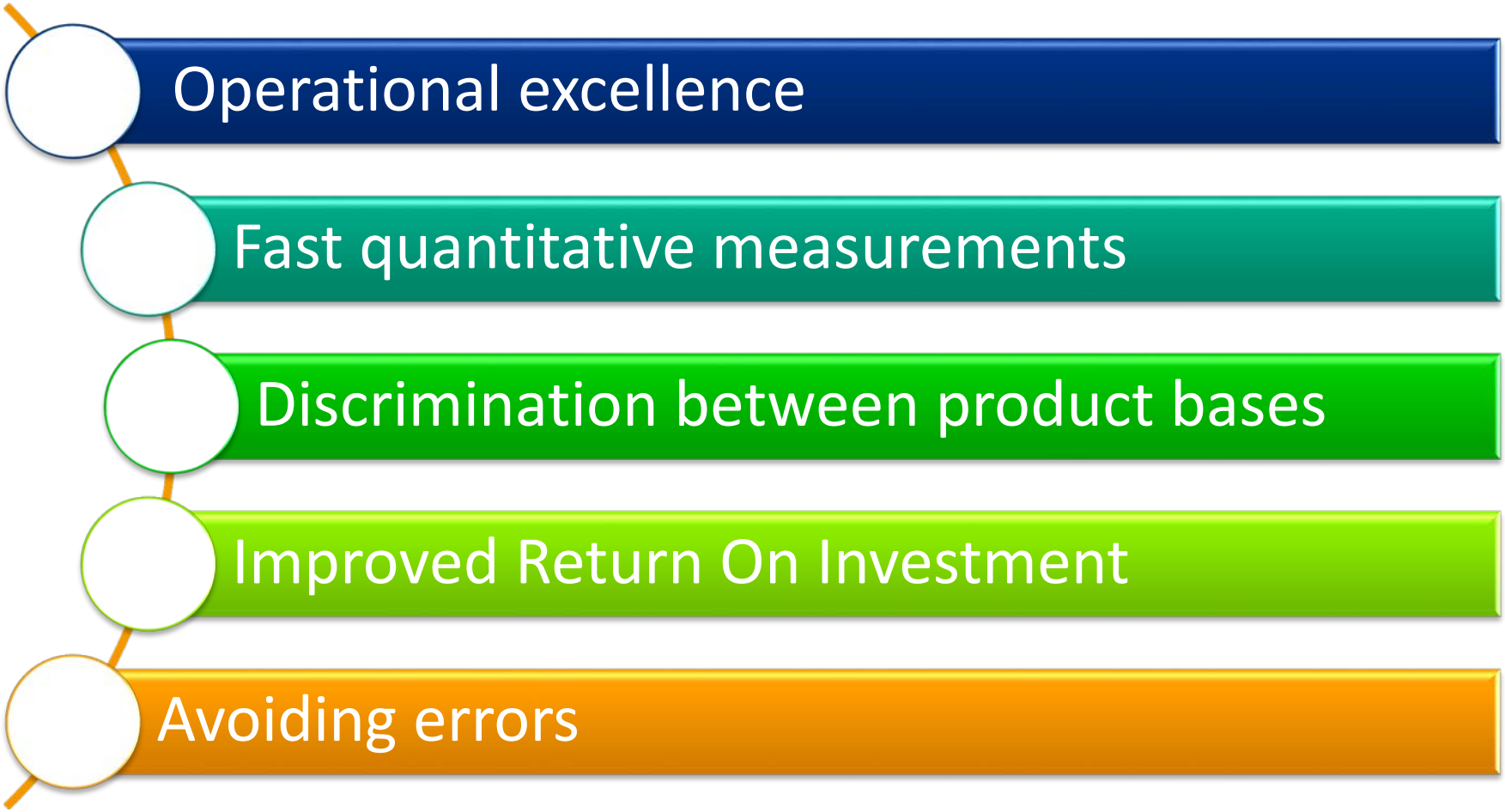
WHAT ARE OUR NEEDS?



WHAT TECHNOLOGY CHOICE FOR OUR NEEDS ?

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WHAT TECHNOLOGY CHOICE FOR OUR NEEDS ?

Raman spectroscopy

- Very discriminant technology
- Not applicable to the entire range of applications (fluorescence)
- Miniaturization of instrumentation started
- High cost

NIR spectroscopy

- Validated for most of the insdustrial applications on FT-NIR instrumentation (except black samples)
- Reasonable cost for « big » applications
- Miniaturization of instrumentation started at very low cost
- Performances to be assessed

X-Ray Fluorescence

- Validated for the insdustrial applications on ED or WD laboratory instrumentation
- Needs disminative elements
- Reasonable cost for « big » applications
- Allows to work on black samples
- Miniaturization of instrumentation started
- Medium cost
- Performances to be assessed

WHAT TECHNOLOGY CHOICE FOR OUR NEEDS ?

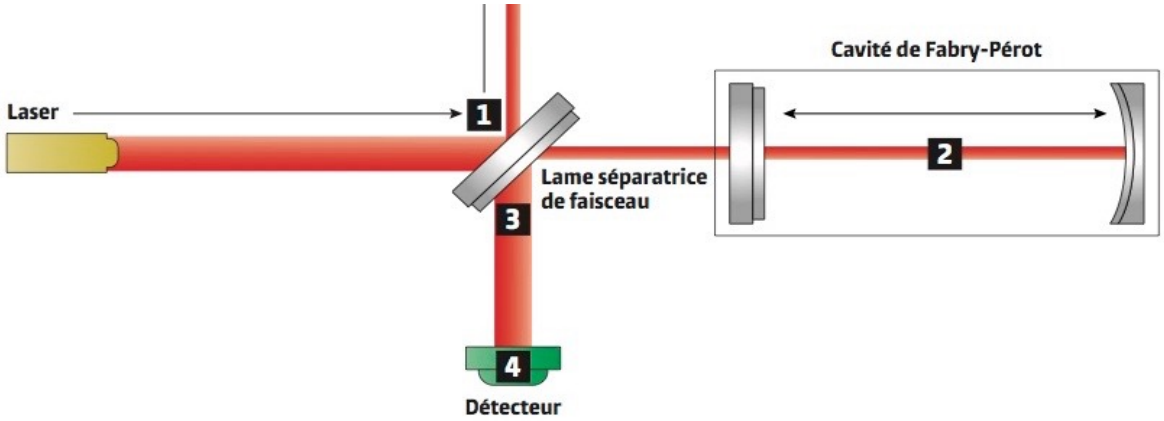
FTNIR

- 50 000€
- Widely used in the industry
- **Technology : Fourrier Transform**
- Wide spectral range
- Qualitative and quantitative analysis

MiniNIR Sensor

- 2-5000€
- Recent on the market
- **Technology : Fabry Pérot**
- Limited spectral range
- Performances to be assessed

FABRY PEROT TECHNOLOGY



- **Fabry Perot Interferometer**
  - 1 λ for one cavity length
  - Cavity length controlled with MEMS (Microelectromechanical systems)

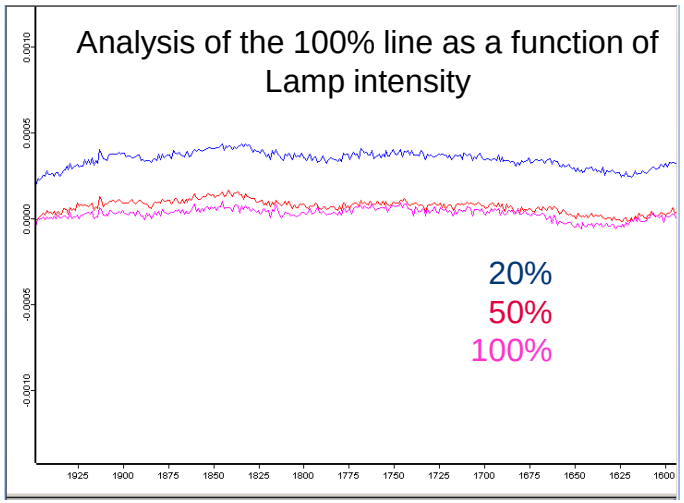
SPECIFICATIONS VALUEs

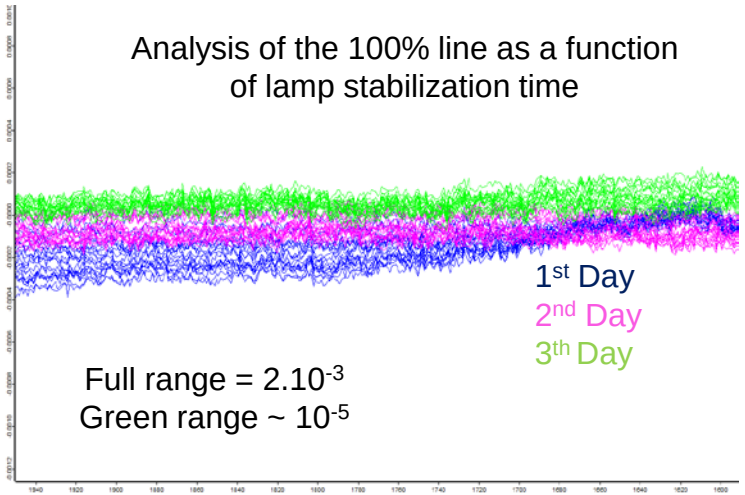
- **Wavelength range**
  - 1.35 – 1.65 µm (NIRONE1.7)
  - 1.55 – 1.95 µm (NIRONE2.0)
  - 1.75 – 2.15 µm (NIRONE2.2)
  - 1.95 – 2.45 µm (NIRONE2.5)
- **Detector type Single element extended InGaAs**
- **Wavelength points Minimum step 0.1 nm,up to 512 in total**
- **SNR (typical, w/o averaging) > 10,000**
- **Size (W x L x H) 60 x 53 x 27 mm3**
- **Wavelength resolution (FWHM)**
  - 14 – 18 nm (NIRONE1.7)
  - 16 – 22 nm (NIRONE2.0)
  - 20 – 26 nm (NIRONE2.2)
  - Not availble (NIRONE2.5)
- **Illumination source 2 tungsten vacuum lamps Bulb life > 40,000 hrs**
- **Wavelength switching time 1 ms**
- **Wavelength temperature response (max.) 0.1 nm/°C**
- **Weight 90g**

WHAT ARE YOURS NEEDS ?

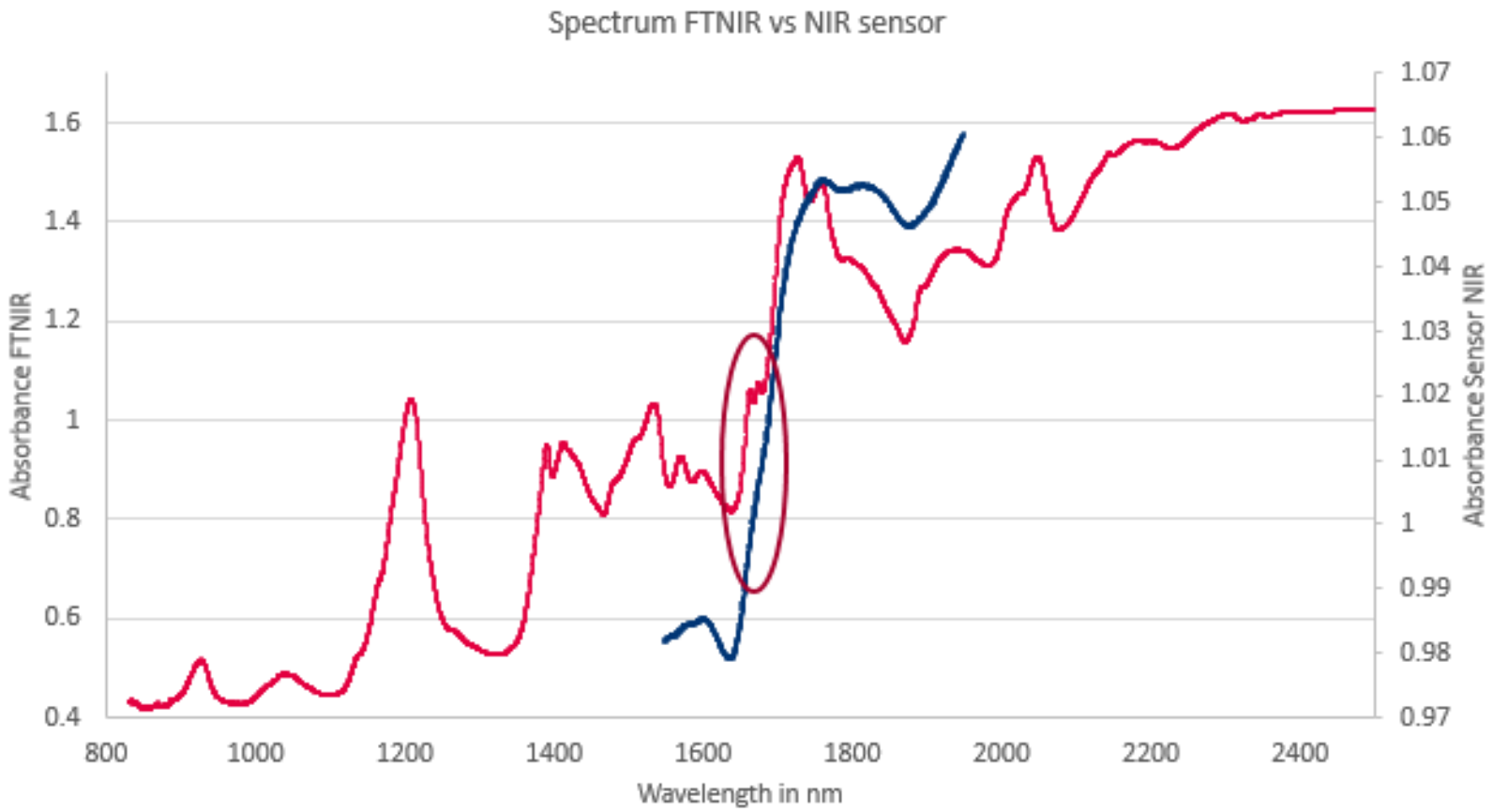
Goal: Analysis time around 20 secondes

- Analysis time = Integration time * Number of Scans * Number of points
- Parameters:
  - Integration time = 0.1ms / step
  - Number of points (Range (1550 – 1950 nm) / Step size (1, 2 or 10nm))

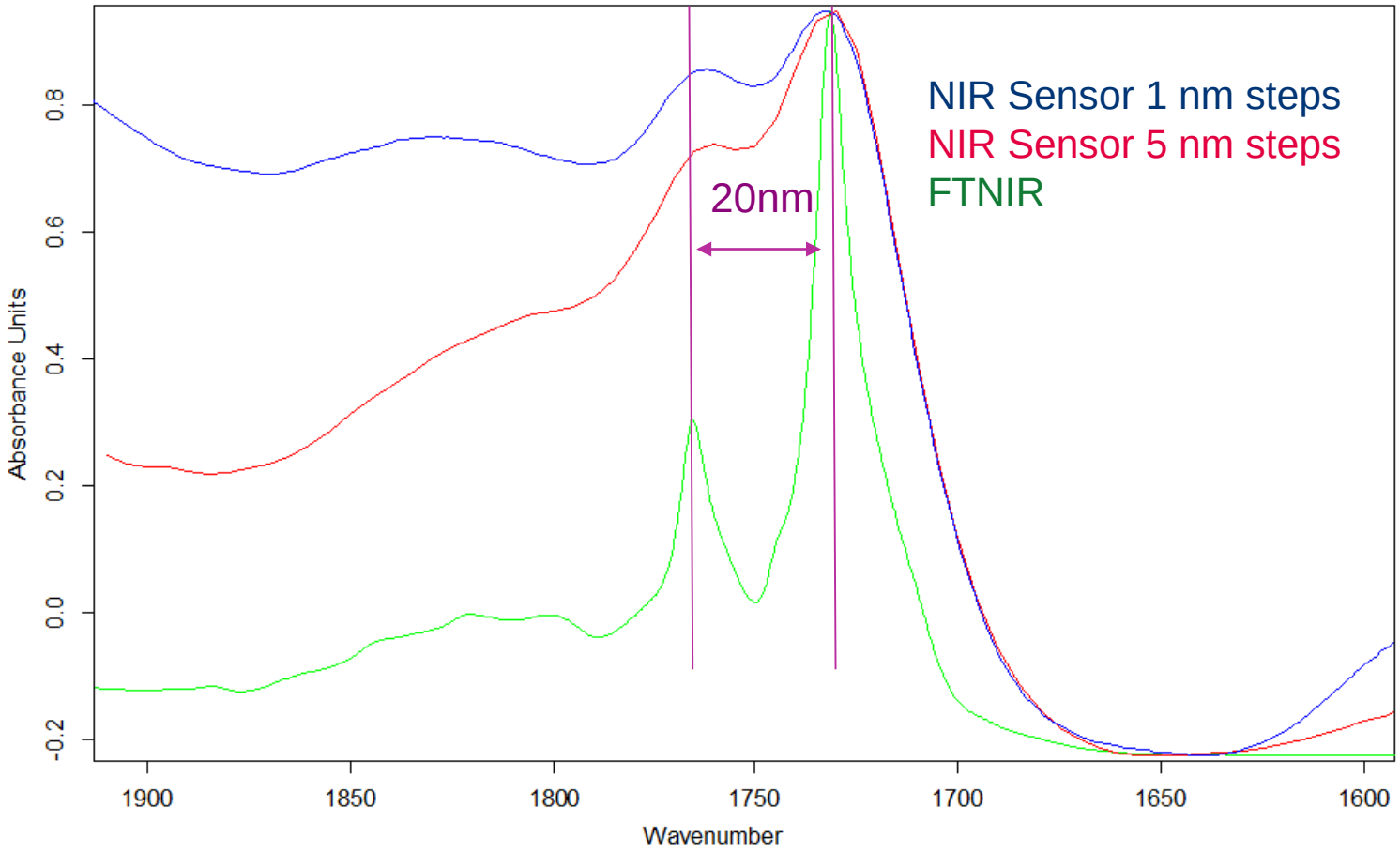




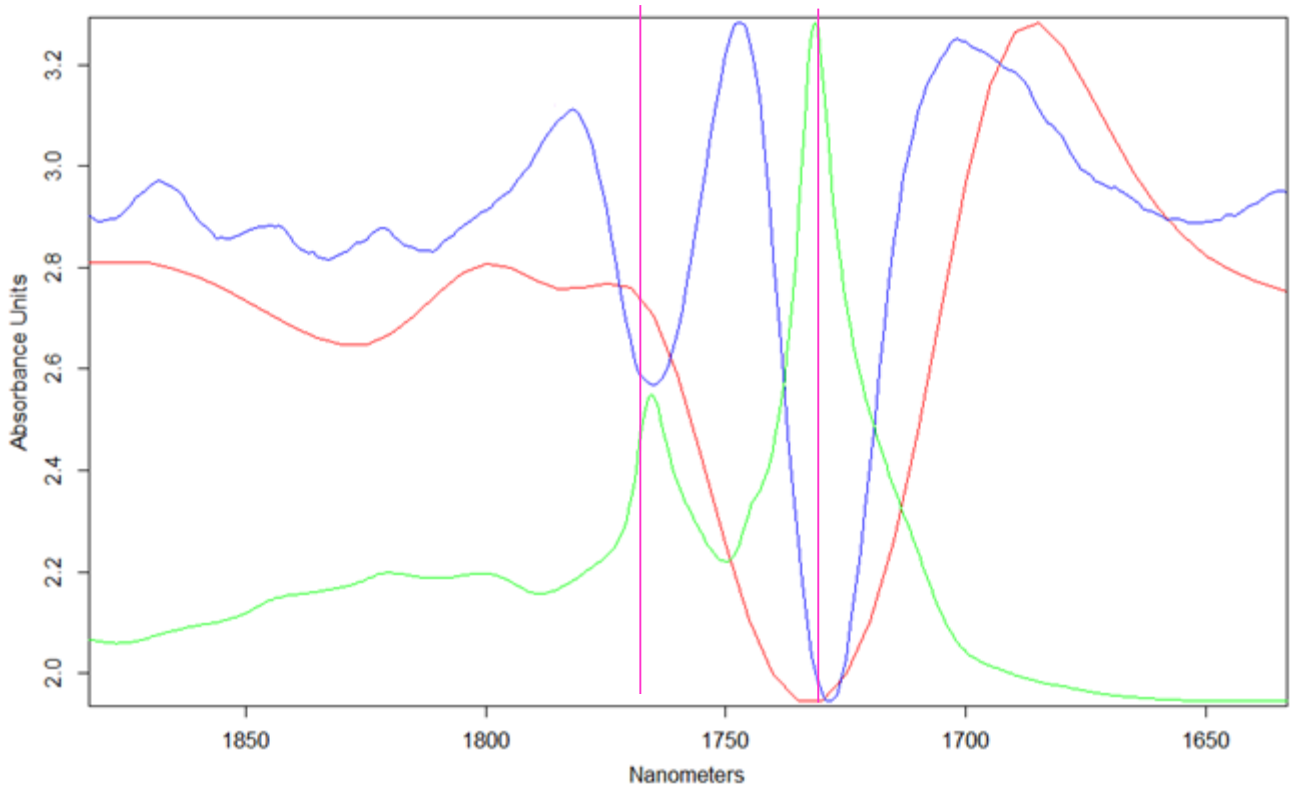
FTNIR VS SENSOR NIR



RESOLUTION : FTNIR VS SENSOR NIR



DERIVATION



2nd dérivative – Sensor NIR 1nm steps
2nd dérivation – Sensor NIR 5nm steps
FTNIR

WHAT RESULTS DID WE OBTAIN ?

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DISCRIMINATION BETWEEN PRODUCT BASES AND /OR QUANTIFICATION

Plasticized products

- Separation of plasticized (PA11 P20, PA11 P40) versus not plasticized (PA11, PA12)
- Separation of plascized products as a function of the plasticizer level (PA11, PA11 P20, PA11 P40)
- Prediction of the amount of plasticizer

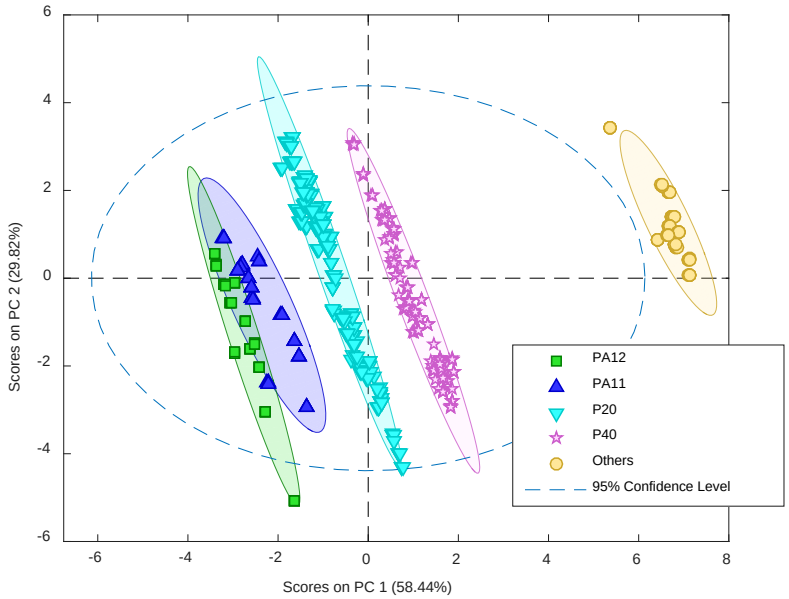
Nature of products

- Separation of PA11 versus PA12 vs other polyamides

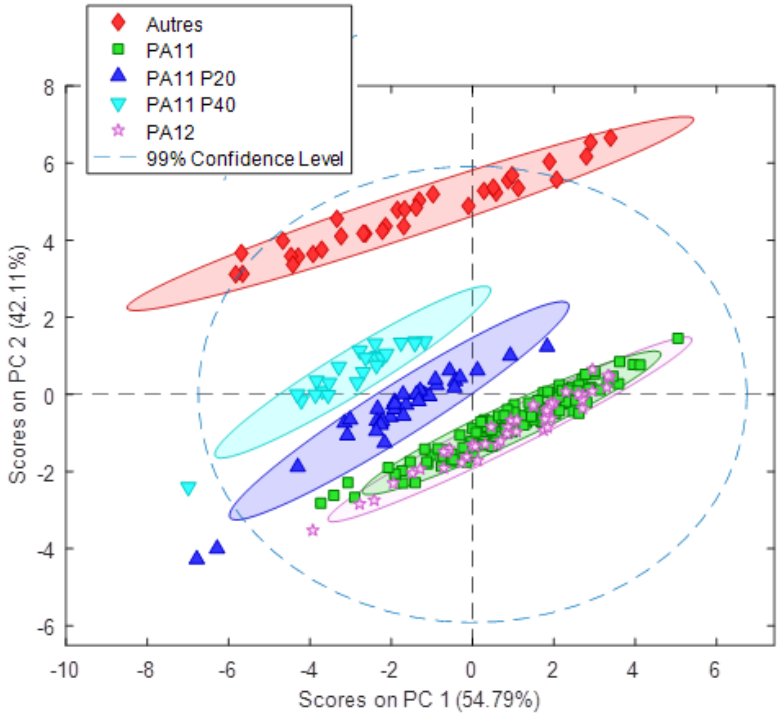
ACP ON THE FT-NIR VS NIR SENSOR

→ *ACP on the 5 classes*

→ *After preprocessing SNV*

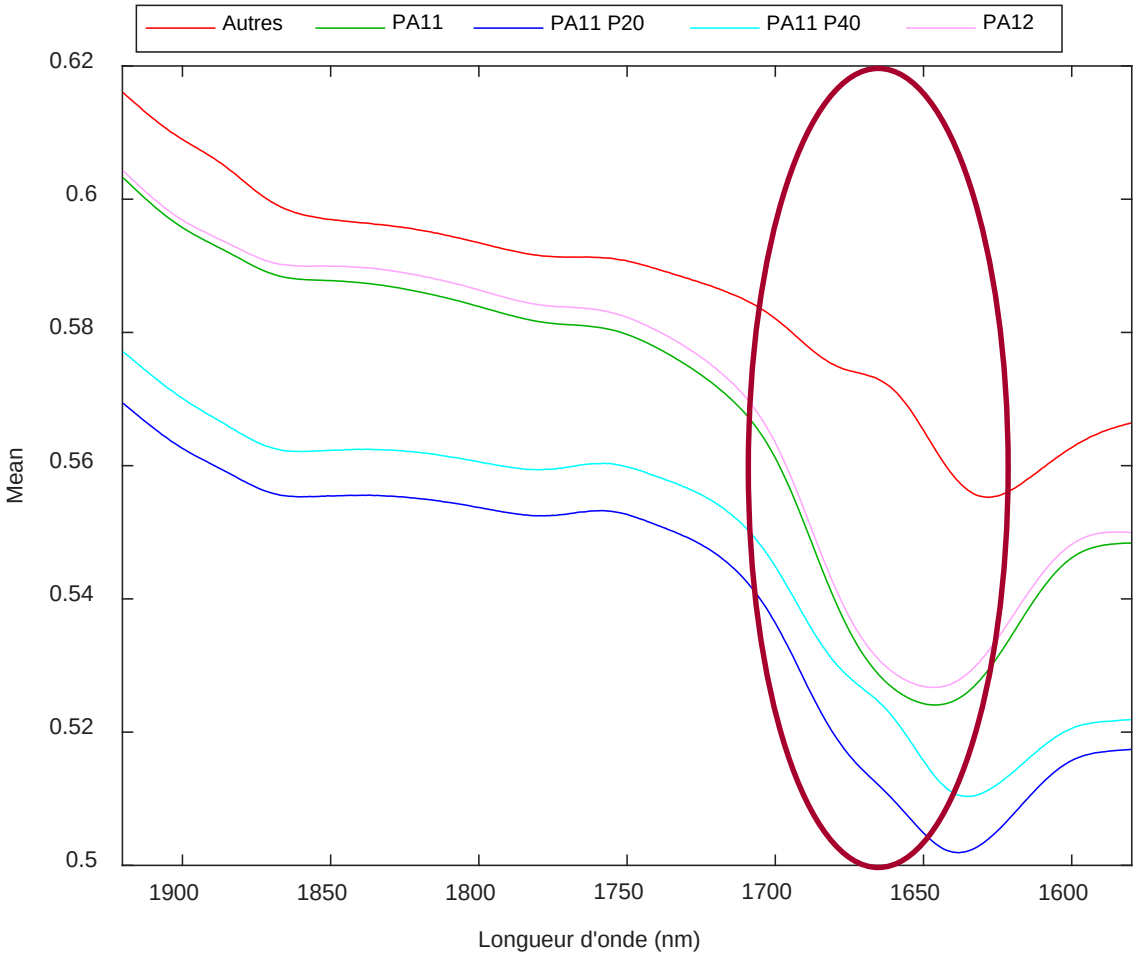


FT-NIR



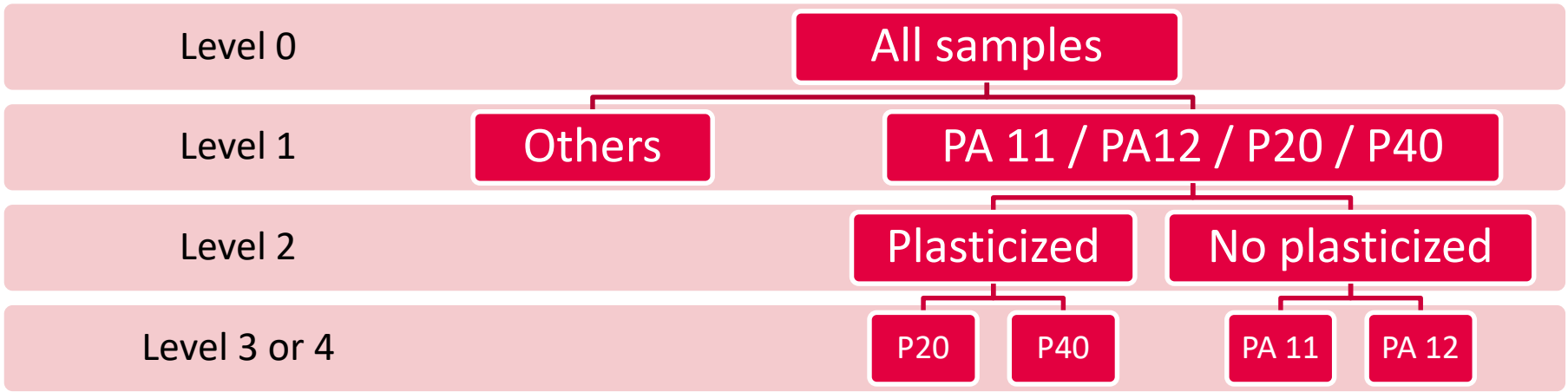
NIR Sensor

MEAN SPECTRA BY CLASS

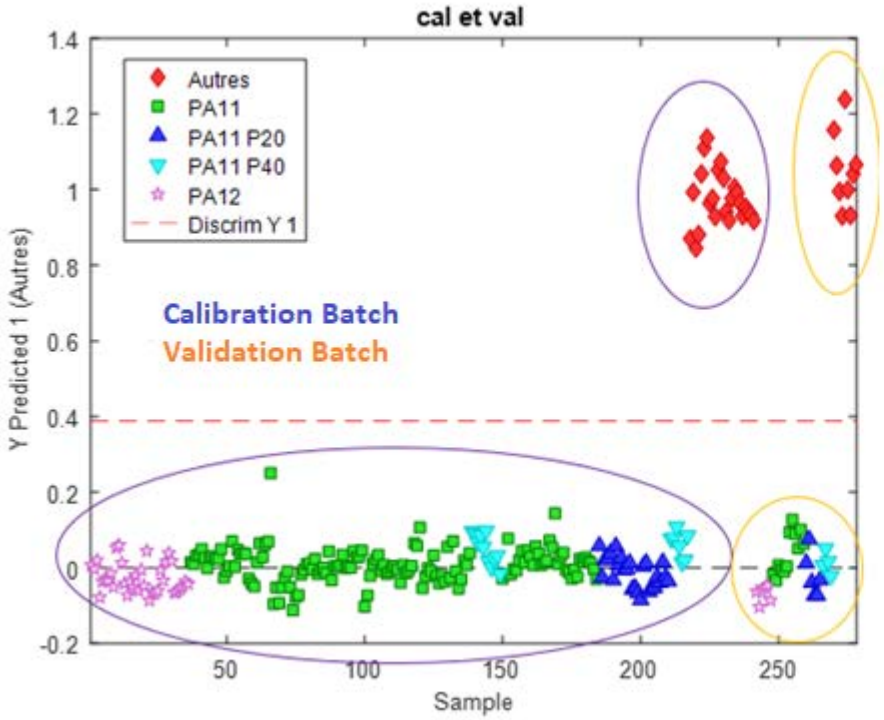


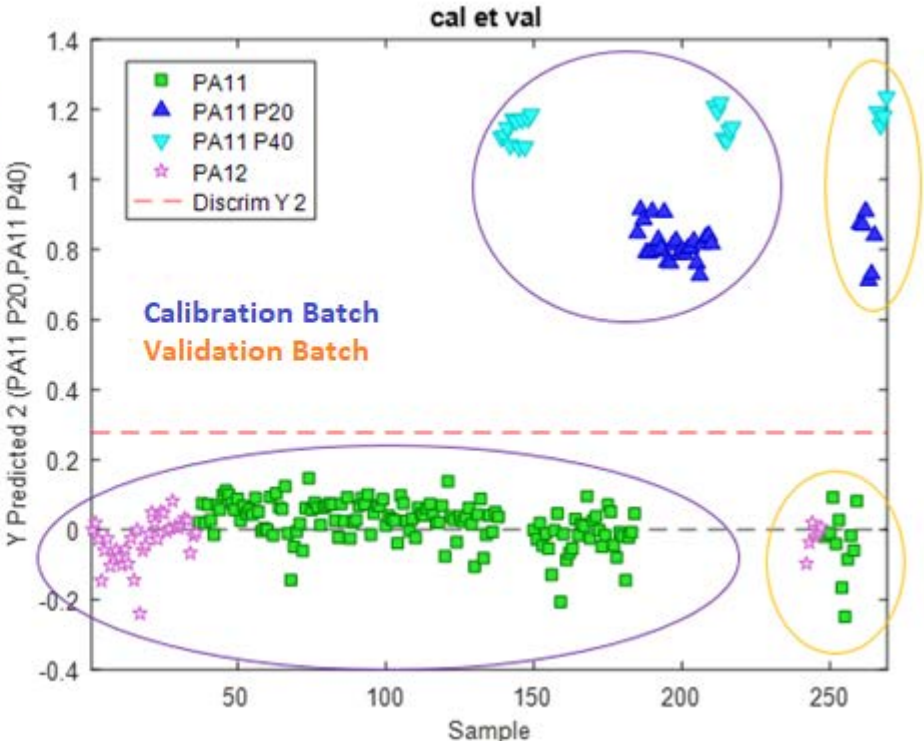
PLS-DA HIÉRARCHICAL

- **Coding in 0 and 1**
- **Descending order of variance**



LEVEL 1: OTHERS VS ALL PA11 AND PA12 SAMPLES
LEVEL 2: PLASTICIZED VS NO PLASTICIZED



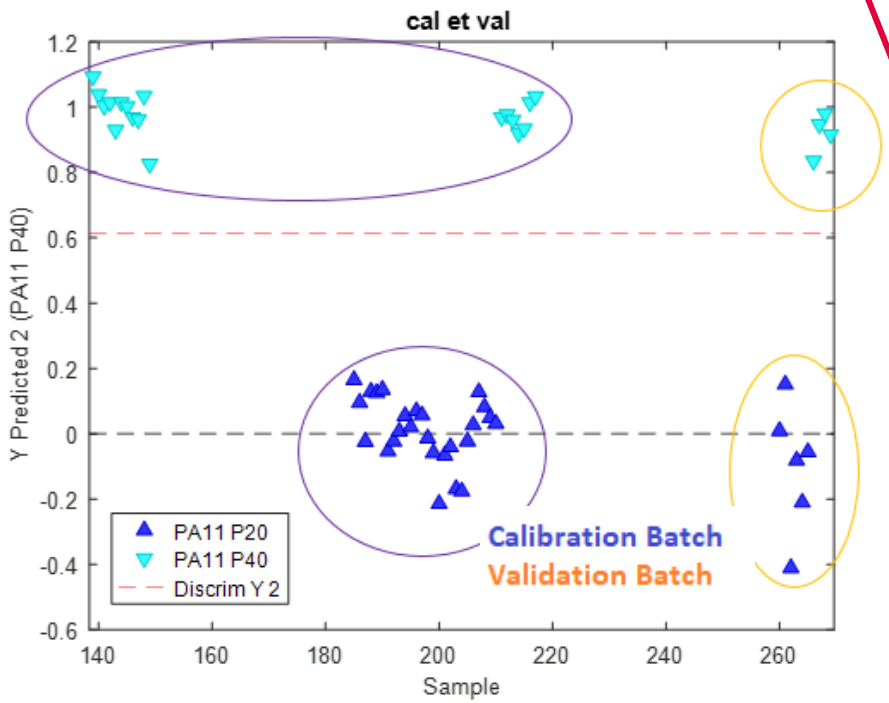


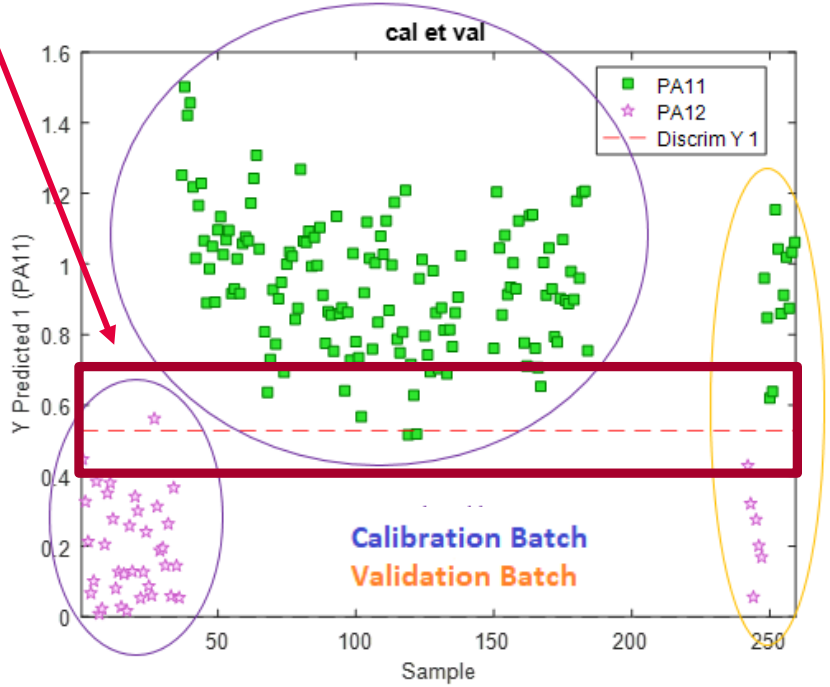
Level 1

Level 2

LEVEL 3: P20 VS P40
LEVEL 4: PA 11 VS PA 12

→ **Level 4: zone of uncertainty between Y = 0,4 and Y= 0,7**



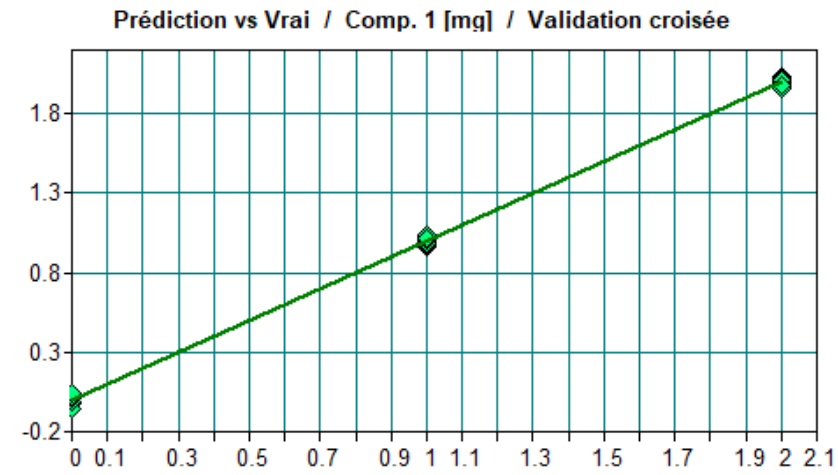


Level 3

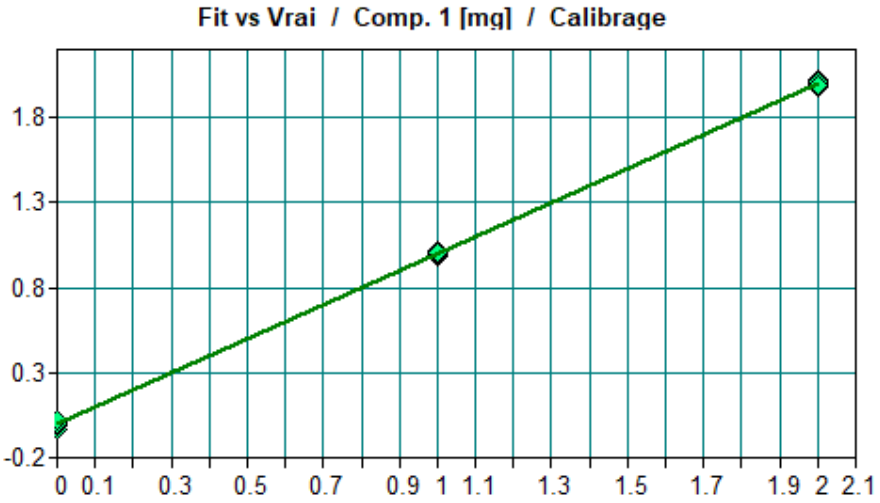
Level 4

PLS ON THE PLASTICIZER CONTENT

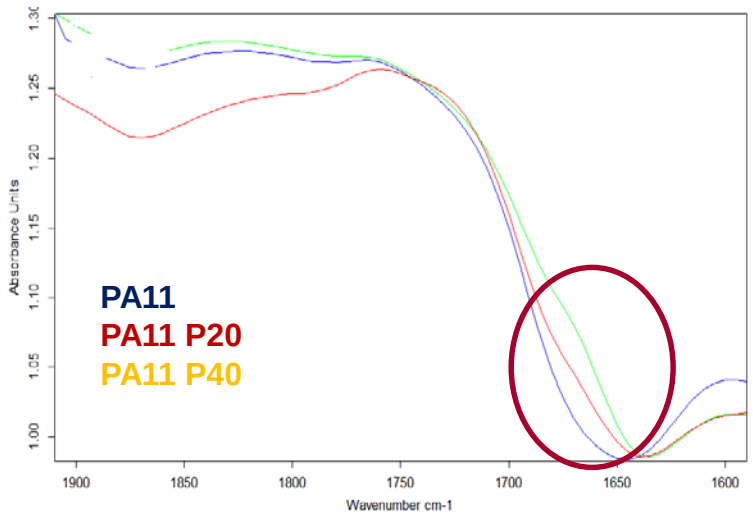
Quantitative analysis is possible



Rang: 8 R^2 = 99.93 RMSECV = 0.0223 Biais: 0.000909 RPD: 36.7
Validation No 3 2018 07 Plastifiant.q2



Rang: 8 R^2 = 99.98 RMSEE = 0.0133 RPD: 66.4
Validation No 3 2018 07 Plastifiant.q2



TO BE USED BY OPERATORS

→ **It's necessary to develop:**

Sampling interface →

Chemometric interface:
Matlab → Exportation to Excel

Computer interface →

CONCLUSION

→ **Mini NIR spectrometer allows to discriminate between our products**

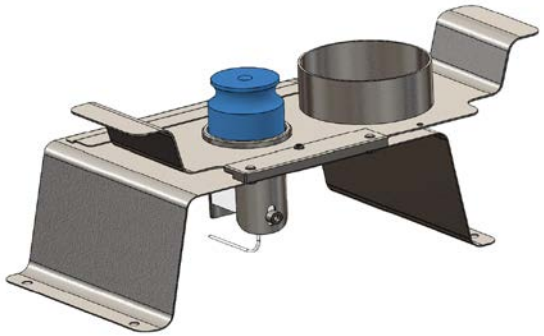
- Plasticized vs un plasticized ➔ Easy
- PA11 vs PA12 ➔ more challenging

→ **Mini NIR spectrometer allows to quantify plasticized content**

- Obvious patern
- Strong concentration variations (%)

→ **Necessory to develop**

- Sampling interface
- Computer interface
- Chemometric interface



THANK YOU FOR YOUR ATTENTION

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