# Application des techniques de spectroscopie vibrationnelle à des analyses en ligne dans les procédés de polymérisation

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Vibrational Spectroscopy, UV-Visible and in / on / at-line analysis

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# Arkema, les polymères, les marchés, le site de Serquigny

**2014**

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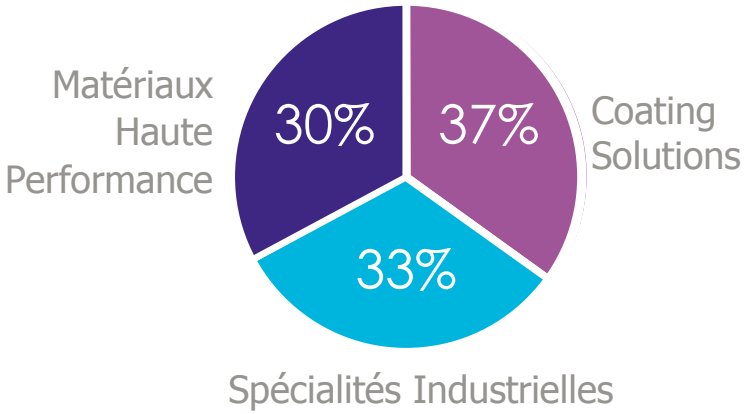
# Arkema en bref

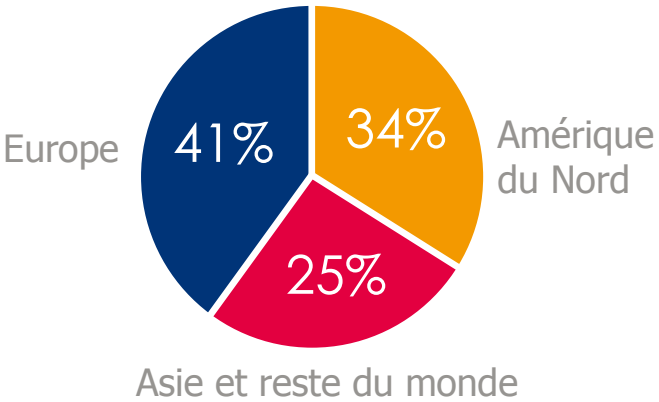
- Acteur mondial de la chimie de spécialités
- Chiffre d'affaires de **6,1 Md€***
- Positions de 1er à 3e mondial sur 90 % du portefeuille d'activités
- **14 000** salariés dans 40 pays
- **90** sites industriels
- **10** centres de R&D

*** Chiffres 2013**

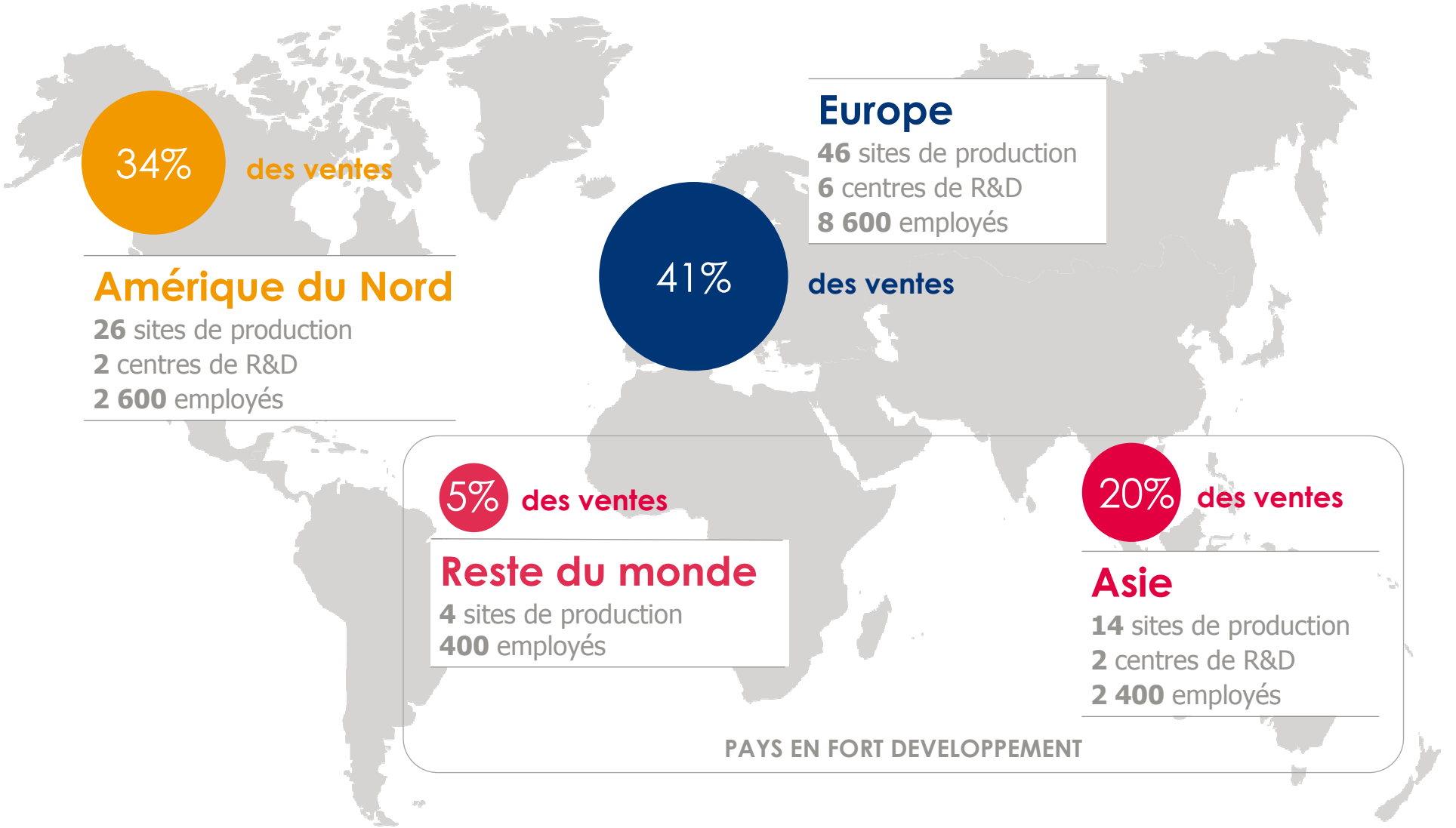
**Ventes par pôle***




**Ventes par région***



# Une présence géographique équilibrée



34% des ventes

## Amérique du Nord

**26** sites de production
**2** centres de R&D
**2 600** employés

## Europe

**46** sites de production
**6** centres de R&D
**8 600** employés

41% des ventes

5% des ventes

## Reste du monde

**4** sites de production
**400** employés

20% des ventes

## Asie

**14** sites de production
**2** centres de R&D
**2 400** employés

PAYS EN FORT DEVELOPPEMENT



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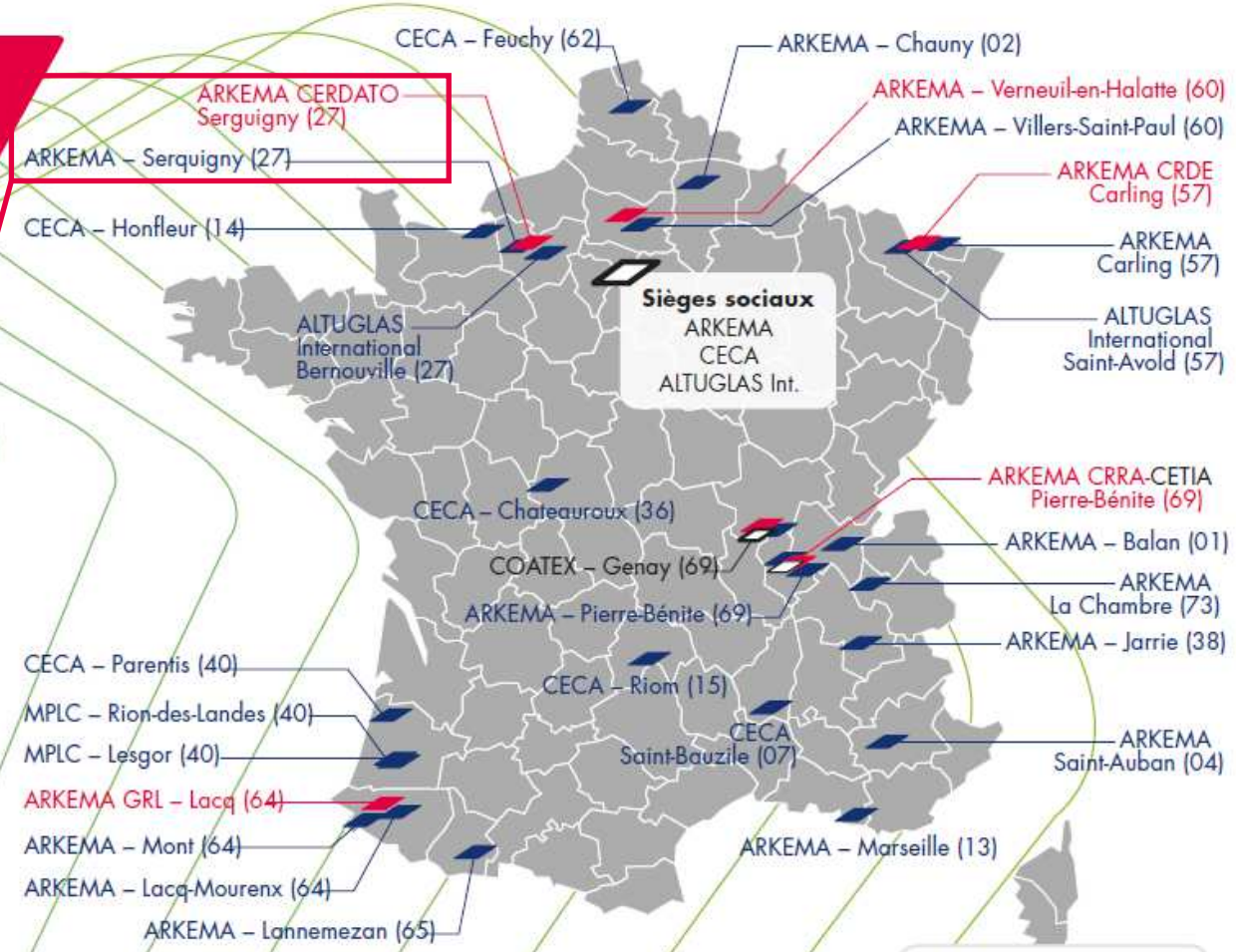
# ARKEMA, PREMIER CHIMISTE FRANÇAIS

**25**
sites industriels en France

**11% DU CA**
du Groupe

près de 6 700 personnes




# ARKEMA en France

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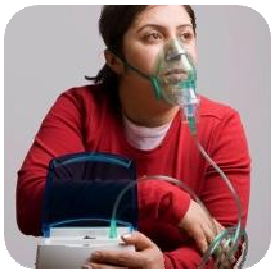
# Trois pôles d'activités

## Matériaux Haute Performance

**Des solutions innovantes et à haute valeur ajoutée**

- Polyamides de spécialités
- Polymères fluorés
- Adsorption/filtration (CECA)
- Peroxydes organiques

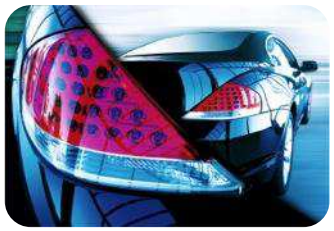



## Spécialités Industrielles

**Une présence mondiale sur des niches industrielles intégrées**

- Thiochimie
- Fluorés
- PMMA (Altuglas International)
- Oxygénés



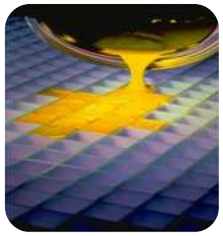



## Coating Solutions

**Des solutions pour les peintures décoratives, les revêtements industriels et applications acryliques en forte croissance**

- Acryliques
- Résines de revêtements
- Résines photoréticulables (Sartomer)
- Additifs de rhéologie (Coatex)





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# Des positions de leader

| POSITION | | PRINCIPAUX CONCURRENTS | % CA GLOBAL |
|---|---|---|---|
| #1 | Polyamides de spécialités | • Evonik<br>• Ems | 13% |
| #1 | PVDF | • Solvay | |
| #1 | Thiochimie | • Chevron Phillips | 9% |
| #2 | Peroxydes organiques | • Akzo Nobel<br>• United Initiators | 4% |
| #2 | Gaz fluorés | • Dupont<br>• Honeywell | 9% |
| #2 | PMMA | • Evonik<br>• Mitsubishi Chemical | 11% |
| #3 | Peroxyde d'hydrogène | • Solvay<br>• Evonik | 4% |
| #3* | Acryliques | • BASF<br>• Dow<br>• Nippon Shokubai | 15% |
| #3 | Coatings | • BASF<br>• Dow | 22% |

Matériaux Haute Performance  Spécialités Industrielles  Coating Solutions

**Parmi les 3 premiers mondiaux sur 90% du portefeuille**



* Après l'acquisition de la 1ère ligne de 160 kt de Jurong en Chine

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# Le site de Serquigny

Une usine de production & Un centre de recherche

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# Usine

Fabrication de polyamides de haute performance

RILSAN® BY ARKEMA

RILSAN® HT BY ARKEMA

RILSAN® FINE POWDERS BY ARKEMA

RILSAN® CLEAR BY ARKEMA

RILSAMID® BY ARKEMA

PEBAX® BY ARKEMA

PEBAX® RNEW BY ARKEMA

**Expéditions :**

**8 % France**

**42 % Europe** (hors France)

**50 % Reste du Monde**

= **92%** **de la production est exportée**

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# CERDATO :

## Centre de Recherche et Développement

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# CERDATO

Sa vocation :

Concevoir, synthétiser, formuler et transformer des polymères de haute performance en vue de leur commercialisation

Les missions :

- Mettre au point de nouveaux matériaux
- Développer de nouvelles applications
- Assurer une Assistance Technique mondiale
- Améliorer nos procédés

Des fondamentaux:

La sécurité toujours en tête
sécurité en action

- La sécurité
- La relation clients
- L'amélioration permanente (qualité ISO9001)

afaq ISO 9001 Qualité AFNOR CERTIFICATION

Effectif:

250 Employés

80 Cadres, dont 50 docteurs-ingénieurs

170 Techniciens et opérateurs
(Bac Pro, DUT, BTS, licence professionnelle…)

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# Les Axes de R&D du CERDATO

## Le Développement de Matériaux Haute Performance et d'Origine Renouvelable

- Rilsan® B
- Pebax® Rnew
- Rilsan® Clear Rnew
- Rilsan® HT
- Rilsan Tie Flex pour MLT
- Polyamide 10.10 Hiprolon

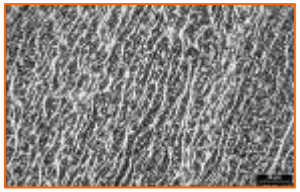




## Les Matériaux Très Haute Performance

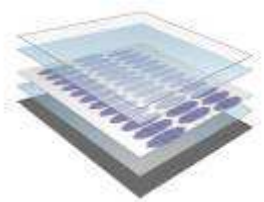
- PEKK
- Polymères Antistatiques Permanents
- Composites thermoplastiques
- Matériaux pour le Laser sintering





## Les Matériaux pour le marché du Photovoltaïque

- **E**vatane®
- Luperox®
- Kynar® Film
- Apolhya® grafted copolymers



## Les Polyoléfines Fonctionnelles pour Structures multicouches

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# Control of polymerisation processes

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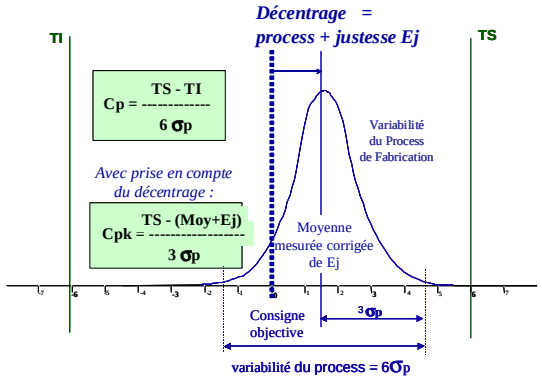
# Introduction

- **In the industrial world, analytical methods are almost always considered to be too slow, too complicated, too hazardous and very often not precise enough. However, it is necessary to get some indications as to conduct the processes.**
- **In the case of polymers, it is necessary to know at least the final state of polymerization which can be given by viscosity in solution or melt flow index measurement in a control lab environment.**
  - These results can be completed by size exclusion chromatography or more sophisticated measurements such as NMR in a research environment.
  - Residual monomers and oligomers can also be measured using gas or liquid chromatography. Most of these properties can also be obtained using vibrational spectroscopy.
- **Vibrational spectroscopy has already an important place in the control labs :**
  - To qualitatively control raw materials,
  - To quantitatively control copolymer contents (EVA, EDA, …) or grafting of reactive groups (Maleic anhydride in functionalized polyolefins).
- **and /or in research labs:**
  - To identify defects or pollutions,
  - To improve the different steps of the process
- **Additionally, the different vibrational spectroscopy techniques have a very good ability for on-line control (especially NIR and Raman).**

# Process control : why?




*"All models are wrong, some can be useful "*
**George Edward Pelham Box** (Statistician)

- **Give on specs products to customers**
- **Avoid manufacturing of bad products**

} Production

- **Improve the process**
  - Liability
  - Productivity
  - Safety
  - Etc …

} Development

- **Understand the process**
- **Develop new process**

} Research

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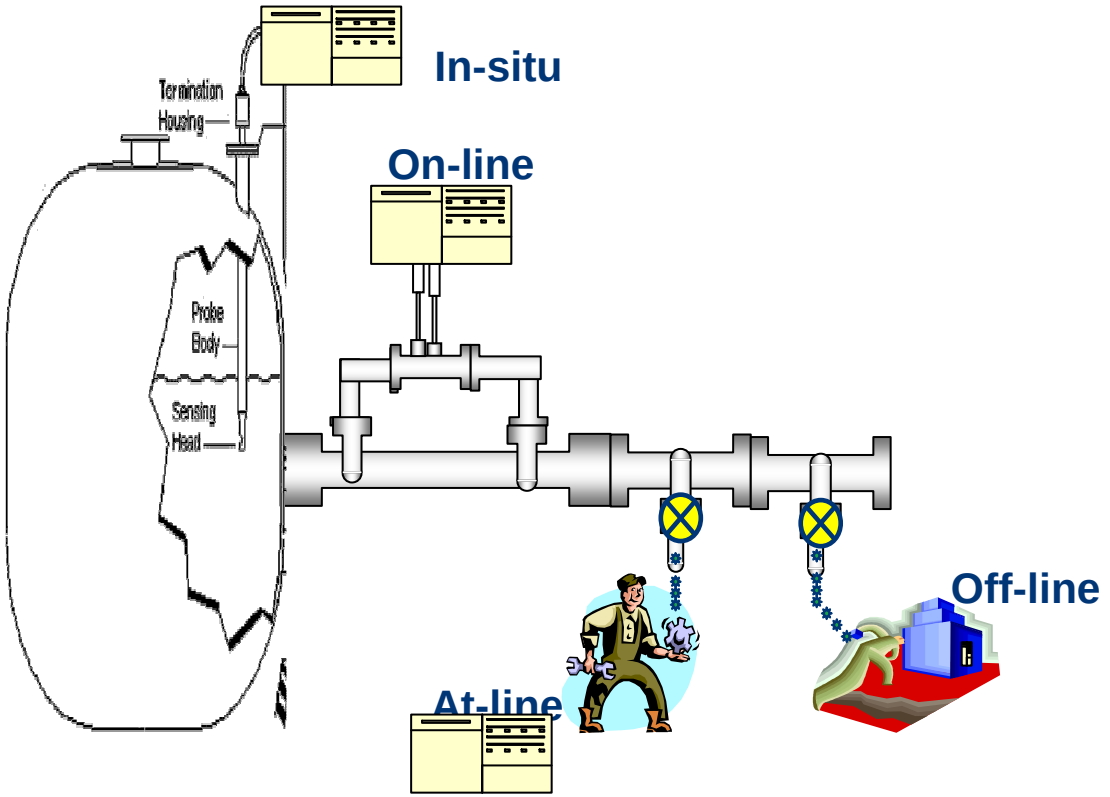
# Process control : How?

- **« off-line » control**
  - Sampling
  - Analysis in QC lab
  - Possibly « sophisticated » Methods
  - Response time can be long
- **« at-line » control**
  - Sampling
  - Analysis in the production area
  - Simple Methods
  - Short response time
- **« In-line or on-line » Control**
  - Sampling loop or in-situ analysis
  - No sample manipulation
  - Quasi immediate response time
  - Information on the process in-situ
  - Maintenance?

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# Quantitative analysis with vibrational spectroscopy

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# Vibrational spectroscopies

MIR : Mid Infrared spectroscopy

- **Based on the absorption of IR light in the region between 2500 nm and 25000 nm (4000 - 400 $cm^{-1}$)**
- **Fundamental vibrations ➔ spectral interpretation based on literature and libraries**
- **Very intense absorption bands**
- **Major limitation ➔ sample preparation (!! ATR is more tricky than it looks!!)**

Raman spectroscopy

- **Based on inelastic interaction between laser light (from UV to Near IR) and molecules in the region between 2500 nm and 25000 nm (4000 - 400 $cm^{-1}$)**
- **Fundamental vibrations ➔ spectral interpretation based on literature and libraries**
- **Low intensity diffusion bands ➔ no sample preparation**
- **Major limitation ➔ fluorescence / sample degradation**

NIR : Near InfraRed spectroscopy

- **In the region between 800 and 2500 nm (12500 - 4000 $cm^{-1}$)**
- **Overtones and combinations of fundamental bands in Mid InfraRed region**
- **10 to 1000 less intense than fundamental bands for the 1st overtone and combination region**
- **technique measuring essentially H bonds such as : -OH , -NH, -CH and their combinations.**
- **Major limitation ➔ spectral interpretation**

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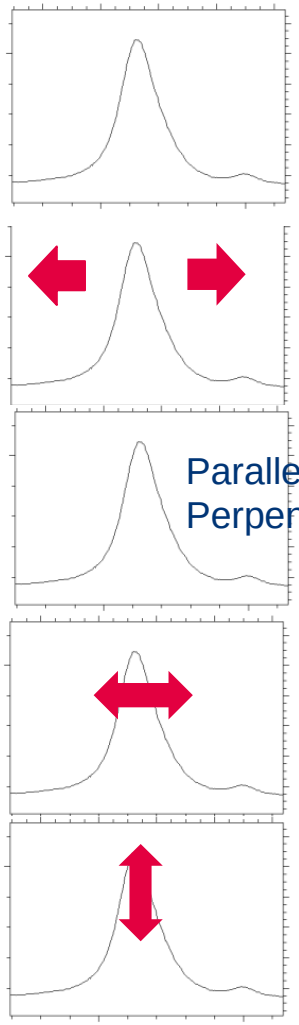
# Vibrational Spectroscopy




Characteristic frequencies → Composition of Material

Changes in frequency → Stress /strain State

Polarization of peak → Crystal symmetry and Orientation

Width of Peak → Quality of Crystal

Intensity of peak → Amount of material

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# Quantitative analysis with vibrational spectroscopy

## *In the laboratory (control or research)*

### Manual methods

- Use of specific vibrational bands (Band ratio) to measure the concentrations
- Simple linear regressions

### Chemometric methods

- Multivariate approach from simple cases to complex mixtures
  - Model development requires a large set of data
  - Can be moved in a production environment

## *At the production floor (at-line/on-line)*

### Chemometric methods

- At-line measurement (mostly NIR)
  - Simplicity / user interface
  - Robustness

### Use of fiber optics

- On-line measurement (NIR and Raman)

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# Characterization of ethylene vinyl acetate copolymers (EVA) by vibrational spectroscopy

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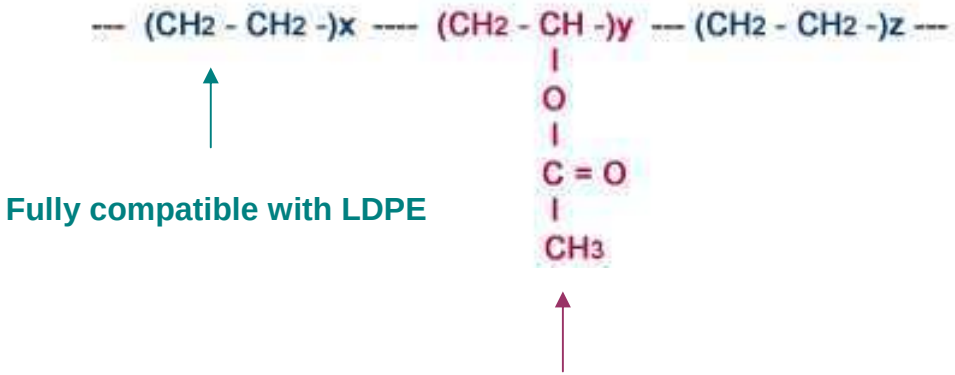
# Evatane®

EVATANE®

*Ethylene - Vinyl Acetate (VA)*




**Evatane® Resins are ethylene copolymers with a high vinyl acetate content (18 to 42%).**

**It is more elastomeric than polyethylene, compatible with a wide range of polymers, and easy to process.**

**Evatane® copolymers are used in many applications for many markets such as :**

- **photovoltaïcs**
- **hot melt adhesives**
- **cables**
- **plastics**
- **automotive**
- **packaging**
- **road bitumen**

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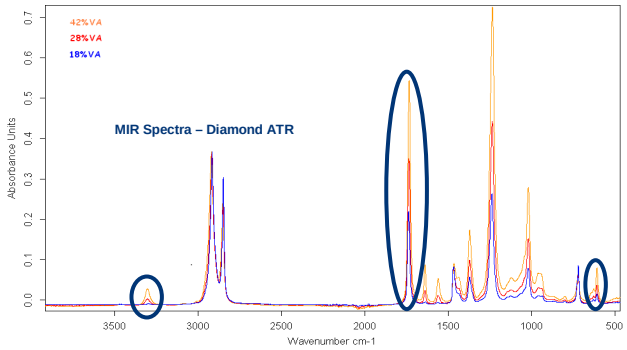
# Quantitative measurements using FTIR
# ISO 8895 - 1998



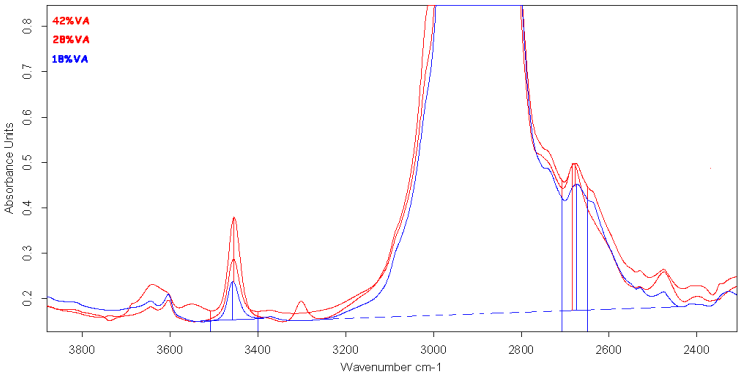

**MIR Spectra – Diamond ATR**

The quantitative analysis is based on the Lambert-Beer relationship between the Absorbance of the IR bands and the concentration of the measured property. The concentrations are obtained using NMR.

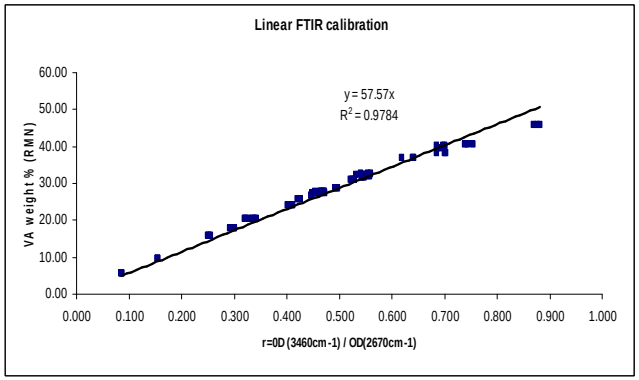
The thickness is corrected by the absorbance of a band independant of the property

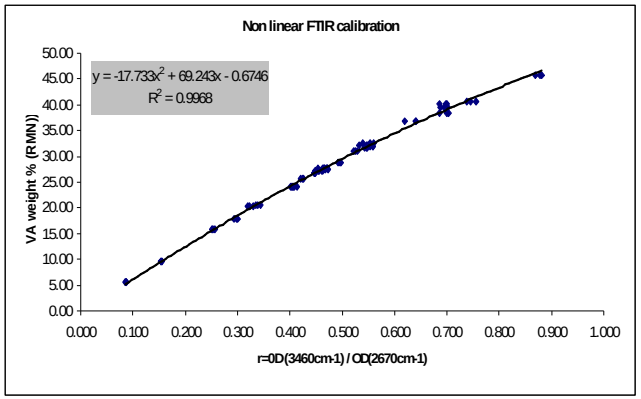
%VA=f ($2\upsilon_{C=O}$ / $2\delta_{CH2}$ band ratio)

- $2\upsilon_{C=O}$ = 3460 $cm^{-1}$
- $2\delta_{CH2}$ = 2670 $cm^{-1}$
- The quantitative measurements are done in transmission mode on 300 µm films. It is necessary to use 2 calibrations (%VA < 30% and > 30%)

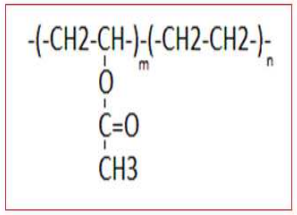



**MIR transmission Spectra –300 microns films**

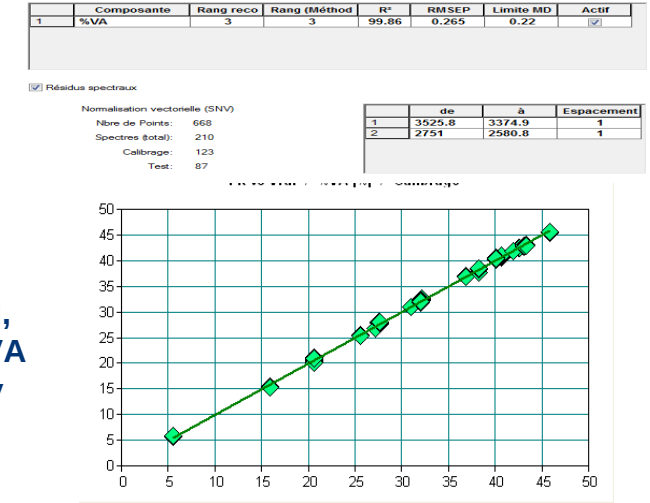



**As mentionned in the ISO method, the linear relationship fails for %VA above 30%. It can be explained by the following equations**




$$\frac{abs\ 3460cm^{-1}}{abs\ 2670cm^{-1}} = \frac{m}{2n+m} = \frac{1-n}{n+1} \neq linear\ (with\ m = 1-n)$$






**Another way around to better take into account the contribution of both co-monomers is to use PLS calibration on the FTIR spectra.**

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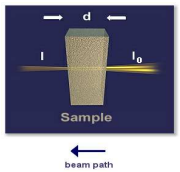
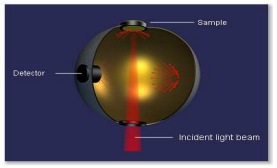
# NIR : From laboratory measurement to at-line and on-line



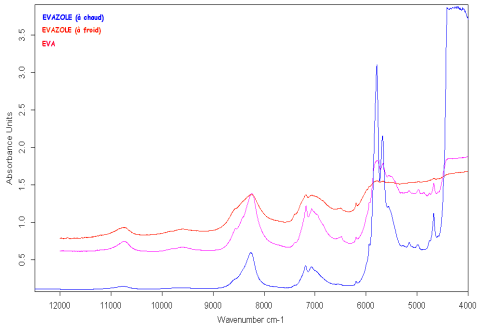




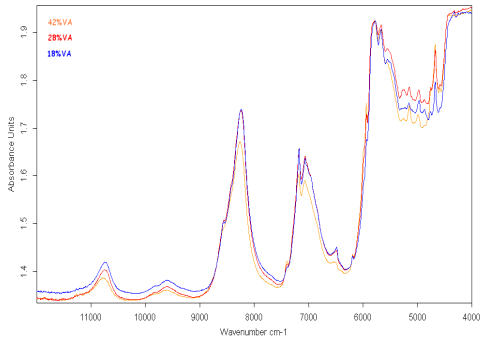
Schematic diagram of an integrating sphere

Probe head adapted for at-line measurement

Probe head adapted for on-line measurement



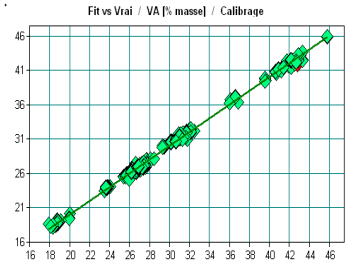

From the top to the bottom :
NIR spectra obtained on granules, gel and melted EVA

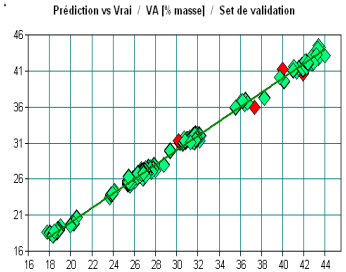



NIR spectra obtained on granules with various %VA content

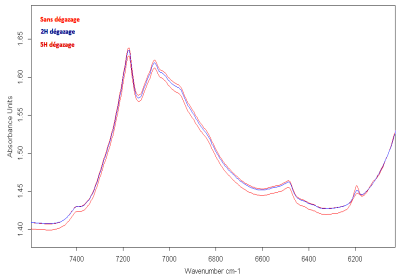
## %VA

| | |
|---|---|
| $R^2$ | 99.56% |
| Bias | 0.006 |
| RMSEP | 0.346 |
| Nbr of factors | 9 |

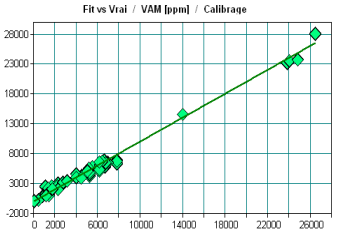


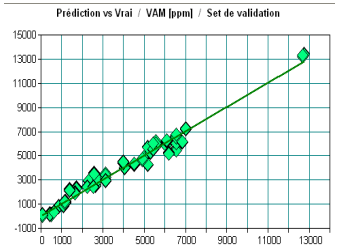




## %residual monomer




| | |
|---|---|
| $R^2$ | 97.37% |
| Bias | -80 |
| RMSEP | 437 |
| Nbr of factors | 4 |




Additionally NIR allows to get an information on the rate of polymerisation which is correlated with the viscosity or the MFI.

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# Solid State Polymerisation of Polyamide powders followed at-line by NIR spectroscopy

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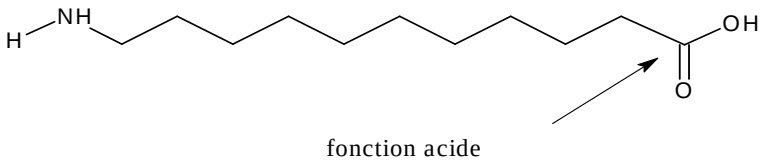
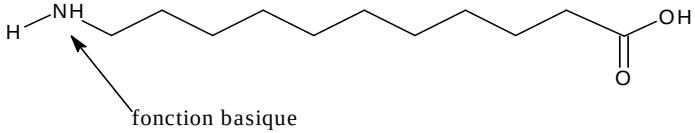
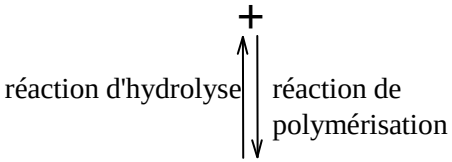
# RILSAN powders viscosity control using Near Infrared Spectroscopy (NIR)

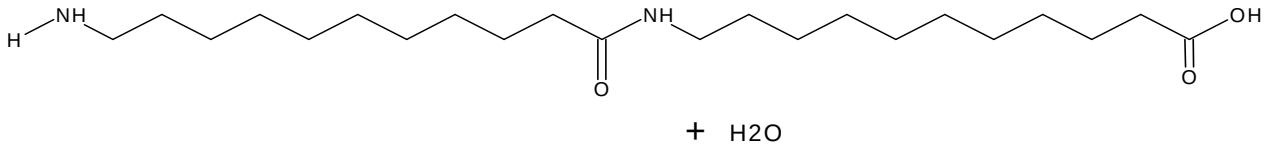
## Process :

- Solid State Polymerization
- Water elimination at high temperature under vacuum




- Reduction of the number of acids and amine end groups
- Increase of the number amide groups

- Viscosity range from 0.5 to 1(0.9 -1.2)
- Acceptation range from 0.03 to 0.06 around final value

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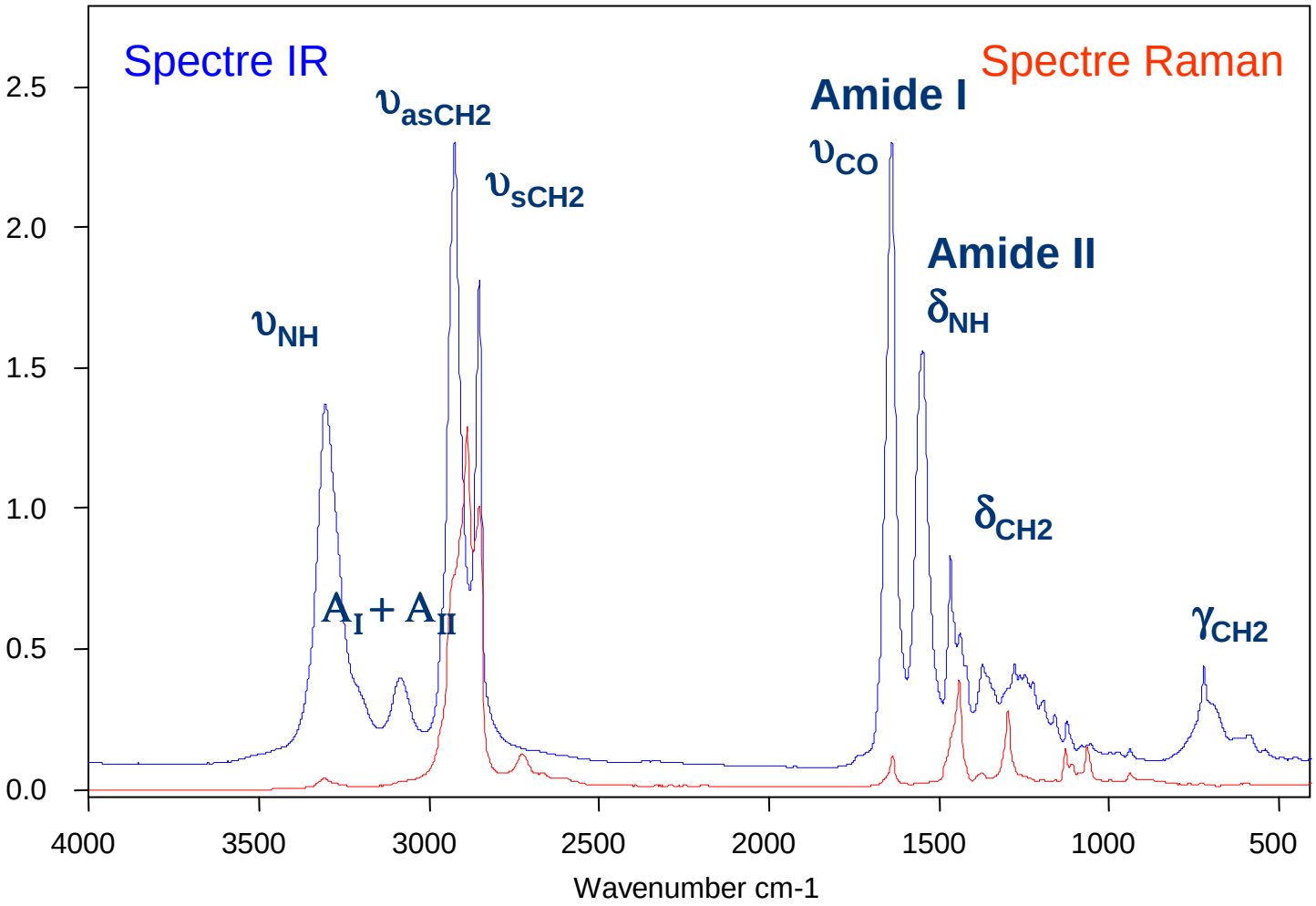
# IR and Raman spectroscopic response for PA11

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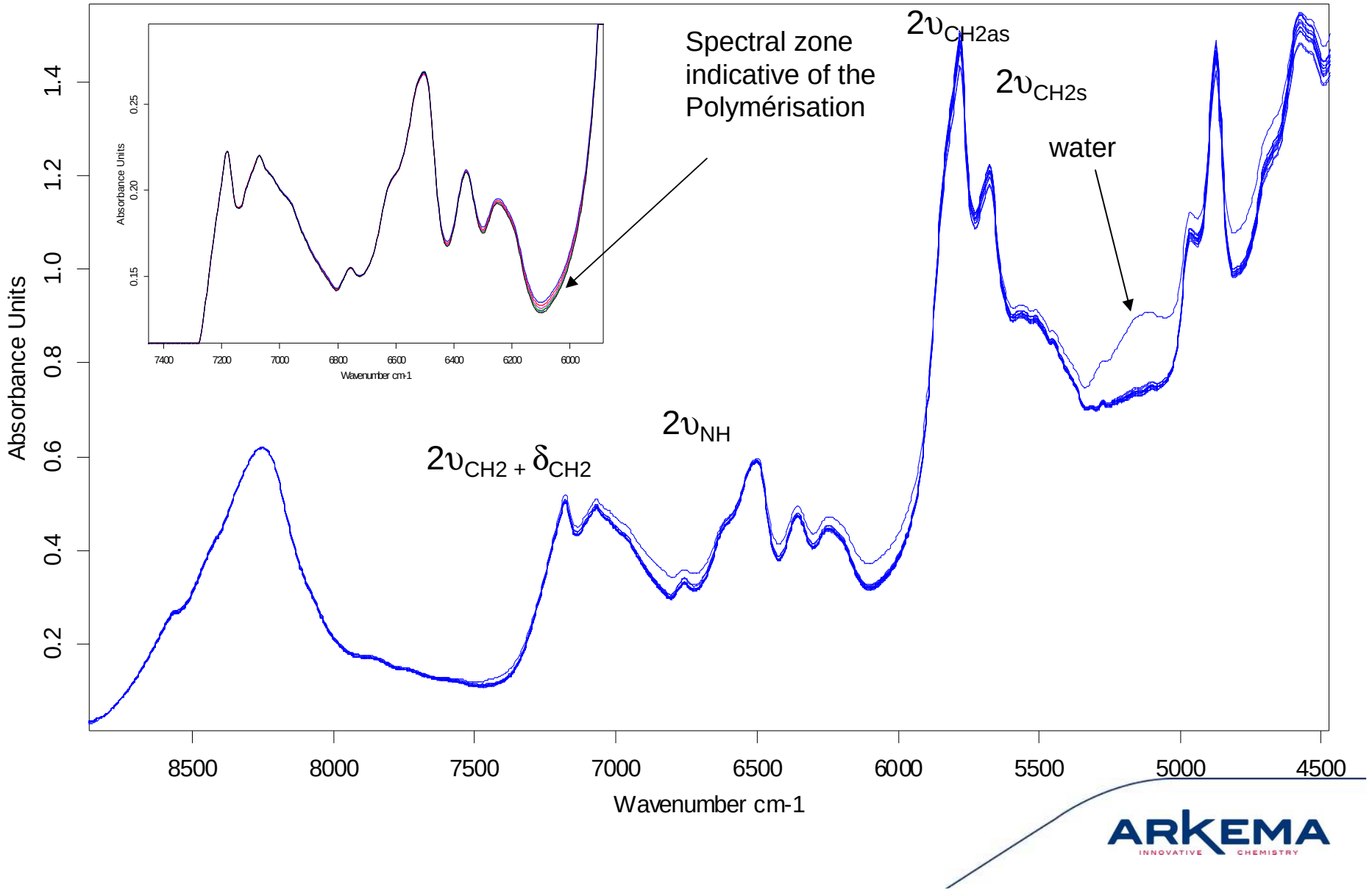
# Variations of the NIR spectra during SSP
# At-line measurements / room temperature



# RILSAN powders viscosity control using Near Infrared Spectroscopy (NIR)

- **Reference method**
  - Inherent viscosity in solution
  - Standard deviation 0.015
  - Measurement time from 1 to 2h

- **NIR spectra contain information on the polymers chain's length**

- **Possibility to correlate NIR with viscosity**
  - $\eta = KM_w^{\alpha}$ with $\alpha \sim 0.5$ (Mark-Houwink relation)

- **Measurement time of about 1 minute**

- **« at-line » measurement by production staff :**
  - response time 10 – 15 minutes (sample temperature decrease)
  - Non contact measurement through a vial

- **Possibility to measure water content**

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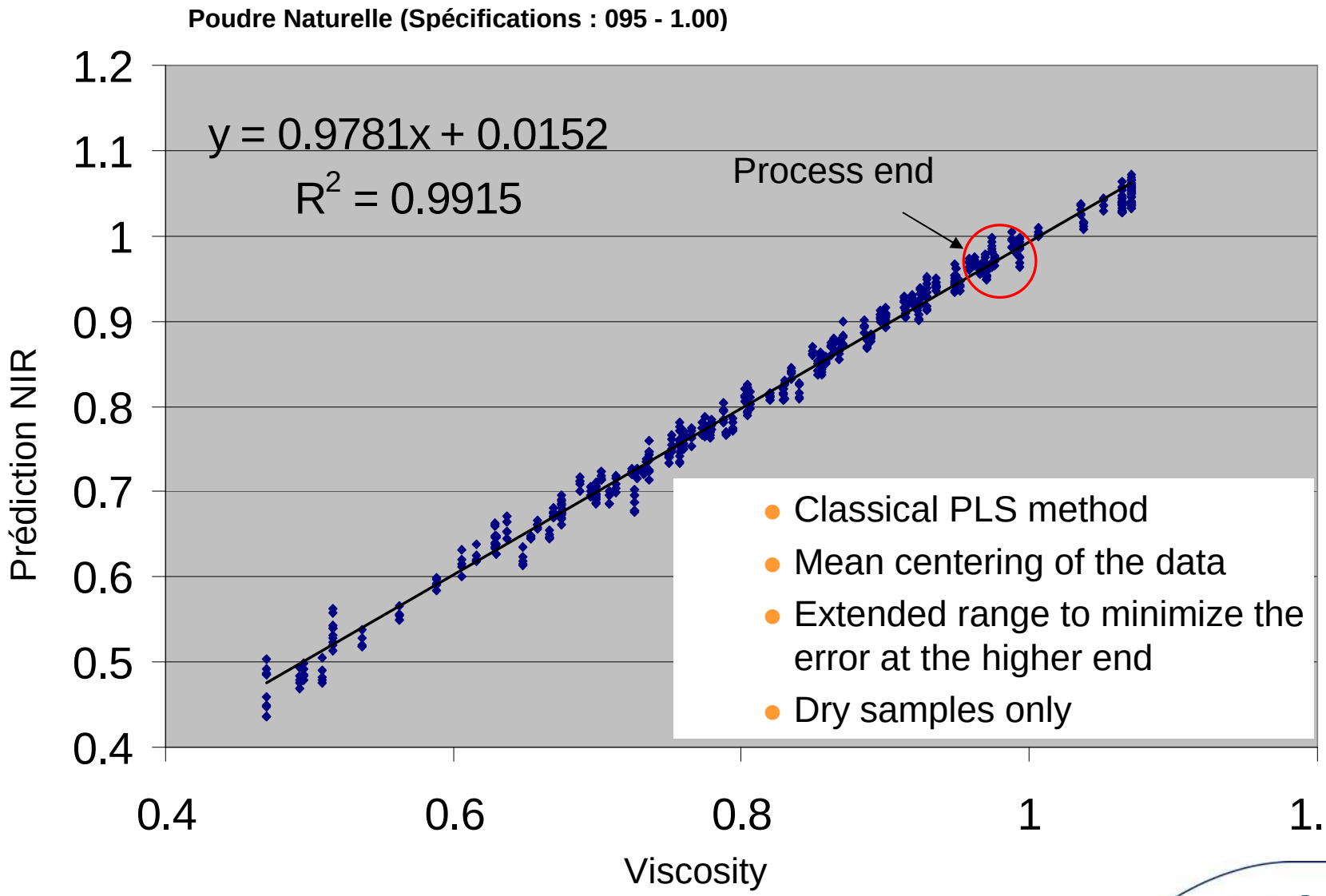
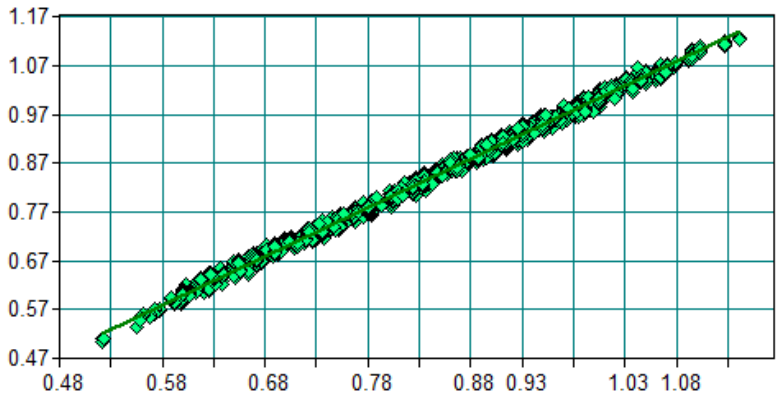
# Calibration curve for SSP
# At-line measurements / room temperature



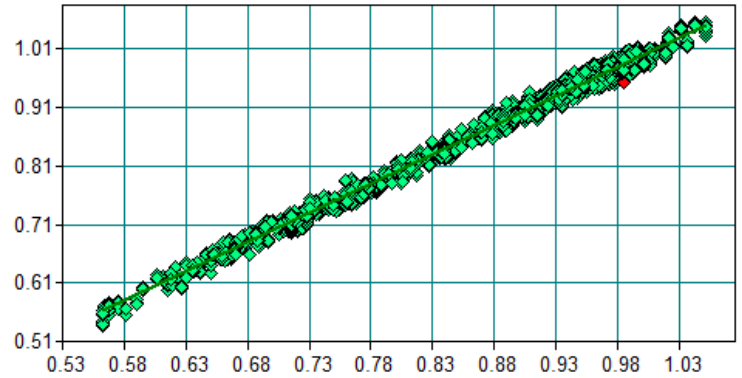
# Inherent viscositv of PA 11 powders

Fit vs Vrai / Visco / Calibrage



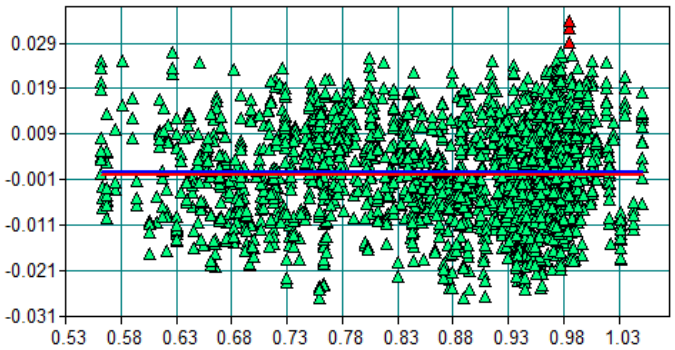

Rang: 19 R² = 99.56 RMSEE = 0.00914 RPD: 15.1
Validation No 2 + 2013 05 29 REV T Nat 2P + 09S.q2

Prédiction vs Vrai / Visco / Set de validation




Rang: 19 R² = 99.11 RMSEP = 0.0111 Biais: 0.000741 RPD: 10.6
Validation No 2 + 2013 05 29 REV T Nat 2P + 09S.q2

Différence vs Vrai / Visco / Set de validation




Rang: 19 R² = 99.11 RMSEP = 0.0111 Biais: 0.000741 RPD: 10.6
Validation No 2 + 2013 05 29 REV T Nat 2P + 09S.q2

- **Method in use at-line in the plant for more than 5 years**
- **Cross validation with inherent viscosity measurement once a year**
- **No obvious spectral feature in the spectra**

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# On-line measurement of the PA11 powder SSP

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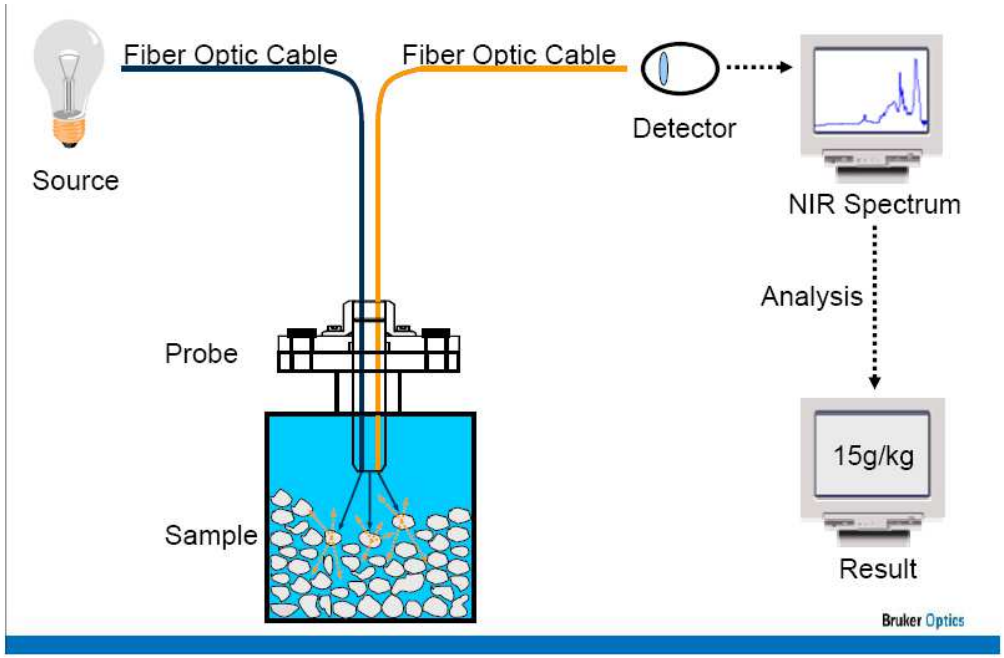
# Experimental setup : pilote and industrial





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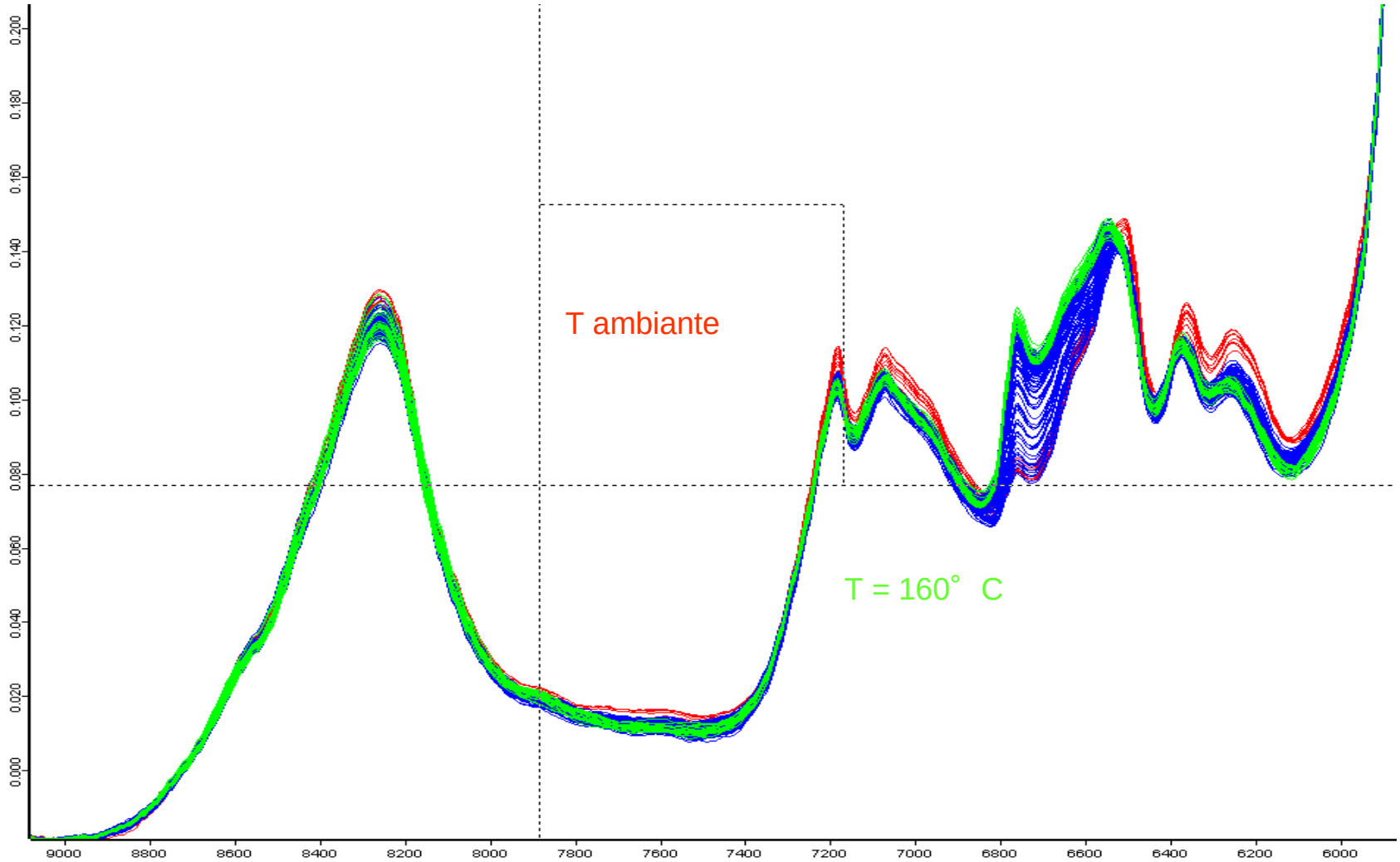
# Evolution of NIR spectra with temperature

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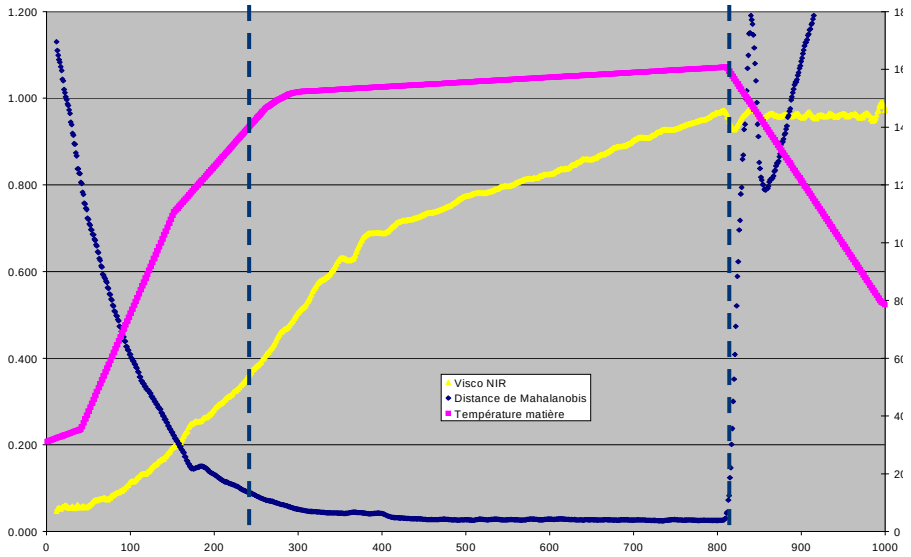
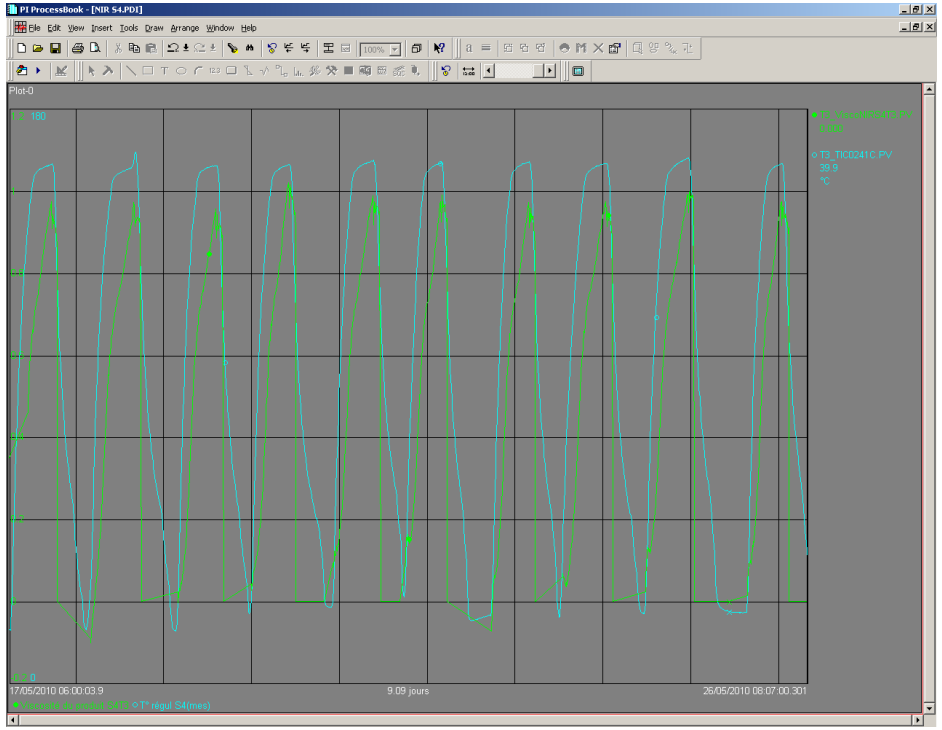
# On-line measurement : plant




- The spectral variations permit to predict temperature
- Developping models in a stable temperature range allows to predict viscosity
- Mahalanobis distance gives a good indication of when to use the viscosity values

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# Technical considerations

- **A lot of sources of variations**
  - Variable Temperature ➔ Models developed in the plateau area (less than 10° C variation)
  - Continuous data collection and moving average on 10 spectra sent to control screen based on Mahalanobis distance
  - Background collection twice a year

  ➔ requires a very stable instrument

- **Data collection leads to large amount of spectra**
  - 1 spectrum every minute
  - Reference samples only once an hour
  - Model development takes a long time
  - Model maintenance needs to be minimum

  ➔ requires a very stable instrument

- **Raman spectroscopy is also well suited for on-line measurements**
  - The technology is more complex and the stability has to be proven
  - Raman is very interesting to understand what's going on in the process
  - A combination of techniques could be of interest

- **The use of MIR spectroscopy is limited for on-line measurements**
  - Necessity to have a very short path length (ATR or thin films)

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# DOES NIR IMPROVE THE PRECISION?

REFERENCE METHODS

- **Most of the time requires a dilution**
- **Takes a long time**
- **Very often based on a small amount of sample**

NIR

- **No sample preparation**
- **Analysis based on a large amount of sample**
- **Rapid analysis → possibility to average signal**
- **High S/N ratio**
- **Use of mathematical treatments and chemometrics analysis**

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# CONCLUSION

- **In the case of solutions, it is possible to calibrate NIR based on gravimetry ➔ NIR gives better results than the reference methods requiring sample preparation**

- **In the case of polymers, the NIR methods can be improved by using a large number of calibration samples.**
  - NIR gives better results than most of the reference methods
  - Calibration transfer increases variability but it can be compensated over time
  - NIR does not suffer from long term variability
  - Sometimes you reach the limits

- **In any cases, NIR gives the results faster and easier once the calibrations are done**

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# GENERAL CONCLUSION

- **Vibrational spectroscopy techniques are complementary**

- **NIR contains most of the information from both the Raman and Mid IR**
  - A good understanding of the fundamental vibrations can be helpful to better develop calibration models in the NIR
  - We need some work to better interpret the NIR spectra

- **Chemometrics is not only for NIR**

- **Raman instrumentation is growing fast**
  - New lasers
  - Edge filters
  - Better use of the detectors

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# Thank you for your attention

**Questions?**

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