

Chimar Hellas S.A.



***A new generation of methodologies  
for on-line monitoring  
of the industrial resin production***

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**6th European Wood-Based Panel Symposium**

**8-10 October 2008 in Hanover/Germany**



- ☐ Recommendation to reclassify formaldehyde emissions - summer of 2004
- ☐ Reduction of the resin mole ratio
- ☐ Need of reliable control of the whole resin synthesis procedure
- ☐ NIR spectroscopy has been applied to many fields of science incl. the wood based panel industry
- ☐ Spectroscopic applications developed and installed industrially by Chimar - GNOSSI™



**Production of  
raw materials**

**Final products**

**NIR technology  
&  
GNOSSI™ software**

**Synthesis of resins**



**Raw materials**

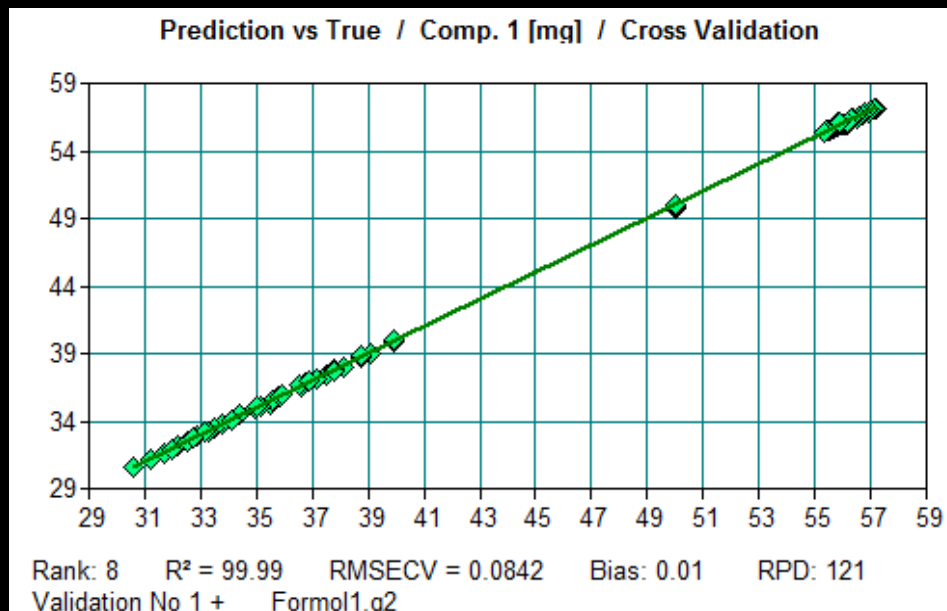
**UREA**

**FORMALDEHYDE**

**FORMOL**

**UFC**

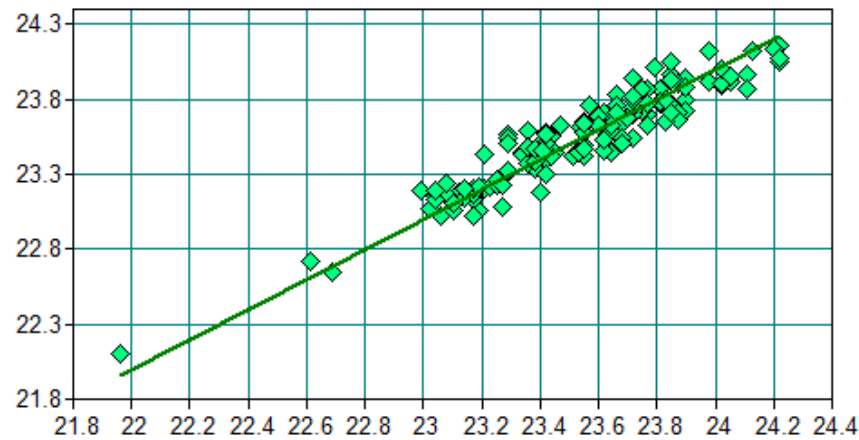
- Formaldehyde concentration



- Urea concentration
- Formaldehyde concentration
- Molar ratio
- Solids content
- Buffer capacity

## UREA

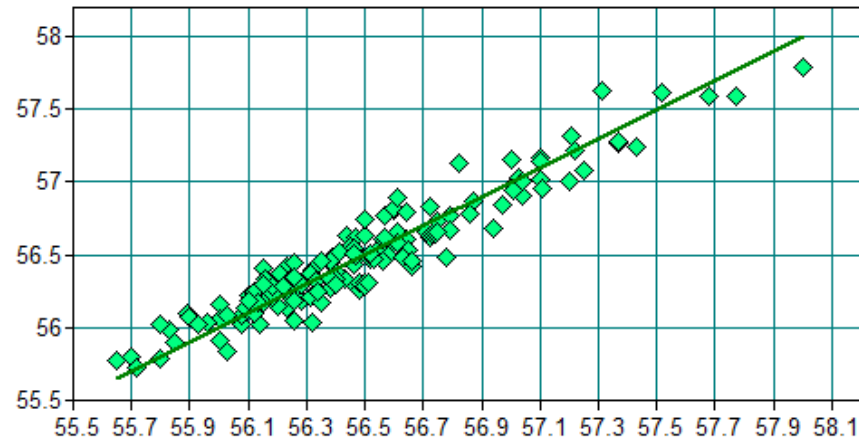
Prediction vs True / uREA [%] / Cross Validation



Rank: 7  $R^2 = 89.34$  RMSECV = 0.115 Bias: -0.00652 RPD: 3.07  
Validation No 12 + UFC\_U\_205.q2

## FORMALDEHYDE

Prediction vs True / Formaldehyde [%] / Cross Validation



Rank: 5  $R^2 = 90.67$  RMSECV = 0.13 Bias: -0.00187 RPD: 3.27  
Validation No 4 + UFC\_F\_205.q2

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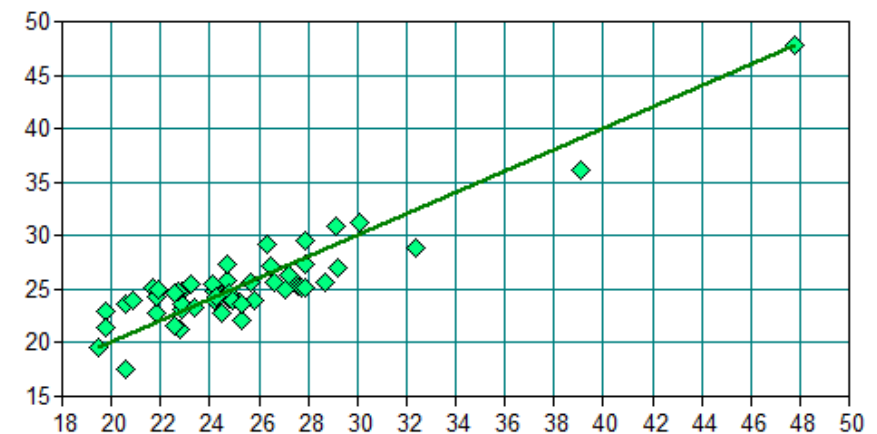


## UFC algorithms

**GNOSI is the unique technique  
that offers**  
reliable, rapid, precise, non-destructive, on  
line and real time measurements  
of UFC production

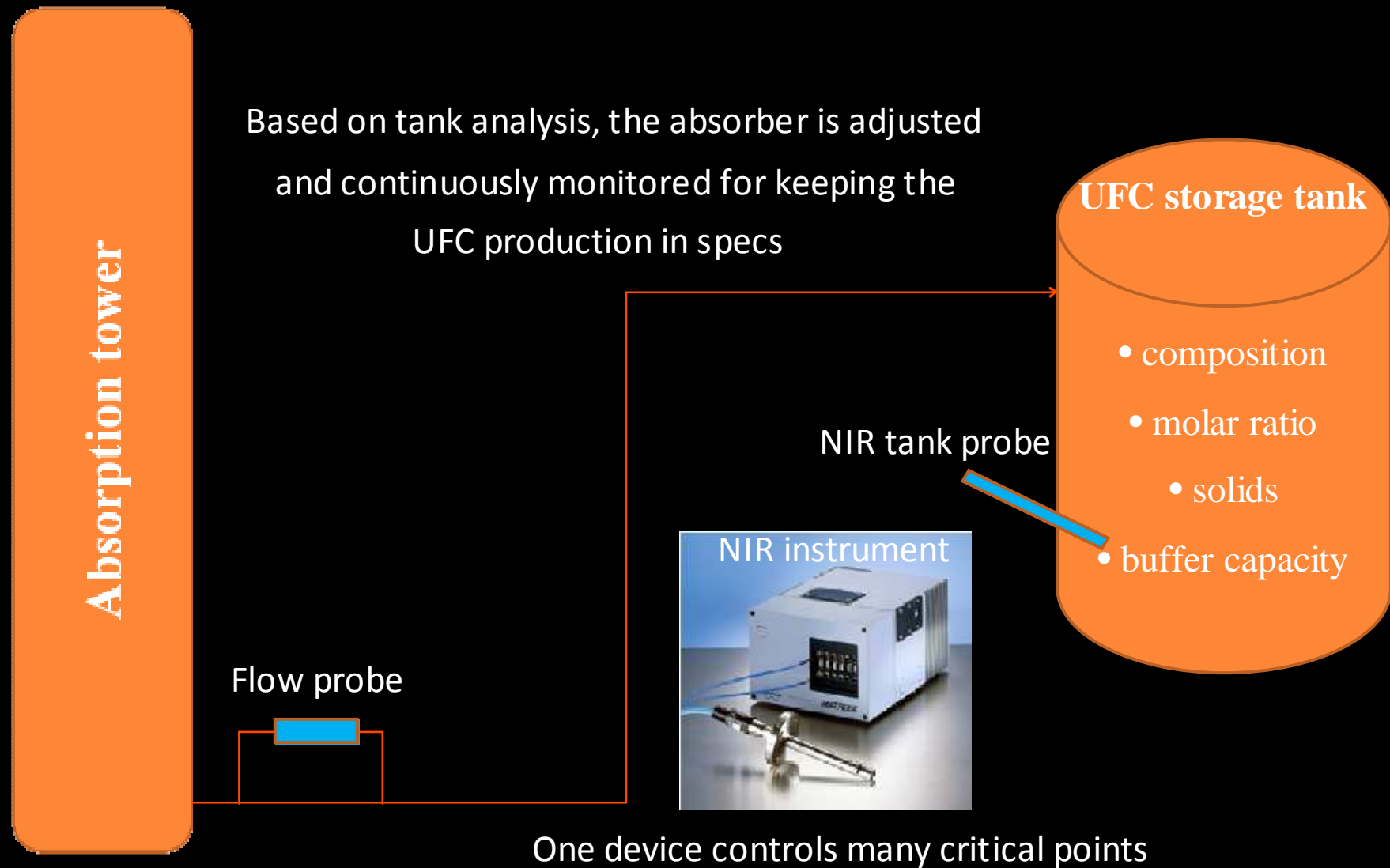
## BUFFER CAPACITY

Prediction vs True / Buffer Capacity [ml] / Cross Validation



Rank: 5  $R^2 = 82.05$  RMSECV = 1.93 Bias: -0.0379 RPD: 2.36  
6 + UFC\_BC.q2

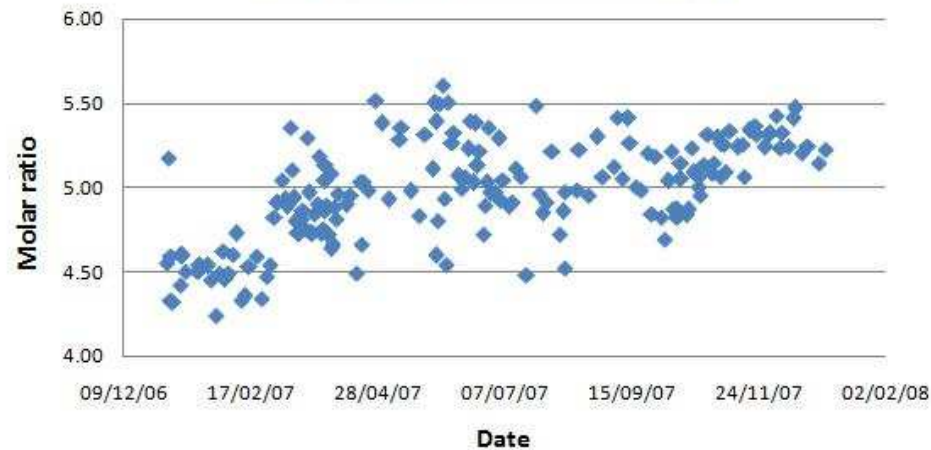
## Industrial application of GNOSST<sup>TM</sup> UFC



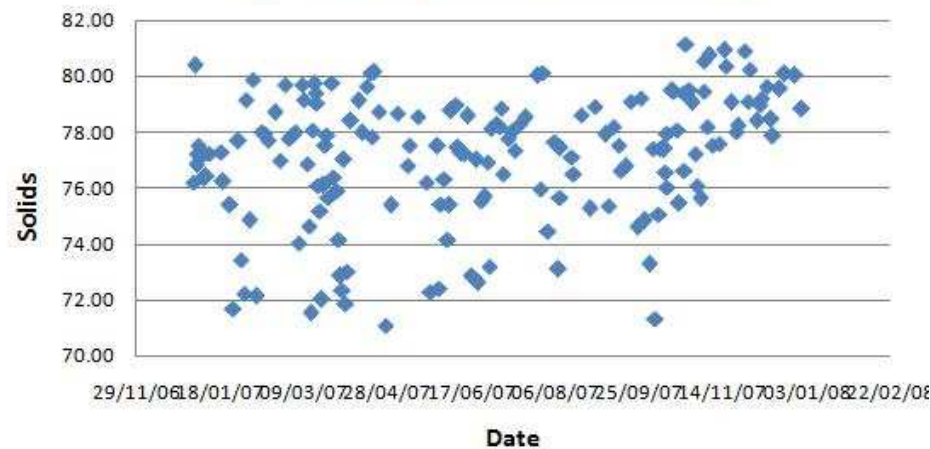


## UF C analysis of storage tanks during 2007 (industrial data)

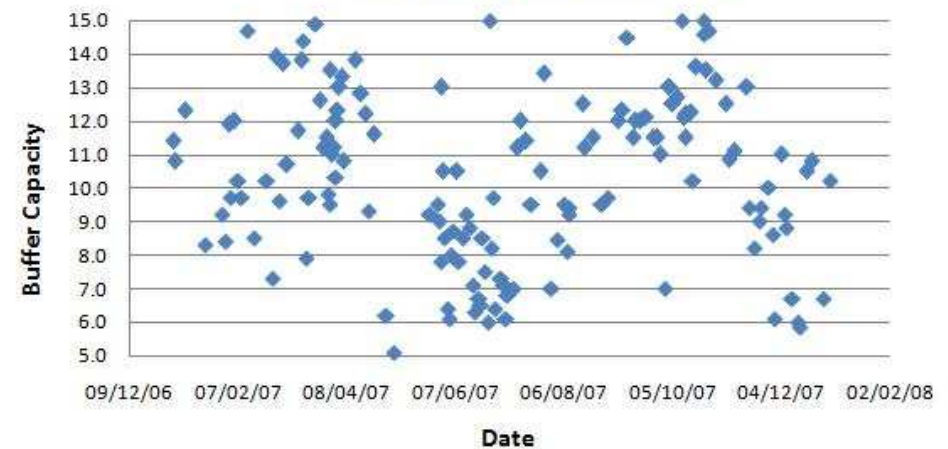
UFC MR (industrial data of 2007)



UFC Solids (industrial data of 2007)



UFC BC (industrial data of 2007)





## Example of GNOSSI™ UFC probe installation



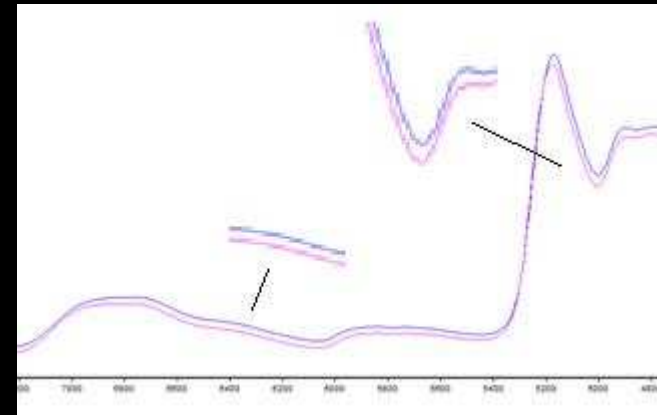
- Installed on a by-pass to the line connecting the absorber to the storage tank
  - Use of a de-aerator to avoid air bubbles
- The probe is installed 50 meters away from the instrument – remote sampling via fibre optics



## Top view of UFC probe



## Typical UFC spectra

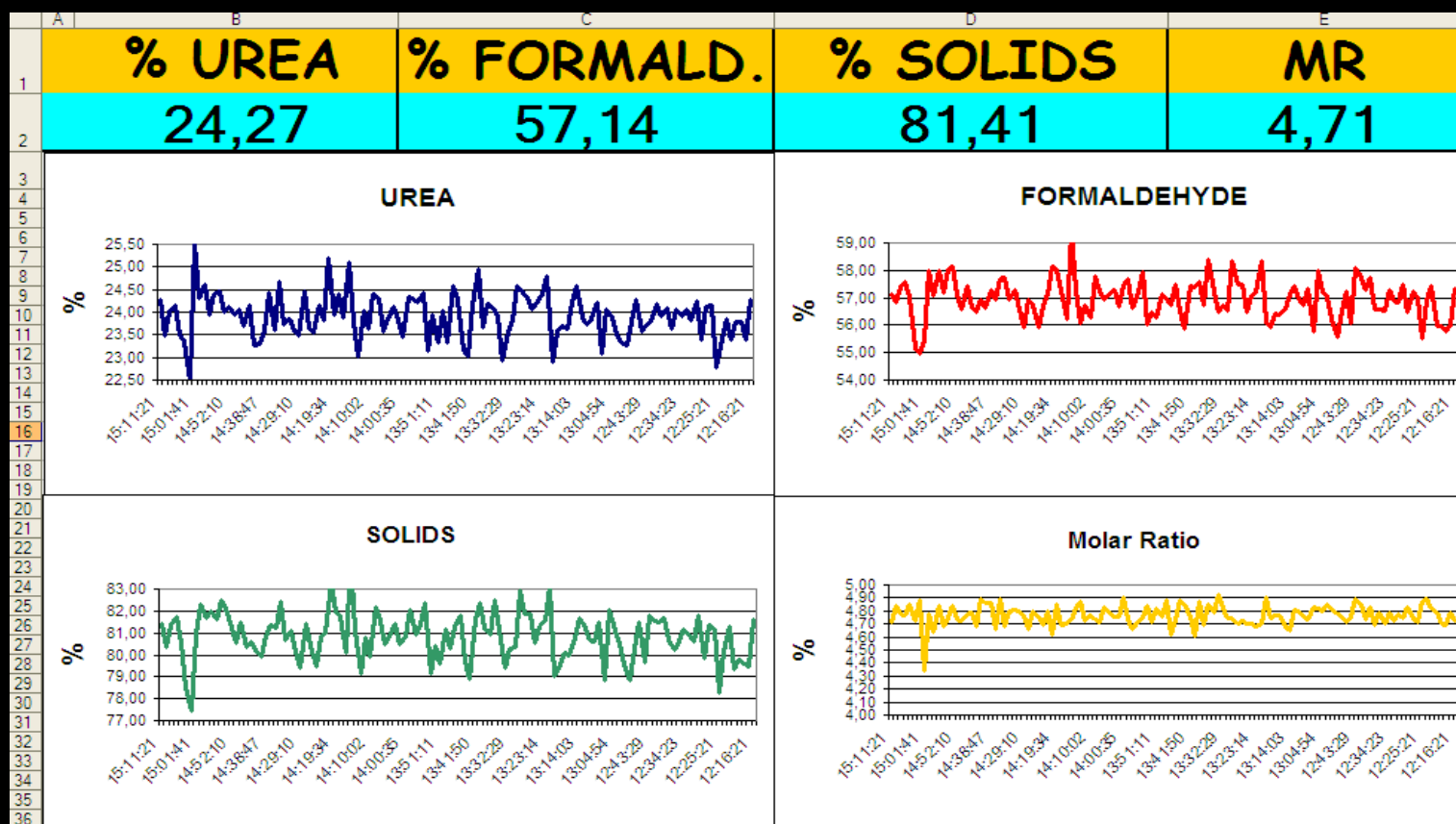


The portion of the **absorbed radiation** depends on the **properties** of the UFC.

The **time evolution** of some **characteristics bands** in the NIR frequency range determines UFC's chemical properties.

The results of the analysis are depicted on graphs in the control room.

# Industrial depiction of results - GNOSSI™ UFC



- GNOSSI™ can be used to:**
- online monitoring
  - control solids  $\Rightarrow$  more consistent product
  - ensure correct Molar Ratio



# **GNOSSI™ for UFC analysis**

## **ADVANTAGES**

- ❑ REAL TIME PRODUCTION CONTROL**
- ❑ ONLINE DETERMINATION OF SOLIDS AND MOLAR RATIO**
- ❑ IMMEDIATE TIME OF RESPONSE - RESULTS EVERY MINUTE OR LESS**
- ❑ NO MANPOWER REQUIRED FOR ANALYSIS**
- ❑ NO MAINTENANCE (EXCEPT IN CASE OF LINE BLOCKAGE)**
- ❑ LOW CONSUMABLES (ONLY PROBE AND FIBER OPTICS CAN BE DAMAGED IF LINE IS BLOCKED)**

# GNOSI™ for resin's synthesis

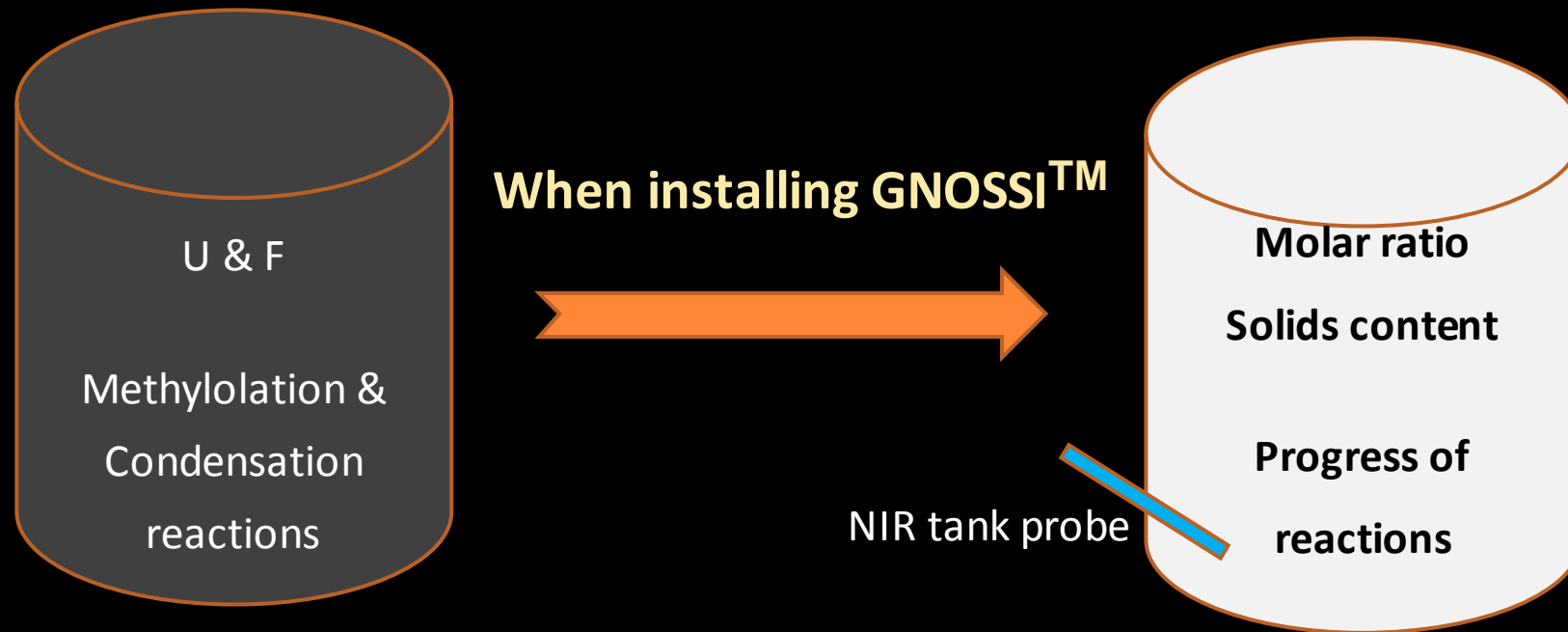


## Inventors of TEM

“...the time to look through materials  
to confirm and prove what is theoretical believed  
just arrived...”

## Chimar Hellas – GNOSI™ software

“...the time to install an eye in the reactor to confirm  
its content and the progress of the condensation just  
arrived...”



❑ **GNOSSI software** is the unique technique that can simultaneously determine numerous parameters of a complex system. When installing a probe in the reactor it stops being a black box.

❑ **Develop check points** on which we confirm the **molar ratio** and the **theoretical solids** content of the reactor.

# Industrial application of GNOSSI™ resins



**NIR tank probe**



**NIR probe installed**

- Practical installation system that allows the daily cleaning of the probe
- Sampling 30 meters away from the NIR instrument
- Depiction of the results on an excel file in the control room



# Predicting the MR & Solids in the reactor

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Calculated values

MR = 4.91 Th. Solids = 58.55%



MR_UI	MR_UII	MR_UIII	MR_UIV
out of range	2.106	out of range	out of range
Solids_UI	Solids_UII	Solids_UIII	Solids_UIV
out of range	66.43	out of range	out of range
Methylation			
in progress			
Condensation			
condensating			
Condensation Speed: normal			

**CASE II**

MR_UI	MR_UII	MR_UIII	MR_UIV
4.907	out of range	out of range	out of range
Solids_UI	Solids_UII	Solids_UIII	Solids_UIV
59.03	out of range	out of range	out of range
Methylation			
in progress			

**CASE I**

Calculated values

MR = 2.10 Th. Solids = 66.20%



**Excellent precision!!!**



## Monitoring the methylation stage

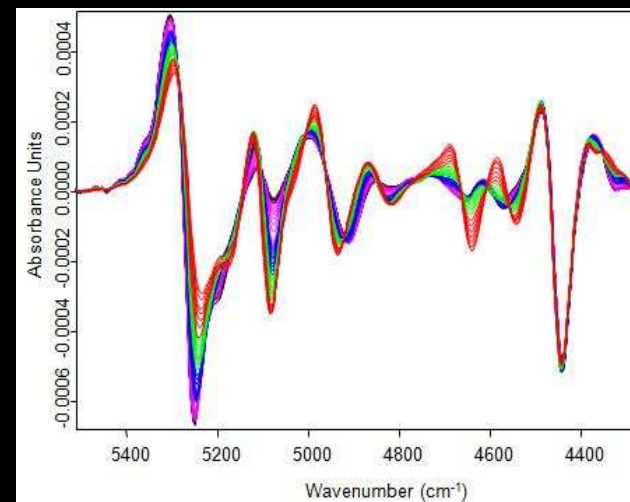
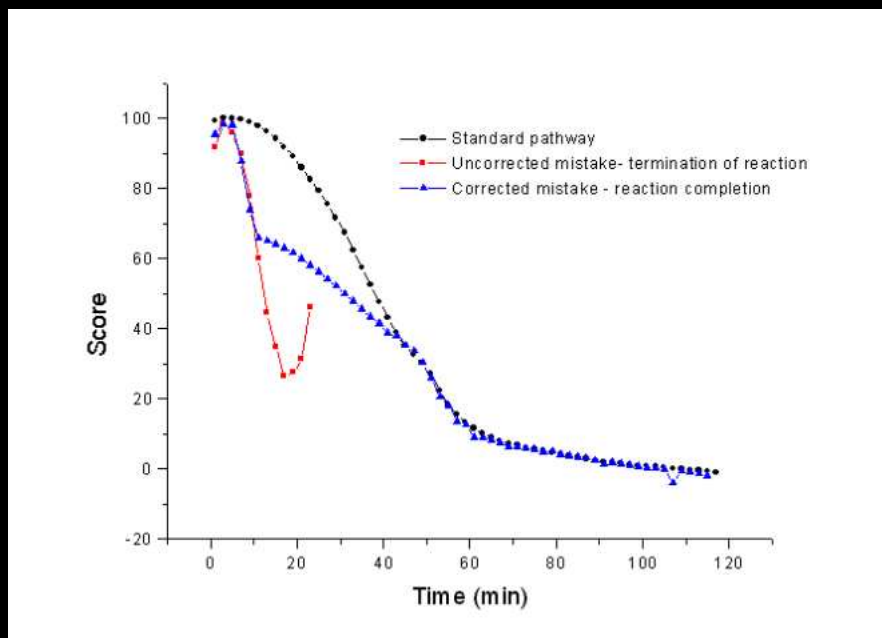
MR_UI	MR_UII	MR_UIII	MR_UIV
4.907	out of range	out of range	out of range
Solids_UI	Solids_UII	Solids_UIII	Solids_UIV
59.03	out of range	out of range	out of range
Methylation			
in progress			

**Methylation completed in 5 min  
instead of expected 10 min**

MR_UI	MR_UII	MR_UIII	MR_UIV
4.906	out of range	out of range	out of range
Solids_UI	Solids_UII	Solids_UIII	Solids_UIV
59.04	out of range	out of range	out of range
Methylation			
end of methylation			

# Monitoring the CONDENSATION stage

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Spectroscopic evolution during condensation

Chimar Hellas has developed indices which indicate the chemical pathway, called “**standard pathway**”.

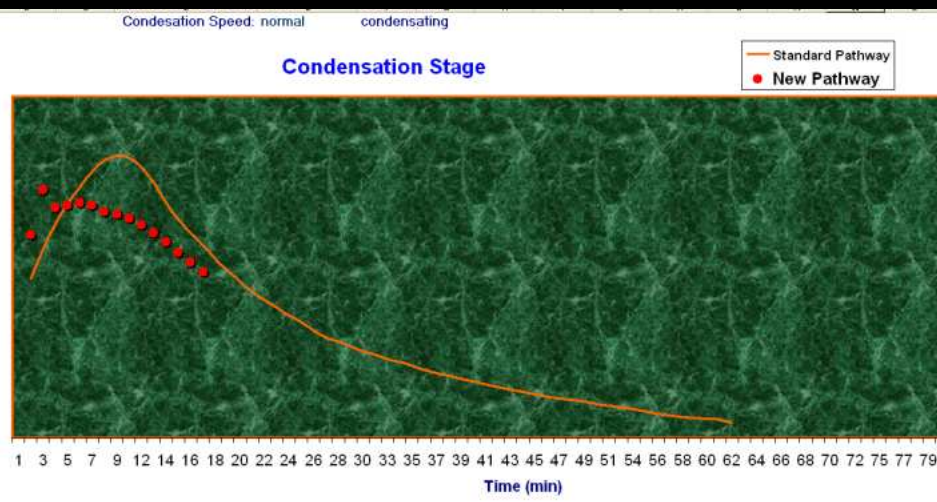
The condensation reaction should **follow the standard pathway**.

**Every deviation** of the standard pathway is an indication that the condensation reaction goes on in a **different way**.

## Industrial example of GNOSSI™ in resins

MR_UI	MR_UII	MR_UIII	MR_UIV
out of range	2.160	out of range	out of range
Solids_UI	Solids_UII	Solids_UIII	Solids_UIV
out of range	66.11	out of range	out of range
Methylolation			
in progress			
Condensation			
condensating			
Condensation Speed: too fast			

- pH was corrected at 4.3 instead of 5.3 when the temperature was 70°C
- condensation was too fast!!
- pH was corrected at 5.3 when T=78°C



The deviation of the new pathway from the standard pathway is a fast indication that the reaction follows a different route.

## Importance of temperature during measuring

Temperature was lower than 80 °C & acid was loaded in the reactor.

The value of the molar ratio is not precise because temperature is not at 80 °C yet.



MR_UI	MR_UII	MR_UIII	MR_UIV
out of range	2.106	out of range	out of range

Solids_UI	Solids_UII	Solids_UIII	Solids_UIV
out of range	66.43	out of range	out of range

Methylation
in progress

Condensation
condensating
Condensation Speed: normal

MR_UI	MR_UII	MR_UIII	MR_UIV
out of range	2.160	out of range	out of range

Solids_UI	Solids_UII	Solids_UIII	Solids_UIV
out of range	66.11	out of range	out of range

Methylation
in progress

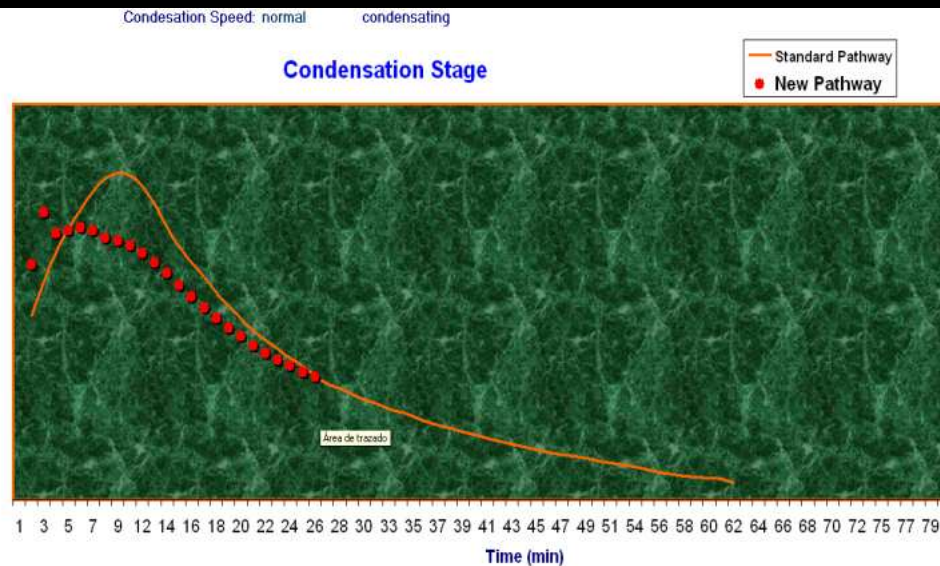
Condensation
condensating
Condensation Speed: too fast

When temperature stabilized at 80 °C the molar ratio turned to 2.10 which was equal to the calculated one.

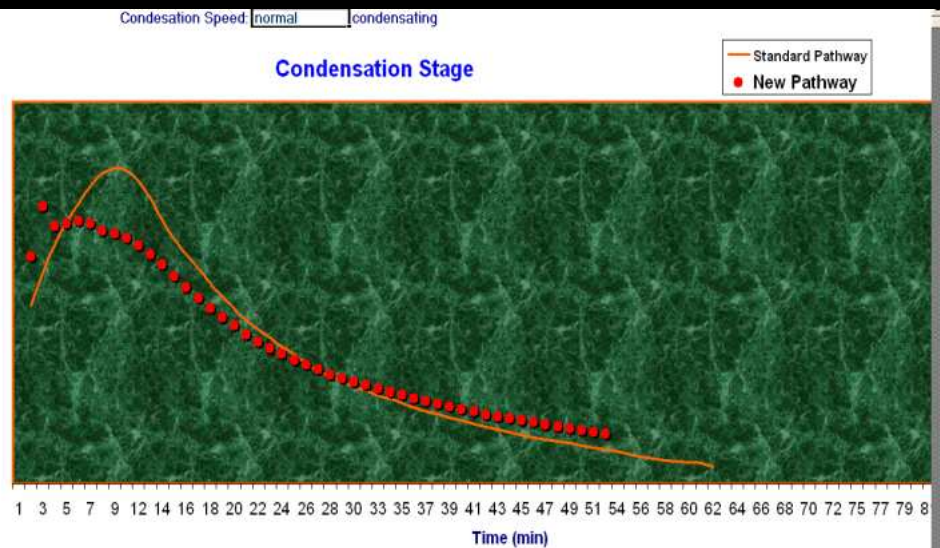


Solids are unaffected!!!

# Predicting the end of the condensation



Path returned to standard pathway but the end of the condensation was at a different value of the condensation index.

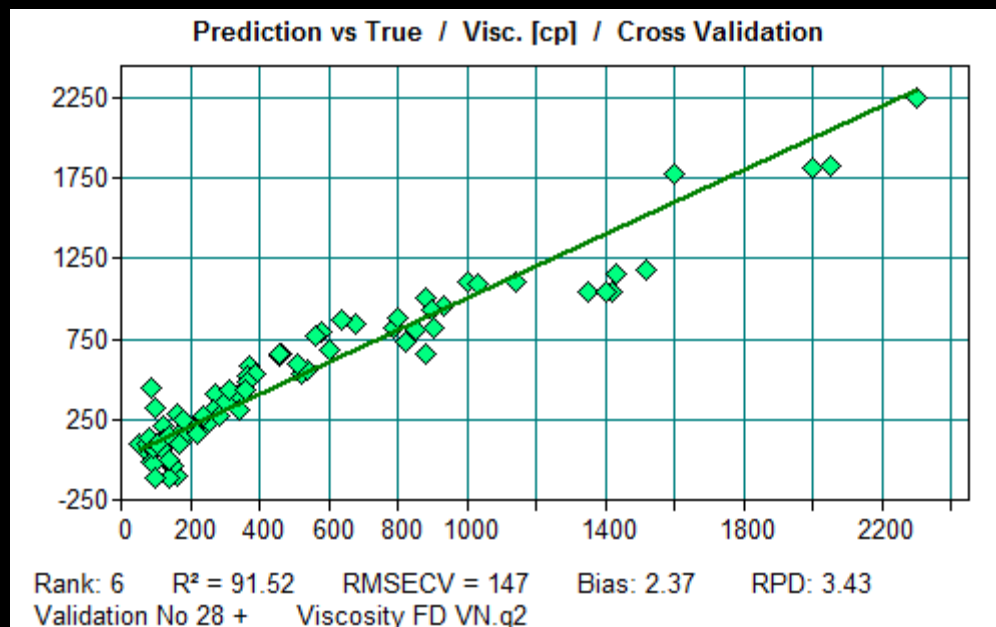


The prediction of the end of the condensation is impossible to be based only on the value of the index.



## Spectroscopic correlation of the progress of the viscosity during condensation stage

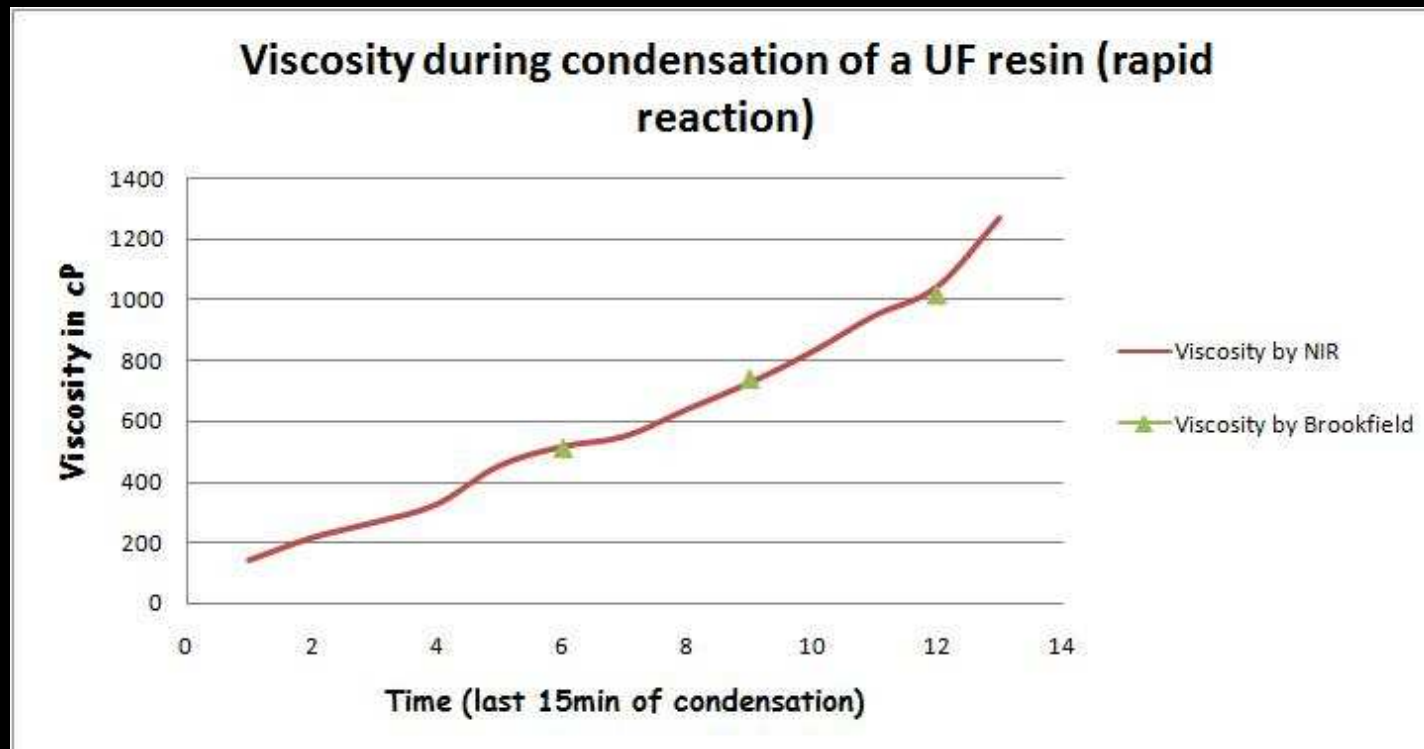
- An innovative spectroscopic methodology for predicting the end of the condensation stage is the correlation of the spectra during the condensation with the progress of the viscosity.
- The chemo metrics algorithm includes a 6 ranks model with  $R^2=91.5\%$  and RMSECV=147.



**Good correlation between NIR and Brookfield results allows predicting when to cut the reaction to achieve desired viscosity.**

## Industrial example I

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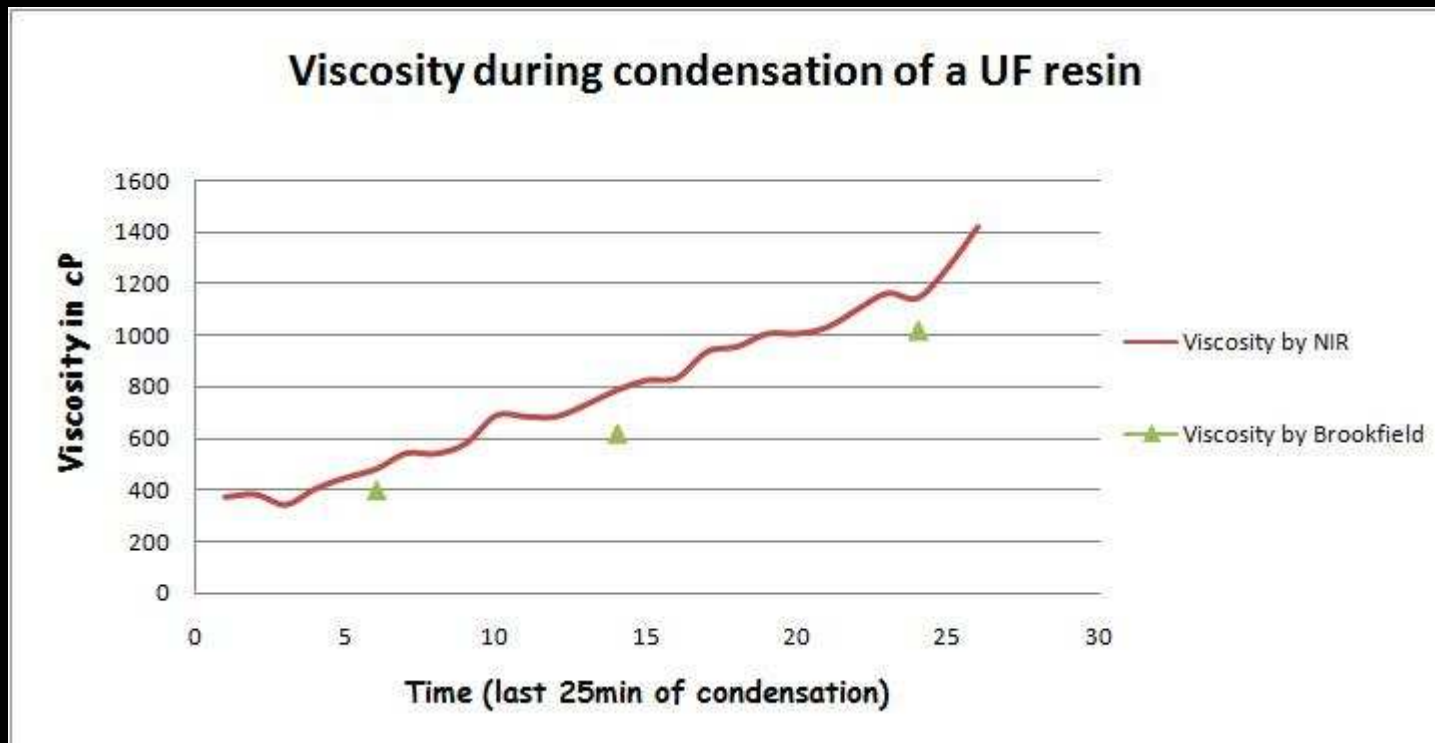


The progress of the viscosity is predicted by GNOSSI™ with excellent precision.



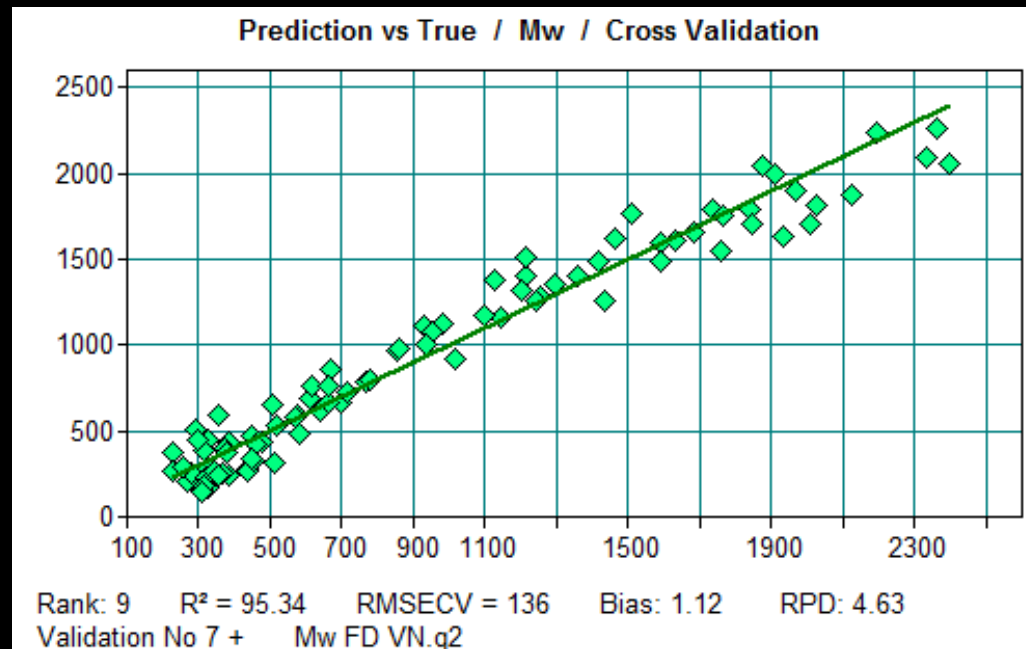
## Industrial example II

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At the end of the condensation the progress of the viscosity is very rapid. Without GNOSSI™ it would be impossible to measure one more sample with Brookfield viscometer.

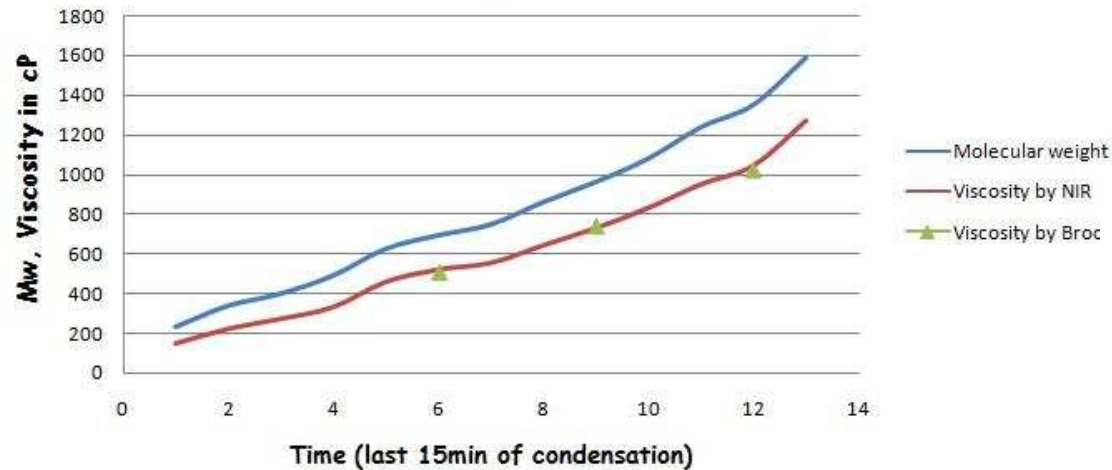
# Spectroscopic correlation of the molecular weight during the condensation stage



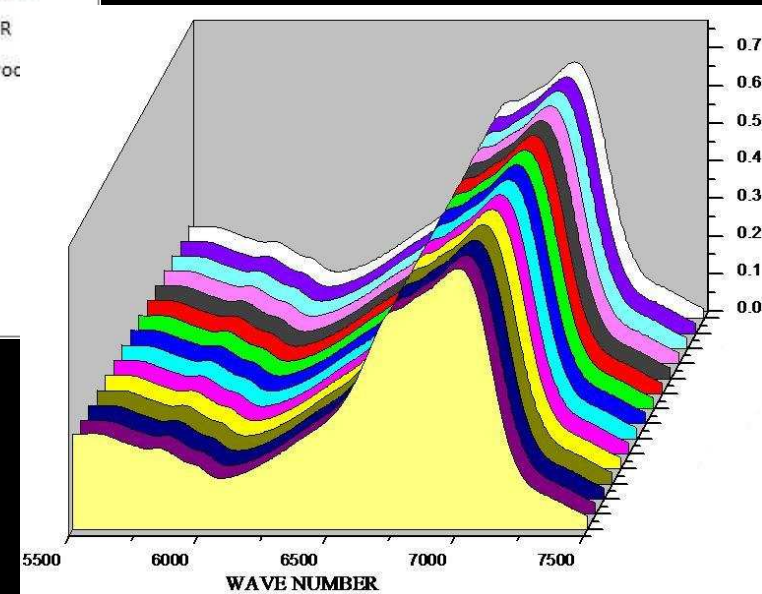
- ✓ GPC analysis of samples during the condensation stage
- ✓ The correlation gives a 9-ranks model with  $R^2=95\%$  and RMQECV=136.

# Industrial example I

Mw and Viscosity during condensation of a UF resin  
(rapid reaction)



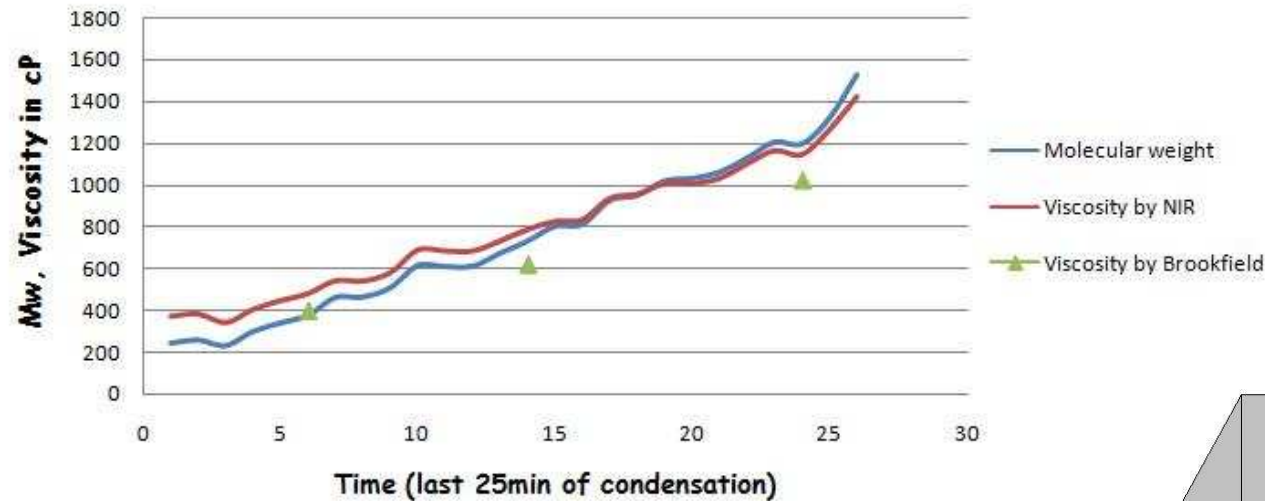
Progress of the molecular weight of the polymer during an industrial condensation.



The variations of the spectra during condensation. The critical wave band is from 5500 up to 7500 wave numbers.

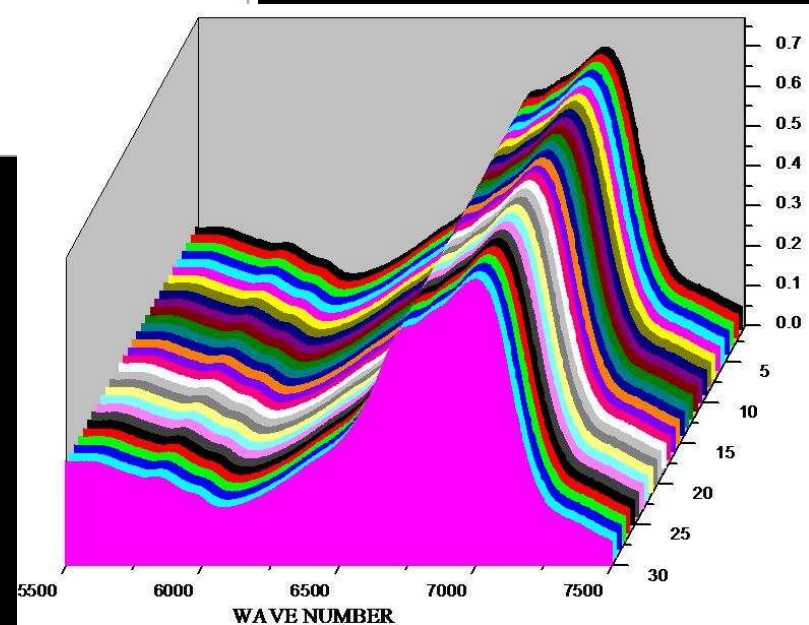
## Industrial example II

Mw and Viscosity during condensation of a UF resin



Progress of the molecular weight of the polymer during an industrial condensation.

The variations of the spectra during condensation.





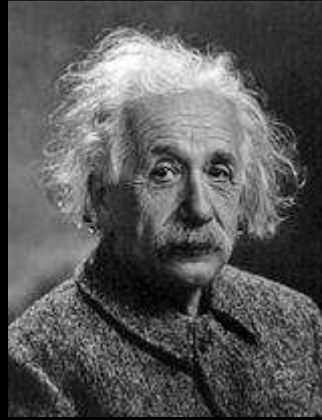
**We afford three spectroscopic models  
that follow the progress of the condensation:**

**the condensation index,  
the progress of the viscosity and  
the progress of the molecular weight.**

**When combining all these we can predict the end of the condensation.**

**But, have we reached the goal?**

**Can we base the prediction of the end of the condensation  
on such a spectroscopic analysis?**



**“...100 experiments that fulfill a law aren’t enough for proving that a theory is correct. One experiment that doesn’t fulfill a law is adequate for proving that the theory is wrong...”**

Unfortunately...

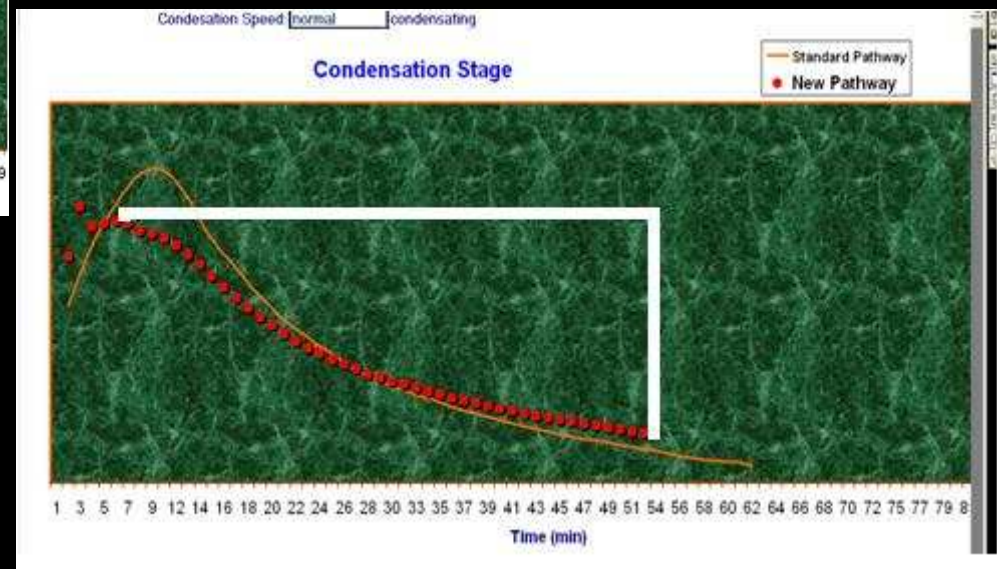
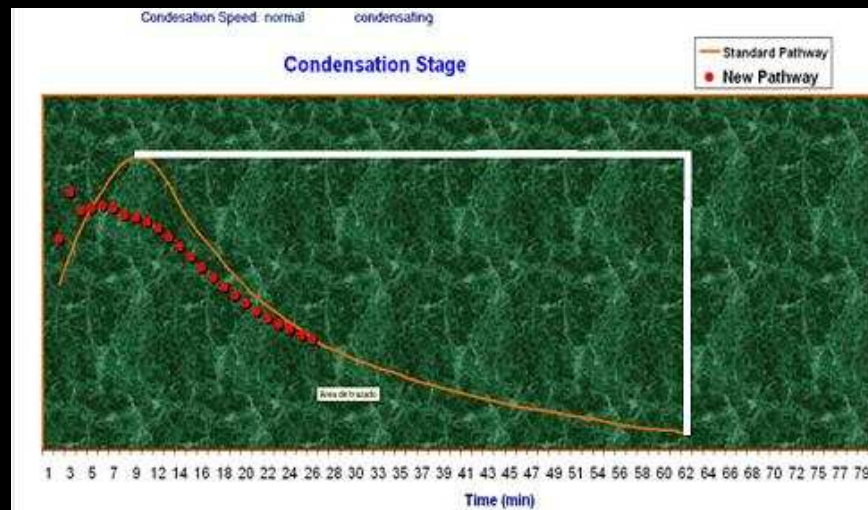
if we cook 100 resin batches by predicting successfully the end of the condensation and we jellify one then we are in trouble.

That’s why we have to insert a final criterion that ensures the end of the condensation.





The area between the curve of the condensation index and a line parallel to axis x that passes from the maximum value of the index is constant.





## Determination of the final molar ratio

MR_UI	MR_UII	MR_UIII	MR_UIV
out of range	out of range	out of range	1.074
Solids_UI	Solids_UII	Solids_UIII	Solids_UIV
out of range	out of range	out of range	74.31
Methylation			
in progress			
Condensation			
condensation ended			
Condensation Speed: not applicable			

Expected final values

1. Molar Ratio = 1.070
2. Th. Solids = 74.23%



**The unique obstacle is**

**that GNOSSI™ software should be adjusted to**

**the settings of each resin plant**

# CONCLUSIONS I

**The NIR technology through the GNOSSI™ software developed by Chimar can successfully be applied to the resin industry for**

- ☐ **Monitoring the production of raw materials (formol and UFC)**
- ☐ **Determine the quality of the stored raw materials allowing the adjustment of the absorber for keeping the production in specs**
- ☐ **Determine the molar ratio of the mixture each time a new component is loaded in the reactor**
- ☐ **Monitoring the progress of the methylation stage**
- ☐ **Monitoring the progress of the condensation stage in terms of viscosity and molecular weight of the polymer**

## CONCLUSIONS II

- ☐ **Detecting abnormalities during the condensation stage**
- ☐ **Determine the properties of the final resin either in the reactor or in the storage tank**
- ☐ **As a technique it is**
  - **non-destructive**
  - **rapid**
  - **precise**
  - **reproducible**
  - **reliable**
  - **in situ and at real time**

# Contact details

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