AALBORG UNIVERSITY

PLS2 regression as a tool for selection of optimal analytical modality

- *a closer look at beer brewing process analysis with alternative spectroscopic data types*

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Aim of the study

- To compare the performance of three different matured spectroscopic techniques for beer brewing process monitoring (complex biochemical matrix)

- To investigate inter-relationships between spectral data types using the PLS2 algorithm

- To quantify the amount of unique information contained in each spectral data type based on bilateral PLS2 (e.g. NIR vs. Raman and vice versa)

- To propose a dedicated PLS2 approach for selection of optimal analytical modality for any given chemical matrix (biochemistry, environmental engineering, bio energy, chemical engineering)

Bilateral PLS2 approach (*in development*)

- Clean-up spectral data for gross outliers and other unrepresentative data. Apply spectral transformation if feasible (e.g. MSC on Raman spectra)

- Perform PLS2 on e.g. MIR (X) vs. Raman (Y). Apply all relevant validation methods to document their individual behaviour

- Switch the two spectral data types, Raman (X) vs. MIR (Y), and redo the PLS2

- Visualise the joint vs. unique information (Validation Variance) for a selected model complexity (no. of PLS components)

Campus-scale brewery at AAU EIT (sponsored by Carlsberg)

Technical summary

2 fermentors approx. 150 L each

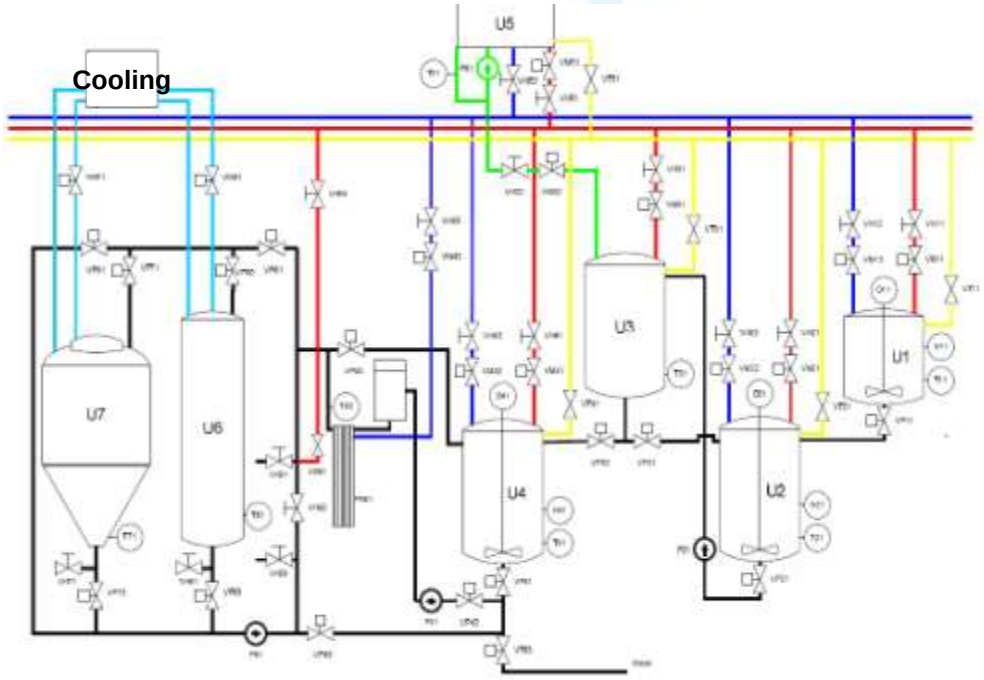
Pre-treatment vessels

Active cooling

Active heating

Ultra-filtration unit

Heat exchanger



Reference: Thygesen and Toft, *Control of brewery*, B.Sc. thesis, AAU EIT, 2006, p. 11

Plant monitored and controlled through LabVIEW™

Future options / ideas

Augment program with chemometric tools:

- online score plots

- early warnings (stuck fermentations)

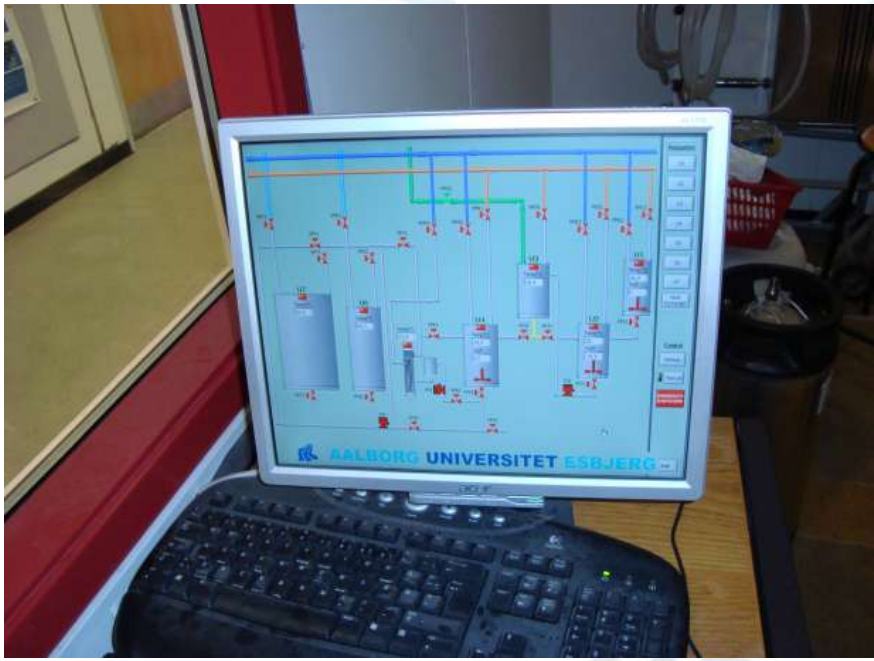
- real time prediction

- automatic process sampling

(Hopefully) leading to:

- comprehensive process documentation

- better tasting campus beer…



Short introduction to the main metabolism

The production path

Crushing/grinding of barley malt

Wort (sugar solution)

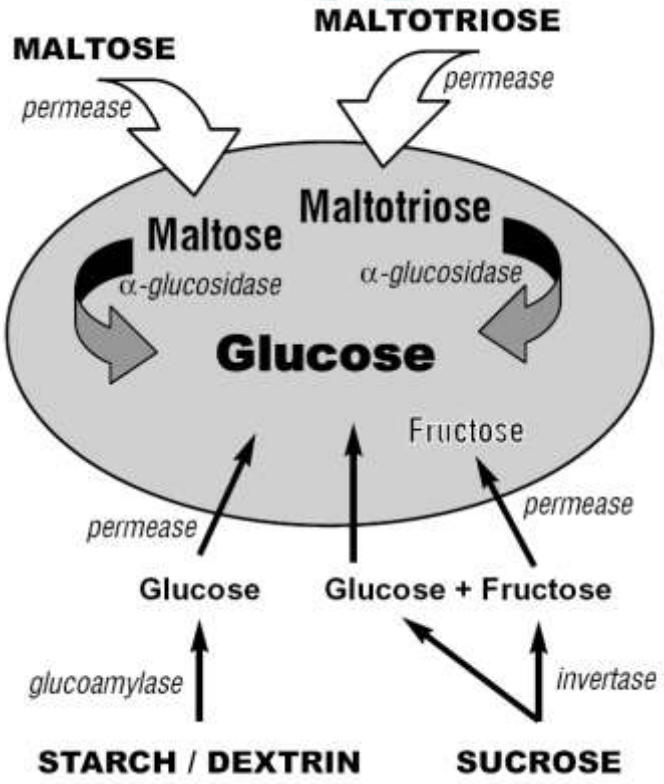
Filtration

Inoculation

Fermentation

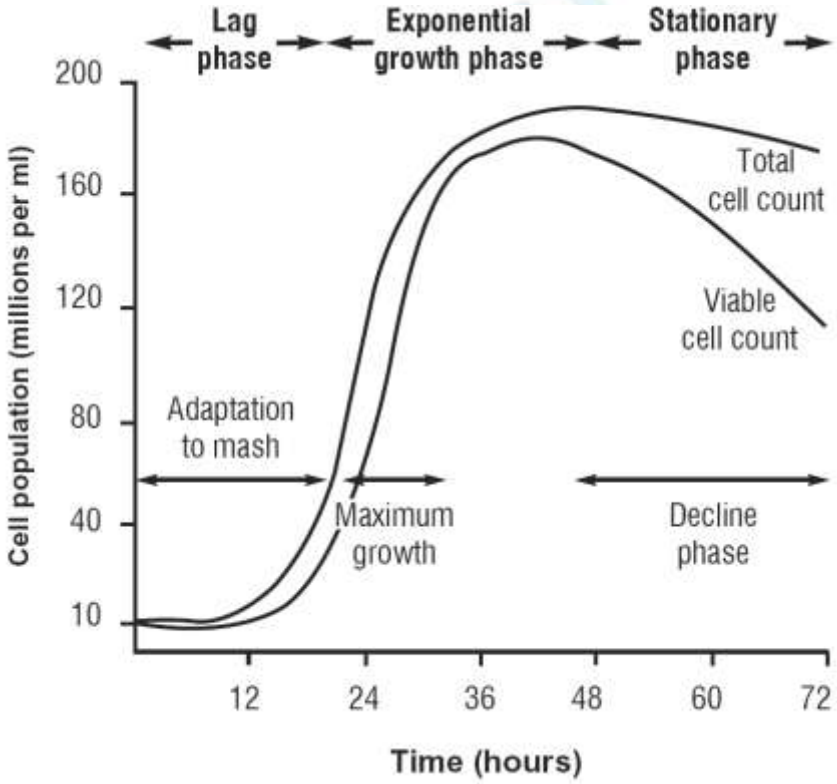
Lager-process

Tapping



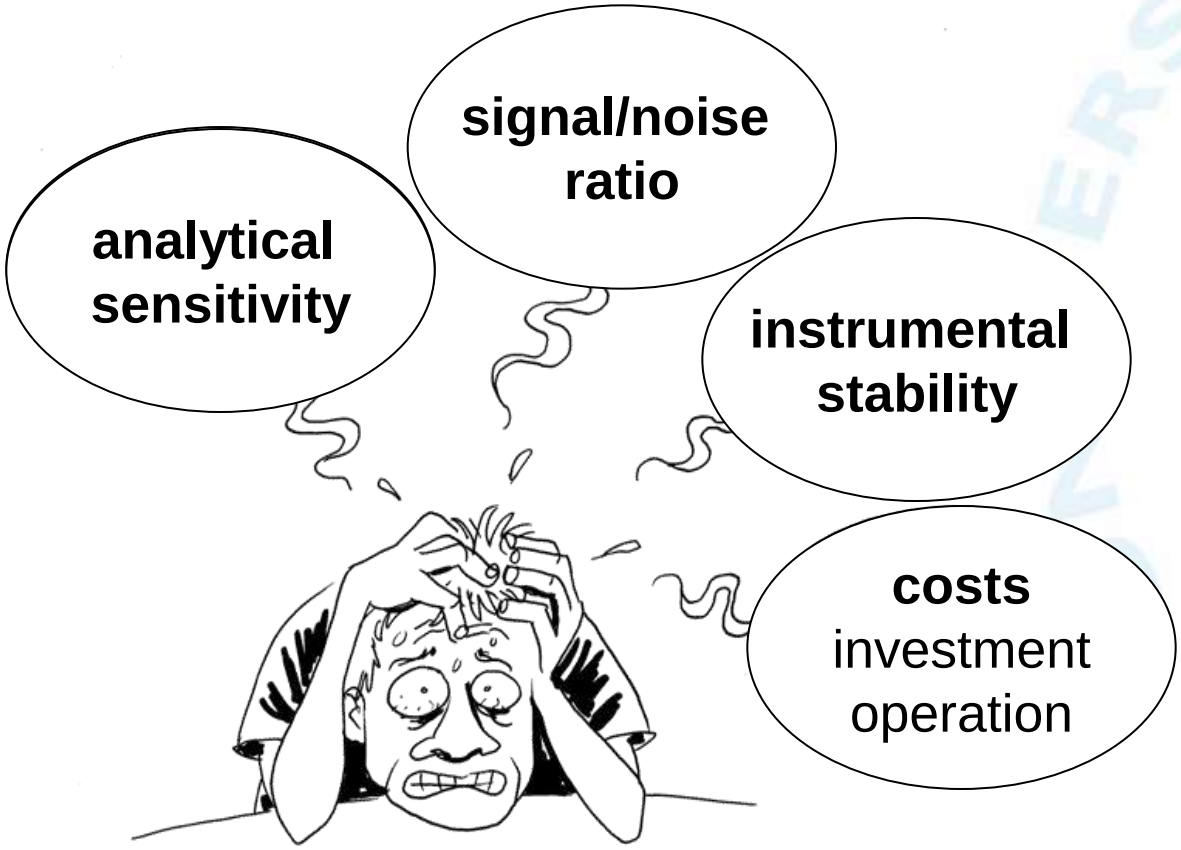
Reference: The Alcohol Textbook, 4th edition (ed. by KA Jacques et al.)

Typical batch fermentation behaviour



Reference: The Alcohol Textbook, 4th edition (ed. by KA Jacques et al.)

Spectroscopic implementation:
- *A few issues worth addressing*



Key to unlocking information in signals: *vibrational Eigen modes*

Based on Classical Mechanics and Molecular Quantum Theory the presence of signals from specific molecules in various spectral data types can be predicted

Infrared spectroscopy represents molecular dipole-dipole interactions

Near infrared spectroscopy represents molecular vibrations, stretching, and rotations

Raman spectroscopy represents scatter of incident laser light

In other words: the chosen spectroscopic techniques represent three different physical phenomena

Features of the chosen spectroscopic techniques

NIR

- Signals have low intensity
- Wide spectral absorption bands
- Very much affected by the presence of water

MIR

- Signals have high intensity
- Generally narrow absorption bands
- Some influence from presence of water and carbon dioxide

Raman

- Signals have very low intensity
- Affected by fluorescence (use excitation laser frequency close to NIR)
- Selective
- Less sensitive to presence of water
- Heats optical sampling area (high power laser excitation technique)

Fourier Transform InfraRed spectroscopy

Spectral range
4 000 – 650 cm^{-1}

Resolution
8 cm^{-1}

Co-adds
64

Background
Ambient air

Temperature
Ambient (22 °C 1 °C)

Mode
Attenuated Total Reflectance

Fourier Transform Near InfraRed spectroscopy

Spectral range
9 000 – 5 500 cm^{-1}

Resolution
16 cm^{-1}

Co-adds
64

Background
Ambient air

Temperature
Ambient (30 °C 1 °C)

Mode
Transmission

Raman laser spectroscopy

Spectral range
3 000 – 200 cm^{-1}

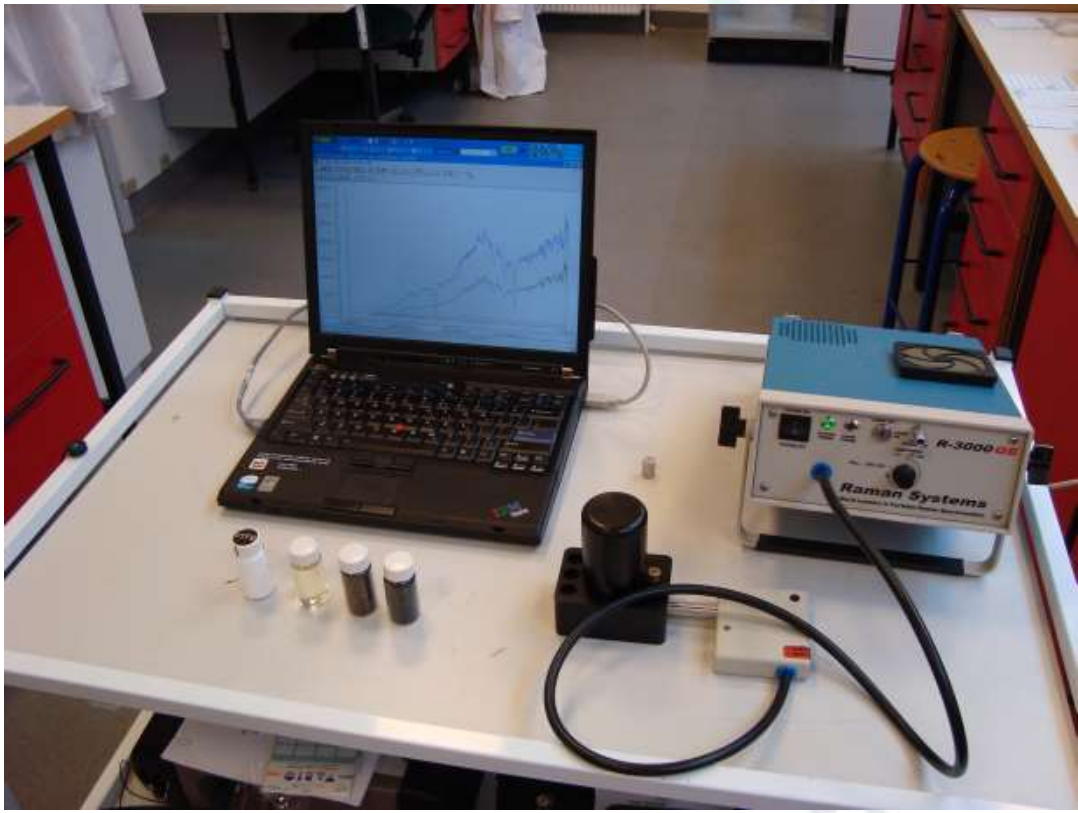
Resolution
10 cm^{-1}

Integration time
1 s

Laser output power
30 mW

Temperature
Ambient (22 °C 1 °C)

Excitation wavelength
785 nm



Wet chemical reference analysis

Analysed parameters

1. Maltotriose (not metabolised by the yeast applied)
2. Maltose
3. Fructose
4. Glucose
5. Sum of the above
6. Ethanol

Method

High Pressure Liquid Chromatography with Refractive Index detection, HPLC-RI

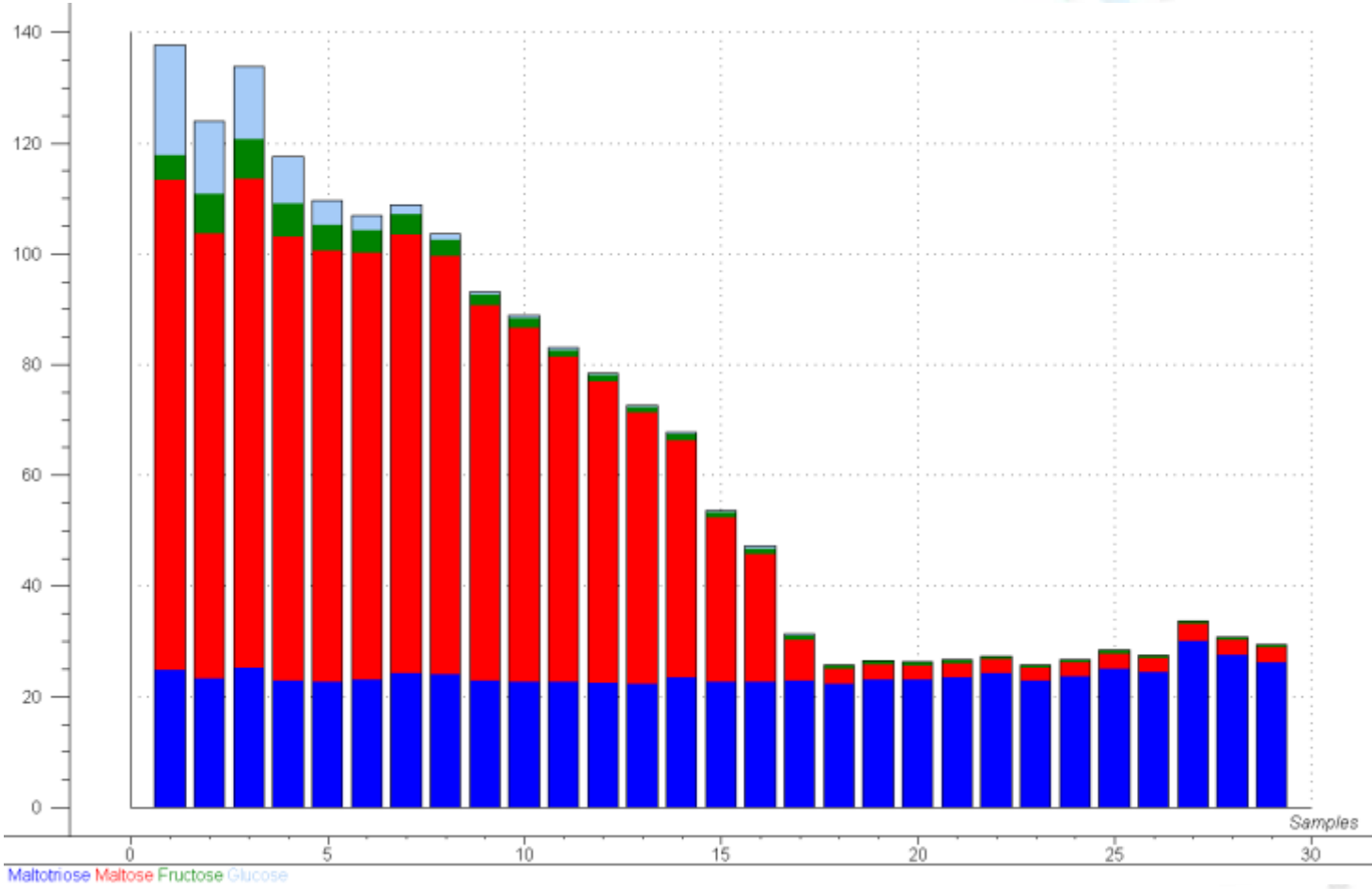
Sample preparation

Dilution with acidic eluent and filtration

Analysis time

Roughly one hour per sample (analysed in duplicate)

Typical sugar utilisation during a fermentation

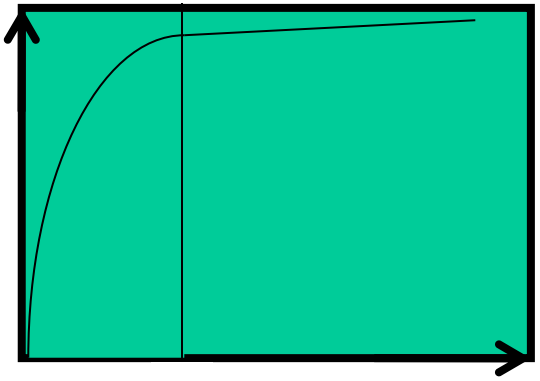


Sneak preview

- more in the accompanying paper

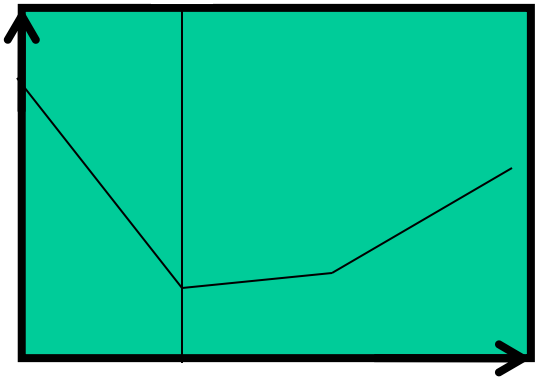
NIR (X) vs. MIR (Y)

Cal var.



PLS comp.

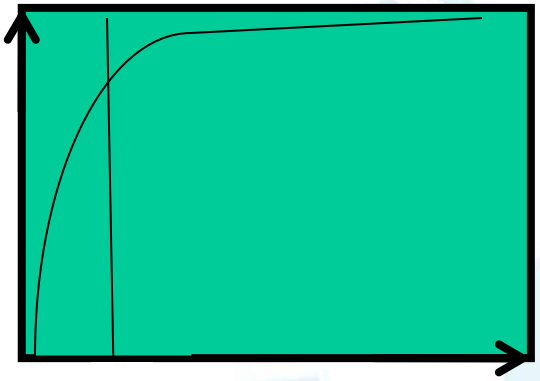
Val var.



PLS comp

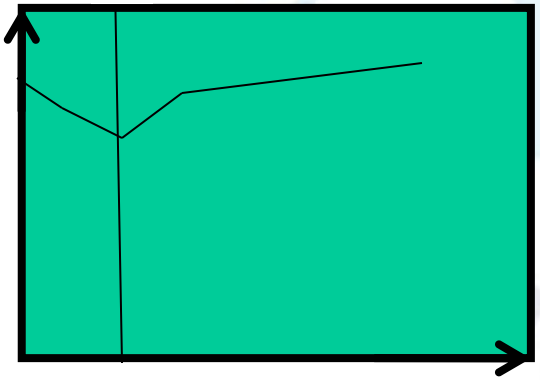
MIR (X) vs. NIR (Y)

Cal var.



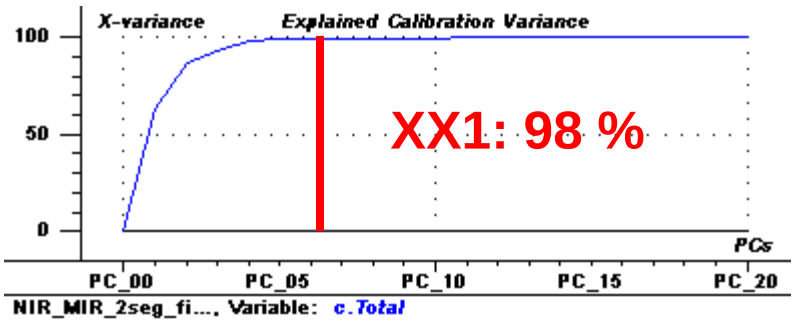
PLS comp.

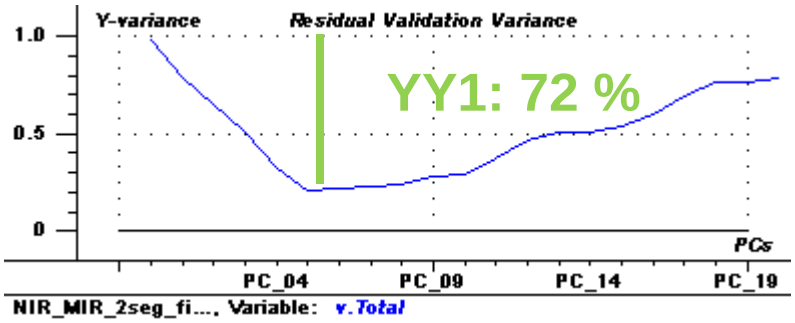
Val var.



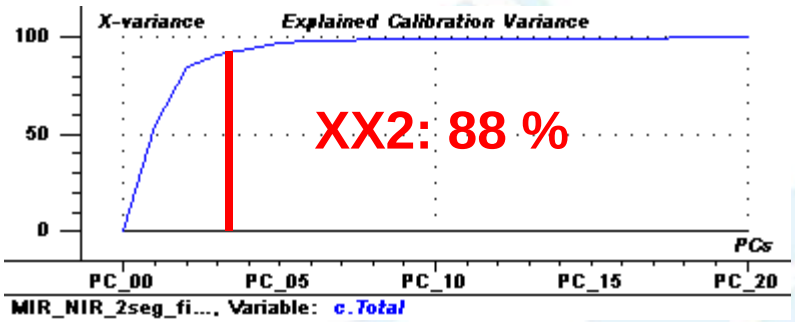
PLS comp

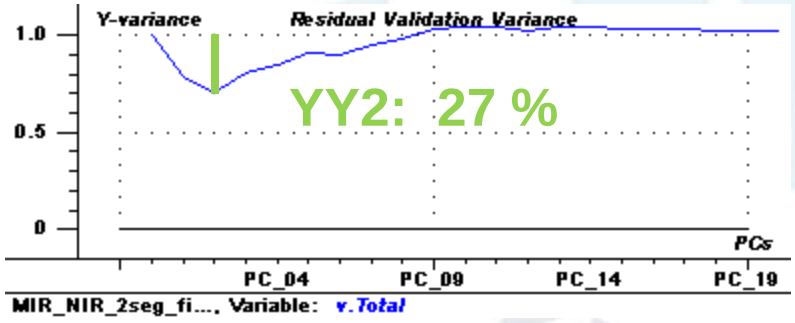
NIR (X) vs. MIR (Y)





MIR (X) vs. NIR (Y)





PLS2 bilateral inter-calibration (A → B)

Route diagram:

1) Is there a satisfactory model?

2) Validation is the answer! (X-val is the right thing **HERE**)

3) If the validation is acceptable: cal-variance (X)? : XX1%

4) Conclusion: XX1 % explains YY1 %

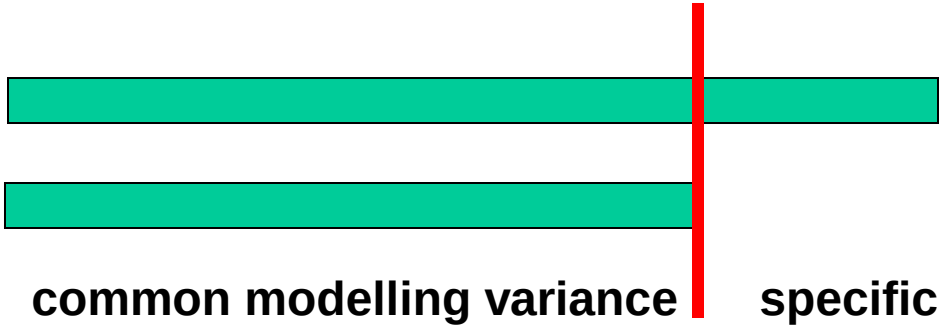
5)Reverse modelling (B→A) and repeat procedure

6) XX2 % explains YY2 %

Inter-calibration insight

1: proportion of the common modelling variance (XX %)

2: proportion specific modelling variance



XX1: 98 %

XX2: 88 %

Thank you for your attention

Avoid spurious correlations - practice SAFE validation