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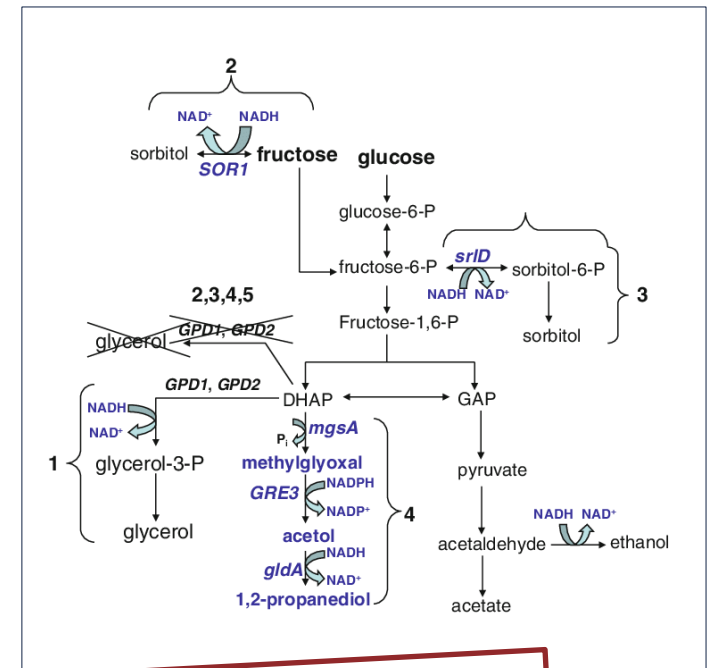
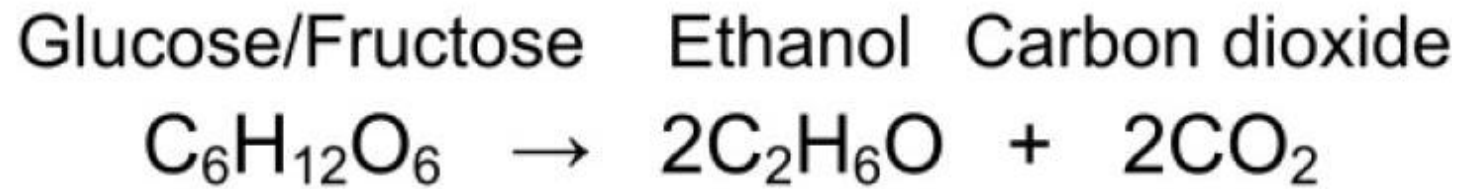
UNIVERSITÀ DEGLI STUDI
DELL'INSUBRIA

APPLICATION OF ATR-MIR AND CHEMOMETRICS FOR THE EARLY DETECTION OF DEVIATIONS DURING THE WINE ALCOHOLIC FERMENTATION PROCESS

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Joan Ferré, Montserrat Mestres, Ricard Boqué

REMOTE SUMMIT ON FOOD QUALITY CONTROL
ANALYTICAL APPROACH
28TH MAY 2020

WINE ALCOHOLIC FERMENTATION



Many other reactions involved

FERMENTATION PROCESS CONTROL

In the cellar
Fermentation temperature
Density
pH
Temperature
Organoleptic Evaluation



Off-flavours

In the laboratory:

Total and volatile acidity
Sugars
SO₂
Assimilable N
Malic/Lactic Acids
...



Low quality wines



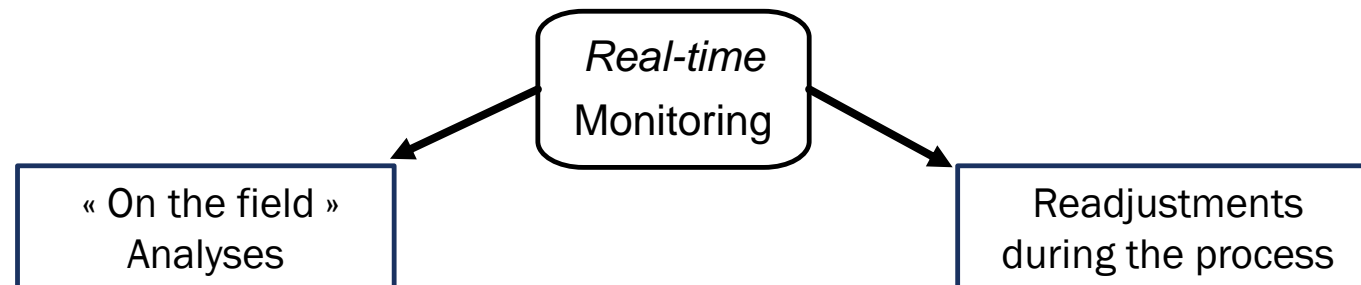
Stuck/Sluggish Fermentations

Bacterial Spoilage

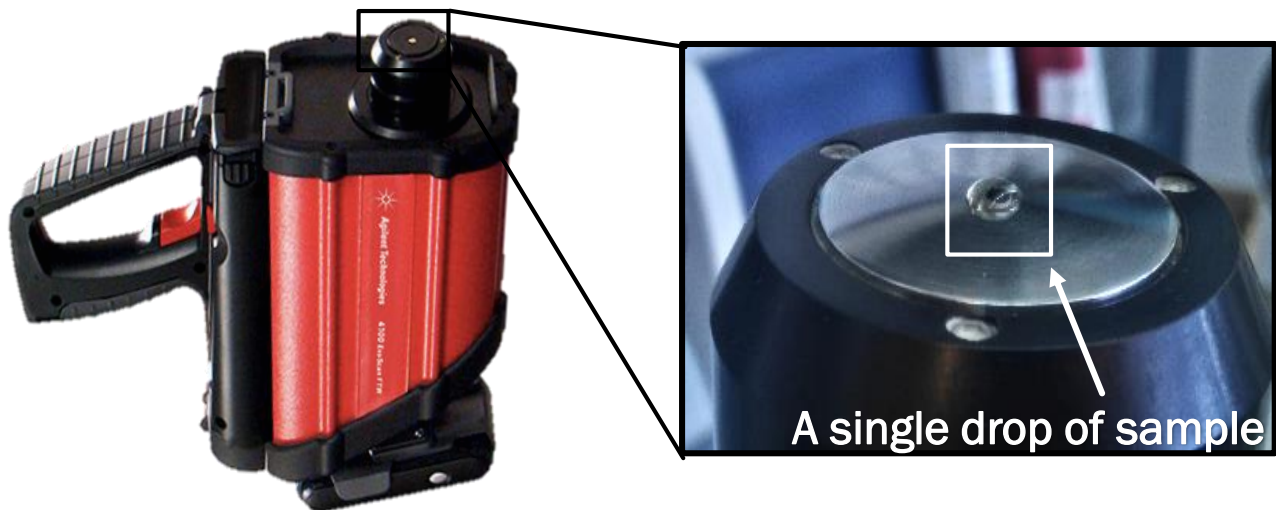
PROCESS ANALYTICAL TECHNOLOGY

“ a system for designing, analyzing, and controlling manufacturing through timely measurements (i.e., during processing) of critical quality and performance attributes of raw and in-process materials and processes, with the goal of ensuring final product quality” (1)

(1) “Guidance for industry: PAT” -2004, U.S. Food and Drug Administration (FDA)



ATTENUATED TOTAL REFLECTANCE (ATR) MIR SPECTROSCOPY



- Advantages:**
- ✓ Fast
 - ✓ Easy to use
 - ✓ Long-term economic
 - ✓ Little or no pretreatment
 - ✓ Portable



**Valuable
PAT tool**

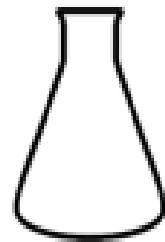
AIM OF THE STUDY

- To determine the usefulness of an ATR-MIR portable device for *at-line* monitoring of small-scale wine fermentations, prior to PAT implementation.
- To detect different undesirable deviations in must fermentation using ATR-MIR and multivariate analysis
- To propose a process control methodology easy to implement and understand

WORK FLOW



Small-scale wine fermentations



NOC

+Wine must
+yeast
+activators
&nutrients



MLF

+Wine must
+yeast
+lactic acid bacteria
+activators
&nutrients



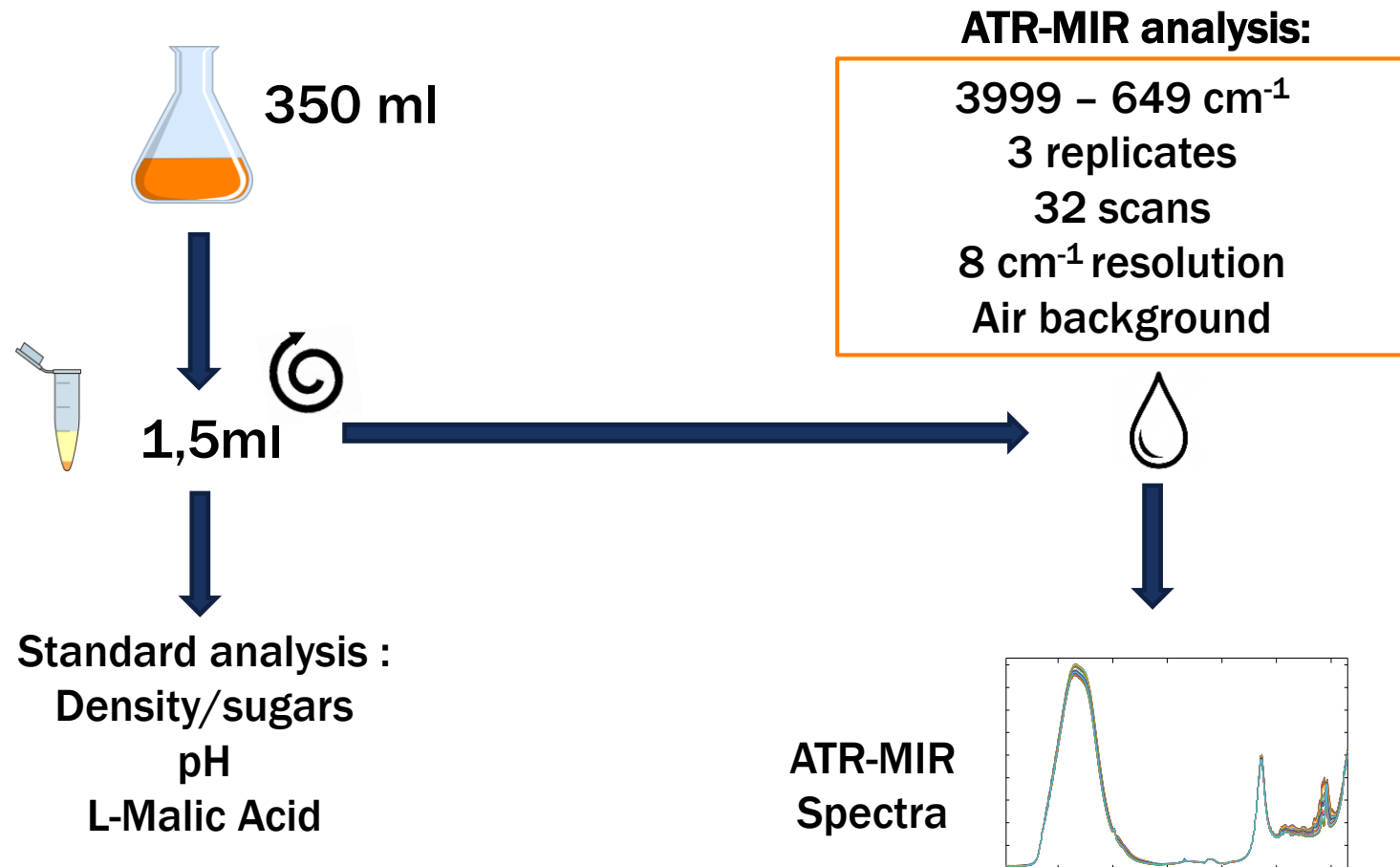
YAN

+Wine must
+yeast
+activators
&nutrients (less quantity)

WORK FLOW

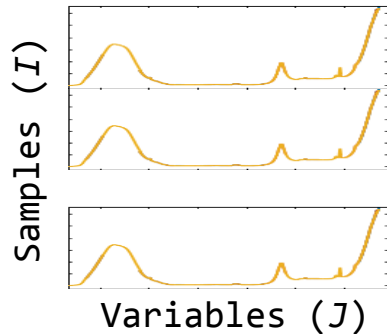


Small-scale wine fermentations

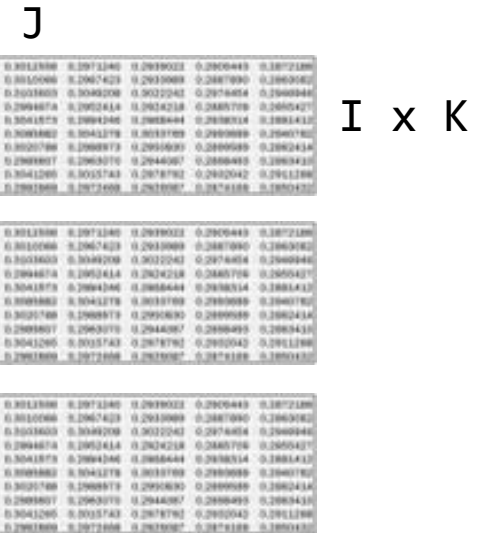
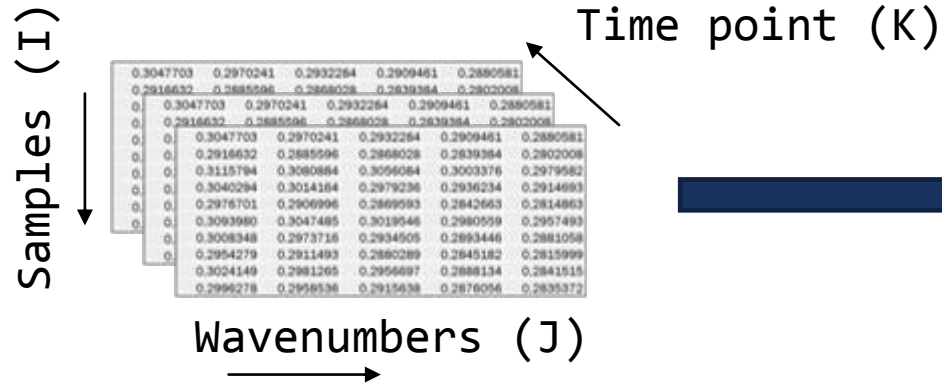


MULTIVARIATE ANALYSIS

Data at k time point



Data for K time points



Exploratory Analysis

Principal Component Analysis (PCA)

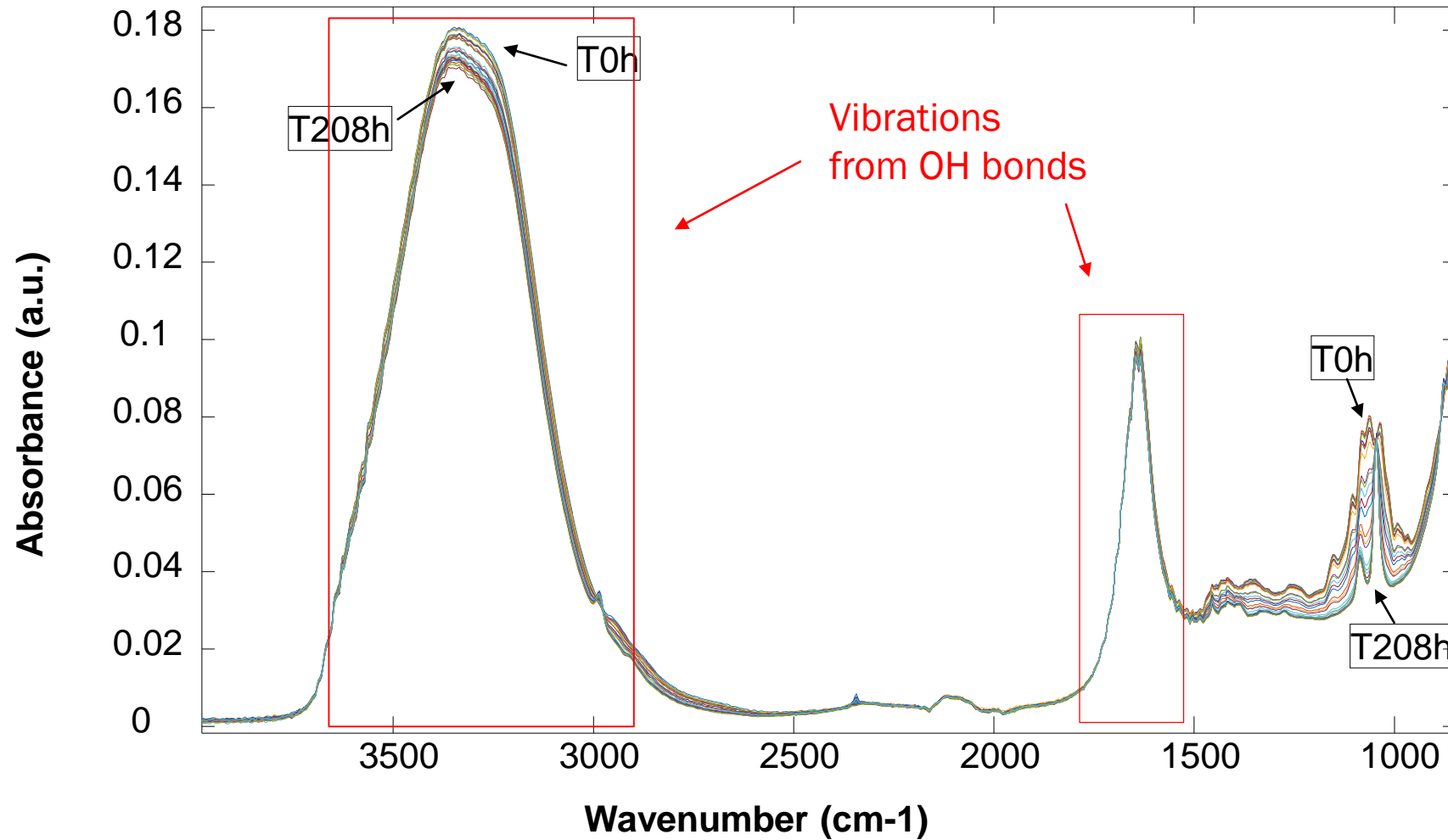
Regression Models

Partial Least Squares (PLS) Regression

Discrimination Models

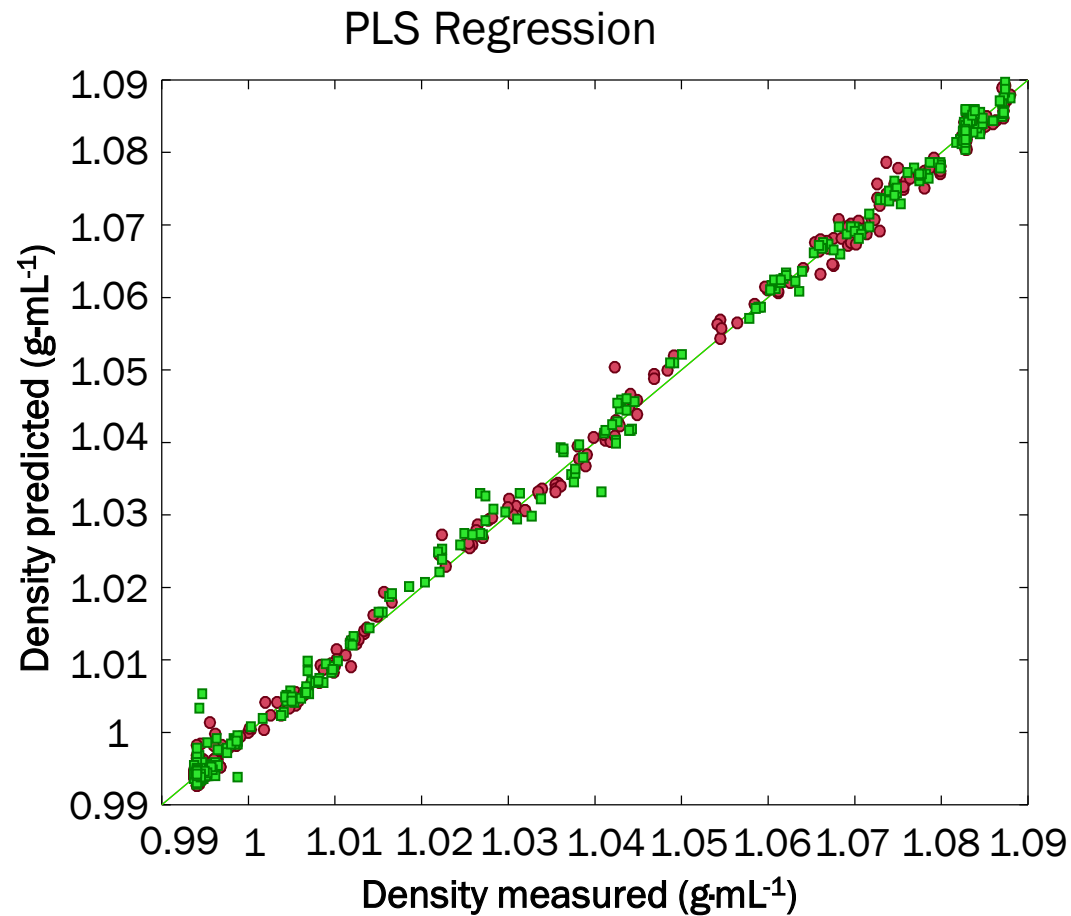
PLS Discriminant Analysis (PLS-DA)

ATR-MIR SPECTRA



PARAMETER PREDICTION (DENSITY)

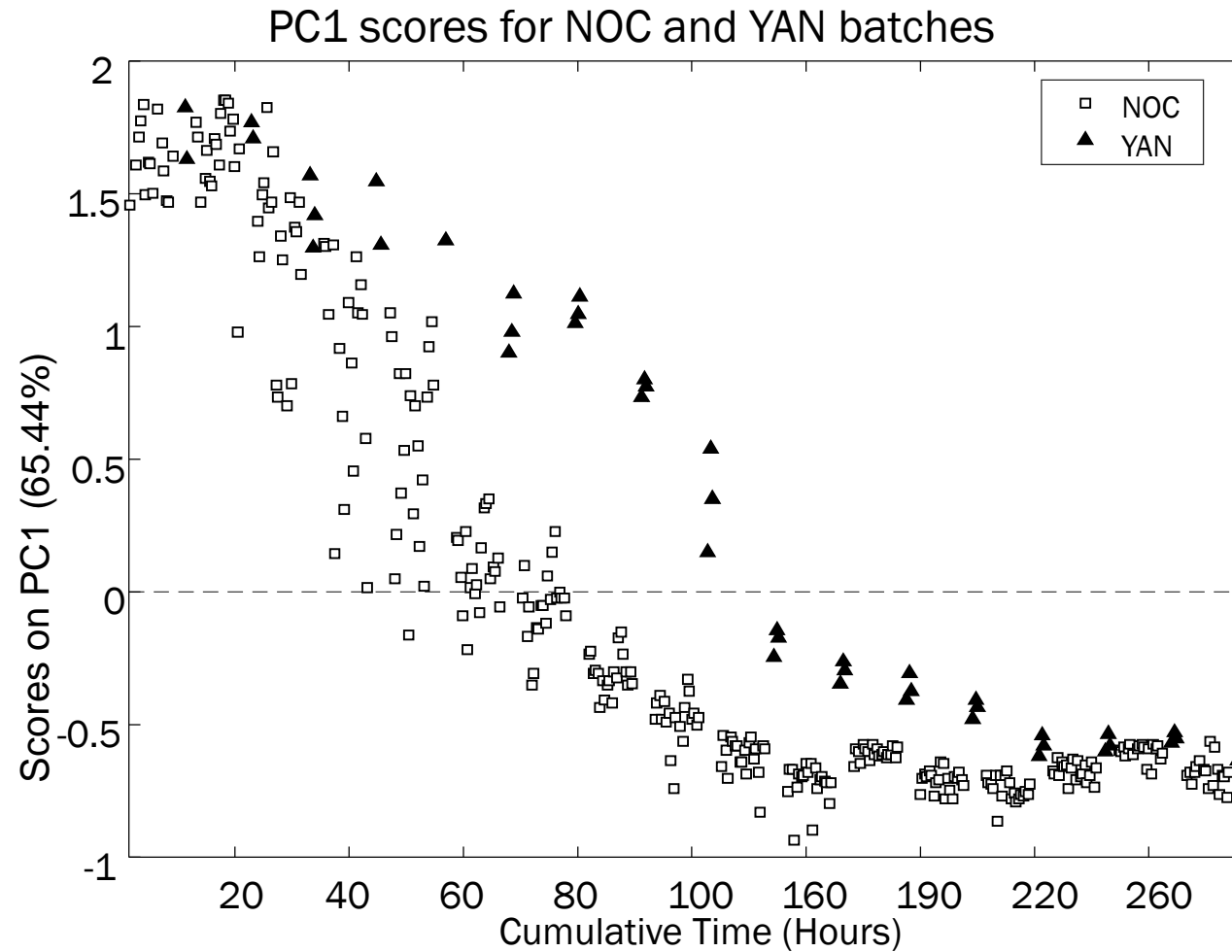
Preprocessing applied:
Smoothing 7 pts
(2nd order polynomial)
SNV
Mean Center



RMSEC: 0,0011 $\text{g}\cdot\text{mL}^{-1}$
RMSECV: 0,0012 $\text{g}\cdot\text{mL}^{-1}$

SLUGGISH FERMENTATIONS

Exploratory Analysis
PCA

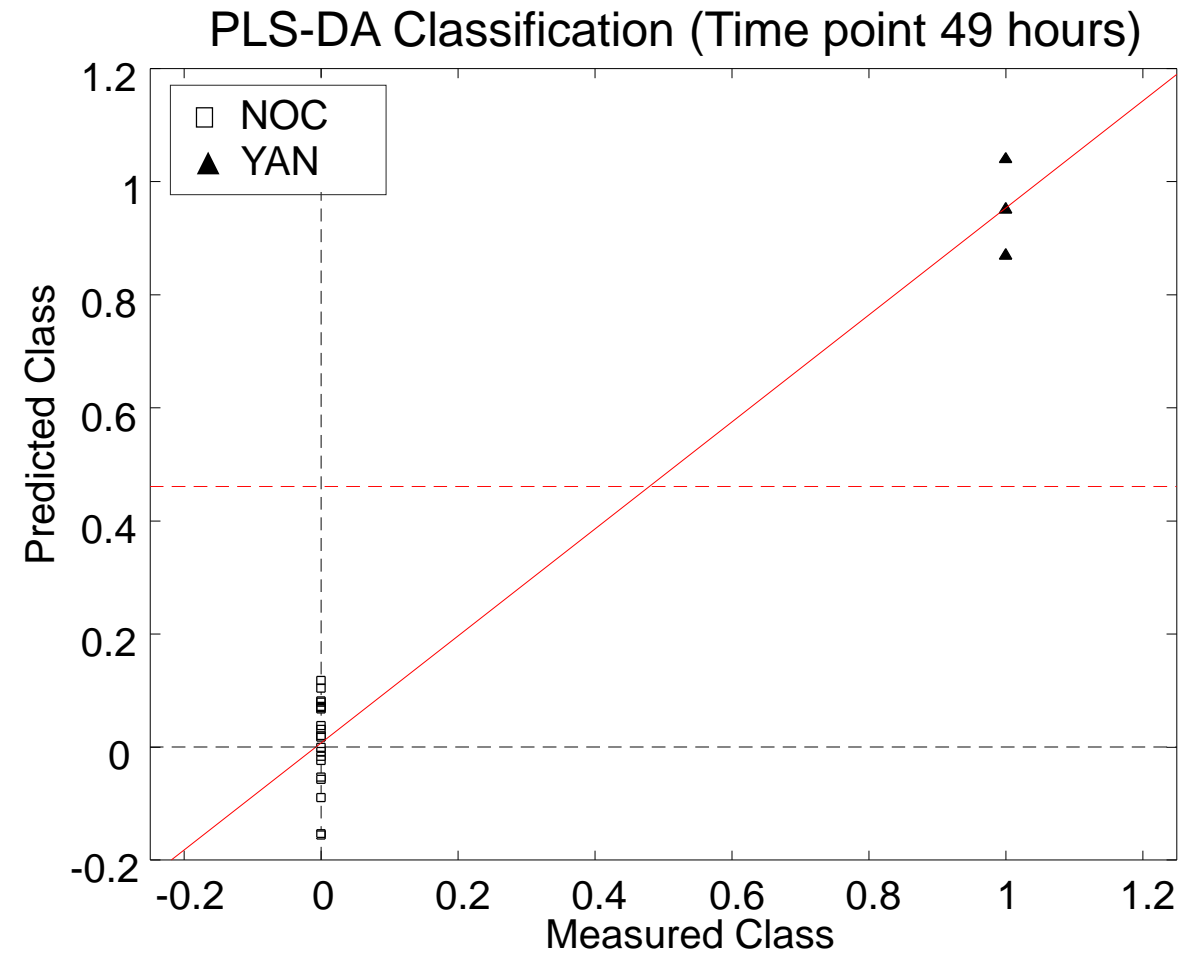


SLUGGISH FERMENTATIONS

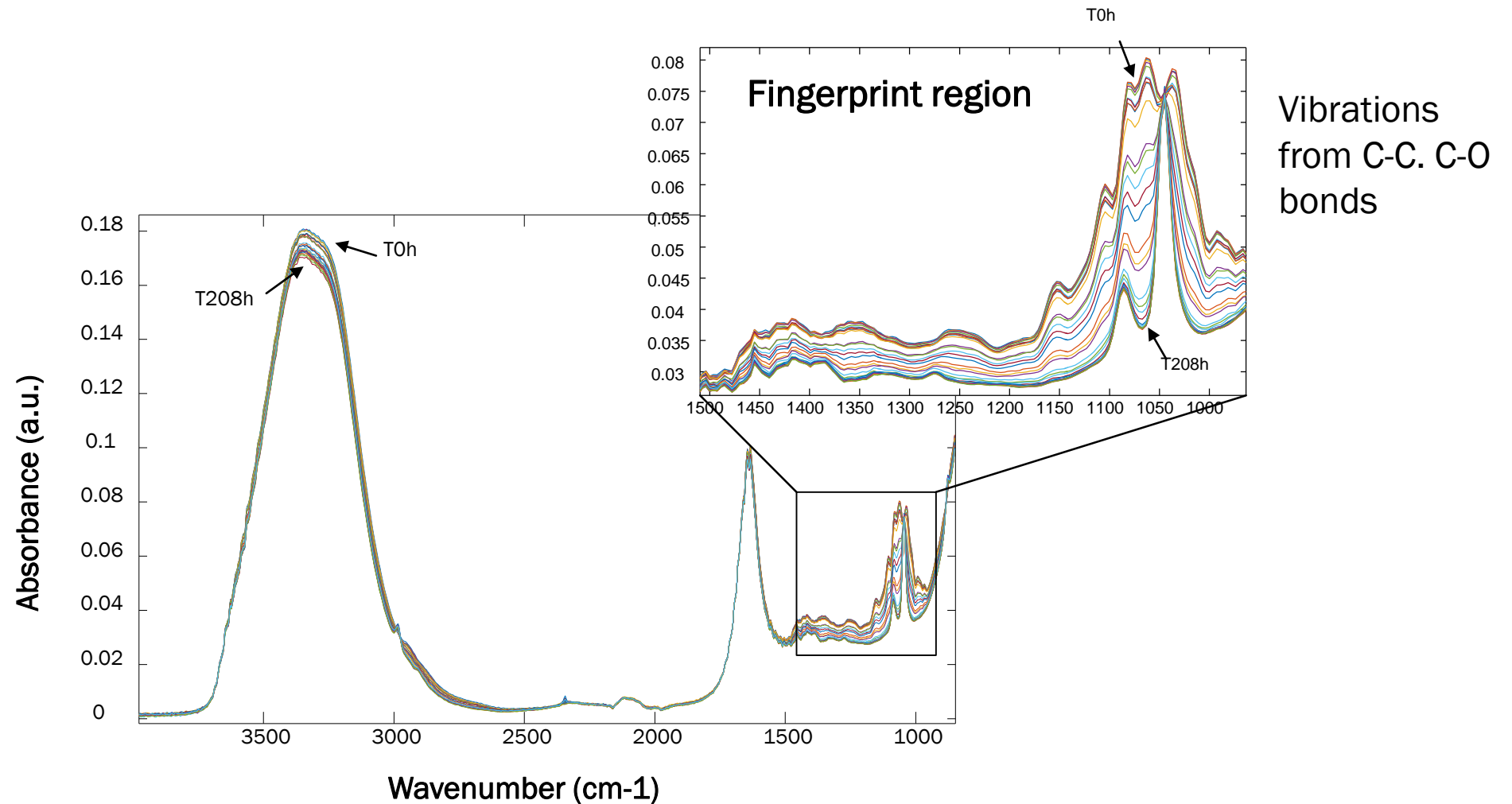
Discriminant Analysis
PLSDA



PLS Regression
for classification

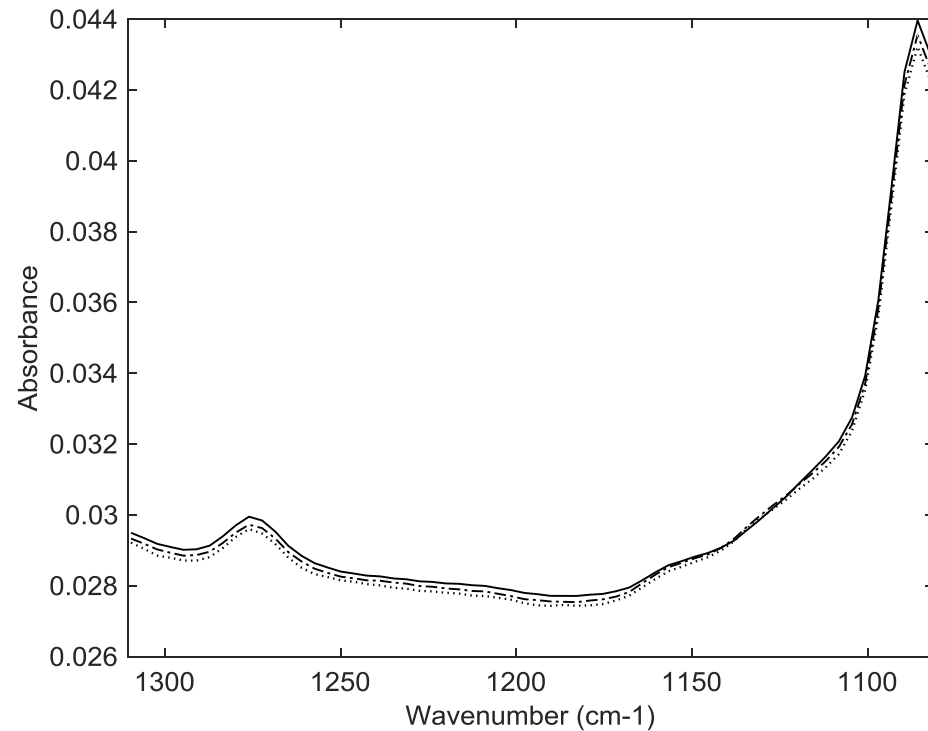


FINGERPRINT REGION

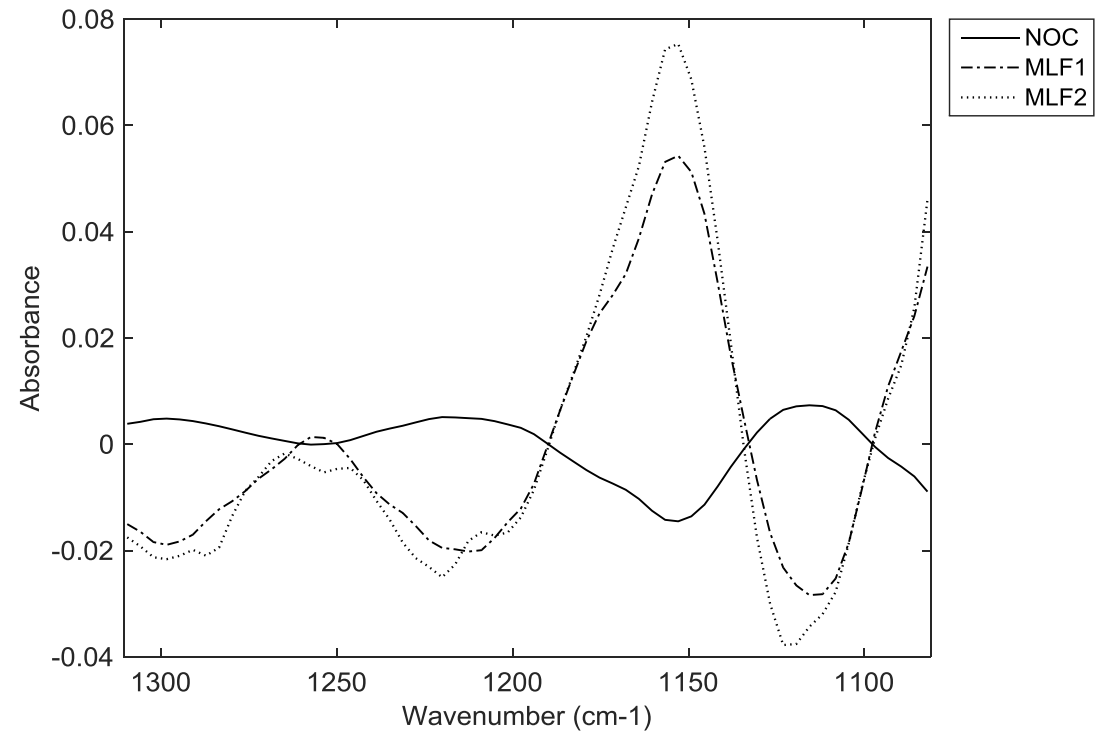


LACTIC ACID BACTERIA SPOILAGE

Raw Spectra (1320 to 1082 cm^{-1})

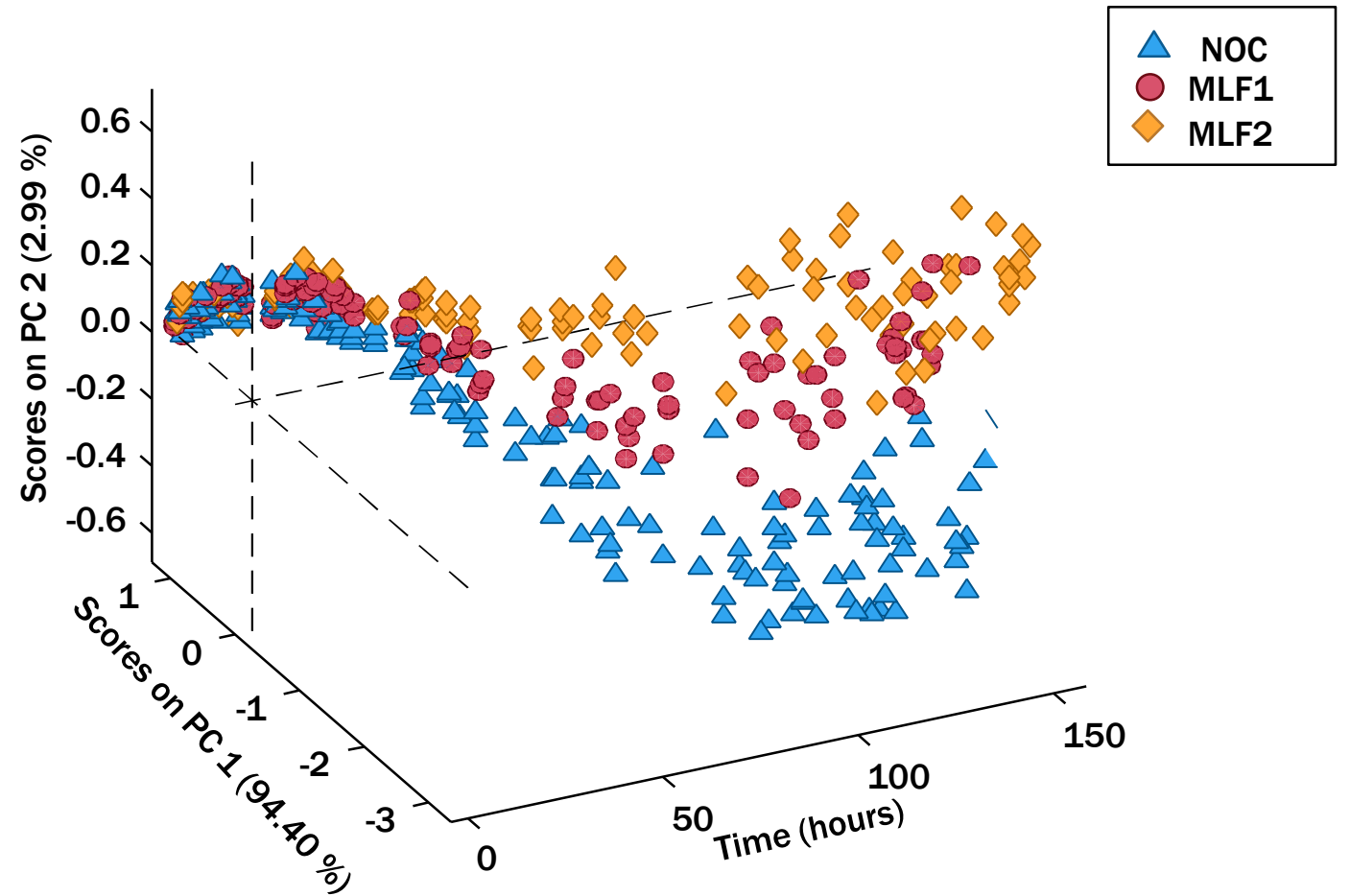


1st derivative, SNV and Mean Center



LACTIC ACID BACTERIA SPOILAGE

Exploratory Analysis
PCA



MULTIVARIATE STATISTICAL PROCESS CONTROL (MSPC)

Q-residuals:

A measure of the residual information between a sample and its projection.

Analysis of the process variations not explained in the NOC-PCA models.

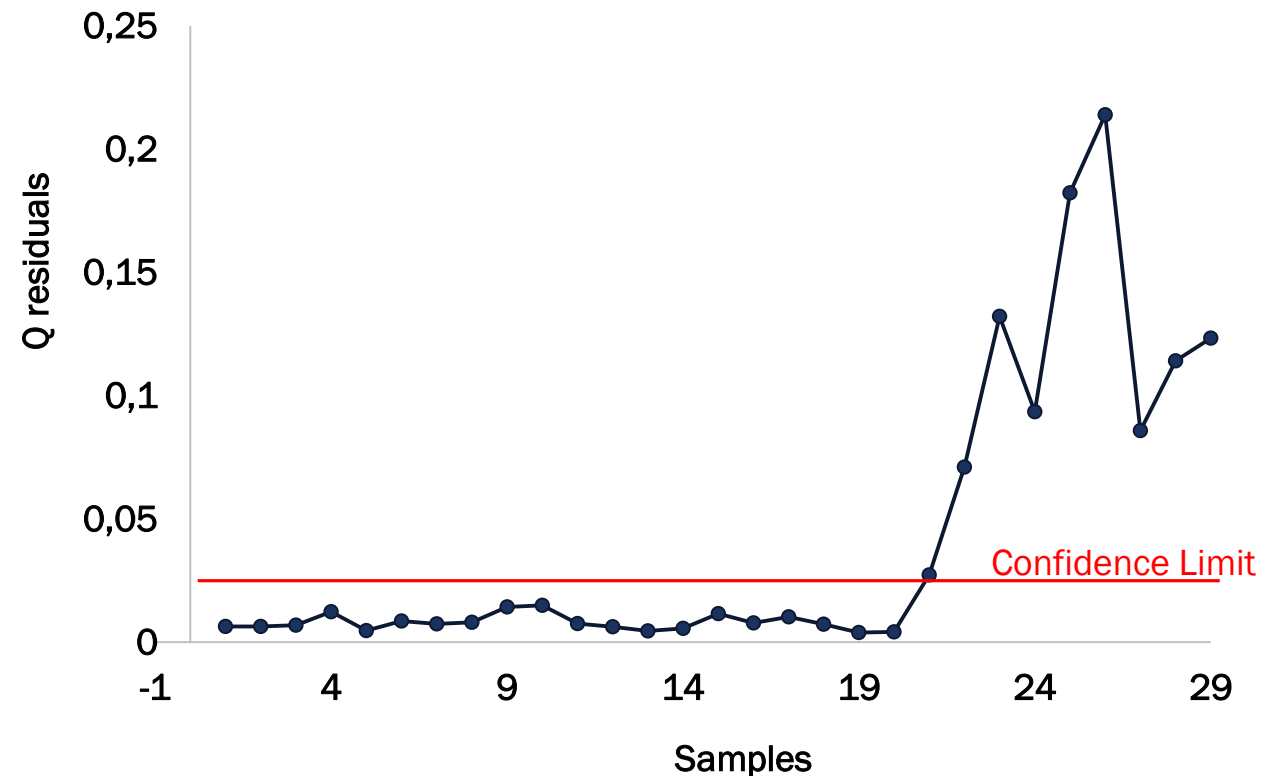
1

NOC-PCA models are built to establish Q-residuals control limits at a certain confidence in the charts.

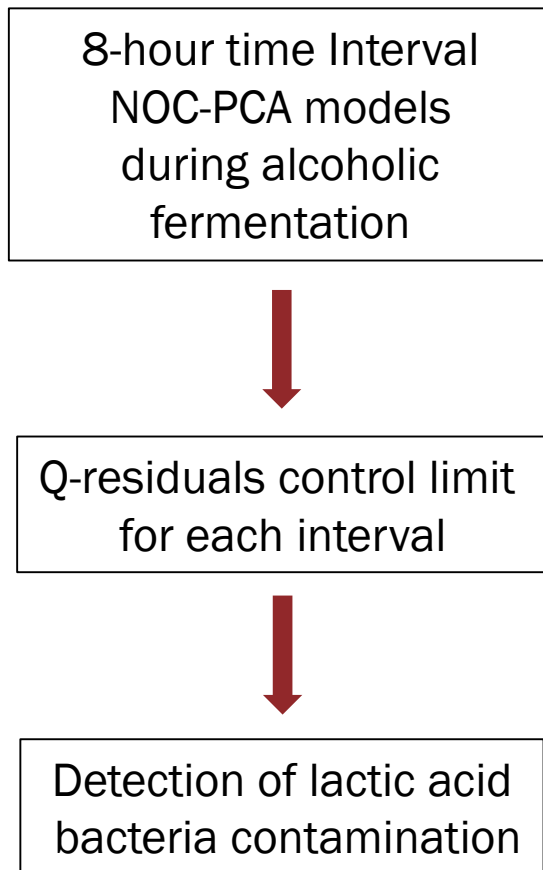
2

New data are monitored using these limits.

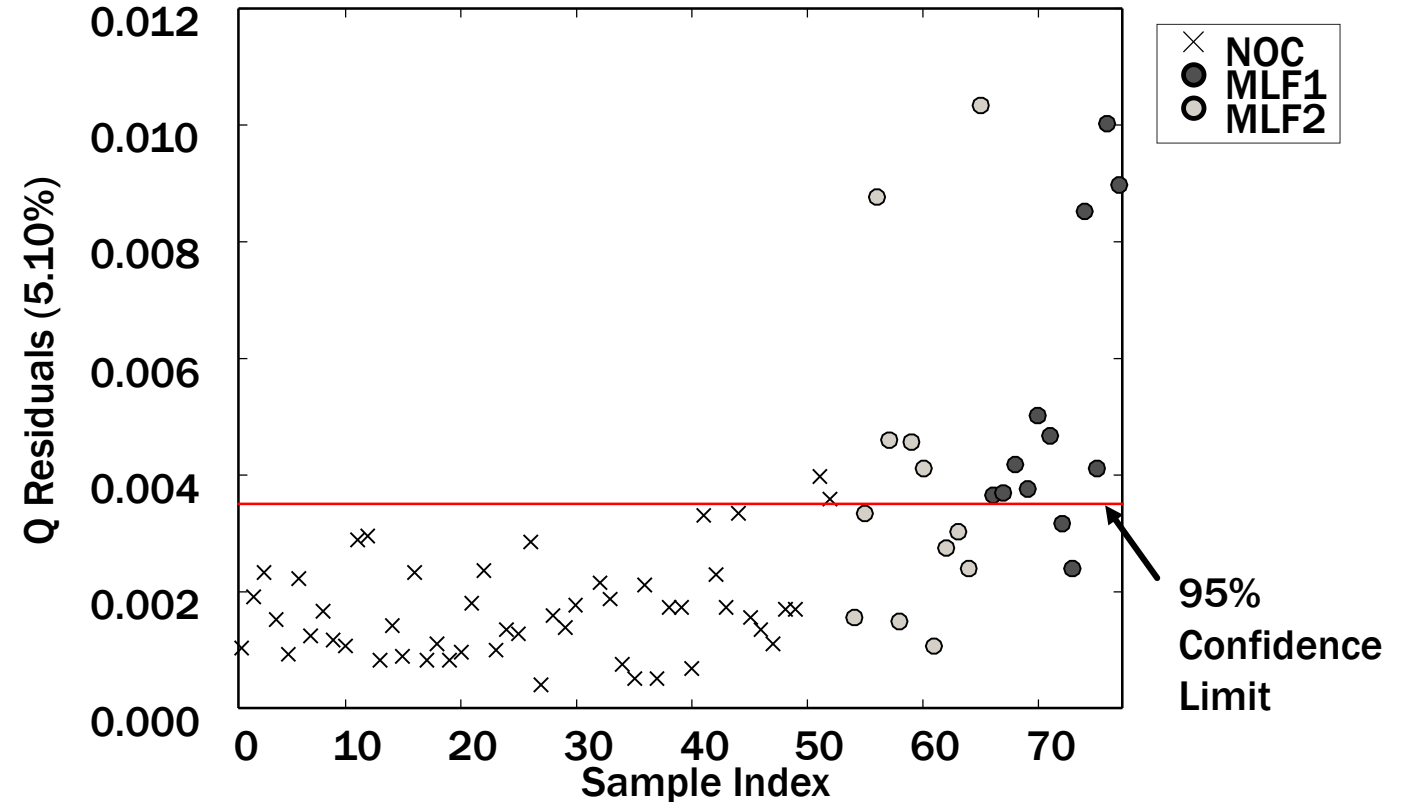
MSPC chart



MULTIVARIATE STATISTICAL PROCESS CONTROL (MSPC)



Time interval from 65 to 72 hours



CONCLUSIONS & FUTURE PERSPECTIVES

- ATR-MIR and PLSR allow the prediction of density with a low RMSECV (0.0012 g-mL⁻¹) throughout the whole alcoholic fermentation process.
- Sluggish alcoholic fermentations were detected at an early stage using PLSDA models.
- Lactic acid bacteria contamination can be early predicted using MSPC charts before the end of alcoholic fermentation, giving the possibility to apply corrective measures.
- The addition of new batches from different fermentations should be studied closely in order to minimize between-experiments variability.
- Early detection of other fermentation deviations will be considered (e.g. stuck fermentations).

THANK YOU VERY MUCH FOR YOUR ATTENTION

Julieta Cavaglia Pietro

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