

Continuous, real-time measurement of black liquor chemical makeup using static optics FTIR spectroscopy

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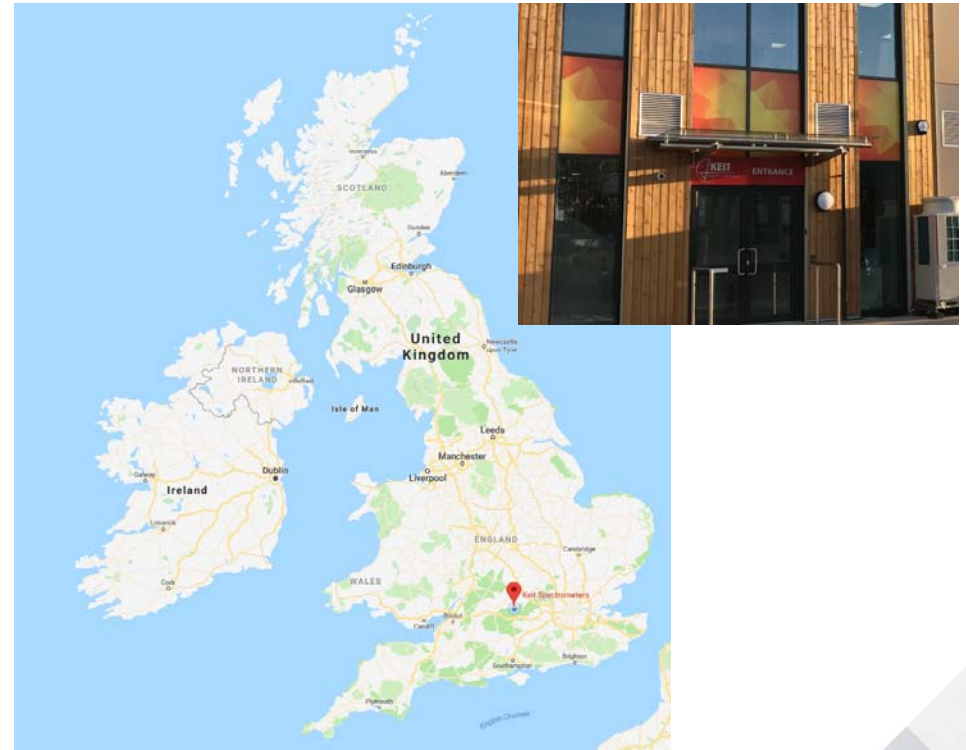
Applications and Data Scientist

Keit Industrial Analytics, UK



Where we are from

- The company is a spin-out from the UK government space research centre near Oxford, UK.
- Its technology was originally designed for a Mars research project.
- Has now been adapted for the chemical industry.



Spectroscopy in process analytics

Simple on-line measurements:

- pH, temperature, oxygen levels, turbidity/optical density measurements etc...
- Parametric measurements – can be used to infer reaction progression

Spectroscopic on-line measurements

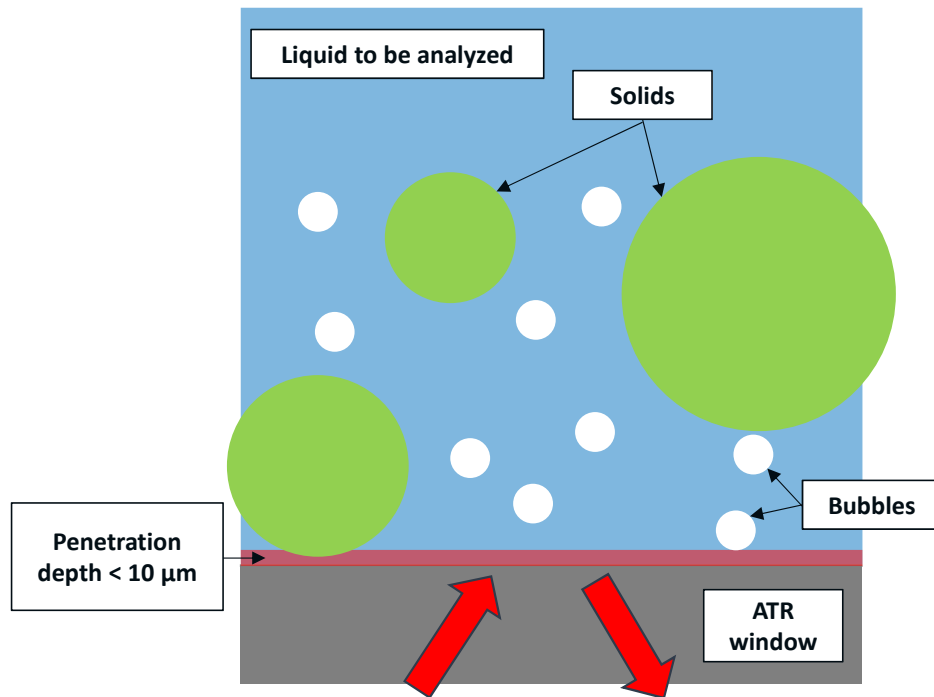
- FTIR, NIR, Raman, UV-vis, fluorescence...
- Real time
- Monitor concentrations using chemometric models

Off-line measurements

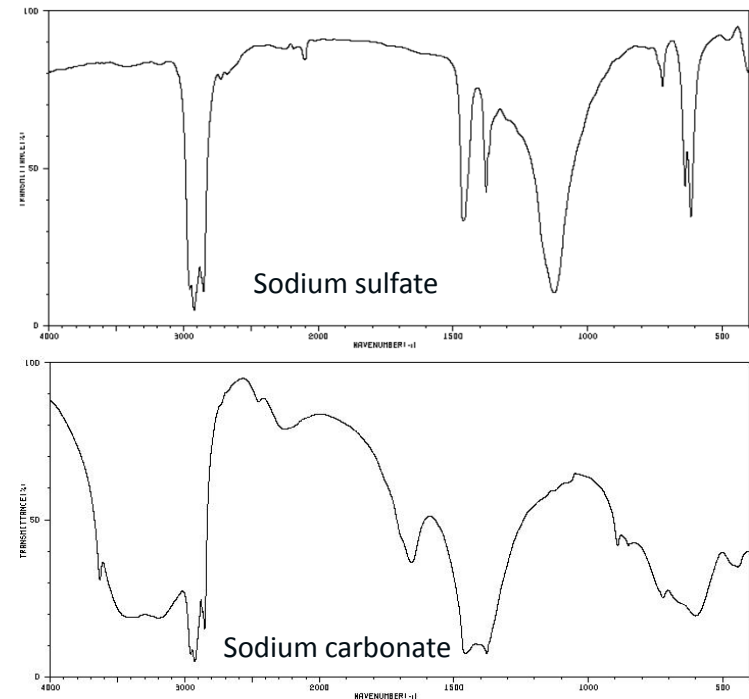
- HPLC, titrations, assays etc...
- Directly monitor concentrations
- Not real time
- Can be dangerous or impractical to remove sample



Spectroscopy in black liquor: ATR mid-IR



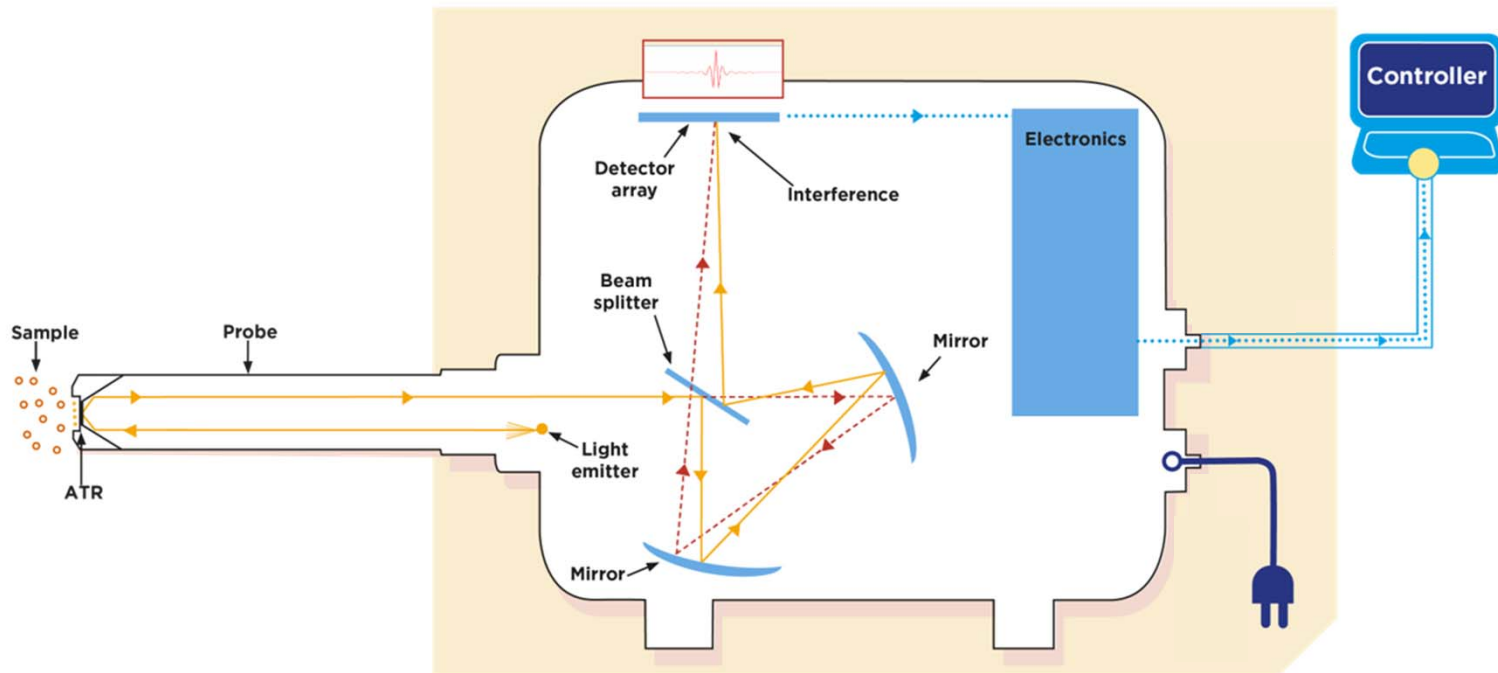
Contact probes are robust to particles and bubbles



Uses the most information-rich part of the IR spectrum



Static optics FTIR spectrometers



Sagnac interferometer, fixed mirrors.

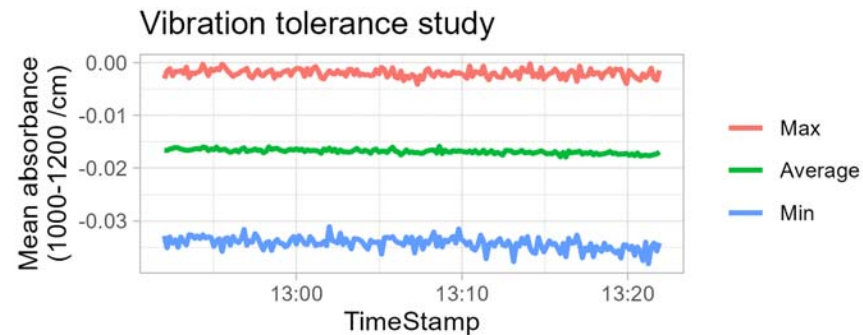
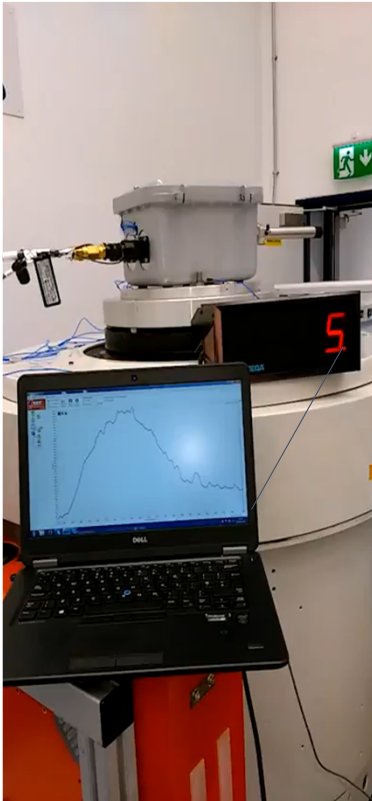
Interferogram resolved in the spatial domain on a detector.

Fourier Transform used to convert interferogram to spectrum.

For Sagnac interferometry: Sagnac, Georges (1913), *Comptes Rendus*, **157**: 708–710



Vibration tolerance of Sagnac instruments



30 minute random all-axes vibration test from 5 to 250Hz

5Hz - $0.0025(\text{m/s}^2)^2/\text{Hz}$

10Hz - $0.04(\text{m/s}^2)^2/\text{Hz}$

50Hz - $0.04(\text{m/s}^2)^2/\text{Hz}$

250Hz - $0.0025(\text{m/s}^2)^2/\text{Hz}$

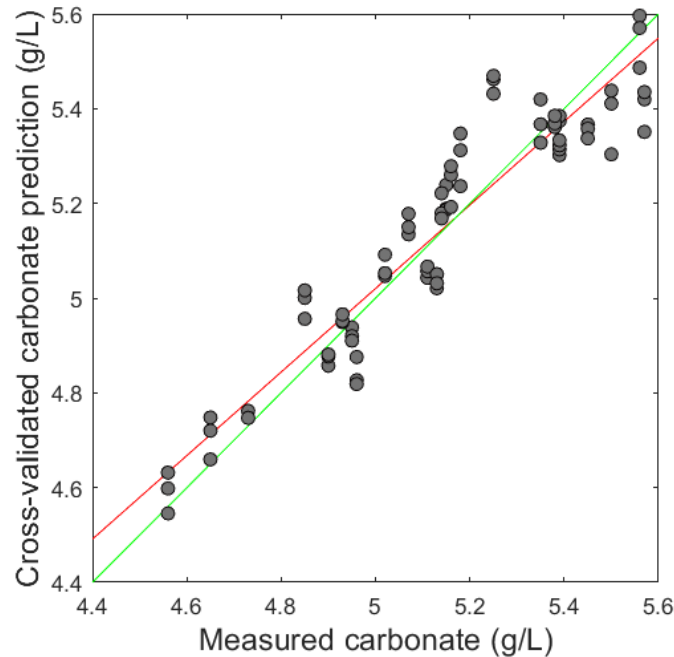
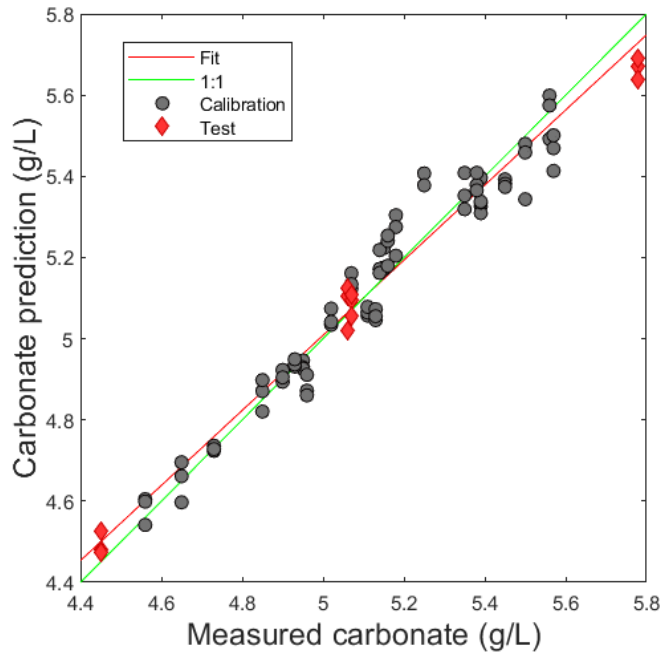
- Sagnac interferometers are robust to vibration.
- Tested to 100x the vibration seen at a pump.
- This allows a Sagnac interferometer to be installed directly into the process pipework of a pulp mill, even if near a pump. Measurements of black liquor can be made *in situ*.



Chemometric methods for process liquid monitoring



Assessing models: cross-validation



Compare chemical measurements vs model predictions.

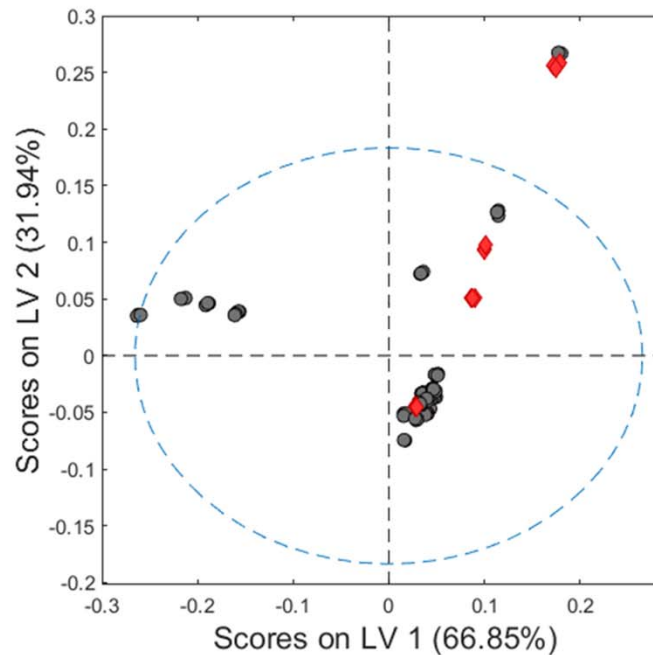
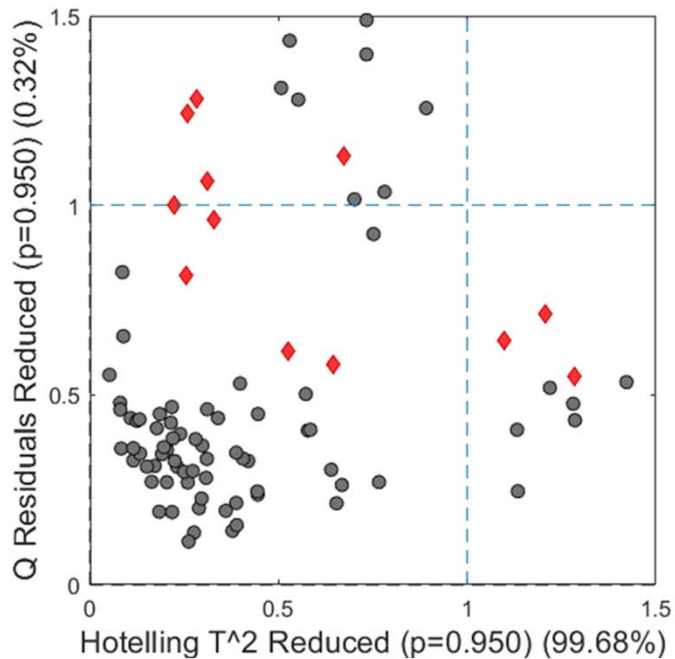
Measure model performance by RMSECV, RMSEP.

Apply preprocessing to reduce the impact of temperature, pressure fluctuations.

PLS with 6 latent variables. Carbonate as CO_3^{2-} in dry solids. RMSECV: 0.09 g/L; RMSEP: 0.07 g/L. Data from a North American strong black liquor installation.



Assessing models: outlier statistics



Look at Hotelling's T2 vs Q residuals, PC/LV space, nearest neighbors. Outliers to exclude?

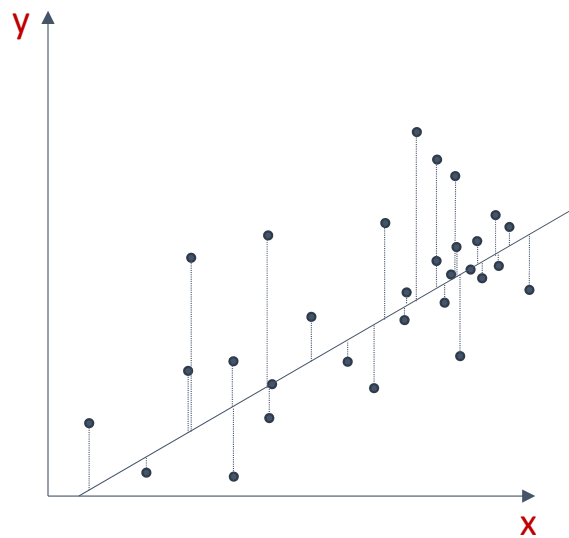
Examine the loadings: do these look like chemical changes?

Re-model in the absence of certain data points. Is the overall model quality improved?

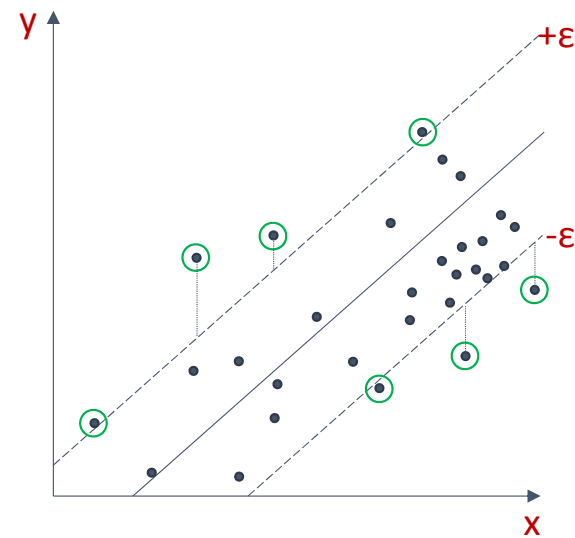
PLS with 6 latent variables. Carbonate as CO_3^{2-} in dry solids. RMSECV: 0.09 g/L; RMSEP: 0.07 g/L.



Support vector regression



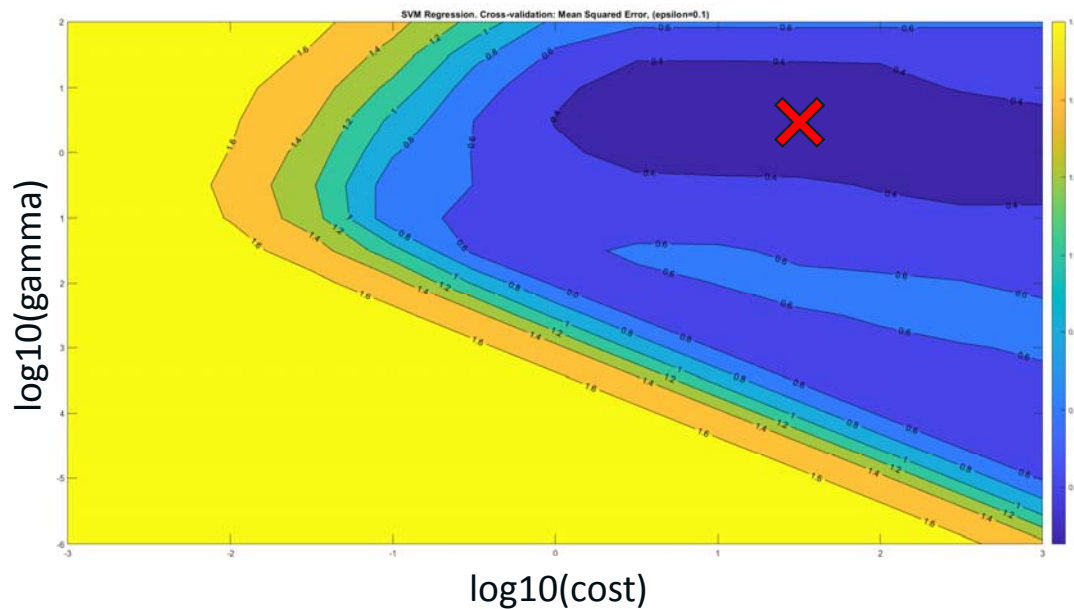
OLS: minimize total residuals



SVR: minimize residuals of support vectors



Support Vector Regression (SVR)



Do compression (PLS or PCA) on training data to reduce number of factors.

Then do hyperparameter tuning:

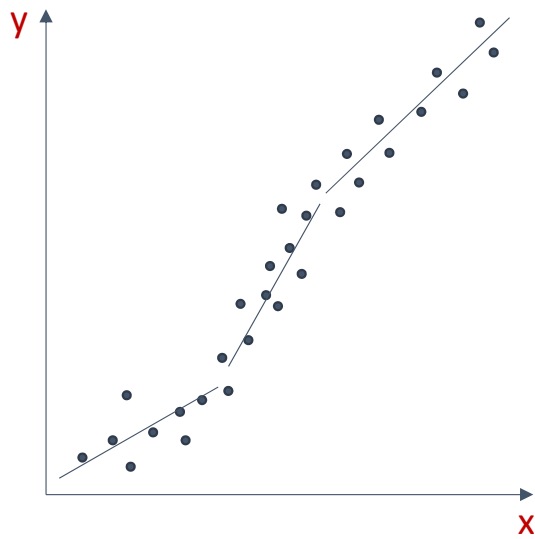
- Cost
- Epsilon
- Gamma

Use RMSECV to settle on best conditions for the SVR.

Then predict the test data.



Locally Weighted Regression (LWR)



For use when chemical concentration has a nonlinear relationship with spectra.

Build a PCA “selector” model. Use this to work out which spectra are most similar (shortest distance in PC space).

Build “local” models (PLS/PCR) for each.

Build local linear models (PLS/PCR) covering the concentration range.



Case study: black liquor monitoring



Instrument installation examples



Instrument installed in weak black liquor line via flow cell

Targeted analytes

- REA
- Total extractives



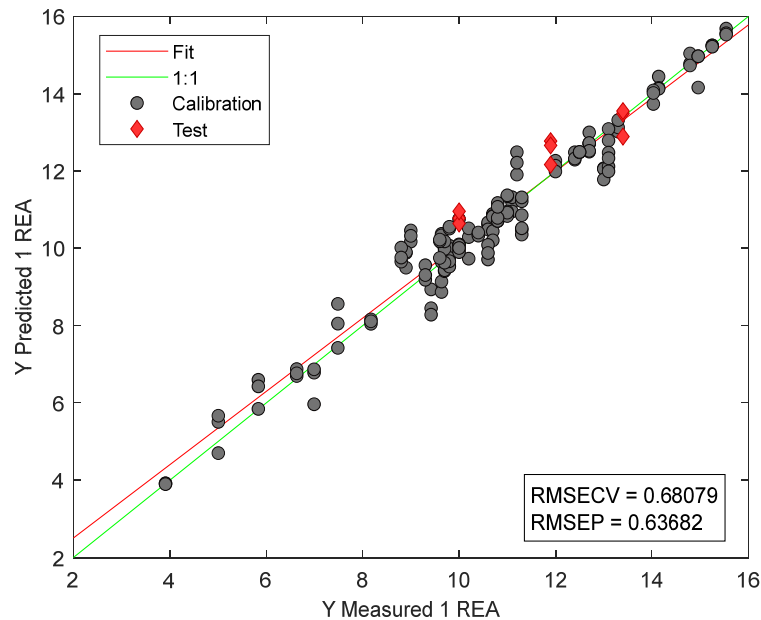
Instrument installed in strong black liquor line via flanged T-piece with supporting cradle

Targeted analytes

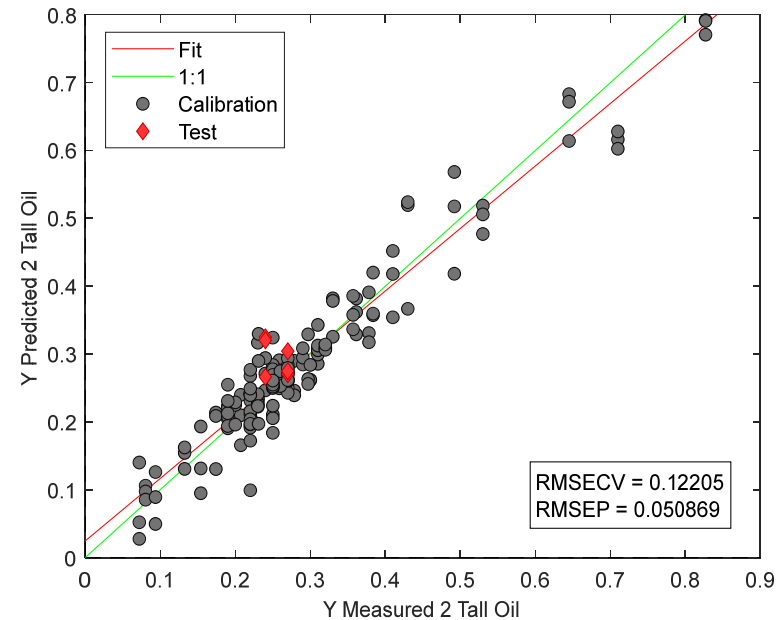
- REA
- Sulfate
- Dissolved Solids



Measurement results: weak black liquor



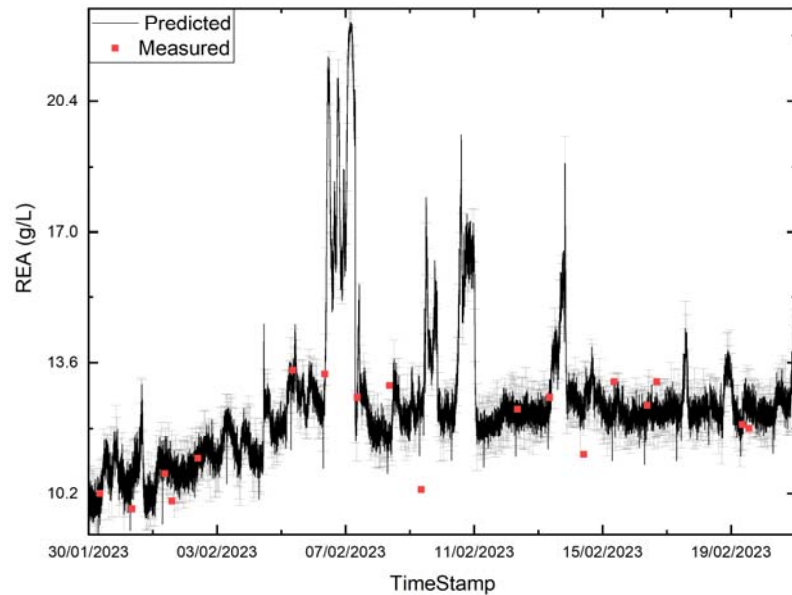
REA: SVR (PLS, 7 LV compression),
SNV. 1048:1444 cm^{-1} . Units:
g/L.



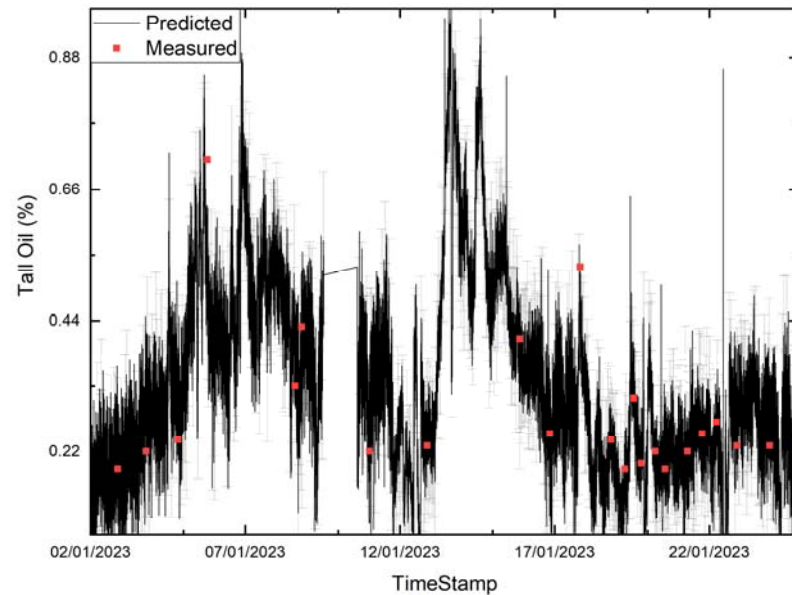
Tall oil: LWR, mean center.
928:1500 cm^{-1} . Units:
wt%.



Measurement results: weak black liquor



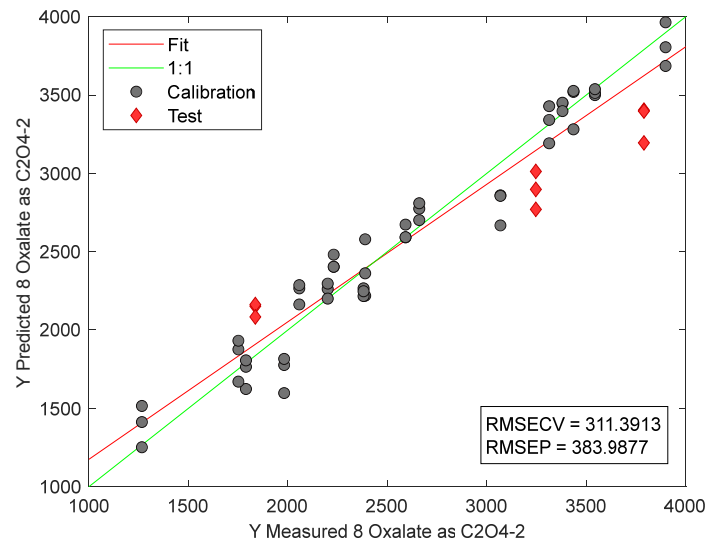
REA modeled with SVR and augmentation with
anonymized datasets from other installations
RMSECV: 0.5 g/L



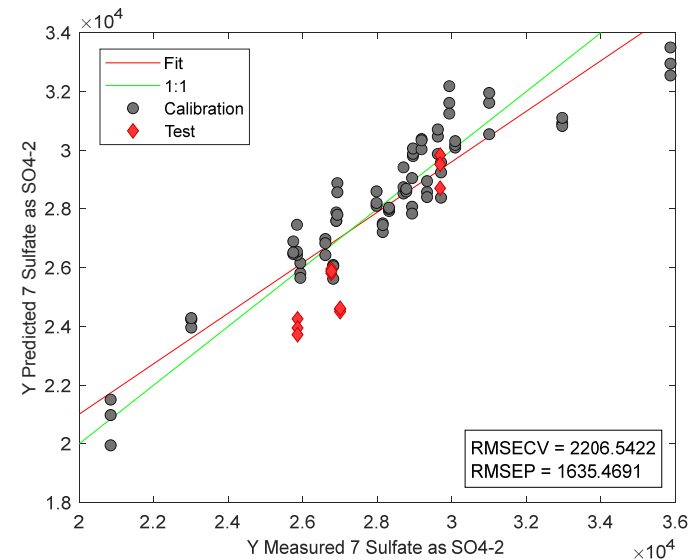
Tail oil modeled with LWR
RMSECV: 0.122 wt%



Measurement results: strong black liquor



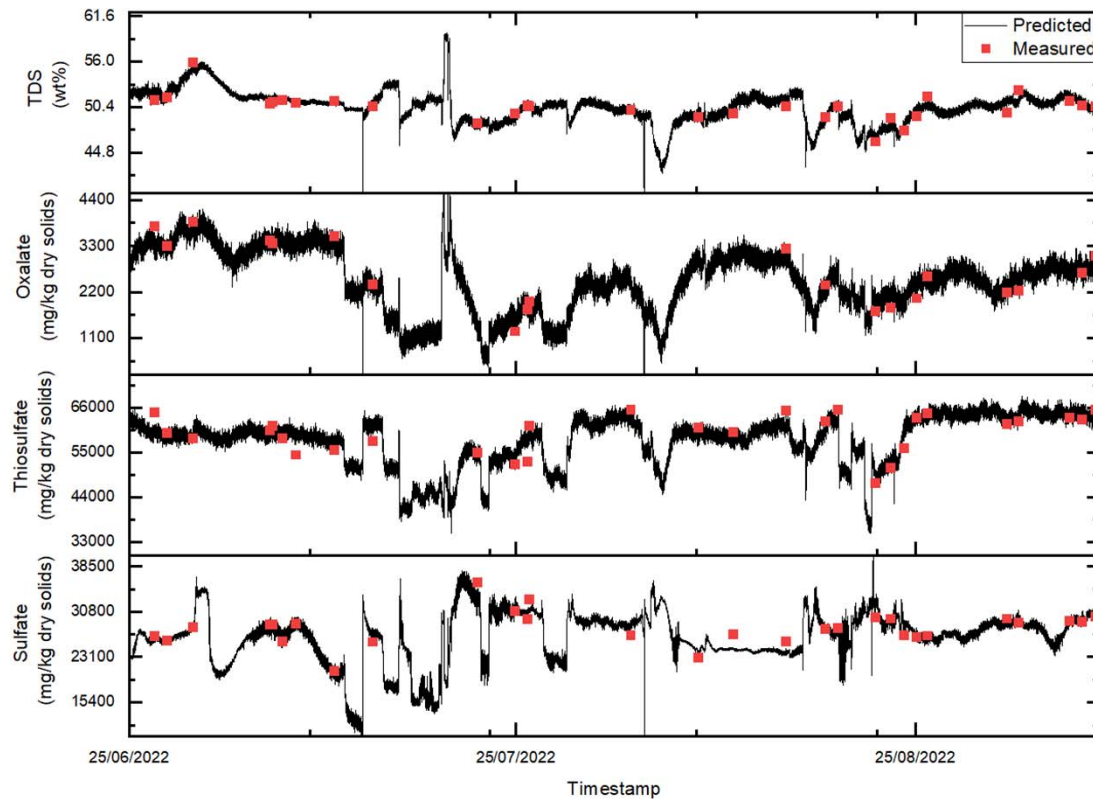
Oxalate: RMSECV 311 mg/kg
PLS (5 LV), 2nd order derivative.



Sulfate: RMSECV 2200 mg/kg
LWR, 1st order derivative, GLSW.



Measurement results: strong black liquor



TDS: RMSECV 0.92 wt%
PLS (4 LV), SNV.

Oxalate: RMSECV 311 mg/kg
PLS (5 LV), 2nd order derivative.

Thiosulfate: RMSECV 3900 mg/kg
LWR, MSC.

Sulfate: RMSECV 2200 mg/kg
LWR, 1st order derivative, GLSW.



Towards global models

- Chemometricians like process variation – plant managers don't!
- Process variation takes time to accumulate.
- Sampling is expensive and hazardous.
- Combining anonymized data from multiple spectrometers enables the building of models from more spectral or chemical variation than any of the individual spectrometers has been exposed to.
- Datasets are curated and incorporated into global models.



Summary

- Process spectroscopy is a data-rich alternative to traditional titrations that greatly reduces the need for sampling.
- Static optics FTIR is robust to the harsh conditions inside a pulp mill.
- Chemometric models can measure many black liquor analytes simultaneously in real time.
- Global models, combining data from many sources, can give high quality predictions immediately on installation.



Any questions?

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