Quantitative resolution of emulsifiers in an agrochemical formulation.

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Context

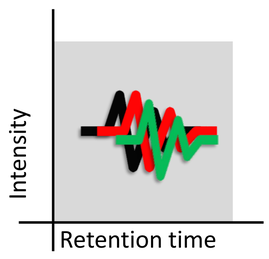
* Emulsifiers stabilise & optimise biological formulations
* Batch to batch variation affects QA, develop model to quantify emulsifiers in blends.
* Quantitation of emulsifiers by LCMS :- co-elution, overlapping peaks, matrix effects; multivariate methods for resolution needed.

Data description & pre-processing

Each formulation is a *mix* of **three emulsifiers/co-formulants (Y1, Y2, Y3)** at the following concentrations

* Low (0.06mg/ml)
* Mid (0.15mg/ml)
* High (0.2399mg/ml)

Objective :- *Create individual models to predict level of each component in any given blend.*

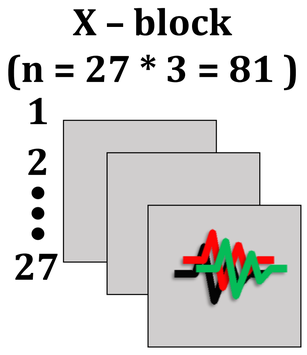


n = 27 unique blends

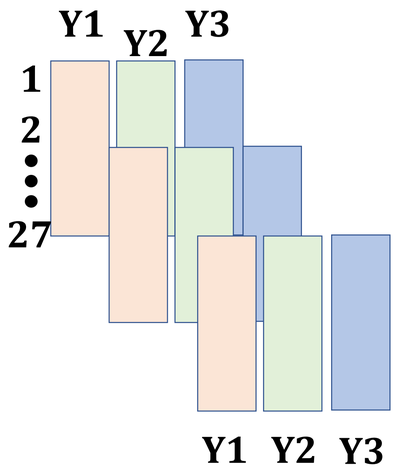
3 replicates

3 concentration values

30-minute LC run (Agilent 1290 Infinity II)

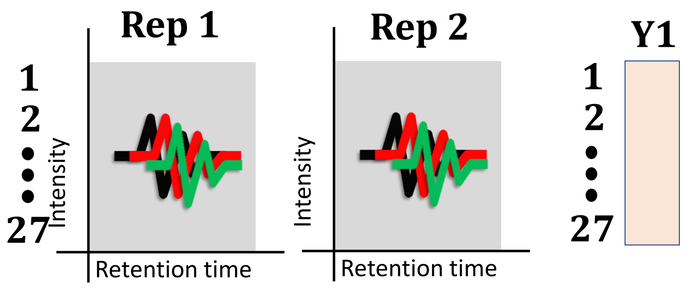


(a) Truncate **X - block** Rt 16 – 27min (*manual varsel*)

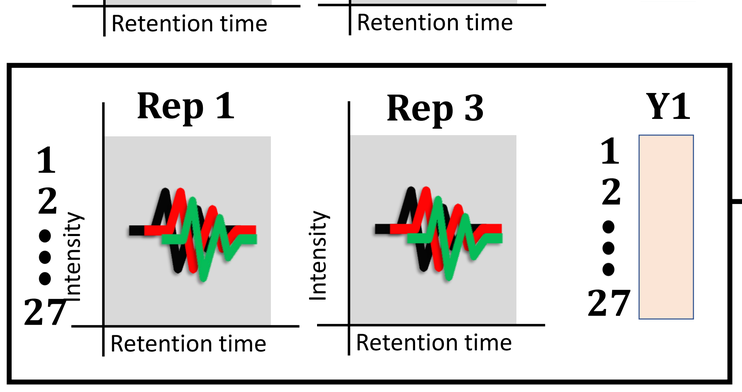


(b) *Autoscale* **X & Y**

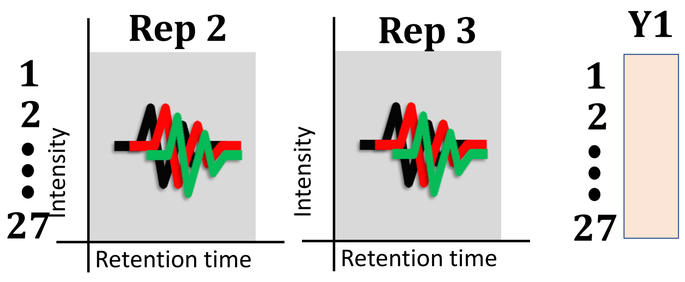
Modelling I (Calibration)



* Create PLSR1 model using n = 27 * 2 as calibration set for **Y1**
* 10-fold cross validation



* Select no. of latent variables based on performance indicators :- **lowest $RMSE_{CV}$, highest R^2_{CV}**



* Check if variable selection needed and/or stable
* Evaluate variability in model performance with respect to cycling of calibration replicates to *select optimal model*

Modelling II (Validation)

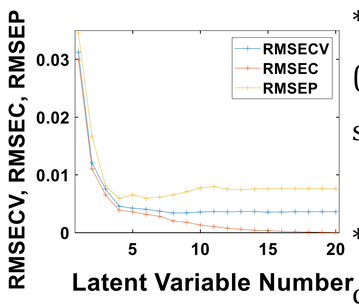
* Apply model on validation set (n = 27),i.e. replicate 2

* Evaluate model performance ;select model with **lowest $RMSE_P$, highest R^2_P**

* Inspect calibration-validation subspace using **Q residuals** to determine if optimal model reached ; consider **exclusion of datapoints** if needed ; consider inclusion of latent variables if needed

* Repeat modelling with **Y2 and Y3** and compare

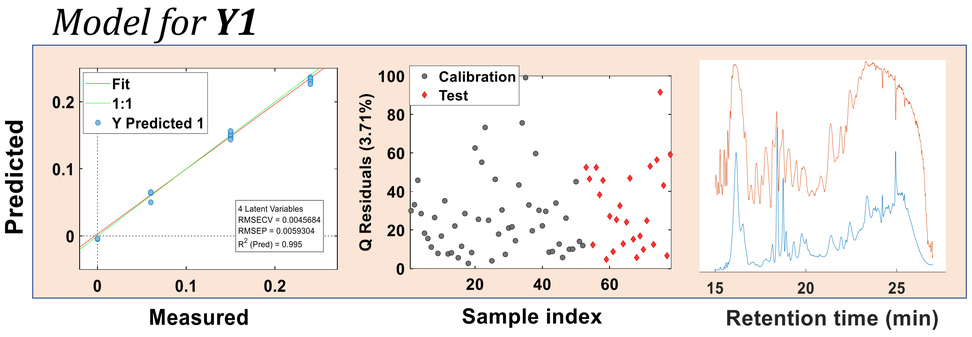
Results & Discussion



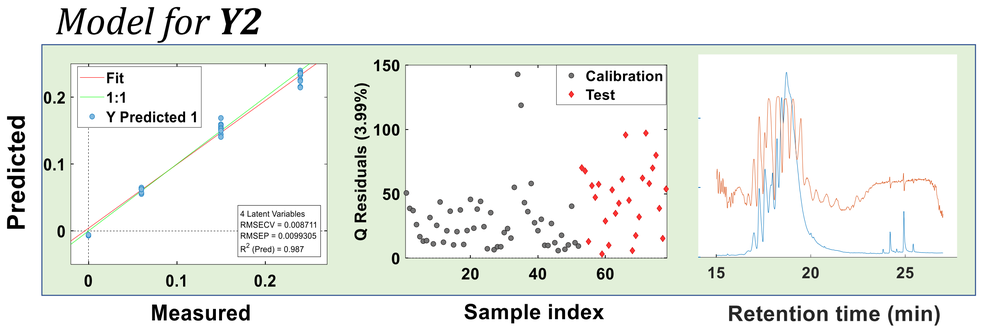
* Lowest $RMSE_{CV}$ for 4 – latent variable model (0.006) and highest **R2** (0.99) for each model separately built for **Y1, Y2 & Y3**

* **Rep 1, Rep 3** selected for calibration :- captures time-based variability, applied to **Rep 2**

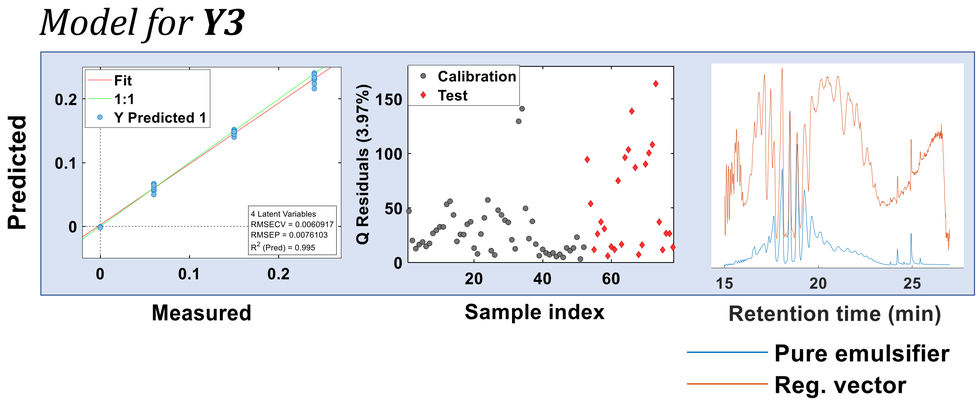
*Model for **Y1***



*Model for **Y2***



*Model for **Y3***



* **Q residual** subspace indicates inclusion of more latent variables could improve model specificity, at the cost of overfitting > more conservative 4 latent variable model preferred to keep predictive performance consistent

* Overlay of 'pure' emulsifier chromatogram with 4-latent variable model regression vector indicates key chromatographic features agree more or less

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