NIR spectroscopy for rapid determination of permethrin or bifenthrin retention in P. radiata sapwood

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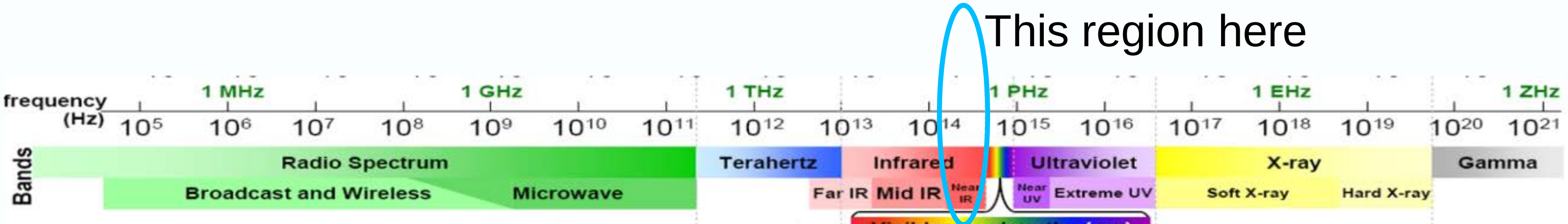
The aim

To develop NIR spectroscopic method(s) for the reliable, rapid, non-destructive determination of pyrethroid (and/or azole) retention in H2F timber.

Why?

The existing AS1605.3 method for testing of retention in timber suffers from (i) considerable sample preparation requirements, (ii) slow throughput and (iii) is prone to error due to variable extraction / analytical efficiencies.

NIR Spectroscopy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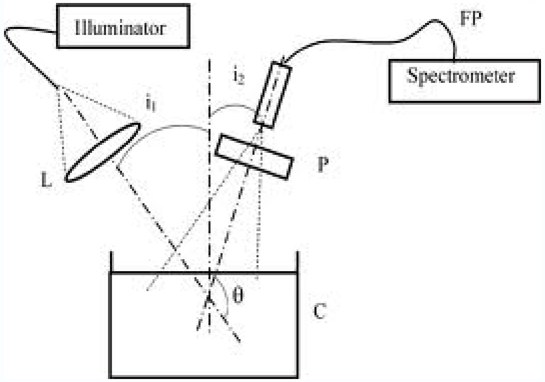
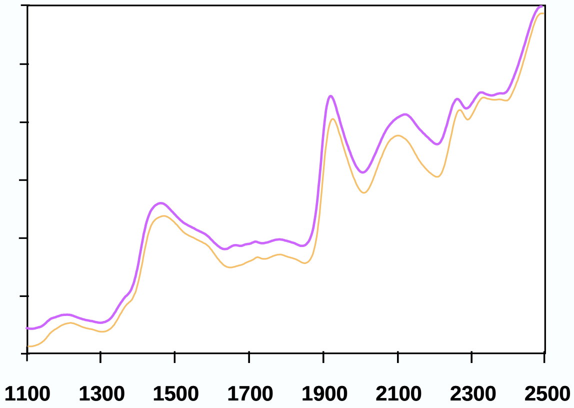
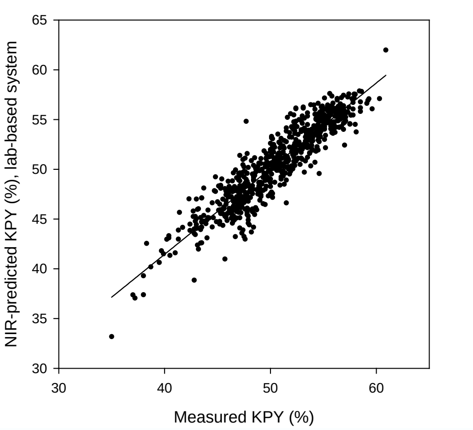
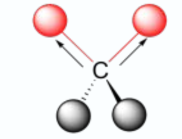
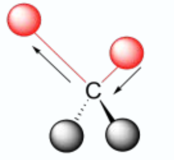


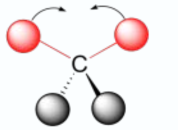


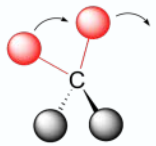
PLS




symmetric stretching


asymmetric stretching


scissoring


rocking

NIR Applications in the Forestry Sector

- Chemical composition
  - Kelley et al 2004, Poke and Raymond 2006, Thumm et al 2010
- Kraft pulp yield
  - Wallbäcks et al 1990; Meder et al 1994, Michell 1995, Schimleck and Michell 1998, Downes et al 2010, 2011, 2012
- Compression wood
  - Meder and Meglen 2012
- Stiffness
  - Thumm and Meder 2001, Meder et al 2003
- Density
  - Hoffmeyer and Pedersen 1995, Mora et al 2008
- Microfibril angle
  - Schimleck and Evans 2002, Zbonak and Bush 2006, Meder et al 2010
- Durability
  - Jones et al 2011, Bush et al 2011

Two special issues of *JNIRS*
2010 18(6) Meder, Trung, Schimleck (Eds) – 16 papers
2011 19(5) Meder and Schimleck (Eds) – 13 papers

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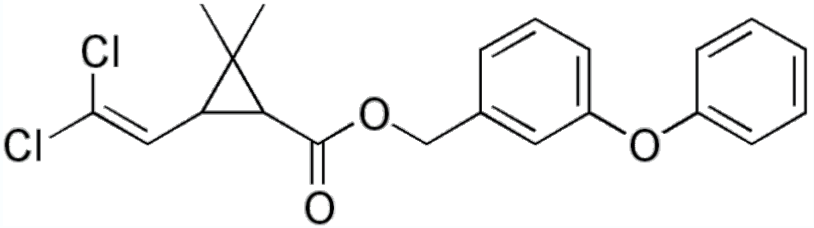
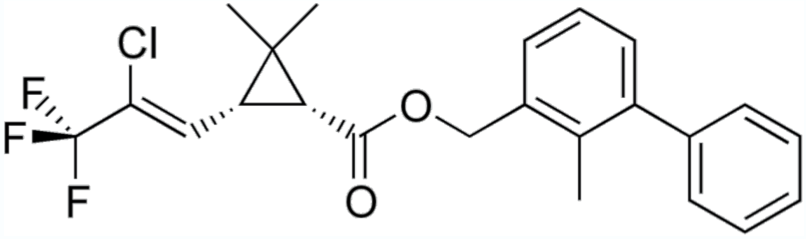
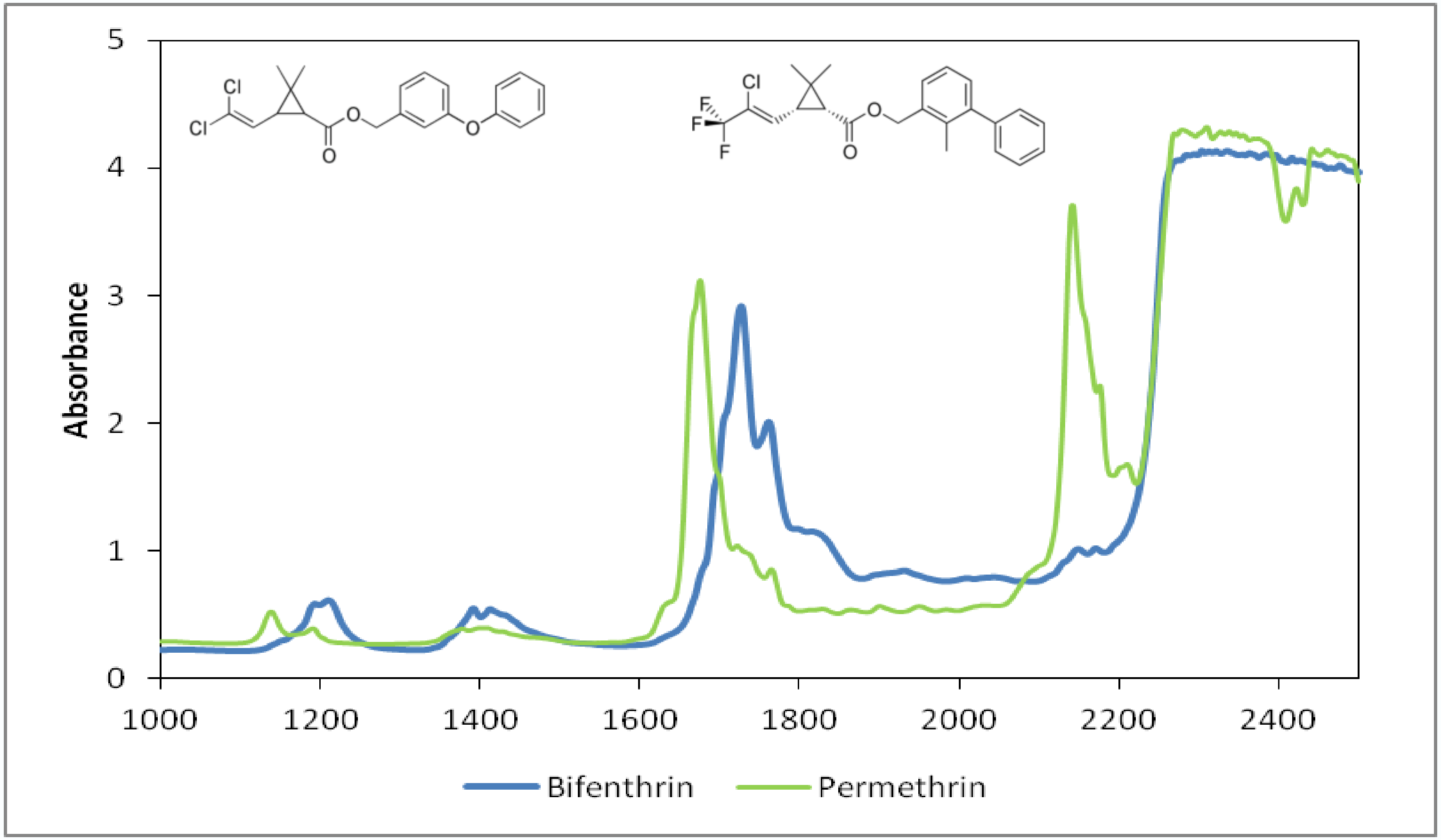
<u>**CCA preservative**</u> So et al 2004

So C-L, Lebow ST, Groom LH, Rials TG (2004) Wood and Fiber Science, 36(3), 329-336

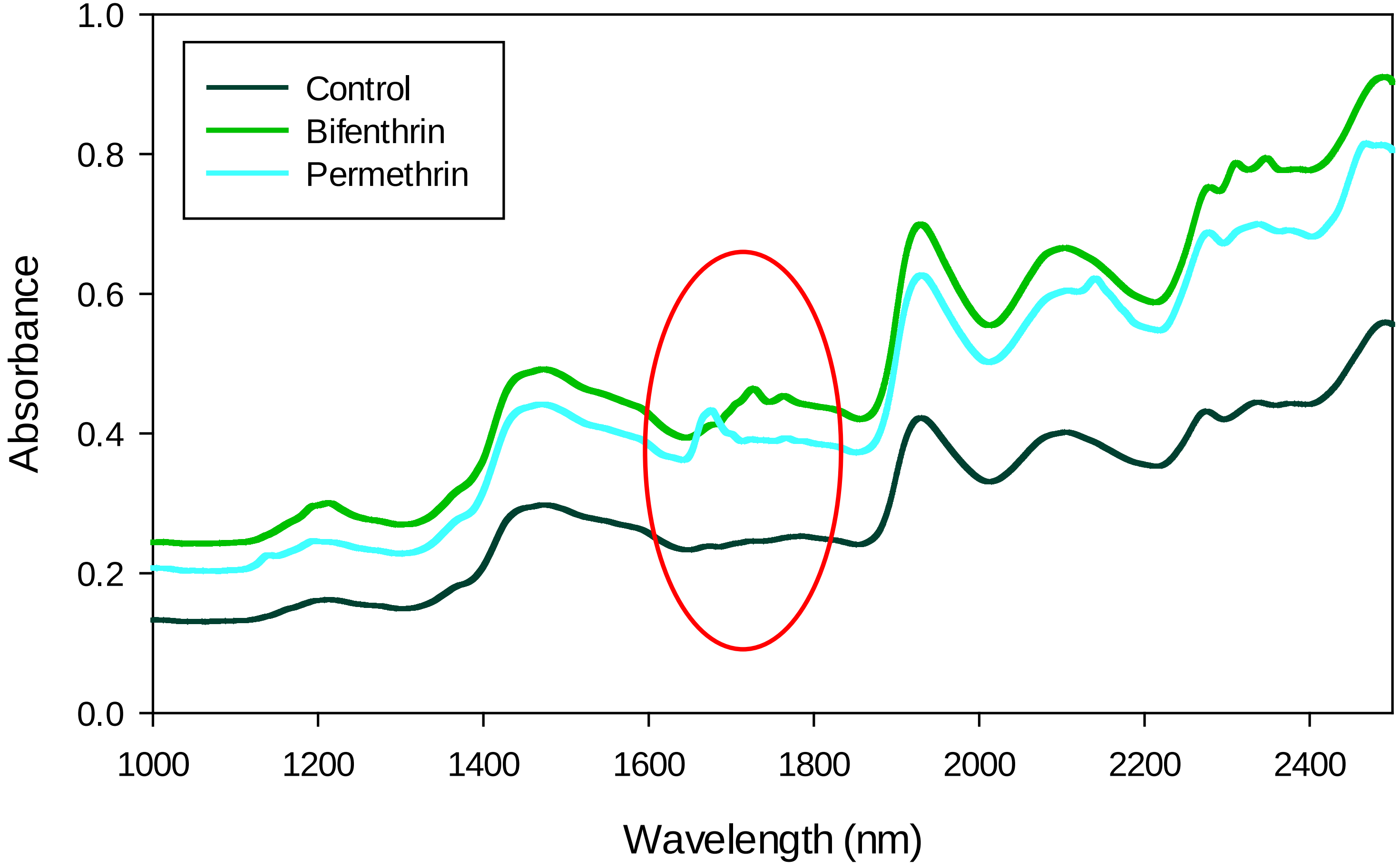




NIR of pyrethroids



NIR of pyrethroid in wood



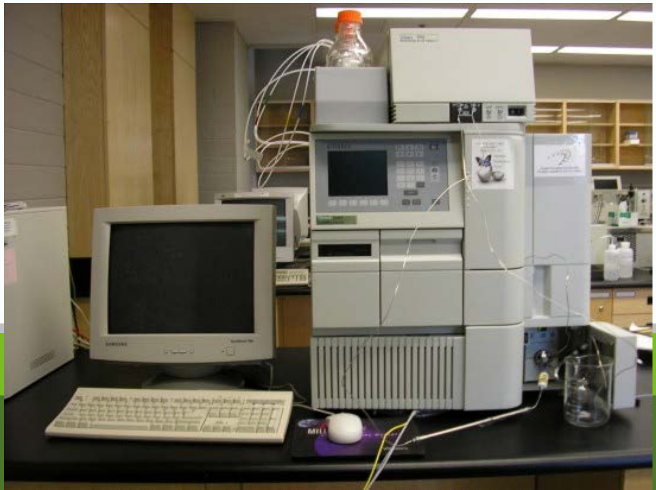
Target treatment

Active	Retention (% m/m)	Retention Depth (mm)
Bifenthrin	0.02	2
Permethrin	0.02	5
Tebuconazole/Propiconazole	0.03	Full penetration (LOSP)

Source: AS1604.1 – 2000

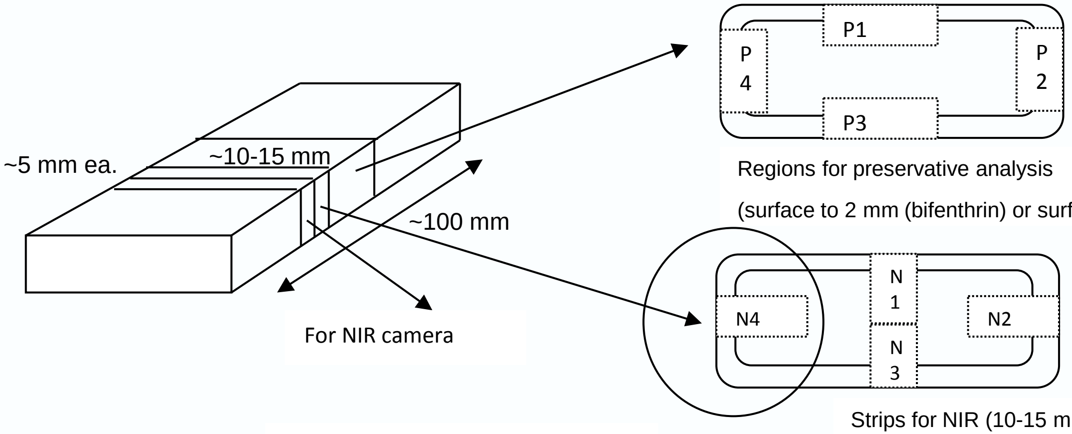
AS1605.3 – Analysis of preservative retention

Bifenthrin	Permethrin
Section 4 faces to a depth of 2 mm	Section 4 faces to a depth of 5 mm
Determine MC	Determine MC
Extract in acetone via sonication	Extract in ethanol via sonication
Analyse bifenthrin concentration via GC-ECD (electron capture)	Analyse permethrin concentration via HPLC with UV detection at 232 nm



Section 1:
H2F Laboratory Calibration

Treatment and sampling of boards

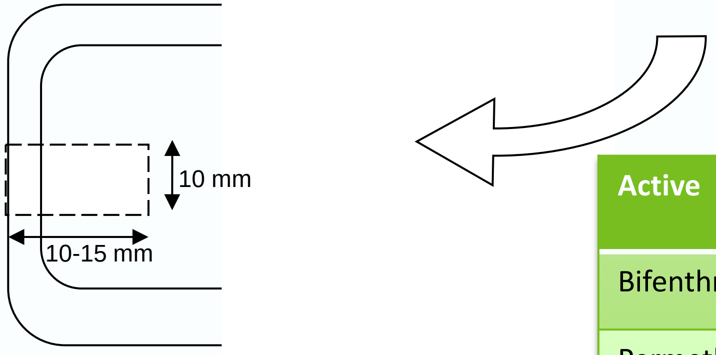


For NIR camera

Regions for preservative analysis

(surface to 2 mm (bifenthrin) or surface to 5 mm (permethrin)

Strips for NIR (10-15 mm deep) from each face



Active	Target Retention (% m/m)	Standard Retention (% m/m)
Bifenthrin	0.015, 0.020, 0.025, 0.030	0.02
Permethrin	0.015, 0.020, 0.025, 0.030	0.02
Tebuconazole/Propiconazole	0.02, 0.03, 0.05, 0.06, 0.07	0.03

4 or 5 boards per treatment level, nominal 90 x 45 mm

NIR of treated wood samples

- Bruker MPA w fibre optic
- Control Development Inc (CDI-256)

Jig constructed to fit fibre optic with 2 mm and 5 mm stops

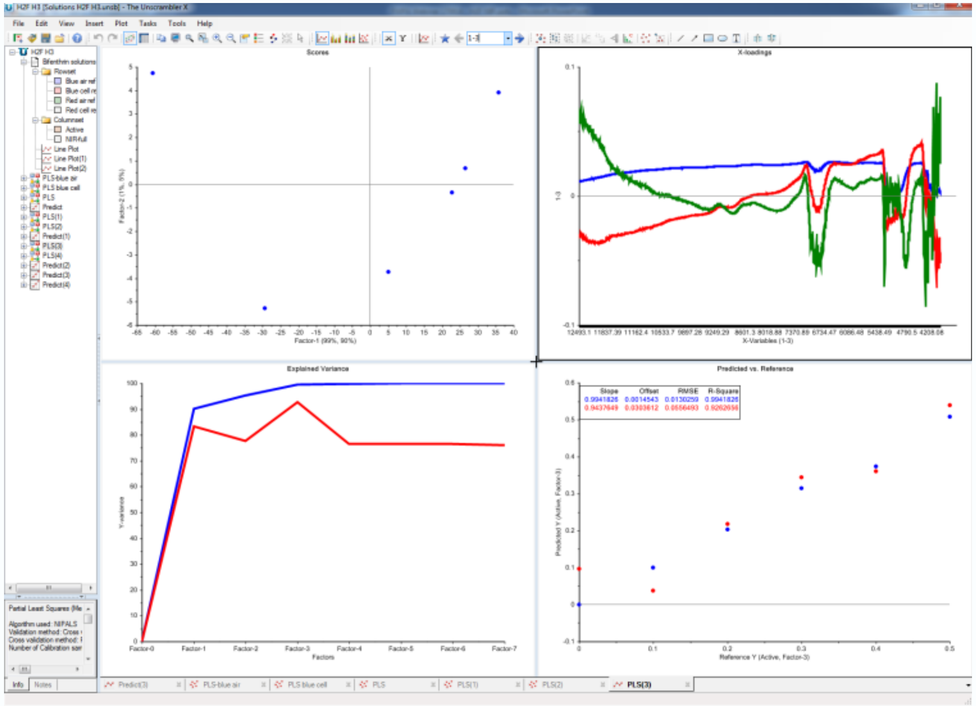
Calibration development

Partial least squares regression

X = NIR spectra

Y = measured retention (or theoretical retention)

The Unscrambler X v10.3



Slope	Offset	RMSE	R-Square
0.9941826	0.0014543	0.0130259	0.9941826
0.9437649	0.0303612	0.0556493	0.9262656

Section 2A:
Results of lab calibration

Calibration statistics (cross validation) Bruker MPA

Active	LV's reqd	R^2 (Calib)	r^2 (CV)	RMSEP
Bifenthrin	5	0.943	0.74	0.003
Permethrin	4	0.974	0.87	0.002
Tebuconazole	6	0.990	0.57	0.008
Propiconazole	6	0.992	0.52	0.009
Total azole	6	0.990	0.55	0.02

CDI

Active	LV's reqd	R^2 (Calib)	r^2 (CV)	RMSEP
Bifenthrin	7	0.921	0.70	0.005
Permethrin	6	0.933	0.79	0.003

Savitzky-Golay 2nd derivative, 15 points, 2nd order polynomial
Cross validation – 10 random blocks

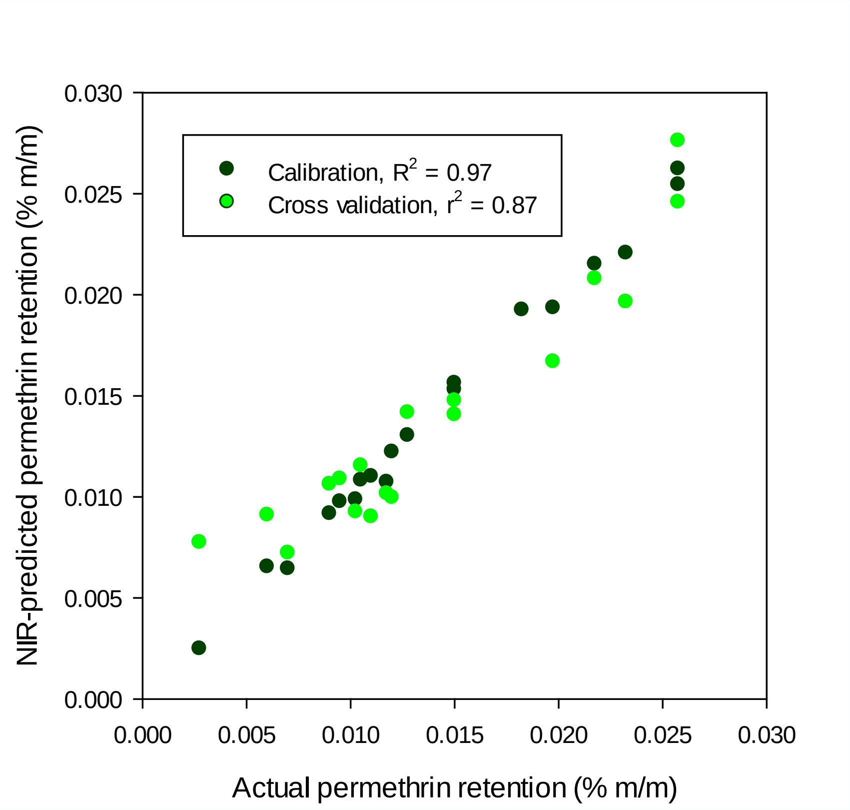
Calibration statistics – reduced range NIR (cross validation)

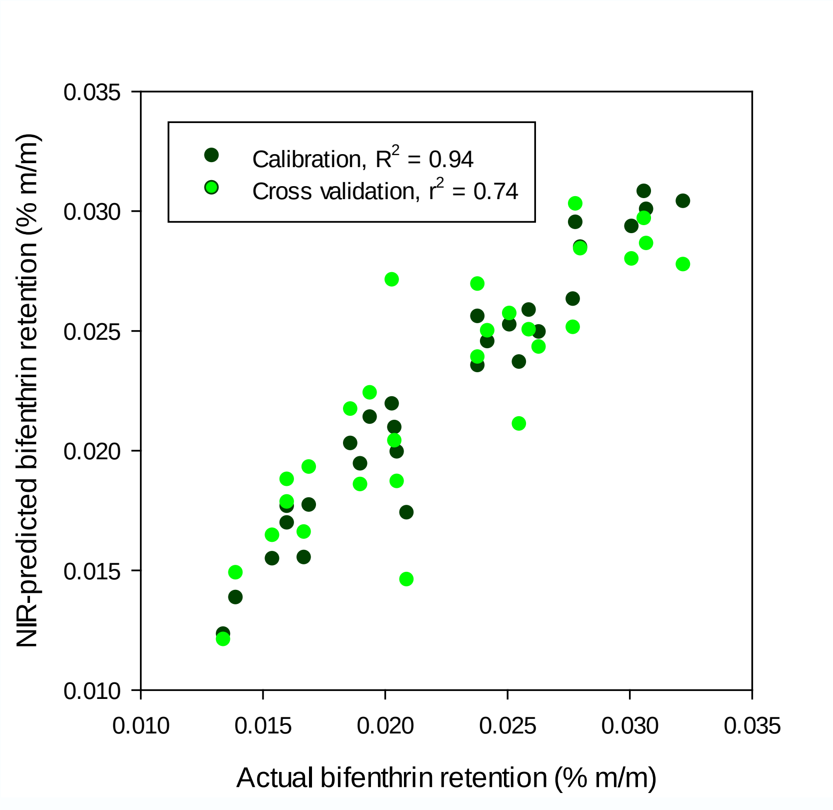
NIR spectra 1600-2400 nm only (common range of low-cost NIR)

Active	LV's reqd	R^2 (Calib)	r^2 (CV)	RMSEP
Bifenthrin	5	0.936	0.82	0.003
Permethrin	5	0.923	0.85	0.003

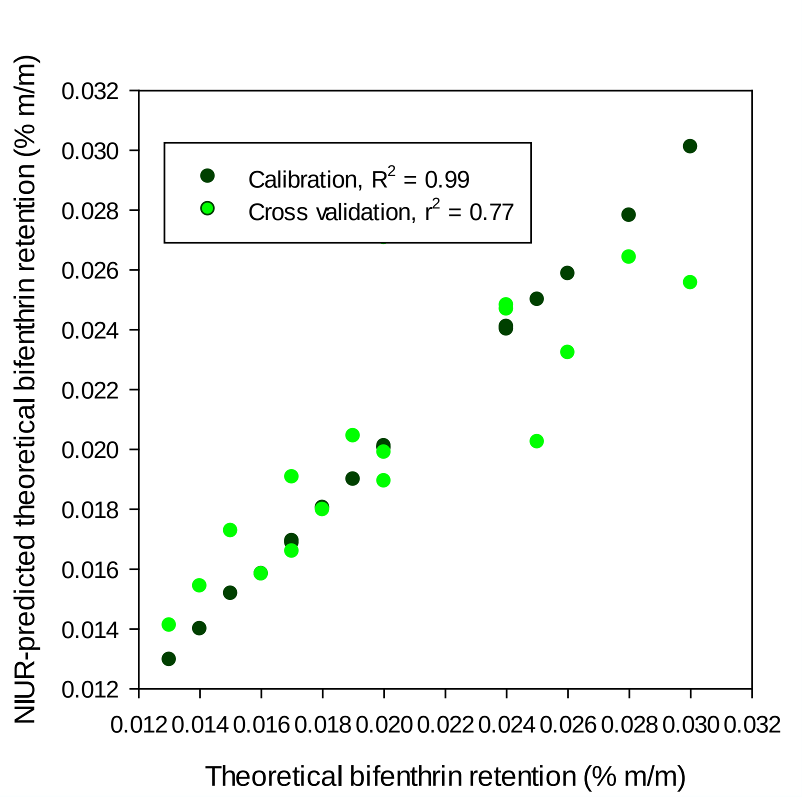
Savitzky-Golay 1st derivative, 15 points, 2nd order polynomial
Cross validation – 10 random blocks

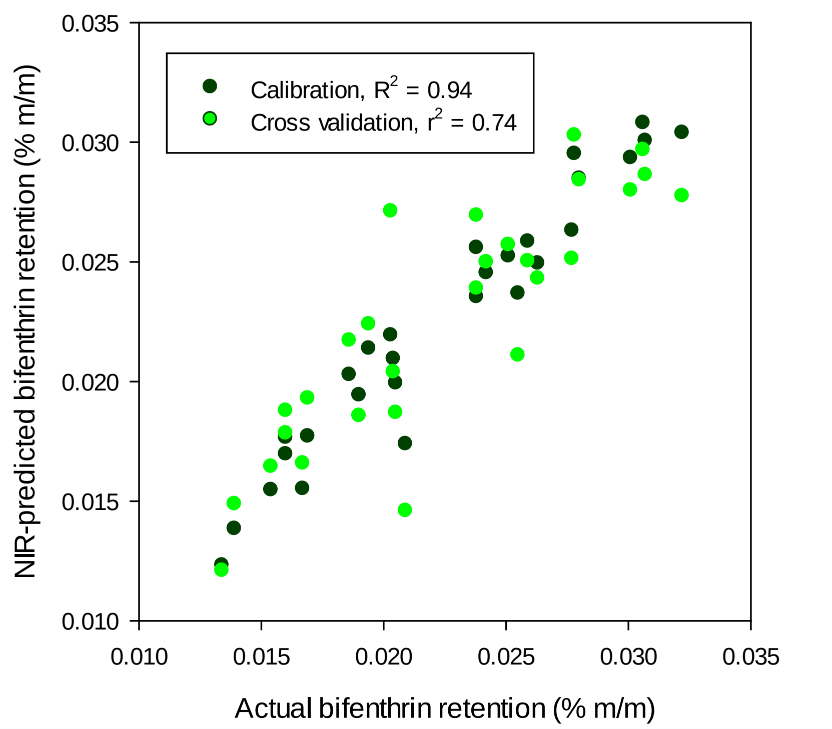
Calibration plots for NIR prediction of permethrin and bifenthrin (MPA)





Calibration of theoretical retention vs calibration of actual retention for bifenthrin





Section 2B:

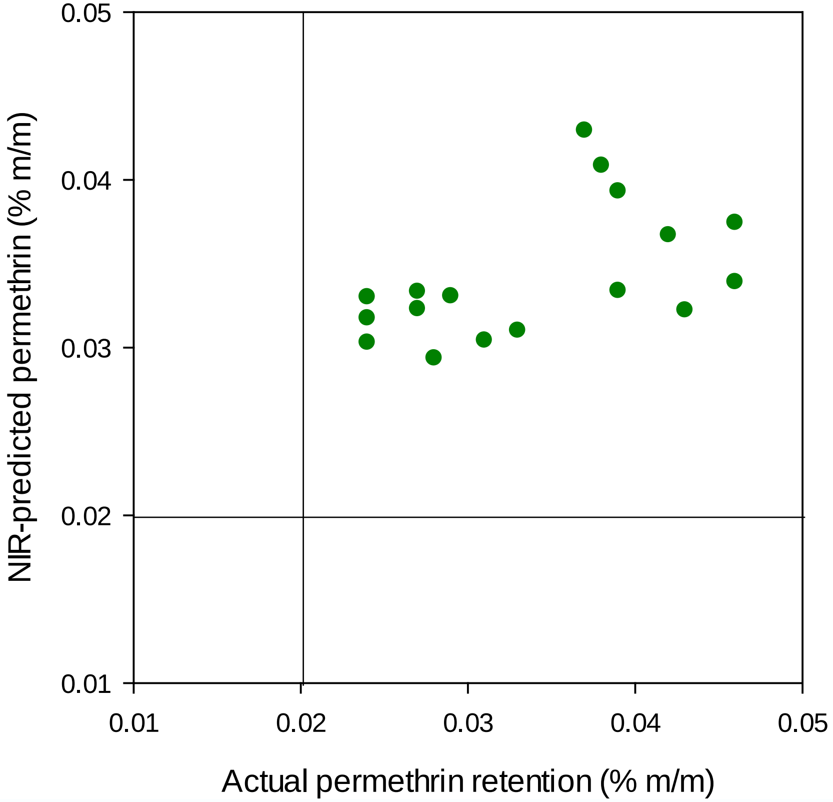
Results of prediction of mill samples

Prediction of permethrin retention in run-of-mill samples

All samples predicted > 0.02 %

All actual values > 0.02 %

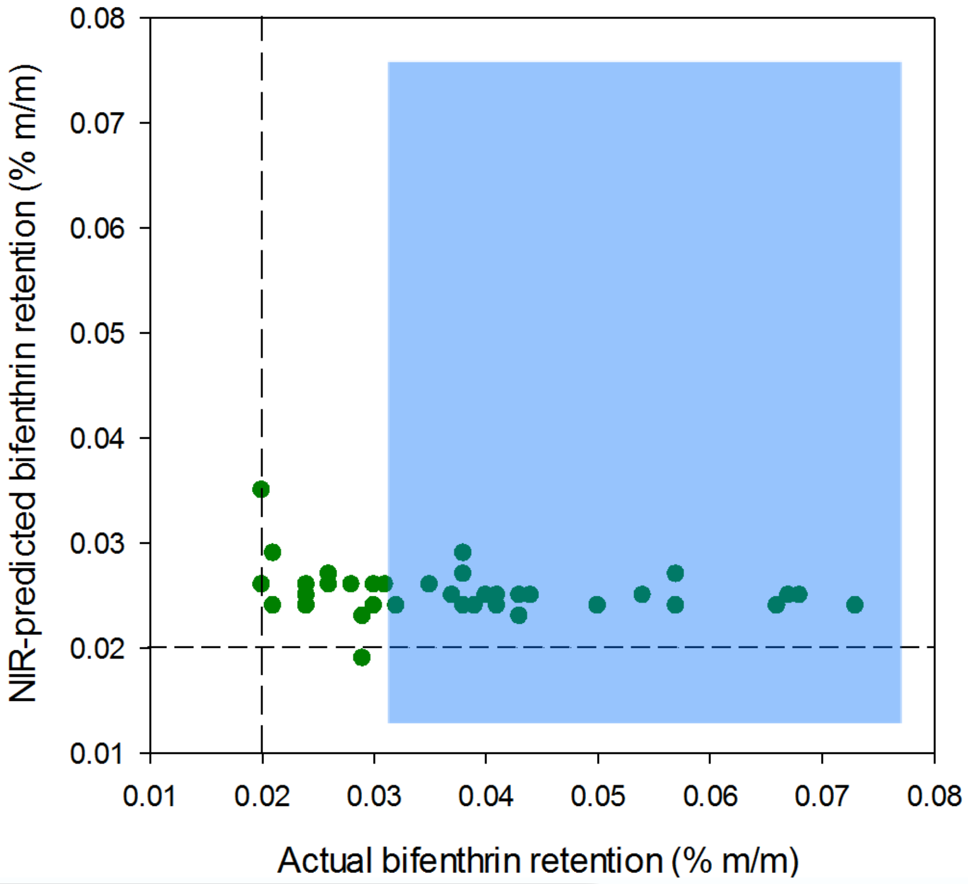
$r^2 = 0.3$



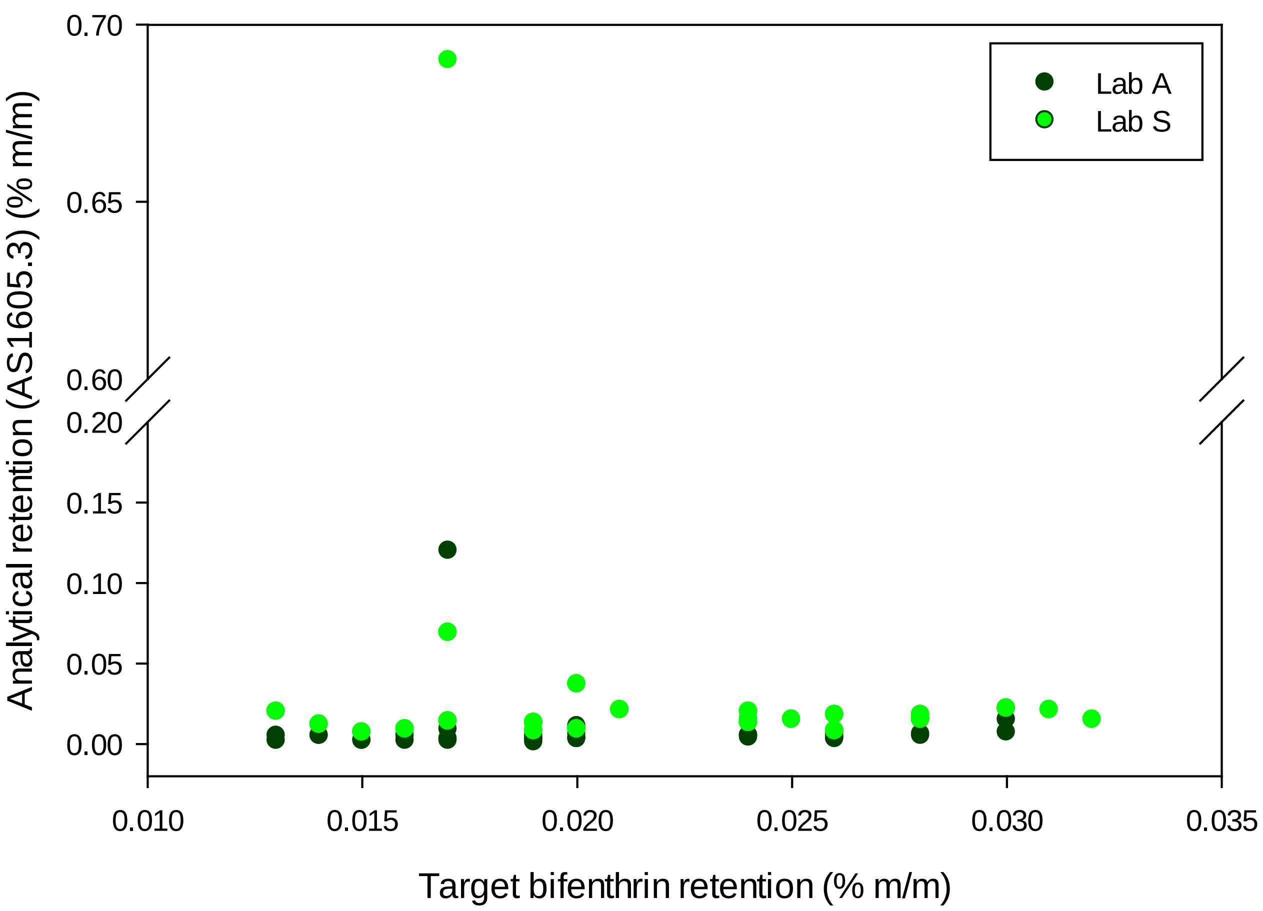
Prediction of bifenthrin retention in run-of-mill samples

- Error in prediction?
    - Range 0.19 – 0.35
    - Std Dev (σ) = 0.002

- Error in actual value?
    - Range 0.020 – 0.074
    - Std Dev (σ) = 0.017



Variability in reference data (bifenthrin)



Potential sources of error

1. Sectioning of analytical subsample. Particularly in the case of bifenthrin where the depth of sample is only 2 mm, there is considerable opportunity for error with analysts reporting that sectioning of subsamples can readily vary between 1.4 and 2.4 mm, representing an error of ±20% (Crimp, pers comm.).

2. Efficiency of active extraction. Extraction of the active from the wood matrix is highly variable and is dependent on both solvent system and extraction type (sonication vs Soxhlet extraction) and has been estimated at between 50 and 80% efficient (Hague, pers comm.; Schoknecht et al. 2008).

3. Stability of calibration standards. Anecdotal evidence suggests that calibration standards for GC or LC are unstable unless stored in dark glass bottles in the dark (Lobb, pers comm.).

Section 3:
Conclusions

Why NIR?

1. Sectioning of analytical subsample. Particularly in the case of bifenthrin where the depth of sample is only 2 mm, there is considerable opportunity for error with analysts reporting that sectioning of subsamples can readily vary between 1.4 and 2.4 mm, representing an error of ±20% (Crimp, pers comm.).

NIR uses a fixed stop on the fibre optic probe to ensure constant depth is measured.

2. Efficiency of active extraction. Extraction of the active from the wood matrix is highly variable and is dependent on both solvent system and extraction type (sonication vs Soxhlet extraction) and has been estimated at between 50 and 80% efficient (Hague, pers comm.; Schoknecht et al. 2008).

NIR does not require extraction. It determines the active in situ.

3. Stability of calibration standards. Anecdotal evidence suggests that calibration standards for GC or LC are unstable unless stored in dark glass bottles in the dark (Lobb, pers comm.).

NIR uses calibration standards that are verified by classical retention analysis.

Conclusions

- NIR can acquire spectra directly from the crosscut surface of wood surfaces for a select depth from surface.
- NIR spectra can be calibrated to predict permethrin and bifenthrin retention.
- As yet it is not reliable for azole retention.

- Total analysis time is the order of minutes.

Conclusions cont’d

- Questions exist around the standard method for determination of bifenthrin, highlighting the potential error in:
  - Sectioning a set depth of envelope for analysis
  - Exhaustive extraction of active
  - Degradation of the calibration standard solutions if not stored correctly

Section 4:
Current and future work

New Calibration using Mill samples

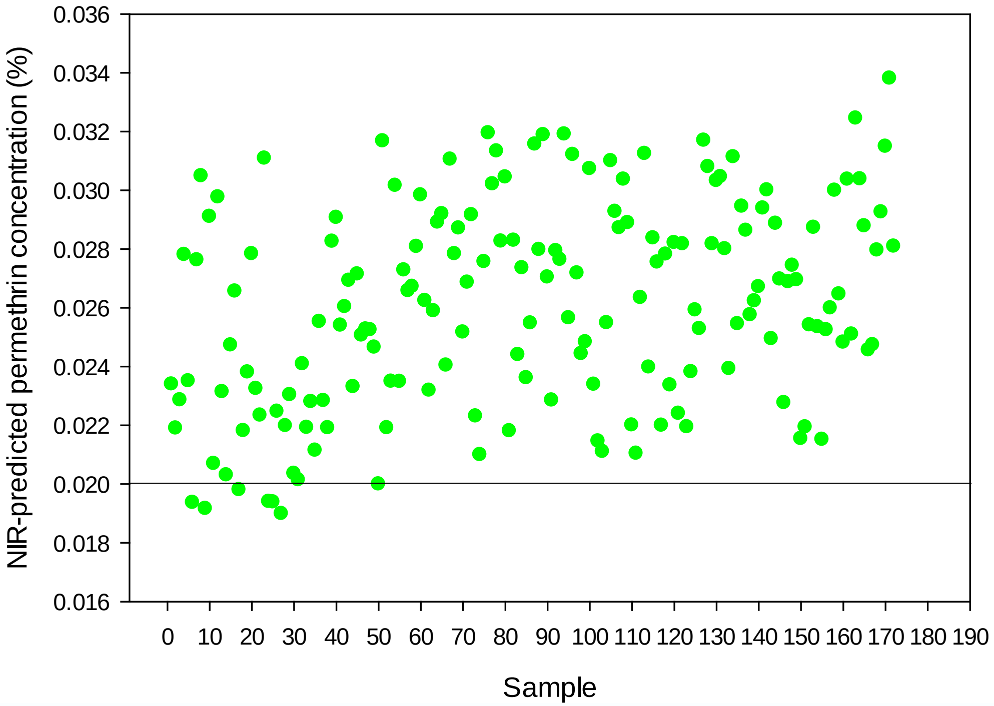
Run-of-mill samples using portable CDI NIR over several days

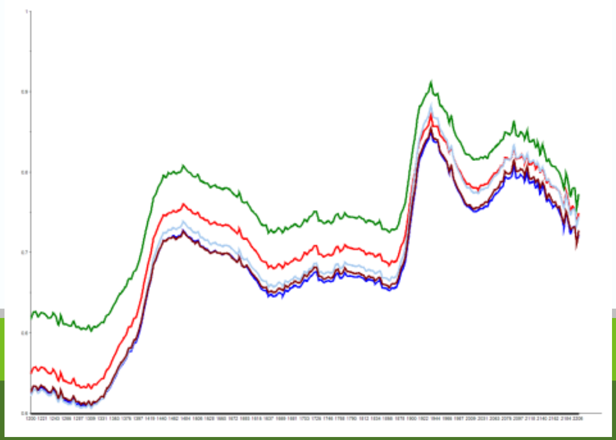
Few initial samples <0.02%

Many samples >0.03%

(costly over treatment)

Problems emerged with noisy spectra in 13 year old portable NIR





Next steps

Consider lab-based instrument for at-line analysis of H2F treated product for quality assurance

Consider use of NIR for treatment formulation analysis

Hardware and software requirements

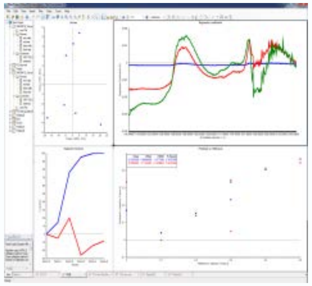
High-end e.g. Bruker Matrix multiplex

- $120,000
- multiple intervention points (treatment tank, final product)

Low-end e.g. Ocean Optics NIRQuest

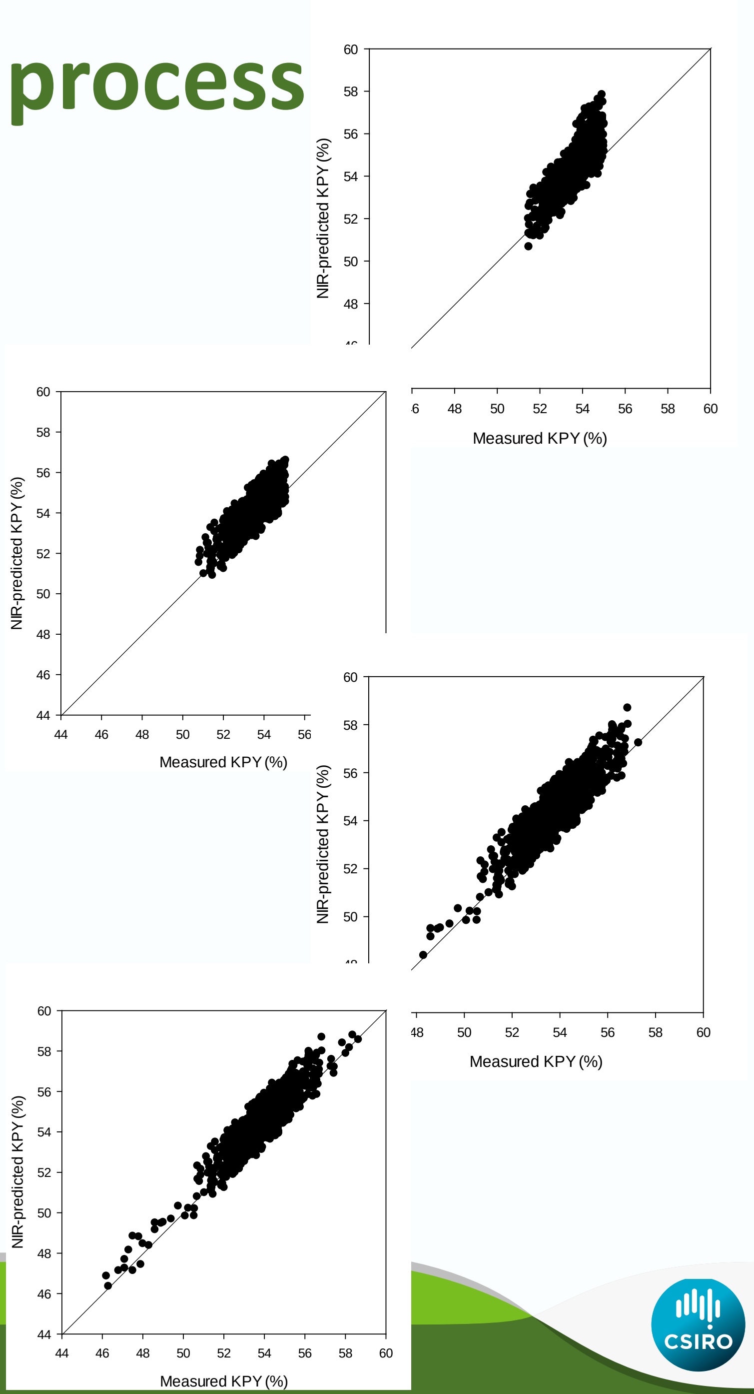
- $35,000
- single intervention point (final product only)

Software e.g. Camo *The Unscrambler*



- $10,000

The calibration/validation process



<u>Iteration</u>

1. Create initial calibration.
2. Use calibration to predict retention of new samples (100 or more)
3. Select 20 samples based on predicted retention – select <u>extreme</u> samples
4. Perform lab QC on those 20 samples to obtain actual retention
5. Create a new retention model
6. Go to Step 2

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Thank you

CSIRO Agriculture Flagship

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