Practical solutions for monitoring Pinot Noir grape and wine phenolics

Bob Dambergs

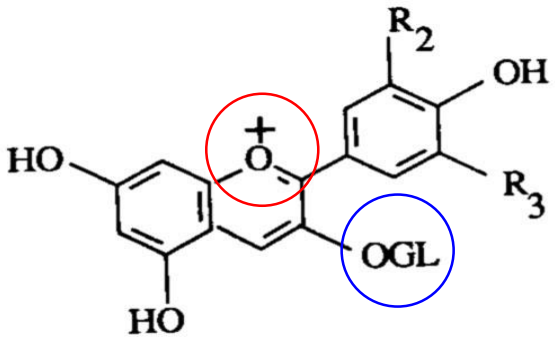
“Perfecting Pinot Noir”

Mornington, 17 June 2015

What defines a red wine?

- Water
- Ethanol
- Organic acids, glycerol
- **Phenolics**
  - tannins, anthocyanins
- Minerals
- Flavour compounds

Anthocyanin facts



Anthocyanins normally have a glucose molecule attached via a glycosidic bond, making them more stable….. “GG”

Anthocyanins also exist as acetyl and courmaryl derivatives which are even more stable

At very low pH (<2) all anthocyanins have a positive charge and are coloured, at wine pH only a small proportion are charged (*Somers assay)

If SO_2 binds to anthocyanins they are colourless (*Somers assay)

React with tannin to form stable pigments

Some tannin facts

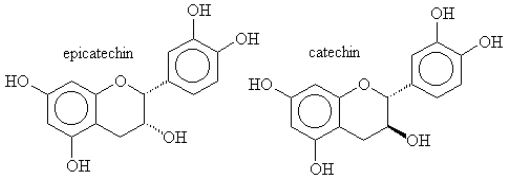
Pigmented tannin colour is less sensitive to pH (*Somers assay)

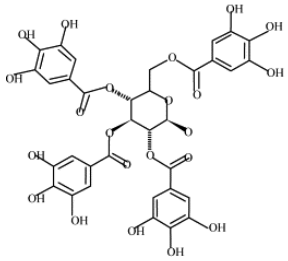
Pigmented tannin colour is not bleached by SO_2
"Non-bleachable pigments" (*Somers assay)

Tannins bind to proteins, to produce astringency, drying chalky characters when they bind to saliva linings of the mouth ….their sensory effect is "tactile" rather than "taste"

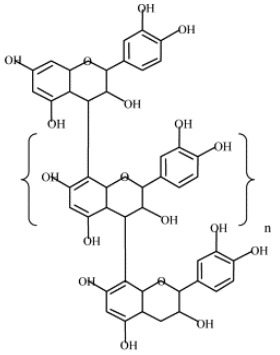
Seeds tannins vary in structure to skin tannin so their chemical reactivity and sensory properties vary

Seed tannin is more difficult to extract than skin tannin



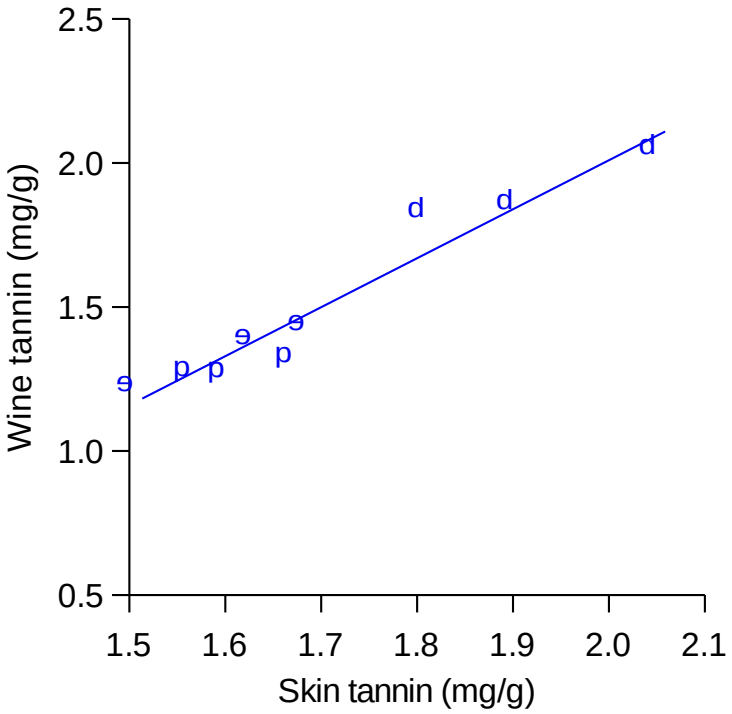


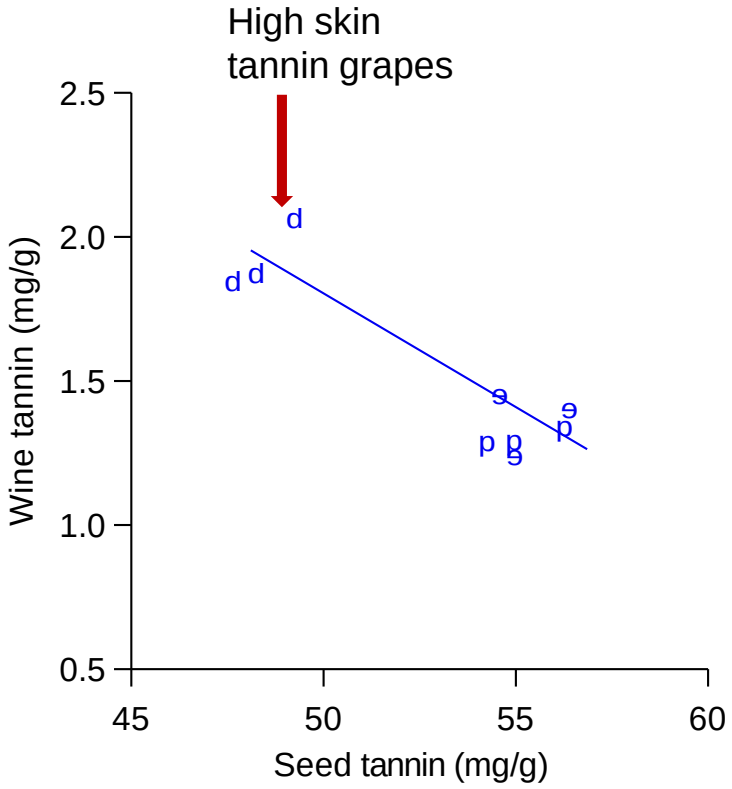
Hydrolysable tannin



Condensed tannin

High seed tannin does not mean high wine tannin



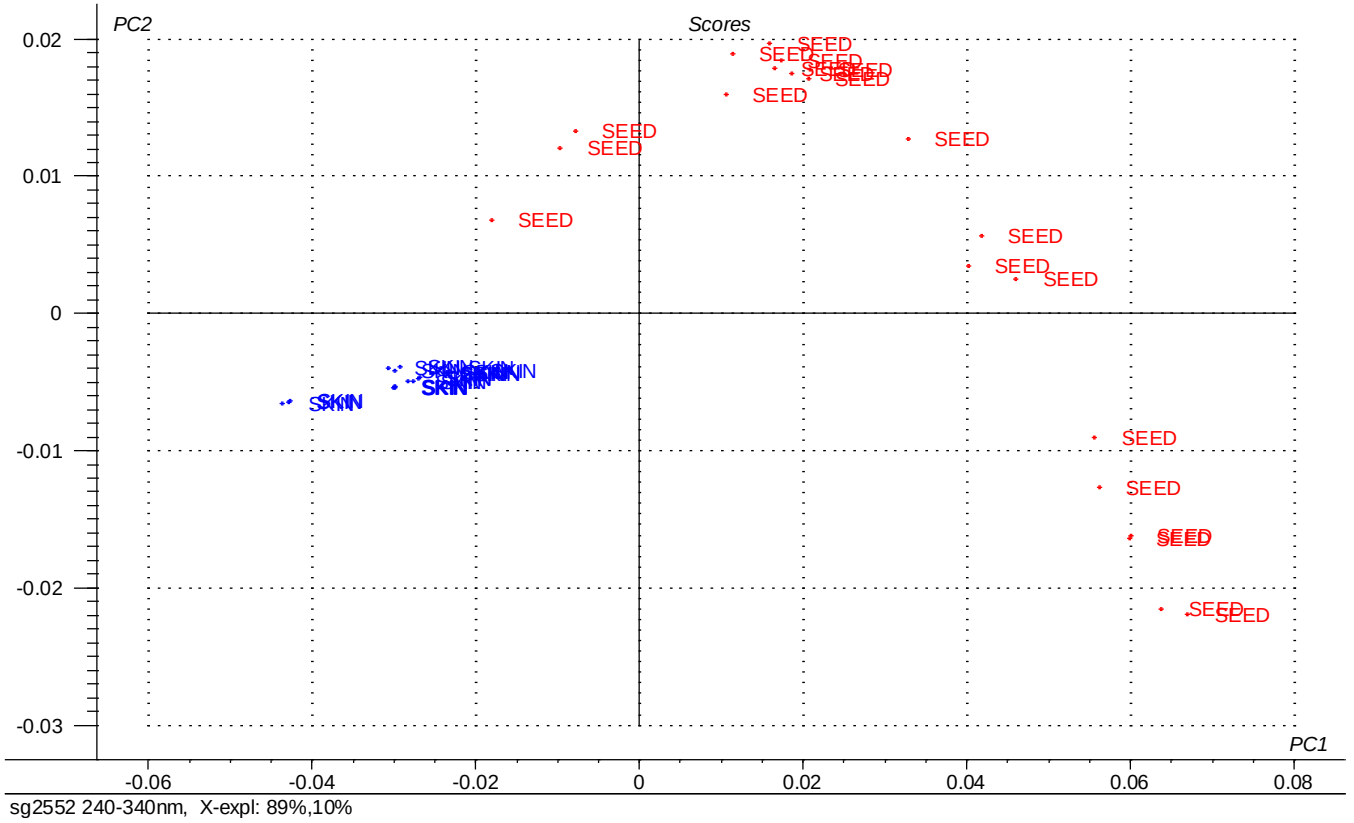


Shiraz grapes

Renata Ristic
University of Adelaide

Seed tannin extraction is more variable than skin tannin

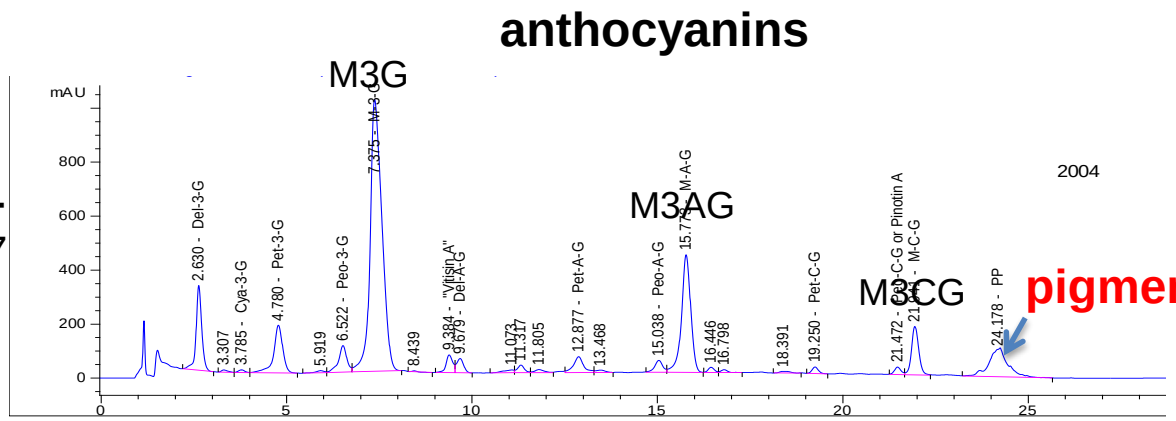
Cabernet Sauvignon



Helen Holt AWRI

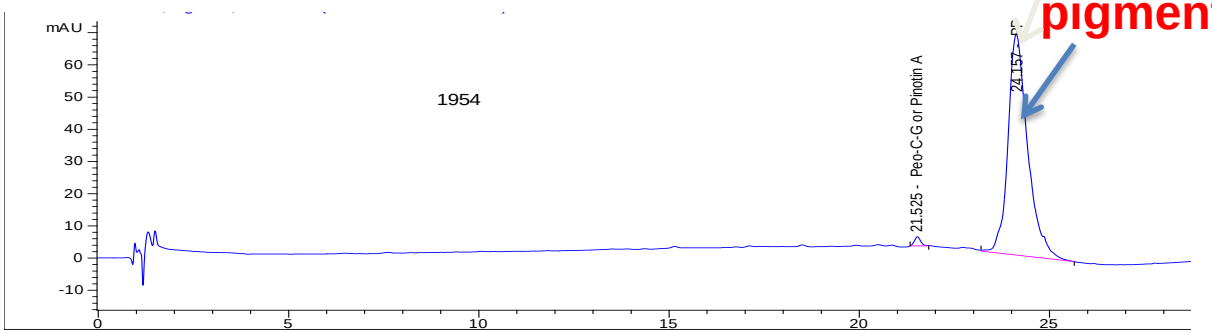
No free anthocyanins in old wines- pigmented tannins dominate colour

Vintage 2004
col dens 11.17
hue 0.70



pigmented tannins

Vintage 1954
col dens 5.50
hue 1.32



pigmented tannins

The physics of gravitation has "Einstein's equation for general relativity"

The chemistry of wine colour has…

…the "Dambergs-Herderich equation"

[PP] = 0.06 [M3G] + 0.04 [T] - 2.88

R^2 = 0.92

PP: pigmented polymers

M3G: malvidin 3-glucoside

T: tannins

Can we compensate for low anthocyanins in Pinot noir by boosting soluble tannin to promote pigmented tannin formation?

Which wine compounds vary in concentration the most?

Alcohol 20%

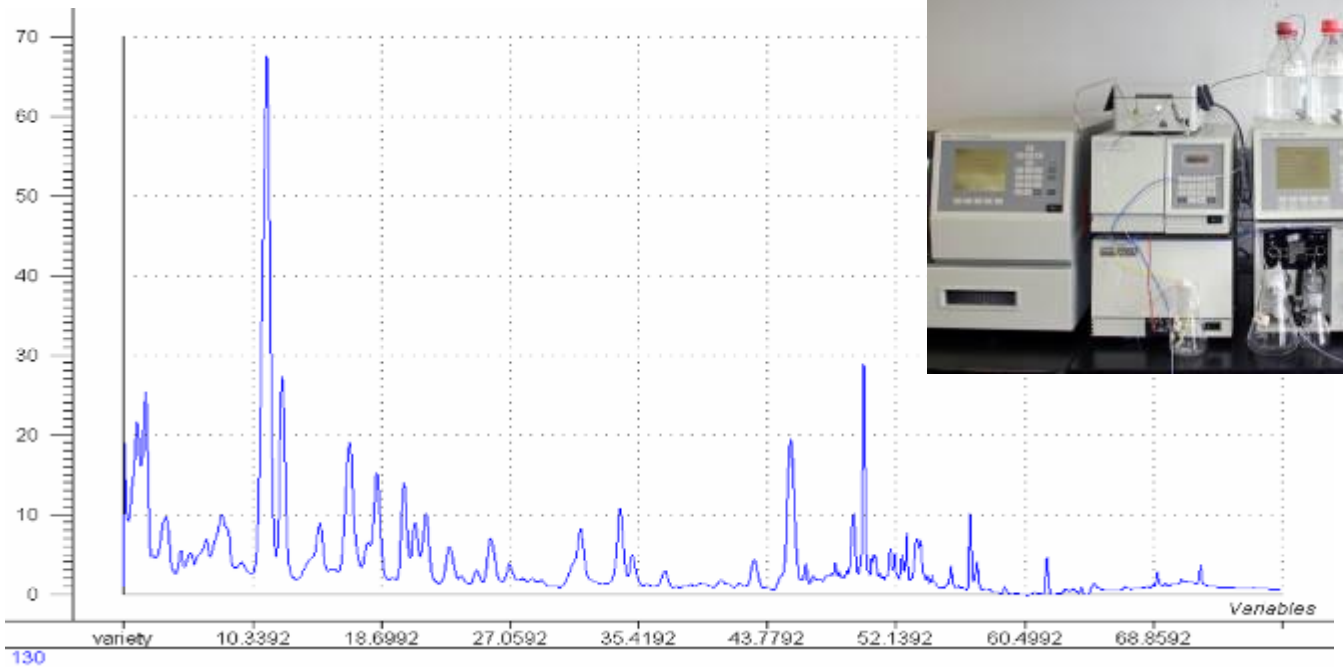
Acidity 20%

Tannin **150%**

We routinely measure alcohol, acid *etc* and have specifications…..but are we measuring tannin?

Measurement of wine tannin and anthocyanin

- HPLC can be used to separate and quantify individual phenolic compounds



BUT….complex, expensive and slow

The Somers measurements: Colour expression of free anthocyanins is sensitive to pH and SO_2

Malvidin-3-glucoside

pH<1.5 pH 3.7 pH 3.7+SO_2

- Polymerised pigments (PP) are less affected by pH and SO_2
- Differential sensitivity of anthocyanins and PP forms the basis of the “Somers measurements”
- Use a combination of absorbance at 420 and 520nm with and without SO_2 and low pH treatment to estimate anthocyanins and PP plus colour density and hue

“Bob’s modified Somers analysis”

Samples are diluted in a wine-like buffer with

— with acetaldehyde added

— with high SO_2 added

(read at 420 and 520 nm)

- provides control of pH, ethanol to minimise their effects on colour
- samples can be read in 10 mm cuvettes instead of 1 mm
- can be adapted for use in a plate reader spectrophotometer

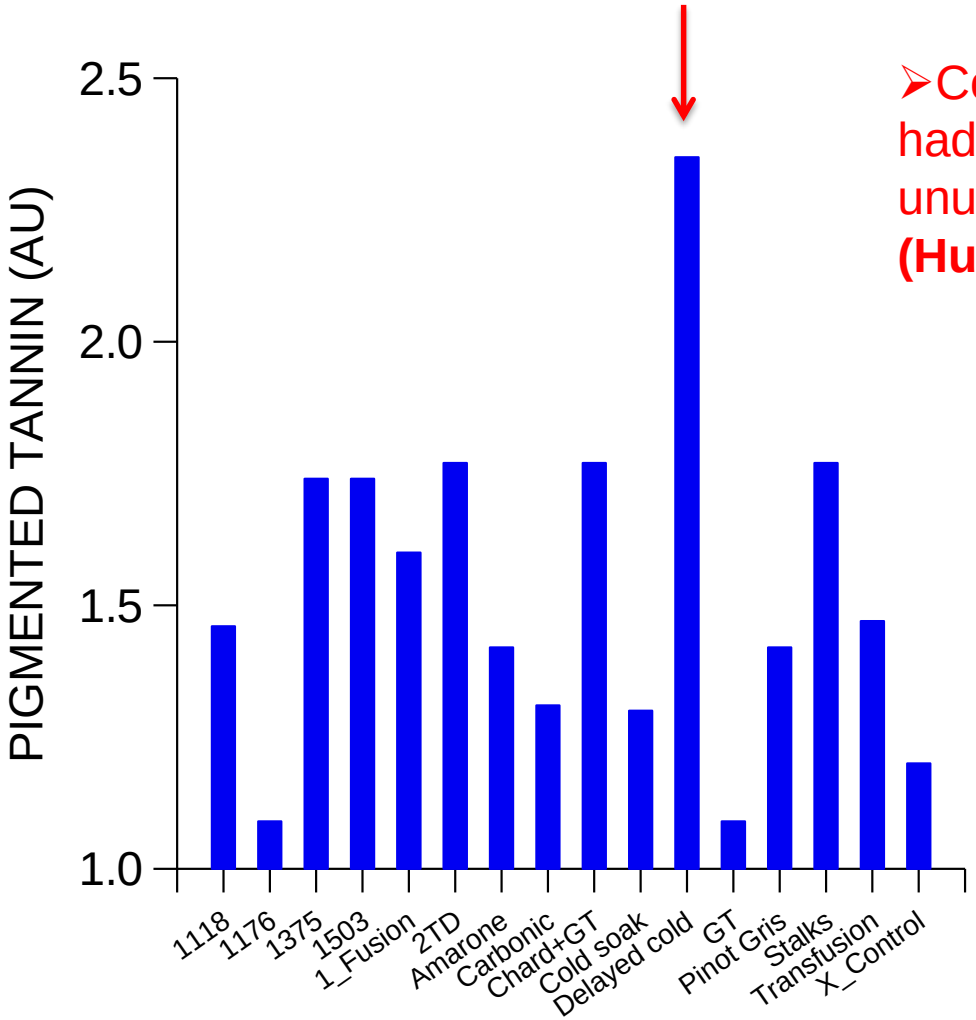
Samples diluted in 1M HCl

(read at 280 and 520 nm)

Phenolics 101: Modified Somers Analysis

- **Total phenolics**
  - Anything that absorbs UV at 280 nm
  - All forms of tannin, anthocyanins, phenolic acids, flavonols etc
- **Hue**
  - The quality of the colour
  - Young wines have purple hues, low hue values
  - Hue increases with age as wines start to develop brown tones
- **Hue SO2**
  - Hue in the presence of high SO2 ie hue of the pigmented polymers
- **Colour Density**
  - Intensity of the colour
- **Total Pigment**
  - Free anthocyanin and pigmented tannin
  - Increases while wine is on skins then decreases gradually with age
- **Free anthocyanin**
  - Increases quickly while on skins (freely soluble)
  - Decreases quickly off skins (after 5 years all consumed)
- **Pigmented tannin** - " pigmented polymers", "non-bleachable pigment"
  - Formation starts during fermentation
  - Gradual increase after wines taken off skins and during maturation
  - Formation promoted by yeast metabolites
  - Formation promoted by micro-oxidation and barrel maturation

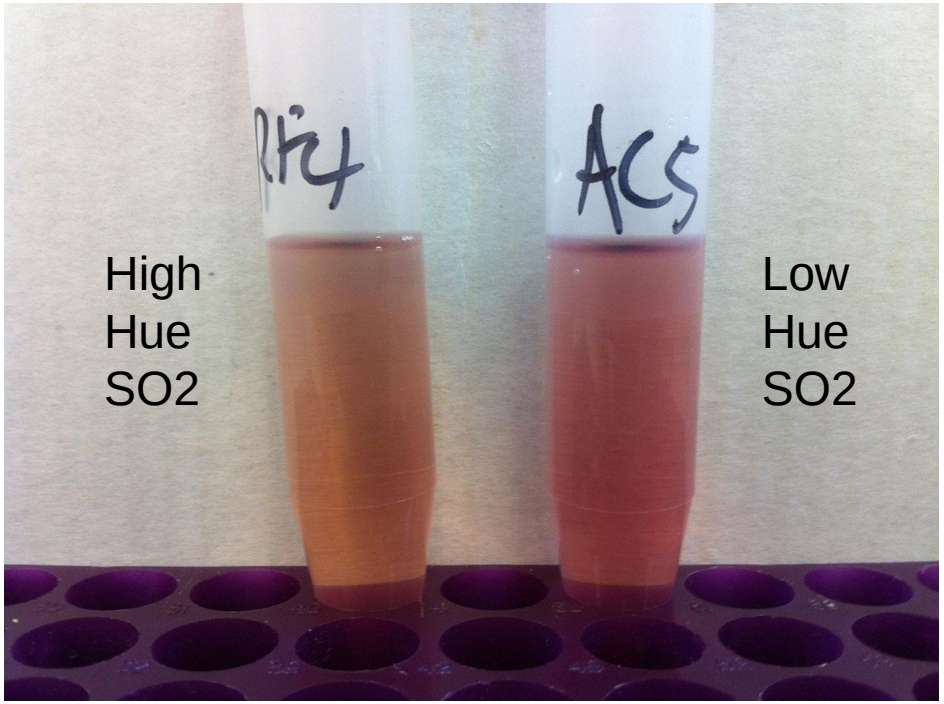
Taming pigmented tannin



➢Cold soak/delayed malo had highest but it was an unusual plummy colour **(Hue_SO_2 !!)**

ICCS Workshop 2-
"Taming the Pinot noir terroir"
with Nick Glaetzer and Jenny Bellon

Hue SO2



- Influenced by yeast strain?
- Influenced by maceration method?
- Influenced by high skin tannin plus high anthocyanin?

Correlation matrix – Somers & HPLC

	Col_Den	Anth_Som	NBP	Phen	M3G	PP
Col. Density	1.00					
Antho_Somers	0.53	1.00				
NBP	0.82	0.03	1.00			
Phenolics	0.87	0.47	0.77	1.00		
M3G_HPLC	0.44	0.97	-0.04	0.34	1.00	
PP_HPLC	0.87	0.17	0.94	0.76	0.10	1.00
Tannin_HPLC	0.24	-0.39	0.58	0.32	-0.39	0.54

KISS

Somers total anthocyanins can replace HPLC anthocyanins
Non bleachable pigment (A_{520} in high $SO_{2)}$ can replace HPLC pigmented polymers

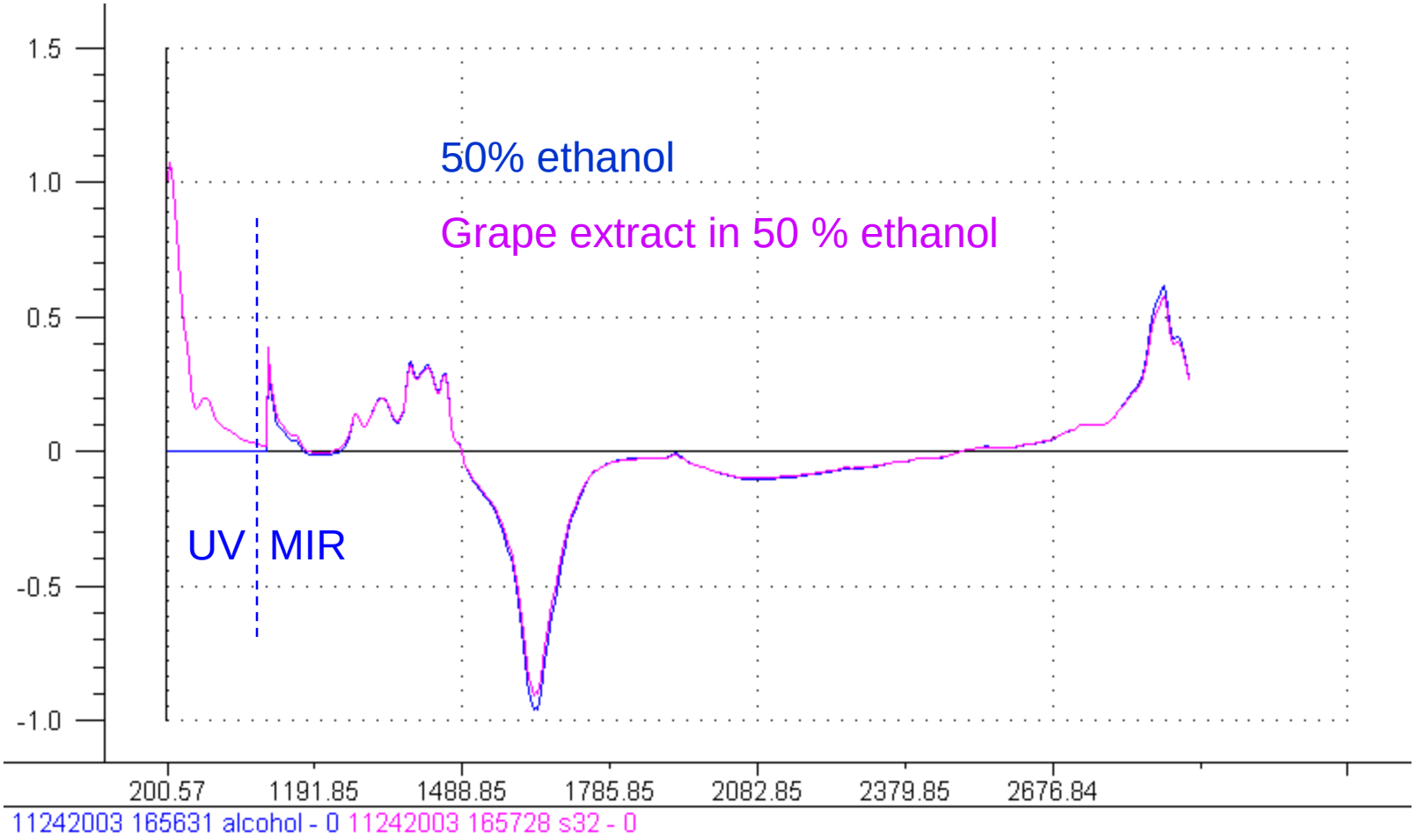
(and new rapid tannin methods can replace HPLC tannin?)

A roadblock to uptake of tannin assays

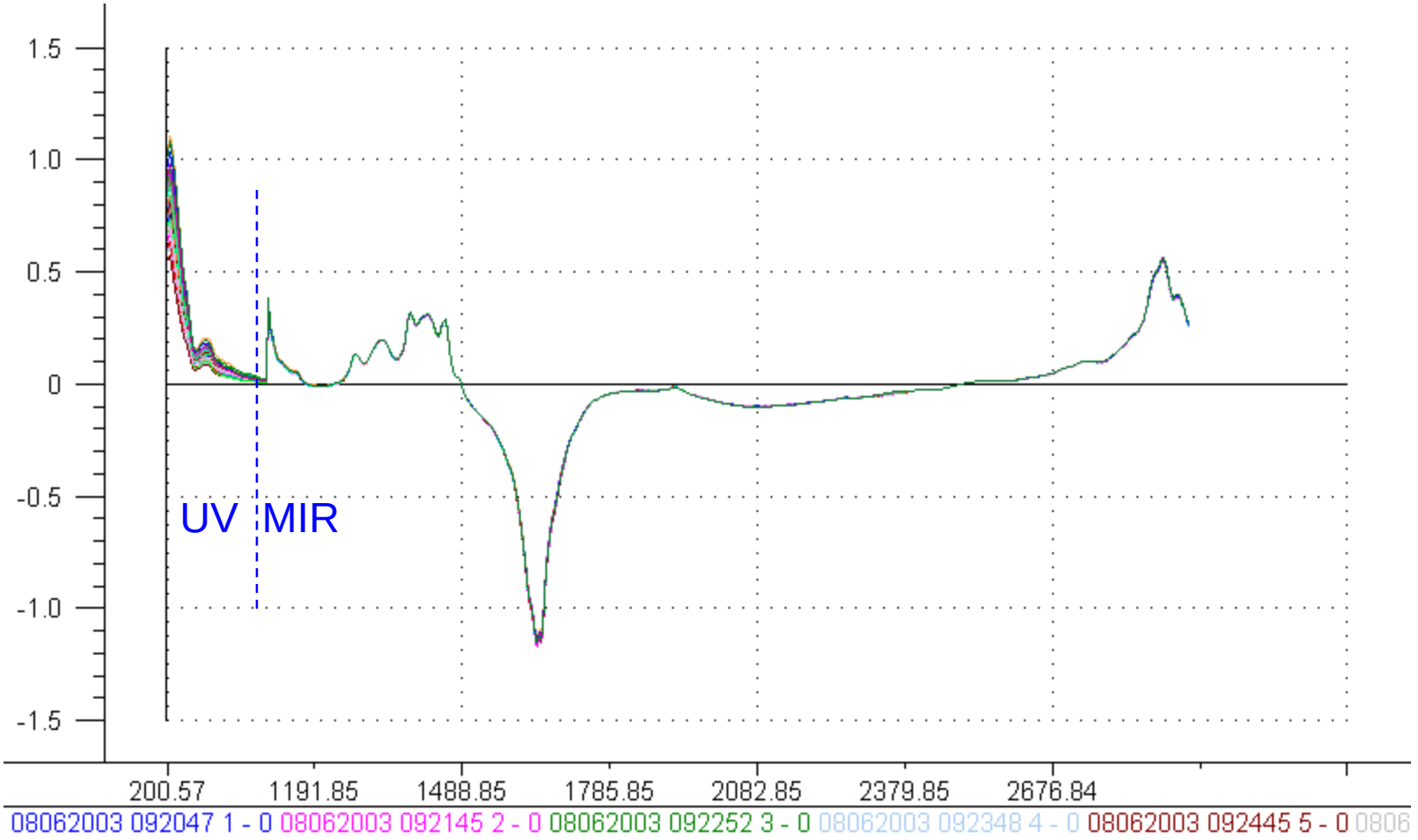
SOLUTION?

Use existing equipment e.g. standard UV-Vis spectrophotometer

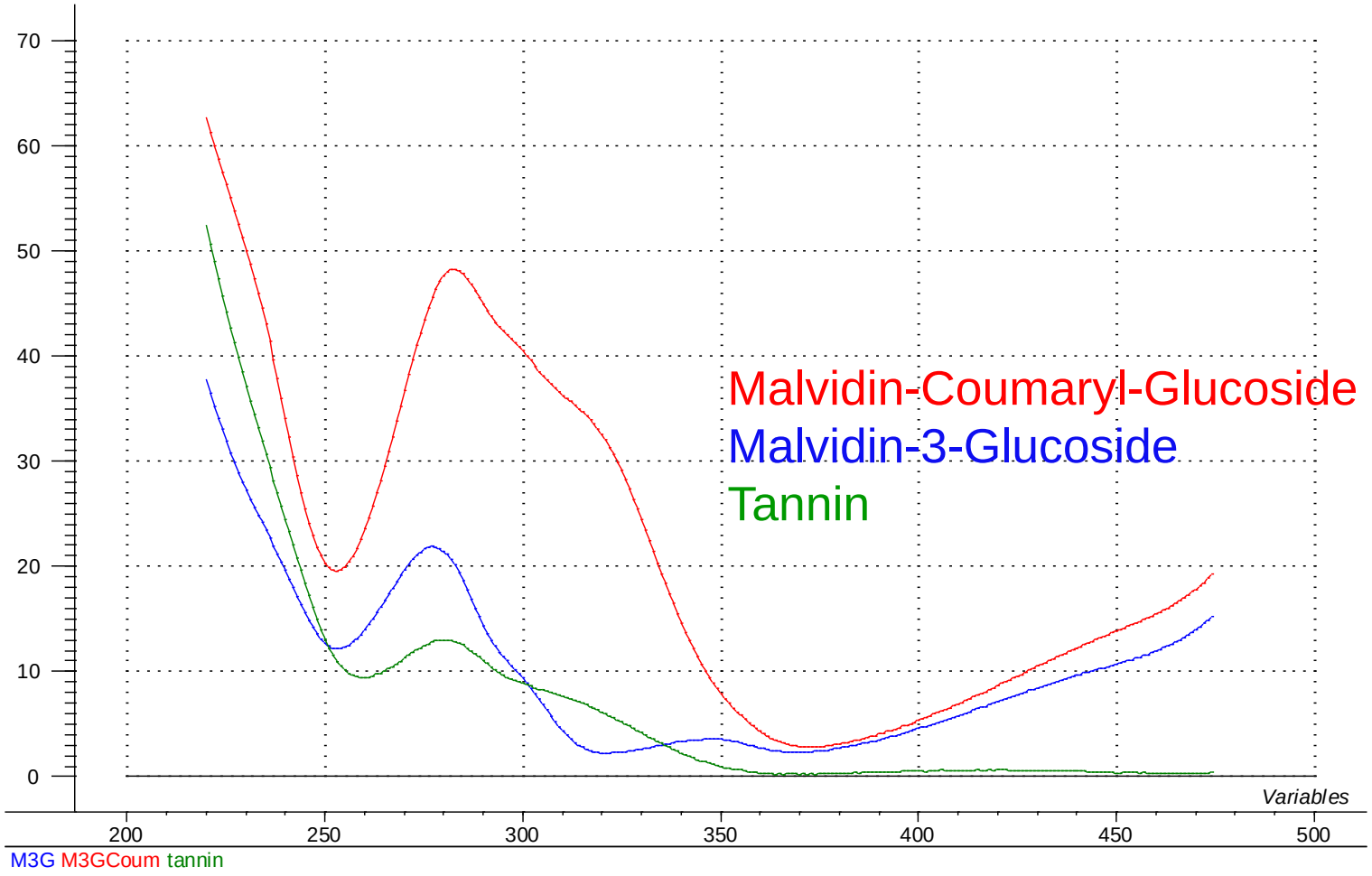
The phenolic-free wine matrix has no UV spectral signal



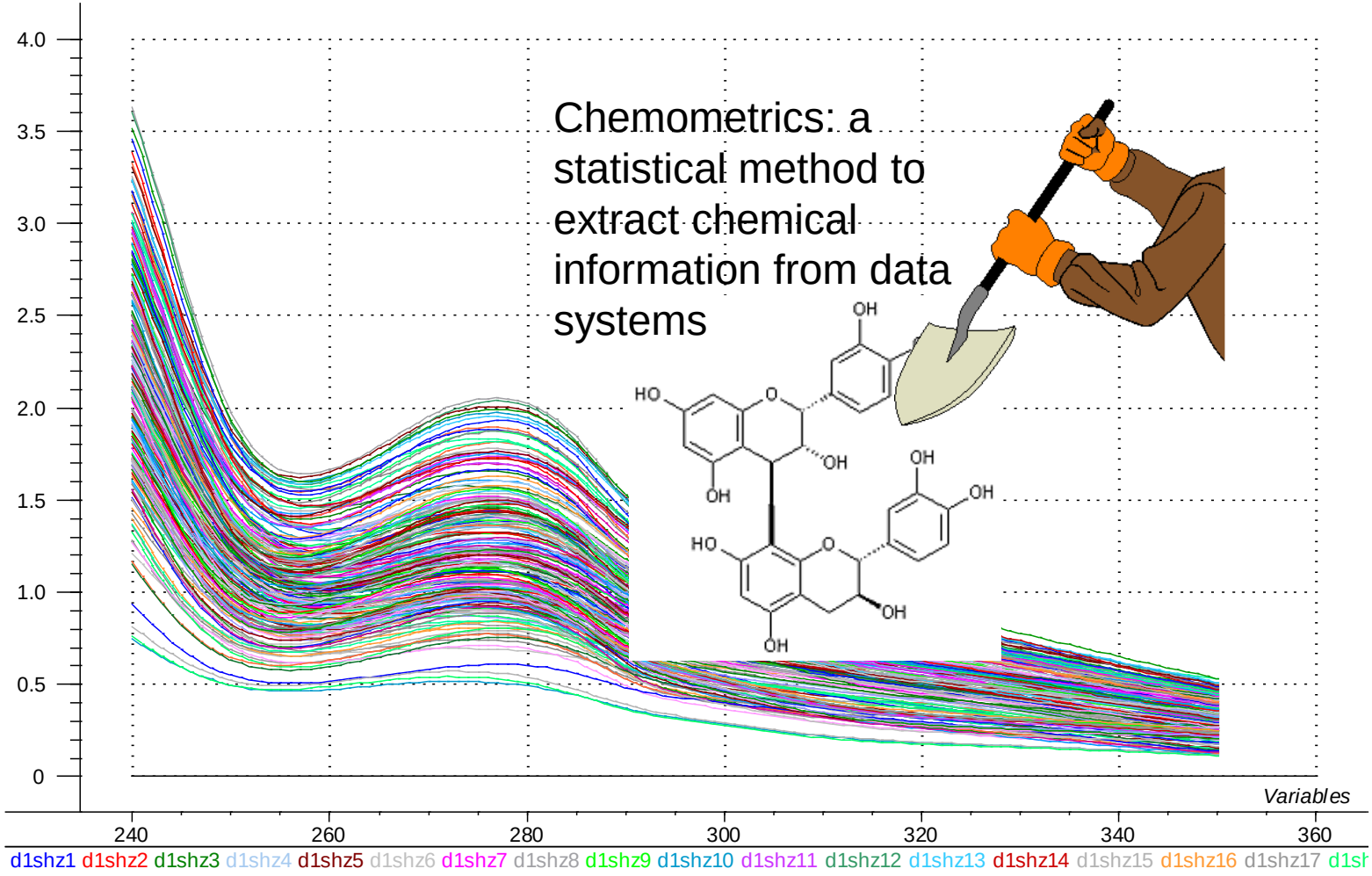
High between-sample variation in UV region of wine spectra



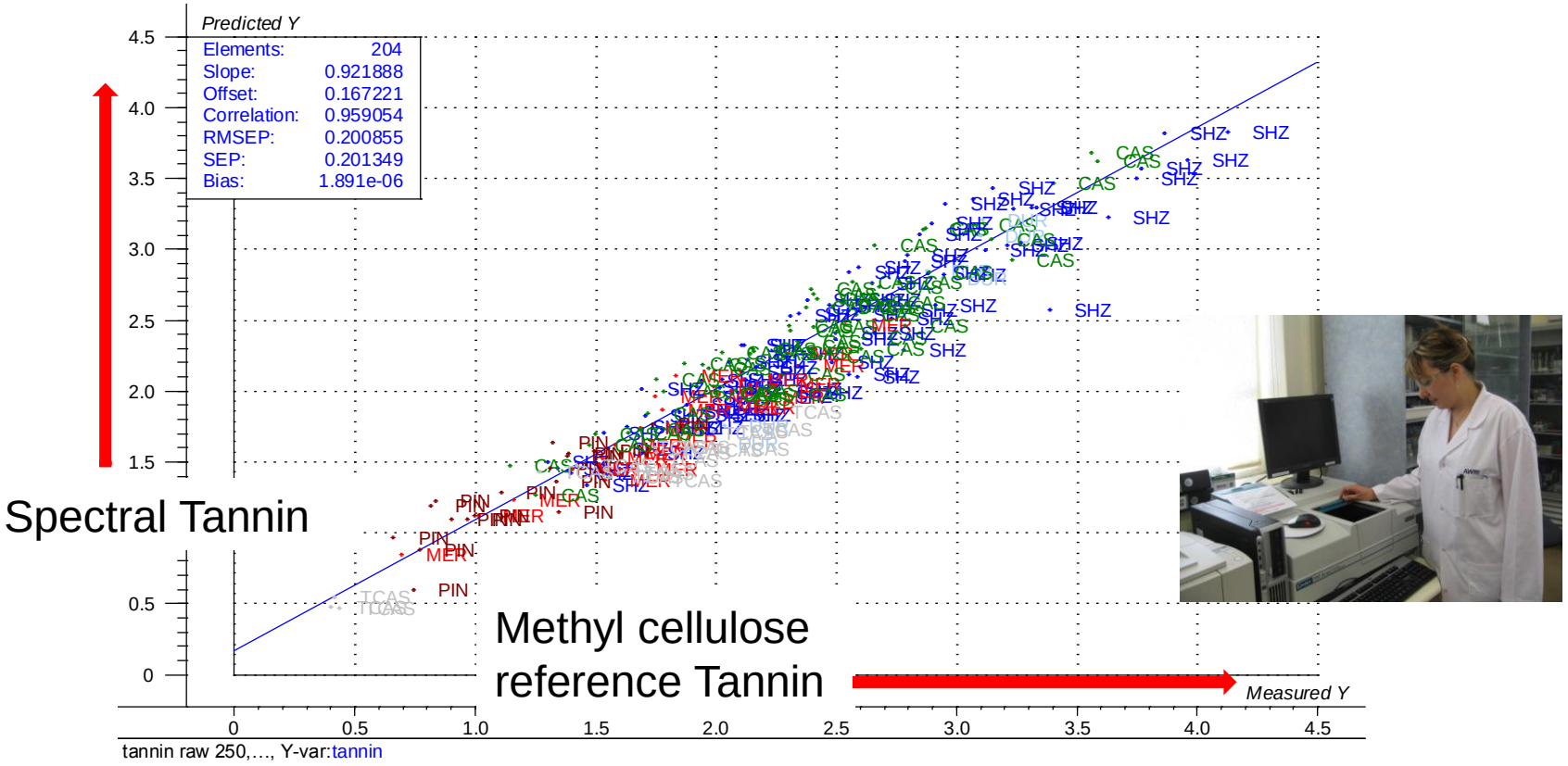
Tannin and anthocyanins have distinct UV spectra



The spectral fingerprint of tannin is buried in wine UV spectra



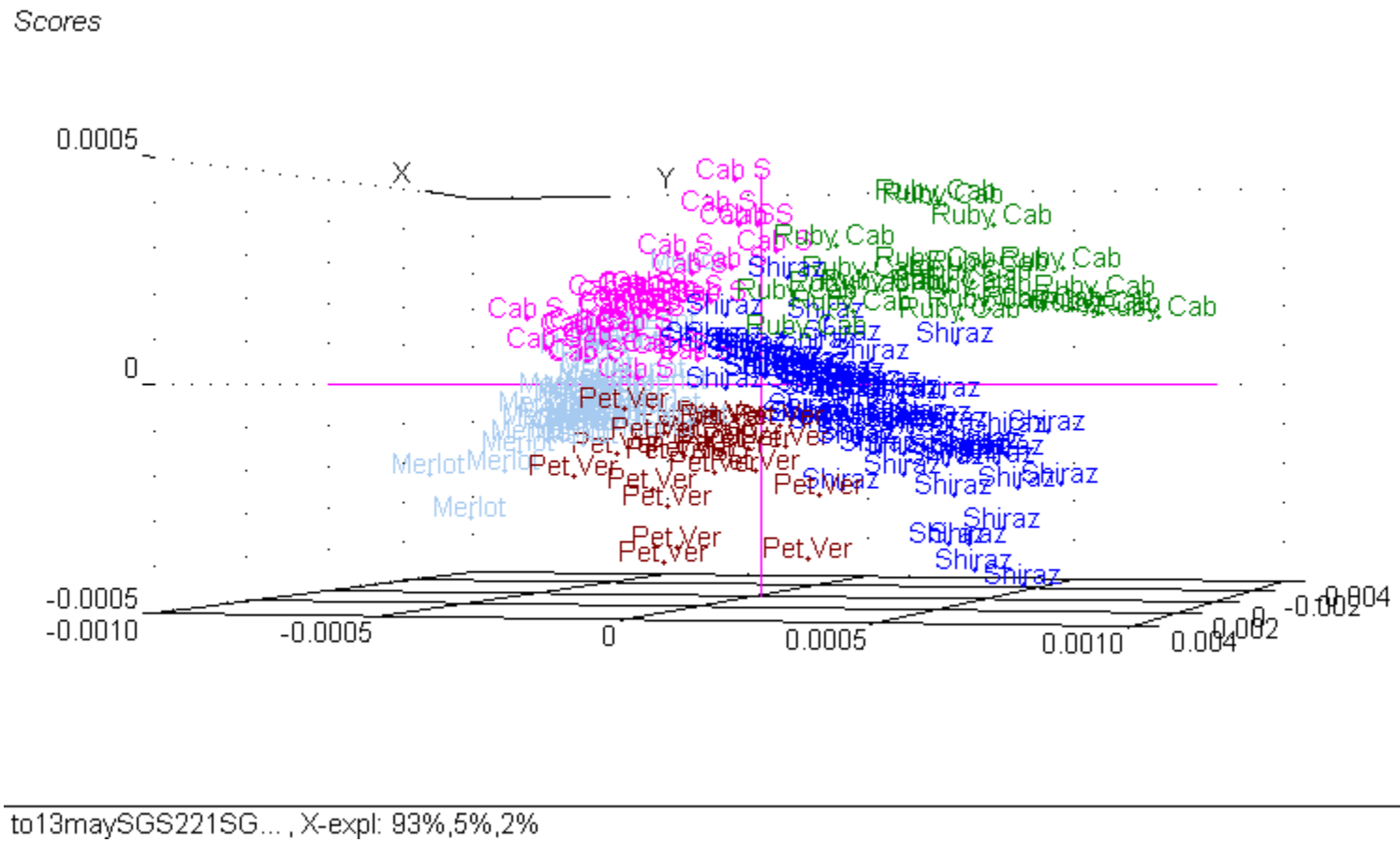
Multiple Linear Regression (MLR) calibration to calculate tannin with 5 UV wavelengths



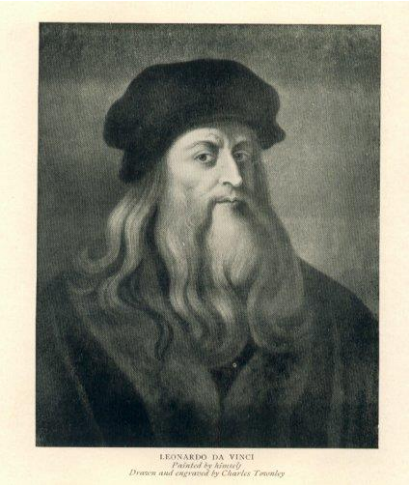
$R^2 = 0.92$

Same standard error as reference method: 0.2 g/L

An added bonus
– varietal discrimination with UV

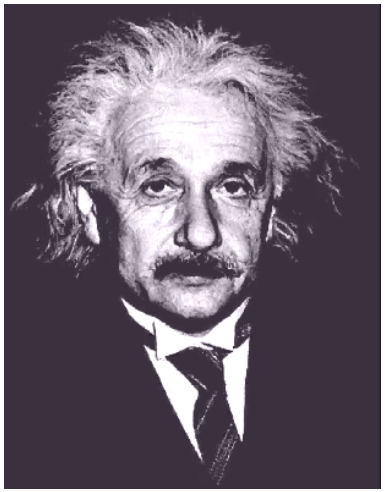


Simplicity



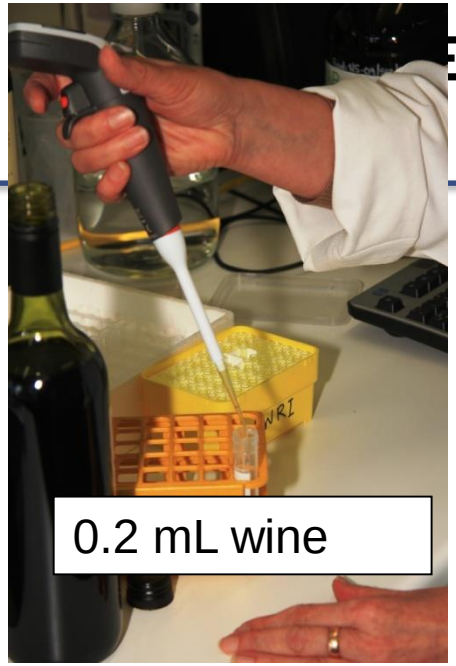
“Simplicity is the ultimate sophistication.”

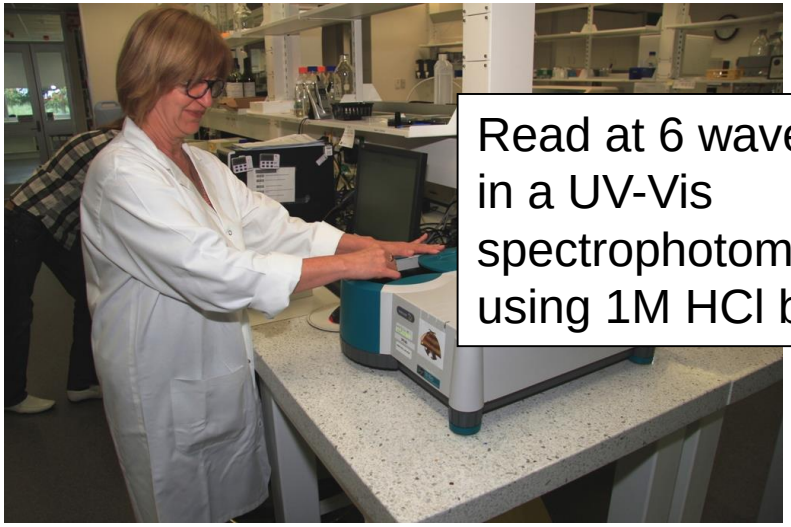
Leonardo da Vinci



“Most of the fundamental ideas of science are essentially simple……..”

Albert Einstein





Calculate

- Tannin
- Total phenolics
- Total Pigment

Additional calculations

- Requires an extra sample prep (dilution in high SO_2 buffer)
- Free anthocyanin
- Pigmented tannin

Simplified wine analysis

Modified Somers and tannin analysis

- Anthocyanin*
- Total pigment*
- Total phenolics*
- Pigmented tannin*
- Total tannin*

**can be analysed with the AWRI Tannin Portal*

- Colour density#
- Hue#

#requires a dilution in wine-like buffer + acetaldehyde

Phenolics 101+1

- **Tannin**
  - **Total tannin i.e. pigmented and non-pigmented**
  - **Increases slowly while wine is on skins (extraction needs alcohol and heat)**
  - **Skin tannin is more readily extracted than seed tannin**
  - **Structure changes with aging**

- **Total phenolics**
  - Anything that absorbs UV at 280 nm
  - All forms of tannin, anthocyanins, phenolic acids, flavonols etc
- **Hue**
  - The quality of the colour
  - Young wines have purple hues, low hue values
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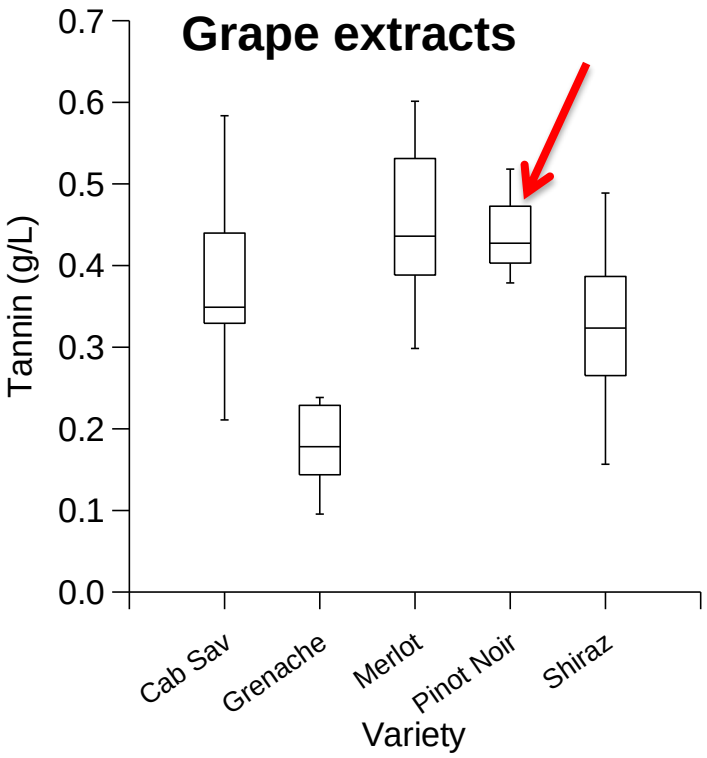
The problem with Pinot phenolics

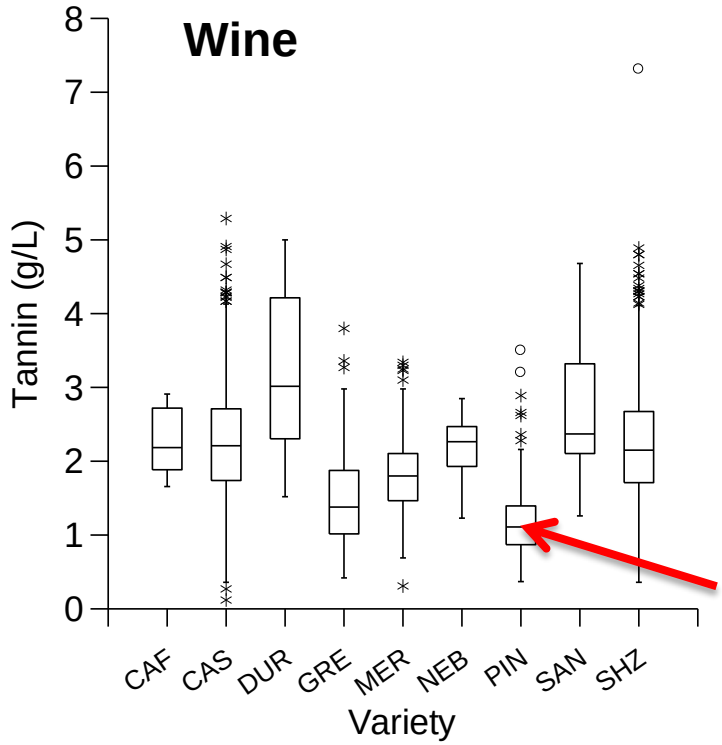
Low total anthocyanins

No acylated or coumarylated anthocyanins

Grapes have high tannin but it's mostly seed tannin

Wines have relatively low tannin and colour





Fixing Pinot noir phenolics with winemaking

…more later from the T3 team (Tasmanian Tannin Trio)

- Anna Carew
- Angela Sparrow
- Bob Dambergs

Acknowledgments

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