Critical analyses for monitoring authenticity - investigating ATR-FT-IR as a tool for the authentication of South African wines.

Dominique Plaatjes, Francois Van Jaarsveld, Wessel du Toit, Karen Freitag, Valmary van Breda, Marieta van der Rijst, Maxine Newman, Craig Paulsen

SASEV 44th Conference

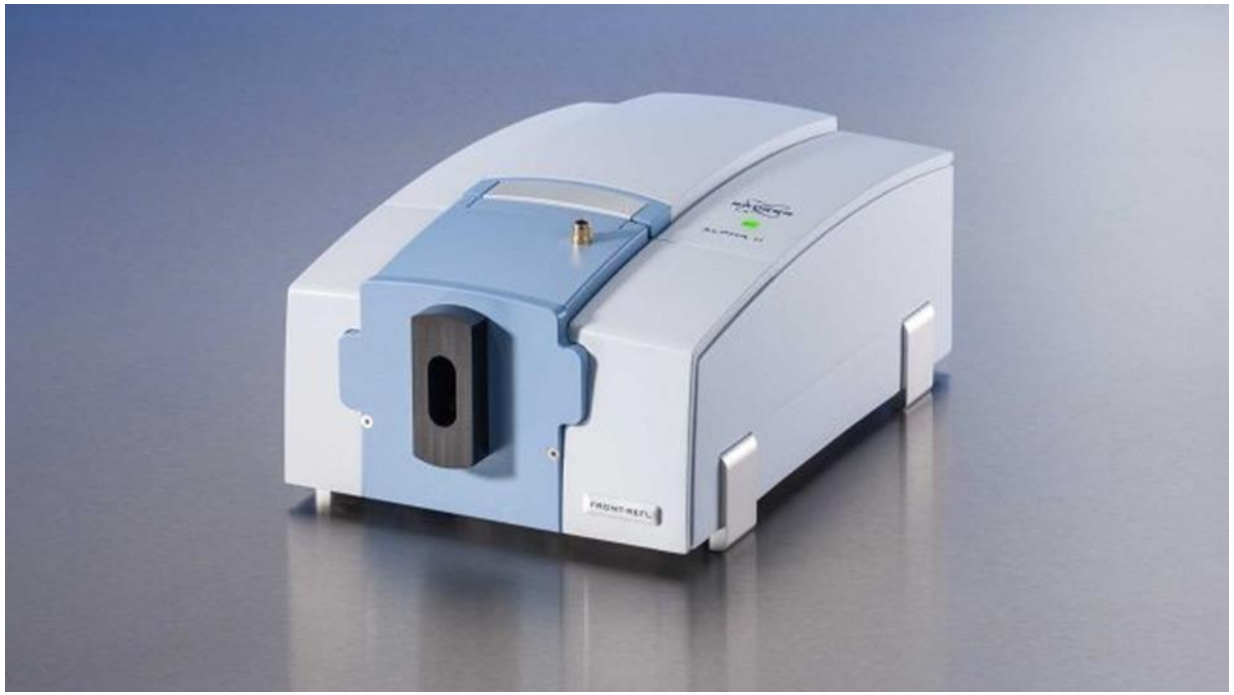
Photo by Stefan Els

Background and introduction

- Ensuring the quality and integrity of wine is a key priority for producers and consumers alike.
- Wine offers rich diversity, and authenticity helps highlight its unique character and origin.
- To support consumer confidence and celebrate genuine products, we make of use the process of authentication.
- Authentication can be done through a variety of classical and chromatographic methods, as well as through various spectroscopic techniques.
- Many of these methods are however not cost effective, and as a result there is an interest in the development of more cost effective methods, to authenticate wine, with a particular interest in export wines.

introduction

- ATR-FT-IR is a type of infrared spectroscopy that typically makes use of mid-infrared spectrum.
- It has previously been used in traceability and authenticity studies.
- It is a more practical method than other analytical techniques.



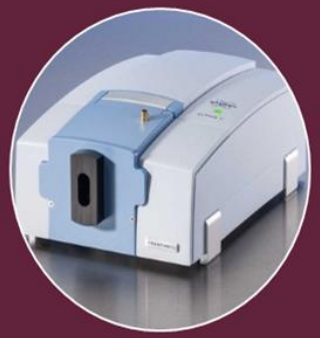
Aim

The aim of this project is to investigate the effectiveness of Attenuated Total reflectance Fourier transform infrared spectroscopy (ATR FT-IR) as a cost-effective screening tool for the authentication of South African wines. The project will look to confirm geographical origin, varietal identification, and vintage of South African wines to see if any distinctions can be drawn. Furthermore the project will look to determine whether microvinified and commercial, and white and red wine models can be used interchangeably.

Objectives

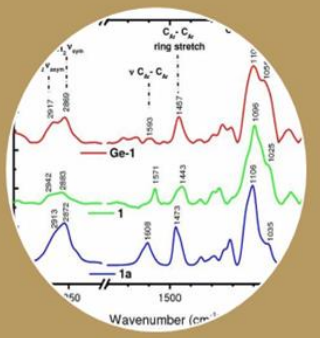
Objective 1

Microvinification of wines from various winemaking regions of South Africa.



Objective 2

Chemical and spectral analysis of microvinified, commercial and intentionally wines using ATR FT-IR analysis on the Alpha II Wine Analyzer.



Objective 3

Confirm the use of vibrational spectroscopies such as ATR-FT-IR combined with chemometric methods for authentication of South African wines.

Methodology

Objective 1:

- Wines (100 p.a.) from various wine production regions of 8 different cultivars were microvinified. According to a specific sampling plan.

- Microvinification was done according to EC regulation N. 2729/2000 and the winemaking protocols of Nietvoorbij Experimental cellar.

- Merlot must was intentionally modified through dilution and chaptalization, this wine was made in a rose style.

Objective 2:

- Alpha II: Rapid analysis of finished wines, using FT-IR technology.

- Analysis was conducted by manually injecting 10ml of wine. Each sample was run in triplicate.

- A calibration was built to quantify 53 additional compounds (as well as the 14 original quantifiable compounds).

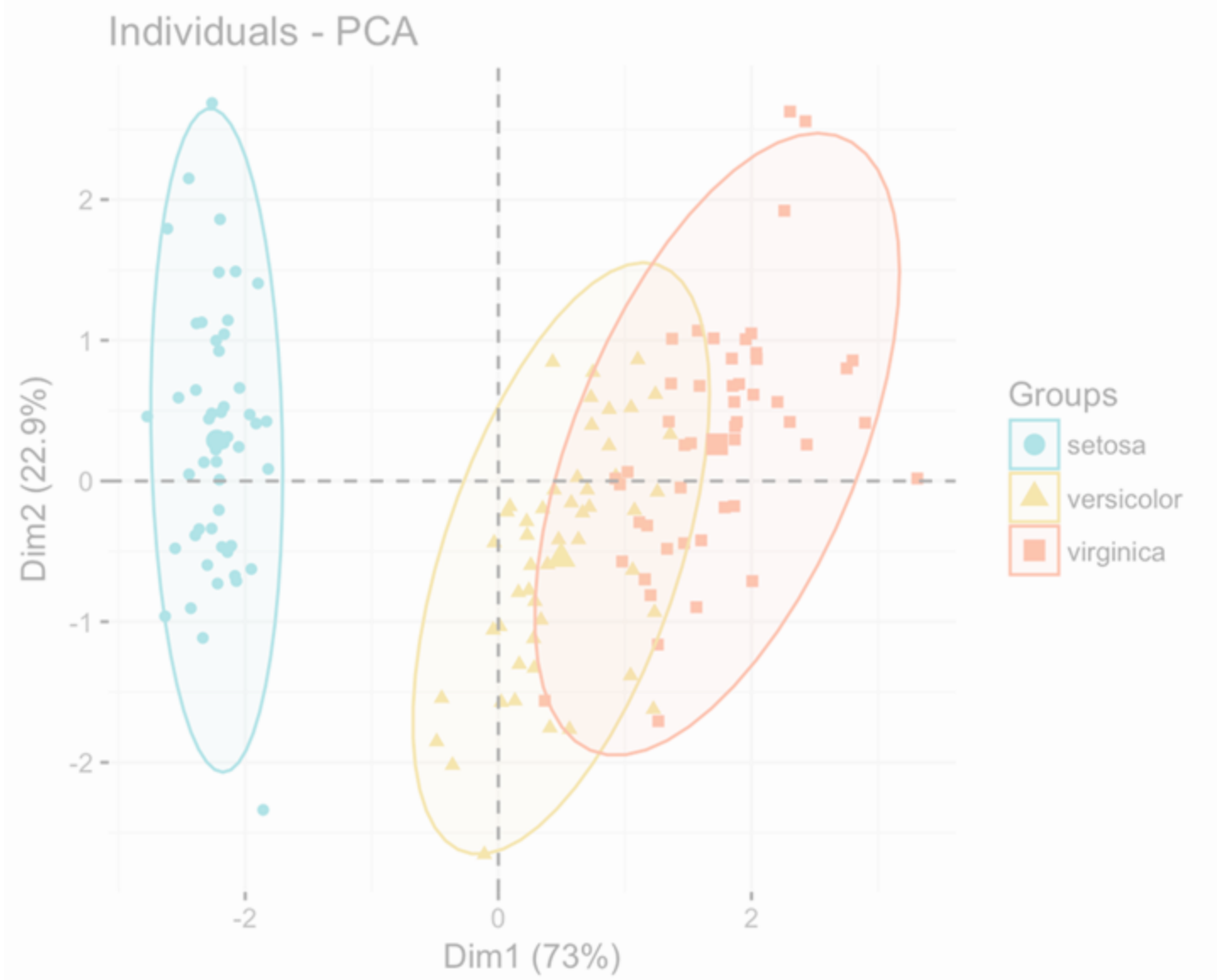
- The calibration data was based off NMR data related to the same wines being analyzed.

Objective 3:
- The mean value of each sample triplicate were used to conduct ANOVA to determine significant compounds.

- PCA, DA and PLS-DA were conducted on mean values to determine whether distinctions can be drawn based off variety, vintage and geographical origin. DA is done using model selection (done using XL-stat).

- Results analysed and reported on.

Quantitative Results



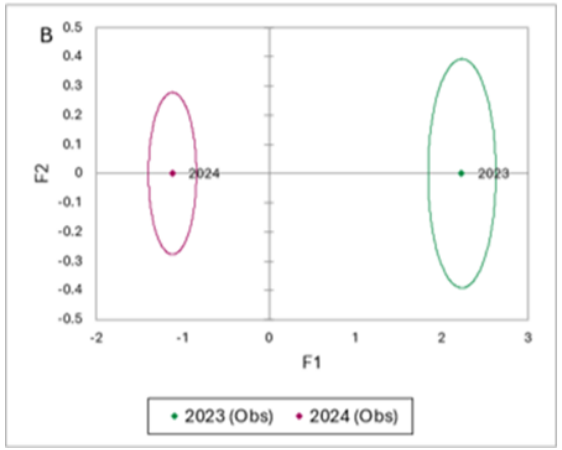
Classification ratings

Table 1. How to interpret classification accuracy levels

Rating	Accuracy Range	Comment
Excellent	90–100%	Strong class separation, robust model
Very Good	80–89%	Reliable, minor misclassifications
Good	70–79%	Acceptable, but room for improvement
Fair	60–69%	Some weaknesses in class prediction
Poor	<60%	Not reliable

Class refers to the different groups the model tries to identify. In this case, they represent different wine cultivars or their regions of origin, or vintage.

Vintage: White- top, Red- bottom

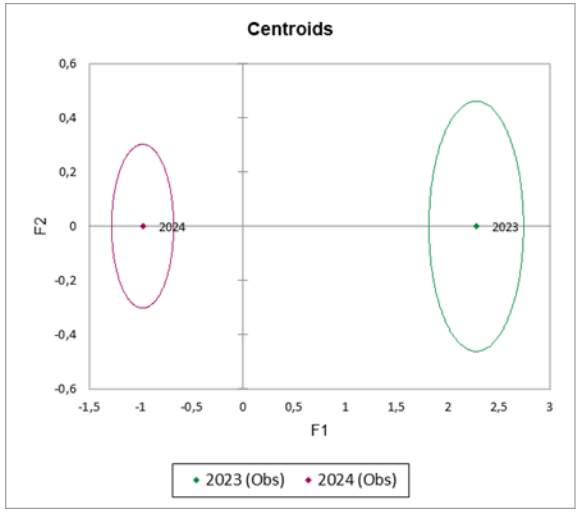


Confusion matrix for the cross-validation results:

from \ to	2023	2024	Total	% correct
2023	24	1	25	96,00%
2024	3	47	50	94,00%
Total	27	48	75	94,67%

Confusion matrix for the training sample (Variable Vintage):

from \ to	2023	2024	Total	% correct
2023	24	1	25	96,00%
2024	2	48	50	96,00%
Total	26	49	75	96,00%



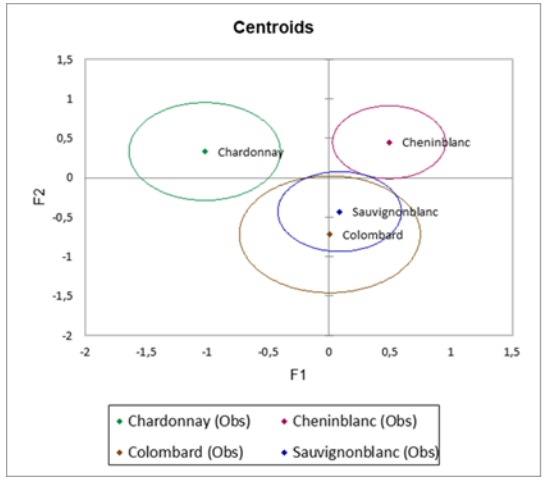
Confusion matrix for the cross-validation results:

from \ to	2023	2024	Total	% correct
2023	15	3	18	83,33%
2024	1	41	42	97,62%
Total	16	44	60	93,33%

Confusion matrix for the training sample (Variable Vintage):

from \ to	2023	2024	Total	% correct
2023	16	2	18	88,89%
2024	1	41	42	97,62%
Total	17	43	60	95,00%

Variety: White- top, Red-bottom

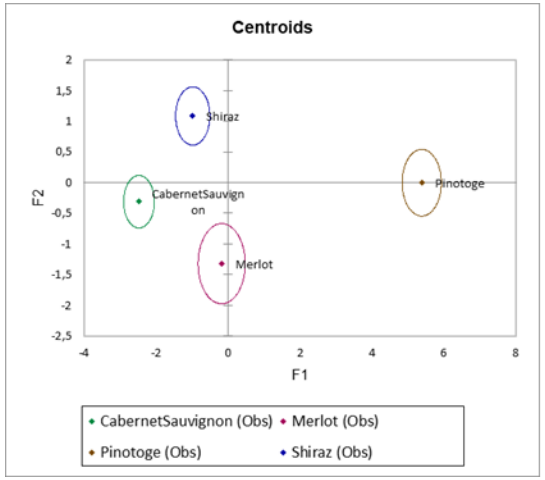


Confusion matrix for the cross-validation results:

from \ to	Chardonnay	Cheninblanc	Colombard	Sauvignonblanc	Total	% correct
Chardonn	5	3	0	2	10	50,00%
Cheninbla	1	13	2	2	18	72,22%
Colombar	2	2	1	2	7	14,29%
Sauvignor	1	6	0	8	15	53,33%
Total	9	24	3	14	50	54,00%

Confusion matrix for the training sample (Variable Cultivar):

from \ to	Chardonnay	Cheninblanc	Colombard	Sauvignonblanc	Total	% correct
hardonna	1	4	0	5	10	10,00%
heninblan	1	14	0	3	18	77,78%
olombarc	2	1	0	4	7	0,00%
vignonbla	1	4	0	10	15	66,67%
Total	5	23	0	22	50	50,00%



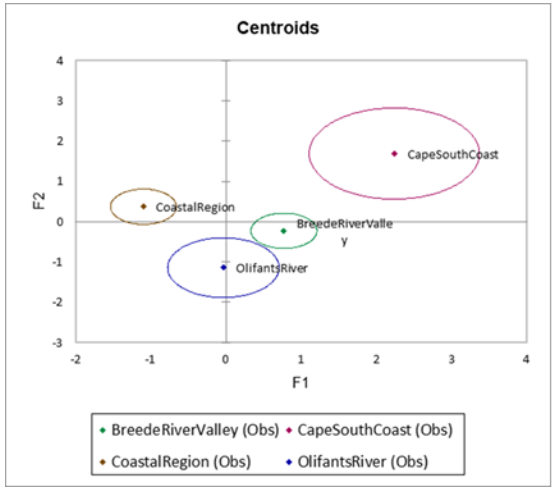
Confusion matrix for the cross-validation results:

from \ to	CabernetSauvignon	Merlot	Pinotoge	Shiraz	Total	% correct
CabernetS	15	3	0	3	21	71,43%
Merlot	0	5	0	4	9	55,56%
Pinotoge	0	0	13	0	13	100,00%
Shiraz	4	0	0	13	17	76,47%
Total	19	8	13	20	60	76,67%

Confusion matrix for the training sample (Variable Cultivar):

from \ to	CabernetSauvignon	Merlot	Pinotoge	Shiraz	Total	% correct
ernetSauvi	19	0	0	2	21	90,48%
Merlot	5	0	3	1	9	0,00%
Pinotoge	0	0	13	0	13	100,00%
Shiraz	8	0	2	7	17	41,18%
Total	32	0	18	10	60	65,00%

Geographical Origin: White-top, Red-bottom

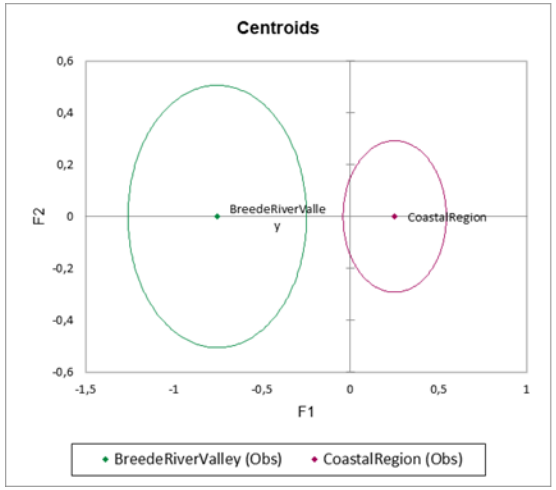


Confusion matrix for the cross-validation results:

from \ to	BreedeRiverValley	CapeSouthCoast	CoastalRegion	OlifantsRiver	Total	% correct
BreedeRiv	13	1	5	1	20	65,00%
CapeSoutl	3	0	0	0	3	0,00%
CoastalRe	3	0	16	1	20	80,00%
OlifantsRi	3	0	2	2	7	28,57%
Total	22	1	23	4	50	62,00%

Confusion matrix for the training sample (Variable Region):

from \ to	BreedeRiverValley	CapeSouthCoast	CoastalRegion	OlifantsRiver	Total	% correct
edeRiverVa	15	0	5	0	20	75,00%
peSouthCc	2	1	0	0	3	33,33%
astalRegi	4	0	16	0	20	80,00%
lifantsRive	7	0	0	0	7	0,00%
Total	28	1	21	0	50	64,00%



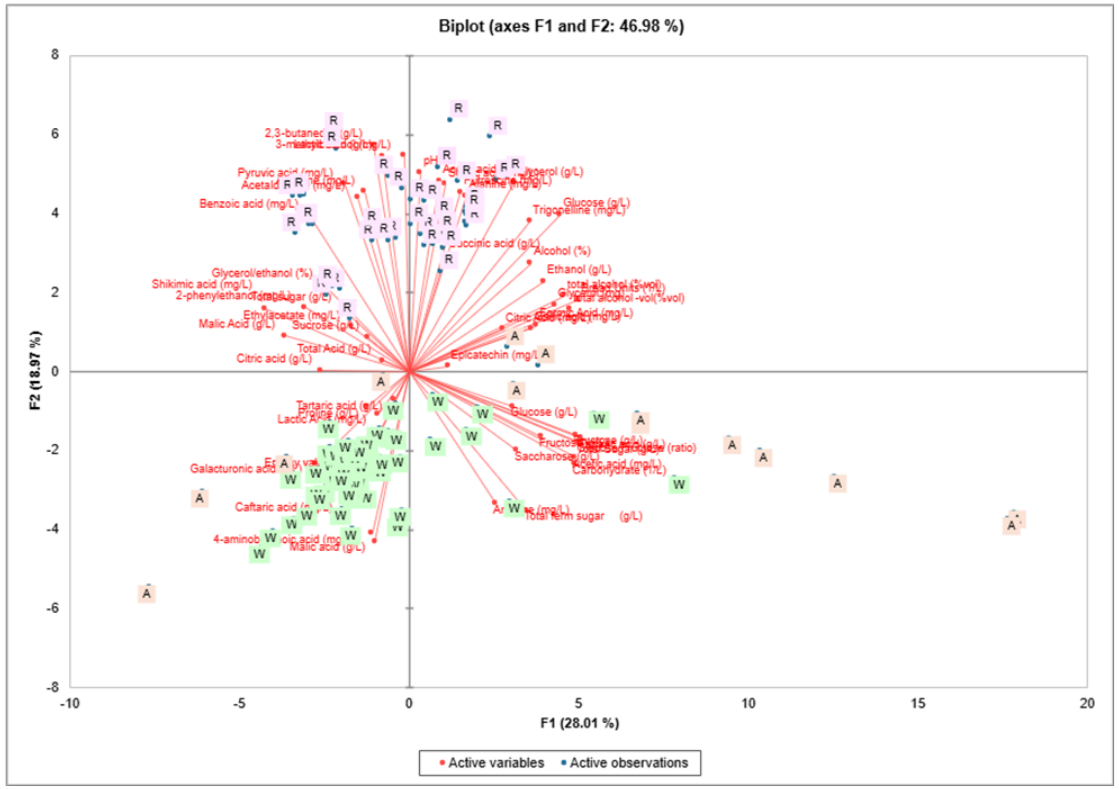
Confusion matrix for the cross-validation results:

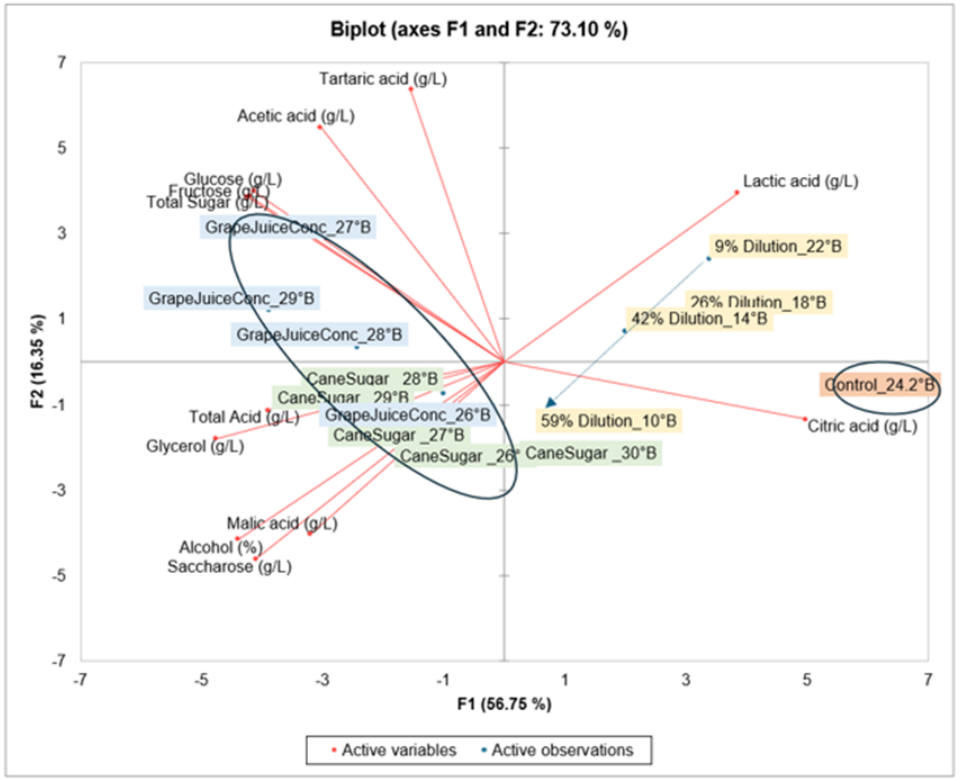
from \ to	BreedeRiverValley	CoastalRegion	Total	% correct
BreedeRiv	2	13	15	13,33%
CoastalRe	1	44	45	97,78%
Total	3	57	60	76,67%

Confusion matrix for the training sample (Variable F

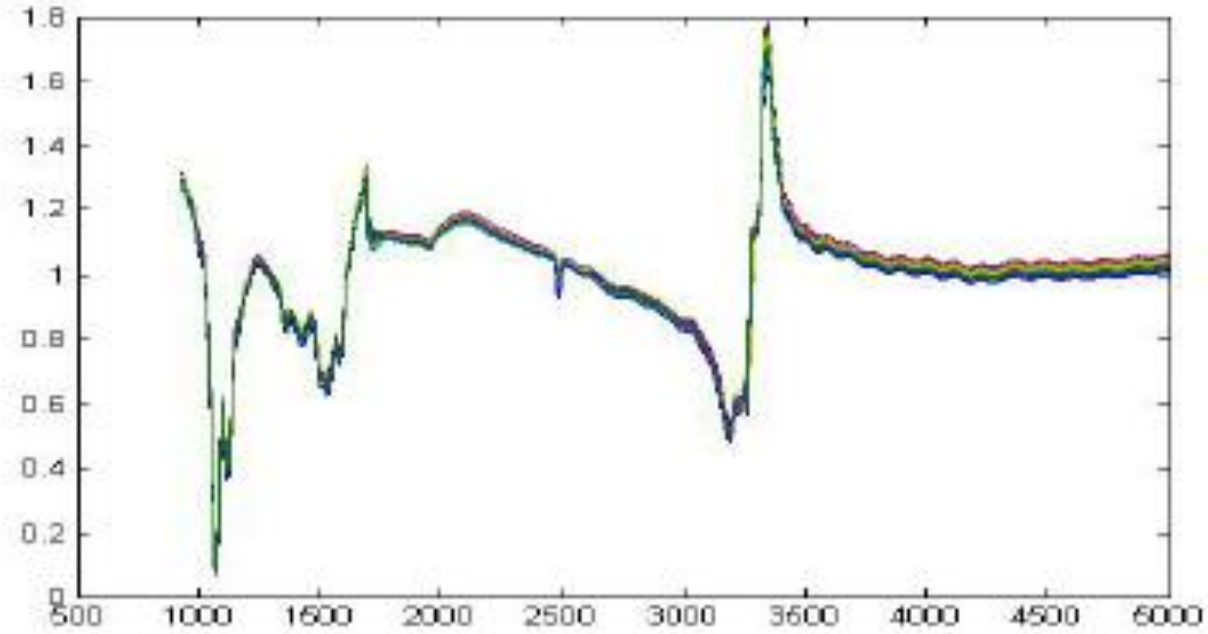
from \ to	BreedeRiverValley	CoastalRegion	Total	% correct
edeRiverVa	2	13	15	13,33%
astalRegi	0	45	45	100,00%
Total	2	58	60	78,33%

Red vs White vs intentionally modified

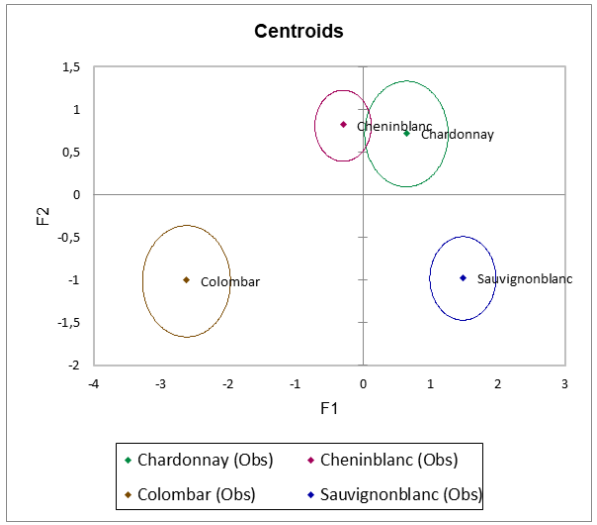




Spectral Results



Variety: White-top, Red-bottom

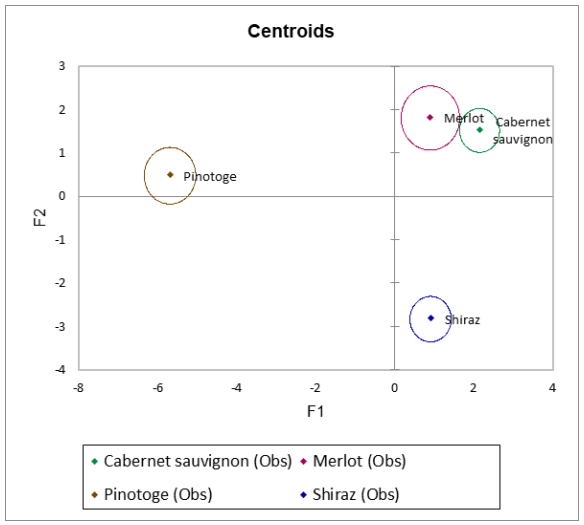


Confusion matrix for the cross-validation results:

from \ to	Chardonnay	Cheninblanc	Colombar	Sauvignonblanc	Total	% correct
Chardonnay	4	4	0	2	10	40,00%
Cheninblanc	3	16	2	1	22	72,73%
Colombar	0	3	6	0	9	66,67%
Sauvignonblanc	1	3	0	12	16	75,00%
Total	8	26	8	15	57	66,67%

Confusion matrix for the training sample (Variable Cultivar):

from \ to	Chardonnay	Cheninblanc	Colombar	Sauvignonblanc	Total	% correct
Chardonnay	0	5	3	2	10	0,00%
Cheninblanc	0	16	2	4	22	72,73%
Colombar	0	2	7	0	9	77,78%
Sauvignonblanc	0	10	2	4	16	25,00%
Total	0	33	14	10	57	47,37%



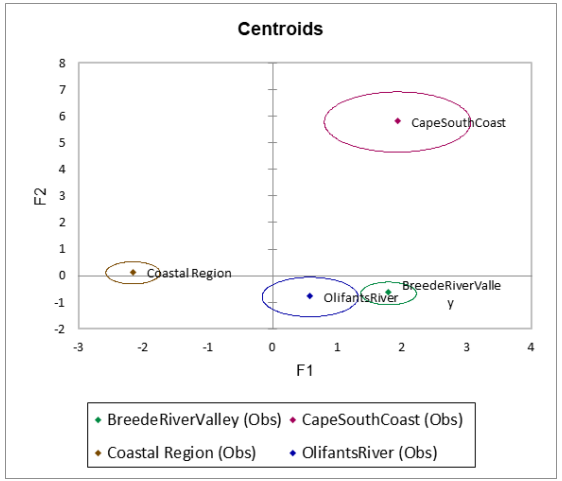
Confusion matrix for the cross-validation results:

from \ to	Cabernet sauvignon	Merlot	Pinotoge	Shiraz	Total	% correct
Cabernet sauvignon	11	3	0	1	15	73,33%
Merlot	2	5	0	0	7	71,43%
Pinotoge	0	0	9	0	9	100,00%
Shiraz	1	0	0	13	14	92,86%
Total	14	8	9	14	45	84,44%

Confusion matrix for the training sample (Variable Cultivar):

from \ to	Cabernet sauvignon	Merlot	Pinotoge	Shiraz	Total	% correct
Cabernet sauvignon	13	0	0	2	15	86,67%
Merlot	6	0	0	1	7	0,00%
Pinotoge	2	0	4	3	9	44,44%
Shiraz	4	0	0	10	14	71,43%
Total	25	0	4	16	45	60,00%

Geographical origin: White- top, Red-bottom

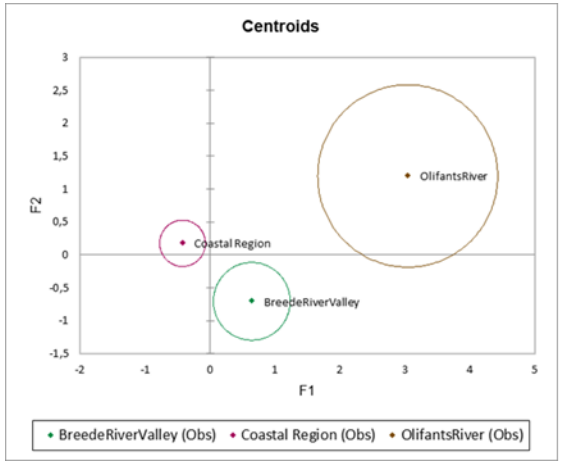


Confusion matrix for the cross-validation results:

from \ to	BreedeRiverValley	CapeSouthCoast	Coastal Region	OlifantsRiver	Total	% correct
BreedeRiverValley	20	0	0	1	21	95,24%
CapeSouthCoast	0	3	0	0	3	100.%
Coastal Region	2	0	20	0	22	90,91%
OlifantsRiver	2	0	2	3	7	42,86%
Total	24	3	22	4	53	86,79%

Confusion matrix for the training sample (Variable Region):

from \ to	BreedeRiverValley	CapeSouthCoast	Coastal Region	OlifantsRiver	Total	% correct
BreedeRiverValley	16	0	5	0	21	76,19%
CapeSouthCoast	2	0	1	0	3	0,00%
Coastal Region	5	0	17	0	22	77,27%
OlifantsRiver	6	0	1	0	7	0,00%
Total	29	0	24	0	53	62,26%



Confusion matrix for the cross-validation results:

from \ to	BreedeRiverValley	Coastal Region	OlifantsRiver	Total	% correct
BreedeRiverValley	4	7	0	11	36,36%
Coastal Region	2	29	0	31	93,55%
OlifantsRiver	0	0	2	2	100,00%
Total	6	36	2	44	79,55%

Confusion matrix for the training sample (Variable Region):

from \ to	BreedeRiverValley	Coastal Region	OlifantsRiver	Total	% correct
BreedeRiverValley	1	10	0	11	9,09%
Coastal Region	1	30	0	31	96,77%
OlifantsRiver	0	2	0	2	0,00%
Total	2	42	0	44	70,45%

Conclusions and future research

- With the available built-in calibration that is provided by the existing software, we can see a fair amount of discrimination for the factors being investigated in the quantitative results, but it would not be considered sufficient for industry use.
- The spectral data provides consistently better overall classification rates and should be considered in the general discrimination and authenticity processes.
- The extension of the calibration will help to increase the robustness of the model and can increase the discrimination capacity and classification rates of the quantified data.

Acknowledgements

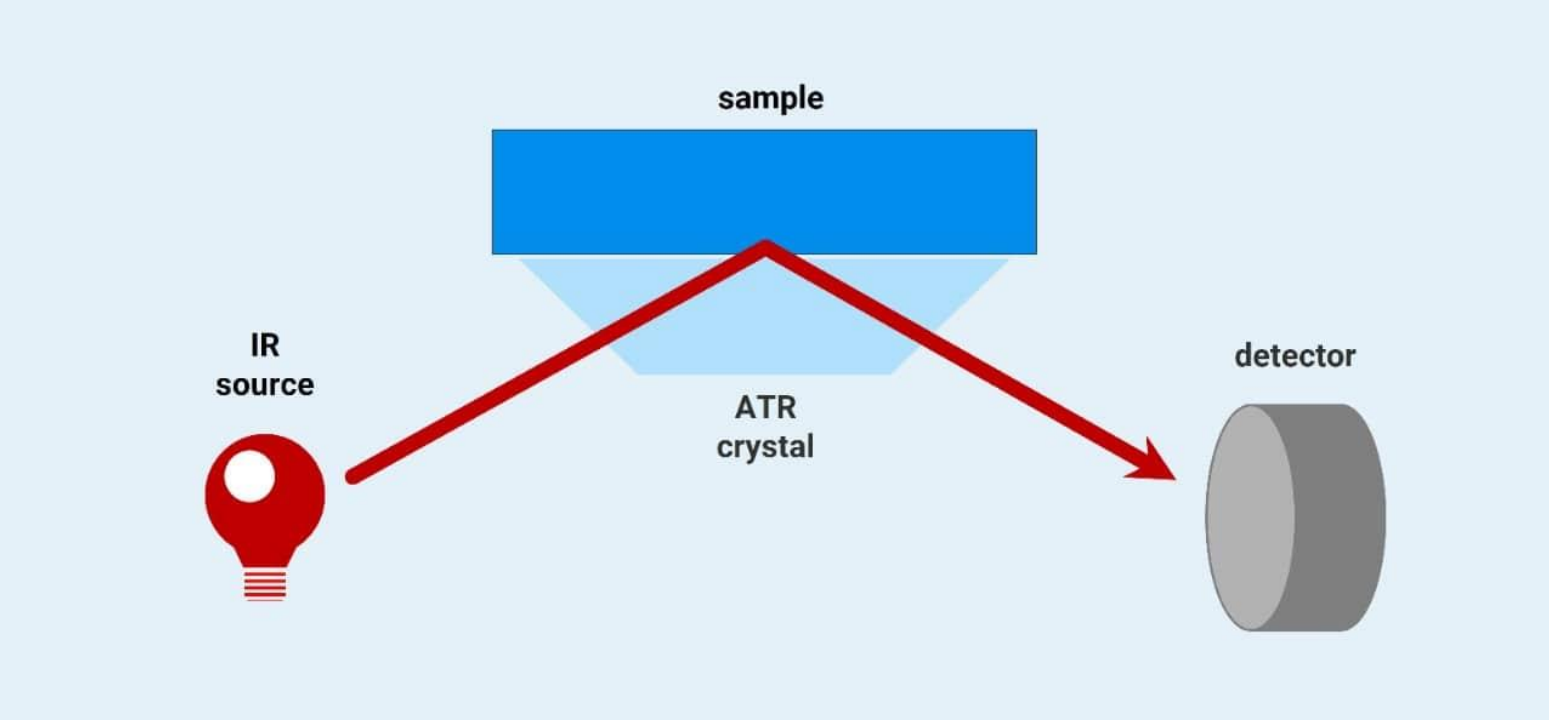
- Agricultural Research Council

- Stellenbosch University

- South Africa Wine


NRF
National Research Foundation
Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT
SAGWRI
South African Grape and Wine Research Institute
SOUTH AFRICA WINE
discover diversity in a glass
Thank you
Enkosi
Dankie
Photo by Stefan Els

How ART-FT-IR works



Example of chemometric techniques that have been applied

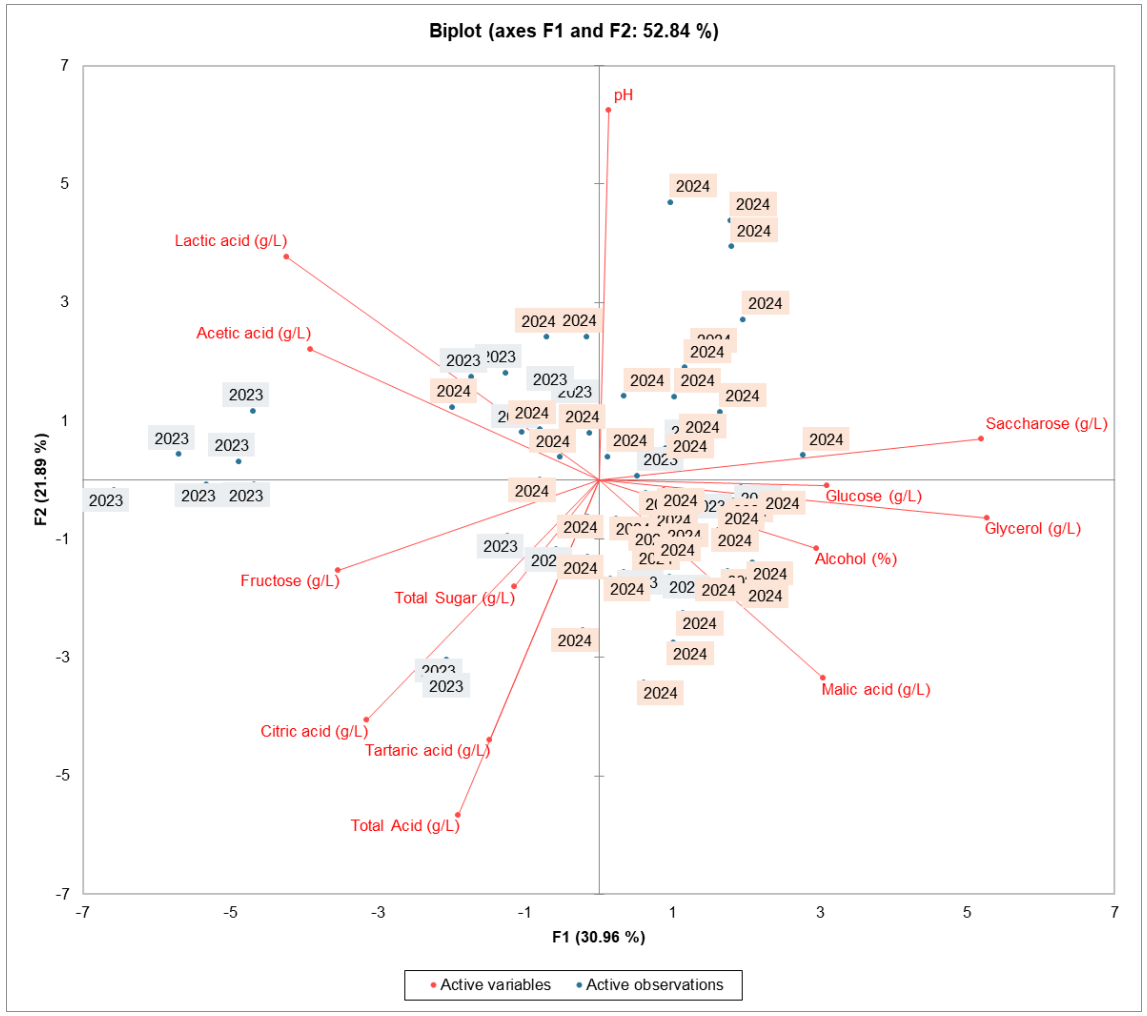
- A Review of Wine Authentication Using Spectroscopic Approaches in Combination with Chemometrics

Table 2. Examples of IR spectroscopy in combination with chemometrics for wine authentication.

Spectroscopic Technique	Spectral Range	Parameters for Authentication	Classification Method [1]	Remark	Reference
MIR	5012–926 cm^{-1}	Discrimination of red and white varieties from Australian regions	PCA, LDA	Correct classification of red varieties, 96% and white varieties, 94%	[26]
UV–Vis, NIR and MIR	400–2500 nm (UV–Vis and NIR) and 4000–400 cm^{-1} (MIR)	Geographical origin of Sauvignon blanc wines from Australia and New Zealand	PCA, SIMCA, PLS-DA	Correct classification using PLS-DA with: UV–Vis, 67%; NIR, 76%; MIR, 90%; and combined IR spectra, 93%	[23]
UV–Vis/NIR	190–2500 nm	Discrimination of white wines (Albariño cultivar) from Rías Baixas subzones in Spain	PCA, LDA, SIMCA, SVM	Correct classification using: LDA, 86%; SIMCA, 56%; and SVM, 84%	[30]
NIR and MIR	1750–1000 cm^{-1} and 4555–4353 cm^{-1}	Geographical origin of Cabernet Sauvignon wines from Australia, Chile, and China	PCA, SIMCA, DA	Correct classification using: SIMCA, 97%, 97%, and 92% for Australian, Chilean, and Chinese wines; and DA, 86%, 85%, and 77%, respectively.	[31]

[1] PCA, principal component analysis; LDA, linear discriminant analysis; SIMCA, soft independent modelling of class analogy; PLS-DA, partial least squares-discriminant analysis; SVM, support vector machine.

- Ask Dr VJV for classificstion table showing percentage classification levels eg good, excellent, bad etc.


Biplot (axes F1 and F2: 52.84 %)
F2 (21.89 %)
F1 (30.96 %)
pH
Lactic acid (g/L)
Acetic acid (g/L)
Saccharose (g/L)
Glucose (g/L)
Glycerol (g/L)
Alcohol (%)
Fructose (g/L)
Total Sugar (g/L)
Malic acid (g/L)
Citric acid (g/L)
Tartaric acid (g/L)
Total Acid (g/L)
Active variables
Active observations

Background and introduction

- ~~Food safety is a great consumer and industry concern.~~
- ~~Wine is one of the most adulterated products on the market.~~
- ~~In order to ensure product compliance and consumer health, we make of use the process of authentication.~~
- Ensuring the quality and integrity of wine is a key priority for producers and consumers alike.
- Wine offers rich diversity, and authenticity helps highlight its unique character and origin.
- To support consumer confidence and celebrate genuine products, we make of use the process of authentication.
- Authentication can be done through a variety of classical and chromatographic methods, as well as through various spectroscopic techniques.
- Many of these methods are however not cost effective, and as a result there is an interest in the development of more cost effective methods, to authenticate wine, with a particular interest in export wines.

(Marianthi Basalekou, Kyriakou and Tarantilis, 2022)
(Christoph Hermann and Wachter, 2015)
(Popîrdă et al., 2021)
(Ranaweera et al., 2021)
(www.oiv.int, n.d.)

introduction

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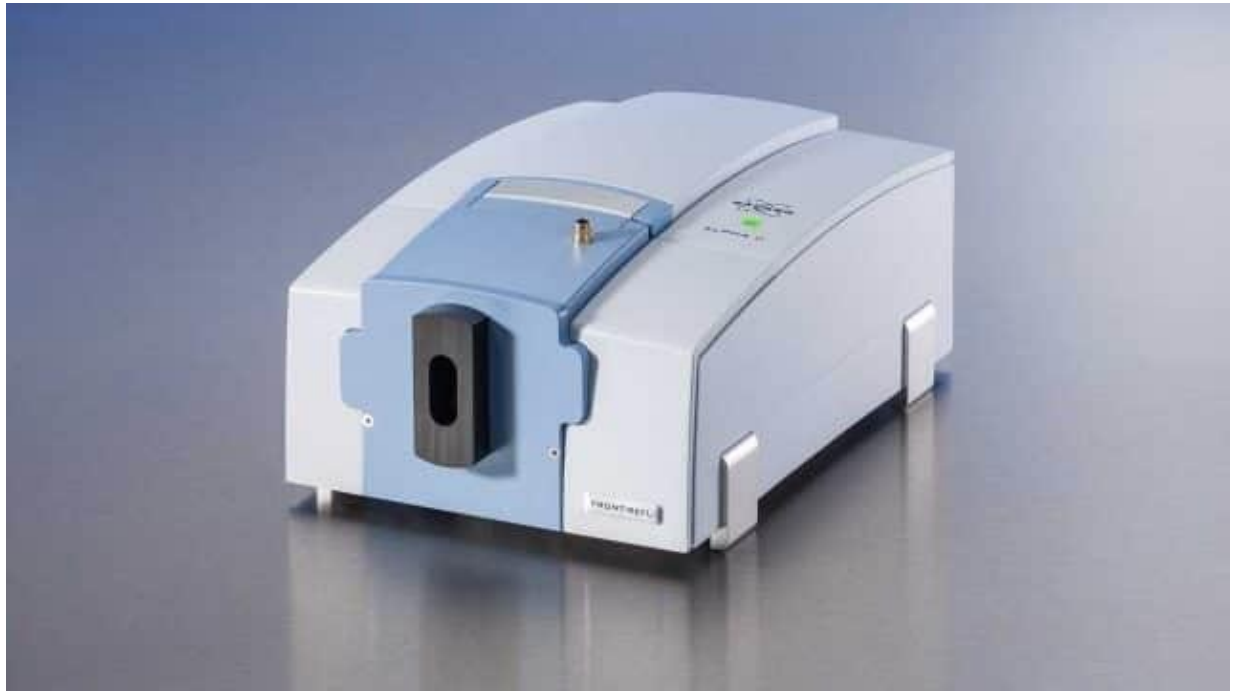
- It has previously been used in traceability and authenticity studies.
- It is a more practical method than other analytical techniques.



(Thanasi, Catarino and Ricardo-da-Silva, 2022)
(Austin Journal of Analytical and Pharmaceutical Chemistry, n.d.)
(Kruzlicova and Gruberova, 2022)
(Griffiths and Airmet, 2010)
(Ranaweera et al., 2021)
(Geană et al., 2019)
(www.bruker.com,n.d.)

Aim

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

SAGWRI South African Grape and Wine Research Institute

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SAGWRI South African Grape and Wine Research Institute

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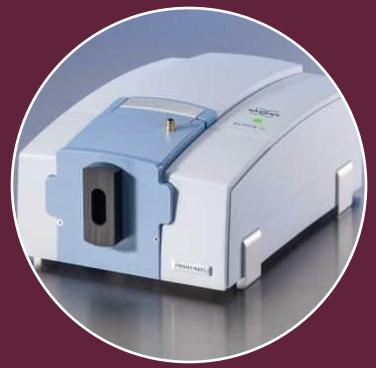
Microvinification of wines from various winemaking regions of South Africa.



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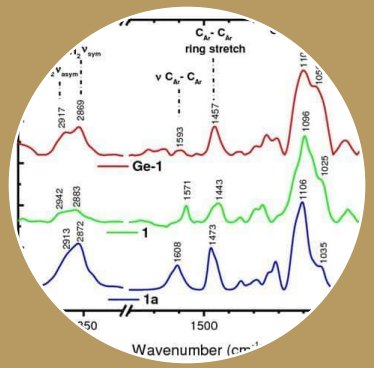
Chemical and spectral analysis of microvinified, commercial and intentionally wines using ATR FT-IR analysis on the Alpha II Wine Analyzer.



Objective 3

Confirm the use of vibrational spectroscopies such as ATR-FT-IR combined with chemometric methods for authentication of South African wines.

Methodology

Stellenbosch UNIVERSITY IYUNIVESITHI UNIVERSITEIT

SAGWRI South African Grape and Wine Research Institute

Objective 1:

- Wines (100 p.a.) from various wine production regions of 8 different cultivars were microvinified. According to a specific sampling plan.

- Microvinification was done according to EC regulation N. 2729/2000 and the winemaking protocols of Nietvoorbij Experimental cellar.

- Merlot must was intentionally modified through dilution and chaptalization, this wine was made in a rose style.

Objective 2:

- Alpha II: Rapid analysis of finished wines, using FT-IR technology.

- Analysis was conducted by manually injecting 10ml of wine. Each sample was run in triplicate.

- A calibration was built to quantify 53 additional compounds (as well as the 14 original quantifiable compounds).

- The calibration data was based off NMR data related to the same wines being analyzed.

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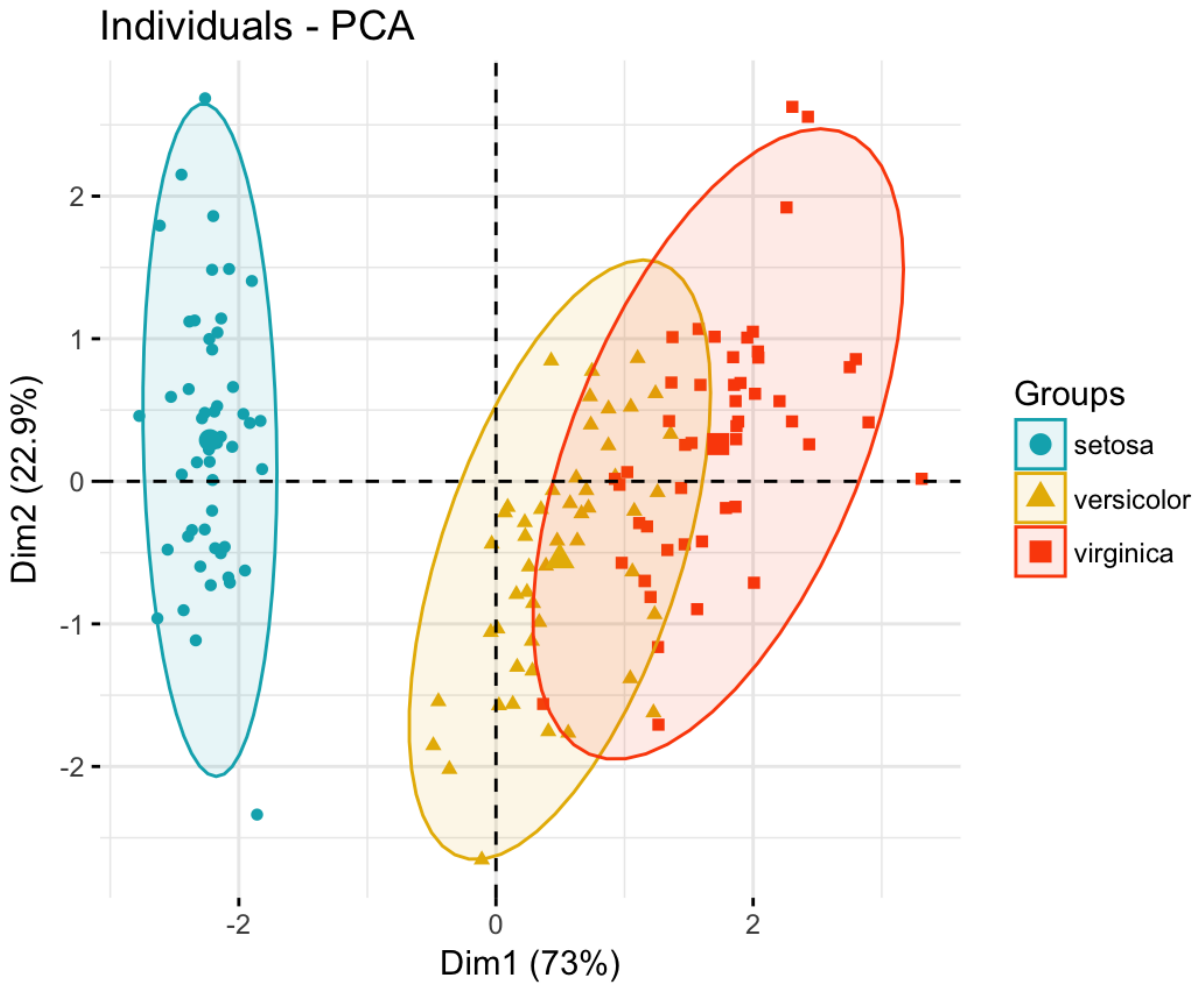
- The mean value of each sample triplicate were used to conduct ANOVA to determine significant compounds.

- PCA, DA and PLS-DA were conducted on mean values to determine whether distinctions can be drawn based off variety, vintage and geographical origin. DA is done using model selection (done using XL-stat).

- Results analysed and reported on.

Quantitative Results



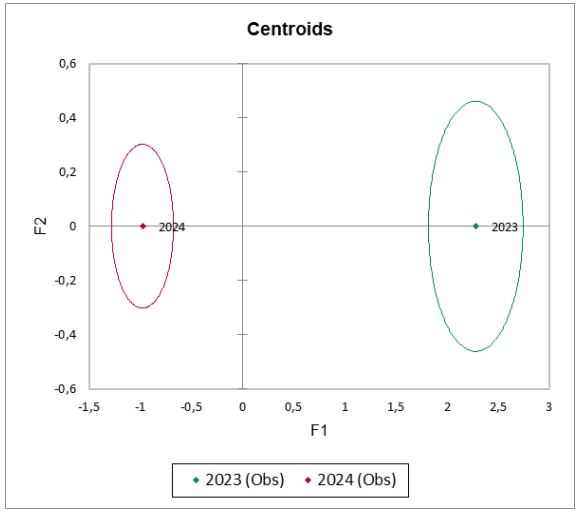
Classification ratings

Table 1. How to interpret classification accuracy levels

Rating	Accuracy Range	Comment
Excellent	90–100%	Strong class separation, robust model
Very Good	80–89%	Reliable, minor misclassifications
Good	70–79%	Acceptable, but room for improvement
Fair	60–69%	Some weaknesses in class prediction
Poor	<60%	Not reliable

Class refers to the different groups the model tries to identify. In this case, they represent different wine cultivars or their regions of origin, or vintage.

Results : Vintage(R-top W-bottom)

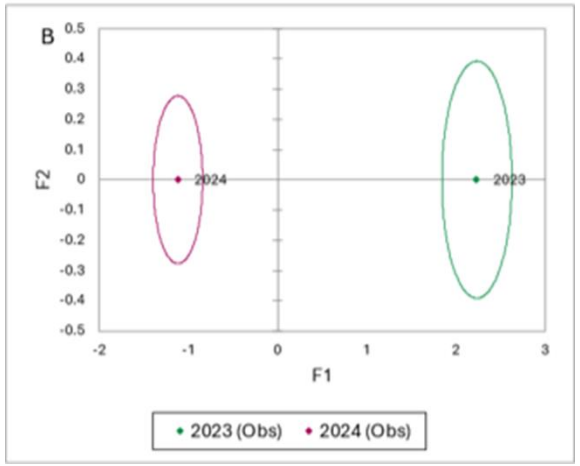


Confusion matrix for the cross-validation results:

from \ to	2023	2024	Total	% correct
2023	15	3	18	83,33%
2024	1	41	42	97,62%
Total	16	44	60	93,33%

Confusion matrix for the training sample (Variable Vintage):

from \ to	2023	2024	Total	% correct
2023	16	2	18	88,89%
2024	1	41	42	97,62%
Total	17	43	60	95,00%



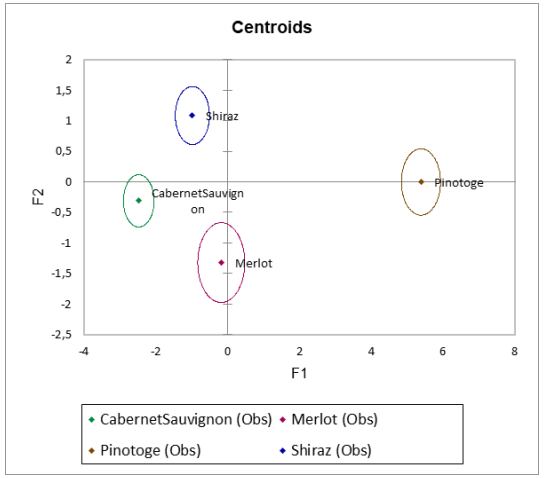
Confusion matrix for the cross-validation results:

from \ to	2023	2024	Total	% correct
2023	24	1	25	96,00%
2024	3	47	50	94,00%
Total	27	48	75	94,67%

Confusion matrix for the training sample (Variable Vintage):

from \ to	2023	2024	Total	% correct
2023	24	1	25	96,00%
2024	2	48	50	96,00%
Total	26	49	75	96,00%

Results : Variety(R-top w-bottom)

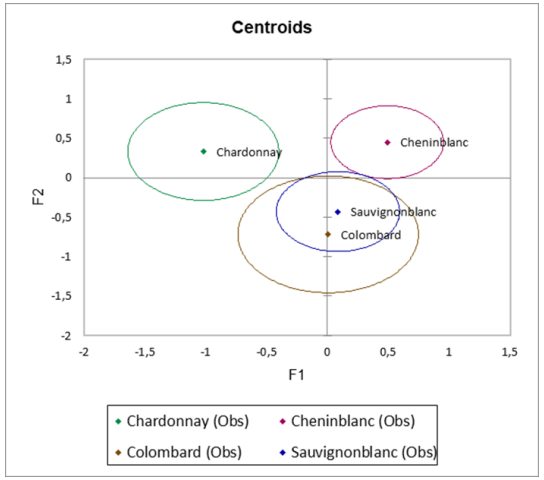


Confusion matrix for the cross-validation results:

from \ to	Cabernet Sauvignon	Merlot	Pinotoge	Shiraz	Total	% correct
CabernetS	15	3	0	3	21	71,43%
Merlot	0	5	0	4	9	55,56%
Pinotoge	0	0	13	0	13	100,00%
Shiraz	4	0	0	13	17	76,47%
Total	19	8	13	20	60	76,67%

Confusion matrix for the training sample (Variable Cultivar):

from \ to	Cabernet Sauvignon	Merlot	Pinotoge	Shiraz	Total	% correct
ernetSauvi	19	0	0	2	21	90,48%
Merlot	5	0	3	1	9	0,00%
Pinotoge	0	0	13	0	13	100,00%
Shiraz	8	0	2	7	17	41,18%
Total	32	0	18	10	60	65,00%



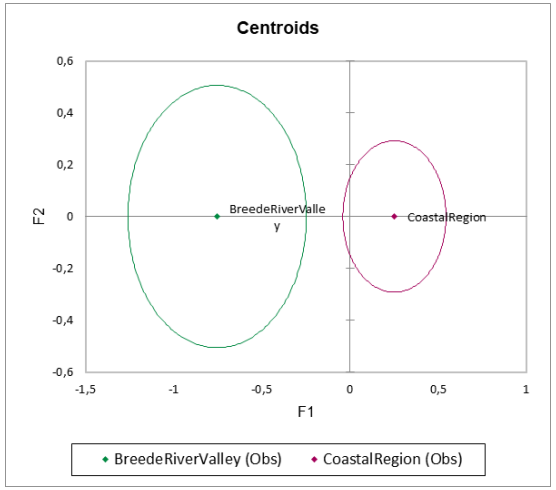
Confusion matrix for the cross-validation results:

from \ to	Chardonnay	Cheninblanc	Colombard	Sauvignonblanc	Total	% correct
Chardonn	5	3	0	2	10	50,00%
Cheninbla	1	13	2	2	18	72,22%
Colombar	2	2	1	2	7	14,29%
Sauvignor	1	6	0	8	15	53,33%
Total	9	24	3	14	50	54,00%

Confusion matrix for the training sample (Variable Cultivar):

from \ to	Chardonnay	Cheninblanc	Colombard	Sauvignonblanc	Total	% correct
hardonna	1	4	0	5	10	10,00%
heninblan	1	14	0	3	18	77,78%
olombarc	2	1	0	4	7	0,00%
uvignonbla	1	4	0	10	15	66,67%
Total	5	23	0	22	50	50,00%

Results : Geographical origin (R-top W-bottom)

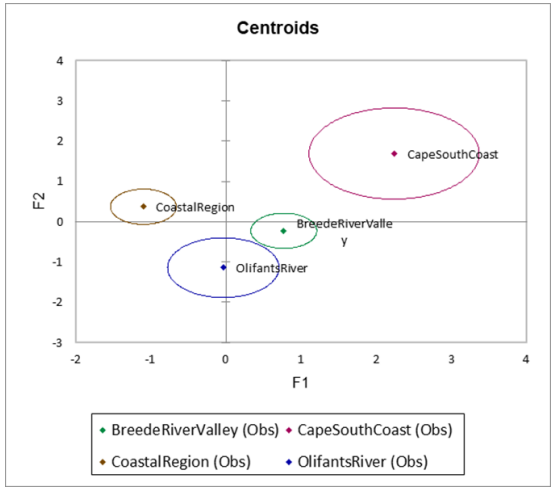


Confusion matrix for the cross-validation results:

from \ to	BreedeRiverValley	CoastalRegion	Total	% correct
BreedeRiv	2	13	15	13,33%
CoastalRe	1	44	45	97,78%
Total	3	57	60	76,67%

Confusion matrix for the training sample (Variable F

from \ to	BreedeRiverValley	CoastalRegion	Total	% correct
edeRiverVa	2	13	15	13,33%
oastalRegi	0	45	45	100,00%
Total	2	58	60	78,33%



Confusion matrix for the cross-validation results:

from \ to	BreedeRiverValley	CapeSouthCoast	CoastalRegion	OlifantsRiver	Total	% correct
BreedeRiv	13	1	5	1	20	65,00%
CapeSoutl	3	0	0	0	3	0,00%
CoastalRe	3	0	16	1	20	80,00%
OlifantsRi	3	0	2	2	7	28,57%
Total	22	1	23	4	50	62,00%

Confusion matrix for the training sample (Variable Region):

from \ to	BreedeRiverValley	CapeSouthCoast	CoastalRegion	OlifantsRiver	Total	% correct
edeRiverVa	15	0	5	0	20	75,00%
peSouthCc	2	1	0	0	3	33,33%
oastalRegi	4	0	16	0	20	80,00%
lifantsRive	7	0	0	0	7	0,00%
Total	28	1	21	0	50	64,00%

Red vs White vs adulterated

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