



The University of Adelaide

Geographic classification of wines using Vis-NIR spectroscopy

Master Thesis

by

Liang Liu

B. Eng. (Shenyang Pharmaceutical University, China)

School of Chemical Engineering

Faculty of Engineering, Computer & Mathematical Sciences

November 2006

Declaration

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis being made available in the University Library.

The author acknowledges that copyright of published works contained within this thesis (as listed below) resides with the copyright holders of those works.

Liang Liu

November 2006

Summary

The determination of wine authenticity and the detection of adulteration are attracting an increasing amount of attention for wine producers, researchers and consumers. Wine authentication and classification based on geographical origin has been widely studied. Most of these studies have achieved successful classification results. However, these studies have involved complicated and expensive procedures. Visible and near infrared spectroscopy (Vis-NIR) is recognized as a rapid and non-destructive technique. In recent years, several studies have been conducted using Vis-NIR spectroscopy to analyze wine for both quantitative and qualitative purposes. The aim of this research was to investigate the geographical classification of wines using Vis-NIR spectroscopy. The effect of temperature and measurement mode (transmission and transreflectance) on Vis-NIR spectra was investigated to identify optimal conditions for wine sample analysis. It was found the optimal temperature is between 30 to 35 °C and the shorter pathlength measurement condition has better prediction ability. Classification by geographical origin using Vis-NIR spectroscopy was investigated for sixty-three Tempranillo wines from Spain and Australia, and fifty Riesling wines from Australia, New Zealand and Europe. Discriminant partial least square regression (DPLS) and linear discriminant analysis (LDA) based on PCA scores were used to perform classification. Over 90% of the Tempranillo wines were correctly classified according to their geographical region using both DPLS and LDA. A classification rate of 72% was achieved for the Riesling wines. Vis-NIR technique provides a similar degree of reliability on wine classification comparable to those obtained using chemical composition. The results of this study demonstrate potential for Vis-NIR spectroscopy combined with multivariate analysis as a rapid method for classifying wines by geographical origin.

Acknowledgements

I wish to express my sincere gratitude to my research supervisors, Dr. Chris Colby and Dr. Daniel Cozzolino. I appreciate their expert guidance and never ending patience. I also thank my co-supervisors, A/Prof. Brian O'Neill, Prof. Derek Abbott and A/Prof. Graham Jones for their helpful guidance and encouragement.

The major part of the work reported in this thesis was performed at the Australia Wine Research Institute, Adelaide, SA. I would like to thank the following staff from AWRI, Dr. Wies Cynkar, Mr. Mark Gishen, Dr. Les Janik, Dr. Robert Damberg, Mr. Geoffrey Cowey, Mr Mathew Holdstock, Dr. Paul Smith, Ms. Megan Mecurio, and their colleagues from the AWRI analytical lab. Their contributions made this work possible.

Finally, I would like to thank my parents and my girlfriend for their continuing love and support throughout my academic career.

List of Publications

Liang Liu, Daniel Cozzolino, Wies Cynkar, Mark Gishen, Christopher Colby. Geographic classification of Spanish and Australian Tempranillo red wines by visible and near infrared spectroscopy combined with multivariate analysis. *Journal of Agriculture and Food Chemistry*. (Published on web 12/08/2006)

Liang Liu, Daniel Cozzolino, Chris Colby, Bob Dambergs, Mark Gishen, Brian O'Neill, Derek Abbott, (2006) Effect of temperature on visible and near infrared spectra of wine. The 12th Australian Near Infrared Spectroscopy Conference, Rockhampton, Queensland, Australia.

Table and Contents

SUMMARY	II
ACKNOWLEDGEMENTS	III
LIST OF PUBLICATIONS.....	IV
LIST OF FIGURES	VII
LIST OF TABLES	IX
CHAPTER 1 INTRODUCTION.....	1
CHAPTER 2 LITERATURE REVIEW	4
2.1 WINE QUALITY CATEGORY – GEOGRAPHICAL ORIGIN	4
2.2 WINE CLASSIFICATION AND AUTHENTICATION.....	5
2.2.1 <i>Sensory evaluation</i>	5
2.2.2 <i>Instrumental analysis</i>	6
2.2.3 <i>Spectroscopic methods</i>	9
2.2.4 <i>Summary</i>	9
2.3 NEAR INFRARED SPECTROSCOPY.....	10
2.3.1 <i>Introduction</i>	10
2.3.2 <i>Effect of Sample presentation on Vis and NIR spectra</i>	10
2.3.3 <i>Use of NIR to classify food based on geographical origin</i>	12
2.3.4 <i>NIR applications on wine analysis</i>	13
SUMMARY AND RESEARCH GAPS	15
CHAPTER 3 MATERIAL AND METHODS.....	16
3.1 WINE SAMPLES	16
3.2 WINE REFERENCE ANALYSIS.....	17
3.3 SPECTROSCOPIC MEASUREMENTS	17
3.4 SPECTRA DATA ANALYSIS	19
3.4.1 <i>Spectra pre-treatment</i>	19
3.4.2 <i>Multivariate analysis</i>	20
CHAPTER 4 EFFECT OF SAMPLE PRESENTATION - SAMPLE TEMPERATURE EFFECT ON THE ANALYSIS OF WINE.....	24
4.1 INTRODUCTION	24
4.2 RESULTS AND DISCUSSION.....	24
4.2.1 <i>Chemical analysis</i>	24
4.2.2 <i>Spectra interpretation and analysis</i>	26

4.2.3 Influence of temperature on the Vis-NIR spectra of wine	29
Summary	36
4.2.4 Principal component analysis	36
4.2.5 Comparison of the prediction ability of different temperatures using PLS	40
CHAPTER 5 EFFECT OF SAMPLE PRESENTATION – MEASUREMENT CONDITION	
EFFECT ON THE ANALYSIS OF WINE	42
5.1 INTRODUCTION	42
5.2 RESULTS AND DISCUSSION.....	42
5.2.1 Chemical analysis	42
5.2.2 Spectra analysis	43
5.2.3 Principal component analysis	45
5.2.4 Comparison using PLS.....	47
CHAPTER 6 USE OF VISIBLE AND NIR TO CLASSIFY TEMPRANILLO WINES BASED	
ON GEOGRAPHICAL ORIGINS	49
6.1 INTRODUCTION	49
6.2 RESULTS AND DISCUSSION.....	50
6.2.1 Chemical analysis	50
6.2.2 Spectra interpretation and analysis.....	51
6.2.3 Principal component analysis	52
6.2.4 Discrimination analysis.....	54
SUMMARY.....	58
CHAPTER 7 USE OF VISIBLE AND NIR TO CLASSIFY RIESLING WINES BASED ON	
GEOGRAPHICAL ORIGINS	59
7.1 INTRODUCTION	59
7.2 RESULTS AND DISCUSSIONS.....	59
7.2.1 Chemical analysis	59
7.2.2 Spectra interpretation and analysis.....	60
7.2.3 Principal component analysis	62
7.2.4 Discrimination analysis.....	65
SUMMARY.....	67
CONCLUSION	69
REFERENCES	71

List of Figures

FIGURE 3. 1 FOSS NIRSYSTEM6500, SILVER SPRING, MD	18
FIGURE 3. 2 SAMPLE PRESENTATION OF TRANSMITTANCE AND TRANSFLECTANCE	19
FIGURE 4. 1 VIS-NIR SPECTRA OF RED WINE SAMPLES AT 5 DIFFERENT TEMPERATURES	27
FIGURE 4. 2 VIS-NIR SPECTRA OF WHITE WINE SAMPLES AT 5 DIFFERENT TEMPERATURES	27
FIGURE 4. 3 SECOND DERIVATIVE SPECTRA OF RED AND WHITE WINE SAMPLES	28
FIGURE 4. 4 WATER SPECTRA AT 6 DIFFERENT TEMPERATURES.....	28
FIGURE 4. 5 VIS-NIR SPECTRA OF ONE RED WINE SAMPLE (Ww1) AT 6 DIFFERENT TEMPERATURES	29
FIGURE 4. 6 SPECTRA AT 1450NM REGION	30
FIGURE 4. 7 SPECTRA AT 2270NM TO 2300NM REGION.....	30
FIGURE 4. 8 SECOND DERIVATIVE SPECTRA AT 1450NM REGION.....	31
FIGURE 4. 9 SECOND DERIVATIVE SPECTRA AT 2270NM TO 2300NM REGION	31
FIGURE 4. 10 LINEAR RELATIONSHIP OF THE ABSORBANCE OF SECOND DERIVATIVE SPECTRA AT 962NM OF RED WINES	32
FIGURE 4. 11 LINEAR RELATIONSHIP OF THE ABSORBANCE OF SECOND DERIVATIVE SPECTRA AT 962NM OF WHITE WINES	33
FIGURE 4. 12 LINEAR RELATIONSHIP OF THE ABSORBANCE OF SECOND DERIVATIVE SPECTRA AT 1412NM OF RED WINES AVERAGE SPECTRA	34
FIGURE 4. 13 LINEAR RELATIONSHIP OF THE ABSORBANCE OF SECOND DERIVATIVE SPECTRA AT 1462NM OF RED WINES AVERAGE SPECTRA	34
FIGURE 4. 14 LINEAR RELATIONSHIP OF THE ABSORBANCE OF RAW SPECTRA OF RED WINES AT 2268 NM.	35
FIGURE 4. 15 LINEAR RELATIONSHIP OF THE ABSORBANCE OF RAW SPECTRA OF RED WINES AT 2306 NM.	36
FIGURE 4. 16 SCORE PLOT OF PC1 AND PC2 OF THE WHITE WINE SAMPLES. NUMBERS REPRESENT THE TEMPERATURES	37
FIGURE 4. 17 EIGENVECTORS OF THE FIRST TWO PCs OF THE PCA FOR WHITE WINES	37
FIGURE 4.18 SCORE PLOT OF PC1 AND PC2 OF THE RED WINE SAMPLES. NUMBERS REPRESENT THE TEMPERATURES	38
FIGURE 4. 19 EIGENVECTORS OF THE FIRST TWO PCS OF THE PCA FOR THE RED WINES.....	38
FIGURE 4. 20 LINEAR RELATIONSHIP BETWEEN THE MEAN SCORE VALUES OF TEMPERATURE RELATED PC OF WHITE RED SAMPLES AND TEMPERATURE VARIATION.....	39
FIGURE 4. 21 LINEAR RELATIONSHIP BETWEEN THE MEAN SCORE VALUES OF TEMPERATURE RELATED PC OF WHITE WINE SAMPLES AND TEMPERATURE VARIATION	39
FIGURE 5. 1 VIS-NIR SPECTRA OF 6 RED AND 6 WHITE WINE SAMPLES AT 0.2 MM PATH LENGTH TRANSFLECTANCE MODE.....	44
FIGURE 5. 2 VIS -NIR SPECTRA OF 6 RED AND 6 WHITE WINE SAMPLES AT 0.4 MM TRANSFLECTANCE MODE	44
FIGURE 5. 3 VIS-NIR SPECTRA OF THE SAME SAMPLE AT THREE DIFFERENT PATH LENGTHS.....	45

FIGURE 5. 4 PCA SCORE PLOT OF THE PC1 AGAINST PC2	46
FIGURE 5. 5 PCA SCORE PLOT OF THE PC1 AGAINST PC3	47
FIGURE 6. 1 SECOND DERIVATIVE OF THE VIS-NIR SPECTRA OF AUSTRALIAN AND SPANISH TEMPRANILLO WINES	52
FIGURE 6. 2 SCORE PLOT OF THE FIRST TWO PRINCIPAL COMPONENTS OF AUSTRALIAN (A) AND SPANISH (S) TEMPRANILLO WINES USING VIS-NIR AFTER SNV AND SECOND DERIVATIVE PROCESSING	53
FIGURE 6. 3 EIGENVECTORS OF THE THREE FIRST PRINCIPAL COMPONENTS OF AUSTRALIAN AND SPANISH TEMPRANILLO WINES USING VIS-NIR AFTER SNV AND SECOND DERIVATIVE PROCESSING	54
FIGURE 6. 4 PARTIAL LEAST SQUARES SCORE PLOT OF THE FIRST TWO PRINCIPAL COMPONENTS OF AUSTRALIAN (A) AND SPANISH (S) TEMPRANILLO WINES USING VIS-NIR PRE-PROCESSED SPECTRA FOR THE CALIBRATION SET	57
FIGURE 7. 1 VIS -NIR RAW SPECTRA OF RIESLING WINES FROM AUSTRALIA, NEW ZEALAND AND EUROPE	61
FIGURE 7. 2 SNV AND 2 ND DERIVATIVE PROCESSED SPECTRA OF RIESLING WINES FROM AUSTRALIA, NEW ZEALAND AND EUROPE	61
FIGURE 7. 3 SCORE PLOT OF THE FIRST 3 PRINCIPAL COMPONENTS OF AUSTRALIAN (AUS), NEW ZEALAND (NZ) AND EUROPEAN (EUR) RIESLING WINES USING VIS-NIR PRE-PROCESSED SPECTRA	62
FIGURE 7. 4 EIGENVECTORS OF THE THREE FIRST PRINCIPAL COMPONENTS OF AUSTRALIAN, NEW ZEALAND AND EUROPEAN RIESLING WINES USING VIS-NIR PRE-PROCESSED SPECTRA	63
FIGURE 7. 5 SCORE PLOT OF THE FIRST 3 PRINCIPAL COMPONENTS OF AUSTRALIAN (AUS), AND EUROPEAN (EUR) RIESLING WINES USING VIS-NIR PRE-PROCESSED SPECTRA	64
FIGURE 7. 6 SCORE PLOT OF THE FIRST 3 PRINCIPAL COMPONENTS OF AUSTRALIAN (AUS) AND NEW ZEALAND (NZ) RIESLING WINES USING VIS-NIR PRE-PROCESSED SPECTRA	64
FIGURE 7. 7 SCORE PLOT OF THE FIRST 3 PRINCIPAL COMPONENTS OF NEW ZEALAND (NZ) AND EUROPEAN (EUR) RIESLING WINES USING VIS-NIR PRE-PROCESSED SPECTRA	65

List of Tables

TABLE 2.1 APPELLATION SYSTEMS OF THE MOST EUROPE WINE PRODUCING COUNTRIES (KOLPAN <i>ET AL.</i> 1996; MACNEIL 2001)	5
TABLE 2. 2 GEOGRAPHICAL CLASSIFICATION OF WINES USING MULTI-ELEMENT AND STABLE ISOTOPE RATIO.	7
TABLE 4. 1 WHITE WINE SAMPLES' CODE, VARIETY, CHEMICAL COMPOSITIONS AND THE CORRESPONDING STATISTICS OF SAMPLE ANALYZED.....	25
TABLE 4. 2 RED WINE SAMPLES' CODE, VARIETY, CHEMICAL COMPOSITIONS AND THE CORRESPONDING STATISTICS OF SAMPLE ANALYZED.....	26
TABLE 4. 3 STANDARD ERROR IN CROSS VALIDATION (SECV) OF PLS PREDICTION FOR CHEMICAL ANALYSIS PARAMTERS.....	41
TABLE 5. 1 SAMPLES' CODE, CHEMICAL COMPOSITIONS AND THE CORRESPONDING STATISTICS OF SAMPLE ANALYSED.....	43
TABLE 5. 2 THE STANDARD ERROR IN CROSS VALIDATION (SECV) OF THE PREDICTION MODELS FOR EACH PARAMETER AT DIFFERENT PATH LENGTH.....	48
TABLE 6. 1 VINTAGE AND ORIGIN OF COMMERCIAL TEMPRANILLO WINE SAMPLES ANALYSED	49
TABLE 6. 2 RANGE OF CHEMICAL COMPOSITION FOR THE AUSTRALIAN AND SPANISH WINE ANALYSED...	51
TABLE 6. 3 LDA CLASSIFICATION RESULTS OF AUSTRALIAN AND SPANISH TEMPRANILLO WINES USING VIS-NIR RAW SPECTRA BASED ON THE FIRST 3 PCs (98% OF THE TOTAL VARIATION)	55
TABLE 6. 4 LDA CLASSIFICATION RESULTS OF AUSTRALIAN AND SPANISH TEMPRANILLO WINES USING VIS-NIR PRE-PROCESSED SPECTRA BASED ON THE FIRST 3 PCs (77% OF THE TOTAL VARIATION) ..	55
TABLE 6. 5 LDA CLASSIFICATION RESULTS OF AUSTRALIAN AND SPANISH TEMPRANILLO WINES USING VIS-NIR PRE-PROCESSED SPECTRA BASED ON THE FIRST 9 PCs (95% OF THE TOTAL VARIATION) ..	56
TABLE 6. 6 DISCRIMINANT PARTIAL LEAST SQUARES (DPLS) CLASSIFICATION RESULTS OF AUSTRALIAN AND SPANISH TEMPRANILLO WINES USING VIS-NIR PRE-PROCESSED SPECTRA	58
TABLE 7. 1 VINTAGE AND ORIGIN OF RIESLING WINE SAMPLES ANALYZED	59
TABLE 7. 2 STATISTICS OF CHEMICAL COMPOSITION FOR RIESLING WINES FROM DIFFERENT GEOGRAPHICAL REGION	60
TABLE 7. 3 LDA CLASSIFICATION RESULTS OF AUSTRALIAN, NEW ZEALAND AND EUROPEAN RIESLING WINES USING VIS-NIR PRE-PROCESSED SPECTRA.....	66
TABLE 7. 4 LDA CLASSIFICATION RESULTS OF EACH TWO REGIONS OF AUSTRALIAN, NEW ZEALAND AND EUROPEAN RIESLING WINES USING VIS-NIR PRE-PROCESSED SPECTRA	66
TABLE 7. 5 DPLS CLASSIFICATION RESULTS OF AUSTRALIAN, NEW ZEALAND AND EUROPEAN RIESLING WINES USING VIS-NIR PRE-PROCESSED SPECTRA	67