CHARACTERIZATION OF SALA MANGO QUALITY ATTRIBUTES VIA VISIBLE AND NEAR INFRARED SPECTROSCOPY TECHNIQUES

OMMI KALSOM MARDZIAH BINTI YAHAYA

UNIVERSITI SAINS MALAYSIA 2015

CHARACTERIZATION OF SALA MANGO QUALITY ATTRIBUTES VIA VISIBLE AND NEAR INFRARED SPECTROSCOPY TECHNIQUES

by

OMMI KALSOM MARDZIAH BINTI YAHAYA

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

MAY 2015

ACKNOWLEDGMENTS

In the name of Allah, the most Gracious, the most Merciful. All Praises be to Allah, I am thankful for the strength and courage. He had granted me to complete this research. And I pray for peace and for blessings on all His noble Prophets and Messengers, and in particular on the last of them all, the blessed Prophet Muhammad.

First and foremost, I would like to convey my deepest gratitude to my supervisor and co-supervisor, Professor Dr Mohd Zubir bin MatJafri and Associate Professor Dr. Azlan Abdul Aziz for their supervision, valuable advice, and guidance from the very early stage of this research as well as giving me extraordinary experiences throughout the work. I am much indebted to both of you for using so much time to read this thesis and gave critical comments about it. You have been a tremendous mentor for me. Thank you for not giving up on me, words cannot express how grateful I am.

Many thanks go to my second co-supervisor, Dr. Ahmad Fairuz bin Omar for his crucial contribution to my study, which made him a backbone of this research and so to this thesis. He also provided me unflinching encouragement and support in various ways. His truly intuition has made him as a constant oasis of ideas and passion in this field, which exceptionally inspire and enrich my growth as a student and a researcher want to be. I have also benefited by advice and guidance from him relentlessly, which always kindly grant me his time, even for answering some of my unintelligent questions about this research and also checked my thesis chapter by chapter. I am indebted to him more than he knows.

I would also like to extend my appreciation to the lab assistants and technicians from School of Physics, especially Mr. Mohtar Sabidin who has given me full assistance in the utilisation of equipments in engineering physics laboratory. A special thanks to all administrative staffs, especially Ms. Salmah Zakaria and Mrs. Salmi Sallih for assisting me in administrative related issues throughout my PhD study in Universiti Sains Malaysia.

Special thanks to Federal Agriculture Marketing Authority (FAMA) negeri Perlis especially Mr. Faisal and the owner of the mango farm who have assisted me and collected the Sala mango fruits sample for my experiment.

It is a pleasure to pay tribute also to the following organizations that have contributed to the successful realization of thesis and funding me throughout my research:

- i. Department of Higher Education (MyPhD scholarship).
- ii. Research University Postgraduate Research Grant (Grant No. 1001/PFIZIK/846084).
- iii. Research University Grant (Grant No: 1001/PFIZIK/811220).

- iv. Fundamental Research Grant (Grant No: 203/PFIZIK/6711349).
- v. Islamic Development Bank, Jeddah.
- vi. Federal Agriculture Marketing Authority (FAMA).

I would like to convey my gratitude wholeheartedly to all my family members, who gave me inseparable support and prayers. To my mother, Siti Jalaha Bakar thank you for sincerely raised me with her caring and gently love. To my father, Yahaya bin Hussin, I know we didn't talk much about my study, but I know your prayers are always with me. To my only sister, Siti Fatimah Roqiah Yahaya, you are my best friend because always being supportive and gave positive comments for me and every time I feel like I am falling, you are always there to pick me up.

Last but not least, a special thanks to my fellow friends who have been there for me throughout the entire process, especially Mr Saumi Syahreza who spending time for collecting my sample in Perlis. And I would like to express my gratitude to Ummi Syuhada Osman whose also spending time to help me completed my experiments. To my only best friend, Nur Farida Saini thank you for spending sleepless night with me and for all the take-outs that you brought back for me. I am grateful to have you guys as friends. I would like to express my apology that I could not mention personally one by one.

TABLE OF CONTENTS

		Page
ACK	NOWLEDGMENTS	ii
TABI	LE OF CONTENTS	iv
LIST	OF TABLES	viii
LIST	OF FIGURES	X
LIST	OF SYMBOLS	XV
LIST	OF ABBREVIATIONS	xvi
LIST	OF PUBLICATIONS	xvii
ABST	`RAK	xviii
ABST	TRACT	XX
~~~		
CHA	PTER 1 - GENERAL INTRODUCTION TO THE RESEARCH	1
1.1	Defining Fruits Quality and Its Assessment Techniques	4
1.2	Principles of Spectroscopy and Its Application in Agriculture	6
1.3	Problem Statement	9
1.4	Research Objectives	10
1.5	Scope of the Study	10
1.6	Thesis Outline	11
CHAI APPR	PTER 2 - LITERATURE REVIEW ON SPECTROSCOPIC ROACHES IN FRUITS' QUALITY ANALYSIS	14
2.1	Fruit Physiology and Quality Attributes	15
	<ul> <li>2.1.1 Fruit Products and Standards</li> <li>2.1.2 Fruits Maturity and Ripeness</li> <li>2.1.3 Change in Sensory Properties During Ripening of Fruits</li> <li>2.1.4 Profile of Mangoes</li> </ul>	16 21 23 33
2.2	Non-spectroscopic Techniques for the Assessment of Qual Attributes	ity 37

2.3	Background and Principles of Vis/NIR 43		43
2.4	Fundan	nental Aspects of Spectroscopy Analysis	44
	2.4.1	Basic Concept of Vis/NIR spectroscopy	47
	2.4.2	Vis/NIR Instrumentation	49
	2.4.3	Fiber Optic Structure and Its Application in Spectroscopy Analysis	51
	2.4.4	Vis/NIR Spectroscopy as Non-destructive Techniques for Fruits Quality Assessment	58
2.5	Chemo	metrics Application in Fruit Analysis	63
	2.5.1	Spectral Data Pre-processing and Application	63
	2.5.2	Calibration Model for Quantitative Analysis	66
2.6	Models	Transfer	69
2.7	Simplif	fied Optical Fiber System for Spectroscopy Application	72
CHAI	PTER 3	-METHODOLOGY	75
3.1	Researc	ch Implication and Implementation	76
3.1 3.2	Researce Instrum	ch Implication and Implementation nental Measurement for Fruits Quality Attributes	76 79
3.1 3.2	Researce Instrum 3.2.1	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement	76 79 80
<ul><li>3.1</li><li>3.2</li></ul>	Researce Instrum 3.2.1 3.2.2	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement	76 79 80 83
3.1 3.2	Researce Instrum 3.2.1 3.2.2 3.2.3	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement	76 79 80 83 85
3.1 3.2	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation	76 79 80 83 85 87
<ul><li>3.1</li><li>3.2</li></ul>	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation 3.2.4.1 Preliminary Samples for Set 1: Sala Mango	76 79 80 83 85 87 88
<ul><li>3.1</li><li>3.2</li></ul>	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation 3.2.4.1 Preliminary Samples for Set 1: Sala Mango 3.2.4.2 Intensive Sample for Set 2: Sala Mango	76 79 80 83 85 87 88 90
<ul><li>3.1</li><li>3.2</li><li>3.3</li></ul>	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4 Vis/NII	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation 3.2.4.1 Preliminary Samples for Set 1: Sala Mango 3.2.4.2 Intensive Sample for Set 2: Sala Mango R Spectroscopic System	76 79 80 83 85 87 88 90 94
<ul><li>3.1</li><li>3.2</li><li>3.3</li></ul>	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4 Vis/NII 3.3.1	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation 3.2.4.1 Preliminary Samples for Set 1: Sala Mango 3.2.4.2 Intensive Sample for Set 2: Sala Mango R Spectroscopic System Jaz Spectrometer	76 79 80 83 85 87 88 90 94 95
<ul><li>3.1</li><li>3.2</li><li>3.3</li></ul>	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4 Vis/NII 3.3.1 3.3.2	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation 3.2.4.1 Preliminary Samples for Set 1: Sala Mango 3.2.4.2 Intensive Sample for Set 2: Sala Mango R Spectroscopic System Jaz Spectrometer QE 65000 Spectrometer	76 79 80 83 85 87 88 90 94 95 98
<ul><li>3.1</li><li>3.2</li><li>3.3</li></ul>	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4 Vis/NII 3.3.1 3.3.2 3.3.3	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation 3.2.4.1 Preliminary Samples for Set 1: Sala Mango 3.2.4.2 Intensive Sample for Set 2: Sala Mango R Spectroscopic System Jaz Spectrometer QE 65000 Spectrometer FieldSpec 3 Spectroradiometer	76 79 80 83 85 87 88 90 94 95 98 101
<ul><li>3.1</li><li>3.2</li><li>3.3</li><li>3.4</li></ul>	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4 Vis/NII 3.3.1 3.3.2 3.3.3 Spectra	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation 3.2.4.1 Preliminary Samples for Set 1: Sala Mango 3.2.4.2 Intensive Sample for Set 2: Sala Mango R Spectroscopic System Jaz Spectrometer QE 65000 Spectrometer FieldSpec 3 Spectroradiometer	<ul> <li>76</li> <li>79</li> <li>80</li> <li>83</li> <li>85</li> <li>87</li> <li>88</li> <li>90</li> <li>94</li> <li>95</li> <li>98</li> <li>101</li> <li>108</li> </ul>
<ul><li>3.1</li><li>3.2</li><li>3.3</li><li>3.4</li></ul>	Researce Instrum 3.2.1 3.2.2 3.2.3 3.2.4 Vis/NII 3.3.1 3.3.2 3.3.3 Spectra 3.4.1	ch Implication and Implementation nental Measurement for Fruits Quality Attributes Firmness Measurement Soluble Solids Content Measurement Acidity (pH) Measurement Sample Preparation 3.2.4.1 Preliminary Samples for Set 1: Sala Mango 3.2.4.2 Intensive Sample for Set 2: Sala Mango R Spectroscopic System Jaz Spectrometer QE 65000 Spectrometer FieldSpec 3 Spectroradiometer I Quantitative Analysis Spectral Pre-processing	<ul> <li>76</li> <li>79</li> <li>80</li> <li>83</li> <li>85</li> <li>87</li> <li>88</li> <li>90</li> <li>94</li> <li>95</li> <li>98</li> <li>101</li> <li>108</li> <li>108</li> </ul>

	3.4.3	Transfer	of Calibration Model	110
		3.4.3.1	Between Jaz Spectrometer and QE 65000 Spectrometer for Set 1	111
		3.4.3.2	Between QE 65000 Spectrometer and FieldSpec 3 Spectroradiometer for Set 2	112
3.5	Optica	ll Fiber Re	d-Green-Blue System	115
	3.5.1	Illuminat	ing Light Source and Sensor	116
	3.5.2 3.5.3	Experime	ed Optical Fiber RGB System ental Procedure for Simplified Optical Fiber Sensor ment	119
CHA	PTER 4	- RESUI	TS AND DISCUSSION	124
4.1	Non-d Mango	estructive by Vis/N	Measurement of Quality Attributes of Intact Sala IR Spectrometric Technique	125
	4.1.1	Characte Mangoes	rization of the Spectral Data Analysing on Sala	126
	4.1.2	Effect of Spectra I	Different Data Pre-Processing Techniques on Features	131
	4.1.3	Performa Wavelen	ance of Different Spectra Pre-Processing and oth Selection	140
		4.1.3.1	Firmness	141
		4.1.3.2	Soluble Solid Content	148
		4.1.3.3	Acidity	155
	4.1.4	Summar	y	167
4.2	Calibr Instrui	ation Tran nents usin	sfer of Intact Sala Mango between Different g Visible spectra	168
	4.2.1	Visible S	pectral Characterization	169
	4.2.2	The Proc	ess of Transfer Calibration Model between Diverse	173
		Instrume	nts	1,0
		4.2.2.1	Calibration Set 1: Between QE 65000 and Jaz	173
			spectrometer	
		4.2.2.2	Calibration Set 2: Between QE 65000 Spectrometer and FieldSpec 3 Spectroradiometer	174
	4.2.3	Performa	ince of Calibration and Prediction	175
		4.2.3.1	Performance of Direct Calibration Transfer for Set 1	176
		4.2.3.2	Performance of Direct Calibration Transfer for Set 2	181
	4.2.4	Summary	y	184

4.3	The Application of Red-Green-Blue Light Emitting Diodes in Measuring Mango Quality Attributes		186
	4.3.1 4.3.2	Simplified Optical Fiber Red–Green–Blue System (OF-RGB) Non-destructive Measurement of Intrinsic Quality Attributes via Optical Fiber Red–Green–Blue System (OF-RGB)	187 191
	4.3.3	Summary	200
CHA	PTER 5	5 - CONCLUSION AND FUTURE RESEARCH	204
5.1	Concl	usion	204
5.2	Future	Research	207
REFI	ERENC	ES	209
APPI	ENDIX	Α	240

## LIST OF TABLES

# External quality attribute of fruits and vegetables

Page

20

Table 2.2 Summary of desirable quality attributes for several 21 fruits collected from a European survey (Barreiro et al., 2004).

(United Nations, 2007).

Table 2.1

- Table 2.3 Summary of organic acids that appear in some fruits 24 (Sortwell et al., 1996).
- Table 2.4 Summary of total SSC and TA for different selected 26 fruits (Paul and Southgate, 1985; Kader, 1998; Kader 1999).
- Table 2.5 Percentage of water in some common raw fruits and 29 vegetables (Bastin, 2011).
- Specification of maturity for harvesting several Table 2.6 32 common fruits (Agritech, 2014).
- Table 2.7 Non-destructive techniques to measure quality 38 factors of horticultural produces (Renu, 2013).
- Table 3.1 Instrumental methods for determination of fruit 80 quality (Barrett et al., 2010).
- Table 3.2 Recommended tip sizes for firmness measurement 81 (Mitcham et al., 1996).
- Table 3.3 Specification of Atago Pal-3 Digital Refractometer 85 (Atago, 2009).
- Table 3.4 Specifications of ExStik PH100 pH meter (Extech 87 Instruments, 2008).
- Table 3.5 Characteristics of fruit samples used for preliminary 89 study.
- Table 3.6 90 Features of mangoes (Sala) used in the experiments.
- Table 3.7 Statistical properties of internal attributes (firmness, 91 SSC and pH) for mango.
- Table 3.8 Jaz spectrometer, QE 65000 spectrometer and 103 FieldSpec 3 Spectroradiometer specifications. (Ocean Optics, 2010).

Table 3.9	LED specifications (Avagotech, 2008).	120
Table 3.10	The specifications of TSL257 (TAOS Inc, 2007).	121
Table 3.11	The samples used in this experiment.	123
Table 4.1	Calibration and prediction results of firmness with different pre-processing techniques through reflectance and interactance measurements.	142
Table 4.2	Calibration and prediction results of SSC with different pre-processing techniques through reflectance and interactance measurements.	149
Table 4.3	Calibration and prediction results of pH with different pre-processing techniques through reflectance and interactance measurements.	155
Table 4.4	Calibration transfer performance and prediction accuracy, using QE 65000 (master) and Jaz (slave) for various wavelength selections.	178
Table 4.5	Calibration transfer performance and prediction accuracy using Jaz (master) and QE 65000 (slave) for various wavelength selections.	179
Table 4.6	Calibration transfer performance and prediction accuracy using QE 65000 (master) and FieldSpec 3 (slave) for various wavelength selections.	182
Table 4.7	Calibration transfer performance and prediction accuracy using FieldSpec 3 (master) and QE 65000 (slave) for various wavelength selections.	183
Table 4.8	Summary of results obtained from optical fiber sensor RGB systems.	196
Table 4.9	Summary of results obtained from measurement using QE 65000 spectrometer.	199
Table 4.10	Summary of results obtained from measurement using FieldSpec 3 spectroradiometer.	200

## LIST OF FIGURES

## Page

Figure 2.1	Fruit products that undergo several processing stages.	18
Figure 2.2	Standards implementation (Meza, 2005).	18
Figure 2.3	Stages of plant development (Watada et al., 1984).	22
Figure 2.4	Trends of mango cultivation area and production value in six different states of Malaysia in 2011 (Ali and Ali, 2013).	34
Figure 2.5	Value imports and exports of mangoes, 2000–2011 (Ali and Ali, 2013).	35
Figure 2.6	Mango specifications based on FAMA grading Index MS 885 (FAMA, 2008).	36
Figure 2.7	Interaction of radiation with matter (Nave, 2005).	45
Figure 2.8	Distribution of light on fruit.	46
Figure 2.9	Schematic of spectra structure correlation and absorption region of main compounds in coffee (Barbin <i>et al.</i> , 2014).	49
Figure 2.10	Basic structures of fiber optic layers (Mahdikhani and Bayati, 2009).	52
Figure 2.11	Schematic diagram of fiber optic sensor system.	56
Figure 2.12	Classification of multivariate data analysis technique for fruit quality evaluation (Elmasry <i>et al.</i> , 2012).	67
Figure 3.1	Complete empirical analyses for fruit quality assessment.	78
Figure 3.2	The firmness measurement of intact mango using Fruit Test Model FT penetrometer from Wagner Instruments (Wagner Instrument, 2008).	83
Figure 3.3	Relationship between the refractive index at 589.3 nm and the percentage of sucrose in a solution of water (Bumgarner and Kleinhenz, 2012).	84
Figure 3.4	Atago Pal-3 Digital Refractometer and materials needed for Brix measurement.	85

Figure 3.5	ExStik PH100 pH meter (Extech Instruments, 2008).	87
Figure 3.6	pH distributions of individual fruits.	89
Figure 3.7	Fruits were placed in the laboratory according to the corresponding indices based on FAMA grading index.	91
Figure 3.8	Intrinsic quality distribution of (a) Firmness (b) SSC (c) pH versus maturity index.	93-94
Figure 3.9	Jaz spectrometer used in the experiment of Sala mango of Set 1.	96
Figure 3.10	Experimental setup for reflectance measurement of mango samples.	98
Figure 3.11	The QE 65000 spectrometer used in the experiment of Sala mango of Set 1 and set 2 (Ocean Optics, 2010).	99
Figure 3.12	Experimental setup for interactance measurement of intact mango.	100
Figure 3.13	Calibration setup for interactance measurement.	101
Figure 3.14	FieldSpec 3 spectroradiometer used in the experiment of Sala mango of Set 2 (ASD Inc, 2010).	102
Figure 3.15	The experimental setup using FieldSpec 3 Spectroradiometer.	104
Figure 3.16	Reflectance spectroscopy measurements on intact mango using QE 65000 and FieldSpec 3 spectrometer.	105
Figure 3.17	Spectra suite software (Astro Physics, 2014).	106
Figure 3.18	RS ³ spectrum display (ASD Inc., 2010).	107
Figure 3.19	The illustration for forward and backward directions of calibration transfer. Forward and backward are transfers of calibration algorithm from the master instrument to a slave instrument for each direction.	112
Figure 3.20	The calibration transfer developed on master instrument (QE 65000 spectrometer) using Field Spec 3 spectroradiometer spectra as slave.	114
Figure 3.21	The calibration transfer developed on master instrument (FieldSpec 3 spectroradiometer) using QE 65000 spectrometer spectra as slave.	114

Figure 3.22	Current flows across LED circuit.	117
Figure 3.23	Circuit design of the op-amp current-to-voltage converter (transimpedance amplifier).	118
Figure 3.24	The single coloured of LED circuit system for Red, Green and Blue.	119
Figure 3.25	Experimental setup for the optical fiber RGB system.	123
Figure 4.1	Typical Vis/NIR spectra of (a) reflectance (b) interactance for index 1 (unripe) to 6 (ripe) of Sala mangoes measured by QE 65000 spectrometer.	130
Figure 4.2	Typical Vis/NIR reflectance spectra for index 1 (unripe) to 6 (ripe) of Sala mangoes measured by FieldSpec 3 spectroradiometer.	131
Figure 4.3	Vis/NIR spectra of intact mango samples for index of maturity 1 to 6 via reflectance measurement measured by QE 65000 spectrometer obtained from: (a) raw spectra, (b) smoothing with Savitzky-Golay and (c) first derivative.	134
Figure 4.4	Vis/NIR spectra of intact mango samples for index of maturity 1 to 6 via reflectance measurement measured by QE 65000 spectrometer obtained from: (a) SNV and (b) MSC.	135
Figure 4.5	Vis/NIR spectra of intact mango samples for index of maturity 1 to 6 via interactance measurement measured by QE 65000 spectrometer obtained from: (a) raw spectra, (b) smoothing with Savitzky-Golay and (c) first derivative.	136
Figure 4.6	Vis/NIR spectra of intact mango samples for index of maturity 1 to 6 via interactance measurement measured by QE 65000 spectrometer obtained from: (a) SNV and (b) MSC.	137
Figure 4.7	Vis/NIR spectra of intact mango samples for index of maturity 1 to 6 via reflectance measurement measured by FieldSpec 3 spectroradiometer obtained from: (a) raw spectra, (b) smoothing with Savitzky-Golay and (c) first derivative.	138
Figure 4.8	Vis/NIR spectra of intact mango samples for index of maturity 1 to 6 via reflectance measurement measured by FieldSpec 3 spectroradiometer obtained from: (a) SNV and (b) MSC.	139

Figure 4.9	Scatter plots of prediction of mango firmness based on MSC-MLR model produced from reflectance technique using QE 65000 spectrometer.	144
Figure 4.10	Scatter plots of prediction of mango firmness based on SNV-MLR model produced from interactance technique using QE 65000 spectrometer.	146
Figure 4.11	Scatter plots of prediction of mango firmness based on MSC-MLR model produced from reflectance technique using FieldSpec 3 spectroradiometer.	147
Figure 4.12	Scatter plots of prediction of mango sugar content based on MSC-MLR model produced from reflectance technique using QE 65000 spectrometer.	150
Figure 4.13	Scatter plots of prediction of mango sugar content based on SNV-MLR model produced from interactance technique using QE 65000 spectrometer.	152
Figure 4.14	Scatter plots of prediction of mango sugar content based on MLR model produced from reflectance technique using FieldSpec 3 spectroradiometer.	154
Figure 4.15	Scatter plots of prediction of mango pH based on first derivative pre-processing produced from reflectance technique using QE 65000 spectrometer.	157
Figure 4.16	Scatter plots of prediction of mango pH based on smoothing pre-processing produced from interactance technique using QE 65000 spectrometer.	159
Figure 4.17	Scatter plots of prediction of mango pH based on MSC pre-processing produced from reflectance technique using FieldSpec 3 spectroradiometer.	161
Figure 4.18	Scatter plots of coefficient of determination versus experimental number for (a) calibration and (b) prediction models using reflectance and interactance measurement techniques.	163
Figure 4.19	Reflectance spectrum of the same 'Sala' mango measured by three different spectrometers for unripe and ripe fruits before calibration transfer for (a) Set 1 and (b) Set 2.	171
Figure 4.20	Predicted versus actual pH of mangoes measured on QE 65000 spectrometer (master instrument) and spectra collected from slave instrument (Jaz	180

spectrometer).

Figure 4.21	Predicted versus actual pH of mangoes measured on Jaz spectrometer (master instrument) and spectra collected from slave instrument (QE 65000 spectrometer).	180
Figure 4.22	Predicted versus actual pH of mangoes measured on QE 65000 spectrometer (master instrument) and spectra collected from slave instrument (FieldSpec 3 spectrometer).	183
Figure 4.23	Predicted versus actual pH of mangoes measured on FieldSpec 3 spectrometer (master instrument) and spectra collected from slave instrument (QE 65000 spectrometer).	184
Figure 4.24	Relationship between coefficient of determination, $R^2$ and individual wavelengths for quantifying the (a) firmness and (b) SSC of mango in visible spectral range measured using QE 65000 spectrometer, FieldSpec 3 spectroradiometer and OF-RGB system.	189
Figure 4.25	Relationship between coefficient of determination, $R^2$ and individual wavelengths for quantifying the pH of mango in visible spectral range measured using QE 65000 spectrometer, FieldSpec 3 spectroradiometer and OF-RGB system.	190
Figure 4.26	Linear relationship between actual and calculated values for firmness measurement measured by OF-RGB system.	192
Figure 4.27	Linear relationship between actual and calculated values for SSC measurement measured by OF-RGB system.	192
Figure 4.28	Linear relationship between actual and calculated values for pH measurement measured by OF-RGB system.	193

## LIST OF SYMBOLS

3	Molar absorptivity
λ	Wavelength
°C	Degree Celsius
°F	Fahrenheit
С	Carbon
С	Molar concentration
g	Gram
Н	Hydrogen
h	Planck's constant
Κ	Kelvin
kgf	Kilogram force
l	Pathlength
0	Oxygen
R	Coefficient of correlation
$R^2$	Coefficient of determination
$R^2_{Cal}$	Coefficient of determination for calibration
R ² _{Pre}	Coefficient of determination for prediction
Si	Silicon
Т	Relaxation time

## LIST OF ABBREVIATIONS

А	Absorbance
ANN	Artificial neural network
API	Active Pharmaceutical Ingredient
ASD	Analytical Spectral Devices
В	Body reflectance
Car	Carotenoids
CCD	Charge coupled device
СТ	Computed tomography
DA	Diode array
FFT	Full Frame Transfer
FHWM	Full half width maximum
FT	Fourier Transform
HPLC	High performance liquid chromatography
IR	Infrared
LED	Light emitting diode
MLR	Multiple linear regression
MRI	Magnetic resonance imaging
MSC	Multiplicative scatter correction
NIR	Near infrared
NMR	Nuclear magnetic resonance
PCA	Partial component analysis
PCR	Partial component regression
PCS	Plastic clad silica
PLS	Partial least square
POF	Plastic fiber optic
RH	Relative humidity
RMSEC	Root mean square error of calibration
RMSECV	Root mean square error of cross-validation
RMSEP	Root mean square error of prediction
ТА	Titratable acidity
TC	Tissue culture
TE	Thermoelectric-cooled
SEP	Standard error of prediction
SSC	Soluble solid content
SG	Smoothing Savitzky-Golay
SNV	Standard normal variate
SWIR	Short wave infrared
UV	Ultraviolet
VIS	Visible
WT	Wavelet transform

## LIST OF PUBLICATIONS

- Yahaya, O. K. M., MatJafri, M. Z., Aziz, A. A. and Omar, A. F. (2014), "Nondestructive quality evaluation of fruit by color based on RGB LEDs system", 2nd International Conference on Electronic Design (ICED), August 19-21, Penang, Malaysia, pp. 230.
- Yahaya, O. K. M., MatJafri, M. Z., Aziz, A. A. and Omar, A. F., "Determining Sala mango qualities with the use of RGB images captured by a mobile phone", PERFIK 2014, National Physics Conference, 18-19 November, Kuala Lumpur, Malaysia.
- Yahaya, O. K. M., MatJafri, M. Z., Aziz, A. A. and Omar, A. F. (2015), "Visible spectroscopy calibration transfer model in determining pH of Sala mangoes. Forthcoming article of Journal of Instrumentation.

## PENCIRIAN SIFAT KUALITI MANGGA SALA MELALUI TEKNIK SPEKTROSKOPI VIS DAN NIR

### ABSTRAK

Pada umumnya, penanam buah-buahan dan pihak berkuasa pertanian tempatan semakin menyedari kepentingan untuk memperoleh buah-buahan yang berkualiti tinggi untuk memenuhi permintaan pasaran, khususnya pengguna. Oleh itu, penilaian kualiti buah segar menggunakan teknik optik melalui pengukuran spektroskopi telah dibangunkan untuk menilai dan mengukur kualiti mangga Sala tanpa memusnahkannya. Dalam kajian ini, beberapa pendekatan dengan pengukuran teknik yang berbeza (iaitu: pantulan dan interaksi) telah dilaksanakan dan kecekapannya dibandingkan dengan menggunakan Jaz, QE 65000 dan FieldSpec 3 spektrometer melalui spektrum yang boleh dilihat dan inframerah berserta sistem pengukuran monokromatik yang boleh dilihat untuk mengukur kekerasan, kandungan pepejal larut (SSC) dan keasidan (pH). Berdasarkan prestasi ramalan, MSC merupakan teknik pra-pemprosesan yang terbaik sebelum regresi linear (MLR) untuk mengukur kekerasan mangga menggunakan QE 65000 spektrometer melalui mod pantulan dengan pekali penentuan ( $\mathbb{R}^2$ ) dan punca min kuasa dua ralat ramalan (RMSEP) masing-masing pada 0.857 dan 1.005 kgf. Untuk kandungan pepejal larut (SSC), SNV merupakan teknik pra-pemprosesan yang terbaik dengan  $R^2 = 0.882$  dan RMSEP = 0.783 °Brix menggunakan QE 65000 spektrometer melalui mod interaksi. Untuk keasidan (pH),  $D^1$  merupakan teknik pra-pemprosesan yang terbaik dengan  $R^2$ = 0.879 dan RMSEP = 0.13 pH menggunakan QE 65000 spektrometer melalui mod pantulan. Hasil kajian menunjukkan bahawa prosedur pemindahan kalibrasi langsung telah berjaya dilaksanakan untuk meramalkan ketepatan pH buah mangga Sala antara instrument yang sama atau berbeza strukturnya. Akhir sekali, sistem yang dicadangkan menggunakan gentian optik Merah-Hijau-Biru telah membuktikan aplikasinya berguna dalam menentukan kualiti mangga Sala kerana ia telah menghasilkan keputusan yang setanding dengan spektrometer komersial, dengan kos yang jauh lebih rendah tanpa analisis yang kompleks.

## CHARACTERIZATION OF SALA MANGO QUALITY ATTRIBUTES VIA VISIBLE AND NEAR INFRARED SPECTROSCOPY TECHNIQUES

#### ABSTRACT

Fruits' growers and local agriculture authorities in general have increasingly realized the importance of acquiring fruits with high quality in order to satisfy the market demands, specifically the consumers. Therefore, quality evaluations of fresh fruits using optical technique through spectroscopy measurement have been developed to non-destructively assess and measure internal quality attributes of Sala mangoes. In this research, several approaches with different technique of measurements (i.e. reflectance and interactance) have been performed and their competences were compared using Jaz, QE 65000 and FieldSpec 3 spectrometers via visible and near infrared spectral as well as visible monochromatic measurement systems for measurement of firmness, soluble solid content (SSC) and acidity (pH). Judging from the prediction performance, MSC was found to be the best preprocessing technique prior to multiple linear regression (MLR) for firmness measurement using QE 65000 spectrometer via reflectance mode with a coefficient of determination  $(R^2)$  and root mean square error of prediction (RMSEP) at 0.857 and 1.005 kgf, respectively. For soluble solids content (SSC), SNV was found to be the best pre-processing technique with  $R^2 = 0.882$  and RMSEP = 0.783°Brix through measurement using QE 65000 spectrometer via interactance mode. For acidity (pH),  $D^1$  was found to be the best pre-processing technique with  $R^2 = 0.879$  and RMSEP = 0.13 pH through measurement using QE 65000 spectrometer via reflectance mode. The results also showed that the direct calibration transfer procedure has successfully implemented to predict the pH of intact Sala mango between similar and differently

structured instruments. Lastly, the proposed simplified optical fiber Red-Green-Blue system has proven its useful application in determining Sala mango qualities since it has produced comparable measurement accuracies with the commercial spectrometers, with much lower cost without complex analysis.

## CHAPTER 1 GENERAL INTRODUCTION TO THE RESEARCH

A fruit is defined in botany as the part of a plant that contains seeds. Fruits develop from the ovary of flower after pollination and subsequent fertilization; they then form a protective covering over the seeds. The Funk & Wagnalls Multimedia Encyclopedia defines a vegetable as the edible product of an herbaceous plant with a soft stem that is usually eaten with meat, fish, and other dishes (Ucdavis, 2012). However, fruits and vegetables can be considered as plants that are usually sweet and fleshy (fruit) or served with a savory dish (vegetable) from a culinary perspective. These culinary definitions do not always match the botanical classifications. For example, cucumbers, tomatoes, and eggplants are classified as vegetables, but are botanically considered as fruits (Smith et al., 1995). Almost all fruits generally have a common structure that comprises of a fruit wall that forms the edible portion of the fleshy part and a pericarp that encloses the seeds (Lifeofplant, 2014). The pericarp can be categorized in three distinct layers from the outer to the inner layer, namely, the exocarp, mesocarp, and endocarp. The exocarp is the outermost layer of the pericarp and forms the tough outer peel of the fruit. The mesocarp is the middle layer or pith of the pericarp located between the exocarp and endocarp, which is the part that is usually eaten. The endocarp is the inner layer of the pericarp that surrounds the thick or hard seed in stone fruits such as mangoes, peaches, and apricots.

Generally, fruits contain sugar (sweetness) and acid (sourness) that provide better flavor to consumers. Fruits can be categorized into several classifications that depend on their environmental conditions, chemical composition, and growing region as described as follows (Kader and Barrett, 2004):

- a. Berries are often associated with fruits that are typically small, juicy, and perishable. They are fleshy fruits that contain many seeds, such as tomatoes, oranges, watermelons, and grapes.
- b. Drupes or stone fruits are often associated with fruits with a hard pit that contains the seed, but the outer skin is soft. Examples of these fruits include peaches, cherries, coconuts, olives, and mangoes.
- c. Pomes are often associated with fruits that have thin skins such as apples, pears, and quince.
- d. Citrus fruits are often considered as acidic fruits. The seeds of these fruits are commonly covered with juicy or bitter fruit segments, such as in lemons, limes, oranges, mandarins, and grapefruits.
- e. Tropical fruits are often associated with fruits grown in warm climates. Examples if these fruits include coconuts, bananas, dates, guavas, mangoes, papayas, carambolas, rambutans, and pineapples.

Fruits are also important to accomplish fluid requirements and for human health since they have provided several essential sources such as vitamins, minerals, fiber, protein, antioxidants, and other substances (Kader, 2008). Therefore, the consumption of fruits with many nutrients can potentially lower the risks of related health problems such as heart disease, diabetes, obesity, and constipation. Consuming a sufficient amount of fruits and vegetables per daily intake can prevent the development of different diseases. Experts from World Health Organization (WHO) recommends that the daily intake of fruits and vegetables for a person should be at least 400 grams to ensure good nutrition and long term health conditions (Agudo, 2004). However, the intakes of fruits are significantly different for different countries and regions. Earlier studies note that fruit consumption can lower the risk of cardiovascular disease (CVD) based on the appropriate daily recommendation of constituents (Bazzano *et al.*, 2002; Liu *et al.*, 2000). Another related study conducted in Boston demonstrates that the intake of an adequate amount of fruit is associated with the reduction in lung cancer for some groups of people (Feskanich *et al.*, 2000).

Besides, eating fruits that have high water content can also generally fulfill nutrient recommendations and maintain the hydration process. This is because fruits contain a large amount of water in proportion to their weights, which makes up approximately 60 percent of the human body weight (Bastin, 1994). Water serves as a form of transportation because it sends oxygen, fat, and glucose to working muscles for their proper functioning, including the regulation of body temperature, food digestion, and waste product elimination (Srivastava, 2014).

Therefore, more attention should be focused on production and quality protection in marketing fresh fruits. Fruit quality can deteriorate when it reaches certain levels, which lead to losses that directly affect the fruits. Losses in fresh fruits between the harvest and postharvest times include several quantitative (e.g., physical injuries, packing material, and water loss) or qualitative factors (e.g., loss of flavor, color changes, and nutritive values). These factors influence fruit quality that can occur in the orchard, during transportation, preservation, storage, and other handling process before these fruits arrive at the market.

Fresh fruits that reach the market are usually incapable of maintaining their looks and conditions as those observed at orchards. They can exhibit different conditions because of the impact or bruises on their surfaces. Some fruit types also cannot maintain their original color and ripeness level during packaging and transporting. Therefore, the total time between harvesting and processing is an

3

important factor in preserving fruit quality and freshness (Kader and Barrett, 2004). The Food and Agriculture Organization (2014) reported that the major causes of food quality changes between production and consumption are insect growth; activities of microorganisms, bacteria, moisture, and rodents; chemical changes during processing or storage; and physical changes during storage because of the poor selection of packaging material. Thus, the assessment of quality parameters is necessary to ensure that poor quality produce is not sold to consumers, who should only purchase fruit that meet the quality standards (Butz *et al.*, 2005; Valero and Ruiz-Altisent, 2000).

#### 1.1 Defining Fruits Quality and Its Assessment Techniques

Most consumers prioritize the quality of fresh fruits before buying the produce from sellers. They also consider the freshness, taste, nutritional value, and non-contaminated conditions of products since buyers are now more interested in quality aspects of fresh fruits. By contrast, consumers tended to buy fruits in the past based mostly on a visual assessment of the product's external appearance such as the size, skin color, and surface. This approach often misleads sellers and buyers. Generally, consumers' perception of quality is significantly influenced by the product's intrinsic attributes and extrinsic indicators, as well as suggestions given by product sellers (Caswell *et al.*, 2002). Understanding consumer perceptions of quality and how they are constructed to improve the connection between supply and demand has been a recurrent theme in the fruit industry over the past few years (Mora *et al.*, 2011). Such perception is important in ensuring that products reach consumers with a high quality standard at an affordable price and provides consumer satisfaction. Increasing the awareness of consumers, particularly in the fruit quality, have driven

this industry to create more research on technology in determining the quality of fruit.

The determination of the internal qualities of fruits is an important indicator for harvesting, transportation, storage, and other handling mechanisms before a product is launched in the market (Lin and Ying, 2009). Thus, developing certain measurements is necessary to meet the demands in maintaining product quality and safety. Different efforts have been made to employ quality parameters for products to meet such expectations. These efforts are also focused on the development of instrumentation or systems for rapid and cost-effective detection that can assess quality attributes. For instance, Prof. Margarita Ruiz-Altisent, who is the director of the Physical Properties Laboratory, has been working on fruit quality assessment for a long time. She has also dealt with theoretical and practical topics that focus on quality specifications and instrumental measurement of fruit quality. Internal quality indices, such as maturity, firmness, soluble solids contents (SSC), and acidity (pH) are important attributes that are more difficult to evaluate than external quality attributes and these measurements require instruments that are commercially available. Nevertheless, assessing these internal quality attributes of fruits are intrinsically destructive and involve invasive measurement that require much time and work (Liu et al., 2010). Therefore, a simple, rapid, and highly accurate technique of quality measurement is needed without destroying these attributes. An increasing interest in employing a non-destructive technique for quality assessment and certifying high quality has been observed in the fruit industry. This condition can match consumer satisfaction and acceptance in making purchasing decisions of fresh fruits, which subsequently enhances the fruits industrial economy. Non-destructive techniques offer some advantages over destructive techniques.

5

The main advantages of non-destructive measurements are that they are repeatable in similar fruits and less variability as a result of random sampling of fruit measurements. This technique can be easily installed online, as well as fast and continuous evaluation on different parts of the same fruit without producing fruit waste and subsequent losses (Yurtlu, 2012). Considering these specialties, many studies on the non-destructive sensing technique have been conducted and implemented for assessing fruits internal quality attributes. For instance, spectroscopy measurement is the most practical and successful technique, which provides a higher chance of assessing quality attributes of fresh fruits such as firmness, soluble solids contents and acidity.

Spectroscopy analysis provides comprehensive information on a chemical, physical, and biological sample (Butz *et al.*, 2005) which proven useful in research laboratory. This technology has been widely and effectively used in different fields of research and application utilities such as food, agricultural, chemical, medical, and pharmaceutical industries (McClure, 2003). In fresh fruits quality assessment, spectroscopy has recently gained a remarkable increase in attention.

#### **1.2** Principles of Spectroscopy and Its Application in Agriculture

Spectroscopy is used in optical analysis to deal with the absorption, emission, or scattering of electromagnetic radiation with matter. Recently, this definition has been expanded to include the study of the interactions of different types of electromagnetic radiation between particles such as electrons, protons, or ions (Stoner, 2014). Spectroscopic techniques are widely used analytical methods in the broad area of science. Each type of spectroscopy provides a different picture and characteristic of matter in the spectrum. Spectrum is simple chart or graph that shows

the variation in intensity of the radiation as a function of the frequency or wavelength (wavelength dependent) (Fusina, 2009).

Different regions in the electromagnetic spectrum such as X-ray radiation, ultraviolet (UV), visible (Vis), and infrared (IR) can be used to interact with matter. The applications of spectroscopy can be widely applied in food and agriculture products particularly in fruits. Several techniques that are normally used are based on solvent extraction, followed by other laboratory procedures that often involve laborious and difficult processing for samples (Munawar, 2014). These techniques are also time consuming and destructive. Therefore, non-destructive spectroscopy techniques are established as an alternative technique for the determination of chemical constituents and quality parameters in overcoming existing destructive technique. The integration of spectroscopy instruments with optical fiber probes provides additional advantages in producing a powerful tool for this application purpose. Interestingly, this combination provides a flexible solution for an adequate optical interface between the spectroscopic instrument and sample to be interrogated (Utzinger and Richards-Kortum, 2003). Upon this inspiration, the research examines on the same concept of measurement techniques to measure and quantify fruit quality attributes. In order to achieve that, it is essential to understand on the phenomenon associated with this area of study which is bounded by the fundamental optical nature.

The spectroscopy technique is obtaining more attention, especially in the field of postharvest quality assessment, because it permits non-invasive analysis. This technique covers a sizeable fraction of the electromagnetic spectrum and can be divided into broad spectral regions: The UV region with wavelengths ranging from 200 nm to 400 nm, VIS region with wavelengths between 380 and 750 nm, and near infrared (NIR) region with wavelengths between 750 and 2500 nm. More importantly, the spectroscopy technique in these spectra regions are rapid, chemical free, and less expensive because they do not require sample processing and obtained information extensively used to detect the chemical composition of food materials (Jing *et al.*, 2010; Santos *et al.*, 2012). This technique is comparable with the available measurement that is often performed in assessing internal quality attributes through different physical techniques (Carlini *et al.*, 2000). The ranges of different spectroscopic techniques are significantly important because the comprehensive information can be obtained from these specific ranges which provide the characteristics and descriptions of the biochemical composition of a sample. For example, if the sample is illuminated with an appropriate wavelength range in the electromagnetic spectrum, certain wavelengths are absorbed and the absorption spectrum can be recorded or conversely, reflected (Butz *et al.*, 2005).

The measurement modes that are usually used in spectroscopy analysis for predicting the quality attributes (i.e. firmness, soluble solids content, and pH) of intact fruits are reflectance, interactance, and transmission. The present study explores the existing techniques with the use of various instrumentations and different statistical analysis, as well as the development of simplified optical instruments for biochemical interpretation. It also introduces new statistical analysis for predicting quality parameter of fruits which is calibration transfer models using direct transfer method for differently structure of spectrometers.

8

#### **1.3 Problem Statement**

The quality of fresh fruits is an important issue worldwide because it is difficult to describe objectively. Consumers have the right to be concerned about quality seals and trust mark on fruits based on sensory aspects such as the shape, size, colour, texture, firmness, and external defects. Thus, sorting and grading the fresh products based on their quality to ensure and maintain the supply chain of acceptable products is essential. FAMA was established as a local organization that is responsible for standardizing fruit quality based merely on their external properties to identify the levels of quality in a commodity for marketing fresh fruit products. Hence, a comprehensive research is needed to examine on the reliability of spectroscopic techniques in measuring fruits' quality.

Here, the non-destructive technique is introduced in this research to quantitatively evaluate fruit quality attributes by measuring firmness, soluble solid content (SSC), and acidity (pH). The main focuses are on investigating several measuring techniques, different statistical analyses, and regression analyses to produce the best correlation results between fruit spectral data and physiological indices (i.e., firmness, SSC, and pH). The possibility of applying these techniques and analyses on spectral data measured using different instrumentations can demonstrate their strength and potential in reducing some of the measurement deficiencies in determining fruit quality attributes and uncover the effective technique in performing optical biophysics analysis. This research also demonstrates the applicability of simple calibration transfer procedures between two similar and two dissimilar structured spectrometers. The main idea is to show the efficiency of different spectrometers in measuring the internal quality of fruits by applying similar calibration algorithms through direct calibration transfer. The research will also

9

present a novel approach for measuring fruits quality attributes through simplified RGB optical fiber sensor system. The methodology involved in this research is considerably important because the perfection of these techniques should be practically applicable for fruits industries.

#### **1.4 Research Objectives**

Thus, the following specific objectives are derived.

- a) To introduce the simplified RGB optical fiber system for the non-destructive measurement of mango quality attributes.
- b) To evaluate the feasibility of Vis/NIR spectroscopy in determining quality attributes of intact mangoes (i.e. firmness (kgf), SSC (^oBrix), and acidity (pH)) at different ripening stages using different types of spectrometers.
- c) To compare the efficiency of different spectra pre-processing techniques (i.e. SG, first derivative, SNV and MSC) prior to the multivariate calibration model (MLR) in the measurement of mango qualities.
- d) To demonstrate the ability of calibration transfer procedures for predicting the acidity of mangoes using different spectroscopic instrumentation.

#### **1.5** Scope of the Study

For this study, Sala mango was selected as research samples since it is Malaysian local fruit. Sala mango is easy to find as there are many mango farms especially in Perlis and there are high demand by Malaysian fresh market and industry. The fruit samples in this research were taken according to FAMA grading indexes with the main purpose to have a maximum possible range of internal quality attributes (i.e. firmness, SSC, pH). For this reason, in this research, other variability that may exist in fruit ripening condition due to differences in botanical approaches are not specifically taken into consideration. At the heart of this research, the nondestructive spectroscopy research was conducted to perform the comparative study between several instrument configurations and sensitivities using different measurement probes and techniques through diverse chemometric techniques. Moreover, this study has also developed and implements new optical fiber system as an alternative to the existing spectroscopy system.

#### **1.6 Thesis Outline**

This thesis structured in five chapters. Chapter 1 expressed a brief explanation of the research that includes meaning of fruit and its quality definitions. This chapter also elaborates some basic concepts of spectroscopy along with its application in agriculture, especially for quality attributes evaluation.

Chapter 2 elaborates on the details concept of fruits quality assurance from physiological and consumers point of views and defined the important fruits' parameters associated with it. On the other hand this chapter reviews recent literatures on non-destructive spectroscopic or non spectroscopic techniques used to evaluate the quality attributes of food, particularly fruits products. This chapter also reviews the application of different spectrometers, measurement methodologies, statistical analyses, and spectral pre-processing methods, as well as the development of simplified optical system based on monochromatic light sources and photo detectors. This chapter discussed topics specifically catered to support the research methods and findings molded by the objectives of this research. Chapter 3 describes the stages of implementation that have been used to complete the entire experiment. This chapter also presents the flow of the research methodology and its implementations. The chapter includes with the introduction of the instrument used in this research, sample characteristics, its preparation, spectroscopic instrumentations and the development of a monochromatic sensory system using LEDs as optical components. The method of using spectroscopic measurements has been implemented using two distinctive approached in achieving the research objectives. First is using instrumentations from Ocean Optics and Analytical Spectral Devices (ASD) for the application of various chemometric analysis. Second, this section introduced new approaches for predicting fruits quality parameter by generating calibration algorithm from one instrument to another.

The results obtained from the whole experiment are discussed in Chapter 4. Chapter 4 is separated into three distinct parts. First part is devoted to the evaluation of the internal quality attributes conducted on Sala mangoes using Vis/ NIR spectroscopy. This part focuses on the comparisons among different spectra preprocessing techniques that include the used of smoothing, first derivative, multiplicative scatter correction (MSC), and standard normal variate (SNV) prior to the prediction model development. The model precision obtained from these Vis/NIR spectra is then compared for each reflectance and interactance mode. Second part discusses a novel direct transfer procedure performed between a Jaz & QE 65000 spectrometer and QE 65000 & FieldSpec 3 spectroradiometer. This analysis was conducted using a visible spectral range only to predict the pH of mangoes. Third part presents the development of an optical fiber sensor using a LEDs system in assessing the internal quality of fruits for firmness, SSC and pH parameters. This novel optical component designed for spectroscopy analysis was compared with the result obtained from commercial spectroscopic measurement using a QE 65000 spectrometer and FieldSpec 3 spectroradiometer within the visible spectra.

Chapter 5 presents the general conclusion for all contents of different works that answer the objectives and recommendations as determined from this study.

## CHAPTER 2 LITERATURE REVIEW ON SPECTROSCOPIC APPROACHES IN FRUITS' QUALITY ANALYSIS

Fruit quality and safety are still recognized as an important topic throughout the world, especially in the fruit production and marketing process that are often related to public health and social progress. The words "quality" and "safety" have different meanings and aspects that depend on fruit classification, target market, criteria, and application (Alander *et al.*, 2013). Fruit quality is usually evaluated by consumers, traders, processors, distributors, and producers on the basis of certain characteristics to ensure product quality. Quality can be simply described as the absence of defects or degree of excellence or superiority. Kader (1999) defines the quality of fresh fruits as a combination of attributes, properties, or characteristics that provides commodity value in terms of human food. Quality has also been defined by several researchers as follows: value (Abbott, 1955; Feigenbaum, 1951), conformance to specifications (Gilmore, 1974; Levitt, 1972), conformance to requirements (Crosby, 1979), fitness for use (Juran, 1988), and meeting and/or exceeding customers' expectations (Grönroos, 1983; Parasuraman et al., 1985). While, the International Organization of Standardization (ISO) defines food quality as "the totality of features and characteristics of a product or service that bear on its ability to satisfy stated or implied needs" (ISO 8402) (Becker, 2000), which is accepted by most people coming from different backgrounds and working in the fruit industry, politics, and sciences. However, consumers' trust on product quality has recently decreased because of the their awareness on the poor quality of fruit products in the market. They have become more health conscious, demanding, and willing to pay a high price for the highest quality of fruits (Alander et al., 2013).

Consumers are more interested in the nutritional quality and fruit taste than its appearance. The quality of fresh fruits normally changes when it moves from the harvest to the consumer. The word quality can be used differently in many ways in defining fresh fruits. For example, these terms include market quality, utilization quality, sensory quality, nutritional quality, ecological quality, external and internal quality, as well as shipping quality. Most of these terms are applied to describe the quality of products which usually mean different things to different customer groups.

Hence, this chapter is catered to describe the concept of fruits quality assurance from physiological and consumer preferences point of view. This chapter also elaborates on different important attributes commonly associated with fruits quality and existing non-spectroscopic measurement techniques. On the other hand this chapter will explain on the theory of spectroscopy as well as the existing spectroscopic technique in the measurement and analysis of fruits quality attributes.

#### 2.1 Fruit Physiology and Quality Attributes

Customers who buy fruit products have the right to obtain a safe product for their consumption. Sometimes, fruits can have good quality just based on its appearance but is actually unsafe because it is contaminated with bacteria, fungi, yeast, moulds, and spoilage that are difficult to detect directly. These factors can contribute to illnesses or serious injuries either directly or indirectly. Thus, fruit safety is the most important component of quality to prevent health problems related to consumers. The World Health Organization (WHO) and Codex Alimentarius Commission have defined fruit safety as the assurance that a product does not cause danger to the consumer when it is prepared or consumed according to its intended use (Codex AlimenC, 2003). Therefore, a systematic approach and comprehensive risk assessment of fruit operations should be adequately performed by producers and handlers. They also need to implement procedures to diminish the potential exposure of consumers to hazards (Rushing, 2010). Good Agricultural Practices and Good Manufacturing Practices regulations are used during the growing, harvesting, processing, storing, packing, and shipping of fruits and vegetables to prevent or minimize the occurrence of hazards or injuries (Rushing, 2010). These management practices are important in maintaining the highest level of product quality and assure safety. Fruit safety and quality assurance generally play an important role in fresh products because once the safety or quality of product decreases, it is difficult to restore.

#### 2.1.1 Fruit Products and Standards

In this industry, fruit products can be categorized according two major uses, namely, fresh market or processing. Fruits can be used in making varieties of products, but some of these fruits harvested for fresh use that do not exceed quality standards should be sold for processing (Lucier *et al.*, 2006). Fruit products are shown in Figure 2.1, where they undergo several processing stages such as whole fruit, pulp, and extraction. Most people consume fruits in processed form as it is more convenient when selecting the products. A survey in the U.S. from 2000 to 2004 shows that among fruits, approximately 60 percent of non-citrus production moves into processing channels, whereas over 70 percent of citrus production is processed and consumed as juice; lower vegetable production also goes into processing that accounts for approximately 50 percent of the total output (Lucier *et al.*, 2006). Food standards consist of precise requirements, specifications, guidelines, or characteristics that can be used to define product quality. These standards function

as the main reference that can be the basis for business transactions and disputes to be settled by regulatory authorities if the transaction is not completed successfully (Rushing, 2010). Having a standard and grade for a common language in business organizations is important to have uniformity in determining the quality of fresh products. Standards can be set by different entities such as governments, the industry itself, producers, buyers, or retailers; however, many standards are also set by nongovernmental organizations (Cuffaro and Giacinto, 2011; Voort et al., 2007). They form a coalition that sets standards to comply with the proper criteria in determining quality products. The Economic Commission on Europe of the United Nations (UN-ECE) has drawn up quality grades and standards to facilitate and regulate national and international trade. This standard is used by different countries as a basis for their national trade as shown in Figure 2.2. Product quality is usually based on the subjective assessment that gives priority on the external properties which can be done by manual inspection and a grading process. Similarly to Malaysia, the quality standards have been set by the Federal Agricultural Marketing Authority (FAMA) also focus on the external attribute of the fruits such as size (weight), color, shape, and absence of defect on the fruits.



Figure 2.1 Fruit products that undergo several processing stages.



Figure 2.2 Standards implementation (Meza, 2005).

Besides, the UN-ECE has established the official standards for fresh fruits with code E.91.II.E.42 that every product in the market has to comply with to improve the globalization of the fresh produce market. The quality attributes that are standardized in this regulatory body are based on some specifications that can be measured directly, such as the size, shape, and presence of external defects or decays. However, other properties such as color distribution of fruits skin and occurrence of off-shapes (subjective judgment) can also be associated with this rule. However, this regulation is invalid for the quality properties that cannot be measured with definite procedures. Thus, all these situations have brought the fresh market to a point where many fruits do not exceed consumer's quality satisfactions. For example, in many cases of beautiful fruits such as peaches and pears are inedible and tasteless, which are also similar to mealy apples (Barreiro et al., 2004). For that reason, most climacteric and citrus fruits such as mangoes and oranges, use "degreening" treatment for the ripening process with controlled conditions to improve the external skin color and taste of fruits that suitable for fresh market value. Calcium carbide and ethylene treatment are also usually applied to these fruits to break down the green chlorophyll pigment in the exterior part of the peel and allow the yellow or orange carotenoid pigments to be expressed. The utilization of these techniques causes the fruits less amount of sugar content or become completely non-existent. Thus, growers and distributors are now developing specifications beyond the legal quality by summarizing the relevant intrinsic properties that the consumer requires, such as firmness, sugar and acid contents, as well as aroma (i.e., juice content has been used as a standard measurement). There are diverse components of quality attributes that are used to evaluate fruits. The quality attributes of fruits can be divided into three classes according to their types of properties and measurement technique that are being used to obtain high quality standard. These external attributes and internal attributes are shown in Table 2.1. Both combinations can determine the acceptability of a product.

Class of attribute	Quality attributes	Measurement of quality attributes
External	Appearance (sight) Feel (touch) Defects	<ul> <li>i) Visual evaluation of size, shape, absence of defects, gloss and colour</li> <li>ii) Size and shape: grade standards</li> <li>iii) Color: indicator of maturity (can be accompanied by visual guides, spectrometers and colorimeters)</li> <li>i) Manual evaluation of firmness and texture (can be measured by mechanical means</li> <li>i) Visual evaluation of absence of defects due to the measured by mechanical means</li> </ul>
		deterioration of color (can be measured by mechanical methods like ultrasound)
Internal	Odor or aroma	<ul> <li>i) Mostly qualitative and subjective evaluation by smelling.</li> <li>ii) Can be done by technical methods (e.g. gas chromatography/mass spectrometers)</li> </ul>
	Taste or flavour	<ul><li>i) Oral tasting (sweetness, bitterness, sourness, astringent and saltiness)</li><li>ii) Technical quantification of taste compounds (e.g. liquid and gas chromatography)</li></ul>
	Texture	i) Includes tenderness, firmness, crispness, crunchiness, chewiness, fibrousnesses (can be measured by applying force to the food; additionally, textural characteristics are evaluated as "mouthfeel")
Hidden	Wholesomeness	<ul> <li>i) Wholesomeness is difficult to measure objectively, but often taken into account in the grading and pricing the produce</li> <li>ii) It can be described as "freshness" produce</li> <li>iii) It also has a "sanitary" component (how clean /hygienic the product is)</li> </ul>
	Nutritive value	<ul> <li>i) Nutritive value is related to the presence and levels of components that support life.</li> <li>ii) Content of nutrients such as fat, carbohydrates, protein as well as essential vitamins, minerals and other substances are important and influence human wellbeing.</li> </ul>
	Safety	<ul> <li>i) Can be measured through the examination of food items with regard to their pathogenic microbial load, content of chemical contaminants or the presence of physical foreign matter in the produce.</li> </ul>

Table 2.1 External quality attribute of fruits and vegetables (United Nations, 2007).Class ofOuality attributesMeasurement of guality attributes

However, the most relevant quality attributes for different fruits collected from a survey in the European Project at FAIR CT 95 0302 with a focus on "Mealiness in fruits" are summarized in Table 2.2. This survey was participated in by 818 consumers, 77 producers, and 26 warehousemen. It was collected from other parallel sources of information. The results in all categories show that internal properties such as firmness or taste contribute to the most significant quality attributes. These results also consider that other important quality attributes such as size, shape, and cleanness are already met (Barreiro *et al.*, 2004). This survey also indicates the prospect of developing instrumentation to measure the quality attribute of fresh fruits that can be used to define consumer choices more clearly. Thus, the properties that consumers relate the perception of quality when eating fresh fruits are indeed internal quality properties' of the product itself. This condition has opened the possibility for analyzing these internal properties and exploring its instrumentations (Barreiro *et al.*, 2004). In order to supply best quality of fruits, the sellers should have clear knowledge on fruit maturation and ripening so that proper decisions regarding fruit handling practices will be concerned.

Type of fruits	Most relevant quality	Second	Third
	attributes		
Apple	Firmness/texture	Bruises	Sugar and acidity
Pear	Firmness	Sugar and acidity	Bruises
Peach	Firmness	Sugar and acidity	Bruises
Apricot	Firmness	Sugar	Colour
Tomato	Colour	Firmness	Sugar and acidity
Melon	Sugar	Colour	-
Citrus	Rots-molds	Blemishes/bruises	Sugar and acidity
Citrus	Rots-molds	Blemishes/bruises	Sugar and acidity

**Table 2.2** Summary of desirable quality attributes for several fruits collected from a European survey (Barreiro *et al.*, 2004).

#### 2.1.2 Fruits Maturity and Ripeness

The words "mature" and "ripe" are always used in describing fruits. In simple definition, mature is defined as "having completed natural growth and development", whereas ripe has several meanings such as (a) having undergone maturation and (b)

having attained a final or desired state (Reid, 2002). Mature and ripe are generally considered to be distinct terms for different stages of fruit and vegetable development as shown in Figure 2.3. Besides, most postharvest technologists define maturity as the level at which fruits and vegetables have reached full development after harvesting and postharvest handling (including ripening where required) (Reid, 2002). The quality, potential shelf-life, and consumer acceptance of fruits and vegetables can also be determined (Crisosto *et al.*, 1995; Singh and Khan, 2010).



Figure 2.3 Stages of plant development (Watada et al., 1984).

Ripeness is the process by which fruits attain their desirable flavor, quality, color, and other sensory properties after transformation occurs from the unripe (mature) to ripe stage (Perotti *et al.*, 2014). Fruits are frequently picked at an early stage to improve handling quality, although physiological and sensory properties changes with the ripening process. (Usenik *et al.*, 2014). Immature fruit do not acquire full flavor and aroma, lack a normal Brix ratio, and will definitely never attain superior eating quality (Tromp, 2005). The fruit is generally developed during ripening with changes in the sensory properties such as taste, color, and sweetness that can make fruits tasty and attractive to eat.

#### 2.1.3 Change in Sensory Properties During Ripening of Fruits

Sensory evaluation analyses measure the interaction of fruits with the senses and human responses to fruit properties. Sensory analysis was first introduced by the US government during and after World War II to improve the quality of food prepared for soldiers (Azodanlou, 2001). This approach was recognized to set up values of acceptance for any given food to maintain their good eating quality and not merely by identifying its nutritional content. Thus, some of the primary sensory properties that identify the indicator for consumer preference and acceptance are described below.

- a. Aroma: To determine the ripeness of a fruit when it reaches the maturity stage after being picked. A bitter and astringent compound begins to emerge but not frequently. It then usually diminishes with the ripening because these aromas are produced to discourage animals or microorganisms from eating the fruit before its seed is ready (Hurley, 2014). Each fruit type has different aromatic characteristics and has distinctive aromas that depend on the combination of concentration and volatile compounds (El Hadi *et al.*, 2013). Aroma is one of the most important fruit characteristics in determining consumer perception and acceptability of the produce.
- b. Taste: Taste is expressed in terms of sweetness and sourness or acidity. It indicates the information on ripeness and eating quality. Sweetness can be determined by the concentration of predominant sugars in fruits. Fructose, sucrose, and glucose are three types of sugars in products that affect taste perception. These sugars are ranked in relation to sucrose in the following order of sweetness: fructose (1.2) > sucrose (1.0) > glucose (0.64) (Kader, 2008).

23

- i. Sugar content also has the same meaning with total soluble solids or SSC that can be easily measured using a refractometer in terms of °Brix. However, complicated procedures are needed for the quantification of individual sugars. SSC relates to sweetness in some fruits such as oranges, whereas the relationship is non-linear other fruits such as tomatoes and mangoes (Baldwin *et al.*, 2014, Malundo *et al.*, 2001).
- ii. Sourness or acidity is determined by the concentration of predominant organic acids with a ranking in relation to citric acid in the following order of sourness: citric (1.0) > malic (0.9) > tartaric (0.8) (Kader , 2008). However, other acids such as amino, fumaric, and ascorbic acids can also contribute to the sourness content. For example, citric acid is normally contained in citrus fruits and tomatoes, tartaric acid is contained in grapes, and malic acid is contained in apples; but some fruits such as melons and bananas have very little natural acid (Wyllie *et al.*, 1995). Table 2.3 lists the predominant acids contained in selected fruits. Different acids can significantly influence the sourness perception that depends on their chemical structure.

Type of fruits	Predominant Acid	Secondary Acids
Apple	Malic acid (95%*)	Tartaric acid, Fumaric acid
Grape	Malic acid (60%*)	Tartaric acid
Grapefruit	Citric acid	Malic acid
Guava	Citric acid	Malic acid
Mango	Citric acid	Malic acid, Tartaric acid
Orange	Citric acid	Malic acid
Peach	Malic acid (73%*)	Citric acid
Pear	Malic acid (77%*)	Citric acid
Pineapple	Citric acid	Malic acid
Strawberry	Citric acid	Malic acid, Tartaric acid
Tamarind	Tartaric acid	Citric acid, Malic acid
Watermelon	Malic acid (99%*)	Fumaric acid

 Table 2.3 Summary of organic acids that appear in some fruits (Sortwell *et al.*, 1996).

*% of the total acid in the fruit