

## CONTENTS

<b>ABSTRACT</b>	ii
<b>ABSTRAK</b>	iii
<b>ACKNOWLEDGEMENT</b>	iv
<b>CONTENTS</b>	v
<b>LIST OF TABLES</b>	ix
<b>LIST OF FIGURES</b>	xi
<b>LIST OF SYMBOLS AND ABBREVIATIONS</b>	xv
<b>LIST OF FORMULA SYMBOLS</b>	xviii

### **CHAPTER 1 INTRODUCTION**

1.1	General Overview	1
1.2	Problem Statement	4
1.3	Research Objectives	7
1.4	Factors Affecting Formaldehyde Emission	8
1.5	Methodologies of Formaldehyde Determination	11
1.6	Formaldehyde Minimisation Solutions	13
1.7	Summary	14

### **CHAPTER 2 LITERATURE REVIEW**

2.1	Moisture Content and Formaldehyde Emission	15
2.2	Wood Species and Formaldehyde Emission	17
2.3	Formaldehyde Evaluation Methodology	20
2.4	Minimisation of Formaldehyde Emission	24

## **CHAPTER 3      METHODOLOGY**

3.1	Chemical and Reagents	27
3.2	Apparatus and Instruments	27
3.3	Wood Material and Preparation of Plywood Panels	28
3.3.1	Sample Preparation by Using Different Moisture Content Veneers	29
3.3.2	Sample Preparation by using Different Timber Wood Species	31
3.4	General Procedure for Formaldehyde Determination	33
3.4.1	Desiccator-Chromotropic Acid (DC-CA) Method	34
3.4.2	Desiccator-Acetyl Acetone (DC-AA) Method	37
3.4.3	Small Chamber-Chromotropic Acid (SC-CA) Method	39
3.4.4	Liquid-Liquid Extraction (LLE) Method	42
3.4.5	Solid Phase Micro-Extraction (SPME) Method	44
3.5	Methodology for Minimisation of Formaldehyde Emission	47
3.5.1	Minimisation by Pre-treatment -Veneer Thickness Control	47
3.5.2	Minimisation by Post Treatment - Chemical Scavenging	48

## **CHAPTER 4      RESULTS & DISCUSSION**

4.1	The Effect of the Variation of Moisture Content on Formaldehyde Emission	49
4.1.1	Results of Formaldehyde Emission with Changes in Moisture Content	50
4.1.2	Discussion of Formaldehyde Emission with Changes in Moisture Content	55

4.2	The Effect of the Variation of Wood Species on Formaldehyde Emission	58
4.2.1	Results of Formaldehyde Emission with Changes in Woody Colour	59
4.2.2	Result of Formaldehyde Emission with Changes in Woody pH	64
4.2.3	Result of Formaldehyde Emission with Changes in Woody Porosity	67
4.2.4	Discussion of Formaldehyde Emission with Changes in Woody Colour	70
4.2.5	Discussion of Formaldehyde Emission with Changes in Woody pH	72
4.2.6	Discussion of Formaldehyde Emission with Changes in Woody Porosity	75
4.3	Relationship of Evaluation Methodology to Formaldehyde Emission	78
4.3.1	Comparison of SPME and Standard Methods for Initial Formaldehyde Emission	79
4.3.2	Comparison of SPME and Standard Methods for Ultra-low Formaldehyde Emission	83
4.3.3	Validation of Methods	87
4.3.4	Correlation of SPME-A with Standard Methods	92
4.3.5	Correlation of SPME-W with Standard Methods	96
4.4	Formaldehyde Minimisation Solutions	99
4.4.1	Results of Formaldehyde Minimisation with Veneer Thickness Control	100
4.4.2	Results of Formaldehyde Minimisation with Scavenging Treatment	102
4.4.3	Discussion of Veneer Thickness Control	105
4.4.4	Discussion of Scavenging Treatment	106

<b>CHAPTER 5</b>	<b>SPME OPTIMISATION</b>	
5.1	SPME Optimisation	110
5.2	Calibration and Background Level	114
<b>CHAPTER 6</b>	<b>CONCLUSION</b>	
6.1	Conclusion	117
6.2	Future Research	119
<b>REFERENCE</b>		121
<b>APPENDICES</b>		

## LIST OF TABLES

Table	Descriptions	Page
Table 1.1	Formaldehyde emission standards for plywood panels in different regions	7
Table 3.1	Urea formaldehyde glue mix formula used for the preparation of plywood panels	29
Table 3.2	Plywood panels formed by veneers with different moisture content combinations	30
Table 3.3(a)	Working parameters of test method using spectrophotometric analysis	33
Table 3.3(b)	Working parameters of test method using chromatographic analysis	33
Table 3.4	The surface veneers of 0.6 mm to 1.8 mm were bond laminated at different pressing times to form 3 ply panels with core veneer consists of fixed thickness	47
Table 4.1.1	Formaldehyde emission analysed by the desiccator-chromotropic acid (DC-CA) method	51
Table 4.2.1	Physical description of various wood species	59
Table 4.2.2	Colour descriptions of different varieties of wood species	61
Table 4.2.3	Formaldehyde emission with woody colour by the small chamber-chromotropic acid (SC-CA) method	61
Table 4.2.4	Formaldehyde emission with woody colour by the liquid-liquid extraction analysed by GC/FID (LLE-FID) method	62
Table 4.2.5	Formaldehyde emission with woody colour by the solid phase micro-extraction sampling from absorbing solution (SPME-A) method	62
Table 4.2.6	Formaldehyde emission with woody colour by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method	63
Table 4.2.7	Formaldehyde emission of solid wood (SW) and plywood (PW) in accordance with the colour of wood species	63

Table 4.2.8	Formaldehyde emission with woody pH in descending trend by the solid phase micro-extraction sampling from absorbing solution (SPME-A) method	65
Table 4.2.9	Formaldehyde emission with woody pH in descending trend by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method	65
Table 4.2.10	Formaldehyde emission with woody porosity in descending pattern by the liquid-liquid extraction analysed by GC/FID (LLE- FID) method	68
Table 4.3.1	Analytical methodologies with their correspondence standards	79
Table 4.3.2	Formaldehyde emission for various plywood species in ascending pattern as evaluated by different methods	80
Table 4.3.3	Correlation coefficient ( $R^2$ ) values of the different methods utilised	88
Table 4.3.4	Repeatability of different methods with respect to original panel	90
Table 4.3.5	Repeatability of different methods with respect to post treated panel	90
Table 4.3.6	The comparison of the LOD and LOQ between different methods	92
Table 4.4.1	Minimisation of formaldehyde emission as affected by veneer thickness	101
Table 4.4.2	Minimisation of formaldehyde emission after scavenging treatment	103
Table 4.4.3	Summary of formaldehyde minimisation after scavenging treatment	104

## LIST OF FIGURES

Figures	Descriptions	Page
Figure 1.1	Classification of wood composite panels by particle size, density and process (FPL 2010).	3
Figure 3.1	The orientation of veneers subjected to different moisture content.	29
Figure 3.2	Cutting plan of a 2440 mm x 1220 mm plywood panel. Test samples of 350 mm x 350 mm were cut at least 25 mm from the end to obtain adequate representation areas within the panel.	32
Figure 3.3	Evaluation methodologies experimental set up	
Figure 3.3 (a)-(b)	The desiccator loaded with test specimens and absorbing solution in the DC-CA method;	34
Figure 3.3 (c)-(d)	The desiccator loaded with test specimens and absorbing solution in the DC-AA method;	37
Figure 3.3 (e)-(f)	The chamber loaded with test specimens and impinge solution in the SC-CA method.	40
Figure 3.4	Evaluation methodologies experimental set up	
Figure 3.4 (a)-(b)	GC/FID and in-solution derivatisation in the LLE-FID method;	43
Figure 3.4 (c)-(d)	GC/ECD and in-solution derivatisation in the LLE-ECD method;	43
Figure 3.4 (e)-(f)	GC/MS and headspace on-fibre derivatisation in the SPME method.	45
Figure 4.1.1	The largest formaldehyde reduction at MC (18/6) was followed by MC (14/6) and MC (10/6) using the desiccator-chromotropic acid (DC-CA) method.	53
Figure 4.1.2	Formaldehyde emission in accordance with various MC as measured by the desiccator-acetyl acetone (DC-AA) method.	53
Figure 4.1.3	Comparison of formaldehyde emission relative to different moisture content combinations by desiccator-chromotropic acid (DC-CA) method.	54
Figure 4.1.4	Comparison of formaldehyde reduction with the decrease of moisture content, MC (18/6) between surface veneer and inner core of plywood using the desiccator-acetyl acetone (DC-AA) method.	54
Figure 4.1.5	The presence of water results in the hydrolysis of the C=N bond and release of the formaldehyde.	56

Figure 4.2.1	Formaldehyde emission of a variety of wood species with respect to woody pH in descending trend by the desiccator-acetyl acetone (DC-AA) method.	66
Figure 4.2.2	Formaldehyde emission of a variety of wood species with respect to woody pH in descending trend by the liquid-liquid extraction analysed by GC/FID (LLE-FID) method.	66
Figure 4.2.3	Formaldehyde emission with different wood porosity in decreasing trend by the solid phase micro-extraction sampling directly from wood specimen (SPME-W) method.	69
Figure 4.2.4	Formaldehyde emission of high porosity plywood (PP > 72 %) in decreasing trend using different test methods.	69
Figure 4.2.5	Formaldehyde emission in decreasing trend shown by solid wood (SW) and plywood (PW) with different colours as performed using the desiccator-acetyl acetone (DC-AA) and small chamber-chromotropic acid (SC-CA) methods.	71
Figure 4.2.6	Formaldehyde emission in decreasing trend shown by solid wood (SW) and plywood (PW) with different colour as performed using the solid phase micro-extraction (SPME-A & SPME-W) and liquid-liquid extraction analysed by GC/FID (LLE-FID) methods.	71
Figure 4.2.7	Linear correlation of formaldehyde emission with woody pH by the solid phase micro-extraction sampling from absorbing solution (SPME-A) method.	73
Figure 4.2.8	Linear correlation of formaldehyde emission with woody pH by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method.	74
Figure 4.2.9	Linear correlation of formaldehyde emission with woody pH by the small chamber-chromotropic acid (SC-CA) method.	74
Figure 4.2.10	The relationship of formaldehyde emissions with woody porosity by the liquid-liquid extraction analysed by GC/FID (LLE-FID) method.	76
Figure 4.2.11	The relationship of formaldehyde emissions with woody porosity by the solid phase micro-extraction sampling from absorbing solution (SPME-A) method.	77
Figure 4.2.12	The relationship of formaldehyde emissions with woody porosity by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method.	77



Figure 4.3.1	The reaction of PFBHA with formaldehyde forms GC compatible formaldehyde-oxime.	82
Figure 4.3.2	The reaction of acetyl acetone with formaldehyde forms yellowish dihydrolutidine (DDL).	82
Figure 4.3.3	The reaction of chromotropic acid with formaldehyde forms purple chromogen.	82
Figure 4.3.4	Formaldehyde emissions in descending trend with respect to different veneer thickness of pre-treatment.	85
Figure 4.3.5	Formaldehyde emissions after scavenging post treatment between the SPME-A and SPME-W in ascending trend with respect to a variety of plywood species.	85
Figure 4.3.6	Similar minimisation trends as performed by different methods.	87
Figure 4.3.7	Relative standard deviation comparison of different testing methods.	89
Figure 4.3.8	Recovery comparison of different testing methods.	91
Figure 4.3.9 (a)-(f)	Relationship of formaldehyde emission of solid phase micro-extraction sampling from absorbing solution (SPME-A) with standard methods for original untreated and post treated panels.	95
Figure 4.3.10 (a)-(b)	Relationship of formaldehyde emission of solid phase micro-extraction sampling from absorbing solution (SPME-A) and air sampling directly from wood specimen (SPME-W) for original untreated and post treated panels.	96
Figure 4.3.11 (a)-(f)	Relationship of formaldehyde emission of solid phase micro-extraction air sampling directly from wood specimen (SPME-W) with standard methods for original untreated and post treated panels.	98
Figure 4.4.1	Formaldehyde minimisation with the increase of veneer thickness in 1.5, 2, 2.5 and 3 fold respectively.	102
Figure 4.4.2	Effectiveness of FS 25 % to minimise formaldehyde emission.	104
Figure 4.4.3	Reaction of melamine with formaldehyde.	106
Figure 4.4.4	Reaction of urea with formaldehyde.	107
Figure 4.4.5	Reaction of sodium hydrogen sulphite with formaldehyde.	107

Figure 5.1	Formaldehyde-oxime peak of first extraction, after 2 times and then 3 times of continuous extraction	111
Figure 5.2	SPME optimisation	113
Figure 5.2 (a)-(b)	Absorbing solution and plywood specimens prepared in headspace vial in the SPME-A and SPME-W methods;	
Figure 5.2 (c)-(d)	PDMS-DVB and the fibre pre-conditioning at the GC port;	
Figure 5.2 (d)-(f)	On-fibre extraction and analyte adsorption at a constant agitation, followed by analyte desorption through the <i>Merlin</i> microseal septum in the gas inlet of GC/MS	
Figure 5.3	Mechanism through which formaldehyde derivatised by PFBHA forms the formaldehyde-oxime	114
Figure 5.4	Mass spectrum of formaldehyde-oxime obtained after SPME-GC/MS analysis and chromatogram of derivatised formaldehyde from specimen <i>kapur</i> .	114
Figure 5.5	Standard calibration curve for formaldehyde quantitative determination by using headspace solid phase micro-extraction (HS SPME) GC/MS.	115

## LIST OF SYMBOLS AND ABBREVIATIONS

AS	absorbing solution
ASTM	American Society for Testing and Materials
BS EN	British European Standard
BV	back veneer
CARB	California Air Resources Board
CE	European Conformity
CNS	Chinese National Standard
CWPs	composite wood products
DC	desiccator
DC-AA	desiccator-acetyl acetone
DC-CA	desiccator-chromotropic acid
DDL	3, 5-diacetyl-1, 4-diacetyldihydrolutidine
ECD	electron capture detector
EI	electron impact ionization
EN	European Standard
EPA	Environmental Protection Agency
FID	flame ionisation detector
FPL	Forest Product Laboratory
FS 25 %	formaldehyde scavenger solution
F/U	formaldehyde and urea molar ratio
F/ (M+U)	formaldehyde and urea with melamine molar ratio
GC	gas chromatography
GC/ECD	gas chromatography in combination of electron capture detector
GC/FID	gas chromatography in combination of flame ionisation detector

GC/MS	gas chromatography in combination of mass spectrometry
HCHO	formaldehyde
HPLC	high performance liquid chromatography
HS	headspace
IARC	International Agency for Research on Cancer
IC	inner core
ISO	International Organization for Standardization
JAS	Japanese Agriculture Standard
JIS	Japanese Industrial Standard
LLE	liquid-liquid extraction
LLE-ECD	liquid-liquid extraction analysed by GC/ECD
LLE-FID	liquid-liquid extraction analysed by GC/FID
LOD	limit of detection
LOQ	limit of quantification
MC	moisture content
MC 10/6	as the moisture content reduced from 10 % to 6 %
MC 14/6	as the moisture content reduced from 14 % to 6 %
MC 18/6	as the moisture content reduced from 18 % to 6 %
MR	moisture resistance
MS	mass spectrometry
NaHSO <sub>3</sub>	sodium hydrogen sulphite
NIOSH	National Institute for Occupational Safety and Health
PDMS-DVB	polydimethylsiloxane-divinylbenzene
PFBHA	<i>O</i> -(2,3,4,5,6 pentafluorobenzyl) hydroxylamine hydrochloride
pMDI	polymethylene diisocyanate

REC	recovery
RSD	repeatability or relative standard deviation
RT	retention time
R <sup>2</sup>	correlation coefficients
SC	small chamber
SC-CA	small chamber-chromotropic acid
SD	standard deviation
SI	standard international unit
SIM	selected ion monitoring
SPME	solid phase micro-extraction
SPME-A	solid phase micro-extraction sampling from absorbing solution
SPME-W	solid phase micro-extraction air sampling directly from wood specimen
SV	surface veneer
SV+IC+BV	combination of inner core in between surface veneer and back veneer
USTIC	United State International Trade Commission
UV-VIS	ultraviolet-visible
VOCs	volatile organic compounds
VS/ VC	veneer surface/ veneer core
VT	veneer thickness
WBP	weather and boiled proof
WHO	World Health Organization

## LIST OF FORMULA SYMBOLS

<i>A</i>	Coefficient of humidity (0.0175)
<i>A<sub>b</sub></i>	Absorbance of a blank solution
<i>A<sub>bs</sub></i>	Absorbance of a sample solution
<i>A<sub>p</sub></i>	Peak area of a sample solution
<i>Blc</i>	Blank value
<i>C</i>	Test formaldehyde concentration level by DC-CA and SC-CA methods, $\mu\text{g/mL}$
<i>C</i>	Formaldehyde concentration of test pieces by DC-AA method, $\text{mg/L}$
<i>Ca</i>	Total quantity of formaldehyde in the sample aliquots taken from the impinge (as determined from the calibration curve) by SC-CA method, $\mu\text{g}$
<i>Co</i>	Corrected formaldehyde concentration level by DC-CA method, $\mu\text{g/mL}$
<i>Cs</i>	Formaldehyde in 4 mL aliquot of sample read from calibration curve by DC-CA method, $\mu\text{g/mL}$
<i>Cs</i>	Parts of formaldehyde per million parts air by SC-CA method, ppm
<i>Ct</i>	Formaldehyde of sampled solution in DC-CA method, $\mu\text{g/mL}$
<i>Ct</i>	Total formaldehyde in the sample by SC-CA method, $\mu\text{g}$
<i>D</i>	Dilution factor, for example: (If no dilution is made, $D= 1$ )
<i>D</i>	Density
<i>e</i>	Natural log base
<i>G</i>	Gradient of calibration curve $(\text{mg/L})^{-1}$
<i>F<sub>a</sub></i>	Aliquot factor (sampling solution volume/ aliquot used)
<i>F<sub>t</sub></i>	Factor multiplied by to convert to 24 °C
<i>H</i>	Actual relative humidity, %
<i>Ho</i>	Relative humidity, %
<i>Int. y</i>	y intercept of calibration curve
<i>m<sub>o</sub></i>	Mass of the test piece after drying, g

$m_H$	Initial mass of the test piece, g
$m/z$	Mass to charge ratio
$P$	Barometric pressure, kPa
$P$	Porosity, %
$R$	Coefficient of temperature (9799)
$t$	Actual temperature, K
$t_o$	Corrected temperature, K
$T$	Temperature of sample air, °C
$V$	Volume of air sampled, L
$V_s$	Volume of air at standard conditions (101 kPa and 298 K), L