CHAPTER THREE

METHODOLOGY

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3.1 Chemical and Reagents

All reagents used were of analytical-reagent grade unless otherwise specified. Acetyl-acetone (Merck), ammonium acetate (Merck), chromotropic acid (Sigma Aldrich, SA), formaldehyde (37% v/v aqueous solution, SA), glacial acetic acid (Merck), hexane for GC (SA), hydrochloric acid 37% (Merck), iodine (Fischer Scientific, FS), methanol (99.8% purity, SA), methyl red indicator (Merck), *O*-(2,3,4,5,6 pentafluorobenzyl) hydroxylamine hydrochloride (98+% purity, SA), potassium dichromate (Merck), potassium hydrogen phthalate (SA), potassium iodide (SA), sodium carbonate (Merck), sodium chloride (SA), sodium hydrogen sulphite (SA), sodium hydroxide (Merck), sodium sulphite (Merck), sodium thiosulphate pentahydrate (FS), starch soluble powder (FS), sulphuric acid 95% to 98% (Merck).

3.2 Apparatus and Instruments

Glass desiccators of 240 mm diameter and small chamber, 0.11 m^3 were used to collect plywood formaldehyde for spectrophotometry analyses. The Shimadzu Model UV-spectrophotometer (UV-1800), achieves a resolution of 1 nm was used to determine the diacetyldihydrolutidine (DDL) peak at 412 nm and the chromogen at 580 nm. For liquid-liquid extraction (LLE), both of the Shimadzu Model gas chromatography (GC 2010P) in combination of flame ionization detection (GC/FID) with the VB-5 capillary column (30 m x 0.25 mm x 0.25 µm) and the Agilent Technologies Model gas chromatography (7890A) in combination of electron capture detector (GC/ECD) with HP-5 GC capillary column (30 m x 320 µm x 0.25 µm) were used.

In solid phase micro-extraction (SPME), the polydimethylsiloxane-divinylbenzene (PDMS-DVB) fibre of 65 µm with 23 gauges (Supelco) was selected because of its high load capacity (Rivero, 2004). It was first conditioned at desorption unit of GC port at 250°C for 30 minutes. All extractions were performed using a CTC combi-PAL automated SPME system (CTC Analytics, Zwingen, Switzerland) with a 32 vial tray holder. It was connected to the Shimadzu Model gas chromatography (GC 2010) coupled with Shimadzu Model mass spectrometer (GC/MS-QP2010 Plus) for chromatography analysis. Compounds were separated by using a 5% diphenyl 95% dimethyl polysiloxane column (Rts-5MS: 30 m x 0.25 mm x 0.25 µm) (Yung & Lo, 2013; 2012).

3.3 Wood Material and Preparation of Plywood Panels

Initially, tropical hardwood species commonly found in Borneo also South East Asia were selected as dominant wood materials in the plywood samples preparation. There were ten timber species of domestic log with diameter of about 50 cm. The logs chosen were healthy and free from physical defects through visual inspection. They were peeled by rotary lathe machine into thin veneer sheets of desire thickness, ranging from 0.6 mm to 1.8 mm.

All veneers were dried through continuous dryer for long grain veneer and roller dryer for short grain veneer except green veneers used in manufacturing plywood of different moisture content (MC). The plywood panels were composed from veneers of the same species in the arrangement of 1.5 mm core veneer between two thinner surface and back veneers of 0.6 mm that laminated perpendicular (Figure 3.1) with urea formaldehyde formulated glue mix, as given in Table 3.1. Glue lamination carried out by roller spreader with a weight of 28 ± 2 g/cm^2. Subsequently, glued layers were delivered for hot pressing

by hydraulic press machine for 150 seconds with 8 kg/cm^2 pressure applied at 115°C. After that, the plywood were sized to 2440 mm length with 1220 mm width and then sanded at its face side. Finally, the three ply plywood panels with average thickness of 2.5 mm were produced in the condition where wood defects were eliminated in the plywood manufacturing flow.

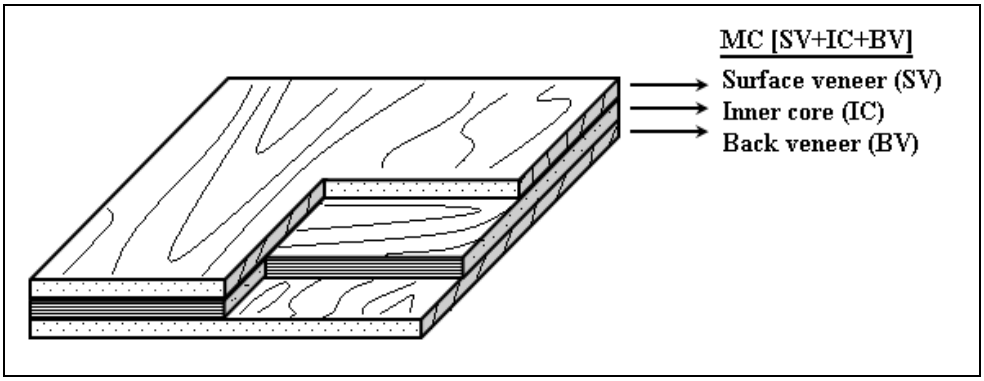


Figure 3.1: The orientation of veneers subjected to different moisture content.

Table 3.1 Urea formaldehyde glue mix formula used for the preparation of plywood panels

Glue mixtures	**Part by weight**
Urea formaldehyde resin	100.0
Wheat flour	20.0
Ammonium chloride	1.2
Melamine	1.2
Urea	2.0

3.3.1 Sample Preparation by Using Different Moisture Content Veneers

In order to achieve moisture content of 6%, 10%, 14% and 18%, green veneers were conditioned using an oven and then left in a controlled atmosphere of 20 ± 2°C and 50 ± 5% relative humidity for approximately 4 hours until they reach room temperature prior glue bonding. These four groups of moisture content were selected by referring to the usual

moisture content of dried wood in accordance with the regular processing parameter besides considering the energy waste plus the deterioration of physical properties of wood veneer. Shrinkage, cracking and warping are the common effects of wood dehydration while blistering, de-bonding or de-lamination are caused by too high moisture content of the wood veneer. Plywood panels were formed by veneers with different moisture content combinations (Table 3.2). Five replicate panels distributed all together thirty sets of sample from each moisture content group. They were prepared for each of the following methods: desiccator-chromotropic acid (DC-CA), desiccator-acetyl acetone (DC-AA) and small chamber-chromotropic acid (SC-CA).

Table 3.2: Plywood panels formed by veneers with different moisture content combinations

MC of IC & SV	**Moisture Content Combination (SV + IC + BV)**			
	6%	10%	14%	18%
6%	6 + 6 + 6	10 + 6 + 10	14 + 6 + 14	18 + 6 + 18
10%	6 + 10 + 6	10 + 10 + 10	14 + 10 + 14	18 + 10 + 18
14%	6 + 14 + 6	10 + 14 + 10	14 + 14 + 14	18 + 14 + 18
18%	6 + 18 + 6	10 + 18 + 10	14 + 18 + 14	18 + 18 + 18

* MC= moisture content; IC= inner core, SV= surface veneer, BV= back veneer

For moisture content determination, test pieces free from loose splinters and sawdust with minimum mass of 20 g were prepared. The initial weight was recorded to an accuracy of 0.01 g immediately after sampling and then placed in a drying oven at temperature of 103 ± 2°C until constant mass has been reached. Constant mass was considered to be reached when the results of two successive weighing operations, carried out at an interval of 6 hours, do not differ by more than 0.1% of the mass of the test piece. After cooled to approximately room temperature in the desiccators, the test pieces were weighted to an accuracy of 0.01 g, rapidly enough to avoid an increase in moisture content greater than

0.1%. Moisture content of each test piece, as a percentage by mass to the nearest 0.1% was calculated based on the following formula:

$$MC = \frac{m_H - m_o}{m_o} \text{ x } 100\%$$

where,

MC = moisture content, %

m_H = initial mass of the test piece, g

m_o = mass of the test piece after drying, g

The moisture content of a board can be obtained by calculating the arithmetic mean of the moisture content of all test pieces taken from the same board and expressed as a percentage to one decimal place (BS EN 322:1993). This oven dry procedure is the sole primary method where it has the highest accuracy or degree of precision for research purpose (Hartley, 2001). Meanwhile, the wood veneers were checked with electronic moisture content meter for double confirmation prior the glue laminating process.

3.3.2 Sample Preparation by Using Different Timber Wood Species

The significant variable considered in this study was the wood species, which in this case were *batai* (*Paraserianthes falcataria*), *binuang* (*Octomeles spp*.), *kapur* (*Dryobalanops spp*.), *keruing* (*Dipterocarpus spp*.), *laran* (*Neolamarckia cadamba*), *magas* (*Duabanga spp*.), *red seraya* (*Shorea spp*.), *sedaman* (*Macaranga*), *white seraya* (*Parashorea spp*) and *yellow seraya* (*Shorea spp*.). All together ten types of domestic timber species were selected as raw material for manufacturing plywood panels.

The timber wood species was classified base to their physical outlook and appearance into two main groups. The first group was pink to dark brown colour, consists of *batai* (BTI), *sedaman* (SDM), *white seraya* (WSY), *kapur* (KPR), *keruing* (KRG) and *red seraya* (RSY). Yellowish *laran* (LRN), *binuang* (BNG), *magas* (MGS) and *yellow seraya* (YSY) were in another group (Table 3.2). Five replicate plywood panels were produced from each species. Within a single panel as illustrated in Figure 3.2, there were twelve sets sample being outlined. Of total fifty panels plywood produced from many kinds of plywood species, there were all together six hundred sets sample prepared for method comparison studies. The DC-AA, LLE and SPME methods shared specimens of set 1 to 6 while samples marked 7 to 12 were evaluated by the DC-CA and SC-CA methods in different specimen dimensions and loading ratio (Table 3.3a; 3.3b).

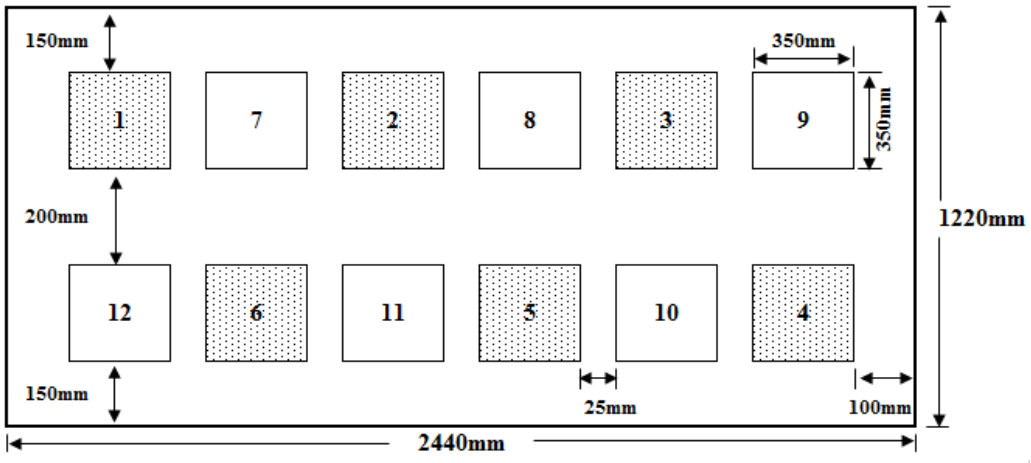


Figure 3.2: Cutting plan of a 2440 mm x 1220 mm plywood panel. Test samples of 350 mm x 350 mm were cut at least 25 mm from the end to obtain adequate representation areas within the panel.

3.4 General Procedure for Formaldehyde Determination

Basically, two major analytical techniques were adopted for comparing the emission of formaldehyde emission in hardwood plywood panels in the current studies. The conventional method was certified spectrophotometric standards: DC-CA, DC-AA and SC-CA. More advance chromatographic method consists of LLE and SPME. The emission values were compared through the following method where the details for all testing methods have been given in section 3.4.1-3.4.5.

Table 3.3(a): Working parameters of test method using spectrophotometric analysis

Method	**DC-CA**	**DC-AA**	**SC-CA**
Specimens	Edge sealed	Edge exposed	Edge sealed
Loading ratio	12.37 m^2/m^3	14.02 m^2/m^3	0.95 m^2/m^3
Sampling	Absorbing solution (H_2O)	Absorbing solution (H_2O)	Impinge solution ($NaHSO_3$)
Detection	UV-VIS (580 nm)	UV-VIS (412 nm)	UV-VIS (580 nm)

* Desiccators-chromotropic acid (DC-CA); Desiccators-acetyl acetone (DC-AA); Small chamber-chromotropic acid (SC-CA)

Table 3.3 (b): Working parameters of test method using chromatographic analysis

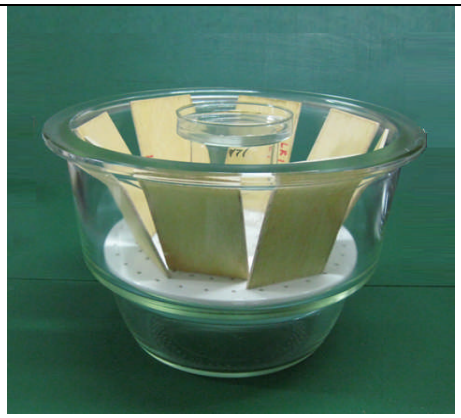
Method	**LLE-FID**	**LLE-ECD**	**SPME-A**	**SPME-W**
Specimens	Edge exposed	Edge exposed	Edge exposed	Edge exposed
Loading ratio	14.02 m^2/m^3	14.02 m^2/m^3	14.02 m^2/m^3	14.09 m^2/m^3
Extraction	Solvent (Hexane)	Solvent (Hexane)	Headspace (H_2O)	Headspace (Wood)
Detection	GC/FID (RT 12 min)	GC/ECD (RT 12 min)	GC/MS (RT 7.5 min)	GC/MS (RT 7.5 min)

* Liquid-liquid extraction analysed by GC/FID and GC/ECD (LLE-FID & LLE-ECD); Solid phase micro-extraction sampling by absorbing solution and air sampling directly from wood specimen (SPME-A & SPME-W)

3.4.1 Desiccator-Chromotropic Acid (DC-CA) Method

According to the testing procedure in the ASTM D5582-00-2006, 8 pieces of 70 ± 2 mm x 127 ± 2 mm specimens were cut from the test sample at least 25 mm from its edges to obtain adequate representation areas within the panel. The edges and ends of each single specimen were coated with paraffin wax with cover no more than 5 mm (3/16 in) of either face around the coated perimeter. Then, the specimens were pre-conditioned with edge and spaced apart, so that air can freely circulate across all surfaces for 7 days ± 4 hours at 24 ± 1.7°C and 50 ± 10% relative humidity. The specimens were arranged at the top of porcelain plate around a 100 mm x 20 mm petri dish that contains 25 mL of distilled water which rests upon on an inverted beaker with a height of 100 ± 7 mm as reservoir support (Figure 3.3a; 3.3b).

(a)



(b)

Figure 3.3 (a)-(b): The desiccator loaded with test specimens and absorbing solution in the DC-CA method.

A desiccator without loaded with test specimens was set as blank sample. The conditioning was conducted in a room maintained at 24 ± 0.6°C and 50 ± 10% relative

humidity where the desiccator, petri dish bottom and distilled water were equilibrated to the same condition. After 2 hours ± 1 minute of conditioning time in a 10.5 L glass desiccator, the 4 mL of the solution sample was pipetted into each of 16 mm x 150 mm screw capped test tube and 0.1 mL of 1% chromotropic acid reagent was dosed in before the 6.0 mL of concentrated sulphuric acid was added. The test tube was mixed adequately by using a vortex mixer. The test tube was then heated at 95°C for 15 ± 2 minutes to ensure complete chemical reaction. After removal, the test tube was left to cool to room temperature. The formaldehyde concentration of each petri dish aliquot in the desiccator was calculated in weight per unit volume:

$$C_t = \frac{C_s}{D \text{ x } 4} \text{ x } F_t \tag{1}$$

$$Cs = \frac{A_{bs} - Blc - Int.y}{G} \tag{2}$$

where,

C_t = Formaldehyde of sampled solution, µg/mL

D = Dilution factor (If no dilution is made, D= 1)

F_t = Factor multiplied by to convert to 24°C

C_s = Formaldehyde in 4 mL aliquot of sample read from calibration curve, µg/mL

A_{bs} = Absorbance value

Blc = Blank value

$Int.\ y$ = y intercept of calibration curve

G = Gradient of calibration curve

Adjustment was made to the desiccators value obtained to a standard temperature of 24°C (Ref: annex A1. Temperature conversion factors for formaldehyde, ASTM 5582-00-2006).

$$C = Co \text{ x } e^{R\left(\frac{1}{t} - \frac{1}{to}\right)} \quad (3)$$

where,

C = Test formaldehyde concentration level, µg/mL

C_o = Corrected formaldehyde concentration level, µg/mL

e = Natural log base

R = Coefficient of temperature (9799)

t = Actual temperature, K

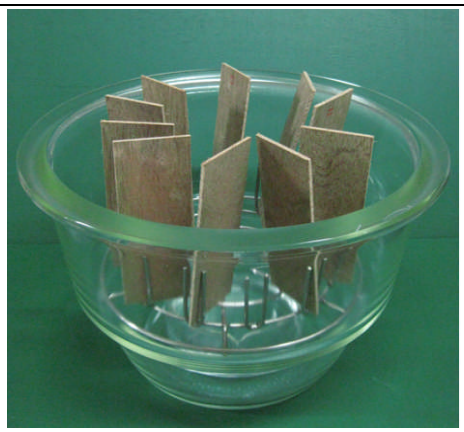
t_o = Corrected temperature, K

A calibration curve was developed by taking 0.1, 0.3, 0.5, 0.7, 1.0 and 2.0 mL standard solution. They were marked up with distilled water to 4 mL and underwent the same mixing process like the other sample solutions as discussed earlier. The solution was then transferred into cuvettes and the absorbance reading against distilled water was recorded. An absorbance above 0.030 for the reagent blank indicates contamination of the reagent blank or improper solution preparation. The calibration curve was obtained by plotting the absorbance against micrograms of formaldehyde in the colour development solution. The gradient and y-intercept was determined from the graph or by calculation.

3.4.2 Desiccator-Acetyl Acetone (DC-AA) Method

In accordance with JAS 233:2008, the quantity of formaldehyde was determined by collecting air-borne formaldehyde in a distilled water reservoir within closed desiccators. It is a commonly used method to determine formaldehyde emission of wood based products. According to the testing procedure, 10 pieces of test specimens in the size of 50 mm x 150 mm were being conditioned in an air tight vinyl bag in a thermostatic room at a temperature of 20 ± 1°C for more than 1 day. After that, they were being placed on a crystallising dish with a diameter of 120 mm and a height of 60 mm that contains 300 mL of distilled water. The crystallizing dish was placed at the centre of a heavy 10.5 L glass desiccator. After conditioning at 20 ± 0.5°C for 24 hours, the distilled water which had absorbed the formaldehyde emitted from the test specimens, were used as sample solution (Figure 3.3c; 3.3d). In order to determine the concentration of background, a blank solution without test sample was analysed.

(c)



(d)

Figure 3.3 (c)-(d): The desiccator loaded with test specimens and absorbing solution in the DC-AA method.

The formaldehyde concentration in the sample solutions and in the blank sample solution was determined by using acetyl acetone luminous intensity absorbance method. 25 mL of sample solution was filled into a vessel and then 25 mL of acetyl acetone ammonium acetate solution was added. Then, it was stoppered tightly and mixed gently. After warming the vessel with a ground-in stopper in water at 65 ± 2°C for 10 minutes, the solution was left shielded in the dark until cooled down to room temperature. Based on the *Hantzch* reaction, the formaldehyde was measured through its reactions with ammonium ions and acetyl-acetone which yielding yellowish DDL (3, 5-diacetyl-1, 4-dihydrolutidine). Qualitative test was carried out at wavelength of 412 nm of spectrophotometer (Yung & Lo, 2013; 2012). The formaldehyde concentration of the sample is calculated by the following formula,

$$C = \frac{(A_d - A_{bs})}{G} \tag{1}$$

where,

C = Formaldehyde concentration of test pieces, mg/L

A_{bs} = Absorbance of a sample solution

A_b = Absorbance of a blank solution

G = Gradient of calibration curve

For the first calibration curve, 5, 10, 20, 50 and 100 mL of standard solution were taken by using a transfer pipette into 100 mL volumetric flasks. It was marked up with distilled water to the specified volume like the other sample solutions. After that, the solution was taken into a cuvettes and the absorbance was measured at the wavelength of 412 nm using a spectrophotometer. The relation between the amount of formaldehyde (0

mg to 3 mg) and absorbance was plotted to obtain calibration curve in the study of moisture content effects to the formaldehyde emission. The blank solution is a reference. The second calibration curve was plotted by standard solution of 0.1, 0.3, 0.5, 0.7, 1.0 and 3.0 mg/L for the other studies: solid wood, methodology evaluation and formaldehyde minimisation. The gradient was determined by reading the graph or through calculation.

3.4.3 Small Chamber-Chromotropic Acid (SC-CA) Method

The standard test method for determining formaldehyde concentration in air from wood products using a small scale chamber was adopted from ASTM D6007-02(2008). In compliance to the value of make-up air flow, Q (the quantity of conditioned and filtered air fed into the chamber per unit time, m^3/h.) dependent on the sample surface area (the total area of all sample faces exposed in the chamber), 6 pieces of 70 ± 2 mm x 127 ± 2 mm specimens were prepared to meet the loading ratio of 0.95 m^2/m^3. The edges and ends of each single specimen were coated with paraffin wax with cover of no more than 5 mm on either face around the coated perimeter. Then, specimens were pre-conditioned on edge and spaced apart, so that air can freely circulate across all surfaces for 7 days ± 4 hours at 24 ± 3°C and 50 ± 5% relative humidity. The chamber was purged by running a blank test, followed by loading in test specimens. The test specimens were placed with a minimum distance of 0.15 m between each other in the chamber and maintained at 25 ± 1°C and 50 ± 4% relative humidity for 2½ hours. At the sampling station, air was bubbled through a single impinge which filled with 20 mL of 1% sodium hydrogen sulphite solution, known also as impinge solution (IS). The airflow was maintained at 1 ± 0.05 L/min for 30 minutes (Figure 3.3e; 3.3f).

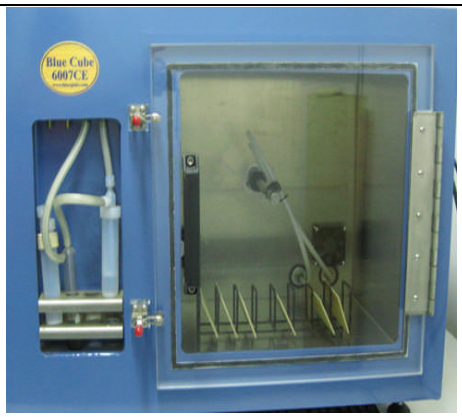
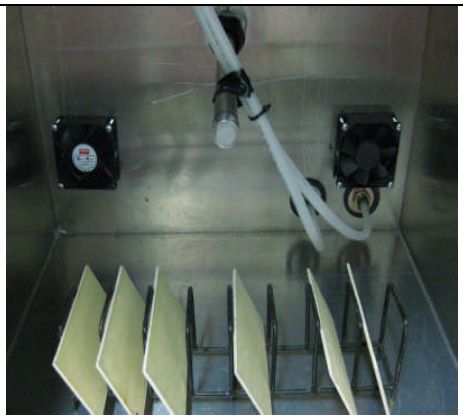
	
(e)	(f)

Figure 3.3 (e)-(f): The chamber loaded with test specimens and impinge solution in the SC-CA method.

Then, 4 mL of sodium hydrogen sulphite solution was transferred into each of the 16 mm x 150 mm screw cap test tubes for duplicate analysis. 0.1 mL of 1% chromotropic acid reagent was added and followed by 6.0 mL of concentrated sulphuric acid. The test tube was mixed adequately by using a vortex mixer and heated at 95°C for 15 ± 2 minutes to ensure complete chemical reaction. After the removal, the test tube was left cool to room temperature. Then, purple colour solution known as chromogen was formed and the absorption spectra was counter checked by spectrophotometer at 580 nm. The absorbance of each sample was recorded where blank solution is a reference. The concentration of formaldehyde was calculated as follows,

$$C_s = \frac{C_t \text{ x } 24.47}{V_s \text{ x } 30.03} \quad (1)$$

$$C_t = C_a \text{ x } F_a \quad (2)$$

$$V_s = \frac{V \text{ x } P \text{ x } 298}{101 \text{ x } (T + 273)} \quad (3)$$

where,

C_s = Parts of formaldehyde per million parts air, ppm

30.03 = Molecular weight of formaldehyde

24.47 = Formaldehyde gas in 1µmol at 101 kPa and 298 K, µL

C_t = Total formaldehyde in the sample, µg

C_a = Total quantity of formaldehyde in the sample aliquots taken from the impinge (as determined from the calibration curve), µg

F_a = Aliquot factor (sampling solution volume/ aliquot used)

V_s = Volume of air at standard conditions (101 kPa and 298 K), L

V = Volume of air sampled, L

P = Barometric pressure, kPa

T = Temperature of sample air, °C

The SC-CA formaldehyde value obtained is adjusted to a standard temperature of 25°C and 50% relative humidity (*Ref: annex A1. Temperature conversion factors for formaldehyde, ASTM D6007-02*)

$$C = Co \text{ x } e^{R\left(\frac{1}{t} - \frac{1}{to}\right)} \quad (4)$$

$$C = C_o[1 + A(H - H_o)] \quad (5)$$

where,

C = Test formaldehyde concentration level, µg/mL

C_o = Corrected formaldehyde concentration level, µg/mL

e = Natural log base

R = Coefficient of temperature (9799)

t = Actual temperature, K

t_o = Corrected temperature, K

A = Coefficient of humidity (0.0175)

H = Actual relative humidity, %

H_o = Relative humidity, %

The solution was transferred into cuvettes and the absorbance reading against distilled water was recorded. An absorbance above 0.030 for the reagent blank indicates contamination of the reagent blank or improper solution preparation. The calibration curve was obtained by plotting the absorbance against micrograms (0.1 to 3.0) of formaldehyde in the colour development solution.

3.4.4 Liquid-liquid Extraction (LLE) Method

The LLE was modified from US Environmental Protection Agency Method 556 (EPA Method 556). The distilled water having absorbed formaldehyde emitted from the test specimens in method DC-AA, also known as absorbing solution (AS) were used. For each sample, a volume of 20 mL was adjusted to pH 4 by adding 0.2 g potassium hydrogen phthalate. It was derivatised with *O*-(2,3,4,5,6 pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) aqueous solution (17 mg/mL) at 35°C for 2 hours before extracted with 4 mL hexane. The extract was shaken manually in first 3 minutes to permit phases to separate and in another 5 minutes after the addition of 0.05 mL concentrated sulphuric acid. The hexane layer flowed on the top was drew off into 3 mL sulphuric acid, 0.2 N for acidic washing. It was shaken for 30 seconds and let stand in 5 minutes for phase separation. The hexane layer was then placed in two 1.8 mL auto-sampler vials per sample.

The concentrations of oxime derivatives (converted from compounds of interest) were then analysed using GC/FID. Another batch of specimens were analysed by GC/ECD simultaneously. Helium with a flow rate of 1.0 mL/min was used as carrier gas in both FID and ECD detections. The temperature program of column was as specified in SPME and total runtime was about 50 minutes, with acquisition from 10 minutes to 40 minutes (Figure 3.4a-3.4d). They shared most of the operation parameters with exception of column specifications as illustrated in section 3.2.

(a)

(b)

(c)

(d)

Figure 3.4 (a)-(b): GC/FID and in-solution derivatisation in the LLE-FID method.
Figure 3.4 (c)-(d): GC/ECD and in-solution derivatisation in the LLE-ECD method.

Analytes in the sample were identified from chromatogram by comparing the retention time (RT) of the suspect peak to the RT of an analyte peak in a calibration standard. The approximate RT for derivatised formaldehyde was as follows: RT 12 min for GC/FID and GC/ECD. The formaldehyde was calculated by formula below,

$$C = \frac{A_p}{G} \quad (1)$$

where,

C = Formaldehyde concentration of test pieces, mg/L

A_p = Peak area of a sample solution

G = Gradient of calibration curve

The calibration curve was obtained by plotting the corresponded peak area against standard formaldehyde solution of 0.1 mg/L to 3.0 mg/L concentrations. These solutions were prepared as per described in section *3.4.2: DC-AA method*.

3.4.5 Solid Phase Micro-Extraction (SPME) Method

The SPME method was conducted in reference to our preliminary experiments and to the findings of other researchers (Yung & Lo 2013; Martos & Pawliszyn, 1998; Saison *et al*., 2009; Lee & Tsai, 2008; Cancho *et al*., 2001; Bao *et al*., 1998). Formaldehyde was collected by absorbing solution (SPME-A) and air sampling directly from wood specimens (SPME-W). For the SPME-A method, the AS of 10 mL collected from DC-AA method was transferred into a 20 mL glass headspace vial. For the SPME-W method, two specimens (1.5 mm x 1.0 mm) were placed in the similar size vial to meet the loading ratio approximating to the DC-AA method (14.0 m^2/m^3). Both vial were covered with magnetic

screw cap and mixed at 50 ± 5°C for 40 minutes in an incubator with agitation speed of 250 rpm to reach gas-liquid equilibration.

In order to determine the concentration of background, a blank solution without test sample was prepared. The SPME fibre PDMS-DVB, 65 µm was first conditioned at GC desorption port at 250°C for 60 minutes in an extra splitless port. Then, it was on-fibre derivatised by 17 mg/mL of PFBHA aqueous solution for 10 minutes. After that, it was possessed for 15 minutes sample adsorption before directly inserted into the GC injector, where the analyte was thermally desorbed at 250°C for 7 minutes (Yung & Lo, 2013; 2012). The formaldehyde-oximes formed on the fibre were desorbed and analysed by GC/MS. Helium with a flow rate 1.0 mL/min was used as the carrier gas. The temperature program used for the column was held at 60°C for 2 minutes, increasing to 90°C at 5 °C/min then 90°C to 250°C at 50 °C/min and a final hold of 5 minutes. The transfer line was set at 250°C (Figure 3.4e; 3.4f).

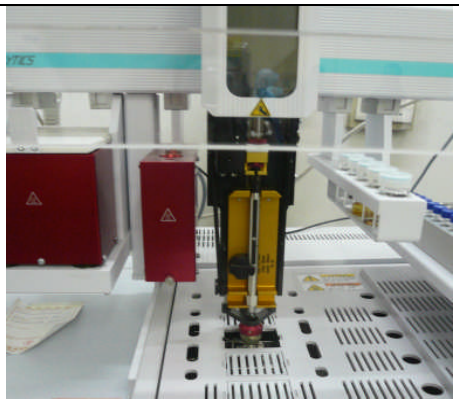
	
(e)	(f)

Figure 3.4 (e)-(f): GC/MS and headspace on-fibre derivatisation in the SPME method.

The approximate RT for interested compound was as follows: derivatised formaldehyde (7.5 min) and non reacted PFBHA (9.0 min). The MS analysis was performed using electron impact ionization (EI) mode for identification and quantified by selected ion monitoring (SIM) mode. Initially, full scan EI data were acquired to determine appropriate masses for SIM. The ion abundance of derivatised formaldehyde was monitored at m/z 181 and 195. The determination of formaldehyde level was performed with external standard.

$$C = \frac{A_p}{G} \tag{1}$$

where,

C = Formaldehyde concentration of test pieces, mg/L

A_p = Peak area of a sample solution

G = Gradient of calibration curve

The relation between formaldehyde amounts of standard solutions and corresponded peak area was plotted to obtain a linear calibration curve. The calibration points were at concentration of 0.1, 0.3, 0.5, 1.0, 2.0 and 3.0 mg/L. Again, the standard solutions were prepared as per described in section *3.4.2: DC-AA method*.

3.5 Methodology for Minimisation of Formaldehyde Emission

The carcinogenic tendency of formaldehyde has awakened the world. Its annual production volume, however, still staying high primarily caused by the chemical's wide array of uses as an incredibly versatile building block. Moreover, it is not at risk for large scale substitution by competing chemicals. The zero emission wood products are simply not reachable under today's promising techniques. Hence, methodologies to deform the formaldehyde released from wood panels are a necessity.

3.5.1 Minimisation by Pre-treatment - Veneer Thickness Control

The thickness of surface veneer was increased and acting as natural barrier to reduce the emission of formaldehyde. Long grain veneers with thickness ranging from 0.6 mm to 1.8 mm were collected from *red seraya* species. They were dried to MC 6% together with the short grain veneers (1.5 mm) for making 3 plies plywood. By following the standard manufacturing process, they were laminated with same urea formaldehyde glue mix in an equivalent glue spreads volume (28 g/ft^2), see Table 3.4.

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

Veneer Thickness (mm)	Plywood Composition	Ratio (VS/VC)	Pressing Time (sec)	Final Thickness (mm)
0.6	0.6 + 1.5 + 0.6	2.5	150	2.5
0.9	0.9 + 1.5 + 0.9	1.7	165	3.0
1.2	1.2 + 1.5 + 1.2	1.3	200	3.6
1.5	1.5 + 1.5 + 1.5	1.0	230	4.2
1.8	1.8 + 1.5 + 1.8	0.8	265	4.8

* VS = veneer of surface; VC = veneer of inner core

3.5.2 Minimisation by Post Treatment - Chemical Scavenging

Though many reduction methods have been used by researchers or manufacturers, the combination of two methods should be a new trial. The first approach was by adding formaldehyde scavengers into current use urea formaldehyde glue mix. In the final 5 minutes of glue mixing period, urea and melamine were added in to become 2.6% of the total new mixture. Then, normal operation procedures were continued until the final hot pressing to form plywood. The newly made plywood was coated with scavenger solution onto both sides of its surface.

As water base scavenger, its major components of urea (22.5%) and sodium hydrogen sulphite (2.5%) were sequentially added into the aqueous solution. The resulting mixture was stirred for 10 minutes at room temperature to form 25% formaldehyde scavenger solution (FS 25%) which was readily to be consumed. For coating the plywood, approximate 5 ± 1 g/ft^2 of FS 25% was sprayed onto the target surfaces. The second approach was advised to be carried out right after hot pressing to facilitate penetration of the scavenging solution. The heat collected and remained also help to dry up the wet surfaces indeed. The existing moist was then dried at 65 ± 5°C for 20 minutes. Over heating is prevented to avoid wrapping on the plywood panels.