

## Integration of Headspace Solid Phase Micro-Extraction with Gas Chromatography for Quantitative Analysis of Formaldehyde

Kong Mun Lo and Yen Li Yung\*

Chemistry Department, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia

\*E-mail: [yyl1007@siswa.um.edu.my](mailto:yyl1007@siswa.um.edu.my)

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A study was carried out to evaluate the solid phase micro-extraction (SPME) for formaldehyde emission analysis of uncoated plywood. In SPME, formaldehyde was on-fiber derivatized through headspace extraction and analyzed by gas chromatography coupled with mass spectrometry (GC/MS). The SPME was compared with desiccators (DC-JAS 233), small-scale chamber (SSC-ASTM D6007) and liquid-liquid extraction (LLE-EPA 556) methods which were performed in accordance with their respective standards. Compared to SSC (RSD 4.3%) and LLE (RSD 5.0%), the SPME method showed better repeatability (RSD 1.8%) and not much difference from DC (RSD 1.4%). The SPME has proven to be highly precise (at 95% confidence level) with better recovery (REC 102%). Validation of the SPME method for formaldehyde quantitative analysis was evidenced. In addition, the SPME by air sampling directly from plywood specimens (SPME-W) correlated best with DC ( $r^2 = 0.983$ ), followed by LLE ( $r^2 = 0.950$ ) and SSC ( $r^2 = 0.935$ ).

**Key Words :** Formaldehyde, Solid phase micro-extraction, Derivatize, GC/MS

### Introduction

Formaldehyde has been declared as a 'human carcinogen' by the International Agency for Research on Cancer (IARC). However, its world demand and consumption, especially in wood resins, is forecast to grow by at least 4% of the annual average from 2009 to 2014.<sup>1</sup> Therefore, the methodology to evaluate formaldehyde emission needs revolution.

Among the existing methods, the desiccator (DC) with static measurements was developed in 1970 and then standardized into the Japanese standard (JAS 233).<sup>2</sup> Thereafter, the dynamic small-scale chamber (SCC) was introduced as defined in the American standard (ASTM D6007).<sup>3</sup> In addition, the liquid-liquid extraction (LLE) and solid phase micro-extraction (SPME) methods were introduced in the present analysis. LLE is the preferred method for air quality evaluation (EPA 556)<sup>4</sup> while SPME is a newer sample preparation method that integrates sampling, extraction, concentration and sample introduction into a single step, as invented by Pawliszyn.

The desiccator and chamber methods have been widely used in the formaldehyde determination of composite wood products (CWP).<sup>5,6</sup> The majority are preferably carried out through spectrophotometric analysis, which was also the popular quality control method in the wood industry.<sup>7-9</sup> However, the longer test duration and larger sample size with a lot of hazardous chemical waste are the remaining drawbacks. Therefore, a simple but advanced technique, such as the SPME, in combination with gas chromatography/mass spectrometry (GC/MS) analysis was suggested. This was compared with standard spectrophotometric analyses and also LLE coupled with GC flame ionization detection

(FID).

Several researchers have discussed the use of SPME but focused on cosmetics, food and biological specimens.<sup>10-12</sup> The SPME literature of CWP is very limited and dominated by that pertaining to qualitative detection.<sup>13</sup> Furthermore, the quantitative analysis of formaldehyde onto a variety of wood species used in fresh plywood was emphasized in the current study instead of the qualitative analysis. Moreover, the derivatization-extraction were facilitated by full automation hence, more promising results were expected.

The formaldehyde regulations target CWP bonded with urea formaldehyde resins (UFR) because they have the tendency to give off gas, which causes indoor air pollution. As a result, the Japanese Government has amended the building standard law to comply with the JAS-Mark (JAS F4, 0.3 mg/L). In 2010, the US President signed the Formaldehyde Standards for CWP Act into law simultaneous with the implementation of the California Air Resources Board regulations (CARB Phase II, 0.05  $\mu\text{g}/\text{mL}$ ).<sup>14</sup> In between, the European Union executed CE-Marking (CE E1, 0.1 ppm).<sup>15</sup> The variety of standards could result in discrepancies in data among distributors, fabricators as well as wood product users. For these reasons, the relationship of the testing methods that complied with different standards is studied while focusing on the commonly used UFR bonded plywood.

The aim of our investigation was to show the compatibility of SPME with the standard methods, and the improved sensitivity of measurement through GC analysis. The influence of wood pH to the formaldehyde emission was also studied. Further works of comparison were carried out to establish the correlations and also to generalize the harmonization among SPME, DC, SSC and LLE methods.

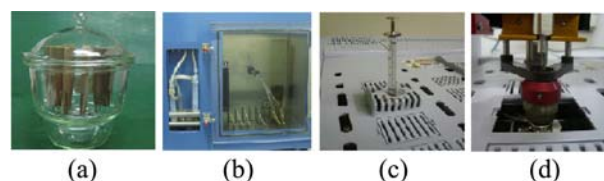
## Experimental

The veneer of 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.) were used. Veneers of the same species were laminated perpendicular in the arrangement of 1.5 mm between two veneers of 0.6 mm with UFR formulated glue-mix, as given in Table 1. Subsequently, they were hot pressed with 8 kg/cm<sup>2</sup> at 115 °C. Five panels of plywood (2.5 mm × 2440 mm × 1220 mm) were produced from each species. Each panel was divided into twelve set samples. The DC, LLE and SPME shared specimens of set 1 to 6 while samples marked 7 to 12 were evaluated by SSC.

All reagents used - chromotropic acid (Sigma Aldrich, SA), formaldehyde 37% (SA), acetyl-acetone (Merck), ammonium acetate (Merck), sodium bisulfite (SA), hexane for GC (SA), *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA, 98 + % purity, SA), potassium hydrogen phthalate (KHP, SA) were of analytical-reagent grade unless otherwise specified.

Glass DC of 240 mm diameter and a SSC of 0.11 m<sup>3</sup> were used in combination with a Shimadzu UV-spectrophotometer (Model UV1800) of 1 nm resolution. For the LLE, the Shimadzu GC/FID (Model 2010P) consisting of a VB-5 capillary column: 30 m × 0.25 mm × 0.25 μm was used. In SPME, divinylbenzene polydimethylsiloxane (DVB-PDMS) fiber of 65 μm with 23 gauges (Supelco) was selected. All extractions were performed using a CTC-Combi-PAL automated SPME system (CTC Analytics, Zwingen, Switzerland). This was connected to a Shimadzu GC/MS (Model GC/MS-QP2010 Plus) and compounds were separated by using a 5% diphenyl 95% dimethyl polysiloxane column (Rts-5MS: 30 m × 0.25 mm × 0.25 μm).

**Procedure: Standard Methods and SPME Methods.** DC and SSC tests were performed as per the experimental condition described in JAS 233 and ASTM D6007, respectively (Fig. 1(a)-(b)). The LLE was modified from EPA 556. For each LLE sample, a volume of 20 mL absorbing solution (AS) was collected from the DC method. This was adjusted to pH 4 by adding 0.2 g KHP and derivatized with PFBHA of 17 mg/mL at 35 °C for 2 hours followed by extraction with 4 mL hexane. The extract was shaken, washed and underwent phase separation. Each sample was split into two 1.8 mL auto sampler vials. The oxime derivative formed was then analyzed using GC/FID (Fig. 1(c)) where the carrier



**Figure 1.** (a)-(d) DC and SSC loaded with plywood specimens. Sample injections performed by LLE and SPME methods.

gas and the column temperature program were as specified in the SPME method. The approximate retention time (RT) for derivatized formaldehyde was 12 min. The emission of different plywood species were quantified by using formula 1, from a calibration curve that was plotted as a response to the corresponding peak area versus the formaldehyde concentration of 0.1-3.0 mg/L.

The SPME method was conducted in reference to our preliminary experiments and to the findings of other researchers.<sup>16-20</sup> Formaldehyde was collected by water reservoir (SPME-A) and air sampling directly from plywood specimens (SPME-W). For the SPME-A method, the AS of 10 mL was transferred into a 20 mL glass headspace vial. For the SPME-W method, two specimens (1.5 mm × 1.0 mm) were placed in similar sized vials to meet the loading ratio approximating to the DC method. Both were conditioned to 50 °C for 40 minutes to reach equilibrium. The DVB-PDMS was first on-fiber derivatized by 17 mg/mL of PFBHA for 10 minutes. Then, it was inserted into the sample (15 minutes) and then introduced into the GC injector for thermal desorption at 250 °C for 7 minutes (Fig. 1(d)). Helium with a flow rate of 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 reaching 250 °C at 50 °C/min and a final hold of 5 minutes. The approximate RT for the interested compound was as follows: derivatized formaldehyde (7.5 min) and unreacted PFBHA (9.0 min). The MS analysis was performed using electron ionization (EI) for identification and quantified by the selected ion monitoring (SIM) mode. The ion abundance of derivatized-formaldehyde was monitored at *m/z* 181 and 195. The calibration points were in the 0.1-3.0 mg/L range and determination of formaldehyde level was performed with external standard.<sup>12</sup>

$$C = A_p/G \quad (1)$$

where,

$C$  = Test formaldehyde concentration (mg/L)

$A_p$  = Peak area of the formaldehyde-oxime

$G$  = Gradient of calibration curve

**Table 1.** Glue-mix formula in the plywood manufacture

Glue mixtures	Parts
Urea formaldehyde resin	100
Wheat Flour	20
Ammonium chloride	1.2
Urea	2

Initial viscosity ~ 3000 cps; glue spreading = 30 ± 2 g/cm<sup>2</sup>

## Results and Discussion

### Initial Experiment: Timber Plywood Species and pH.

As shown in Table 2, plywood samples of a variety of timber species gave different emissions of formaldehyde although they were bonded with the same glue-mix in equivalent

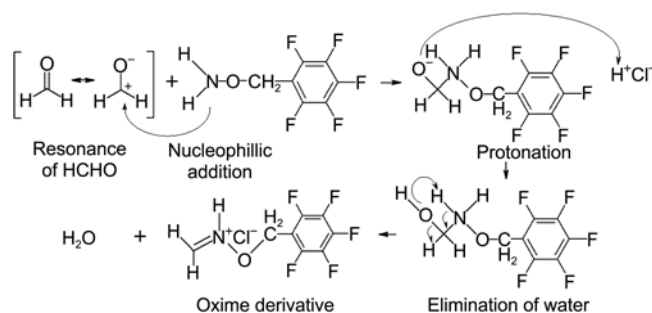
**Table 2.** Mean value of formaldehyde emission subjected to different wood species and pH value

Plywood	pH	Formaldehyde emission (ppm), n = 30				
		DC	SSC	LLE	SPME	
					A	W
KPR	4.7	0.27	0.07	0.07	0.30	0.35
RSY	4.9	0.34	0.08	0.24	0.37	0.43
KRG	5.3	0.41	0.09	0.32	0.44	0.48
SDM	5.3	0.49	0.10	0.42	0.54	0.59
MGS	5.5	0.60	0.15	0.69	0.76	0.91
BTI	5.8	0.58	0.11	0.59	0.70	0.83
WSY	5.9	0.67	0.18	0.72	0.86	0.99
YSY	6.1	0.80	0.20	0.96	1.11	1.18
LRN	6.2	0.97	0.21	1.21	1.20	1.48
BNG	6.2	0.97	0.22	1.84	1.46	1.65

\*(KPR = kapur, RSY = red seraya, KRG = keruing, SDM = sedaman, BTI = batai, MGS = magas, WSY = white seraya, YSY = yellow seraya, LRN = laran, BNG = binuang)

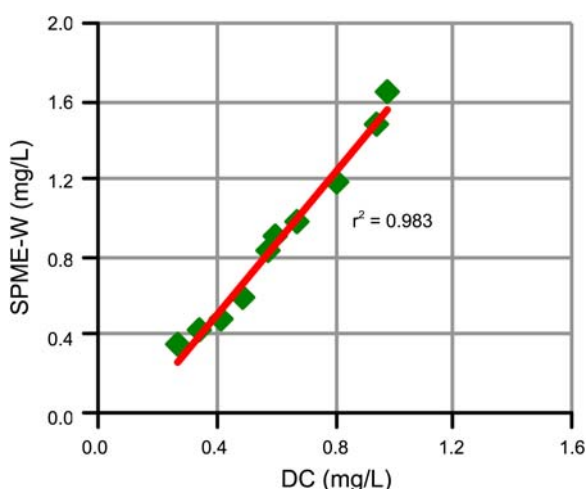
spread volume and produced under the same manufacturing procedures. Generally, it was expected that only the free formaldehyde from uncured UFR and hydrolysis of glue bond-line contributed to the emission. The increasing concern in respect of the natural wood character and a thorough investigation of the pH effects on formaldehyde emission are discussed. Initially, the pH was determined by immersing 1 g of wood-flour (passed through a mesh screen of 0.279 mm) in 20 mL distilled water for 20 minutes of extraction. The greatest emission measured by the SPME-A and SPME-W methods was found for the least acidic *binuang* plywood, followed by *laran*, *yellow seraya* and then the more acidic (pH < 6) plywood with the lowest being *kapur*. The solid wood is believed to emit formaldehyde that occurs naturally and it exhibited pH in the acidic level.<sup>21-24</sup> Wood veneers that are more acidic, when bonded to form plywood, tend to emit a lower amount of formaldehyde. In contrast, less acidic wood substrates retard the adhesive cure rate, which tends to deteriorate the bond integrity of plywood and enhances its formaldehyde emission, especially in the presence of water. The decreasing trend of formaldehyde emission by DC, SSC and LLE methods were also found to be paralleled to the reduction in wood pH. Therefore, the pH effect of tropical hardwood species to the formaldehyde emission was significant.

**SPME Validation and Calibrations.** The validation of SPME method was carried out by establishing the following criteria - linearity, precision, recovery and detection limits. Its equation and regression linearity is  $Y = 3085559X - 16888$  ( $r^2 = 0.998$ ) where  $Y$  representing peak area of the formaldehyde-oxime and  $X$  was the formaldehyde concentration in mg/L. This exhibited better linearity in comparison with the SSC ( $r^2 = 0.991$ ) and not much difference from DC ( $r^2 = 0.999$ ) and LLE ( $r^2 = 0.997$ ). Method precision in terms of the relative standard deviation (RSD) and the recovery (REC) were evaluated using a blank sample spiked with standard formaldehyde solution, 1 mg/L. Compared to the

**Figure 2.** Mechanism of formaldehyde derivatized by PFBHA, which forms the formaldehyde-oxime.

SSC (RSD 4.3%) and LLE (RSD 5.0%), the SPME method showed better repeatability (RSD 1.8%). Although it did not perform as well as DC (RSD 1.4%), the SPME has proved to be a reliable alternative for the determination of volatile formaldehyde. The variety of test methods gave satisfying REC except for the SSC, which only gave a REC of 80%. The SPME method gave the best REC of 102%. Meanwhile, the DC (REC 97%) and LLE (REC 92%) were located between them. The REC obtained has polished the performance of SPME and further improved its feasibility for plywood-formaldehyde quantitative analysis. In addition to the SPME method, the limit of detection (LOD) and limit of quantization (LOQ) of 0.01 mg/L and 0.02 mg/L were obtained, thus enlarging the coverage of the SPME for trace levels of formaldehyde determination which can be used as targets for coated plywood in future research efforts. These achievements confirm that SPME is highly sensitive for formaldehyde analysis. The SPME method gave satisfying results with high consistency and validity. This was achieved by the use of correct fiber and excellent derivatizing agent. The DVB-PDMS fiber has been reported to give a maximum response, while the PFBHA of 17 mg/mL reacted completely with aldehyde within a few seconds, forming a GC compatible oxime (Fig. 2).<sup>16,17,19,22</sup> Meanwhile, the automated system further improved the precision of SPME method.<sup>20</sup>

**Relationship of SPMEs with Standard Methods.** The trends of formaldehyde emission, as measured by both SPME-A and SPME-W, paralleled with other methods. A linear regression analysis was done for SPME-W and corresponding DC data, producing the best correlation coefficient,  $r^2 = 0.983$  (Fig. 3). It was followed by  $r^2 = 0.977$  between SPME-A and DC. As evaluated by the Student's t-test, both achieved a confidence level of 95%, which indicates that the SPMEs were comparable to the DC method. The good correlation of SPME-A and DC could be caused by both methods sharing the same source of AS. Meanwhile, a similar specimen loading ratio generated a better correlation between the DC and SPME-W methods. The direct extraction from plywood specimens could eliminate the risk of lost analyte, and, therefore a higher reading by the SPME-W method was obtained. The higher diffusion of the formaldehyde in air than in water best explains this finding.<sup>19</sup> In addition, the shorter testing time by using smaller test samples has evidenced the high efficiency and applicability of the



**Figure 3.** Relationship of formaldehyde concentration as measured by the SPME-W and DC methods.

#### SPME-W method.

An obvious difference was found between the SPME-A and SPME-W with the SSC. They presented an empirical correlation with  $r^2 = 0.941$  and  $r^2 = 0.935$ , which were also the lowest among the others. The initial difference is most likely attributed to the edge sealing effects. Unlike the SPMEs, the SSC collects formaldehyde liberated from the specimen's surface excluding its edges, which were well sealed with paraffin wax. Previous work showed that the emission from the edges is much higher than the three-layer parquet floor surface.<sup>25</sup> The differences could also have been caused by different loading values and the total exposed area of the sample in which the ratio for the SPMEs is 1.4 more than the SSC method. Higher loading configurations together with the open edge specimens resulted in greater emission, and, consequently, gave a greater concentration value in the SPMEs. These results respond in parallel to the observation of Kim *et al.*,<sup>26</sup> who found that the formaldehyde value of CWP decreased when the edges were sealed. The correlation between SPMEs and the LLE produced satisfying linear regressions with  $r^2 \sim 0.95$ . Compared to SPMEs, approximately 81% of the sample by LLE showed a lower formaldehyde magnitude. This could result from incomplete extraction and the lost of analyte. According to EPA 556, the formaldehyde in AS has to be extracted into hexane because the capillary column is intolerant of water phases. However, some residue of the formaldehyde remains and is not extracted due to the greater chemical attraction of the formaldehyde to water than any other organic solvent.<sup>27</sup>

#### Conclusion

The application of headspace SPME-W combined with GC/MS has proven to be suitable for plywood formaldehyde quantitative analysis. Its validation was evidenced by giving better linearity ( $r^2 = 0.998$ ) and improved sensitivity. It was highly precise with its satisfying repeatability (RSD 1.8%). In terms of REC and detection limits, the SPME method

performed better than the existing methods with REC 102% and LOQ 0.02 mg/L being obtained. The SPME-W method used in the current study correlated best with the DC, followed by LLE and SSC at a confidence value of 95%. The correlations generated could contribute enormously to harmonize the variations among the different testing methods. In addition, more environment-benign principles have been implemented in the use of the SPME methods through their solvent-less extraction technology, in heading towards green analytical chemistry.

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