

Evaluation of Solid Phase Micro-extraction with Standard Testing Method for Formaldehyde Determination

Y. L. Yung and Kong Mun Lo

Abstract—In this study, solid phase micro-extraction (SPME) was optimized to improve the sensitivity and accuracy in formaldehyde determination for plywood panels. Further work has been carried out to compare the newly developed technique with existing method which reacts formaldehyde collected in desiccators with acetyl acetone reagent (DC-AA). In SPME, formaldehyde was first derivatized with O-(2,3,4,5,6 pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA) and analysis was then performed by gas chromatography in combination with mass spectrometry (GC-MS). SPME data subjected to various wood species gave satisfactory results, with relative standard deviations (RSDs) obtained in the range of 3.1-10.3%. It was also well correlated with DC values, giving a correlation coefficient, RSQ, of 0.959. The quantitative analysis of formaldehyde by SPME was an alternative in wood industry with great potential

Keywords—Formaldehyde, GCMS, Plywood and SPME

I. INTRODUCTION

FORMALDEHYDE released from plywood (PW) commonly determined through chamber or desiccators (DC) in United State and Asia-Pacific regions. Although these methods have been used for formaldehyde comparison by several researchers [1] and [2], longer test duration and larger sample size were the remained drawbacks. There is a need for more advance and efficient technique like solid phase micro - extraction (SPME) which requires smaller sample size besides possessing rapid extraction with promising precision. Several researchers have discussed the use of SPME but limited to aromatic, drugs and pharmaceutical analyses [3] and [4]. The application of SPME for plywood is rarely found before this. The wood-formaldehyde analyses are preferably carried out through spectrometric method [5] and [6]. Within current works, gas chromatography coupled with mass spectrometry (GC-MS) was compared with standard ultraviolet-visible (UV-VIS) spectrophotometry.

Y. L. Yung. Author is with the Chemistry Department, Faculty of Science, University of Malaya, 50600 Kuala Lumpur, Malaysia (+60128155481, e-mail: yyl1007@siswa.um.edu.my).

Dr. Kong Mun Lo is working as a lecturer in Chemistry Department, Faculty of Science, University of Malaya, 50600 Kuala Lumpur, Malaysia (+60379674262, e-mail: kmlo@um.edu.my).

The aim of our investigation was initially to improve the methodology sensitivity and accuracy in formaldehyde determination for plywood panels by superseded with SPME-GCMS. Further work has been carried out to compare the newly developed technique with the existing method which reacts formaldehyde collected in desiccators with acetyl acetone reagent (DC-AA)

II. MATERIAL

A. Chemical and Reagents

Formaldehyde 37% v/v aqueous solution, (Merck), Hydrochloric acid 37% (Merck), Sodium sulfite (Merck), Acetyl-Acetone (Merck), Ammonium Acetate (Merck), Glacial Acetic Acid (Merck), Iodine (Merck), Potassium Dichromate (Merck), Potassium Iodide (Merck), Sodium Hydroxide (Merck), Sodium Thiosulfate Pentahydrate, Hexane for GC (SA), Methanol (99.8% purity, SA) and O-(2,3,4,5,6 Pentafluorobenzyl) hydroxylamine hydrochloride (98+% purity SA).

B. Sample Preparations

The wood species used to manufacture plywood sample includes binuang (*Octomeles* spp.), batai (*Falcataria*), kapur (*Dryobalanops* spp.), keruing (*Dipterocarpus* spp.), laran (*Neolamarckia cadamba*), magas (*Duabanga* spp.), red seraya (*Shorea* spp.), sedaman (*Macaranga* spp.), white seraya (*Parashorea* spp) and yellow seraya (*Shorea* spp.). Five replicate plywood panels were prepared for DC-AA and SPME tests

C. Apparatus and Instrument

The Shimadzu Model UV-1800 UV-spectrophotometer, achieves a resolution of 1 nm was used in DC-AA method. Divinylbenzene Polydimethylsiloxane (DVB-PDMS) SPME fiber of 65 μ m with 23 gauge (Supelco) was selected and the extractions were performed using a CTC-Combi-PAL automated SPME connected to gas chromatography coupled with Shimadzu Model GC MS-QP2010Plus mass spectrometer. Compounds were separated by using a 5% diphenyl 95% dimethyl polysiloxane column with 30m length, 0.25 mm i.d. and 0.25 μ m film thickness (Rts-5MS, Restek).

III. METHOD

A. Desiccators-Acetyl Acetone Method (DC-AA)

Glass desiccator of 240mm diameter was used to collect wood formaldehyde since the method first created in 1973.

The test specimens were being placed on top of 300ml distilled water at the centre of desiccators at $20\pm 0.5^\circ\text{C}$ for conditioning in 24 hours. Ammonium acetate and acetyl acetone (A4) solution of 25 ml was mixed gently with equal volume of sample solution in vessels and being warmed at $65\pm 2^\circ\text{C}$ for 10 minutes [7]. Base to the Hantzsch reaction, the formaldehyde was measured through its reactions with ammonium ions and acetyl-acetone which yielding diacetyl dihydrolutidine (DDL). Qualitative test was carried out at wavelength of 412nm of spectrophotometer and blank solution was a comparator.

The formaldehyde concentration of each aliquot was calculated in:

$$C = Fx(Ad - Ab) \quad (1)$$

Where,

C= Formaldehyde concentration of test pieces (mg/l)

Ad= Absorbance of a sample solution

Ab= Absorbance of a blank solution

F= Inclination of calibration curve (mg/l)

B. Solid Phase Micro-Extraction (SPME)

The distilled water also known as absorbing agent (AS), having absorbed formaldehyde was measured to a volume of 10ml into a 20ml glass headspace vial later covered with magnetic screw cap. The samples were mixed at 60°C for 40 minutes in incubator to reach gas-liquid equilibration. The DVB-PDMS fiber was first on-fiber derivatized by 10ml of PFBHA aqueous solution (15mg/ml) for 10 minutes. Then, it was possessed for 15 min sample adsorption before directly inserted into the GC injector, where the analyte was thermally desorbed at 250°C for 7 min. The formaldehyde-oxime formed on the fiber was analyzed by GC-MS. Helium was the carrier gas with flow rate 1.0ml/min. The temperature program of the column used is 60°C for 2 min, increasing to $60\text{-}90^\circ\text{C}$ at $5^\circ\text{C}/\text{min}$ then $90\text{-}250^\circ\text{C}$ at $50^\circ\text{C}/\text{min}$ and a hold 5 min. The mass spectrophotometer analysis was performed using electron impact ionization (EI) in full scan from 150 to 275 m/z.

The target analyte was identified and quantified as,

$$C = FxAd \quad (2)$$

Where,

C= Formaldehyde concentration of test pieces (mg/l)

Ad= Absorbance of a sample solution

F= Inclination of calibration curve (mg/l)

IV. RESULTS AND DISCUSSION

The formaldehyde emission evaluated by SPME and DC-AA method onto the same plywood panels was compared. SPME values were ranging from 1.3 to 5.7mg/l whereas 0.30-0.97mg/l for the DC-AA method. Higher emission values were recorded by using SPME method. It was most likely attributed by the use of DVB-PDMS fiber which capable to optimize the extraction of oxime-derivatives for quantitative analysis [8]. Before proceed the extraction, the fiber was first derivatized in PFBHA solution and it was known as the most appropriate formaldehyde derivatizing agent. As the result, the derivatization and extraction for formaldehyde had been

enhanced and thus giving greater concentration value. Besides that, the yellowish DDL formed in DC-AA method was sensitive compound. It could be decomposed under light source exposure until deteriorate its absorbance value easily in the photometry analysis.

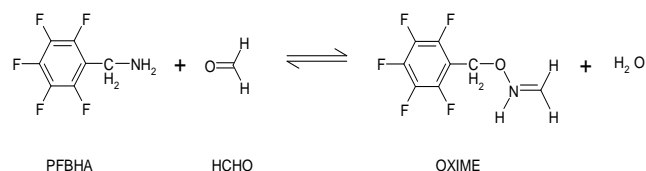


Fig. 1 Reaction scheme of PFBHA and formaldehyde to form the formaldehyde-oxime

Although the formaldehyde emissions of the same panel

TABLE I
FORMALDEHYDE CONCENTRATION AND REPEATABILITY COMPARISON
SUBJECTED TO VARIOUS WOOD SPECIES

Sample	Repeatability, RSD	
	DC-AA (%)	SPME (%)
YS	1.0%	5.7%
WS	1.2%	3.7%
LR	1.3%	6.6%
BT	1.4%	6.9%
BN	1.7%	1.8%
KP	1.8%	10.3%
KR	1.8%	9.3%
RS	2.1%	3.1%
SD	2.2%	6.3%
MG	3.9%	3.1%
Min	1.0%	1.8%
Max	3.9%	10.3%

analyzed by spectrometry and chromatography methods were different, both vary with wood species in similar trend. For example, BN emitted the highest formaldehyde whereas the lowest was KP as measured by both of the DC-AA and SPME methods. The influence of wood species to formaldehyde emission was discovered but current studies focus more towards the method comparison including testing condition and parameters as well. SPME data subjected to various wood species gave satisfying relative standard deviation (RSD) in the range of 3.1-10.3%. It has showed its high consistency and validity although not perform as well as DC (below 3.9%). The repeatability of SPME methods was assessed and it has a great potential to become a new alternative for wood formaldehyde quantitative analysis. As evaluated by Student's t-test, SPME data achieved confidence level of 95% which indicates its testing results obtained were comparable.

A good correlation (Fig. 2) was achieved in between SPME and DC-AA. It could partially caused by both methods sharing the same sources of AS. Furthermore, the diffusion of formaldehyde into a smaller headspace during SPME was in favored [9]. With the effect of agitations [10], the extraction

efficiency has been strongly improved. As a consequence, optimized SPME method forms good correlation with the ordinary method.

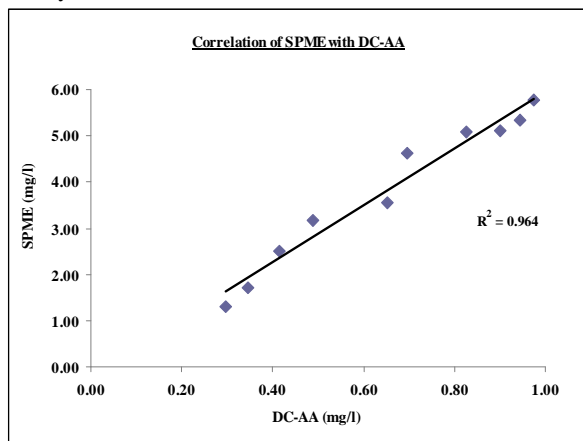


Fig. 2 Relationship of formaldehyde concentration as emitted from plywood panels measured by SPME and DC methods

The calibration curve was used for the formaldehyde analysis and it was formed by linking peak area (GC) or absorbance value (UV) with formaldehyde standard solution of increasing consistencies in the range of 0.5-10 mg/l, see Fig. 3. The six point calibration curve was formed to cover the possible concentration deviation. A good linearity was generated with correlation coefficient, RSQ= 0.999 for both SPME and DC. This achievement has established the effectiveness of the SPME for formaldehyde analysis of plywood panels. During this study, the 'zero formaldehyde' was not achieved and interference of background air quality could be the root cause besides resulted from airborne formaldehyde emitted from wooden furniture and wall panels, consumer products, clothing and fabrics [11].

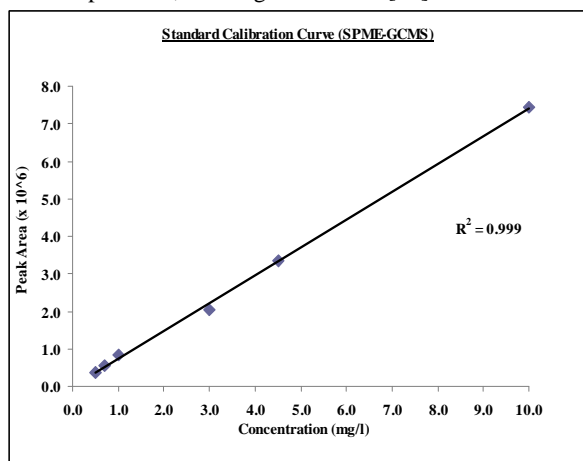


Fig. 3 Standard calibration curve for formaldehyde quantitative determination by using HS-SPME-GCMS

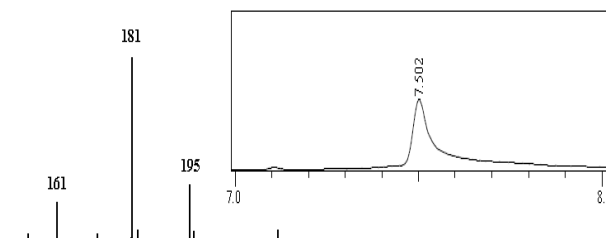


Fig. 4 Mass spectrum of formaldehyde-oxime obtained after SPME-GCMS analysis and chromatogram of derivatized formaldehyde from specimen KP

V. CONCLUSION

The application of SPME combined with GCMS was proven to be a suitable method for wood formaldehyde quantitative analysis with better sensitivity and highly precise of the maximum RSD approximately to 10%. In the comparison with conventional method, the SPME correlated well with DC (RSQ above 0.96) at confidence value of 95%. With gradual improvement, SPME will become more reliable with the contemporary techniques complied.

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