CHAPTER FIVE

SPME OPTIMISATION

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5.1 SPME Optimisation

The formaldehyde concentration of different wood species was quantified by the measurement on the oxime derivative formed. However, the inconsistent readings were noticed in the repeatability evaluation in the earlier stage of the current studies.

In fact, the *O*-(2,3,4,5,6 pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) was substantially fragmentised in the formation of formaldehyde-oxime, as indicated by the decrease of the corresponding peak area. Figure 5.1 demonstrates approximately 50% decreased in the second time and at least 60% decreased in the third time of continuous extraction. It was also learnt that the consumption of derivatisation reagent increased in response to the analytes with greater concentration. Thereafter, the solid phase micro-extraction (SPME) fibre is reloaded with PFBHA each time before proceeding to a new sample extraction. For better derivatisation, freshly prepared PFBHA is used with no more than 20 injection cycles. As a consequence, the method's precision has been improved through more effective fibre adsorption, which leads to the completeness of the formaldehyde extraction.

After the continuous trial, the heating temperature of extraction at 45°C was found to stimulate the formaldehyde migration to the headspace of the samples and further enhance the diffusion in both the solid phase micro-extraction sampling from absorbing solution (SPME-A) and air sampling directly from wood specimen (SPME-W) tests (Figure 5.2). This helped to improve the method sensitivity by accelerating the on-fibre extraction (Gioti

et al., 2007). As a result, formaldehyde is well extracted onto the PFBHA derivatised fibre. The results obtained in Chapter 4 clearly indicate that the extraction was maximised and that the risk of sample degradation at higher temperature (Barrio *et al*., 2006) could be eliminated. This is mainly because of the high reactivity and volatility of formaldehyde even at room temperature (WHO, 2002).

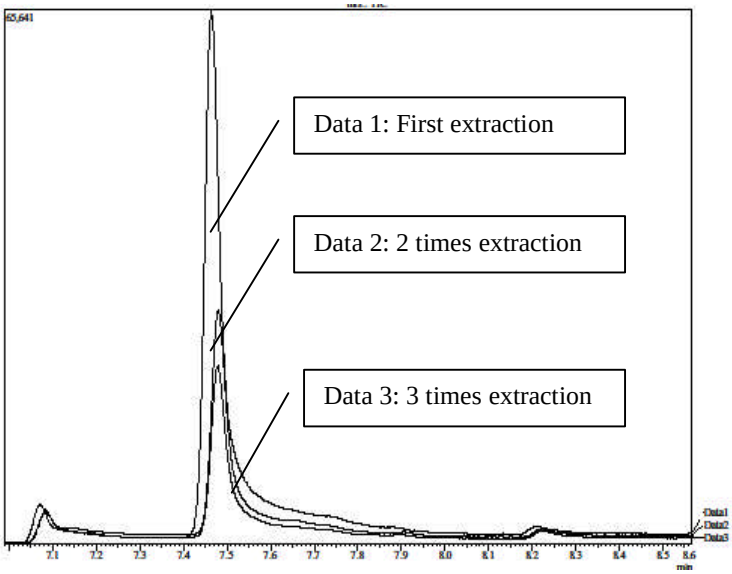


Figure 5.1: Formaldehyde-oxime peak of first extraction, after 2 times and then 3 times of continuous extraction

In order to enrich the emission of formaldehyde in the headspace of SPME-A and SPME-W, the agitation speed was maintained at 250 rpm along derivatisation loading and sample extraction although a faster speed of 500 rpm and even 1100 rpm have been used for beer wort and blood samples, respectively (Schutter *et al*., 2008; Deng *et al*., 2004). This is to prevent the fibre from tearing off easily and frequent splashing of the sample onto the fibre. Also, the water sample in SPME-A is less viscous than the blood specimens tested. In addition, air sampling directly from wood specimens was performed using the

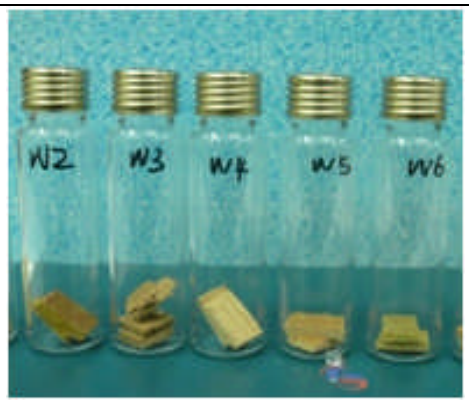
SPME-W method. The incubation and extraction assisted with constant agitation helps to improve the evenness of formaldehyde emission (Figure 5.2).

In addition, the extraction time of 40 minutes was found to be sufficient as there was no significant increase of formaldehyde-oxime peak in responding to the extended interval. Finally, a desorption time of 10 minutes at 60°C was then fixed for automated gas chromatography mass spectrometry (GC/MS) analysis and also for ensuring that the total analyte has been transferred through injection with no carry over problem. The following analyses were continued at the optimum conditions for SPME (Figure 5.2).

The formaldehyde derivatised by PFBHA forms the GC compatible formaldehyde-oxime as shown in Figure 5.3. The extraction profiles were studied for approximately 60 minutes. In between, the standard and sample solutions showed two well defined peaks. A sharp peak at approximately 7.5 min (Figure 5.4) and a broad peak at 9.0 min were acquired. The mass spectra of Peak 1 and Peak 2 were identified by using Shimadzu Lab Solution MS library, as formaldehyde-oxime or the products of derivatisation and non-reacted PFBHA, respectively.

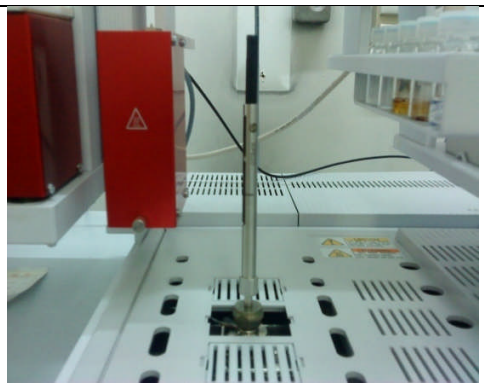
The selected ion monitoring (SIM) mode was applied to improve the sensitivity of the MS detection by referring to previous studies (Barrio *et al*., 2006). The chromatograms acquired in SIM correspond with *m*/*z* 181, 195, 161 and 117. The reference mass spectrum, however, is dominated by *m*/*z* 181 peak, which corresponds to the pentafluorobenzyl group. The other peaks are likely to be generated by non-fragmented PFBHA or other carbonyl compounds.

(a)



(b)

(c)



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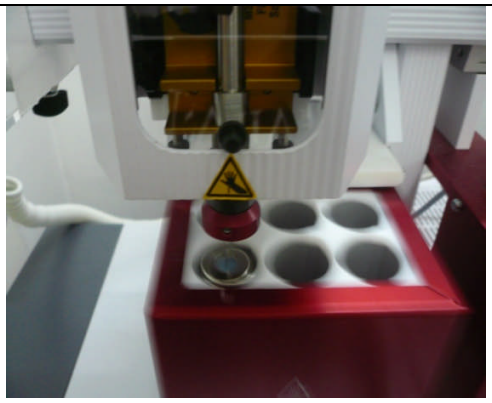

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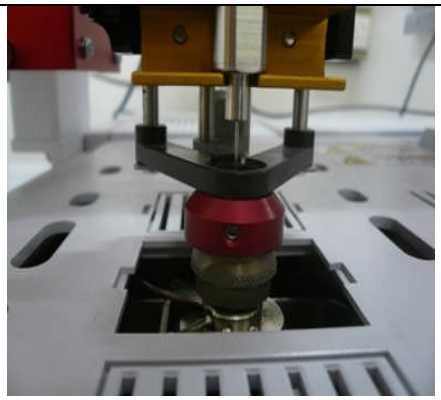

(f)

Figure 5.2 SPME optimisation
(a)-(b): Absorbing solution and plywood specimens prepared in headspace vial in the SPME-A and SPME-W methods;
(c)-(d): PDMS-DVB fibre and the fibre pre-conditioning at the GC port;
(e)-(f): On-fibre extraction and analyte adsorption at a constant agitation, followed by analyte desorption through the *Merlin* microseal septum in the gas inlet of GC/MS.

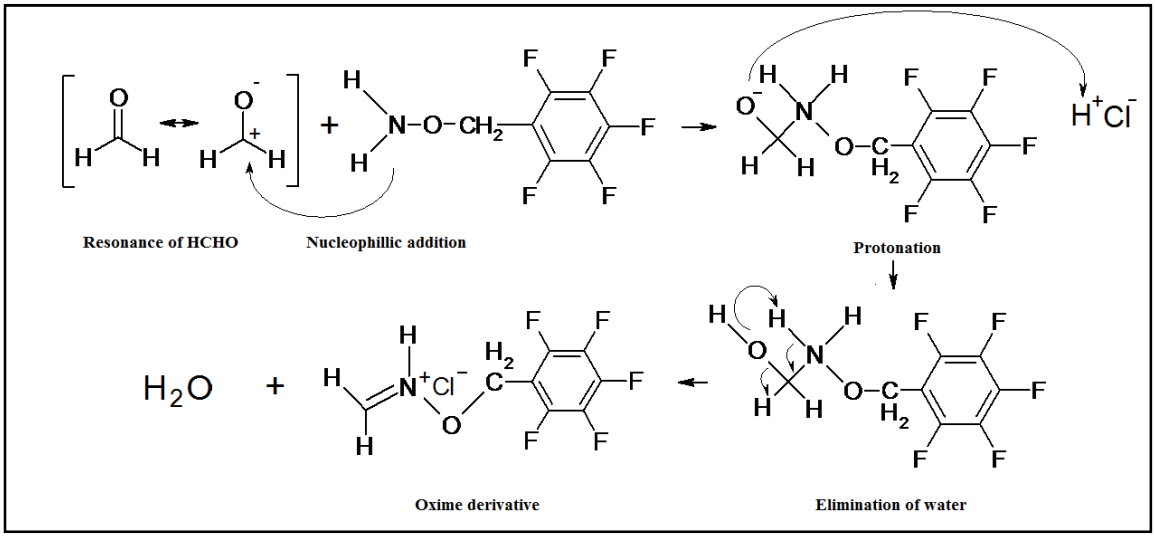

Figure5.3: Mechanism through which formaldehyde derivatised by PFBHA forms the formaldehyde-oxime

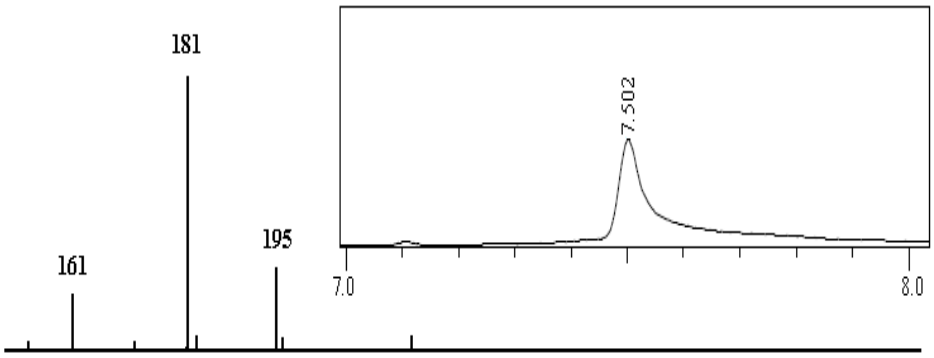

Figure 5.4: Mass spectrum of formaldehyde-oxime obtained after SPME-GC/MS analysis and chromatogram of derivatised formaldehyde from specimen *kapur*.

5.2 Calibration and Background Level

A calibration curve is used for the formaldehyde analysis on moisture content and numerous wood species evaluations. It was formed by plotting the peak area with the formaldehyde standard solution with increasing consistencies in the range of 0.1 mg/L to 3 mg/L (Figure 5.5). A good linearity was generated with the correlation coefficient, R^2 =

0.9982 by the SPME. Its calibration equation is $Y = 3085559X - 16888$, where Y represents the peak area of the formaldehyde-oxime and X was the formaldehyde concentration in mg/L. The linear curve was used for solid wood, original untreated and also treated plywood panel evaluation, giving a formaldehyde concentration from ultra-low to a higher level. A six point calibration curve was formed to cover the possible deviation in concentration (Yung & Lo 2012, 2013).

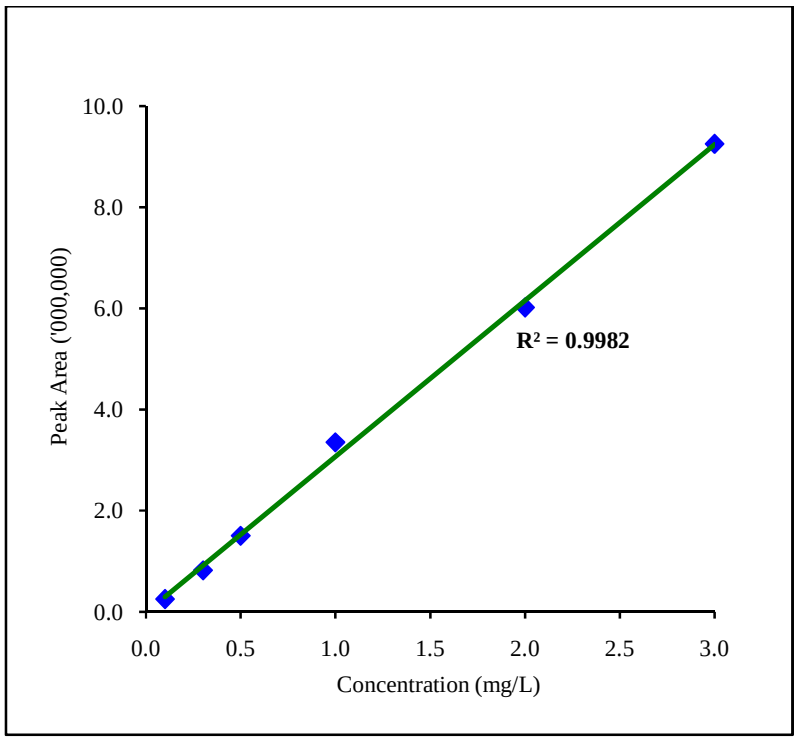

Figure 5.5: Standard calibration curve for formaldehyde quantitative determination by using headspace solid phase micro-extraction (HS SPME) GC/MS.

The effectiveness of the SPME methods for plywood formaldehyde analysis has been established. The satisfying regression value of 0.9982 and very low relative standard deviation of 1.8% by SPME method have exhibited its better linearity and precision in comparison with other methods. Meanwhile its sensitivity for volatile formaldehyde analysis is evidenced. The additional studies carried out showed the better performance of

SPME-W method in terms of repeatability and consistency for evaluation of both the high and ultra-low level of formaldehyde. It is also best correlated with the standard methods that adapted spectrophotometric and chromatographic analysis. In addition, the longer storage interval for solid specimens could be remarkable advantage for the SPME-W method with no better substitution. With gradual improvement, it will become more reliable than the application of the contemporary techniques complied (Yung & Lo 2012).

In this study, ‘zero formaldehyde’ was not achieved, even for the blank sample. The interference of background air quality could be the root cause. In the indoor air, the level of formaldehyde fluctuated and was often higher as a result of the airborne formaldehyde emitted from wooden furniture and wall panels. Other than that, it may be released from building materials, consumer products, tobacco smoke, clothing and fabrics (Roffael, 2006). To eliminate these influences in current research, the researcher developed a prevention method by placing activated carbon around headspace vials overnight before the sample loading. The same treatment was applied to the desiccator and chamber methods.