CHAPTER 3

RESULTS AND DISCUSSION

In this work passive sampler for determination of formaldehyde indoors was developed and validated in the self-constructed exposure chamber.

3.1 Determination of formaldehyde by spectrophotometry

3.1.1 Calibration curve of formaldehyde

Formaldehyde bisulfite adduct collected was determined using the linear regression equation of the calibration curve prepared from different concentrations of formaldehyde standard solutions in a range of 0.5 – 10.0 µg/ml as shown in Table 3.1 and Figure 3.1.

Table 3.1 Absorbance of formaldehyde

Formaldehyde (n=3) µg/ml	**Absorbance**
0.0	0.0004±0.0003
0.5	0.0311±0.005
2.0	0.1123±0.002
4.0	0.2011±0.006
6.0	0.3023±0.005
8.0	0.4001±0.006
10.0	0.5060±0.006

In this method metatrioxane and paraformaldehyde as well as dimethoxymethane represent positive interferences. Large amounts of phenols cause a negative interference which may completely mask color formation. For analysis of samples containing phenol, color development may be accomplished by using 1 ml of 10% instead of 1% chromotropic acid to decrease the phenol interference. However, the process does not collect phenol efficiently and therefore any potential interference is expected to be minimal.

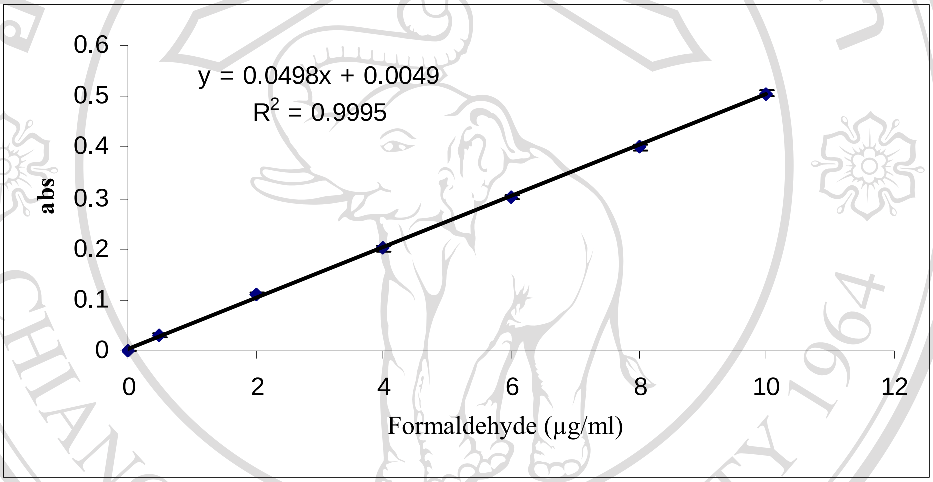

Figure 3.1 Calibration curve of formaldehyde

3.1.2 Linearity of range

The linear dynamic range (LDR) was investigated by varying concentrations of the analyte from 0.5 to 14 µg/ml. After that those concentrations were plotted against their absorbance the relative standard deviation (RSD) was lower than 5 % (n= 3). Moreover, high correlation efficiency (R^2 = 0.9965) was obtained as shown in Figure 3.2.

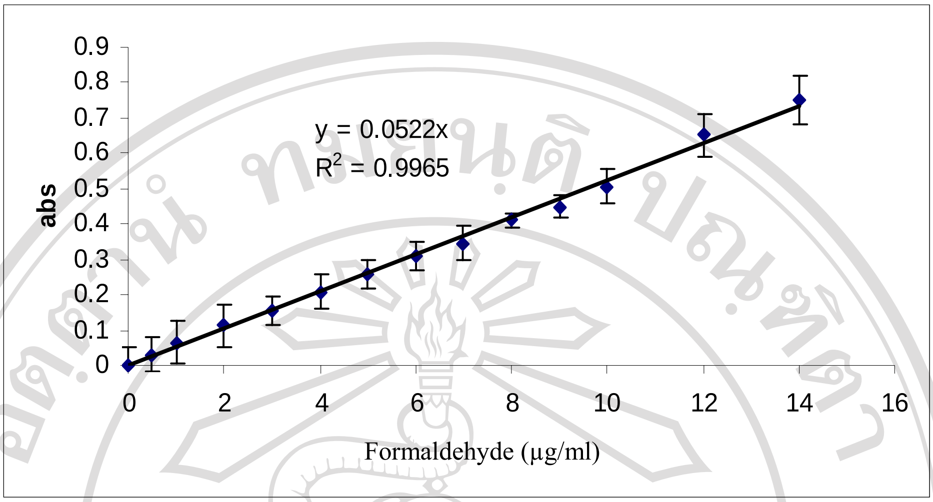

Figure 3.2 Linear dynamic range of CTA method

According the method, the LOQ is 1 μg/ml but in this test, the LOQ can be accepting at 0.5 μg/ml %RSD ≤5.

3.2 Detection limit of spectrophotometry

The detection limit was obtained by use of linearity curve of formaldehyde concentration with good correlation (r^2= 0.999) as shown in Figure 3.1. The detection limit was calculated using the equation 2.17 (topic 2.10.1) and the data of blank measurements are shown in Table 3.2. The method detection limit (MDL) and limit of quantification (LOQ) of spectrophotometry for formaldehyde measurements were 0.007 and 0.023 μg/ml, respectively.

Table 3.2 Detection limit of spectrophotometry for formaldehyde

N	absorbance	Formaldehyde (μg/ml)
1	0.0004	0.008
2	0.0002	0.004
3	0.0005	0.010
4	0.0002	0.004
5	0.0004	0.008
6	0.0003	0.006
7	0.0002	0.004
8	0.0004	0.008
9	0.0005	0.010
10	0.0004	0.008
mean	**-**	**0.007**
SD	**-**	**0.0023**
MDL (3×SD)	**-**	**0.007**
LOQ (10 ×SD)	**-**	**0.023**

3.3 Optimization of passive sampler

3.3.1 Detection limit of formaldehyde passive sampler

Detection limit of formaldehyde passive sampler is shown in Table 3.3 – 3.4. Using the standard deviation of the field blank, the limit of detection (LOD) values of the formaldehyde passive sampler were 0.21 mg/m^3 (0.17 ppm) for 8 hours and 0.06 mg/m^3

(0.05 ppm) for 24 hours exposure. The limits of quantification (LOQ) values were 0.70 mg/m^3 (0.56 ppm) and 0.20 mg/m^3 (0.16 ppm) for 8 and 24 hours, respectively.

Table 3.3 Detection limit of formaldehyde passive sampler for 8 hours exposure.

Replication number	absorbance	Formaldehyde		
		µg/ml	Mass µg	mg/m^3
1	0.0041	0.082	0.246	0.204
2	0.0051	0.102	0.306	0.254
3	0.0045	0.090	0.270	0.224
4	0.0037	0.074	0.222	0.184
5	0.0021	0.042	0.126	0.105
6	0.0029	0.058	0.174	0.144
7	0.0024	0.048	0.144	0.119
8	0.0015	0.030	0.090	0.075
9	0.0013	0.026	0.078	0.065
10	0.0012	0.024	0.072	0.060
mean	**-**	-	-	**0.143**
SD	-	-	-	**0.070**
LOD (3×SD)	-	-	-	**0.200**
LOQ (10×SD)	-	-	-	**0.700**

Table 3.4 Detection limit of formaldehyde passive sampler for 24 hours exposure.

Replication number	absorbance	Formaldehyde		
		µg/ml	µg	mg/m^3
1	0.0051	0.102	0.306	0.085
2	0.0051	0.102	0.306	0.085
3	0.0045	0.090	0.270	0.075
4	0.0057	0.114	0.342	0.095
5	0.0041	0.082	0.246	0.068
6	0.0059	0.118	0.354	0.098
7	0.0044	0.088	0.264	0.073
8	0.0015	0.030	0.090	0.025
9	0.0043	0.086	0.258	0.071
10	0.0042	0.084	0.252	0.070
mean	-	-	-	**0.074**
SD	-	-	-	**0.020**
LOD (3×SD)	-	-	-	**0.060**
LOQ (10×SD)	-	-	-	**0.200**

3.3.2. Determination of total air resistance

Comparison has been done between passive samplers enclosed with and without membrane. Then LF/AF value (see Table 3.5) from the experiment for evaluation of air resistance was calculated with eq. 2.3 (topic 2.7.2).

The diffusion coefficient of formaldehyde in air, calculated with eq. 1.6 was 1.6 x 10^{-5} m^2 s^{-1} at a temperature of 298 K (Gillettr, *et al,* 2000).

A total air resistance of the passive sampler was 382.3 m^{-1} (see detail in the appendix A). Dimension factors of formaldehyde passive sampler are shown in Table 3.5.

Table 3.5 Dimension factor of formaldehyde passive sampler for total air resistance determination

Factor	**value**
AR (area of tube)	1.32 x 10^{-4} m^2
AF (total pore area of Teflon filter)	-
LF (thickness of Teflon filter)	-
LR (length of tube)	5 x 10^{-2} m
LBL (laminar boundary layer depth)	5 x 10^{-3} m
Total resistance	382.3 m^{-1}

In this parameter, the total air resistance can be classified into 3 parts, which are laminar boundary layer (LBL), thickness of Teflon filter (LF) and Length of the tube (LR). **The LBL** part depends on wind speed and pressure in the atmosphere which affects to the thickness of the LBL. If pressure and wind speed are low, it results in increasing the thickness of the LBL. The LBL value used in this work come from the experiment of Gillettr and Ayers in 2000 as shown in Table 3.5. The thickness of Teflon filter **(LF)** part depends on both thickness and pore-size of membrane which affect to diffusion rate of gas and duration time to get into steady state. Length of tube (LR) can control the diffusion rate to constant. The long tube can increase the resistance of diffusion or decrease the time to steady state.

3.3.3 Selection of types of adsorbent

The selection of impregnated paper is important for development of an effective passive sampler. The performance of passive sampler depends on the appropriate impregnated paper which present highly adsorption of sorbent and easy desorption. The hydrophilic property of a impregnated paper results in capacity of adsorption and desorption of the analyte and influencing accuracy and precision of the sampler. All types of impregnated paper were cleaned with DI water and dried in an oven before use. They were placed in the diffusion tube and an impregnated with 100 µl of 1% bisulfite solution. The efficiency of impregnated paper was tested in the exposure chamber by evaluation of percentage recovery value. The result is shown in Figure 3.3 and Table 3.6. It was found that the cellulose Whatman No.6 (96±3%) gave the highest recovery value unless the Whatman 40 (117±8%) was excluded due to its overestimated value and too high %RSD value. The RCB-test showed no significant difference at 95% confidence level between Whatman No. 1 and No. 6. Then, Whatman No. 6 was chosen as an adsorbent for this study due to its hydrophilic properties, easy to adsorb and desorbs formaldehyde and inexpensive. The GFA and GFC also provided quite high recovery (91±3%) and 93±5%, respectively). However, they were not selected due to some inappropriate properties such as ability of adsorption for solution (after pre-washed and dried) as well as their high cost.

Table 3.6 Percent recovery of formaldehyde from different types of adsorbent

Absorbance Types	mean (mg/m^3) (n=5)	SD	%RSD	% Recovery
Whatman No. 1	59.2	0.5	3.8	93±2
Whatman No. 6	61.1	0.7	4.7	96±3
Whatman No. 40	74.1	2.0	11.0	117±8
GF	51.8	2.0	13.0	82±7
GFA	58.0	1.0	5.0	91±3
GFC	58.9	1.0	8.7	93±5

Note Formaldehyde concentration was 14.5 mg/m^3 , % RH = 60 %, T = 30 °C and wind speed = 0.0 m/ s.

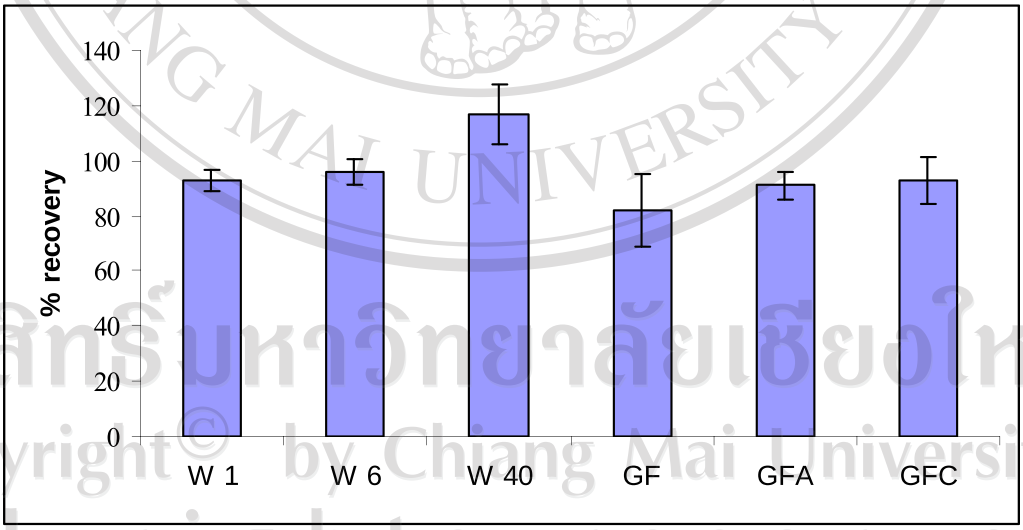

Figure 3.3 Percent recovery of the formaldehyde from difference types of adsorbent

3.3.4 Selection types of diffusion tube

The passive diffusion tube first was introduced by Palmes and Gunnison (1973) for workplace monitoring. The sampling of the diffusion tube bases on the principle of molecular diffusion. The concentration of gas was classically determined from the collected amount of the analyte divided by the sampling time and the sampling rate by applying Fick's first law.

Type of diffusion tube was studied for the suitability of diffusion of gas from ambient air. Diffusion tube types including PP, PE and PS were tested as described in a topic 2.7.4. The PS tube is transparent, while the PE and PP are less transparent. However, the properties of those three types are similar in term of water sorption rate, which is 0.01% for PE and PP and 0.06% for PS. The values indicated hydrophobic property. In this work, the open end of the diffusion tube was closed the with a Teflon membrane to reduce meteorological effect. It was found that the PP diffusion tube gave the highest percent recovery of formaldehyde with good precision (low % RSD value) as shown in Table 3.7 and Figure 3.4. Comparison of PP, PE and PS using RCB-test showed significant difference at 95% confidence level (see Appendix D). The PP tube was therefore chosen for further study.

Table 3.7 Types of diffusion tube and their percent recoveries for formaldehyde

Types	Formaldehyde Conc. mg/m^3	SD	%RSD	%Recovery
PP	5.34	3.0	4.7	83±3
PE	4.88	6.0	12.0	66±6
PS	4.03	1.0	2.0	63±1

Note Formaldehyde concentration was 6.4 mg/m^3 , % RH = 50±3 %, T = 31±2 °C and wind speed = 0.0 m/s.

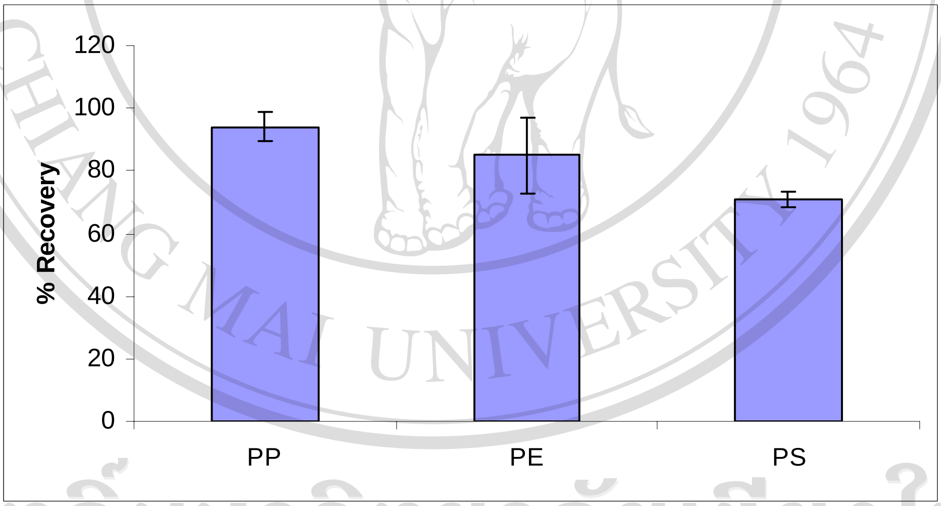

Figure 3.4 Types of diffusion tube and percent recovery of formaldehyde

3.3.5. Desorption efficiency and number of filter layers

The number of adsorbent relate to the extraction efficiency of method. Then the optimization of this parameter has to test for optimum of adsorbent.

The initial extraction procedure followed the guidelines of the 3M Company for use and extraction of the 3M 3721 Formaldehyde Monitor (see Appendix C). Three milliters of distilled water was added to each filter paper and allowed eluting for 30 minutes. A 2 aliquot of the eluate was transferred to a test tube for color development (topic 2.4.2).

Determination of desorption efficiency was done by spiking of 20 µg formaldehyde standard onto the sorbent (Whatman No.6). Layer of the filter paper ranked from 1 to 5 were put in the tubes. Six replications of each condition were prepared. The results in term of percent recovery are shown in Figure 3.5. It was found that 1 and 2 layers of filter paper provided good percent recovery of formaldehyde with good precision (5 and 4 %RSD, respectively). Even though there was no significant difference found between usage of 1 and 2 layers of filter paper, the 2 layers of filter paper was chosen because it provided the higher percent recovery and better precision value. High number of layers affects to variation of determination because more adsorbent layer might adsorb more analyte into it that can cause low extraction efficiency.

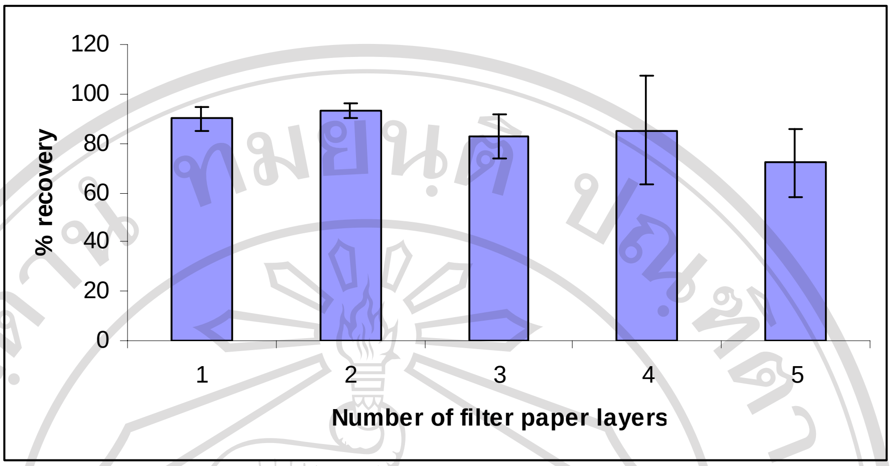

Figure 3.5 Percent recoveries of formaldehyde from different numbers of filter layers

Table 3.8 Percent recoveries of formaldehyde from different number of filter layers (n = 6)

Number of filter layers	Replication number	Formaldehyde absorbance	Formaldehyde µg /ml	Formaldehyde µg	Mean (mg/m^3)	SD	% RSD	% Recovery
1 layer	1	0.3712	6.1	18.3	**18.0**	**0.9**	**5.0**	**90±5**
	2	0.3745	6.1	18.4				
	3	0.3561	5.8	17.5				
	4	0.3970	6.5	19.5				
	5	0.3561	5.8	17.5				
	6	0.3456	5.7	17.0				
2 layers	1	0.3945	6.5	19.4	**18.5**	**0.5**	**2.8**	**93±3**
	2	0.3684	6.0	18.1				
	3	0.3714	6.1	18.3				
	4	0.3654	6.0	18.0				
	5	0.3825	6.3	18.8				
	6	0.3764	6.2	18.5				
3 layers	1	0.3188	5.2		**16.5**	**1.5**	**8.9**	**83±9**
	2	0.3155	5.2	15.5				
	3	0.3530	5.8	17.4				

Table 3.8 (continued)

Number of filter layers	Replication number	Formaldehyde			Mean (mg/m^3)	SD	% RSD	% Recovery
		absorbance	µg /ml	µg				
	4	0.3224	5.3	15.9				
3 layers	5	0.3897	6.4	19.2				
	6	0.3160	5.2	15.5				
	1	0.3955	6.5	19.4				
	2	0.3465	5.7	17.0				
	3	0.4517	7.4	22.2				
4 layers	4	0.2540	4.2	12.5	**16.9**	**3.7**	**22.1**	**85±22**
	5	0.3540	5.8	17.4				
	6	0.2640	4.3	13.0				
	1	0.2870	4.7	14.1				
	2	0.3454	5.7	17.0				
	3	0.3412	5.6	16.8				
5 layers	4	0.3001	4.9	14.8	**14.5**	**2.1**	**14.7**	**72±14**
	5	0.2488	4.1	12.2				
	6	0.2450	4.0	12.0				

3.3.6 Storage stability

Thirty five samplers were exposed to 14.5 mg/m^3 formaldehyde at 80 % relative humidity, 30 °C for 4 hours in the exposure chamber. Five samplers of those were analyzed within 1 day. Half of the remain samplers was stored at 4 ºC and another half was kept at room temperature (27±1ºC). Each set (5 samplers) of those was analyzed every week. The results showed recovery value in the range of 80 – 120 % (Figure 3.6). It can be concluded that the formaldehyde trapped in the passive sampler can be stored at least 3 weeks at room temperature with no loss. Comparison using RCB-test showed no significant difference of the storage duration at 99% confidence level.

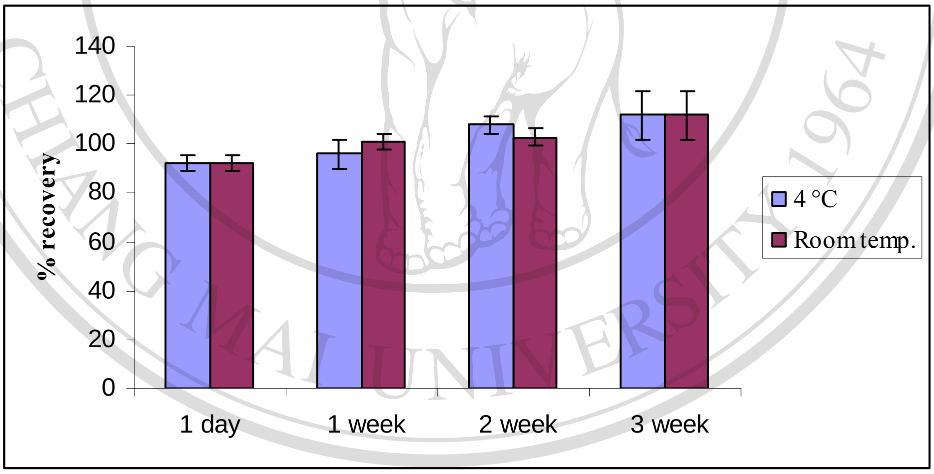

Figure 3.6 storage stability of formaldehyde passive sampler

In the past, bisufite adduct form was used to purify the aldehyde group which presented in a crystal with stable properties. Then the bisulfite adduct is useful for keeping the analyte stable. Moreover, there was no interference in the process.

3.4 Validation of passive sampler

Validation of passive sampler has been investigated by focusing on the effects of reverse diffusion, sampler orientation, temperature and humidity effects. The passive sampler was evaluated under controlled laboratory conditions as well as in the field.

3.4.1 Validation of wind velocity effect

Several investigations demonstrated that wind speed may affect the reliability of diffusive samplers due to variations of the effective diffusion path length (Pozzoli and Cottica, 1987; Zurlo and. Andreoletti, 1987; Gair and Penkett, 1995). Both low and high wind speeds may be a source of error. On conditions with low air velocity a static layer of air in front of the sampler may cause an increase of the diffusive path length. On the other hand, high wind speeds may shorten the effective diffusion path length (CEN prEN 13528- . 3, 1999). In both cases, the use of the geometric length of the sampler may bias the calculation of ambient concentration. Then, close of the open end of the diffusive tube with a Teflon membrane can be used for accuracy in calculation of concentration.

Wind velocity was varied by apply the voltage to the fan inside the exposure chamber, where the diffusion tubes were fixed at the sampling holder. Preliminary measurement of wind velocity inside the chamber was necessary to set up the wind profiles in order to select positions of tubes in accordance to the voltage of fans. A total of 45 measurements including 3 levels of formaldehyde concentration (3, 7 and 18 mg/m^3) and 3 levels of wind velocity in the range of 0.0 – 1.5 m/s have been performed. These experiments were carried out for 4 hours at a relative humidity of 80±3%, temperature of

30±2 °C and 3 - 18 mg/m^3 formaldehyde concentration. The formaldehyde concentration in the atmosphere inside the exposure chamber measured with these samplers was significantly lower than the measurement with gas collector (Figure 2.10).

The results are shown in Figure 3.7 where % recoveries versus wind velocities were presented. It was found that the wind velocity in a range of 0.0-1.5 m/s were not influent to accuracy and precision of sampling. The thickness of the stagnant air at the boundary l-ayer of the membrane was effect to speed of diffusion rate. According to Perez-Ballesta *et al*. (1993), the dependence of the thickness of boundary (**δ**) on wind speed; **W** (m/s) can be expressed by eq. (3.1) where k_1 is a constant and n = 0.5 for laminar flow and n = 0.2 for turbulent flow.

$$\boldsymbol{\delta = k_1/W^n} \qquad 3.1$$

The thickness of boundary was decreased. Then, the resistance of diffusion was also decreased.

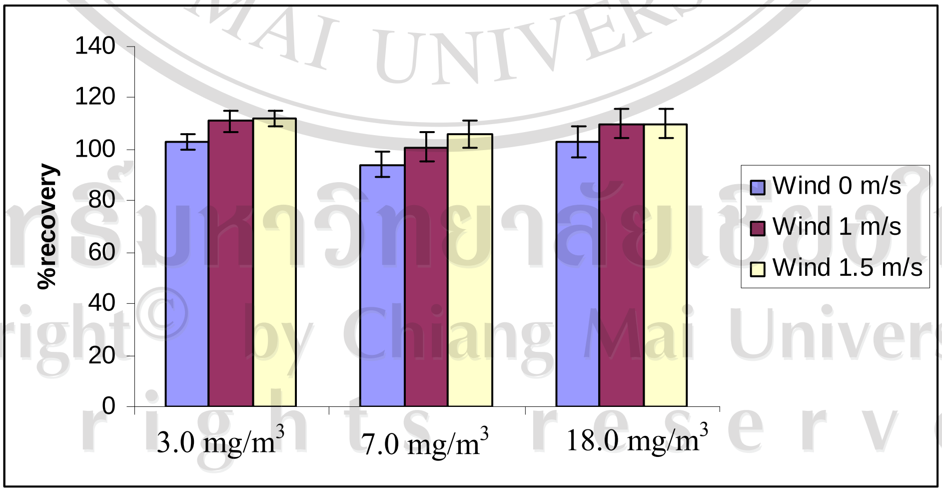

Figure 3.7 Wind velocity effect on efficiency of formaldehyde sampler

Table 3.9 Wind velocity effect on the sampling

Low concentration level (3.0 mg/m^3)

Wind speed (m/s)	Replication number	absorbance	Formaldehyde			mean(mg/m^3)	SD	%RSD	% recovery
			µg/ml	µg	mg/m^3				
	1	0.2355	4.62	13.9	3.2				
	2	0.2336	4.58	13.7	3.1				
0.00	3	0.2400	4.71	14.1	3.2	3.1	0.10	3.1	**103.5**
	4	0.2277	4.46	13.4	3.1				
	5	0.2217	4.35	13.0	3.0				
	1	0.2699	5.29	15.9	3.6				
	2	0.2501	4.90	14.7	3.4				
1.00	3	0.2343	4.59	13.8	3.1	3.3	0.18	5.4	**111.3**
	4	0.2409	4.72	14.2	3.2				
	5	0.2511	4.92	14.8	3.4				
	1	0.2660	5.22	15.6	3.6				
	2	0.2610	5.12	15.4	3.5				
1.50	3	0.2470	4.84	14.5	3.3	3.4	0.22	6.5	**112.0**
	4	0.2553	5.01	15.0	3.4				
	5	0.2246	4.40	13.2	3.0				

Table 3.9 Wind velocity effect on the sampling. (continued)

Medium concentration Level (7.0 mg/m^3)

Wind speed (m/s)	Replication number	absorbance	Formaldehyde µg/m^3	Formaldehyde mass µg	Formaldehyde mg/m^3	mean(mg/m^3)	SD	%RSD	% recovery
	1	0.4940	9.69	29.1	6.6				
	2	0.4730	9.27	27.8	6.3				
0.00	3	0.4870	9.55	28.6	6.5	6.6	0.27	4.1	**94.7**
	4	0.5276	10.35	31.0	7.1				
	5	0.4910	9.63	28.9	6.6				
	1	0.4980	9.76	29.3	6.7				
	2	0.5181	10.16	30.5	6.9				
1.00	3	0.5260	10.31	30.9	7.0	7.1	0.39	5.5	**101.4**
	4	0.5771	11.32	33.9	7.7				
	5	0.5300	10.39	31.2	7.1				
	1	0.5883	11.54	34.6	7.9				
	2	0.5700	11.18	33.5	7.6				
1.50	3	0.5902	11.57	34.7	7.9	7.5	0.41	5.5	**107.5**
	4	0.5411	10.61	31.8	7.3				
	5	0.5194	10.18	30.6	7.0				

Table 3.9 Wind velocity effect on the sampling. (continued)

High concentration level 18.0 mg/m^3

Wind speed (m/s)	Replication number	absorbance	Formaldehyde µg/ml	Formaldehyde mass µg	Formaldehyde mg/m^3	mean(mg/m^3)	SD	%RSD	% recovery
	1	1.4400	28.24	84.7	19.3				
	2	1.4230	27.90	83.7	19.1				
0.00	3	1.4087	27.62	82.9	18.9	18.7	0.64	3.4	**103.7**
	4	1.3761	26.98	80.9	18.4				
	5	1.3191	25.86	77.6	17.7				
	1	1.4598	28.62	85.9	19.6				
	2	1.5810	31.00	93.0	21.2				
1.00	3	1.4260	27.96	83.9	19.1	20.0	1.09	5.4	**110.9**
	4	1.5710	30.80	92.4	21.1				
	5	1.4095	27.64	82.9	18.9				
	1	1.3830	27.12	81.4	18.5				
	2	1.4170	27.80	83.4	19.0				
1.50	3	1.6027	31.43	94.3	21.5	19.9	1.16	5.9	**110.4**
	4	1.5211	29.83	89.5	20.4				
	5	1.4940	29.29	87.9	20.0				

3.4.2 Validation of relative humidity effect

High humidity level may affect the sorption capacity of adsorbing material and boundary layer on the barrier membrane. In this test, different levels of relative humidity were simulated with a hygrometer coupled to an exposure chamber by varying proportions of dried air flow (through drying columns and humidifier unit) mixed with humid air (water steam). Various humidity levels of 30, 60 and 80 % were set for low, medium and high relative humidity, respectively. Sets of five passive samplers were simultaneously exposed for 4 hours to 3 and 16 mg/m^3 formaldehyde at facial velocity of 0.0 m/s and different levels of humidity as described above. Average formaldehyde concentration in the atmosphere inside the exposure chamber measured with both passive samplers and the gas collector, presented no difference. The result is shown in Figure 3.8 and Table 3.10. It was found that the level of humidity in atmosphere was not impact to the accuracy of sampling.

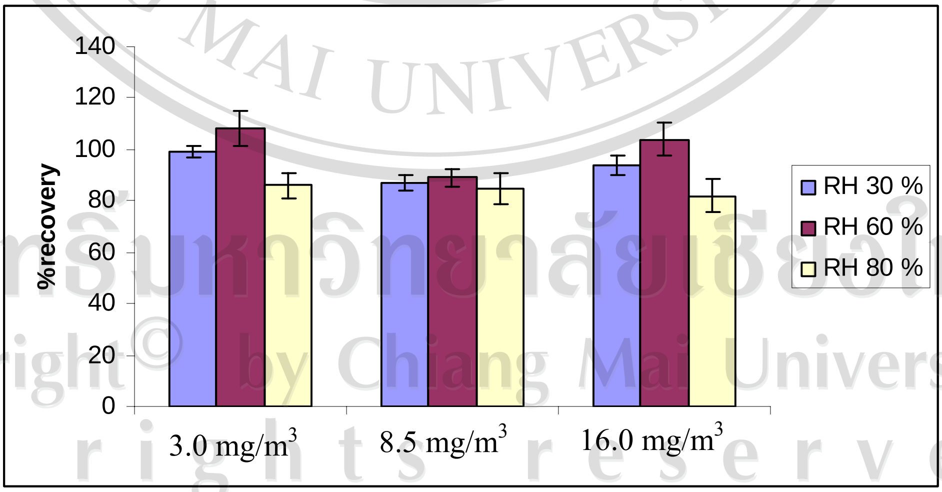

Figure 3.8 Relative Humidity effect on capacity of formaldehyde passive sampler

Table 3.10 Validation of relative humidity effect on the sampling

Low concentration level 5.2 mg/m^3

Relative Humidity (%)	Replication number	absorbance	Formaldehyde µg/ml	Formaldehyde µg	Formaldehyde mg/m^3	mean(mg/m^3)	SD	%RSD	% recovery
	1	0.3744	7.34	22.0	5.0				
	2	0.3821	7.49	22.5	5.1				
30 %	3	0.3970	7.78	23.4	5.3	**5.2**	**0.13**	**2.56**	**99.1**
	4	0.3921	7.69	23.1	5.3				
	5	0.3764	7.38	22.1	5.0				
	1	0.2400	4.71	14.1	3.2				
	2	0.2518	4.94	14.8	3.4				
60%	3	0.2327	4.56	13.7	3.1	**3.2**	**0.11**	**3.3**	**108**
	4	0.2473	4.85	14.5	3.3				
	5	0.2362	4.63	13.9	3.2				
	1	0.202	4.00	11.9	2.71				
	2	0.2009	3.90	11.8	2.69				
80 %	3	0.1910	3.70	11.2	2.56	**2.59**	**0.11**	**4.08**	**86.5**
	4	0.1911	3.70	11.2	2.56				
	5	0.1831	3.60	10.8	2.45				

Table 3.10 Validation of relative humidity effect on the sampling (continued)

Medium concentration level (8.5 mg/m^3)

Relative Humidity (%)	Replication number	absorbance	Formaldehyde			mean(mg/m^3)	SD	%RSD	% recovery
			µg/ml	mass µg	mg/m^3				
	1	0.5440	10.67	32.0	7.30				
	2	0.5210	10.22	30.6	7.00				
30 %	3	0.5170	10.14	30.4	6.90	**7.40**	**0.51**	**6.88**	**87.3**
	4	0.5921	11.61	34.8	7.90				
	5	0.5964	11.69	35.1	8.00				
	1	0.5800	11.37	34.1	7.80				
	2	0.5918	11.60	34.8	7.90				
60%	3	0.5527	10.84	32.5	7.40	**7.60**	**0.25**	**3.30**	**89.0**
	4	0.5473	10.73	32.2	7.30				
	5	0.5662	11.10	33.3	7.60				
	1	0.5213	10.20	30.7	6.99				
	2	0.5893	11.60	34.7	7.90				
80 %	3	0.4903	9.60	28.8	6.57	**7.17**	**0.48**	**6.75**	**84.3**
	4	0.5310	10.40	31.2	7.12				
	5	0.5431	10.60	31.9	7.28				

Table 3.10 Validation of relative humidity effect on the sampling (continued)

High concentration level (16 mg/m^3)

Relative Humidity (%)	Replication number	absorbance	Formaldehyde µg/ml	Formaldehyde µg	Formaldehyde mg/m^3	mean(mg/m^3)	SD	%RSD	% recovery
	1	1.1440	22.43	67.3	15.3				
	2	1.0821	21.22	63.7	14.5				
30 %	3	1.2070	23.67	71.0	16.2	**15.1**	**0.71**	**4.72**	**94.3**
	4	1.1200	21.98	65.9	15.0				
	5	1.0764	21.11	63.3	14.4				
	1	1.2400	24.31	72.9	16.6				
	2	1.2518	24.55	73.6	16.8				
60%	3	1.2327	24.17	72.5	16.5	**16.6**	**0.11**	**0.60**	**104.0**
	4	1.2473	24.46	73.4	16.7				
	5	1.2362	24.24	72.7	16.6				
	1	0.9213	18.10	54.2	12.34				
	2	1.0589	20.80	62.3	14.19				
80 %	3	1.0241	20.10	60.2	13.72	**13.12**	**0.86**	**6.56**	**82.0**
	4	0.9102	17.80	53.5	12.20				
	5	0.9820	19.30	57.8	13.16				

3.4.3 Validation of temperature effect

The diffusion (uptake) rate of the analyte is influenced by temperature; a factor which is, in turn, caused by the dependency of the diffusion coefficient on temperature. Theoretically a slight increase in uptake rate unit: (cm^3/s) is predicted to be about 0.5%/K (Gillettr, *et al*, 2000). If using a non-ideal sorbent, a temperature dependency of the sorption coefficient of the analyte should also be expected. This will cause a decrease in the uptake rate.

A set of passive samplers (n = 10) was simultaneously exposed to the atmosphere containing 3-18 mg/m^3 formaldehyde, at temperature of 24, 30 and 37 °C and facial velocity of 0.0 m/s for 4 hours. Average formaldehyde concentration in atmosphere inside exposure chamber was measured with both passive samplers and the gas collector. It was assumed that temperature may have a pronounce effect on the uptake rate. It was found that 3 concentration levels were not influent by temperature ranged 24 – 37 °C. The recoveries of the formaldehyde sampling are in acceptable range as shown in Figure 3.9 and Table 3.11. Although, the temperature can be effected to diffusion rate (Ballarch. *et al*, 1999).

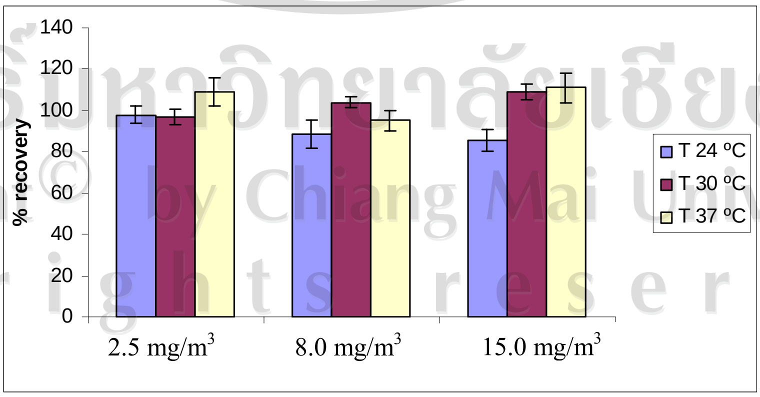

Figure 3.9 validation of temperature effect on capacity of formaldehyde passive sampler

Table 3.11 Validation of temperature effect on the sampling

Low concentration level 2.5 mg/m^3

Temperature (°C)	Replication number	absorbance	Formaldehyde µg/ml	Formaldehyde µg	Formaldehyde mg/m^3	Mean (mg/m^3)	SD	% RSD	% Recovery
24 ºC	1	0.195	3.8	11.5	2.61	**2.52**	**0.10**	**4.12**	**100.9**
	2	0.1766	3.5	10.4	2.37				
	3	0.185	3.6	10.9	2.48				
	4	0.1891	3.7	11.1	2.53				
	5	0.1951	3.8	11.5	2.61				
30 ºC	1	0.18	3.5	10.6	2.41	**2.44**	**0.17**	**6.76**	**97. 8**
	2	0.1998	3.9	11.8	2.68				
	3	0.1717	3.4	10.1	2.3				
	4	0.1708	3.4	10.1	2.29				
	5	0.1897	3.7	11.2	2.54				
37 ºC	1	0.2483	4.9	14.6	3.33	**3.29**	**0.17**	**5.24**	**109.7**
	2	0.2251	4.4	13.2	3.02				
	3	0.2346	4.6	13.8	3.14				
	4	0.2403	4.7	14.1	3.22				
	5	0.2587	5.1	15.2	3.47				

Table 3.11 Validation of temperature effect on the sampling (continued)

Medium concentration level 8 mg/m^3

Temperature (°C)	Replication number	absorbance	Formaldehyde µg/ml	Formaldehyde mass (µg)	Formaldehyde mg/m$^{3)}$	mean(mg/m^3)	SD	%RSD	%Recovery
	1	0.5060	9.9	29.8	6.78				
	2	0.5466	10.7	32.2	7.32				
24 ºC	3	0.5150	10.1	30.3	6.90	**7.08**	**0.3**	**4.0**	**88.6**
	4	0.5210	10.2	30.6	6.98				
	5	0.5551	10.9	32.7	7.44				
	1	0.6490	12.7	38.2	8.70				
	2	0.6098	12.0	35.9	8.17				
30 ºC	3	0.6217	12.2	36.6	8.33	**8.38**	**0.2**	**2.9**	**104.8**
	4	0.6085	11.9	35.8	8.15				
	5	0.6389	12.5	37.6	8.56				
	1	0.5830	11.4	34.3	7.81				
	2	0.5951	11.7	35.0	7.97				
37 ºC	3	0.5460	10.7	32.1	7.32	**7.64**	**0.3**	**3.5**	**95.5**
	4	0.5634	11.0	33.1	7.55				
	5	0.5878	11.5	34.6	7.88				

Table 3.11 Validation of temperature effect on the sampling (continued)

High concentration level 15 mg/m^3

Temperature (°C)	Replication number	absorbance	Formaldehyde µg/ml	Formaldehyde µg	Formaldehyde mg/m^3	mean(mg/m^3)	SD	%RSD	%Recovery
	1	1.0600	20.8	62.4	14.20				
	2	0.9160	18.0	53.9	12.27				
24 ºC	3	0.9011	17.7	53.0	12.07	**12.82**	**0.8**	**6.5**	**85.5**
	4	0.9521	18.7	56.0	12.76				
	5	0.9555	18.7	56.2	12.80				
	1	1.2964	25.4	76.3	17.37				
	2	1.1608	22.8	68.3	15.56				
30 ºC	3	1.2170	23.9	71.6	16.31	**16.35**	**0.8**	**5.0**	**109.0**
	4	1.1608	22.8	68.3	15.55				
	5	1.2637	24.8	74.3	16.94				
	1	1.2300	24.1	72.4	16.48				
	2	1.3595	26.7	80.0	18.22				
37 ºC	3	1.1546	22.6	67.9	15.47	**16.75**	**1.2**	**7.0**	**111.7**
	4	1.3563	26.6	79.8	18.17				
	5	1.2587	24.7	74.0	16.87				

3.4.5 Effect of orientation of passive sampler

The ambient air face velocity and orientation of the sampler can affect the performance and reliability of diffusive samplers because they may influence the effective diffusion path length (Underhill and Feigley, 1991; Gair and Penkett, 1995). The diffusion path length is a function of the length and cross-sectional area of the diffusion space within the sampler. Both low and high wind speeds may be sources of error. If wind speed falls, the effective path length may increase, causing a decrease in uptake rates. Conversely, high wind speeds may reduce the effective path length and increase the uptake rate (Gair and Penkett, 1995).

In the orientation experiment, 15 samplers were placed at the holder in different directions including 5 upright vertical, 5 upside down vertical and 5 horizontal directions. They were exposed for 24 hours at the study site (the Institute of Language, CMU). The results of 3 different orientations were not significantly different at 95% confidence level using RCB-test. This means orientation position was not affected to the sampling. The limitation of this test was low wind speed (0.00-0.05 m/s) in the sampling site. Therefore, it can not exactly indicate that orientation was not influent to the sampling. The formaldehyde concentration levels of 3 different orientations are shown in Figure 3.10 and Table 3.12.

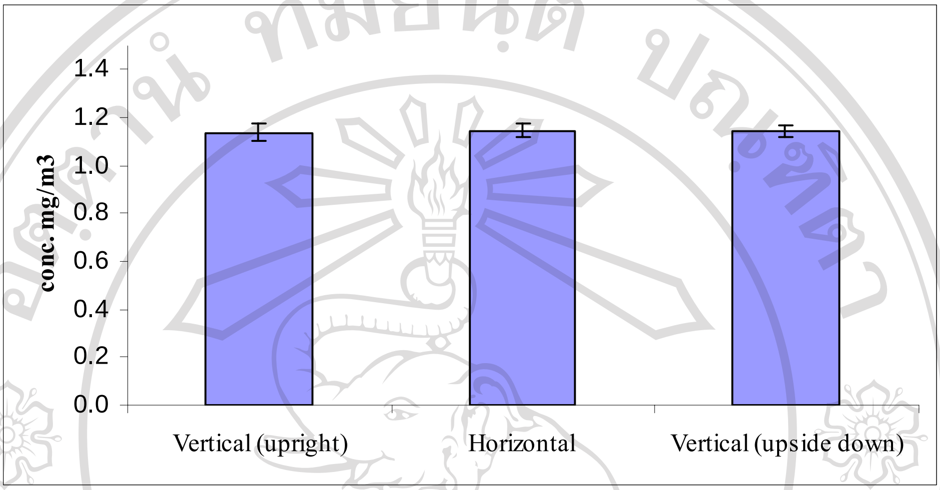

Figure 3.10 Effect of sampler of orientation on absorbance formaldehyde concentration

Table 3.12 Effect of sampler of orientation on absorbance formaldehyde concentration

Orientations (direction)	Replication number	abs	Formaldehyde			mean (mg/m^3)	SD	%RSD
			µg/ml	µg	mg/m^3			
	1	0.0829	1.38	4.1	1.15			
	2	0.0804	1.34	4.0	1.11			
Vertical (upright)	3	0.0784	1.31	3.9	1.08	**1.14**	**0.04**	**3.33**
	4	0.0850	1.42	4.3	1.18			
	5	0.0842	1.40	4.2	1.16			
	1	0.0832	1.39	4.2	1.15			
	2	0.0820	1.37	4.1	1.13			
Horizontal	3	0.0802	1.34	4.0	1.11	**1.15**	**0.03**	**2.27**
	4	0.0850	1.42	4.3	1.18			
	5	0.0842	1.40	4.2	1.16			

Table 3.12

(continued)

Orientations	Replication number	absorbance	Formaldehyde			mean (mg/m^3)	SD	%RSD
			µg/ml	Mass (µg)	mg/m^3			
Vertical (upside down)	1	0.0820	1.37	4.1	1.13	1.14	0.02	2.04
	2	0.0804	1.34	4.0	1.11			
	3	0.0824	1.37	4.1	1.14			
	4	0.0845	1.41	4.2	1.17			
	5	0.0842	1.40	4.2	1.16			

Note Meteorological conditions: wind speed = 0.05 m/s, T = 25.6 - 28.1ºC and RH % = 40 - 45 %.

3.4.6 Effect of reverse diffusion

The possibility of reverse diffusion was investigated by exposure of 10 diffusive samplers at known concentration in the exposure chamber for 4 hours. The aim of this test was to check if back diffusion took place in the samplers. The prepared passive samplers were exposed to the 26 mg/m^3 formaldehyde inside the exposure chamber at 50 % relative humidity and 26°C. The first set of the samplers (n=5) was exposed for 4 hours and immediately extracted to find out formaldehyde concentration, while the second set (n=5) was exposed further to clean air (zero concentration of formaldehyde) for another 4 hours prior to extraction. It was found that both sets showed no significant difference using RCB-test 95% confidence level and gave recovery values in an acceptable range as shown in Table 3.13 and Figure 3.11. It can be concluded that the reverse diffusion effect was not influent to the sampling due to stability of bisulfite adducts form and dimension of passive sampler.

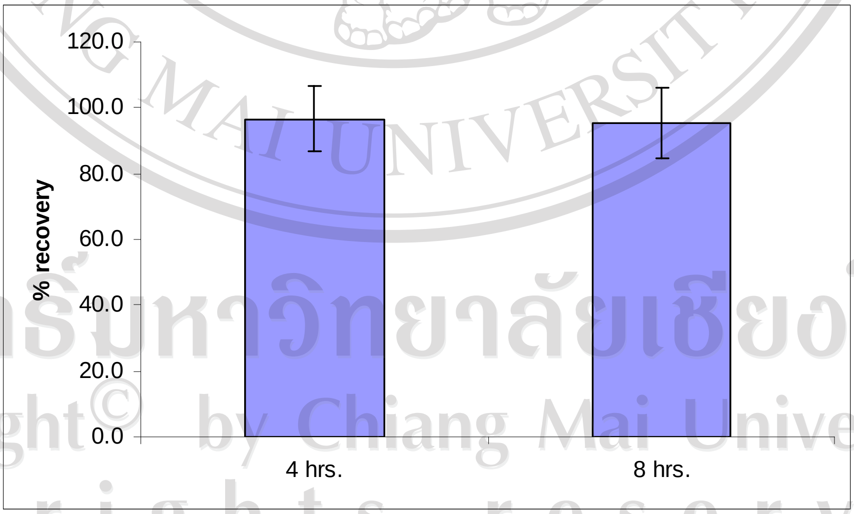

Figure 3.11 Effect of reverse diffusion on formaldehyde passive sampler

Table 3.13 Effect the reverse diffusion on formaldehyde passive sampler

Exposure duration	Replication number	absorbance	Formaldehyde		
			µg/ml	µg	mg/m^3
4 hours	1	0.2388	4.68	14.05	22.38
	2	0.2559	5.02	15.05	23.98
	3	0.2680	5.25	15.76	25.11
	4	0.2658	5.21	15.64	24.91
	5	0.3109	6.10	18.29	29.13
		Mean	-	-	**25.10**
		SD	-	-	**2.50**
		%RSD	-	-	**9.95**
		% recovery	-	-	**96.5**
8 hours	1	0.2583	5.06	15.19	24.20
	2	0.2934	5.75	17.26	27.49
	3	0.2500	4.90	14.71	23.42
	4	0.2946	5.78	17.33	27.60
	5	0.2295	4.50	13.50	21.50
		Mean	-	-	**24.85**
		SD	-	-	**2.66**
		%RSD	-	-	**10.69**
		% recovery	-	-	**95.6**

Note Formaldehyde concentration was 26 mg/m^3, % RH = 60 %, T = 30 °C and wind speed = 0.0 m/s.

3.5 Determination of formaldehyde indoors

Formaldehyde is released into home and workplace from a variety of indoor sources. Some resins, or glues, used to bind wood chips or fibers into plywood, particleboard, and other pressed wood products, contain formaldehyde. Cabinetry and some floor and wall materials are often made from such products. Formaldehyde is also used in fabrics to impart wrinkle resistance or to fix color, and in some consumer products it is used as a hardening agent or preservative. Also, formaldehyde is a by-product of combustion processes, such as wood burning, gas appliance use, and cigarette smoking. Formaldehyde is usually present at lower (but not necessarily healthful) levels in outdoor air. It is emitted in car exhaust and from some industrial sources, and is also created from chemical reactions in the air among combustion pollutants, such as those in automobile exhaust (CEPA, 2004).

In this study, the Language Institute, Chiang Mai University was chosen as the study site because it is a new building and contains the potential sources i.e. pressed wood furnitures and the floor covered by carpet. This expected of using formaldehyde for protecting.

3.5.1 Sampling duration

Normally, the sampling period of indoor site can be classifies into three periods, including short term exposure limit (STEL) for 15 minutes, eight hour exposure evaluation (an 8 hr TWA for work place) and 24 hours for in home. This study aims to test the formaldehyde level in duration of medium to long term levels from 8 hours to 7 days (29 CFR Part 1910.1000).

The formaldehyde passive samplers were exposed at the Language Institute, Chiang Mia University for different sampling duration including 8, 24 hours and 2, 3, 4, 5, 6, 7 days**.** The values of mean formaldehyde concentration of 5 replicates subtracted with blank value were calculated in concentration (mg/m^3) as shown in Figure 3.12 and Table 3.14.

It was found that sampling durations of 8 and 24 hours were sufficient and suited for determination of formaldehyde. Long sampling time affected to mass collected and precision of the sampling due to stability and diffusion limits. The diffusion limit depends on the dimension of the sampler such as size of cross section (capacity of sorbent) which affect to rate of diffusion ($C_1 - C_0$) in long time exposure. Due to the capacity of sorbent and diffusion length of the sampler were limited so that it reached the steady state within the time of less than a day. Then, even the samplers were continuously exposed, the rate of collection will continuously decrease after 24 hours. In case of application for long time exposure, capacity of sorbent and diffusion length of the sampler must be increased. Table 3.15 shows differences of difference of formaldehyde concentrations and exposure duration. In Figure 3.12, the line was drawn from an average concentration of each sampling duration to the others (Figure 3.12). The slope ($m = \Delta C/\Delta t$) of each two points was calculated from this data, a group was constructed. It was found that steep of the slope was decreasing when the exposure duration was longer. Higher slope values indicate faster rate of gas diffusion results sooner steady state. The highest slope value was found between 8 hours and 1 day exposure duration. Then, the passive samplers were tested again in order to check the precision of the sampling for 8 and 24 hours. The results are shown in Figure. 3.13 and Table 3.16 . It was found that both duration showed no significant difference using RCB-test 95% confidence level.

Table 3.14 Effect of sampling duration on formaldehyde concentration

Sampling duration	Replication number	absorbance	Formaldehyde			Mean	SD	%RSD
			μg/ml	μg	mg/m^3			
	1	0.0250	0.42	1.25	1.03			
	2	0.0240	0.40	1.20	1.00			
8 hours	3	0.0285	0.48	1.43	1.18	**1.090**	**0.10**	**7.30**
	4	0.0261	0.44	1.31	1.08			
	5	0.0280	0.47	1.40	1.16			
	1	0.0612	1.02	3.06	0.846			
	2	0.0623	1.038	3.12	0.862			
1 day	3	0.0620	1.033	3.10	0.858	**0.813**	**0.23**	**7.76**
	4	0.0570	0.95	2.85	0.788			
	5	0.0516	0.86	2.58	0.714			
	1	0.1031	1.718	5.16	0.713			
	2	0.1030	1.717	5.15	0.712			
2 days	3	0.1131	1.885	5.66	0.782	**0.733**	**0.26**	**4.91**
	4	0.1012	1.687	5.06	0.70			
	5	0.1102	1.837	5.51	0.762			
3 days	1	0.1486	2.477	7.43	0.685			
	2	0.1203	2.005	6.02	0.555			
	3	0.1348	2.247	6.74	0.621	**0.631**	**0.82**	**11.90**
	4	0.1230	2.050	6.15	0.567			
	5	0.1582	2.637	7.91	0.729			
4 days	1	0.1451	2.418	7.26	0.502			
	2	0.1412	2.353	7.06	0.488			
	3	0.1845	3.075	9.23	0.638	**0.502**	**1.22**	**16.86**
	4	0.1383	2.305	6.92	0.478			
	5	0.1171	1.952	5.86	0.405			

Sampling duration	Replication number	absorbance	Formaldehyde µg/ml	Formaldehyde Mass (µg)	Formaldehyde mg/m^3	Mean	SD	%RSD
	1	0.1367	2.278	6.84	0.378			
	2	0.1450	2.417	7.25	0.401			
5 days	3	0.1510	2.517	7.55	0.418	**0.424**	**0.73**	**9.51**
	4	0.1603	2.672	8.02	0.443			
	5	0.1746	2.910	8.73	0.483			
	1	0.166	2.767	8.3	0.383			
	2	0.1511	2.518	7.56	0.348			
6 days	3	0.1886	3.143	9.43	0.435	**0.395**	**1.40**	**16.33**
	4	0.1413	2.355	7.07	0.326			
	5	0.2100	3.500	10.5	0.484			
	1	0.1953	3.255	9.77	0.386			
	2	0.2439	4.065	12.20	0.482			
7 days	3	0.2142	3.570	10.71	0.423	**0.419**	**1.05**	**9.89**
	4	0.2178	3.630	10.89	0.430			
	5	0.1912	3.187	9.56	0.378			

Note Meteorological conditions: wind speed = 0.08 m/s, T = 24.6 - 27.4ºC and RH % = 42- 50 %.

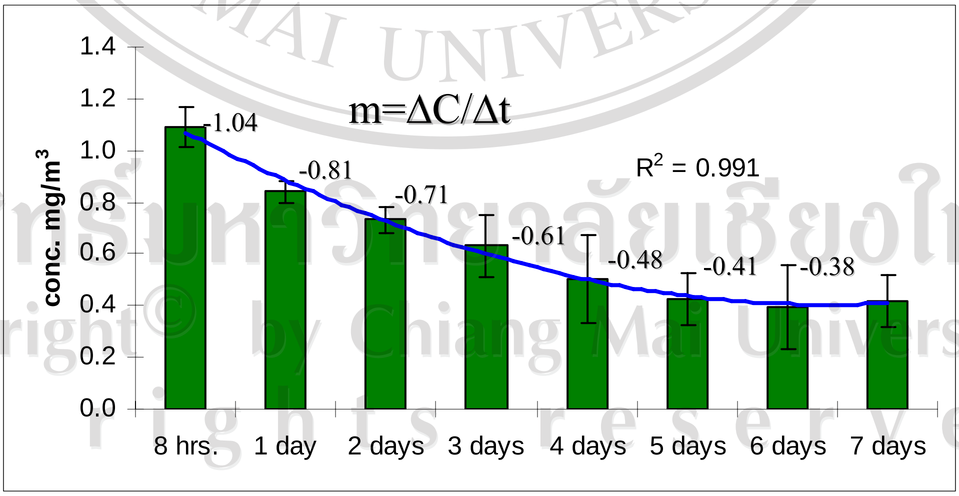

Figure 3.12 Formaldehyde concentrations of different sampling duration

Table 3.15 Difference of formaldehyde concentrations and exposure duration

slope	C_1 (mg/m^3)	C_2 (mg/m^3)	ΔC (C_2-C_1)	t_1 (hours)	t_2 (hours)	Δt (t_2-t_1)	m ($\Delta C/\Delta t$)
m_1	1.09	0.84	-0.25	8	24	16	-1.04
m_2	0.84	0.73	-0.11	24	48	24	-0.81
m_3	0.73	0.63	-0.10	48	72	24	-0.71
m_4	0.63	0.50	-0.13	72	96	24	-0.61
m_5	0.50	0.42	-0.08	96	120	24	-0.48
m_6	0.42	0.39	-0.03	120	144	24	-0.41
m_7	0.39	0.42	0.30	144	168	24	-0.38

Table 3.16 Indoor formaldehyde concentrations of 8 and 24 hours

Day	Replication number	absorbance	Formaldehyde µg/ml	Formaldehyde Mass(µg)	Formaldehyde mg/m^3	Mean mg/m^3	SD	%RSD
		1	0.4200	1.25	0.0250	1.03		
		2	0.4000	1.20	0.0240	1.00		
	Day 1	3	0.4800	1.43	0.0285	1.18	**1.09**	**0.08**
		4	0.4400	1.31	0.0261	1.08		
		5	0.4700	1.40	0.0280	1.16		
8 hrs.								
		1	0.4700	1.40	0.0280	1.16		
		2	0.4300	1.28	0.0256	1.06		
	Day 2	3	0.4200	1.26	0.0251	1.04	**1.09**	**0.06**
		4	0.4600	1.37	0.0273	1.13		
		5	0.4200	1.25	0.0250	1.04		

Day	Replication number	absorbance	Formaldehyde			Mean	SD	%RSD
			μg/ml	Mass(μg)	mg/m^3	mg/m^3		
24 hrs	Day 1	1	1.1500	3.46	0.0691	0.95	**0.98**	**0.03**
		2	1.1900	3.56	0.0711	0.98		
		3	1.1900	3.56	0.0712	0.98		
		4	1.2400	3.71	0.0742	1.02		
		5	1.1800	3.55	0.0710	0.98		
	Day 2	1	1.2100	3.62	0.0723	1.00	**1.00**	**0.02**
		2	1.2400	3.71	0.0742	1.02		
		3	1.1700	3.51	0.0701	0.97		
		4	1.1900	3.57	0.0713	0.98		
		5	1.2400	3.71	0.0741	1.02		

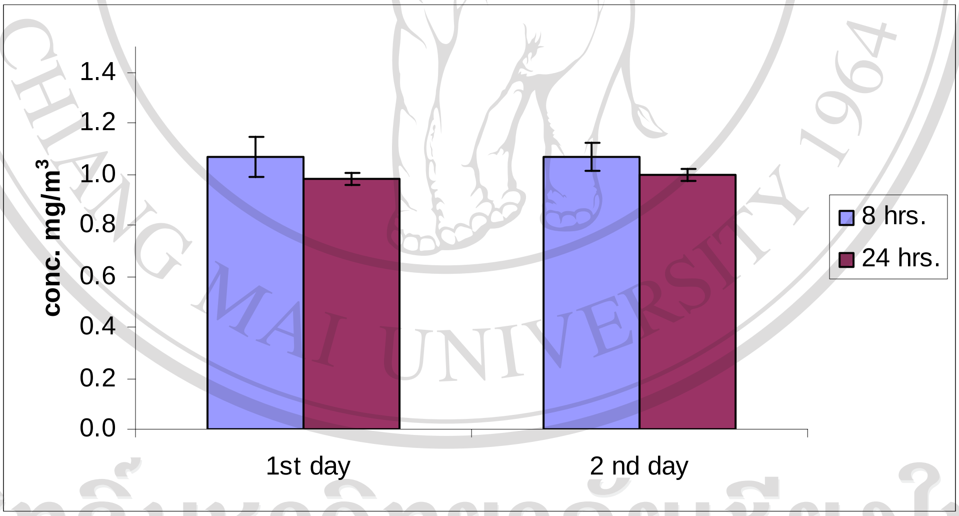

Figure 3.13 Indoor formaldehyde concentrations of 8 and 24 hours

3.5.2 Comparison of self-constructed sampler with a commercial sampler

A set of 5 samplers and 3 filed blanks of self-constructed formaldehyde passive sampler and one of commercial passive sampler (SKC inc.) were placed in a work place at Language Institute of Chiang Mai University for 8, 24 hours and 7 days exposure. The performance of the self-constructed sampler was evaluated by comparing its formaldehyde concentration with the values measured by the commercial passive sampler (SKC inc.). All the tests were conducted during January to February 2007. The temperature, relative humidity and wind speed during the test were 25-33 ºC, 30-60 % and 0.00 - 0.010 m/s, respectively. The percent difference (% diff) of the concentration measured by the two methods was calculated using

$$\textbf{\% Diff} = \left[\frac{C_{\text{self-constructed}} - C_{\text{commercial}}}{C_{\text{commercial}}}\right] \times 100$$

The percent difference of the concentration measured by the two equipments was calculated using the above equation where $C_{\text{self-constructed}}$ is the formaldehyde concentration measured by the passive sampling method, and $C_{\text{commercial}}$ is the formaldehyde concentration measured by the commercial passive sampler (SKC inc.).

The percent differences of the concentrations measured by the self invented and commercial sampler (SKC inc.) were 7.2 %, 13.0 % and 29.1- 29.6 % for 8, 24 hours and 7 days, respectively (Table 3.17-3.19 and Figure 3.14). It was found that the self-constructed sampler was appropriated for 8 and 24 hours. The concentrations obtained from the self-constructed sampler were slightly less than those from commercial passive sampler (SKC inc.) in every sampling. The SKC sampler was designed for long term monitoring (5 - 7 days) according to the instruction in a Catalog No.526-100. The SKC sampler tended to have higher sorbent capacity than the self-constructed sampler for long term exposure. The self-constructed sampler can also use for long exposure by adjustment of some parameters such as increasing of sorbent diameter and length of a tube. Considering the slope of the graph as shown in Figure

3.15, it was found that both samplers were not different in term of formaldehyde concentrations collected.

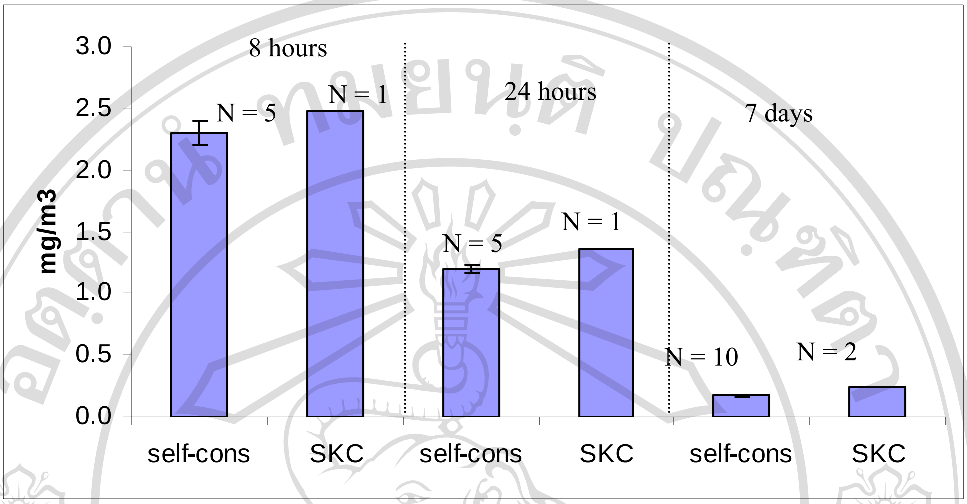

Figure 3.14 Comparison of indoor formaldehyde concentrations collected by SCS and commercial one

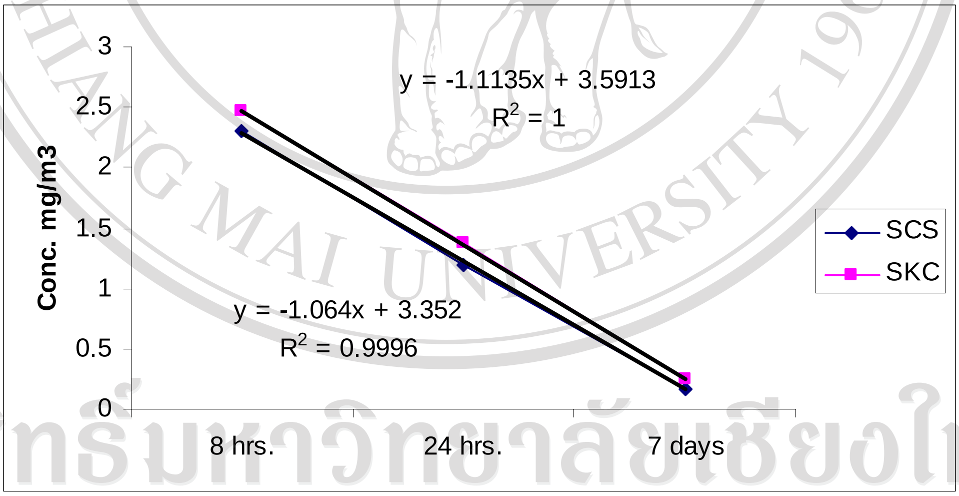

Figure 3.15 The slope of decreasing of concentration for 8 hours to 7 days

Table 3.17 Comparison of indoor formaldehyde concentrations collected by Self-constructed sampler and commercial sampler (SKC) at 8 hours exposure duration.

Exposure duration	Replication number	abs	Formaldehyde µg/ml	mass (µg)	mg/m^3
8 hours	**Blank**	0.0015	0.030	0.090	0.075
	Blank	0.0013	0.026	0.078	0.065
	Blank	0.0012	0.024	0.072	0.060
	mean	-	-	-	**0.066**±0.008
	SCS1	0.0467	0.908	2.724	2.260
	SCS2	0.0481	0.936	2.808	2.330
	SCS3	0.0457	0.888	2.664	2.210
	SCS4	0.0460	0.894	2.682	2.225
	SCS5	0.0507	0.988	2.964	2.459
	mean	-	-	-	**2.300±0.10**
	SKC	**0.0660**	**1.320**	**3.960**	**2.475**
	% Diff (SCS & SKC)	-	-	-	**7.2 %**

Note Meteorological conditions: wind speed = 0.04 m/s, T = 28.5 - 30.7ºC and RH % = 35- 40 %. **SCS =Self-Constructed Sampler**

3.18 Comparison of indoor formaldehyde concentrations collected by Self-constructed sampler and commercial sampler (SKC) at 24 hours exposure duration.

Exposure duration	**Replication number**	**abs**	**Formaldehyde**		
			μg/ml	**μg**	**mg/m^3**
	Blank	0.0021	0.042	0.126	0.105
	Blank	0.0029	0.058	0.174	0.144
	Blank	0.0024	0.048	0.144	0.119
24 hrs	**mean**		-	-	**0.123±0.002**
	SCS1	0.0892	1.500	4.500	1.234
	SCS2	0.0874	1.500	4.400	1.209
	SCS3	0.0842	1.400	4.200	1.165
	SCS4	0.0875	1.500	4.400	1.210
	SCS5	0.0842	1.400	4.200	1.165
	mean	-	-	-	**1.200±0.03**
	SKC	**0.1314**	**2.200**	**6.600**	**1.370**
	% Diff SCS & SKC	-	-	-	**13%**

Note Meteorological conditions: wind speed = 0.04 m/s, T = 28.5 - 30.7ºC and RH % = 35- 40 %. **SCS =Self-Constructed Sampler**

Table 3.19 Comparison of indoor formaldehyde concentrations collected by Self-constructed sampler and commercial sampler (SKC) at 7 days exposure duration.

Exposure duration	Replication number	Formaldehyde			
		abs	µg/ml	mass (µg)	mg/m^3
7 days	**Blank**	0.0015	0.030	0.090	0.025
	Blank	0.0043	0.086	0.258	0.071
	Blank	0.0042	0.084	0.252	0.070
	mean				**0.055±0.026**
	SCS1	0.0788	1.576	4.728	0.187
	SCS2	0.0702	1.404	4.212	0.166
	SCS3	0.0754	1.508	4.524	0.179
	SCS4	0.0714	1.428	4.284	0.169
	SCS5	0.0749	1.498	4.494	0.178
	SCS6	0.0778	1.556	4.668	0.184
	SCS7	0.0602	1.204	3.612	0.143
	SCS8	0.0692	1.384	4.152	0.164
	SCS9	0.0716	1.432	4.296	0.170
	SCS10	0.0762	1.524	4.572	0.181
	mean	-	-	-	**0.172±0.01**
	SKC1	0.1350	2.700	8.100	**0.240**
	SKC2	0.1446	2.892	8.676	**0.257**
	% Diff SCS & SKC	-	-	-	**29.1%**

Note Meteorological conditions: wind speed = 0.04 m/s, T = 28.5 - 30.7ºC and RH % = 35- 40 %. **SCS =Self-Constructed Sampler**