CHAPTER 3

RESULTS AND DISCUSSION

3.1 Calibration curves of VOC standards.

VOCs were determined using the linear regression equation of the calibration curves prepared from different concentrations in a range of 0.1-7.0 μg/mL. Calibration curve was constructed using peak area ratios of standard/internal standard (y axis) and concentration of VOCs in a unit of μg/mL (x axis) as shown in Table 3.1, and Figure 3.1.

3.2 Validation methods of GC-FID

3.2.1 Precision of GC-FID

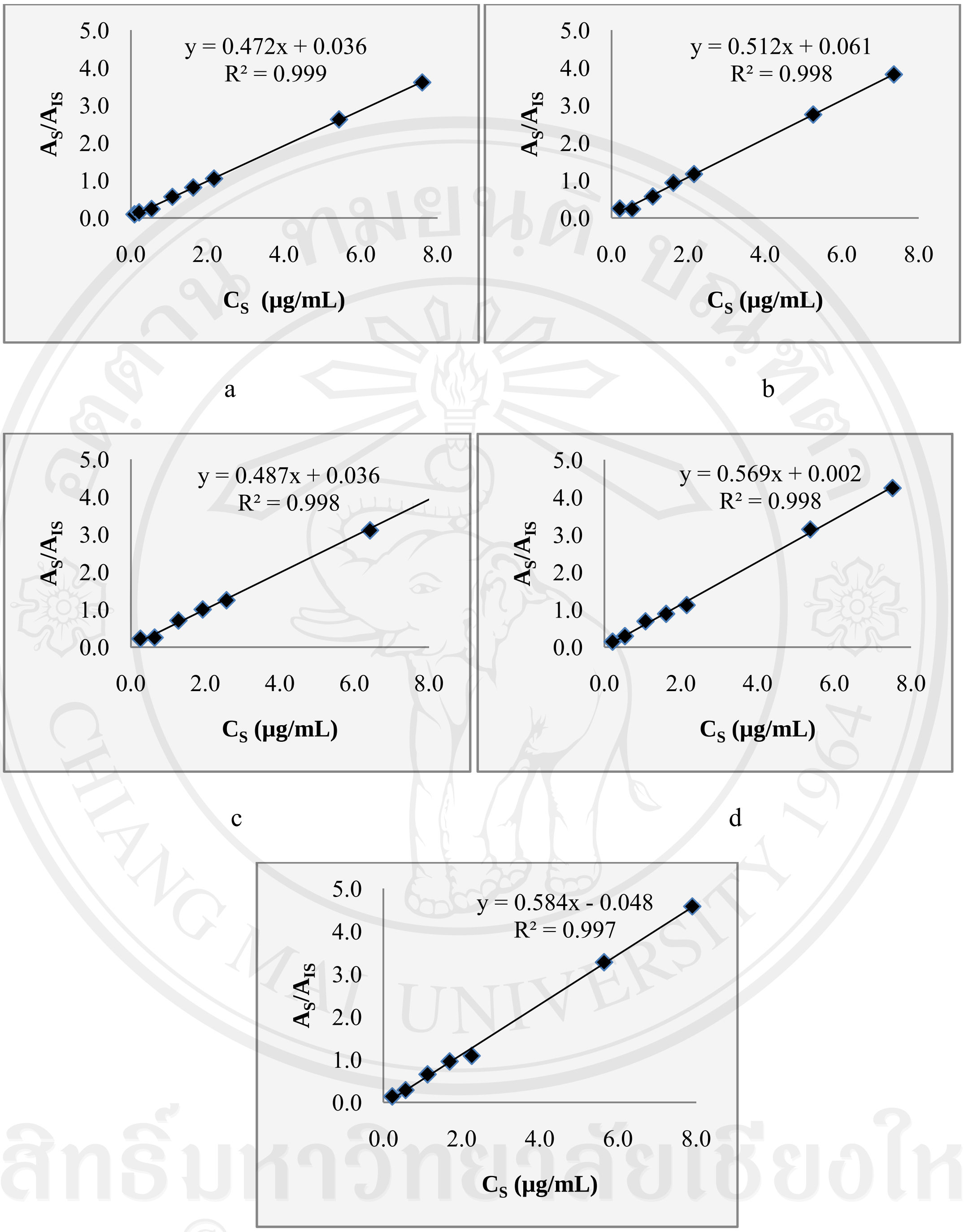
The precision of VOCs analysis was calculated in terms of repeatability and reproducibility. The repeatability and reproducibility were calculated in terms of percent relative standard deviation (% RSD).

(1) Repeatability

The repeatability of 2 μg/mL of mixed VOCs standard VOCs analyzed by GC-FID were calculated as % RSD as shown in Table 3.2. All VOCs show low % RSD (□5%) except for toluene-d_8 (10%). The results show good repeatability for all target VOCs.

Table 3.1 Area ratio and concentration of benzene

Benzene		Toluene		Toluene-d_8		p-Xylene		Styrene	
Concentration (µg/mL)	**Area ratio**	**Concentration (µg/mL)**	**Area ratio**	**Concentration (µg/mL)**	**Area ratio**	**Concentration (µg/mL)**	**Area ratio**	**Concentration (µg/mL)**	**Area ratio**
0.1	0.10	-	-	-	-	-	-	-	-
0.2	0.15	0.2	0.25	0.3	0.23	0.2	0.15	0.2	0.14
0.5	0.24	0.5	0.24	0.6	0.26	0.5	0.29	0.6	0.29
1.1	0.57	1.1	0.57	1.3	0.71	1.1	0.69	1.1	0.66
1.6	0.81	1.6	0.94	1.9	1.00	1.6	0.89	1.7	0.96
2.2	1.05	2.1	1.17	2.6	1.25	2.3	1.12	2.3	1.09
5.4	2.63	5.3	2.76	5.3	3.11	5.6	3.15	5.6	3.28
7.6	3.61	7.4	3.83	9.0	4.45	7.9	4.25	7.9	4.59



a b

c d

e

Figure 3.1 Calibration curve of a) benzene, b) toluene, c) toluene-d_8, d) p-xylene and e) styrene

Table 3.2 Repeatability of VOCs analysed by GC-FID

No. of injection	Concentrations (µg/mL)				
	Benzene	**Toluene**	**p-Xylene**	**styrene**	**toluene-d8**
1	2.06	2.24	2.52	2.59	3.01
2	2.13	2.26	2.38	2.47	3.66
3	2.02	2.27	2.49	2.60	3.66
4	2.08	2.20	2.30	2.42	3.13
5	2.16	2.25	2.52	2.54	2.99
6	2.11	2.23	2.28	2.36	3.67
7	2.06	2.24	2.52	2.59	3.01
average	**2.09**	**2.24**	**2.43**	**2.51**	**3.31**
SD	**0.05**	**0.02**	**0.11**	**0.10**	**0.34**
% RSD	**2.23**	**0.99**	**4.44**	**3.86**	**10.3**

(2) Reproducibility

Reproducibility of 2 µg/mL of mixed VOCs standard solution was injected to GC-FID under the optimum conditions for 7 days. The signals of VOCs from GC-FID were converted to concentrations by comparison of the internal standard curves and calculated to % RSD as shown in Table 3.3. RSD of the analytes were in a range from 6-7.7 %, except toluene-d_8 was highest (15%), cause peak overlap between contaminant peak and toluene for integrate area.

Table 3.3 Reproducibility of VOCs analysis by GC-FID

No. of injection	concentrations (µg/mL)				
	Benzene	**Toluene**	**p-Xylene**	**Styrene**	**Toluene-d_8**
1	1.99	2.17	2.35	2.40	3.36
2	2.12	2.37	2.63	2.75	2.87
3	2.31	2.48	2.65	2.71	2.84
4	2.21	2.41	2.63	2.70	2.88
5	2.22	2.59	2.80	2.92	3.40
6	1.98	2.29	2.61	2.64	2.40
7	2.38	2.67	2.89	2.92	2.17
8	2.43	2.65	2.90	2.91	3.26
average	**2.21**	**2.45**	**2.68**	**2.74**	**2.90**
SD	**0.17**	**0.18**	**0.18**	**0.18**	**0.44**
% RSD	**7.62**	**7.24**	**6.71**	**6.56**	**15.3**

3.2.2 Detection limit of GC-FID for VOCs analysis

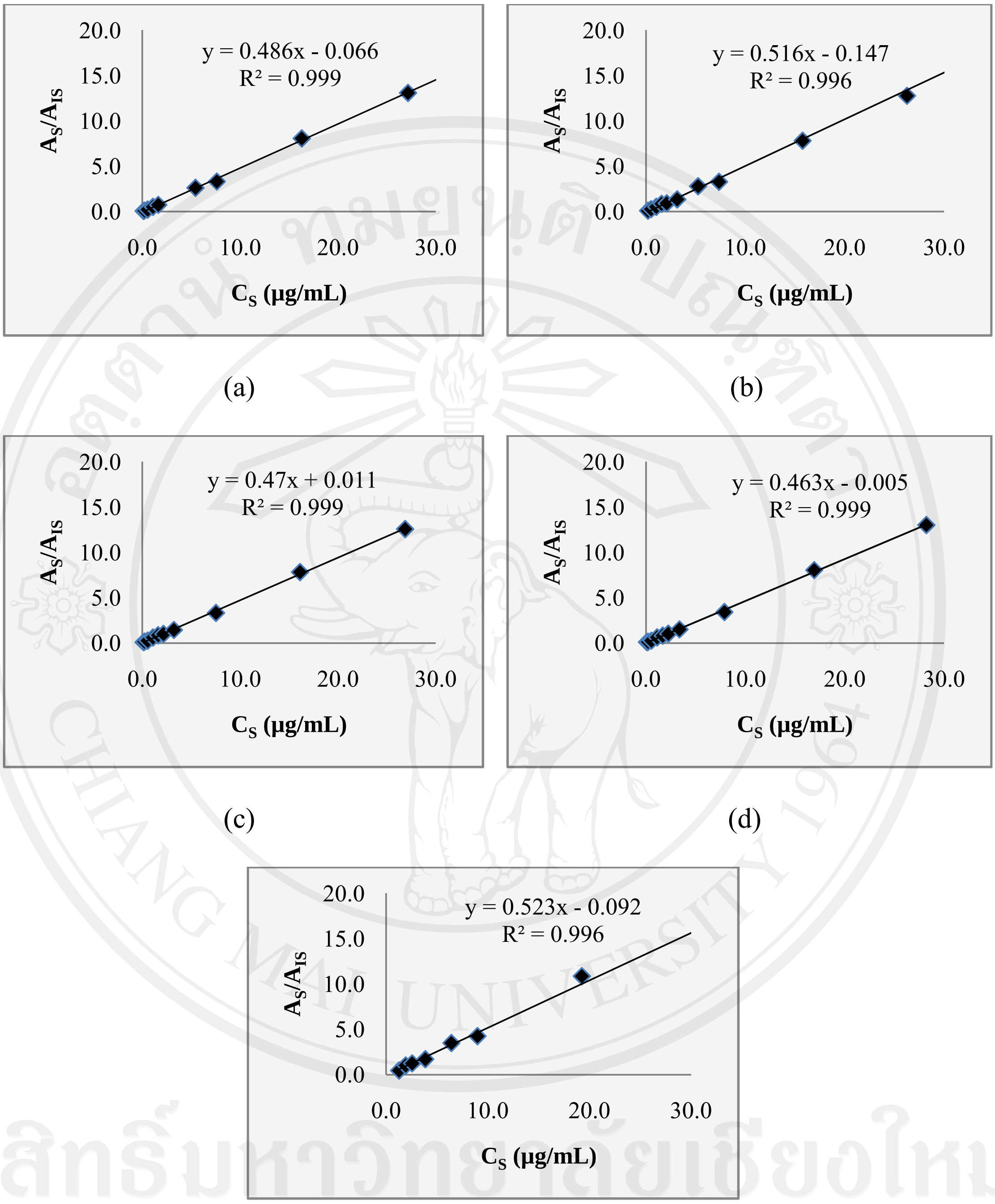
The instrument detection limit (IDL) is the lowest amount of analyte which can be detected with an acceptable statistical significance. According to Taylor (1987), IDL was calculated as three times of standard deviation (SD) of the noise at zero concentration. In this study, IDL was obtained by injections of 0.5 µg/mL standard solution. The IDLs of GC-FID for VOC analysis ranged from 0.17-0.29 µg/mL and the LOQ of GC-FID for VOC quantified range from 0.6-1.0 µg/mL (Table 3.4).

Table 3.4 Detection Limit of GC-FID for VOC analysis

Analysis times	Concentrations (µg/mL)				
	Benzene	**Toluene**	**p-Xylene**	**Styrene**	**Toluene-d8**
1	0.58	0.33	0.50	0.78	0.68
2	0.48	0.45	0.42	0.65	0.73
3	0.55	0.39	0.50	0.79	0.69
4	0.56	0.29	0.64	0.78	0.63
5	0.78	0.33	0.40	0.78	0.59
6	0.56	0.44	0.45	0.60	0.61
7	0.66	0.44	0.53	0.78	0.73
SD	**0.10**	**0.07**	**0.08**	**0.08**	**0.06**
IDL (3×SD)	**0.29**	**0.20**	**0.24**	**0.23**	**0.17**
LOQ (10×SD)	**1.00**	**0.70**	**0.80**	**0.80**	**0.60**

3.2.3 Linear dynamic range (LDR)

The linear dynamic range (LDR) was investigated by varying concentration of the analytes from 0.20-30.00 µg/mL (benzene and toluene) and 0.20-25.00 µg/mL (p-xylene and styrene). After that those concentrations were plotted against their area ratio between standard and internal standard with concentration of standard. High correlation efficiency ($R^2 > 0.995$) was obtained for all VOCs as shown in Figure 3.2.



(a) (b) (c) (d) (e)

Figure 3.2 Linear dynamic range of (a) benzene, (b) toluene, (c) p-xylene, (d) styrene and (e) toluene-d_8

3.2.4 Optimization of GC-FID condition

The column temperature is one of the important parameters in gas chromatography technique, since it leads to peak resolution. The temperature programs were used to minimize the time for separating the VOCs while narrowing peak widths. Results of the temperature program optimization condition (No. 1-5) are shown in Table 3.5 and Figure 3.3. Peaks No.1, 2, 3, 4, 5 and 6 are benzene, 1,4-difluorobenzene (internal standard), toluened8 (surrogate standard), toluene, p-xylene and styrene, respectively. The analysis time of condition No.1, No.2, No.3, No.4 and No.5 was 16.67, 10.00, 7.14, 10.41 and 9.40 minutes, respectively. The analysis times of condition No.1 was the longest and condition No.5 provided acceptable analysis time and good separation between toluene and toluene-d_8 (Figure 3.3 (e). The retention time of benzene, 1,4-difluorobenzene (IS), toluene-d8 (surrogate standard), toluene, p-xylene and styrene were 3.49, 3.67, 5.19, 5.29, 8.15 and 8.66 minutes, respectively as shown in Table 3.6. Therefore condition No.5 was selected for VOCs analysis.

Table 3.5 Optimized GC-FID conditions

No.	Ramp rate (°C/minutes)	Initial Temperature (°C)	Final temperature (°C)	Hold time (minutes)	Analysis Times (minutes)
1	3	50	100	-	16.6
2	5	50	100	-	10.0
3	7	50	100	-	7.14
4	3	50	60	2	
	7	60	100	-	10.4
5	1	50	55	-	
	3	55	60	-	
	15	60	100	-	9.40

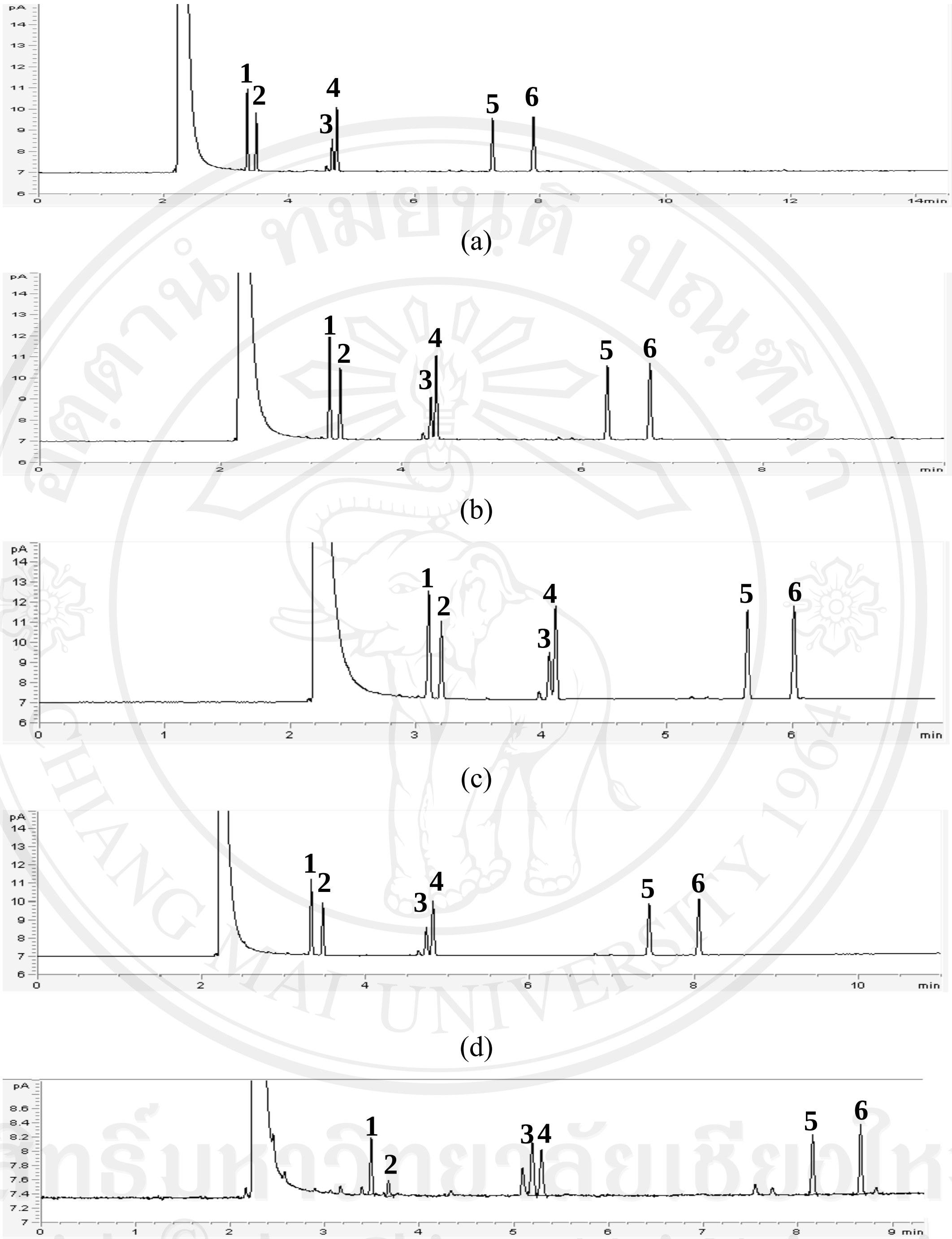


Figure 3.3 Chromatograms of mixed 10 μg/mL VOC standards at different conditions (Table 3.5), (a) No.1, (b) No.2, (c) No.3, (d) No.4 and (e) No.5. Peak 1, 2, 3, 4, 5, 6 are benzene, 1,4-difluorobenzene, toluene-d_8, toluene, p-xylene and styrene, respectively.

Table 3.6 Retention time of VOCs under optimum condition

VOCs	Retention Time (minutes)
Benzene	3.45
1,4-difluorbenzene (IS)	3.67
Toluene-d_8 (surrogate standard)	5.19
Toluene	5.29
p-Xylene	8.15
Styrene	8.66

3.3 Efficiency of methanol and acetonitrile for VOCs absorption

3.3.1 Operation time for VOCs absorption

VOC was collected in canister, polymer bag are often used, but collection of only the VOC portion is possible by trapping on a sorbent adsorption. Sorbent absorption including siliga gel, activated charcoal, anasorb 747, carboxens, porous polymers and carbon molecular sieves were solvent desorption reported by Haper, *et al* (2000). This new method for experiment was used solvent collected VOC. This experiment was optimized sampling times for VOCs by varies operation times using the methanol on testing chamber (see topic 2.5.1). The different operation times such as 15, 30, 45 and 60 minutes were varied. The amount of VOCs was calculated in terms of percent recovery. The 15 minutes operation time provides 24-44% VOC recoveries. The 30 minutes operation time provides 46-73% VOC recoveries. The 45 minutes operation time provides 51-84% VOC recoveries and the 60 minutes operation time provides 86-115% VOC recoveries. The operation time at 60 minute provided the highest percent recoveries for all VOCs as shown in Table 3.7

and Figure 3.4. Recoveries of VOCs in 3 collectors are shown in Figure 3.5. VOC in 3 collectors was decreased.

Table 3.7 Percent recoveries of VOCs absorbed by methanol operated in the testing chamber

Time	**Repeat**	**Percent recoveries of VOCs**				
		Benzene	**Toluene**	**Toluene-d8**	**p-Xylene**	**Styrene**
15	1	32.8	42.2	49.5	29.8	33.7
	2	28.5	31.9	40.4	21.5	22.0
	3	25.7	32.6	40.7	20.5	22.0
	average	**29.0**	**35.5**	**43.5**	**23.9**	**25.9**
	SD	**3.56**	**5.74**	**5.18**	**5.06**	**6.76**
	% RSD	**12.3**	**16.2**	**11.9**	**21.1**	**26.2**
30	1	45.6	77.2	103.3	57.4	55.6
	2	46.6	43.8	53.8	48.7	35.9
	3	67.3	36.0	61.6	33.8	ND
	average	**53.2**	**52.3**	**72.9**	**46.6**	**45.8**
	SD	**12.3**	**21.9**	**26.6**	**11.9**	**13.9**
	% RSD	**23.1**	**41.8**	**36.5**	**25.6**	**30.4**
45	1	60.1	72.1	90.4	50.3	57.5
	2	54.4	57.8	77.6	48.5	56.9
	3	67.8	66.6	81.9	54.2	53.7
	average	**60.8**	**65.5**	**83.3**	**51.0**	**56.0**
	SD	**6.77**	**7.19**	**6.55**	**2.88**	**2.06**
	% RSD	**11.1**	**11.0**	**7.86**	**5.64**	**3.69**
60	1	78.3	98.2	115	82.3	90.5
	2	99.2	113	121	100	110
	3	85.5	100	108	75.4	80.9
	average	**87.7**	**104**	**115**	**86.1**	**93.8**
	SD	**10.6**	**8.02**	**6.64**	**12.9**	**14.8**
	% RSD	**12.1**	**7.70**	**5.78**	**15.0**	**15.8**

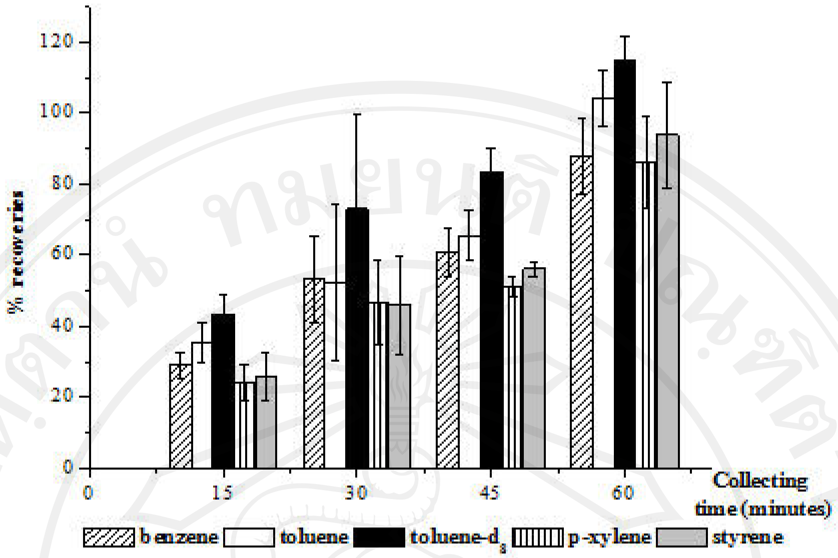


Figure 3.4 Percent recoveries of VOCs absorbed by methanol obtained from different operating time

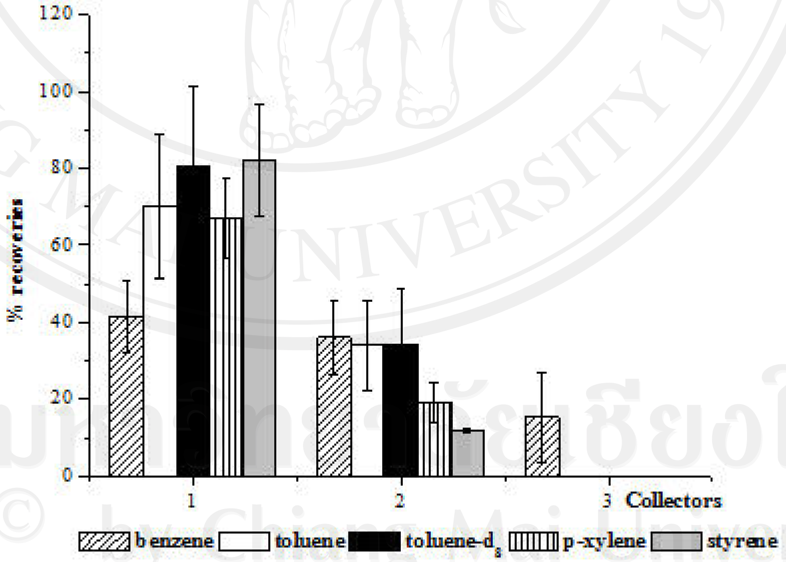


Figure 3.5 Percent recovery of VOCs in 3 collectors of methanol at 60 minutes operating time

3.3.2 VOCs absorption efficiency of methanol and acetonitrile

VOCs absorption efficiency was tested in the testing chamber (topic 2.5.2) and calculated in terms of percent recovery. Percent recoveries of VOCs in methanol and acetonitrile are shown in Table 3.8 and Figure 3.6. It was found that methanol was better solvent than acetonitrile in terms of VOCs absorption efficiency. Percent recoveries of VOCs in methanol were 86-114 %, while those in acetonitrile were 53-73 %. Methanol was higher than acetonitrile.

The polarity index of methanol with 5.1 and acetonitrile was 5.8 which higher than methanol. Therefore VOCs were more soluble in methanol than acetonitrile.

Table 3.8 Comparison of VOC percent recoveries obtained with methanol and acetonitrile

Solvents	**Replication No.**	**% Recoveries**				
		Benzene	**Toluene**	**Toluene-d_8**	**p-Xylene**	**Styrene**
Methanol	1	99.2	113.2	121	100	110
	2	85.5	100.8	107	75.4	80.9
	3	87.7	104.1	114	86.1	93.8
	Average	**87.7**	**104**	**114**	**86.1**	**93.8**
	SD	**10.6**	**8.02**	**6.64**	**12.9**	**14.8**
	% RSD	**12.1**	**7.70**	**5.78**	**15.0**	**15.8**
Acetonitrile	1	66.9	71.4	84.2	60.3	32.4
	2	53.8	77.2	57.7	92.5	82.4
	3	54.8	63.2	79.6	46.2	46.2
	average	**58.4**	**70.6**	**73.9**	**66.3**	**53.7**
	SD	**7.33**	**4.30**	**14.2**	**23.7**	**25.8**
	% RSD	**12.6**	**12.6**	**19.2**	**35.7**	**48.1**

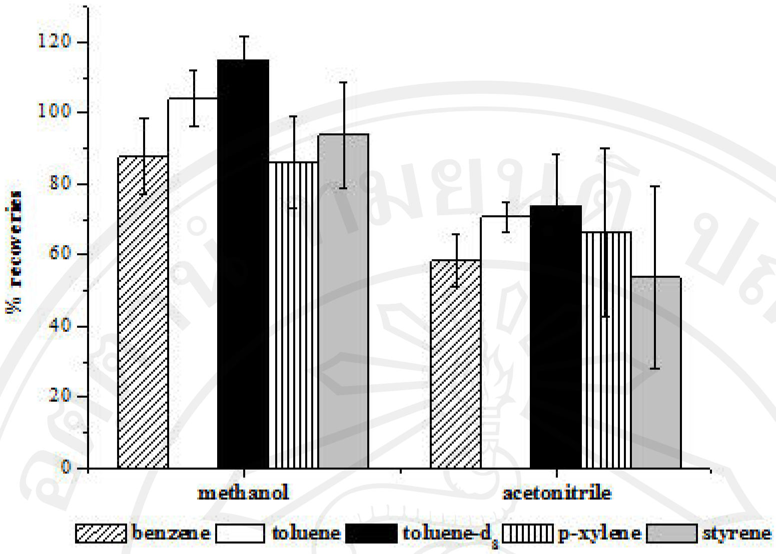


Figure 3.6 Comparison of percent recoveries of VOCs in methanol and acetonitrile solvents.

3.3.3 Testing of VOC absorption by methanol

VOC absorption efficiency by methanol (topic 3.3.2) was tested in the chamber. The operation time at 60 minutes provided the highest percent recoveries for all VOCs. Comparison of absorption efficiency of VOC between 30 and 100 µg was used in this condition as shown in Table 3.9. The absorption efficiency was calculated in term percent recovery.

30 and 100 µg amount of VOCs were collected in methanol high percent recoveries were obtained in a range of 87-122 µg / mL. Therefore, methanol was a suitable solvent for collecting of VOCs from biomass burning.

Table 3.9 Percent recoveries of VOCs (30 and 100µg) in methanol

VOCs concentration	Replication No.	% Recoveries				
		Benzene	**Toluene**	**Toluene-d_8**	**p-Xylene**	**Styrtene**
30 µg	1	99.2	113	121	100	110
	2	85.5	100	108	75.4	80.9
	3	87.7	104	115	86.1	93.8
	average	**87.6**	**104**	**115**	**86.1**	**93.8**
	SD	**10.6**	**8.02**	**6.64**	**12.9**	**14.8**
	% RSD	**12**	**8**	**6**	**15**	**16**
100 µg	1	92.3	126	112	106	124
	2	100	124	121	131	148
	3	114	87.2	90.5	79.9	95.1
	average	**103**	**112**	**108**	**106**	**123**
	SD	**11.4**	**21.8**	**15.8**	**25.6**	**26.9**
	% RSD	**11**	**19**	**15**	**24**	**22**

3.4 Determination of VOCs emitted from biomass burning on combustion chamber

3.4.1 Identification of VOCs from biomass burning by GC-MS

Identification of benzene, toluene, m,p-xylene and styrene from biomass burning was performed by GC-MS. The results of VOCs from burning of rice straw, maize residue and leaf litter are shown in Table 3.10.

Table 3.10 Retention times, target ions and percentage of quality of VOCs obtained from GC-MS

Peak no.	**Name**	**RT (min)**	**Target ion**	**Match Quality (%)**		
				Rice straw	**Maize residue**	**Leaf litters**
1	benzene	2.39	78	90	72	93
2	toluene	3.67	91	81	76	91
3	p-xylene	6.32	91	43	30	97
4	styrene	7.07	104	83	90	95

3.4.2 Emission factors of VOCs from biomass burning in the combustion chamber

1, 2 and 3 g of rice straw, maize residue and leaf litters were burnt under the optimum conditions of the combustion chamber. Table 3.11 shows amount of VOCs emitted from each type of biomass burning in the chamber. Example of chromatogram of VOCs from biomass burning is shown in Figure 3.7. The amounts of VOCs in 7 collectors of rice straw burning, maize residue and leaf litters are shown in Figure 3.8. The lower EF of benzene, toluene, m,p-xylene and styrene from rice straw burning were 14, 3, 1 and 2 mg/kg reported by Jenkins, et al. (1999).

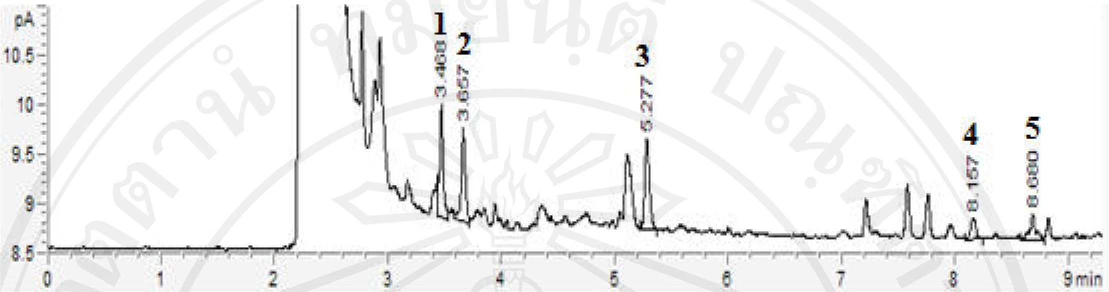


Figure 3.7 Chromatogram of VOCs emitted from rice straw burning 1) benzene 2) 1,4-difluorobenzene (IS) 3) toluene, 4) m,p-xylene and 5) styrene

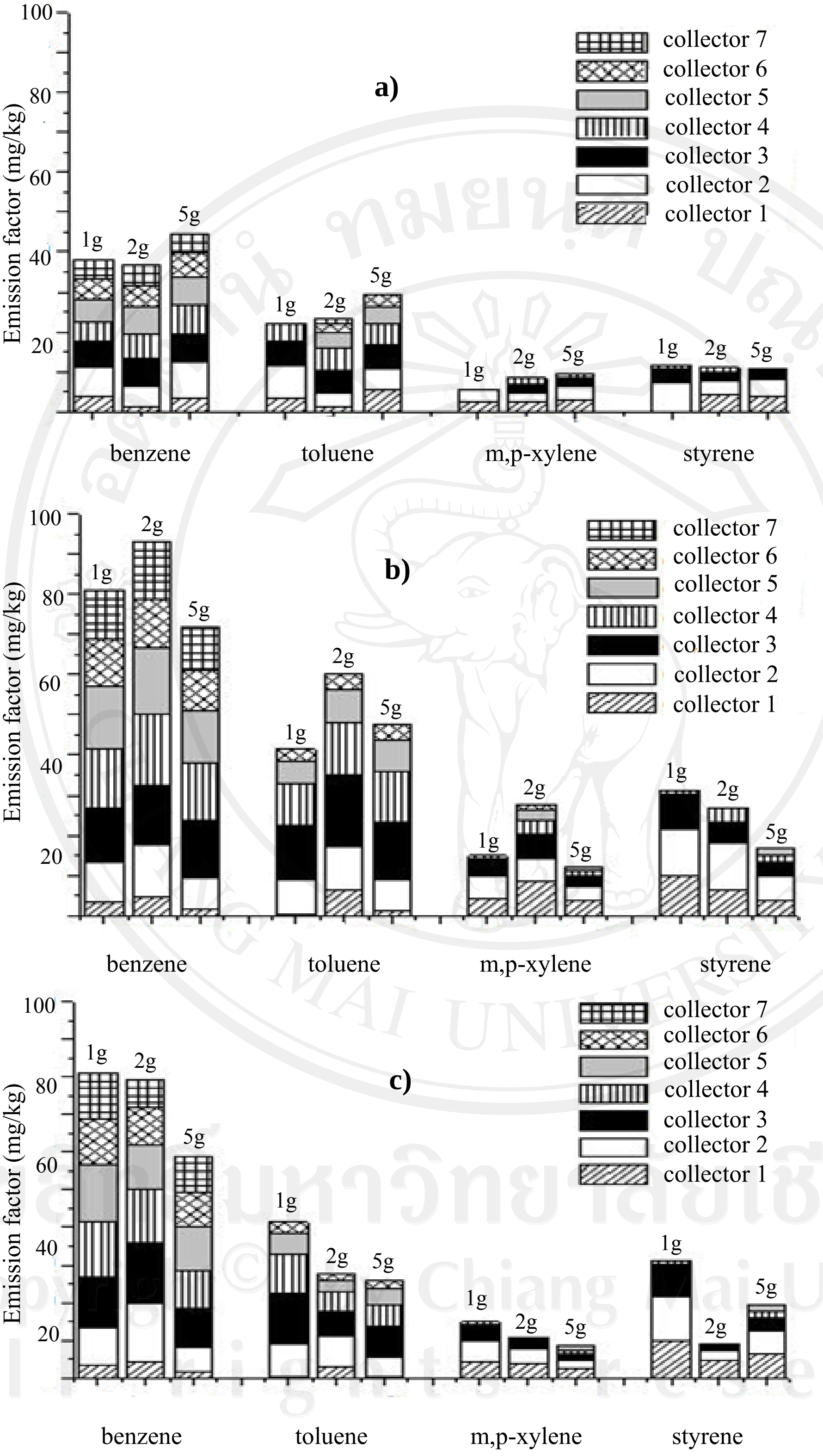


Figure 3.8 Emission factors of VOCs in 7 collectors from a) rice straw b) maize residue and c) leaf litter

Table 3.11 Emission factors of VOCs from biomass burning

Biomass	**Mass**	**VOCs (mg/kg)**			
(n=5)	**(g)**	**Benzene**	**Toluene**	**p-Xylene**	**Styrene**
Rice straw	1	37.9±8.70	22.1±7.72	5.39±1.70	9.46±3.82
	2	37.2±9.96	20.5±5.88	7.07±3.07	9.58±5.56
	5	32.2±12.0	28.8±12.8	10.1±2.68	8.10±2.97
	average	35.8±10.2	23.8±8.80	7.50±2.50	9.00±4.10
	% RSD	28.6	37.0	33.0	45.5
Maize residue	1	81.0±22.4	41.4±14.5	14.8±4.10	31.1±8.33
	2	93.3±20.7	61.4±17.0	18.0±9.02	23.7±6.43
	5	71.7±5.23	51.0±9.36	8.58±2.40	16.3±2.55
	average	82.0±16.1	51.3±13.6	13.8±5.20	23.7±5.8
	% RSD	19.6	26.6	37.5	24.3
Leaf litters	1	51.2±11.4	38.7±14.0	6.36±4.70	11.5±9.20
	2	79.2±42.4	27.1±13.4	7.38±4.04	7.15±2.99
	5	58.6±13.1	26.8±8.33	7.57±3.50	18.2±8.80
	average	63.0±22.3	30.9±11.9	7.10±4.10	12.3±7.00
	% RSD	35.4	38.6	57.4	57.0

3.4.3 Determination of emission rate

The emission rate (ER) is the multiplication of emission factor (EF) and the amount of crop residue burnt in the field annually (kg/area/year). The emission rates of VOCs from biomass burning of rice straw, maize residue and leaf litters are shown in Table 3.12.

Table 3.12 Emission rate of VOCs from biomass burning in Mae Rim District

Biomass	VOCs	EF (mg/kg)	Annual Burning mass* (kg/year)	ER** (kg/year)
Rice straw	Benzene	35.7±9.91	10,316,768	369
	Toluene	23.8±9.35		245
	m,p-Xylene	7.50±3.11		77.6
	Styrene	9.60±3.94		99.3
Maize residue	Benzene	82.0±18.9	264,704	21.7
	Toluene	51.3±15.5		13.6
	m,p-Xylene	13.8±6.79		3.66
	Styrene	23.7±8.52		6.27
Leaf litters	Benzene	63.0±27.4	251,920	15.9
	Toluene	30.9±12.7		7.77
	m,p-Xylene	7.10±3.82		1.79
	Styrene	12.3±8.40		3.09

*See Table 2.7 (page 48)

** ER = EF × Annual burning mass