CHAPTER 3

RESULTS AND DISCUSSION

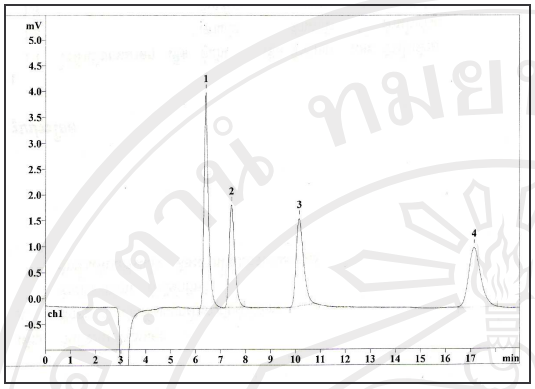
In this work NO_2, SO_2 and O_3 were collected by passive sampling technique and then determined by both ion chromatography (IC) and spectrophotometry under the optimum conditions.

3.1 Ion chromatagraphy

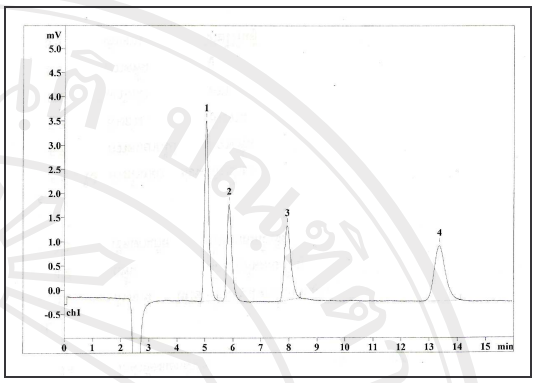
NO_2, SO_2 and O_3 in form of NO_2^-, SO_4^{2-} and NO_3^-, respectively, were determined by IC under the optimum conditions.

3.1.1 Optimization of ion chromatograph

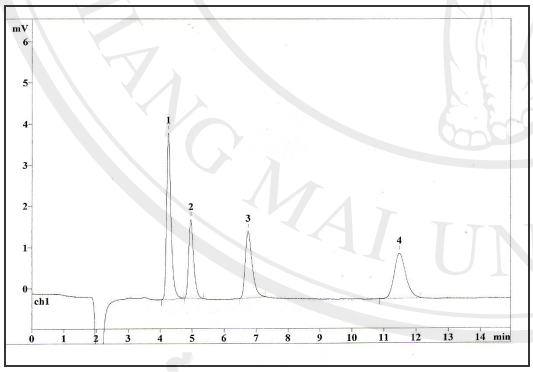
The optimum mobile phase composition and its flow rate were obtained by considering the resolution between Cl^- peak and NO_2^- peak due to their relative close retention times. The resolution (Rs) of these two peaks was calculated as shown in Table 3.1. Effects of mobile phase compositions on retention time of ion peak were tested at different flow rates. Chromatogram analyte were shown in Fig 3.1 and 3.2. Peak 1 is cholide (Cl^-), peak 2 is nitrite (NO_2^-), peak 3 is nitrate (NO_3^-) and the last peak is sulfate (SO_4^{2-})



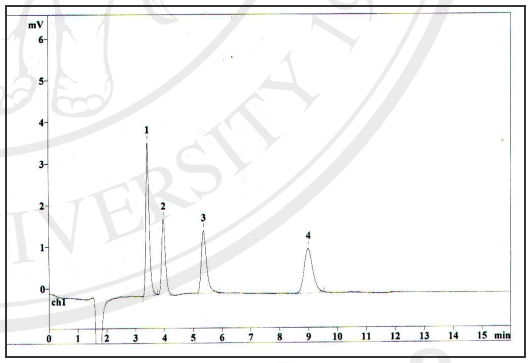
A. Flow rate of 0.8 ml/min



B. Flow rate of 1.0 ml/min

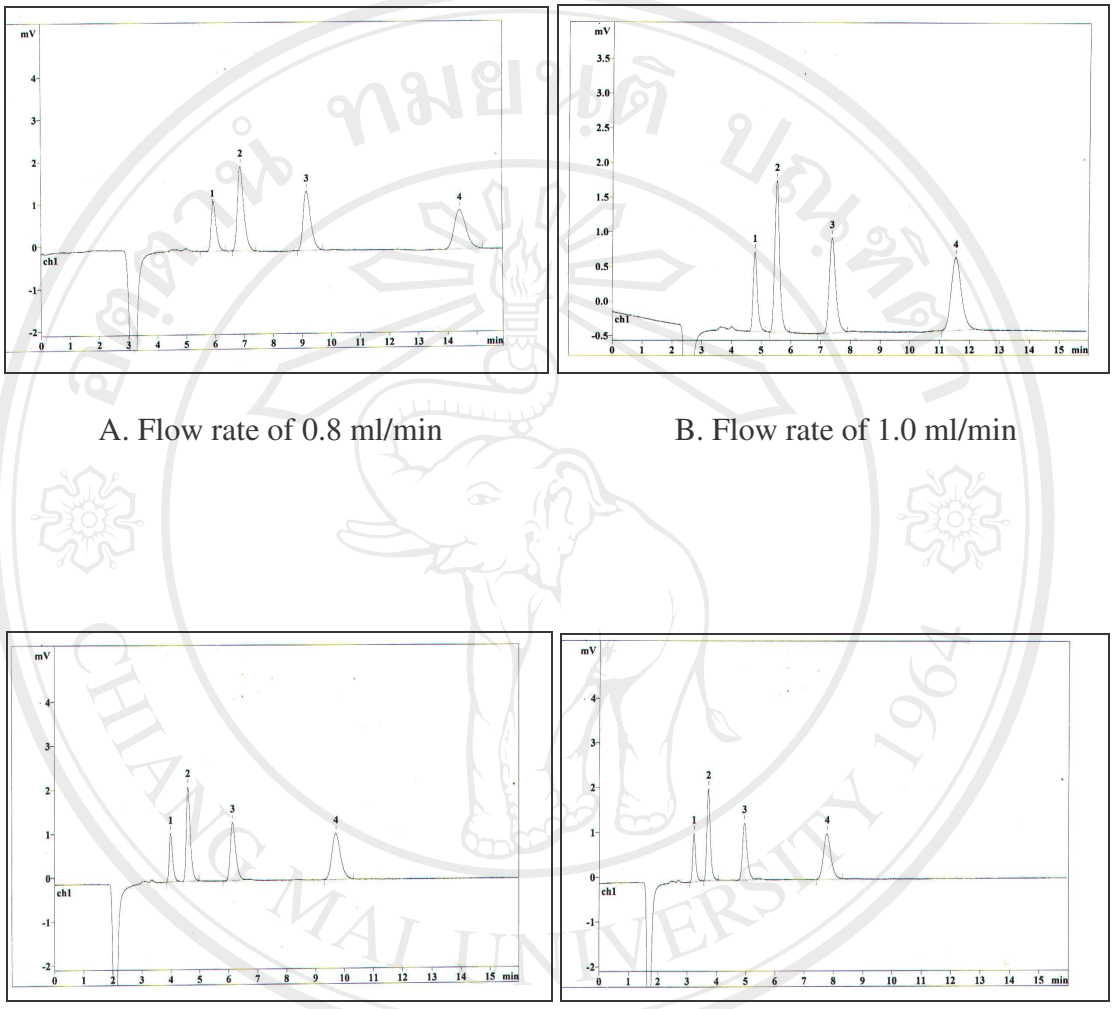


C. Flow rate of 1.2 ml/min



D. Flow rate of 1.5 ml/min

Fig 3.1 The chromatogram obtained from mobile phase 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3



A. Flow rate of 0.8 ml/min

B. Flow rate of 1.0 ml/min

C. Flow rate of 1.2 ml/min

D. Flow rate of 1.5 ml/min

Fig 3.2 The chromatogram obtained from mobile phase 2.0 mM $NaHCO_3$/2.4 mM Na_2CO_3 /5% acetone

Table 3.1 The resolutions of Cl^- and NO_2^- peaks

Flow rate (ml/min)	Mobile phase 1				Mobile phase 2			
	t_R (min)		Time of analysis (min)	Resolution (Rs)	t_R (min)		Time of analysis (min)	Resolution (Rs)
	Cl^-	NO_2^-			Cl^-	NO_2^-		
0.8	6.4	7.4	19	2.9	5.9	6.9	16	2.3
1.0	5.1	5.9	15	2.0	4.8	5.5	13	2.2
1.2	4.3	4.9	13	1.9	4.0	4.6	11	2.0
1.5	3.4	3.9	10	1.5	3.2	3.7	9	1.6

Mobile phase 1 ; 1.7 mM $NaHCO_3$/ 1.8mM Na_2CO_3

Mobile phase 2 ; 2.0 mM $NaHCO_3$/ 2.4mM Na_2CO_3/ 5% acetone

From Table 3.1, the peak resolutions obtained from all conditions were higher than 1.5. It means that all tested conditions can completely separate peaks of Cl^- peak and NO_2^-. The results obtained showed no differences between two mobile phase compositions. Due to the reason that the mobile phase 1 (1.7 mM $NaHCO_3$/ 1.8mM Na_2CO_3) was without organic solvent unlike the mobile phase 2. The organic solvent could contaminate the analytical long term usage. Moreover, acetone which is a toxic substance could affect human health.

The flow rate of mobile phase was also tested. The higher the flow rate is, the shorter analysis time and higher column pressure are. The most appropriate flowrate was the one with not too long analysis time and not too high pressure. Therefore the mobile phase with flow rate of1 ml/min was selected.

Therefore, the optimum mobile phase composition was 1.7 mM $NaHCO_3$/ 1.8 mM Na_2CO_3 with the flow rate 1.0 ml/min.

The conditions of IC used in this work are shown in table 3.2.

Table 3.2 Conditions of Ion chromatograph

Item	Condition
Column	Metrosep A SUPP 4-250 Size : 4 x 250 mm Part.size : 9 μm
Mobile phase	1.7 mM $NaHCO_3$/ 1.8 mM Na_2CO_3
Flow rate of mobile phase	1.0 ml/min
Suppressor	Anion self-generating suppressor with milli-Q water/ 100 mM H_2SO_4
Detector	Conductivity
Temperature	35.0^oC
Pressure	Maximum 10 MPa
Sample loop volume	20 μl
Analysis time	15 min

3.1.2 Precision of ion chromatograph

A) Repeatability

The repeatability is the results of standard deviation (SD) of measurements repeated by the same analyst on the same instrument within a shot time period. The repeatability was checked by injecting a 0.2 ppm mixed standard solution of NO_2^-, NO_3^- and SO_4^{2-} into ion chromatographic system under the optimum conditions. The repeatability of ion chromatograph is shown in Table 3.3.

Table 3.3 Repeatability of ion chromatograph

No. of injection	t_R (min)			Peak area (mV*sec)			Concentration (ppm)		
	NO_2^-	NO_3^-	SO_4^{2-}	NO_2^-	NO_3^-	SO_4^{2-}	NO_2^-	NO_3^-	SO_4^{2-}
1	6.61	9.03	18.20	65.1	110.6	128.6	0.203	0.202	0.243
2	6.55	8.89	18.21	64.8	106.7	136.4	0.201	0.201	0.260
3	6.60	9.01	18.21	72.0	113.8	132.7	0.224	0.208	0.251
4	6.60	9.00	18.20	66.9	113.6	130.6	0.209	0.208	0.247
5	6.59	8.98	18.19	64.5	114.7	127.3	0.201	0.210	0.241
6	6.58	8.96	18.19	74.7	114.1	130.6	0.233	0.209	0.247
7	6.57	8.94	18.20	68.6	112.9	128.3	0.214	0.211	0.243
8	6.57	8.92	18.23	64.4	115.4	127.5	0.201	0.211	0.241
9	6.56	8.90	18.25	75.4	115.4	126.6	0.235	0.210	0.240
10	6.55	8.90	18.20	70.4	114.8	143.1	0.220	0.200	0.270
11	6.56	8.90	18.23	64.2	109.4	127.8	0.200	0.206	0.242
Avrg	6.58	8.95	18.21	68.3	112.9	130.9	0.213	0.207	0.248
SD	0.02	0.051	0.019	4.242	2.799	4.966	0.013	0.004	0.009

B) Reproducibility

The reproducibility was checked by injecting a 0.2 ppm mixed standard solution of NO_2^-, NO_3^- and SO_4^{2-} into the optimum conditions of ion chromatographic system at 3 different days. The results of reproducibility were estimated by standard deviation (SD) and the related values as shown in Table 3.4.

Table 3.4 Reproducibility of ion chromatograph

Day	Rt (min)			Peak area (mV*sec)			Concentration (ppm)		
	NO_2^-	NO_3^-	SO_4^{2-}	NO_2^-	NO_3^-	SO_4^{2-}	NO_2^-	NO_3^-	SO_4^{2-}
1	6.60	8.91	18.23	66.9	112.6	130.6	0.215	0.209	0.247
2	6.58	8.90	18.25	75.3	115.5	126.7	0.235	0.210	0.240
3	6.56	8.80	18.23	64.1	109.4	127.8	0.210	0.200	0.242
Avrg	6.58	8.87	18.24	68.8	112.5	128.4	0.220	0.207	0.243
SD	0.02	0.06	0.01	5.8	3.1	2.0	0.013	0.006	0.004

The results of repeatability and reproducibility showed that the optimum conditions of ion chromatograph used in this experiment provided very good precision for NO_2^-, NO_3^- and SO_4^{2-} determinations.

3.1.3 Detection limit of ion chromatograph

The detection limit (DL) was checked by 2 methods. The first method was done by injecting a 0.2 ppm mixed standard solution of NO_2^-, NO_3^- and SO_4^{2-} into the optimum conditions of ion chromatographic system. The detection limit was obtained from 3 times of standard deviation (SD) of measurements repeated by the same analyst on the same instrument (Taylor, 1987). The detection limit of NO_2^-, NO_3^- and SO_4^{2-} were 0.029, 0.012 and 0.023 ppm, respectively as shown in table 3.5.

Table 3.5 The detection limit of ion chromatograph (First method)

No. of injection	Concentration (ppm)		
	NO_2^-	NO_3^-	SO_4^{2-}
1	0.203	0.202	0.243
2	0.201	0.201	0.260
3	0.224	0.208	0.251
4	0.209	0.208	0.247
5	0.201	0.210	0.241
Avrg	**0.208**	**0.206**	**0.248**
SD	**0.010**	**0.004**	**0.008**
DL	**0.029**	**0.012**	**0.023**

The second method was done by using a linear equation of mixed standard solution 0.2 to 1.0 ppm of NO_2^-, SO_4^{2-} and NO_3^- (Miller and Miller,1998). The detection limit as shown in Table 3.6 was calculated with the help of equation 2.2 (see Appendix B).

Table 3.6 The detection limit of ion chromatograph (second method)

Conc. (ppm)	**Peak area**		
	NO_2^-	**NO_3^-**	**SO_4^{2-}**
0.2	6.49	5.76	6.35
0.4	13.00	11.00	13.10
0.6	19.00	16.90	19.90
0.8	25.50	22.10	26.80
1.0	32.10	28.60	34.10
R^2	**0.9998**	**0.9986**	**0.9998**
DL	**0.017**	**0.012**	**0.017**

3.2 Development of passive sampler for determination of pollutant gases

Passive sampler for determination of pollutant gases has been developed. In the step of sampling, both sampler and blank have to be exposed. The blank test is necessary due to it provides level of contamination including contribution from transport and exposure as well as during chemical analysis and preparation. The amount of gases in sampling tubes was subtracted from blank tubes to obtain the real value.

3.2.1 Sorbent

The selection of sorbent is important for passive sampler. The performance of passive sampler depended on the appropriate sorbent which highly sorption efficiency (Brown, 2002). Reverse diffusion can be also occurred if the vapor pressure of the analyte at the sorbent surface is greater than the external concentration. He suggested to use sorbent with high sorption capacity and low vapor pressure of sorbed material or of the reaction product formed by reactive sorbent.

All sorbents used for NO_2 analysis were impregnated with trapping solution and placed in diffusion tube. The first experiment was conducted in the laboratory (indoor exposure). Each sorbent was cleaned and dried before using. A 50-µl of absorbing solution (20% TEA) was dropped into sorbent. Among the sorbents examined, the glass fiber filter GF/A gave the highest value of absorptivity as shown in Fig 3.3. Therefore, it was chosen as an absorption filter in this study.

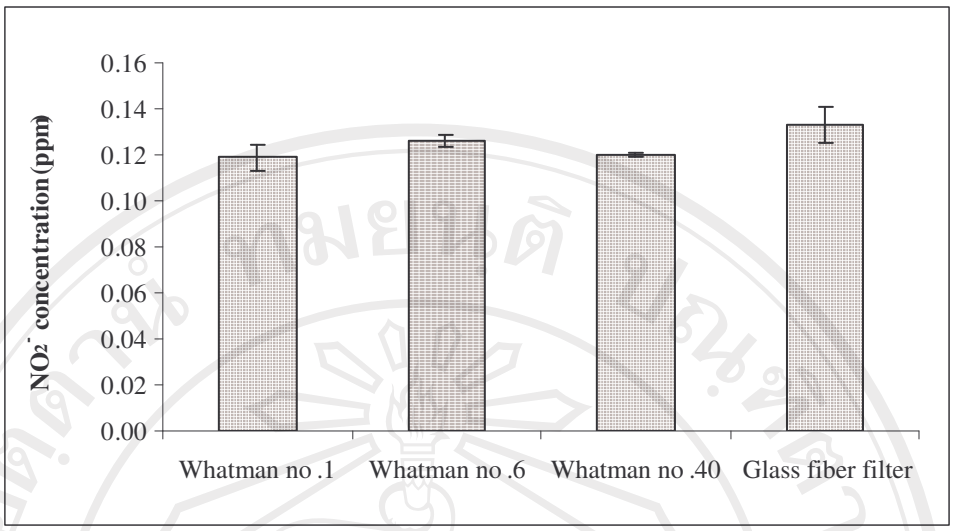


Fig 3.3 The sorbent absorptivity comparison (n=5)

3.2.2 Diffusion tube

Two types of diffusion tube, PE and PS were used as diffusion tube for setting up of passive samplers. The PE tube was 5.40 cm long, 1.40 cm i.d. with a PE cap. The PS tube was 5.40 cm long, 1.20 cm i.d. with a PE cap. Their efficiencies have been compared after 1 week indoor and outdoor exposure. All passive samplers were extracted and determined by IC.

Two-sample student's *t*-test (two-tailed) was used to estimate level of significance of any difference obtained from PE and PS tubes for NO_2 measurement. The highest amount of NO_2 was obtained from PE passive sampler as shown in Fig 3.4. However, the *t*-test indicated that the amount of NO_2 was not significantly different when exposed at indoor site ($p \leq 0.01$). Contrastingly, in the outdoor exposure the difference of NO_2 intake was found (99% confidence level or $p \leq 0.01$).

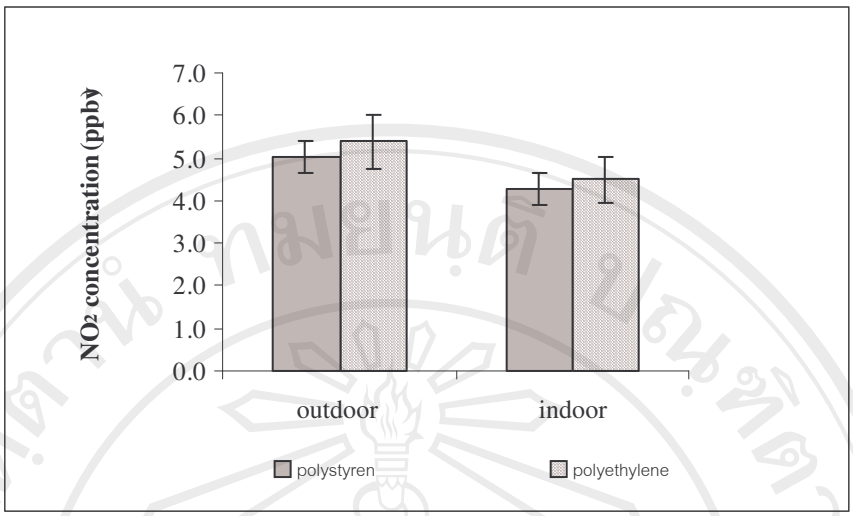


Fig 3.4 Comparison of diffusion tube efficiency (n=5)

The diffusion tubes were also applied for SO_2 determination. The scatter plot diagrams (Fig 3.5 and 3.6) were drawn for the measurements of NO_2 and SO_2 form PE and PS tubes both for indoor and outdoor exposure.

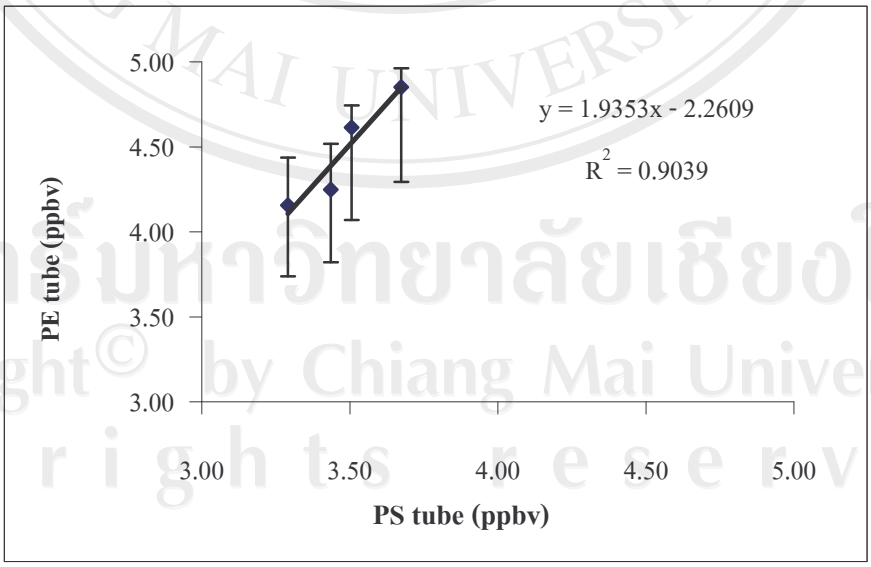


Fig 3.5 Correlation of NO_2 (ppbv) measurement from PE and PS tube

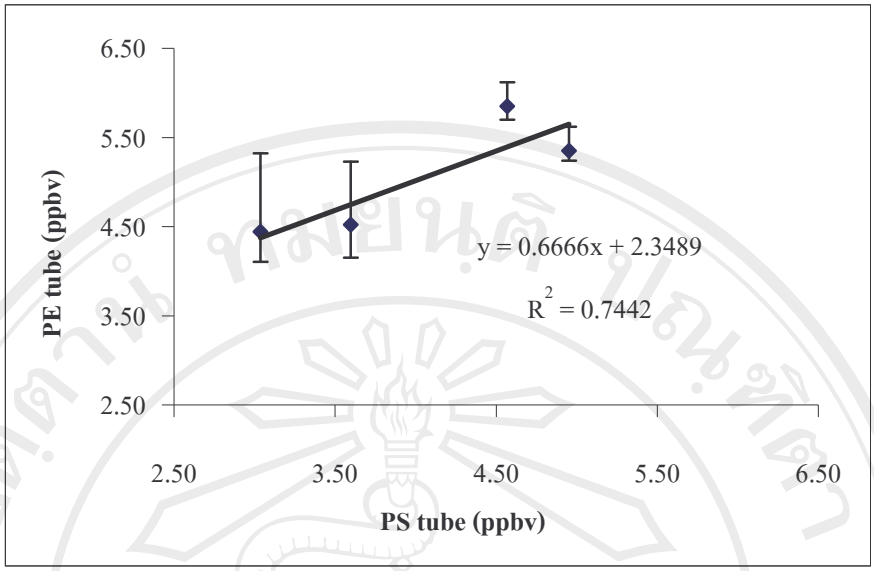


Fig 3.6 Correlation of SO_2 (ppbv) measurement from PE and PS tube

A strong correlation (r^2=0.9039) was found between PS and PE tubes of NO_2 measurements whereas the correlation of SO_2 measurement from PS and PE tubes was 0.7442.

The PS tube is almost 100% transparent, while, the PE tube is less transparent. Therefore, the diffusion tube made form PS tube obviously has more effect from light, which lead to photodegradation of trapped gases. It was found that sampler made of transparent polythene tube give results of determination of NO_2 up to 50 % lower than samplers protected against sunlight (Krochmal and Gorski, 1991).

3.3 Determination of nitrogen dioxide (NO_2)

3.3.1 Calibration curve of NO_2

NO_2 collected in diffusion tube was presented in form of NO_2^-. The NO_2^- concentration was determined by both IC and spectrophotometry and

then calculated by using the regression equation of the calibration curve prepared form the standard NO_2^- solution as shown in Fig 3.7 and 3.8.

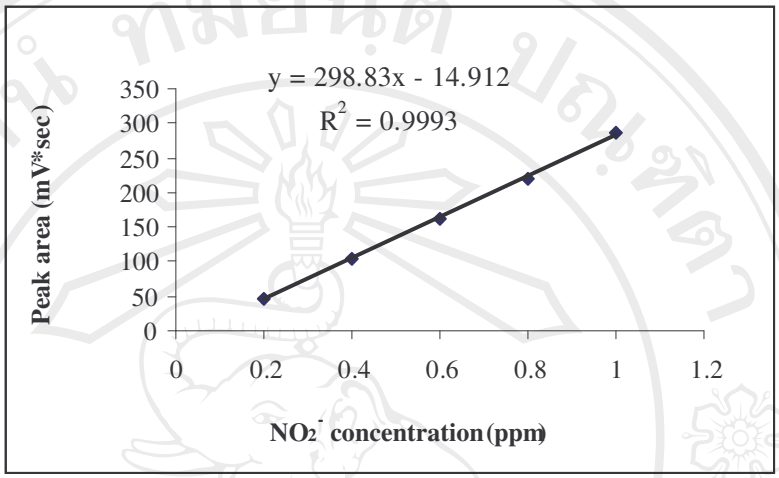


Fig 3.7 Standard curve of NO_2^- determined by ion chromatography

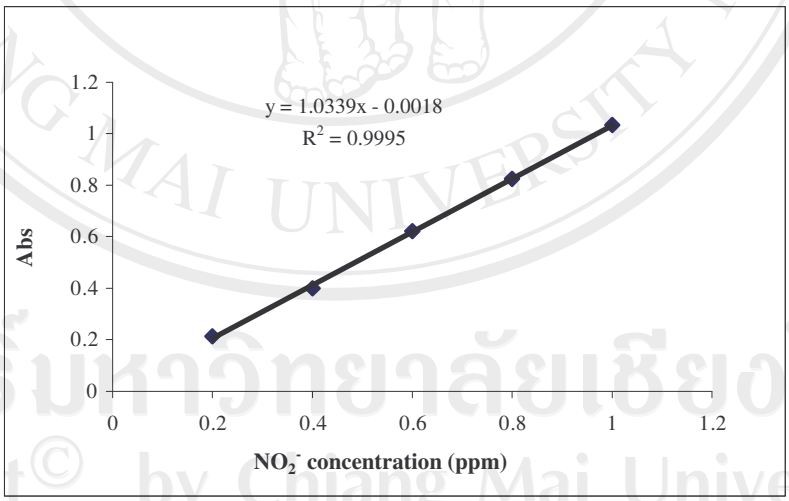


Fig 3.8 Standard curve of NO_2^- determined by spectrophotometry

3.3.2 Detection limit of spectrophotometry

The detection limit was obtained by using a linearity curve of different NO_2 concentrations with very good correlation ($r^2 \geq 0.9995$). The detection limit of spectrophotometer for NO_2 was 0.025 ppm, which calculated with the help of equation 2.2 (see Appendix B).

3.3.3 Selection of absorbing solution for NO_2^-

Four different types of absorbing solution had been tested to compare their efficiencies. They were (1) 20% TEA, (2) 12% TEA/4% glycerol, (3) KI / $NaASO_2$ / ethylene glycol / NaOH in methanol, and (4) methanolic NaI / NaOH. The amount of NO_2 trapped after 1 week indoor exposure was determined by both IC and spectrophotometry.

TEA is a compound widely used for trapping NO_2 and SO_2 due to its high collection efficiency (Sickles *et al*., 1990). The product of absorption of NO_2 in TEA solution is nitrosodiethanolamine (Aoyama and Yashiro, 1983) this compound, however, can be determined in the same way as nitrite.

Levaggi *et al*. (1972) proposed the reaction product as triethanolamine nitrite and triethanolamine nitrate as shown below

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2 \qquad \text{.....(3.1)}$$

$$HNO_3 + HNO_2 + 2N(CH_2CH_2OH)_3 \longrightarrow N(CH_2CH_2ONO_2)(CH_2CH_2OH)_2 + N(CH_2CH_2ONO)(CH_2CH_2OH)_2 + H_2O \qquad \text{.....(3.2)}$$

Triethanolamine (TEA) Triethanolamine-nitrate Triethanolamine-nitrite

Later, Gold (1977) identified the reaction product as nitrite and triethnolamine nitrate but recently Glasius *et al* (1999) identified it as triethanolamine N-oxide and the following reaction scheme was proposed.

$$2NO_2 + N(CH_2CH_2OH)_3 + 2OH^- \longrightarrow 2NO_2^- + {}^-O\text{-}N^+(CH_2CH_2OH)_3 + H_2O \quad \text{.....(3.3)}$$

This mechanism was obtained from the reaction as shown below;

$$N(CH_2CH_2OH)_3 + H_2O \longrightarrow (CH_2CH_2OH)_3NH^+ + OH^- \quad \text{.....(3.4)}$$

$$2OH^- + 2NO_2 + H_2O \longrightarrow NO_3^- + NO_2^- + H_2O \quad \text{.....(3.5)}$$

$$NO_3^- + N(CH_2CH_2OH)_3 \longrightarrow NO_2^- + ON(CH_2CH_2OH)_3 \text{ (N-Oxide)} \quad \text{.....(3.6)}$$

This is supported by the observation of Palmes and Johnson (1987). The alkaline reaction of the extract due to presence of TEA (pH about 10) prevent oxidation of nitrites to nitrates (Krochmal and Kanila, 1997).

NO_2 is dissolved in a basic solution of NaOH, it disproportionates to $NaNO_3$ and $NaNO_2$.

$$2NO_2(g) + 2NaOH(aq) \longrightarrow NaNO_2(aq) + NaNO_3(aq) + H_2O(l) \quad \text{.....(3.7)}$$

Using of NaOH / NaI absorbing solution, NO_2 is absorbed in the filter and the iodide reduce NO_2 to nitrite (NO_2^-). The hydroxide is converted to carbonate during sampling due to uptake of carbon dioxide.

The results of NO_2 trapped after 1 week indoor exposure are shown in Fig 3.9.

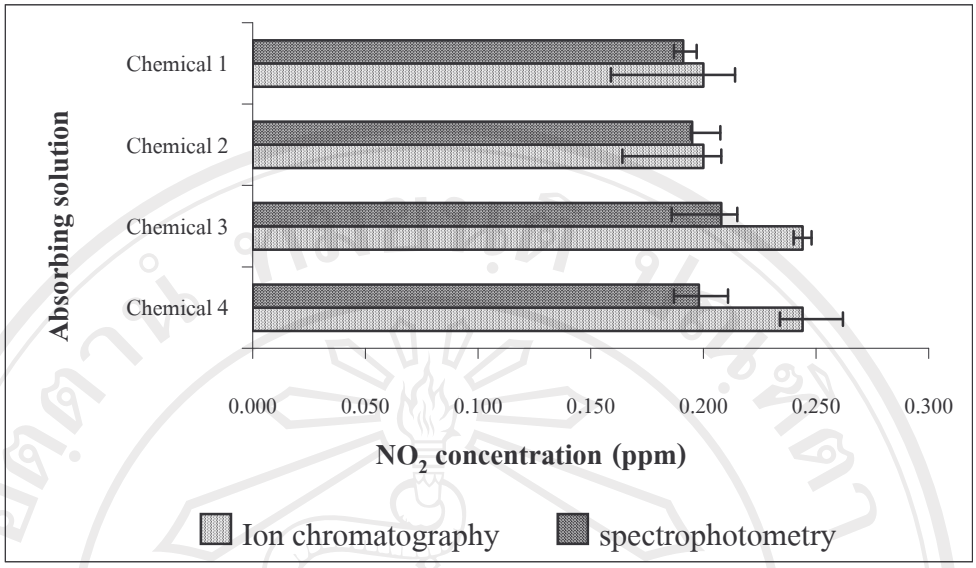


Fig 3.9 Absorbing efficiency comparison of NO_2

Chemical 1; 20% TEA

Chemical 2; 12% TEA/4% glycerin

Chemical 3; KI / $NaASO_2$ / ethylene glycol / NaOH in methanol

Chemical 4; methanolic NaI / NaOH

All types of absorbing solution can be applied for absorbing of NO_2 in ambient air due to no significantly different ($p \leq 0.01$). In the same absorbing solution, the amount of NO_2^- obtained form both IC and spectrophotometry determination was not significantly different ($p \leq 0.01$). However, there was a problem of analysis by ion chromatographic system. A large interference peak from NaOH used in an absorbent appeared in the chromatogram. Moreover, there was a peak drop at the retention time about 8.5 min as shown in an appendix D. Therefore, chemical 3 and 4, which have NaOH composition , were not chosen as the reasons mentioned above.

TEA solution is the appropriate absorbing solution for NO_2. The amount of NO_2 uptake depended on the amount of TEA in solution. In this experiment the mix of 4% glycerol in 12% TEA gave lower SD than 20% TEA absorbing solution. The used of glycerin (Helaleh *et al*., 2002) or ethylene glycol (Ferm, 1997) further improves the collection efficiency at low humidities and stabilizes trapped gases.

The results agreed with the reporting by Kirby *et al*. (2002), he found that there may be insufficient water molecules available in 50% v/v of TEA to achieve equilibrium dissociation. A very large excess of TEA is present on meshes, a significant proportion of this may actually be unavailable to NO_2 molecule arriving at the sampler meshes. The absorption between nitrite ion and TEA is restricted by lack of hydroxy ion in the solution. They also found that TEA in deionized water are closed to NO_2 concentration for chemiluminescence measurements and they found that no difference of NO_2 uptake between compared the aliquot volume in the range 25-50 μl.

Moreover, the efficiency of TEA decreased at low temperature. The freezing point of TEA is indeterminate (17.9-21.2 ^{o}C). Solidification of TEA on sorbent could lead to reduce gases uptake. Hargreaves, 1989 found that relative humidity (RH) in the range 50-100% had no effect on samplers. Palmes and johnson, (1987) reported a reduced NO_2 uptake rate for dry air (RH=0%). The study showed that the hydration of TEA is an essential part of the process of NO_2 absorption and subsequent conversion to nitrite. Therefore, in this study, the solution of 4% TEA in 12% TEA was chosen to be the absorbing chemical.

3.3.4 Determination of NO_2 by spectrophotometry

Nitrite (NO_2^-) can be determined by spectrophotometry for determination of NO_2^-, The nitrite in solution diazotises the sulphanilamide and the diazonium salt formed couples with the N-(1-Napthyl) ethylenediamine dihydrochloride (NEDA) to form a purple azodye. The reaction involved are shown in Fig 3.10 (BCH 5112, 2003).

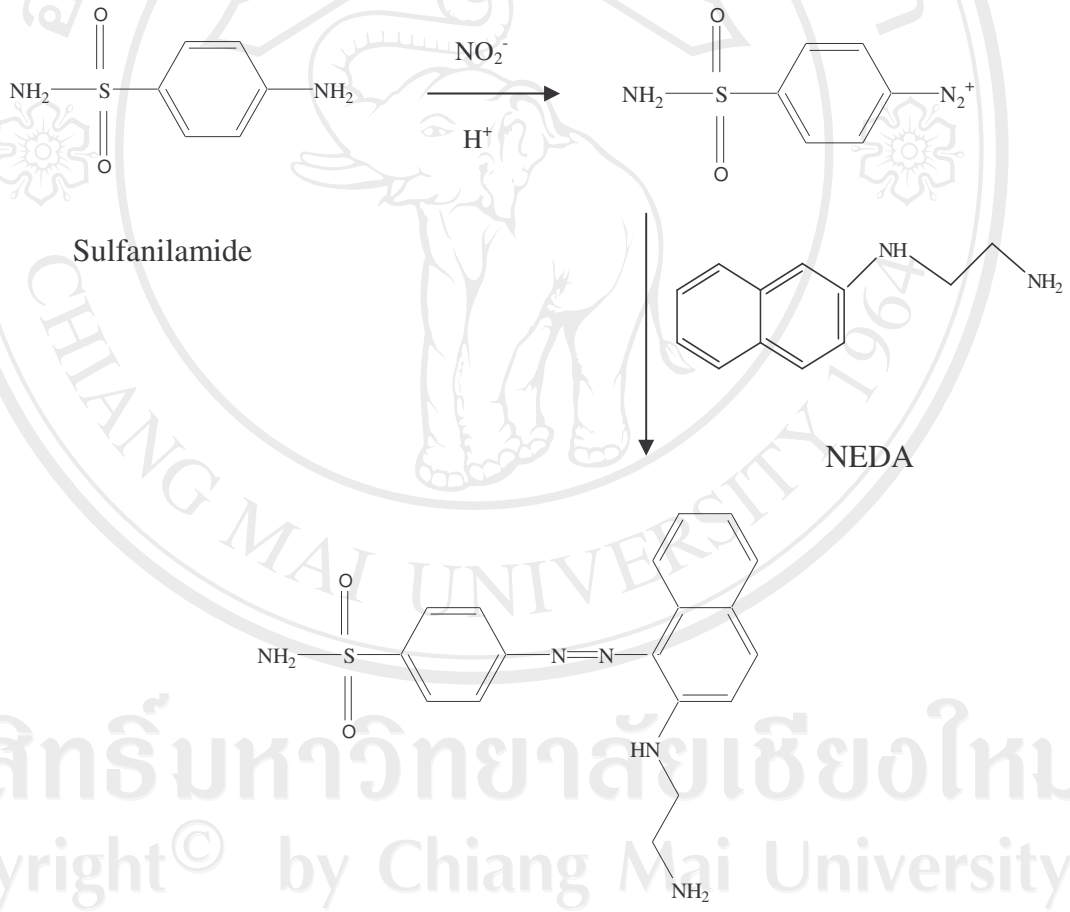


Fig 3.10 The NO_2 formation for determined by spectrophotometry

A) Optimization of color development for NO_2 determination by spectrophotometry

The stability of color has been investigated. Two parts of 0.2-1.0 ppm NO_2^- standard solution was mixed with one part of Salzmann reagent and then leave it for 5-25 min. It was found that the solution was completely mixed after 10 minutes as show in Fig 3.11.

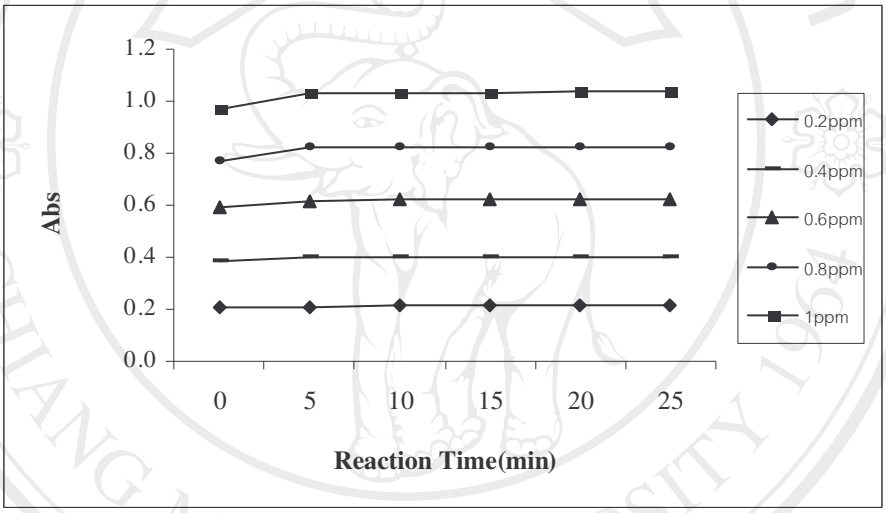


Fig 3.11 Color stability of NO_2^- (n=5)

Color development maximizes at a pH of less than two (Sawicki *et al*., 1963; Macchi and Cescon, 1970). Phosphoric acid was therefore added to the reagents to increase acidity since unlike hydrochloric acid it gives rapid and maximum color development (Jacobs and Hochheiser, 1958).

3.3.5 Extraction process of NO_2

NO_2 was analysed in form of NO_2^-. Extraction conditions have been tested by spiking 20 µl of 100 ppm of NO_2^- standard solution onto the sorbent (Whatman GF/A) placed in 5 diffusion tubes. After that, 4 ml of milli-Q water was then added. Extraction conditions including time of extraction and techniques (used and non-used of ultrasonicator) were tested. Percent recoveries were calculated in order to see the efficiency of each condition. The result of NO_2^- extraction is shown in Fig 3.12.

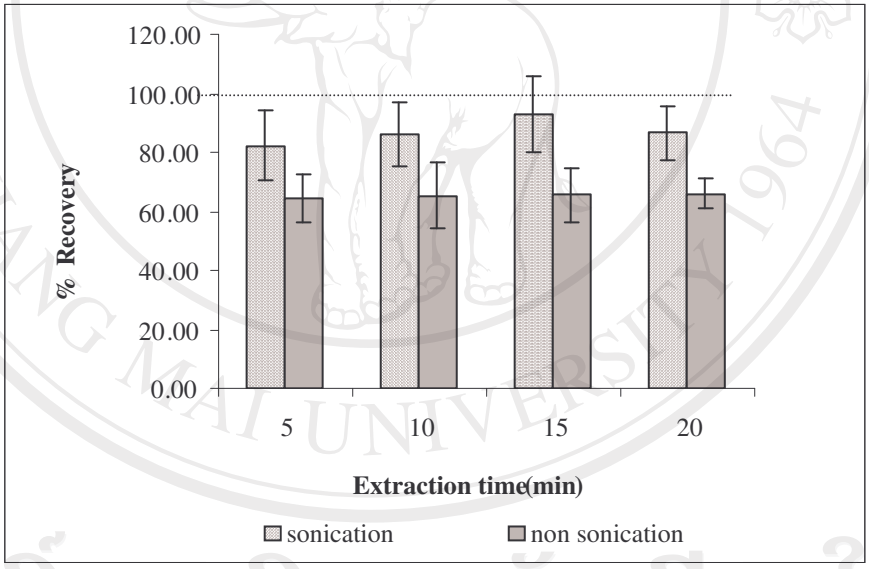


Fig 3.12 Percent recovery of NO_2^- extraction

The recoveries of NO_2^- from extraction with helping of ultrasonicator for 5, 10, 15 and 20 min were 82.3, 86.0, 92.6 and 86.5 %, respectively, while those of non using ultrasonicator were 64.4, 65.4, 65.5 and 66.0 %, respectively.

It was found that extraction with helping of ultrasonicator gave higher recovery than non using ultrasonicator. Although Krochmal and Kanila (1997)

reported that no ultrasonic bath is needed as the substances of interest (NO_2^-) are easily soluble in water (In addition, to avoid another contaminants dissolved in water). The extraction time was varied from 5-20 min. it was found that extraction by 15 min was the appropriate extraction condition for NO_2.

In conclusion, optimum extraction condition for NO_2 determination was 4 ml of milli-Q water with 15 min ultrasonication.

3.3.6 Study of sampling period

The passive samplers for NO_2 sampling were exposed at Chaingmai Governmental Office Center (site A) for 1, 3, 5 and 7 days (11/10/05-17/10/05). Then NO_2 concentrations were determined by IC. The values of median NO_2 concentration of 5 replicates subtracted with blank value are compared with the day average values of active sampling (PCD data) using max and min values to illustrate error bar as shown in Fig 3.13.

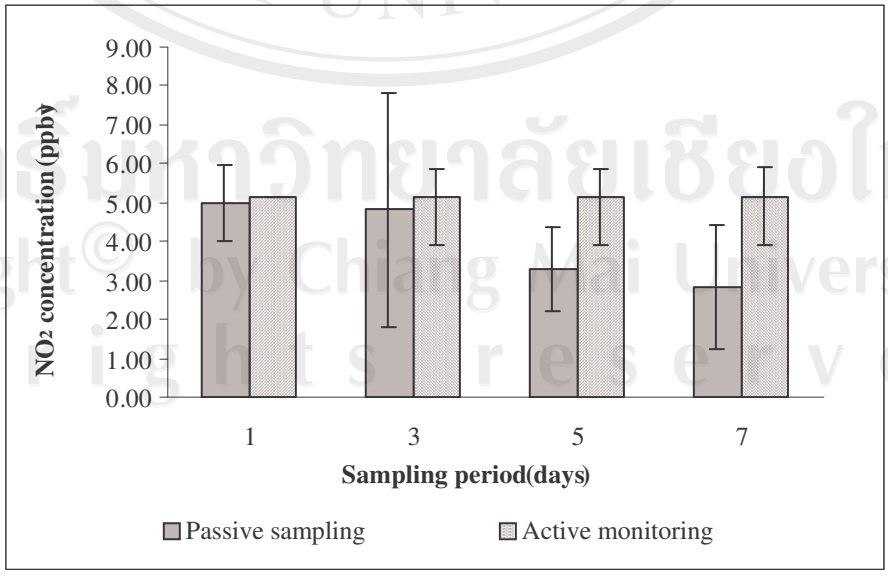


Fig 3.13 Study of sampling period for NO_2

It was found that 24 hr exposure was sufficient for measurement NO_2 in ambient air. The NO_2 concentrations from both techniques well agreed with each others. However, the absorptivity was also depended on concentration of pollutant at the sampling site. For longer exposure (≥ 3 days), results obtained from passive sampling showed lower concentration of NO_2 in comparison to active monitoring.

This result is well-agreed with the finding of Krochmal and Kanila (1997). They reported that light and temperature were found to be major factor for stability of the NO_2-TEA adduct during storage. Santis *et al* (2001) reported that it is important to note that 2-week exposure is much lower than the corresponding result divided from two week subsequent week because photodegradation may be occurred taking the temperature increasing. NO_2-TEA could be loss when leave for a long time.

3.3.7 Correlation of NO_2 concentration determined by passive and active sampling

NO_2 concentrations obtained from passive samplers determined by IC and spectrophotometry were compared with those of automatic active monitoring (chemiluminescence) by using the data from the same day. The correlation is shown in Fig.3.14 and 3.15.

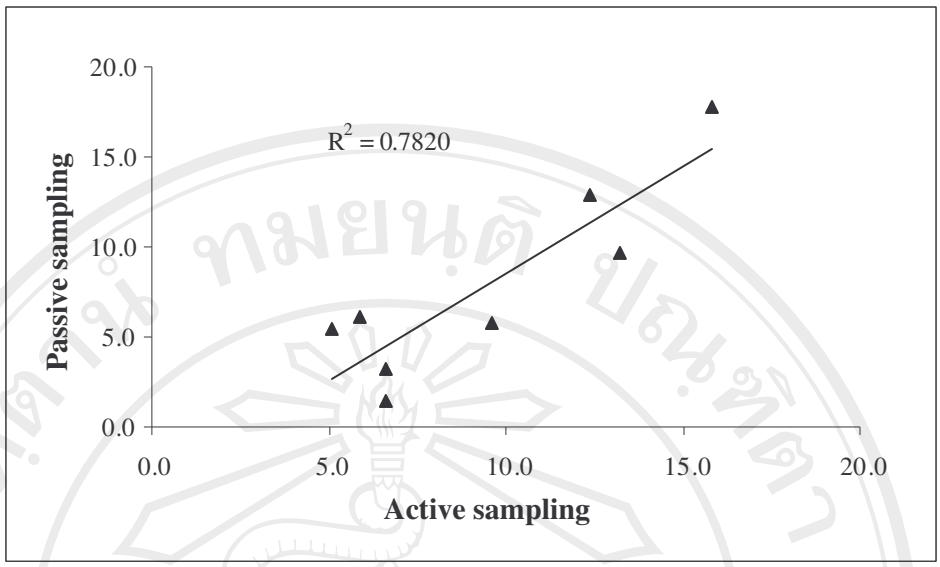


Fig 3.14 Correlation of NO_2 concentration obtained from passive sampling (ion chromatography) and active monitoring

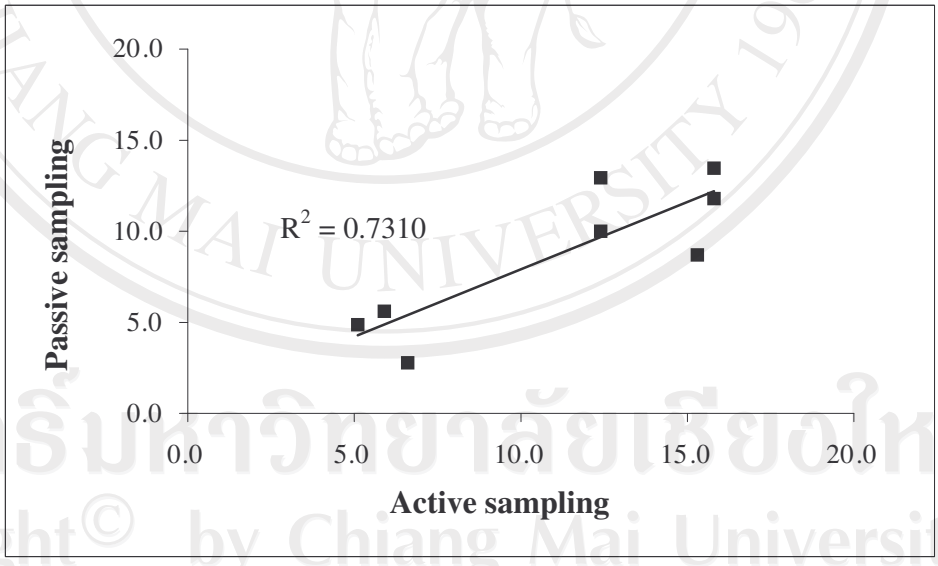


Fig 3.15 Correlation of NO_2 concentration obtained from passive sampling (spectrophotometry) and active monitoring

NO_2 concentrations from passive sampling and IC determination were relative good correlated with those from active monitoring (r^2=0.7820), while the correlation was less in spectrophotometry (r^2=0.7310).

3.4 Determination of sulfur dioxide (SO_2)

3.4.1 SO_2 determination by ion chromatography

A. Calibration curve

SO_2 collected in diffusion tube was presented in form of SO_4^{2-}. The SO_4^{2-} was determined by IC by using the regression equation of the calibration curve prepared from the standard SO_4^{2-} solution as shown in Fig 3.16.

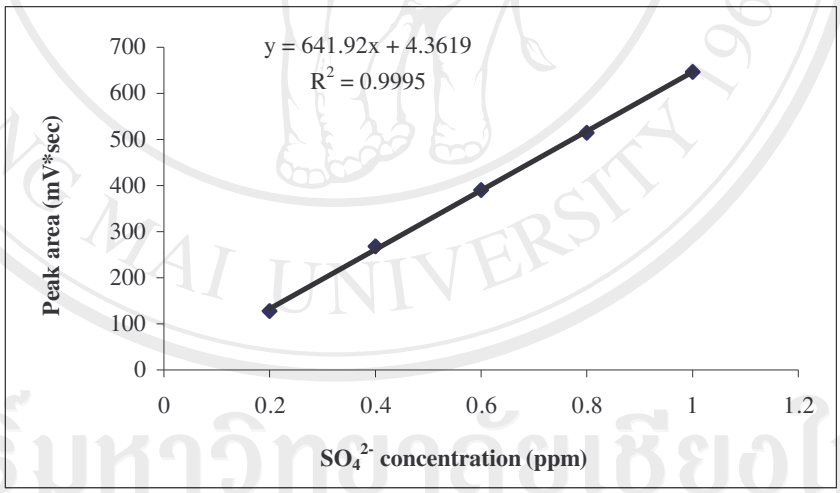


Fig 3.16 Calibration curve of standard SO_4^{2-} solution

B. Selection of absorbing solution for SO_2

Four types of absorbing solution have been tested to compare their efficiencies of SO_2 absorption. There were (1) 20% TEA, (2) 12% TEA / 4% glycerin, (3) 2M Na_2CO_3 and (4) methanolic NaOH. The diffusion tubes with these different absorbing solutions were exposed for a week in the lab. There was 5 replicates and another 3 blanks for each condition. The amount of SO_2 in form of SO_4^{2-} after 1 week indoor exposure was determined by IC as shown in Fig 3.17.

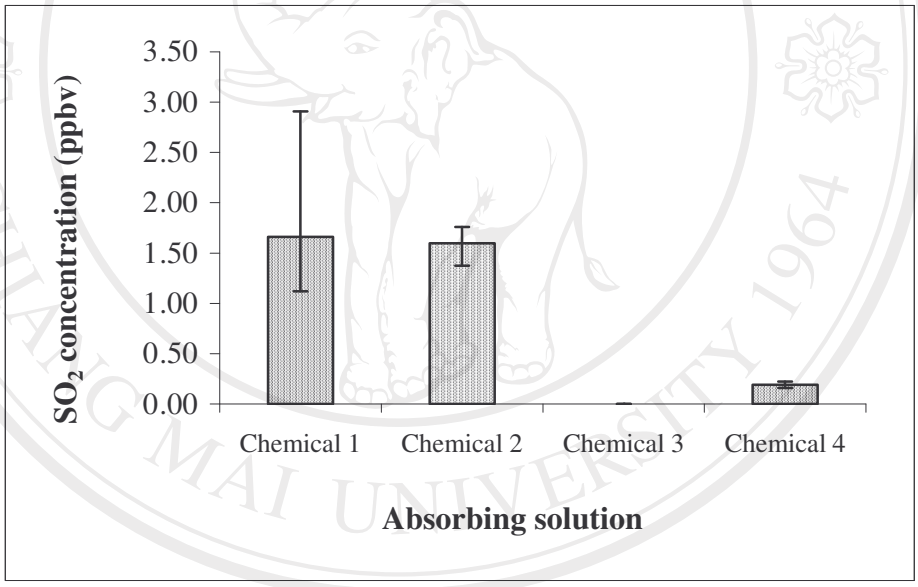


Fig 3.17 Absorbing efficiency comparison of SO_2

Chemical 1; 20% TEA

Chemical 2; 12% TEA / 4% glycerin

Chemical 3; 2M Na_2CO_3

Chemical 4; methanolic NaOH

It was found that chemical 1 (20% TEA) absorbing solution had no significantly different ($p \leq 0.01$) with chemical 2 (a mix of 12% TEA/ 4% glycerin) absorbing solution but higher variation. The SO_2 concentrations obtained from both TEA solutions were higher than methanolic NaOH and Na_2CO_3. Moreover, Na_2CO_3 solution had no ability to absorb SO_2 in the air. Although, previous work (Mulik, 1991) reported that this solution can absorb SO_2. It may be due to the helping of viscous properties of glycerin added in the Na_2CO_3 solution. One more important point was that both of Na_2CO_3 and methanolic NaOH caused problem of analysis in ion chromatographic system as the same case of NO_2 determination. Therefore, the appropriate absorbing solution for SO_2 is 4% glycerin in 12% TEA solution.

B.1 The reaction of SO_2 and absorbing solution

TEA is a compound widely used for trapping NO_2 and SO_2 due to it's highly collection efficiency (Sickles *et al*., 1990).

Krochmal and Kalina (1997) report that, Both sulfite (SO_3^{2-}) and SO_4^{2-} are formed when TEA absorbing is used. However, long period of exposure of passive samplers and small volume of absorbing solution required lead to oxidation of SO_3^{2-} to SO_4^{2-} during sampling and storage of samplers.

Ion chromatography has sufficient limit of determination of SO_4^{2-}, similar to that of NO_2^- determination, and the peak of SO_4^{2-} is well separated.

SO_2 dissolved in basic solution NaOH or KOH to form SO_3^{2-} and were then convert to SO_4^{2-} form.

The atmospheric reactions of SO_2 are very complex. It can react with the hydroxyl radical to form an HSO_3 radical, which can react with another hydroxyl radical to form water and SO_3^{2-} or H_2SO_4.

$$SO_2 + OH^{\bullet} \longrightarrow HSO_3^{\bullet}$$

$$HSO_3^{\bullet} + OH^{\bullet} \longrightarrow SO_3^{2-} + H_2O \text{ or } H_2SO_4$$

or $$H_2SO_4 + NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

or $$2KOH\,(aq) + H_2SO_3\,(aq) \rightleftharpoons K_2SO_3\,(aq) + 2H_2O$$

$$SO_3^{2-} + H_2O \longrightarrow H_2SO_4$$

C. Sampling period for determination of SO_2 by ion chromatography

The passive samplers were exposed at Chaing Mai Governmental Office Center (site A) for 1, 3, 5 and 7 days. Then SO_2 concentrations were determined by IC. The amount of SO_2 is the median value of 5 replicates subtracted with blank value. Their concentration were compared with the values obtained from PCD monitoring station (24 hr average) in the same of time using max and min values to illustrate error bar as shown in Fig 3.18.

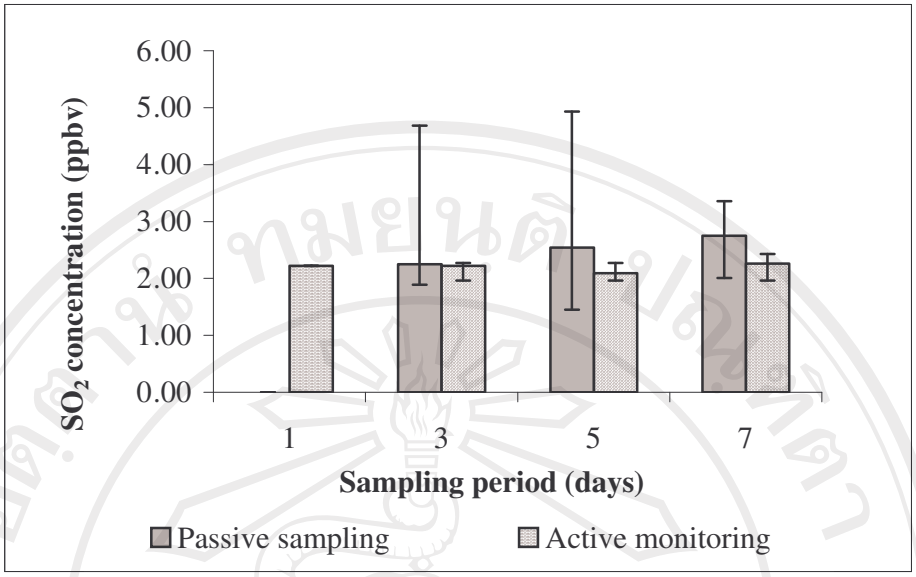


Fig 3.18 Study of sampling period for SO_2 by ion chromatography

Using passive sampler, SO_2 was not detected in 24 hr sampling period. The measurement showed the increasing amount of SO_2 with the sampling period. The results agreed with Kabindra (2004). He reported that 4 weeks exposure gave overestimate SO_2 higher than 2 weeks exposure. The overestimation of SO_2 measurements can be caused by interferences from wall deposition of SO_4^{2-} aerosols (Kasper-Giebl and Puxbau, 1999). In this study, the diffusion tubes were fixed inside the boxes to avoid interferences. Dust particles were still deposited on wall of the tubes. These dusts might contain SO_4^{2-} ion leading to overestimation of SO_2 concentrations as far as expose for long time. The porous membrane at the open end of the tube is necessary to avoid the interference from SO_4^{2-} aerosol. These membranes can also help minimize the effect from wind driven mixing of air at the mount of tube (Campbell *et al.*, 1994). Tube with two caps might also be helpful so that the cap with sampling

medium and the tube parts could be disassembled. The body of the tube can then be cleaned to avoid the SO_4^{2-} aerosol deposition on the inner surface of the tube before extraction (Plaisance *et al*., 2002). The passive samplers used in this study do not have porous membrane and the wall of tube cannot be cleaned because they have only one cap. These might lead to SO_2 overestimation.

3.4.2 SO_2 determination by spectrophotometry

A. Calibration curve

The tetrachloromercurate solution collected SO_2 in from of SO_3^{2-}, which was determined using the regression equation of calibration curve prepared from the SO_3^{2-} standard solution as shown in Fig 3.19.

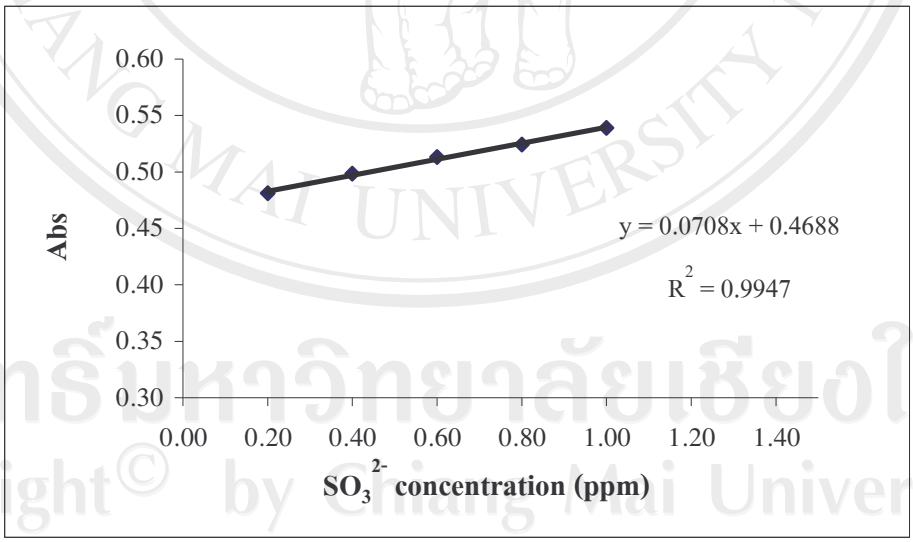


Fig 3.19 Calibration curve of standard SO_3^{2-} solution

SO_2 present in the ambient air reacts with tetrachloromercurate (TCM; $HgCl_4$) and then form a stable complex, dichlo-sulfito mercurate (DSM),

which is subsequently reacted with acid bleached pararosaniline dye and formaldehyde (HCHO) to develop an intensely color pararosaniline methyl sufonic acid (West and Gaeke, 1956) as shown in Fig 3.20; the intensity color is measured spectrometrically at 550 nm, with in the Beer's law application range.

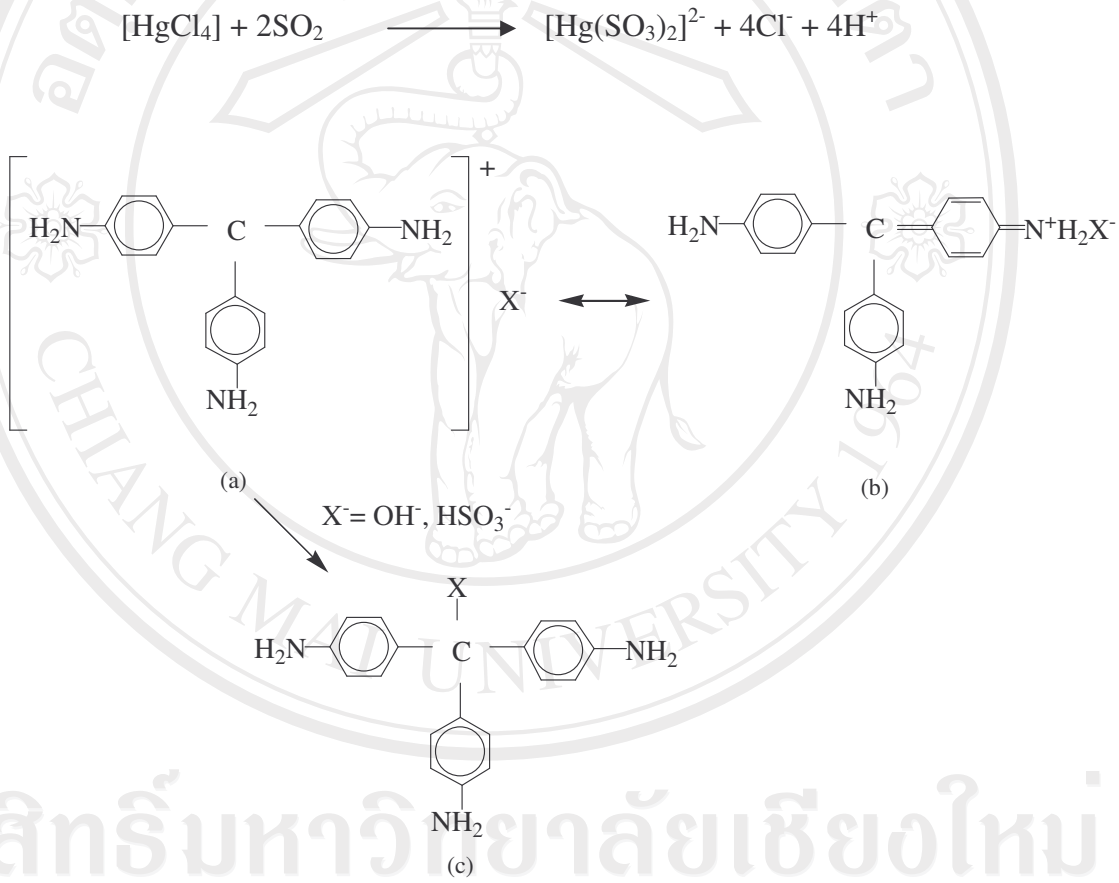


Fig 3.20 Structure of pararosaniline and related compounds (Purnendu, K *et al*., 1980)

TCM was only used for trapping SO_2 in the case of determination by spectrophometric system because TCM form a stable complex with SO_2 in forms of SO_3^{2-}, which can completely develop color solution with reagent.

Among the various manuals monitoring system, the pararosaniline dye-based colorimetric method has been adopted as a reference technique by the US-EPA and certain European countries for calibration of continuous recorders, and is also widely used in developing countries for the determination of SO_2 in ambient air. Goyal (2001) reported that the pararosaniline method shows high collection efficiency, acceptable sensitivity and can be used for long sampling duration. It is economical compared to automatic analysis.

B. Detection limit of spectrophotometry

The detection limit was obtained by the use of linearity curve of different SO_2 concentrations as shown in Fig 3.28 with very good correlation (r^2=0.9947). The detection limit was calculated with the help of equation 2.2 (see Appendix B). The detection limit of spectrophotometry for SO_2 was 0.367 ppm.

C. Testing of absorbing solution volume and sampling period for determination of SO_2 by spectrophotometry

After TCM was selected as the absorbing solution for SO_2, its volume was varied in order to gain optimum absorption. The experiment was set based on two purposed including testing of TCM volume and sampling period. 50µl and 2 ml of 4 M TCM were used and applied at PCD monitoring station (Yupparaj Wittayalai School) for 1,3 and 5 days. 50µl TCM was used to impregnate the sorbent, while 2 ml TCM was used as the absorbing solution without sorbent as a medium. The data obtained was compared with the day average values obtained from PCD automatic UV-fluorescence. The result is shown in Fig 3.21.

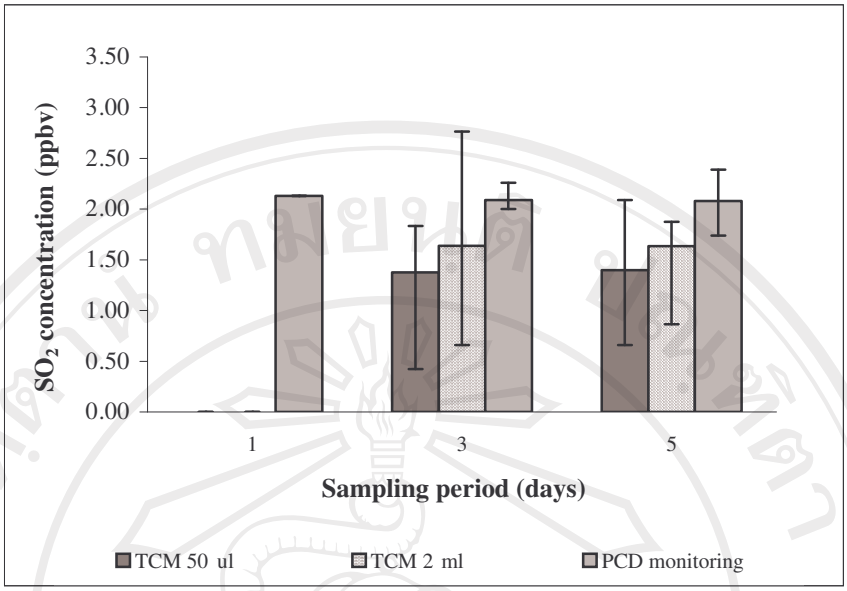


Fig 3.21 Testing of absorbing solution volume and sampling period for determination of SO_2 by spectrophotometry

The result showed that using of 2 ml and 50 µl of 4 M TCM impregnated onto the sorbent gave no different of SO_2 concentration ($p \leq 0.01$). However, SO_2 trapped by TCM was lower than active monitoring. One day exposure was not sufficient for determination of SO_2 in ambient air by passive sampler. Using of TCM in passive sampler gave approximately 30% SO_2 concentration lower than data obtained from automatic active technique in both 3 and 5 days sampling period.

Kass and Ivaska (2001) reported that the reaction between pararosaniline and sulfite is rather slow. When low concentration of SO_2 was determined the sensitivity of Schiff reaction (pararosaniline reaction) should be increase. This can be done by having separated reagent components and a different addition sequence.

Nevertheless, Krochmal and Kalina (1997) preliminary studies has been checked that the widespread spectrophotometric West-Gaeke method (pararosaniline

method) of determination of SO_2 can not be successfully applied for analysis of passive samplers due to oxidation of sulfites.

3.4.3 Extraction process of SO_2

The final products of absorbing solution reacted with SO_2 were in form of both SO_4^{2-} and SO_3^{2-}. Extraction conditions for SO_4^{2-} including time consuming and technique (with and without using ultrasonication) have been optimized by spiking SO_4^{2-} standard solutions onto the sorbent (Whatman GF/A), which was placed in diffusion tube. According to both of SO_4^{2-} and SO_3^{2-} can be dissolved in water, 4 ml of milli-Q water was then added. After extraction, SO_4^{2-} was determined by IC under optimum conditions.

Extraction conditions for SO_3^{2-} have also been optimized as the same way as SO_4^{2-} extraction by spiking SO_3^{2-} standard solution onto the sorbent. SO_3^{2-} was measured by spectrophotometry after reacted with pararosaniline reagent at the appropriate conditions described in section 2.4.6 and the results were shown in Fig 3.22 and 3.23.

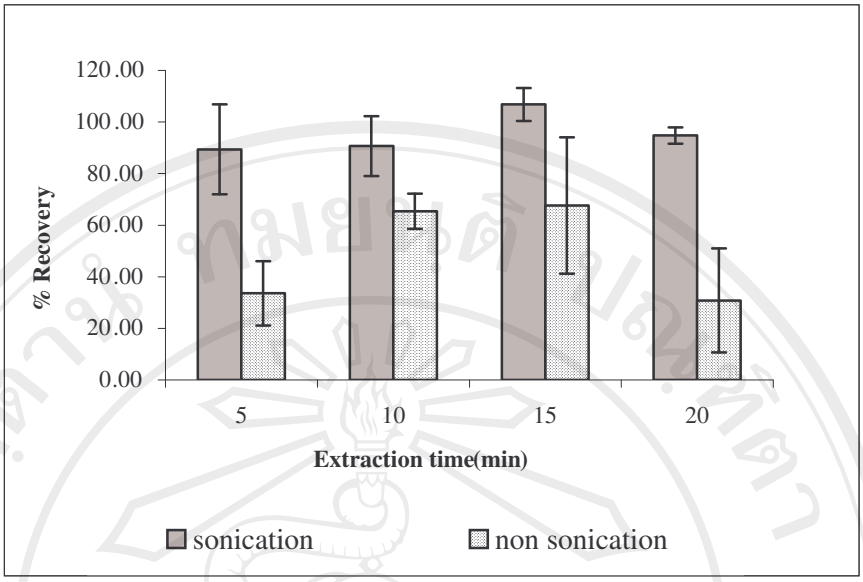


Fig 3.22 Percent recovery of SO_4^{2-} extraction

The recoveries of SO_4^{2-} from extraction with helping of ultrasonicator for 5, 10, 15 and 20 min were 89.4, 90.7, 106.8 and 94.8 %, respectively, whereas those of non using ultrasonicator were 33.6, 65.4, 67.6 and 30.8 %, respectively.

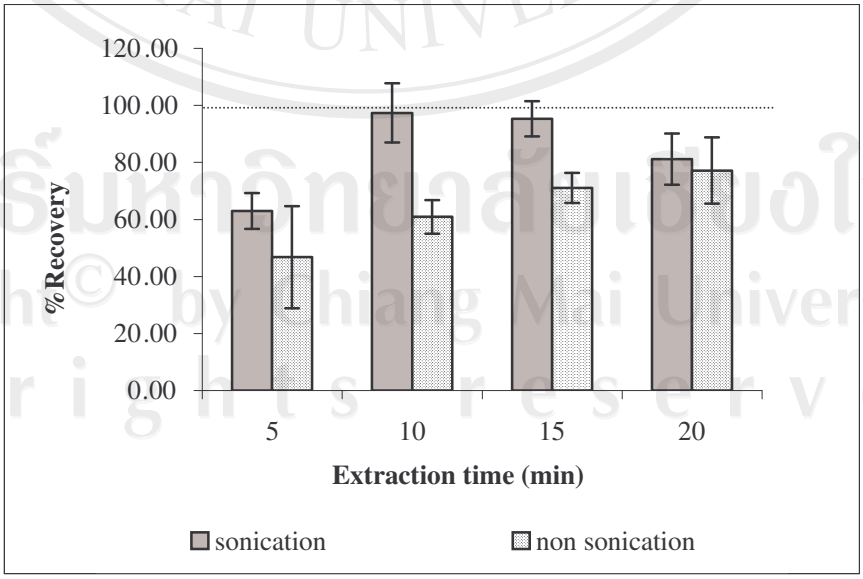


Fig 3.23 Percent recovery of SO_3^{2-} extraction

The recoveries of SO_3^{2-} from extraction with helping of ultrasonicator for 5, 10, 15 and 20 min were 63.0, 97.3, 95.3 and 81.2 %, respectively, while those of non using ultrasonicator were 46.8, 60.9, 71.1 and 77.1 %, respectively.

Extraction with helping of ultrasonicator gave higher recovery than non using ultrasonicator. The extraction time of both methods was varied from 5-20 min. it was found that extraction by 15 and 10 min with sonication was the appropriate extraction condition for SO_4^{2-} and SO_3^{2-}, respectively.

3.4.4 Correlation of SO_2 determination by passive and active samplings

The correlation curve was plotted between SO_2 concentrations obtained from passive samplers determined by IC and spectrophotometry and those of automatic active monitoring by using the data from the same day. The correlations are shown in Fig.3.24 and 3.25.

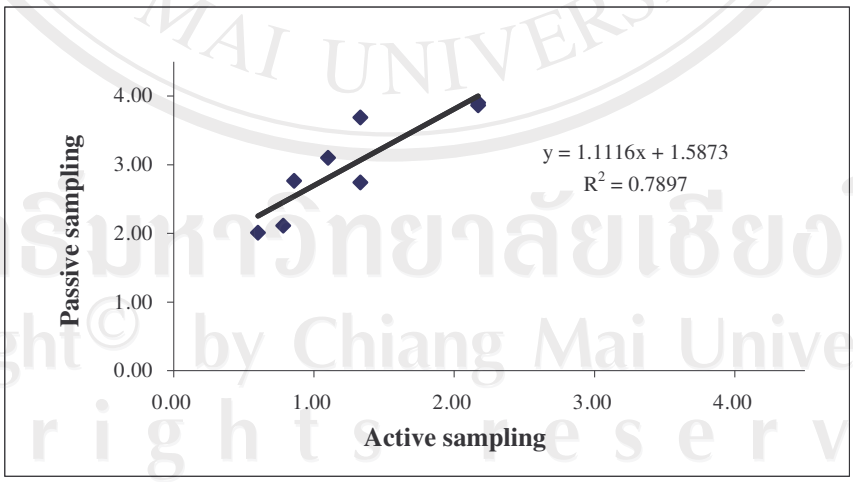


Fig 3.24 Correlation of SO_2 obtained from passive sampling (determined by IC) and active monitoring

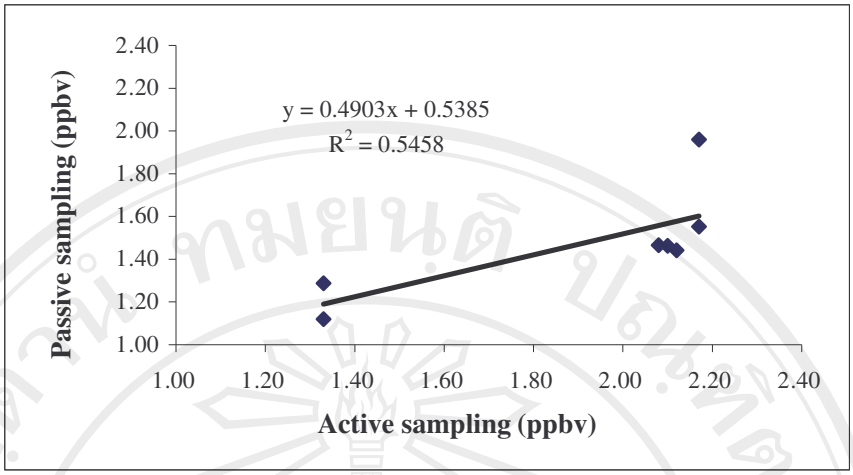


Fig 3.25 Correlation of SO_2 determination by spectrophtometry from passive sampling and active monitoring

SO_2 concentrations from passive sampling were correlated with those from active monitoring. However, the correlation of SO_2 concentrations in passive samplers determined by IC was more correlated with active monitoring than SO_2 in passive samplers determined by spectrophotomertry.

3.5 Effect of glycerin for determination of NO_2 and SO_2

Absorbing solutions were prepared in various conditions by adding glycerin varying from 2 to 10% and compared with non adding one. The 50 µl of each of the 2, 4, 6, 8 and 10% glycerin in 20% TEA solution were impregnated onto the glass fiber filter placed in the polyethylene tubes. Each condition consisted of 3 blanks and 5 collecting samplers.

All of passive samplers were exposed for 1 week at PCD monitoring site (Chiang Mai Governmental Office Center). NO_2 and SO_2 were extracted and then subsequently determined by IC.

The results of glycerin volume and amount of detected NO_2 and SO_2 are shown in Fig 3.26 and 3.27. The concentrations of each gas was the median value of 5 replicates. It was found that the concentrations of both NO_2 and SO_2 obtained from various ratio of glycerin were only slightly different. It indicated that the increasing amount of glycerin mixed with absorbing solution did not have an effect to the amount of gases trapped. The *t*-test showed no significantly different ($p \leq 0.01$).

Ferm (1991) reported that, the use of glycerin further improves the collection efficiency at low humidity and stability. His report agreed with Helaleh (2002), who suggested that ethylene glycol was used as a hygroscopic compound to keep the trapping reagent at constant humidity.

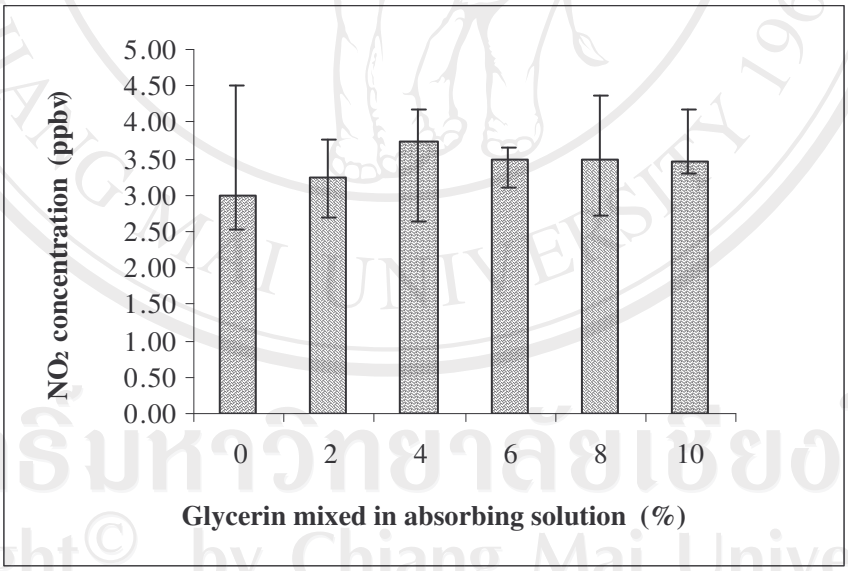


Fig 3.26 Effect of glycerin for determination of NO_2

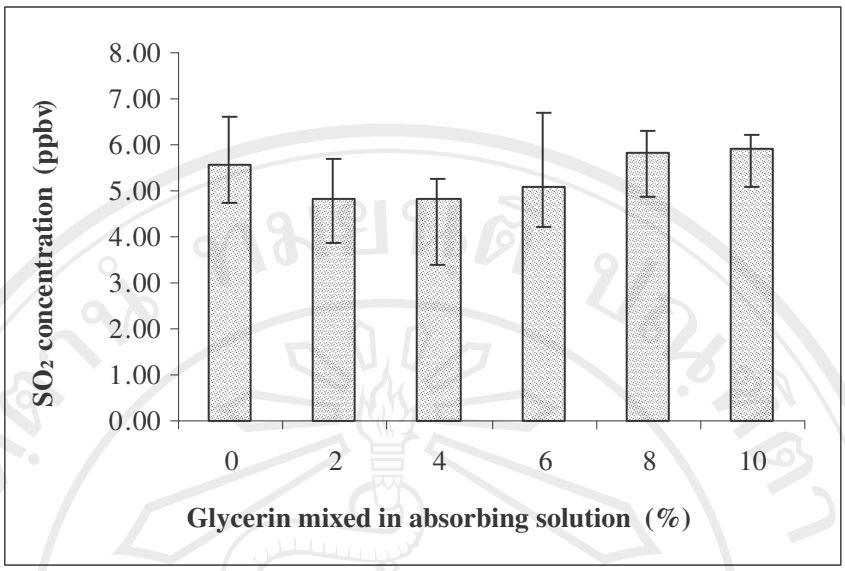


Fig 3.27 Effect of glycerin for determination of SO_2

3.6 Determination of ozone (O_3)

3.6.1 Calibration of ozone

A. Determination of ozone by ion chromatography

Ozone was collected by using $NaNO_2$ solution or a mix of $NaNO_2$/ Na_2CO_3/ ethylene glycol as absorbing solution. It was presented in form of NO_3^- and determined by using the regression equation of the calibration curve prepared from the NO_3^- standard solution as shown in fig 3.28.

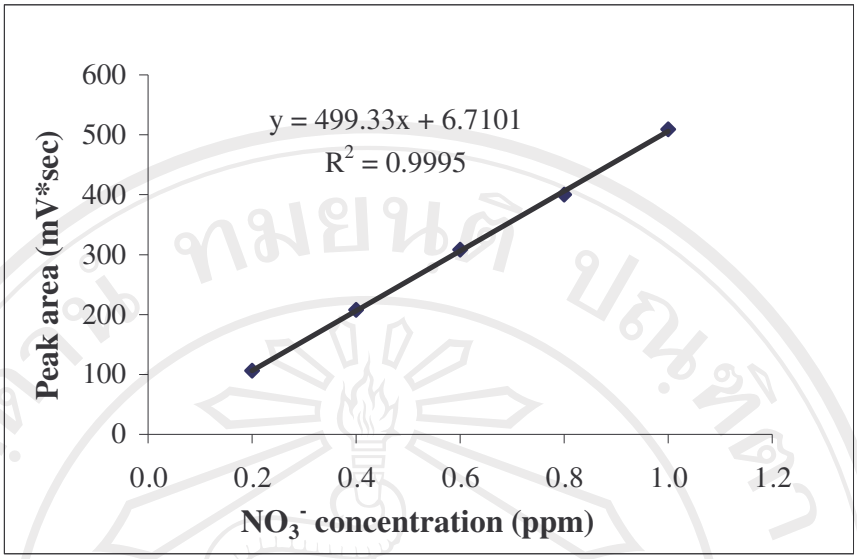


Fig 3.28 Calibration curve of standard NO_3^- solution

B. Determination of ozone by spectrophometry

Ozone was collected by using DPE as absorbing solution. It was presented in form of pyridine 4-aldehyde, which reacted with 3-MBTH to form the yellow azine (pyridine-4-aldehyde-3-methyl-2-benzothiozolyl azine). Then the complex was determined by spectrophotometry at 432 nm. The calibration curve was prepared from the standard pyridine-4-aldehyde solution as shown in fig 3.29.

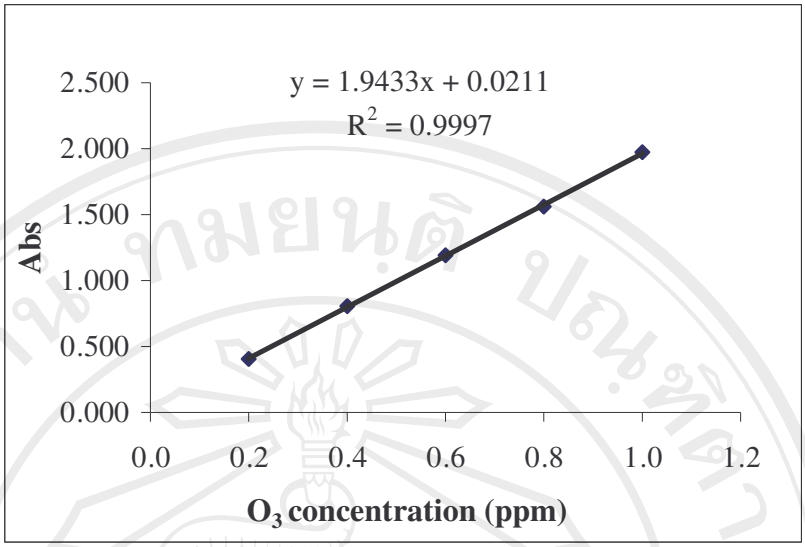


Fig 3.29 Calibration curve of standard O_3

C. Detection limit of spectrophotometry

The detection limit was obtained by the use of linearity curve of SO_2 concentrations with very good correlation (r^2=0.9997) as shown in Fig 3.29. The detection limit of spectrophotometry for ozone was 0.091 ppm by calculation using equation 2.2.

3.6.2 Selection of absorbing solution for ozone

Four absorbing solution including (1) 0.1% $NaNO_2$, (2) 0.1% $NaNO_2$/ 0.1% Na_2CO_3/ 1% ethylene glycol, (3) 0.1% DPE (1,2-di-(4-pyridyl)ethylene) in methanol and, (4) 0.5% DPE in glacial acetic acid have been tested to compare their efficiencies in ozone absorption.

The first two types of absorbing solution (1) and (2) collected O_3 in form of NO_3^- were subsequently determined by IC. Calculation of ozone concentration was done based on the following reaction (Helaleh *et al*., 2002)

$$NO_2^- + O_3 \longrightarrow NO_3^- + O_2$$

Another two absorbing solution (3) and (4), the final product was determined by spectrophometry at 432 nm. Calculation of ozone concentration was done based on the following reaction (Fig 3.30)

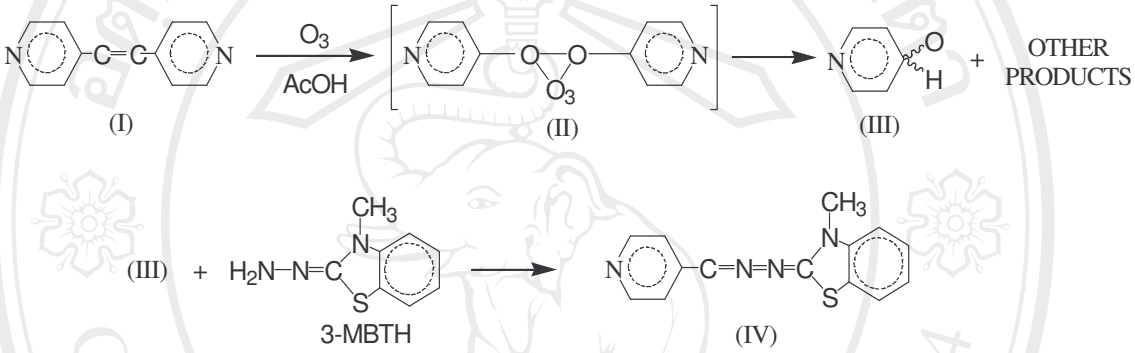


Fig 3.30 Probable reaction sequence of O_3 (Thomas and Daniel, 1966)

The probable overall reaction is depicted by the sequence given in Fig 3.39. l, 2-di-(4-pyridyl)-ethylene (I) react with O_3 in ambient air to form ozonide intermediate (II) which upon hydrolysis yields pyridine-4-aldehyde (III) , among other products. The pyridine-4-aldehyde is then reacted with 3-MBTH to form the yellow azine (IV). The stability time of forming yellow color was studied by leaving the mixtures in 3 conditions (room temperature, 30 ^oC for 1 hr, and in boiled water for 20 min). The result showed that color was completely developed at about 20 min. The absorbance (Abs) of all tested condition was not different. Therefore, 20 min at the room temperature was selected as the color developing condition as shown in Fig 3.31.

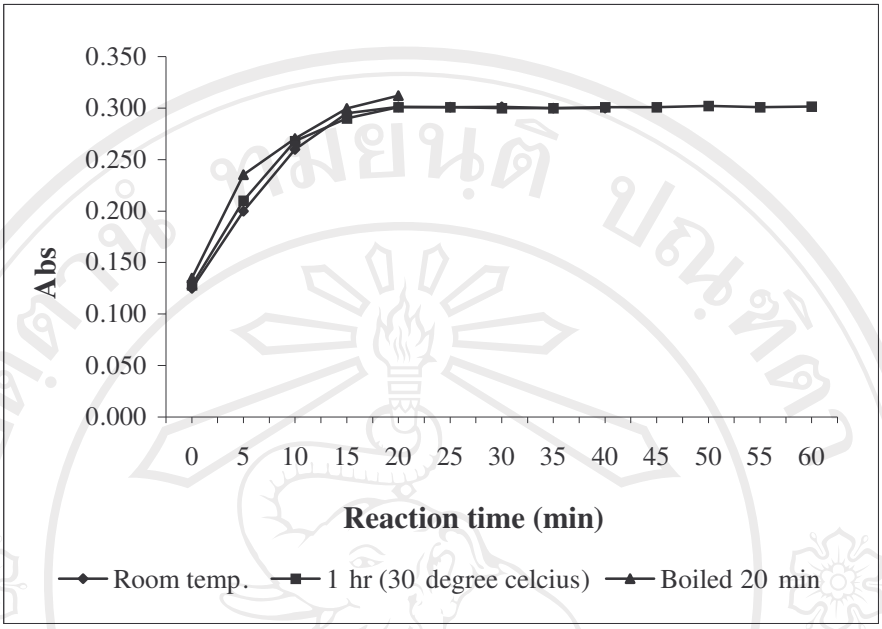


Fig 3.31 Color stability for O_3 determination

The results of ozone absorptivity from both methods are shown in Fig 3.32. It was found that all of absorbing chemicals can be applied for indoor O_3 determinations. Absorbing efficiencies obtained from solutions consisted of $NaNO_2$ (1 and 2) were not significantly different. However, they presented higher O_3 concentration than the absorbing solution consisted of DPE (3 and 4). The absorption efficiencies of both DPE solutions were not significantly different. However, DPE / glacial acetic acid (4) might not suitable because its strong smell, which annoying the surrounding environment.

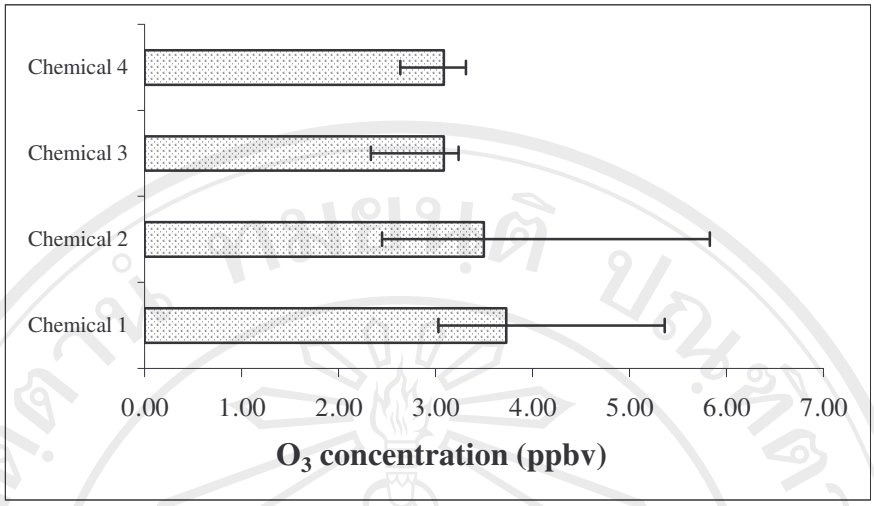


Fig 3.32 Absorbing efficiency comparison of O_3

Chemical 1; 0.1% $NaNO_2$

Chemical 2; 0.1% $NaNO_2$/ 0.1% Na_2CO_3/ 1% ethylene glycol

Chemical 3; 0.1% DPE / methanol

Chemical 4; 0.5% DPE in glacial acetic acid

Thomas and Daniel (1966) tested several solvents to dissolve DPE and methanol was one of that. They also commented that DPE dissolved in water will effect on final color development probably because of decreased collecting efficiency.

Helaleh *et al*. (2002) reported that nitrite (NO_2^-) collected at absorbent filter surface can be readily oxidized to nitrate (NO_3^-) when O_3 present in air sample. Reaction between nitrite and ozone is pH dependent with a rate constant that increases with pH. Thus, sodium carbonate was used to keep the collecting medium alkaline and to ensure that the oxidation reaction was O_3 specific. Ethylene glycol was used as a hygroscopic compound to keep the trapping reagent at constant humidity (Helaleh *et al.*, 2002). Therefore, the mix of 0.1% $NaNO_2$/ 0.1% Na_2CO_3/ ethylene glycol was

more appropriate absorbing solution than 0.1% $NaNO_2$ in case of ozone determination by IC.

3.6.3 Extraction process of ozone

The final products of O_3 reacted with absorbing solution were presented in forms of NO_3^- and pyridyl-4-aldehyde. Extraction conditions have been optimized by spiking 20 µl of 100 ppm NO_3^- standard solution onto the sorbent (Whatman GF/A) placed in diffusion tube. After that 4 ml of milli-Q water was added. The concentration of NO_3^- was determined by IC. The results of NO_3^- extraction are shown in Fig 3.33.

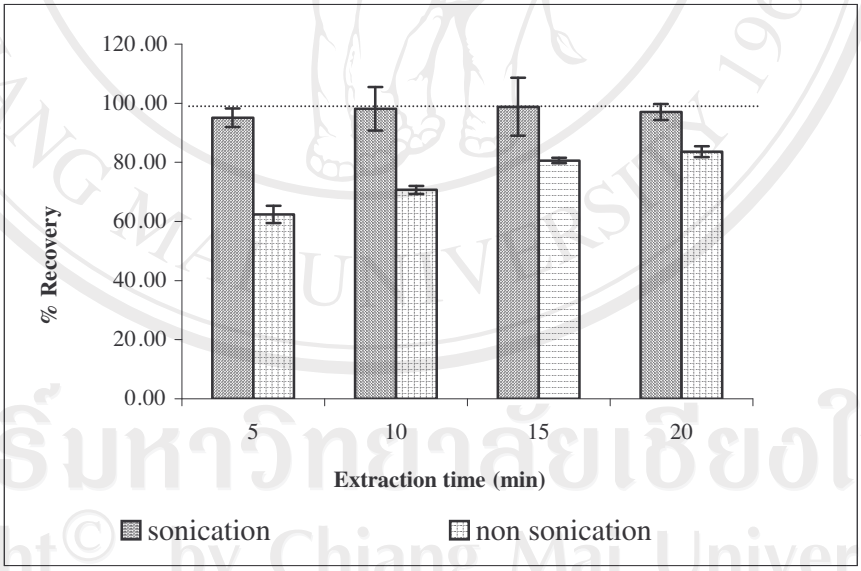


Fig 3.33 Percent recovery of NO_3^- extraction

The recoveries of NO_3^- from extraction with helping of ultrasonicator for 5, 10, 15 and 20 min were 95.1, 98.1, 98.8 and 97 %, respectively, whereas those of non using ultrasonicator were 62.4, 70.7, 80.6 and 83.6 %, respectively.

The extraction of pyridyl-4-aldehyde which is representative of O_3 when detected by spectrophotometry was done by spiking 20 µl of 100 ppm of pyridyl-4-aldehyde onto the sorbent (Whatman GF/A), which was placed in diffusion tube. After that 2 ml of milli-Q water was added. The concentration of pyridyl-4-aldehyde was determined by spectrophotometry that mentions in section 2.12.6. The results of pyridyl-4-aldehyde extraction were shown in Fig 3.34.

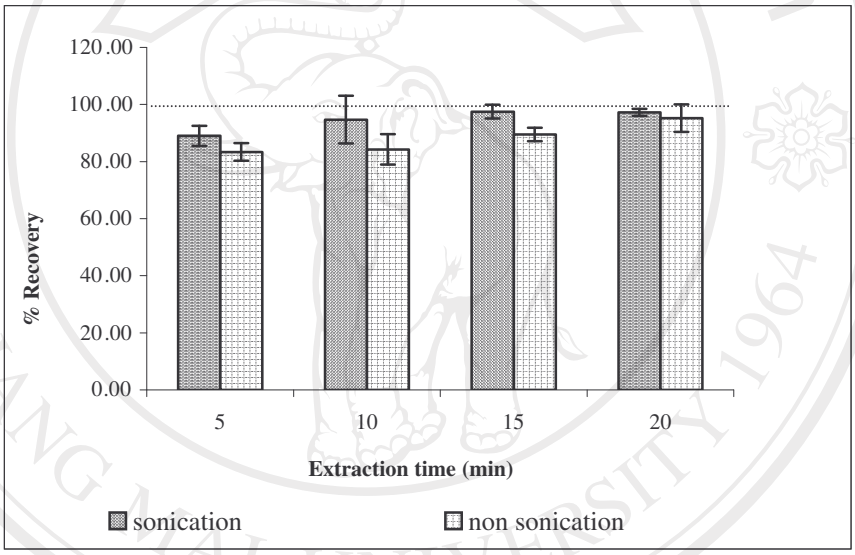


Fig 3.34 Percent recovery of pyridyl-4-aldehyde extraction

The recoveries of pyridyl-4-aldehyde from extraction with helping of ultrasonicator for 5, 10, 15 and 20 min were 89.0,94.4, 97.5 and 97.2 %, respectively, whereas those of non using ultrasonicator were 83.4, 84.3, 89.5 and 95.2 %, respectively.

Extraction with helping of ultrasonicator gave higher recovery than non using ultrasonicator. The appropriate extraction condition for pyridyl-4-aldehyde 15 min with ultrasonication.

3.6.4 Outdoor ozone measurement

After testing of O_3 absorbing solution, the mix of $NaNO_2$ / ethylene glycol / Na_2CO_3 and DPE / methanol was used for O_3 determination by IC and spectrophotometer, respectively.

At first, the absorbing solutions was impregnated onto the sorbent (Whatman GF/A) placed in PE tube. Then all passive samplers (5 collecting samplers and 3 blanks) were exposed at Chiangmai Governmental Office Center for 1 week. The results of outdoor ozone measurement are shown in Fig 3.35.

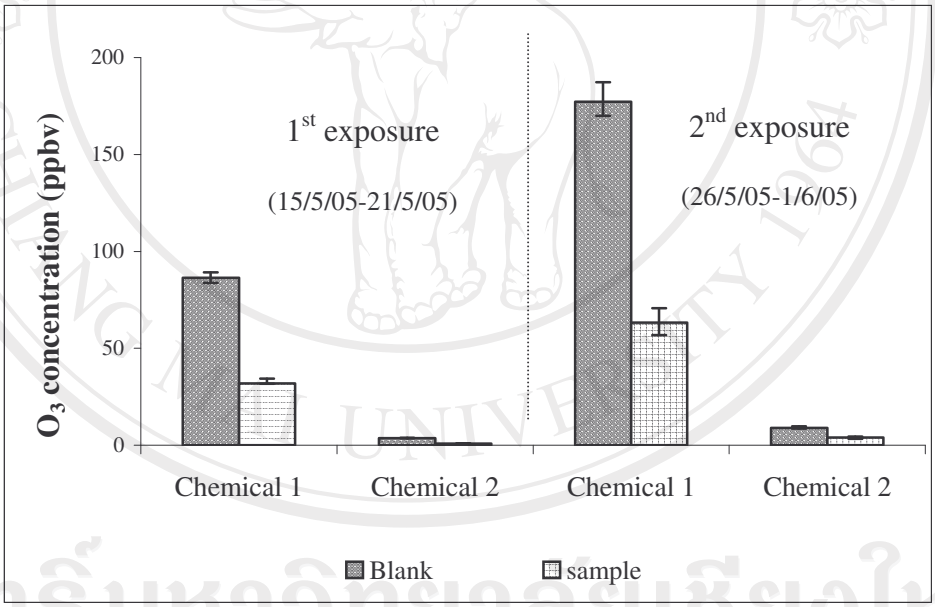


Fig 3.35 Outdoor O_3 measurement using original passive samplers

Chemical 1; $NaNO_2$ / ethylene glycol / Na_2CO_3

Chemical 2; DPE / methanol

It was found that, the O_3 concentrations in blank tubes were approximate 2 times higher than in the sampling tubes. The sunlight radiation causes increasing of temperature in the tubes and the photolysis of NO_2 on the sorbent surface or inside the tubes occurred. The equation of NO_2 photolysis is shown as follow.

$$NO_2 + \text{light } (h\nu) \longrightarrow NO + O^{\bullet}$$

$$O^{\bullet} + O_2 \longrightarrow O_3$$

To overcome this problem, the passive sampler had been developed by wrapping the diffusion tubes by aluminium foil, and the cover was changed to increase cover area and light protection. All conditions tested are shown in Table 3.7. The results of O_3 measurement are shown in Fig 3.36.

Table 3.7 Outdoor O_3 measurement conditions

Set	Absorbing chemical	Cover	Type of tube	Determination
1	$NaNO_2$ / Na_2CO_3 / ethylene glycol	original	Foil-wrapped tube	IC
2		new	Foil-wrapped tube	
3		new	No wrapping	
4	DPE / Methanol	original	Foil-wrapped tube	Spectrophotometry
5		new	Foil-wrapped tube	
6		new	No wrapping	

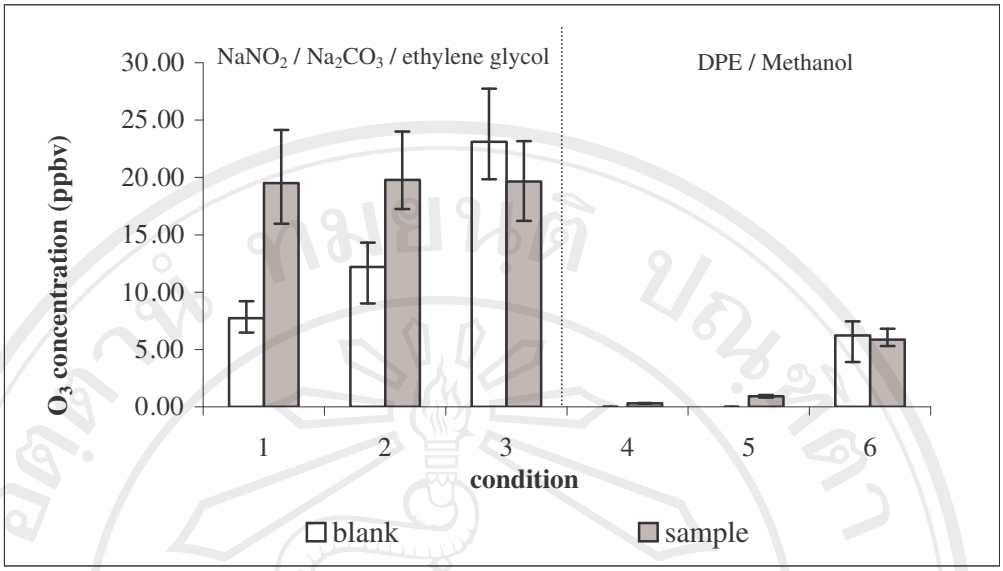


Fig 3.36 Comparison of outdoor O_3 measurement in different conditions

Fig 3.36 shows that foil-wrapped tubes (conditions 1, 2, 4 and 5) gave higher O_3 concentrations in sampling tubes than blank tubes. The DPE absorbing chemical showed very low ozone absorptivity. It should be further developed to achieve the optimum conditions by considering the outdoor parameters that affect the absorptivity. The DPE solution can stabilize ozonide or final product (pyridine-4-aldehyde), because ozone reacts vigorously with alkenes to form unstable compounds (initial ozonides) which rearrange spontaneous (and often noisily) to form compounds known as ozonide. The ozonide, themselves are very unstable compounds and low molecular weight. It often explode violently (Solomons, 1997).

3.6.5 Optimization of absorbing solution for determination of ozone by spectrophotometry

In previous study, Thomas and Daniel (1996) used DPE solution to measure ozone in ambient air using active method. 50 μl DPE solution is very small volume that might be lost during exposure. Reducing the sampling period might be overcome this problem as had been studied by Hangartner (1990). Ozone was collected in the diffusion sampler for 8 hour exposure, however, it was not succeed if the measured value is below 108 $\mu g/m^3$.

In order to trap ozone in ambient air, passive sampler was modified by wrapping tube with aluminium foil. The absorbing chemical for O_3 determination by spectophotometry was also optimized. All passive samplers were exposed at the PCD monitoring site (Yupparaj Wittayalai School) for 24 hr on 22/9/05 and 4/10/05.

The passive samplers were divided into 2 sets. Each set consisted of 3 blanks and 5 collecting samples. The results from both conditions were compared with PCD data as shown in Fig 3.37.

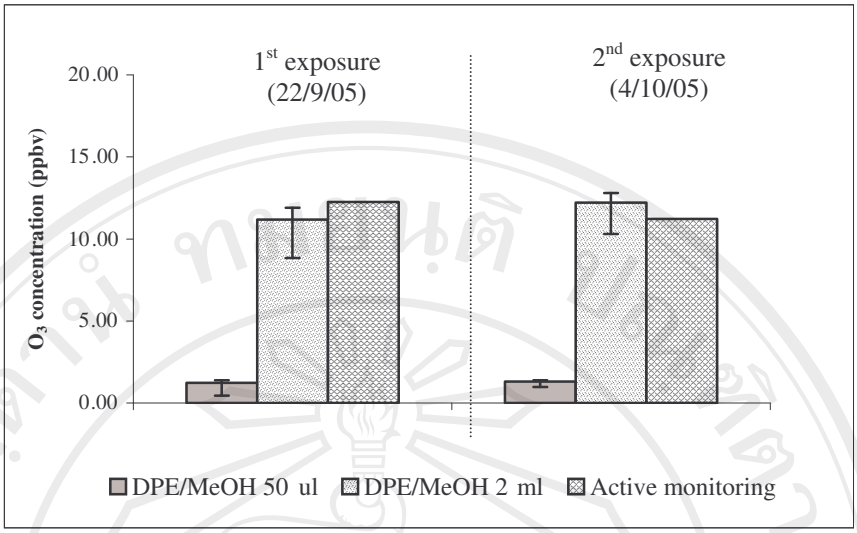


Fig 3.37 Optimization of absorbing solution for determination of O_3 by spectrophotometry

From Fig.3.37 the amount of ozone was obtained from 24 hrs exposure. It was found that 2 times testing of ozone measurement by using 2 ml of DPE / MeOH as absorbing solution gave the ozone concentration very close to data obtained from active monitoring.

3.6.6 Study of sampling period of ozone measurement

Ozone was measured by using the modified passive sampler (foil-wrapped tube) in different sampling periods for O_3 collected. All passive samplers were exposed on 4/10/05 at the PCD monitoring site (Yupparaj Wittayalai School) for 8 and 24 hr.

The passive samplers were divided into 3 sets. Each set consisted of 3 blanks and 5 collecting samples.

In the first set, 50 µl of a mix of $NaNO_2$, Na_2CO_3 and ethylene glycol was used as the absorbing solution. O_3 was extracted and determined by IC.

In the second and the third set, 50 µl and 2 ml of DPE / MeOH was used as the absorbing solution, respectively. O_3 was extracted and determined by spectrophotometry. The results from all conditions were compared with PCD data as shown in fig 3.38.

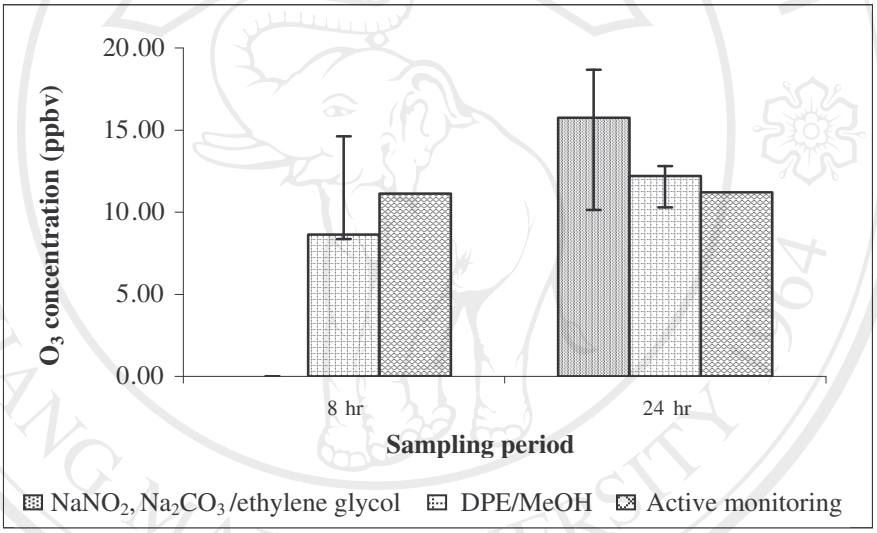


Fig 3.38 Sampling period of ozone measurement

The exposure period of ozone, 8 hr and 24 hr, was compared by using the selected absorbing chemicals and passive sampler. Fig 3.38 shows that ozone was not collected by a mix of $NaNO_2$, Na_2CO_3 and ethylene glycol cannot collect O_3 at 8 hr unlike in 24 hr exposure. On the other hand, the 2 ml of DPE / MeOH could collect O_3 in both sampling periods. However, 24 hr exposure presented close ozone amounts among them.

3.6.7 Correlation of O_3 determination by passive sampling and active monitoring

The correlation curve was plotted between O_3 concentration data obtained from passive samplers determined by IC and spectrophotometry and those of automatic active monitoring by using the data from the same day. The correlation is shown in Fig.3.39 and 3.40.

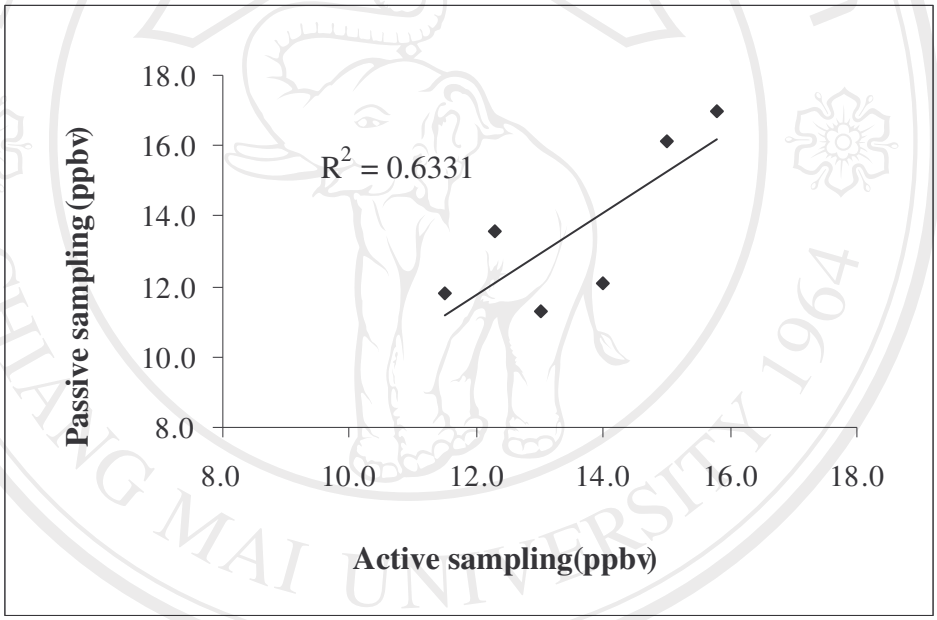


Fig 3.39 Correlation of O_3 concentration obtained from passive sampling (determined by IC) and active monitoring

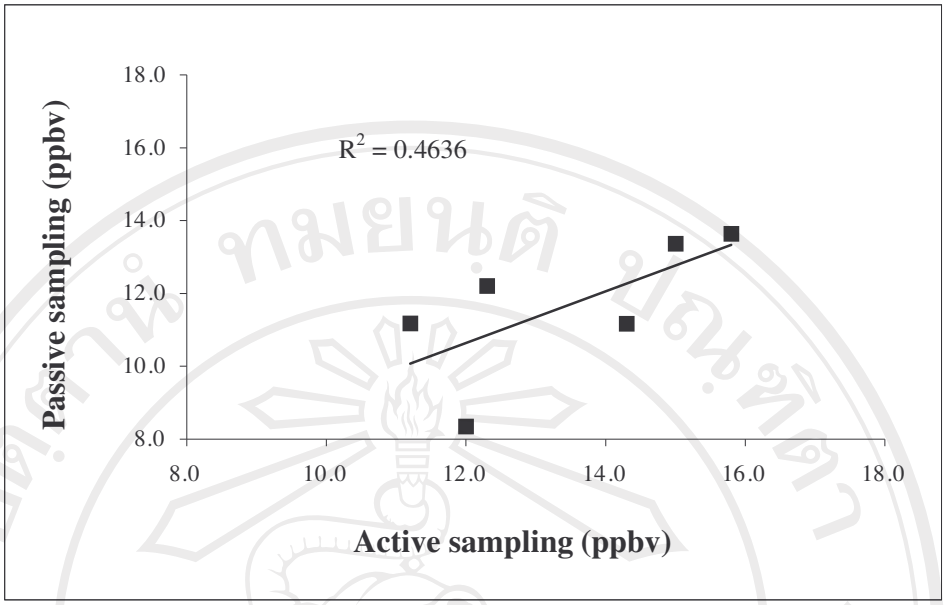


Fig 3.40 Correlation of O_3 concentration obtained from passive sampling (determined by spectrophotometry) and active monitoring

O_3 concentration determination by IC from passive sampling were correlated with those from active monitoring (r^2 = 0.6331) and more correlated than those determined by spectrophotomertry (r^2 = 0.4636).

3.7 The application of passive samplers for determination of NO_2, SO_2 and O_3

The optimum passive samplers (Table 3.8) were applied for determination of NO_2, SO_2 and O_3 at 3 sampling sites for 2 times. The results are shown in Fig 3.41-3.46. The passive sample consists of the PE tube and Glass fiber filter (GF/A) were used for setting up a passive sampler. Each set consisted of 3 blanks and 5 collecting samples.

Table 3.8 The conditions of passive samplers for determination of NO_2, SO_2 and O_3

Pollutant gas	Absorbing solution	Sampling period (days)	Analysis method
NO_2	50 µl of 12% TEA/ 4% glycerin	1	IC
			Spectrophotometry
SO_2	50 µl of 12% TEA/ 4% glycerin	3	IC
	2 ml of 4M TCM	3	Spectrophotometry
O_3	50 µl of 0.1% $NaNO_2$/ 0.1% Na_2CO_3/ ethylene glycol	1	IC
	2 ml of 0.1% DPE / methanol	1	Spectrophotometry

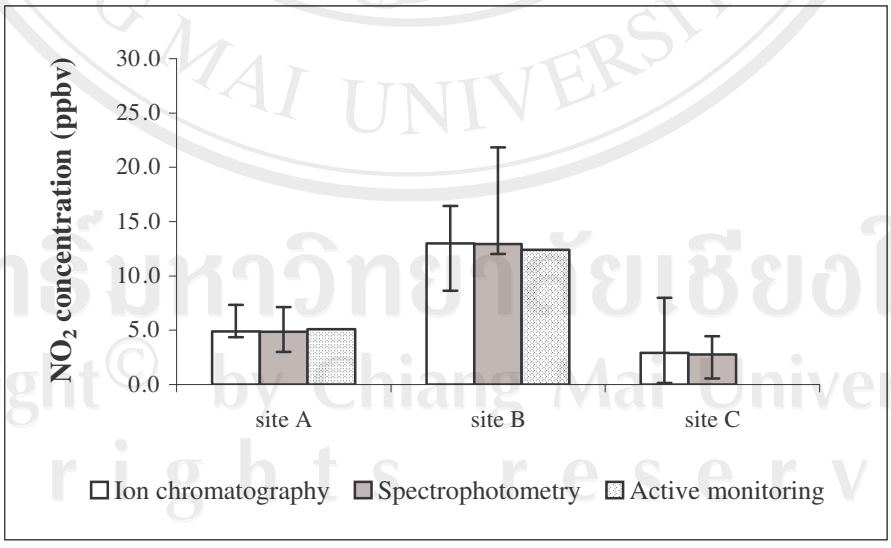


Fig 3.41 Median NO_2 concentrations (24 hr) on 11/10/05

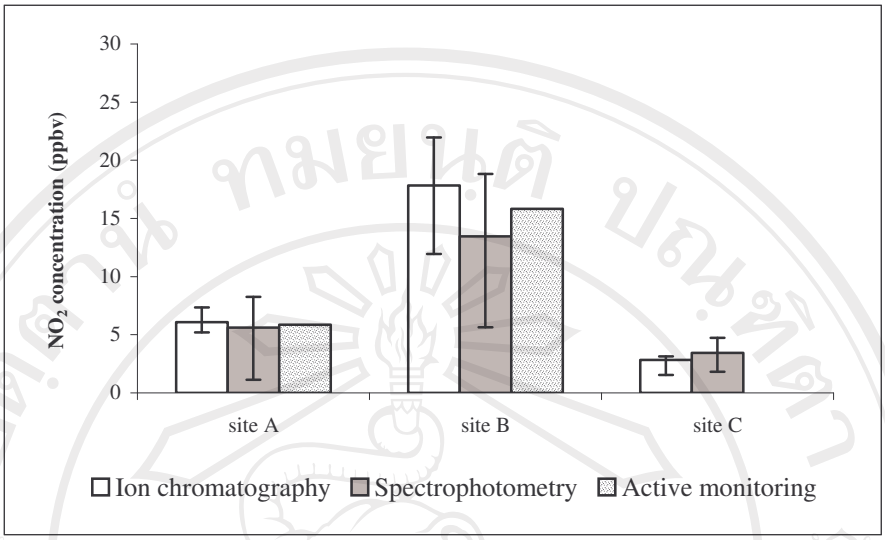


Fig 3.42 Median NO_2 concentrations (24 hr) on 12/10/05

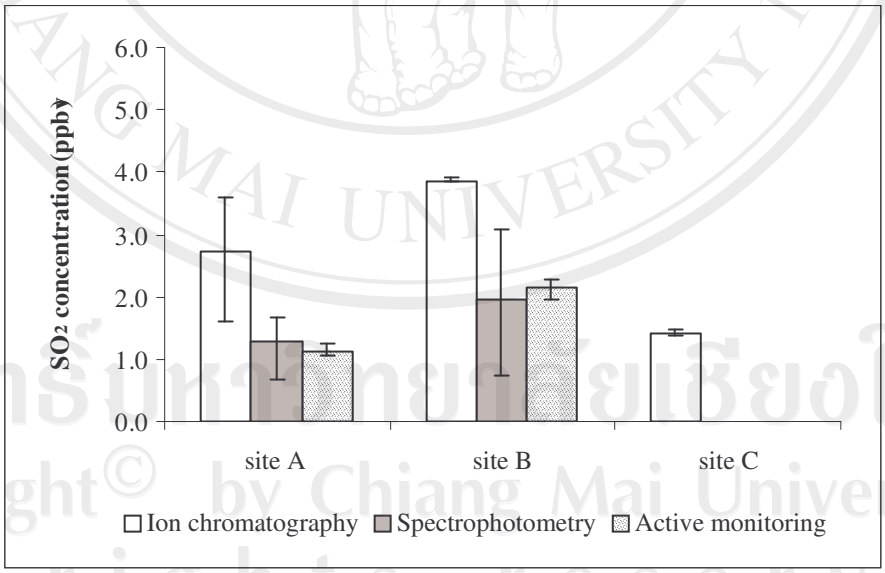


Fig 3.43 Median SO_2 concentrations (3 days) on 11/10/05-13/10/05

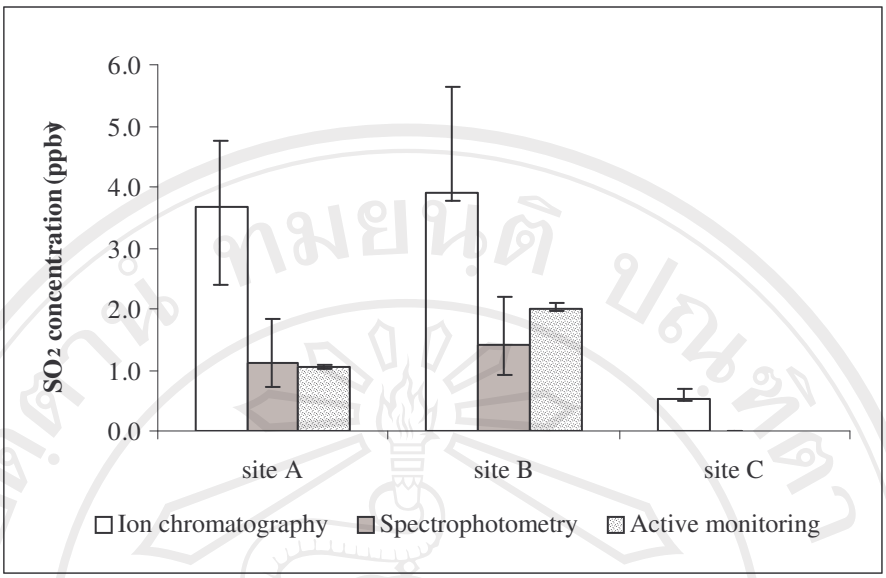


Fig 3.44 Median SO_2 concentrations (3 days) on 13/10/05-15/10/05

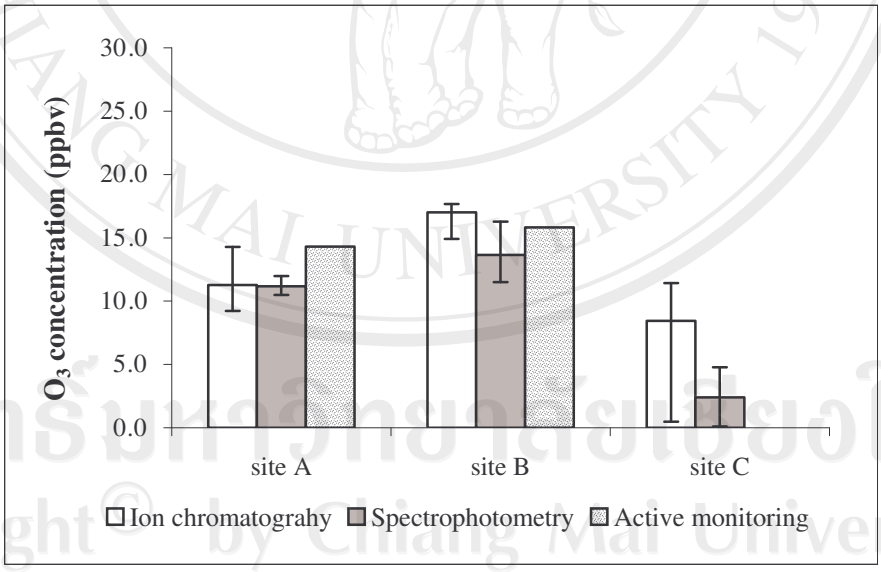


Fig 3.45 Median O_3 concentrations (24 hr) on 11/10/05

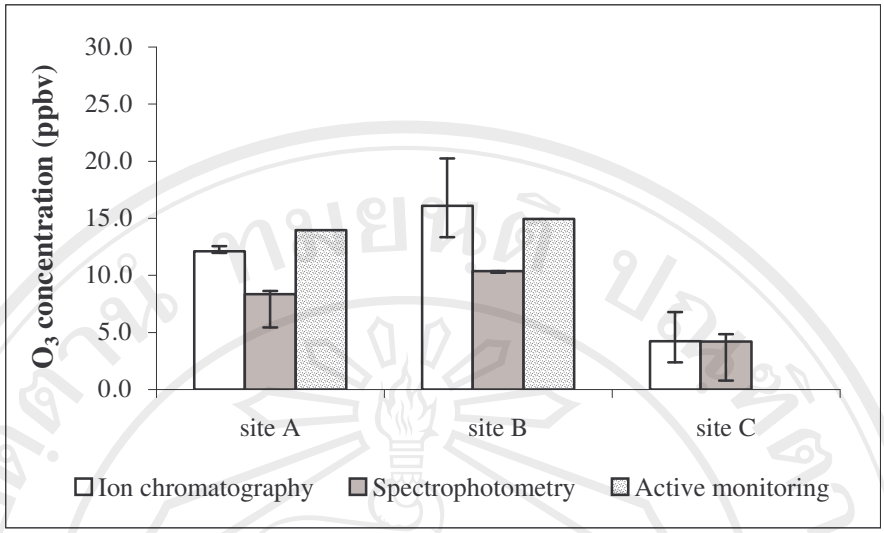


Fig 3.46 Median O_3 concentrations (24 hr) on 12/10/05

The application of passive sampling technique showed the values of pollutant gases relatively close to the values obtained from active monitoring. Site B showed the highest level of pollution because it is located at the center of Chiang Mai City, in which was disturbed by human activities were high and probably the main source contributed to the level of pollutant. Site C was indicated as rural area and found to have least level of pollution. The accuracy of the method was done by comparing of measured values with active measurement and expressed as percent difference. Precision of the measurement was done by observation of the variation of measured values and expressed as % RSD as shown in Table 3.9.

Table 3.9 Precision and accuracy of NO_2, SO_2 and O_3 determination by passive sampling. Exposure for NO_2 and O_3 on 11/10/05 (1^{st} exposure) and 12/10/05 (2^{nd} exposure), exposure for SO_2 on 11-13/10/05 (1^{st} exposure) and 13-15/10/05 (2^{nd} exposure)

Site	Exposure	Analysis method	NO_2				SO_2				O_3			
			Median (ppbv)	% diff	Avg. (ppbv)	%RSD	Median (ppbv)	% diff	Avg. (ppbv)	%RSD	Median (ppbv)	% diff	Avg. (ppbv)	%RSD
site A	1^{st}	IC	4.878	-5.1	5.587	1.4	2.743	+144.9	2.618	3.0	11.282	-21.1	11.735	7.4
		Spectrophotometry	4.875	-5.2	8.112	14.4	1.288	+15.0	1.247	24.0	11.170	-21.9	11.253	2.7
		Active sampler (ppbv)	5.140				1.120				14.300			
	2^{nd}	IC	6.079	+3.6	4.461	0.9	3.687	+251.1	3.573	10.8	12.108	-13.3	12.361	0.7
		Spectrophotometry	5.625	-4.2	4.287	13.7	1.120	+6.7	3.398	7.6	8.355	-40.2	7.183	10.7
		Activesampler(ppbv)	5.870				1.050				13.960			
site B	1^{st}	IC	12.990	+4.5	13.040	2.7	3.865	+79.8	3.854	0.3	17.002	+7.4	18.303	1.0
		spectrophotometry	12.928	+4.0	14.087	25.6	1.960	-8.8	1.990	18.0	13.644	-13.8	13.906	7.4
		Active sampler (ppbv)	12.430				2.150				15.830			
	2^{nd}	IC	17.846	+12.8	17.346	3.4	3.905	+94.3	4.146	11.7	16.098	+7.7	16.087	6.2
		spectrophotometry	13.463	-14.9	17.610	20.8	1.424	-29.2	ND	40.9	10.366	-30.7	10.344	0.580
		Active sampler (ppbv)	15.820				2.010				14.950			
site C*	1^{st}	IC	2.923		2.378	2.9	1.424		1.436	0.4	8.449		6.734	16.1
		spectrophotometry	2.777		2.549	23.7	ND		ND	ND	2.390		2.555	25.0
	2^{nd}	IC	2.831		2.502	0.6	0.529		0.503	1.5	4.237		4.348	6.3
		spectrophotometry	ND		ND	ND	ND		ND	ND	4.329		2.176	34.2

* % Difference (%diff) was not calculated due to lacking of data from active sampler

Concentrations of NO_2 collected by passive samplers and determined by IC and spectrophotometry were not different from each other. However, the variation of values (%RSD) obtained from spectrophotometry was higher than that of IC. When comparing the passive-NO_2 values with the active sampler, the difference value was less than 5.2%, which was very low except for the second measurement in site B using the spectrophotometry.

SO_2 concentrations from passive sampler determined by IC was very different from those determined by spectrophotometry and active monitoring. The concentration determined by IC gave overestimate value (> 79.8% difference) from active sampler. On the other hand, determination by spectrophotometry gave relatively close value to active monitoring (< 29.2% difference). Sensitivity of spectrophotometry was quite low, which can be seen from the slope of standard calibration curve (slope = 0.0708). This causes high variation in measurement because only little change in absorption value affect a lot on concentration of gas. Therefore, the variation (%RSD) values of IC measurement was lower than that of spectrophotometry. The overestimation of SO_2 measurements can be caused by interferences from wall deposition of SO_4^{2-} aerosols (Kasper-Giebl and Puxbau, 1999). The dusts might contain SO_4^{2-} ion leading to overestimation of SO_2 concentrations as far as expose for long time. Extraction of SO_2 from passive sampler tube for IC determination was done by directly adding milli-Q water into the tube and sonicating, while this for spectrophotometry was done by taking 1 ml of absorbing solution in the diffusion tube mixed with pararosaniline reagent in the test tube. Therefore, the effect of wall deposition of SO_4^{2-} aerosol could be affected to the extraction technique for IC determination, which illustrated almost 2 times

overestimated SO_2 values comparing with active analyzer. The using of porous membrane at the mouth of the tube is one of the necessary to avoid the interference from SO_4^{2-} aerosol. Fig 3.47 shows the particle (PM_{10}) in Chiang Mai ambient air in 2005 (data from Chiang Mai Governmental Office Center). It was found that SO_2 concentrations obtained from passive sampling determined by IC trended to be increased with the amount of PM_{10}.

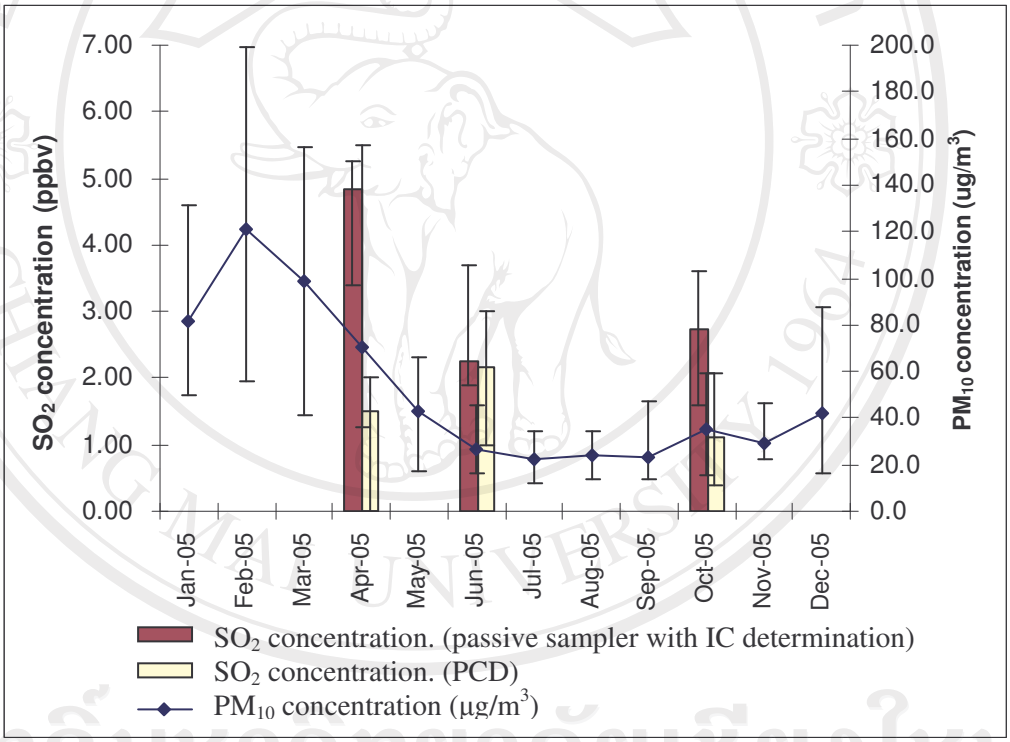


Fig 3.47 Relation of PM_{10} concentration and SO_2 in ambient air at Chiang Mai Governmental Office Center

O_3 concentration measured by passive sampler and determined by both IC and spectrophotometric system were not different from each other and relatively closed to active sampling. IC determination showed both over- and underestimate values with

error less than 21.1% from active analyzer, whereas O_3 from spectrophotometry showed only the underestimate values, which was in the range of 13.0-40.0%. However, the higher variation (%RSD) was found in O_3 determination by spectrophotometry.