CHAPTER 3

RESULTS AND DISCUSSION

In this work passive sampler for determination of nitrogen dioxide in ambient air were developed and validated.

3.1 Optimization method for nitrogen dioxide

The standard NISOH method was chosen and applied for determination of nitrogen dioxide in ambient air by passive sampler. Triethanolamine (TEA) is a compound widely used for trapping NO_2 in ambient air (Ozden and Dogeroglu, 2007; Gerboles *et al*, 2005 and Plaisance *et al*, 2003). TEA absorbs not only NO_2, but also SO_2 in ambient air. Therefore SO_2 can compete with NO_2 to be absorbed by TEA and presents in form of sulfate (Krochmal and Kalina, 1997). Fortunately concentration of SO_2 in ambient air is much lower than NO_2, therefore SO_2 is not much interfere with the sampling. The product of the reaction of NO_2 with TEA solution is nitrosodiethanolamine (Aoyama and Yoshiro, 1983 cited by Glasius *et al*, 1999). The compound can be determined by spectrophotometry. Glasius *et al* (1999) identified it as triethanolamine N-oxide and the following reaction scheme was proposed.

$$2NO_2 + N(CH_2CH_2OH)_3 + 2OH^- \longrightarrow 2NO_2^- + {}^-O\text{-}N^+(CH_2CH_2OH)_3 + H_2O \qquad (3.1)$$

This mechanism was obtained from the reaction as shown below

$$\underset{\text{triethanolamine}}{N(CH_2CH_2OH)_3} + H_2O \longrightarrow (CH_2CH_2OH)_3NH^+ + OH^- \qquad (3.2)$$

$$2OH^- + 2NO_2 + H_2O \longrightarrow NO_3^- + NO_2^- + H_2O \qquad (3.3)$$

$$NO_3^- + N(CH_2CH_2OH)_3 \longrightarrow \underset{\text{triethanolamine N-oxide or nitrosodiethanolamine}}{NO_2^- + ON(CH_2CH_2OH)_3(\text{N-oxide})} \qquad (3.4)$$

Nitrite (NO_2^-) can be determined by spectrophotometry. Nitrite in solution reacts with sulphanilamide and form a diazonium compound, which on coupling with N-(1Napthyl) ethylenediamine dihydrochloride (NEDA) form purple azodye (Varshney and Abhai, 2003). The reactions involved are shown in Figure 3.1.

Figure 3.1 The NO_2 formation for determined by spectrophotometry

3.1.1 Reaction time of color development for NO_2

After Saltzmann reagent was added for color development of nitrite standard solution, reaction time was observed. 1 ml of 0.2-1.0 mg/L nitrite standard solution was mixed with 2 ml of Saltzmann reagent and left for 0-25 minutes prior to spectrophotometry measurement. It was found that the solution was completely mixed after 10 minutes as shown in Table 3.1 and Figure. 3.2. Therefore, after mixing of standard solution and Saltzmann reagent, the solution needs to be left for at least 10 minutes prior to process the next step.

Table 3.1 Reaction time of color forming for NO_2 determination

Concentration of NO_2^- (mg/L)	**Mean absorbance (n=3)**					
	0 min	**5 min**	**10 min**	**15 min**	**20 min**	**25 min**
0.2	0.0505	0.0633	0.0641	0.0650	0.0656	0.0654
0.4	0.1168	0.1291	0.1298	0.1305	0.1309	0.1307
0.6	0.1766	0.1794	0.1910	0.1915	0.1919	0.1907
0.8	0.2107	0.2205	0.2253	0.2276	0.2280	0.2273
1.0	0.2959	0.3052	0.3175	0.3175	0.3188	0.3168

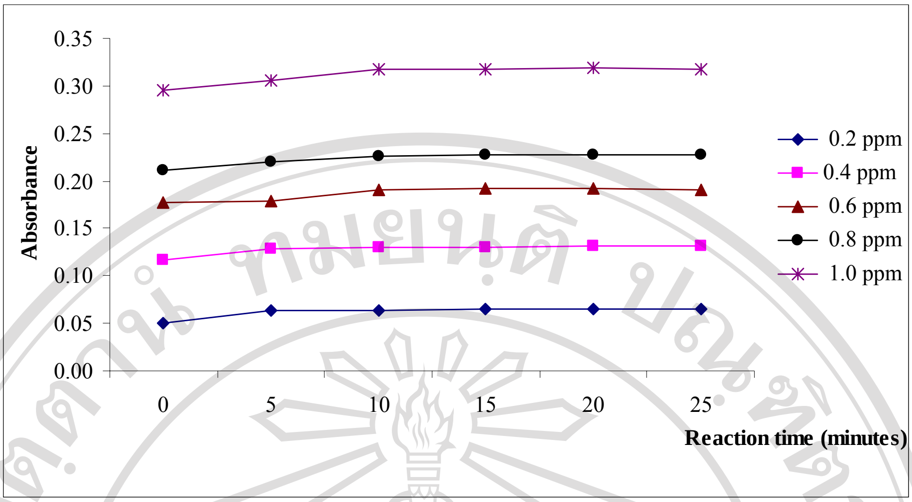

Figure 3.2 Reaction time of color developing for NO_2

3.1.2 Extraction time

NO_2 was analyzed in form of NO_2^-. Extraction time have been tested by spiking 20 µl of 100 mg/L of NO_2^- standard solution onto the sorbent (Whatman GF/A) in 3 diffusion tubes. Extraction was done as described in topic 2.4.2. Times of extraction (5-25 minutes) were tested. Percent recoveries of NO_2^- were calculated in order to see the effect of extraction duration as shown in Table 3.2. Percent recoveries of NO_2^- from extraction of 5, 10, 15, 20 and 25 minutes were 84±2, 92±2, 94±3, 92±2, and 92±2, respectively. The optimum extraction time of NO_2 from the sampler was at 15 minutes.

3.2 Analytical Characteristics

3.2.1 Linear range

1 ml of nitrite standard was mixed with 2 ml of Saltzmann reagent and stand for 10 minutes. Absorbances of nitrite standard solutions (0.02-10 mg/l) were measured at 540 nm. Concentrations were plotted against their absorbance as shown in Table 3.3 and Figure 3.3. The linear dynamic range was obtained in the range of 0.02-1.70 mg/L.

Table 3.2 Percent recoveries of NO_2^- extraction

Extraction time (minute)	**Replication number**	**absorbance**	**NO_2^- (mg/L)**	**Mean**	**SD**	**%Recoveries**
5	1	0.2630	0.84	0.84	0.02	84$\pm$ 2
	2	0.2580	0.82			
	3	0.2671	0.86			
10	1	0.2908	0.94	0.93	0.02	92$\pm$ 2
	2	0.2806	0.90			
	3	0.2932	0.95			
15	1	0.2808	0.90	0.94	0.03	94$\pm$ 3
	2	0.3030	0.98			
	3	0.2935	0.95			
20	1	0.2805	0.90	0.93	0.02	92$\pm$ 2
	2	0.2914	0.94			
	3	0.2905	0.94			
25	1	0.2807	0.90	0.94	0.03	92$\pm$ 2
	2	0.2909	0.94			
	3	0.2924	0.94			

Table 3.3 Linear dynamic ranges of nitrite standard

Concentrations of NO_2^- standard solution (mg/L)	**Absorbance**	**SD**
0.02	0.0070	0.0027
0.04	0.0123	0.001
0.10	0.0342	0.001
0.20	0.0654	0.002
0.40	0.1249	0.0028
0.60	0.1690	0.0051
0.80	0.2181	0.011
1.00	0.2833	0.003
1.30	0.3660	0.0092
1.50	0.4194	0.0048
1.70	0.4577	0.0081
2.00	0.4958	0.0067
4.00	0.7231	0.0031
6.00	0.7802	0.0017
8.00	0.7992	0.0057
10.00	0.8039	0.0063

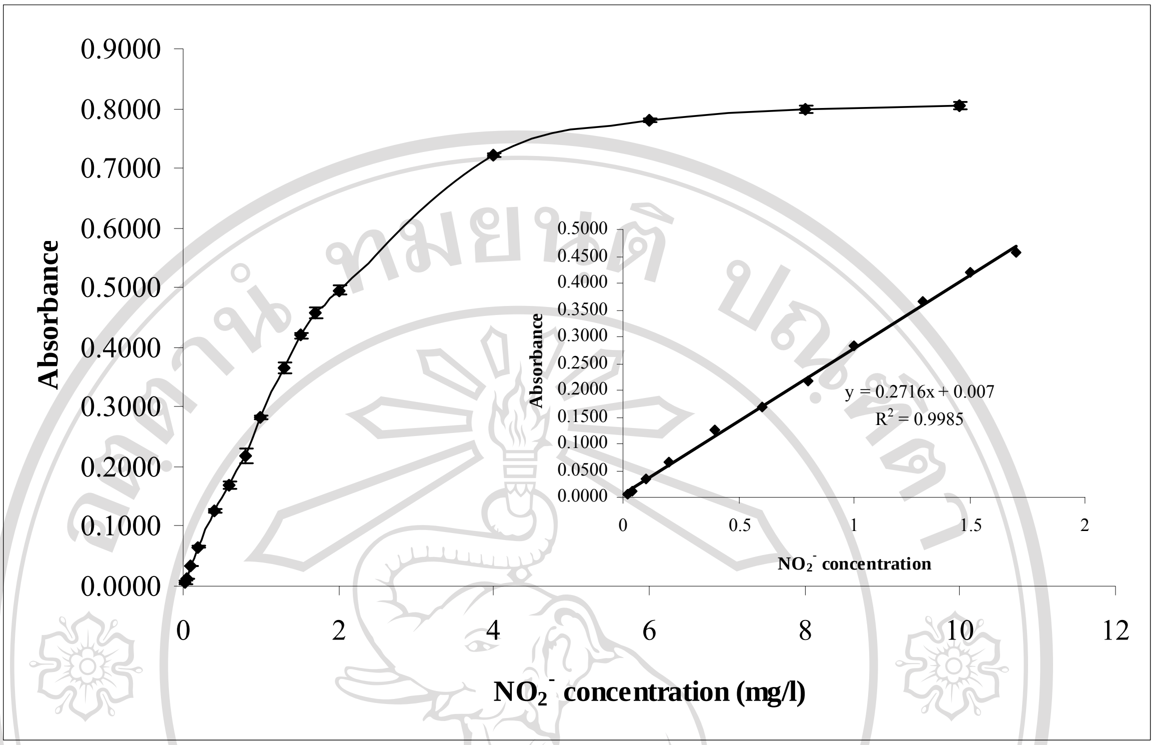

Figure 3.3 Linear dynamic ranges of nitrite standard

3.2.2 Calibration curve of nitrogen dioxide

Nitrogen dioxide trapped in diffusion tube was presented in the form of nitrite (NO_2^-). The NO_2^- concentration was determined using the linear regression equation of the calibration curve prepared from different concentrations of nitrite standard solutions in the range of 0.02-0.10 mg/L as shown in Table 3.4 and Figure 3.4. Linear regression analysis of the nitrogen dioxide as absorbance unit (Y) versus various nitrite concentrations in mg/L (X) yielded an equation: $Y = 0.2763x + 0.0053$ ($r^2 = 0.9989$).

Table 3.4 Absorbance of nitrite standard solution

Nitrite (mg/L)	Absorbance
0.02	0.0070
0.04	0.0123
0.1	0.0342
0.2	0.0654
0.4	0.1249
0.6	0.1690
0.8	0.2181
1	0.2833
1.3	0.3660
1.5	0.4194

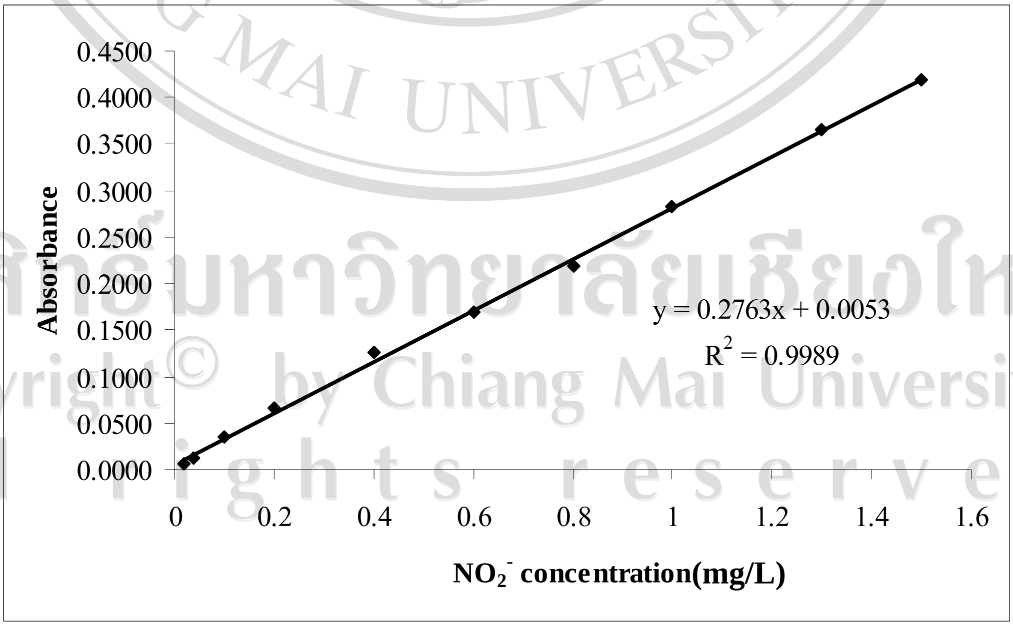

Figure 3.4 Calibration curve of nitrite standard solution

3.2.3 Limit of detection and limit of quantification

The limit of detection (LOD) was obtained by use of linearity curve of nitrite standard concentration with high correlation (r^2 >0.99). LOD was calculated using the equation 2.3 and 2.4 (topic 2.7.4) and the result is shown in Table 3.5. Ten measurements of 0.02 mg/L standard solution were done and absorbances obtained were calculated back into concentrations. LOD and limit of quantification (LOQ) were calculated by 3 times and 10 times of standard deviation (SD) obtained from those ten measured concentrations. LOD and LOQ of spectrophotometry for nitrite measurement were 0.01 and 0.03 mg/L, respectively.

3.2.4 Repeatability and reproducibility

The repeatability of the system was determined by repeating measurements of 0.2 mg/L nitrite solution for 10 replicates analysis. The reproducibility of the system was pursued by preparing 10 solutions of 0.2 mg/l nitrite solution followed by analysis in the same manner. The results obtained are summarized in the Table 3.6. The repeatability and reproducibility of the method were reported in term of %RSD and values were 2.2 and 2.7 %, respectively.

Table 3.5 Limit of detection and limit of quantification of spectrophotometry for nitrite

Number	**Absorbance**	**Nitrite (mg/L)**
1	0.0069	0.010
2	0.0061	0.008
3	0.0051	0.004
4	0.0074	0.012
5	0.0047	0.003
6	0.0060	0.007
7	0.0070	0.011
8	0.0067	0.010
9	0.0046	0.003
10	0.0044	0.002
Average		**0.0075**
Standard Deviation (SD)		**0.0035**
LOD (3*SD)		**0.01**
LOQ (10*SD)		**0.03**

Table 3.6 Repeatability and Reproducibility of spectrophotometry

No. of injection	**Repeatability (mg/L)**	**Reproducibility (mg/L)**
1	0.210	0.199
2	0.219	0.209
3	0.223	0.196
4	0.221	0.200
5	0.221	0.211
6	0.223	0.198
7	0.225	0.206
8	0.212	0.198
9	0.221	0.209
10	0.223	0.209
Average	**0.220**	**0.203**
Standard Deviation (SD)	**0.005**	**0.006**
% RSD	**2.2**	**2.7**

3.3 Development of passive samplers

Passive sampler for determination of NO_2 has been developed by selection of appropriate materials for each component.

3.3.1 Sorbent type

The selection of sorbent type is important for development of an effective passive sampler. The performance of sampler depends on appropriate sorbent which highly sorption efficiency and easy desorption (Murad *et al*., 2002). Four different types of pre-cleaned sorbent including Whatman No.1, No.6, No.40 and glass fiber (GF/A) were tested by impregnated with trapping solution (50 µl of 20% TEA), placed in diffusion tubes and exposed for 24 hours outdoor. Results are illustrated in Table 3.7 and Figure 3.5. It was found that the GF/A provided the highest value of NO_2 (40.5 ppbv) and less difference (6.2%) from value of chemiluminescence technique (43.2 ppbv). However, the ANOVA test showed no significant difference ($\alpha = 0.05$) between types of sorbent. According to properties of cellulose and glass fiber, the glass fiber is more stable in long run, while cellulose fiber contains lignin, which will be decomposed in alkaline condition (OH^-). Therefore GF/A was chosen as an absorption filter for NO_2 in this study.

Table 3.7 Concentrations of nitrogen dioxide from different types of sorbent

Absorbent types	**Mean NO_2 concentration (n=5)**		**SD (ppbv)**	**%RSD (ppbv)**	**% Difference from reference value ***
	µg/m^3	**ppbv**			
Whatman No.1	71.5	38.7	3.8	9.9	9.9
Whatman No.6	71.5	38.7	5.1	13.4	9.9
Whatman No.40	69.8	37.7	3.2	8.6	12.1
Whatman GF/A	80.0	40.5	4.4	11.1	6.2

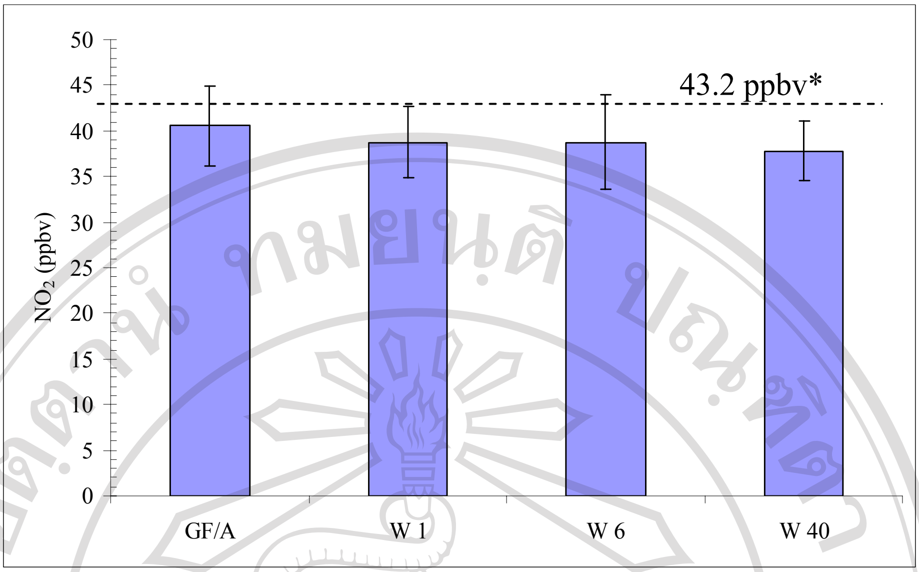

Figure 3.5 Concentration of nitrogen dioxide from different types of sorbent

* Reference value obtained from chemiluminescence measurement of the air quality monitoring station (PCD) at Yupparaj Wittayalai School

3.3.2 Cleaning of the sorbent filter

Filter cleaning technique were investigated to select the one with the lowest contaminant in the sorbent filter (GF/A). The test has been run followed the instruction in a topic 2.9.2. Only in a step of exposure, the tubes were always closed same as blank. Table 3.8 illustrates the concentrations of NO_2 in the sorbent exposed in the field. It is clear that cleaning technique B provided lower NO_2 value than technique A (Soak in deionized water). Therefore, techniques B (soak in deionized water and sonicating) was chosen and used for absorbent filter cleaning in this study.

Table 3.8 Nitrite concentration in the sorbent filter after cleaning by different techniques

Technique	**Cleaning procedure**	**Replication number**	**Nitrite concentration (mg/L)**	**Average ± SD (mg/L)**
A	Soak in deionized water for 30 minute	1	0.067	0.060±0.008
		2	0.054	
		3	0.064	
		4	0.049	
		5	0.065	
B	Soak in deionized water and sonicate for 30 minute	1	0.015	0.019±0.003
		2	0.022	
		3	0.020	
		4	0.021	
		5	0.015	

3.3.3 Type of diffusion tube

Two types of diffusion tube including PE (5.4 cm long and 1.4 cm i.d.), and two sizes of PP (5.3 cm long and 1.3 cm i.d. and 7.7 cm long and 1.6 cm i.d.) were tested to find out their efficiencies in 24 hours exposure. It was found that concentrations of nitrogen dioxide obtained from different types of diffusion tube (n=5) were not significantly different ($\alpha = 0.05$) testing by ANOVA as shown in Table 3.9 and Figure 3.6. However a shorter PP tube (5.3 cm) was chosen due its low cost and locally available.

Table 3.9 Concentrations of NO_2 from different types and different sizes of diffusion tube

Types of diffusion tube	**Mean concentration (ppbv)**	**SD**	**%RSD**	**% Difference from reference value***
PE	32.2	2.1	6.6	6.8
PP1	31.7	3.4	10.8	6.1
PP2	31.2	3.3	10.5	4.23

Note PP1; Length (L) = 5.3 cm, internal diameter (i.d.) = 1.3 cm

PP2; Length (L) = 7.7 cm, internal diameter (i.d.) = 1.6 cm

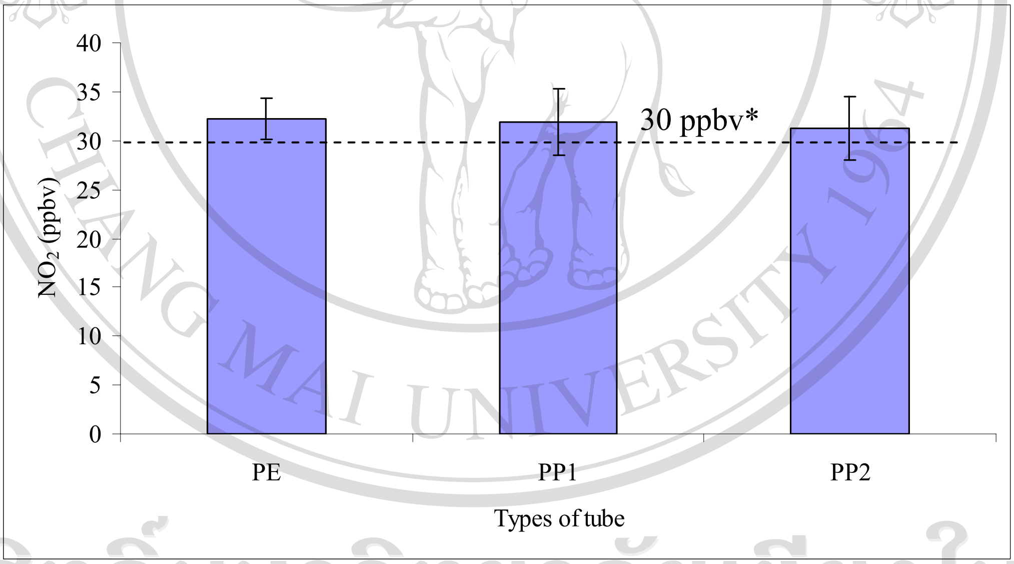

Figure 3.6 Concentration of NO_2 from different types and different sizes of diffusion tube

* Reference value obtained from chemiluminescence measurement of the air quality monitoring station (PCD) at Yupparaj Wittayalai School

3.3.4 Use of membrane as part of diffusion tube

Yanagisawa et al. (1986) modeled the wind influence on the overall mass transfer showing that the uptake rate increases with higher wind speed. An effective and practical way for reducing the effective of air turbulence is use of protective boxes (Plaisance *et al*, 2004) and a Teflon membrane placed at the open end of diffusion tube (Gerboles *et al*, 2005).

For the diffusion tube, without membrane, the uptake rate can be calculated using the coefficient of diffusion and the dimension of the sampler (Gerboles *et al*, 2005). In addition of the membrane introduces a resistance to molecular diffusion. Air resistance was calculated with equation 1.7 (page 13).

NO_2 concentrations obtained from the diffusion sampler with and without Teflon membrane were 11.9 ± 2.0 and 11.6 ± 1.4 ppbv, respectively (Table 3.10). They were not significantly different ($\alpha = 0.05$). However, a passive sampler with membrane has less value of standard deviation.

Table 3.10 Concentration of NO_2 from diffusion tubes with and without membrane

Diffusion tube	Replication number	NO_2 concentration (µg/m^3)	NO_2 concentration ppbv	Mean (ppbv)	SD	% RSD	% Difference from reference value *
Without membrane	1	27.6	14.8	11.9	2.0	17.2	1.9
	2	23.7	12.7				
	3	22.3	11.9				
	4	20.3	10.9				
	5	17.3	9.3				
With membrane	1	22.7	12.2	11.6	1.4	12.4	1.7
	2	17.0	9.1				
	3	22.8	12.2				
	4	21.8	11.7				
	5	23.7	12.7				

*Reference value obtained from chemiluminescence measurement of the air quality monitoring station (PCD) = 11.7 ppbv

3.3.5 Sampling duration

The nitrogen dioxide passive samplers were exposed at the Yupparaj Wittayalai School, for 1, 3, 5 and 7 days. The values of mean nitrogen dioxide concentration of 5 replicates subtracted with blank value were calculated in concentration (ppbv) as shown in the Figure 3.7 and Table 3.11. It was found that exposure duration provided no significant difference ($\alpha = 0.05$) of NO_2 levels (ANOVA test). However, 1 day of exposure showed less percent difference of NO_2 concentration comparison to PCD's value. Long sampling time affected to mass diffusion limit depends on the dimension of the sampler such as size of cross section (capacity of sorbent) which affect to rate of diffusion in the long time exposure. The rate of collection will continuously decrease after 1 day. In case of application for long time exposure, capacity of sorbent must be increased.

Table 3.11 Sampling duration of nitrogen dioxide

Sampling duration	**Replication number**	**NO_2 concentration**		**Mean (ppbv)**	**% RSD**	**% Difference from reference value***
		$\mu g/m^3$	**ppbv**			
1 day	1	12.6	6.7	9.0	19.1	24.4
	2	17.6	9.4			
	3	16.9	9.0			
	4	15.8	8.4			
	5	21.5	11.5			
3 days	1	15.7	8.4	8.6	12.6	26.0
	2	15.7	8.4			
	3	17.7	9.5			
	4	20.0	10.3			
	5	11.3	6.0			
5 days	1	15.0	8.0	8.3	2.3	29.0
	2	15.7	8.4			
	3	15.9	8.5			
	4	15.1	8.1			
	5	15.5	8.3			
7 days	1	19.7	10.5	7.2	33.6	36.7
	2	13.4	7.1			
	3	9.3	4.9			
	4	8.9	4.7			
	5	14.5	7.7			

*Reference value obtained from chemiluminescence measurement of the air quality monitoring station (PCD); 1 day = 12, 3 day =11.7, 5 day = 11.2, 7 day = 11.2

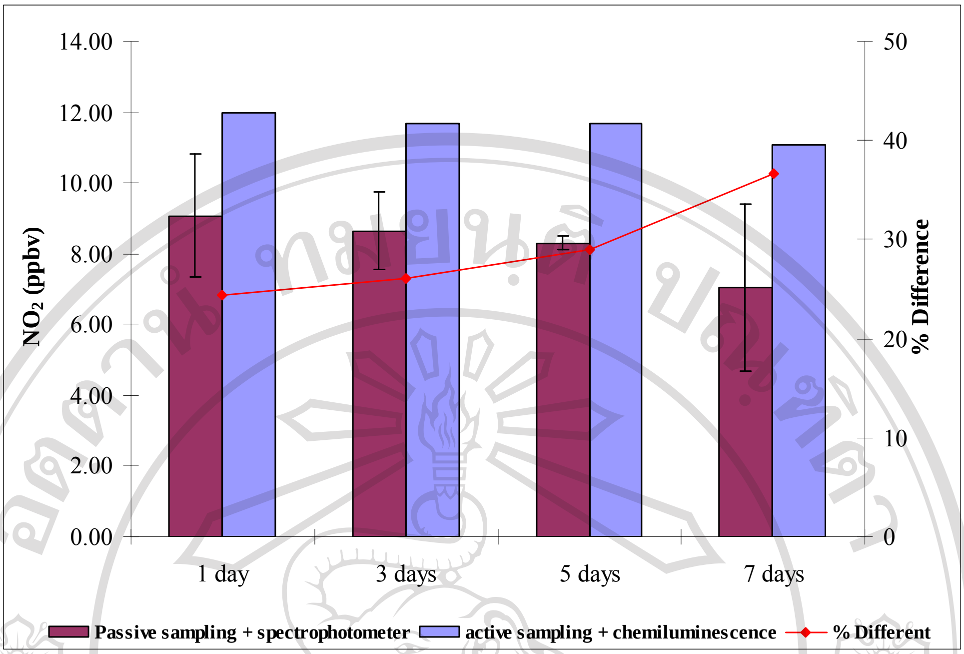

Figure 3.7 Comparison of nitrogen dioxide concentrations from passive and active sampling

3.4 Comparison of nitrogen dioxide concentrations from passive and active sampling

The propose of air sampling is to get some air to an analyzer without changing the analyte concentration. Active air sampling is a process to collect air sample by using a pump to control air flow rate. Therefore air volume collected at a certain time is known. Sampling involves the collection of targeted matter, while the sampling flow rate is required to obtain the transfer volume of the matter to be measured. Thus, when sampling is carried out, transfer volume of the targeted matter is obtained as dynamic or static flow rates using the sampling rate. Passive sampling is using diffusion of air and absorption of pollutant for collection of air sample (Ministry of the Environment Japan, 1999).

NO_2 concentrations from optimum of passive sampler were comparing with chemiluminescence technique from PCD. The Chemiluminescence is the emission of light. Another gas phase reaction is the basis of nitric oxide detection in analytic instruments applied to environmental air quality testing. Ozone is combined with nitric oxide to form nitrogen dioxide in an activated state, and decays to ground state with photon emission. The flux density is measured with a photomultiplier (Colls, 2002).

To prove the efficiency of passive sampling device, comparison between nitrogen dioxide concentrations obtained from 24 hours exposure of passive samplers and those from active sampling (chemiluminescence determination) has been conducted at Yupparaj Wittayalai School from March to December, 2007. Time series of nitrogen dioxide concentrations are illustrated in Table 3.12 and Figure 3.8. Concentrations of nitrogen dioxide obtained from passive sampling are plotted against those from active sampling as shown in Figure 3.9 and good correlation ($r = 0.924$) is obtained. Concentrations of NO_2 from both techniques were not significantly different ($\alpha = 0.05$). Mean relative standard deviation (RSD) representing precision of NO_2 concentrations obtained from passive sampling ($n=5$) was 15.7%, while mean of difference values of NO_2 concentrations obtained from passive and active samplings were 16.0% (Table 3.12).

Those of results presented in this worked agree with Ayers (1998) and Plaisance (2004) who also found that Concentrations of nitrogen dioxide obtained from passive sampling (Ferm diffusion sampler; Long 10 mm and 25 cm i.d. and Palmes diffusion tube: Acrylic diffusion tube; long 7.1 cm, 0.935 m^2 cross sectional area) are good correlation with active sampling ($r^2 = 0.890$ and $r = 0.867$, respectively)

Table 3.12 Nitrogen dioxide concentration (ppbv) obtained from active and passive samplings

Time	**Active sampling**	**Passive sampling**		**% difference**
		Mean (n=5)	**% RSD**	
13/03/2007	44.20	39.59	9.9	-10.4
15/03/2007	34.00	33.70	12.8	-0.9*
16/03/2007	30.60	36.29	18.3	+18.6
19/03/2007	29.30	28.25	18.2	-3.6
23/03/2007	24.60	23.47	17.2	-4.6
26/03/2007	31.00	40.53	13.6	+30.7
28/03/2007	27.40	33.47	18.5	+22.2
15/05/2007	12.00	10.05	32.8	-16.3
24/05/2007	14.30	18.50	11.8	+29.4
5/06/2007	11.40	9.06	19.1	-20.5
17/06/2007	10.80	11.76	46.1	+8.9
18/06/2007	11.10	17.94	30.5	+61.6**
19/06/2007	25.00	22.89	4.8	-8.4
20/06/2007	11.60	15.22	5.5	+31.2
21/06/2007	12.70	18.24	14.7	+43.6
16/07/2007	16.70	13.27	8.5	-20.5
18/07/2007	12.80	11.27	14.0	-12.0
23/07/2007	9.70	10.46	11.5	+7.8
7/11/2007	11.90	11.10	15.1	-6.7
13/11/2007	15.80	13.20	26.0	-16.5
15/11/2007	18.20	17.32	8.5	-4.8
3/12/2007	21.20	20.63	4.7	-2.7
10/12/2007	20.50	20.69	8.9	+0.9*
16/12/2007	22.30	20.44	12.6	-8.3
25/12/2007	18.00	19.63	8.7	+9.1
Average ± SD	**19.88± 8.95**	**19.48± 9.66**	**15.7± 9.60**	**16.0**

* Minimum

** Maximum

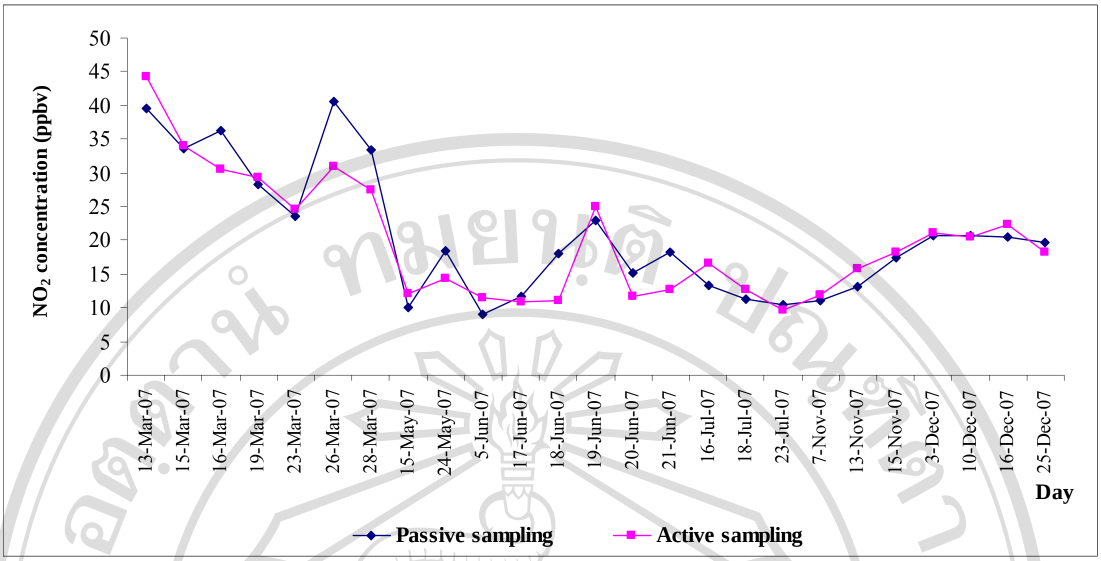

Figure 3.8 The concentrations of nitrogen dioxide from passive sampler and chemiluminescence measurements

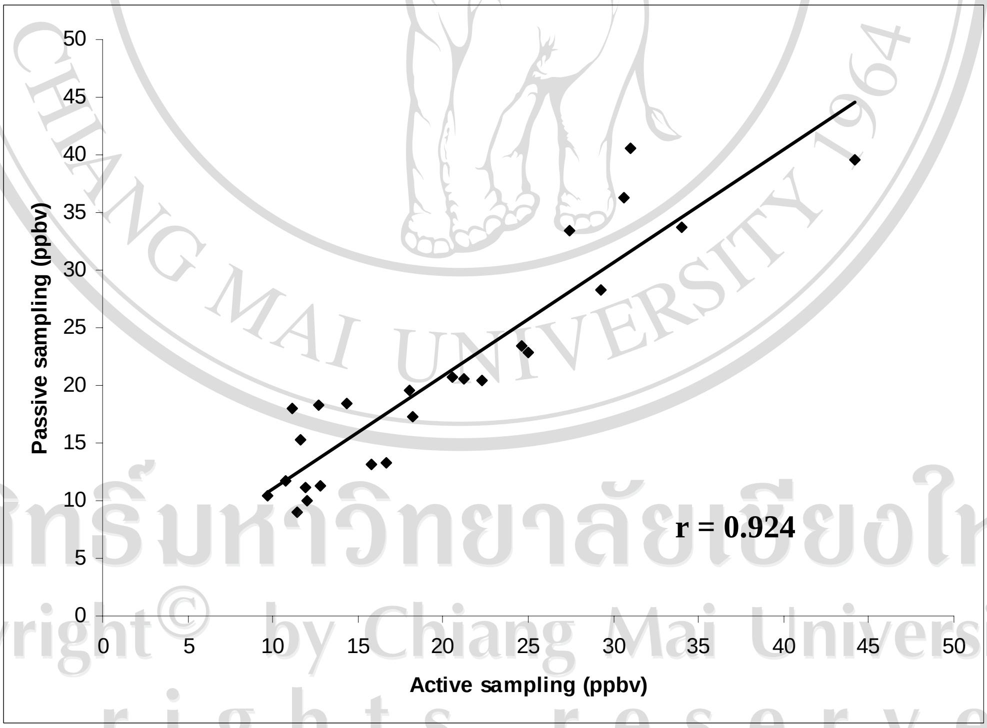

Figure 3.9 Correlation of nitrogen dioxide concentrations determined by passive and active samplings

3.5 Construction of nitrogen dioxide test kit and reliability testing

Determination of nitrogen dioxide can be performed by spectrophotometry. However, this technique needs analyse proficiency. Therefore use of a test kit is a good option because it is simple, quick and easy. Precision and accuracy of the values obtained is acceptable and reliable, if quality control and quality assurance are well performed. In this study experimental work aims to develop a test kit for determination of nitrogen dioxide in ambient air using passive sampling technique. The nitrogen dioxide test kit was designed and constructed (Figure 3.10). It consists of a passive sampler, chemical reagents and standard color chart. The color chart was constructed by Adobe Illustrator program. The stability of test kits was tested. Validation of test kit was test by comparing measured NO_2 concentrations with the PCD chemiluminescence technique. The questionnaire for survey research was also performed.

Figure 3.10 Nitrogen dioxide test kit

3.5.1 Construction of nitrogen dioxide standard color chart

1 ml of nitrite standard solutions (0.03-1.5 mg/l) was mixed with 2 ml of Saltzmann reagent and left for 10 minutes until colors appear as shown in Figure 3.11. It was found that the color can be categorized based on its visual distinguish ability among the different concentrations. The color can be divided into 6 categories (Figure 3.12) belong to the solution with different nitrite concentrations, which are 0.03 mg/l (light misty rose), 0.06 mg/l (misty rose), 0.1 mg/l (light pink), 0.4 mg/l (pink), 0.8 mg/l (hot pink) and 1.5 mg/l (deep pink). The standard color chart was constructed by Adobe Illustrator program, established the relationship between amounts of nitrite standard solution with color chart. Unit conversion of nitrogen dioxide concentration from unit of part per million (ppm) was converted to part per billion by volume (ppbv) as shown in appendex A.

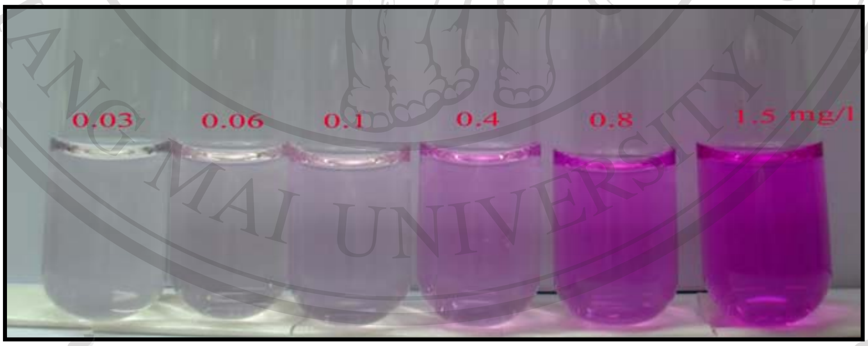

Figure 3.11 Visual color of nitrite solution at different concentration

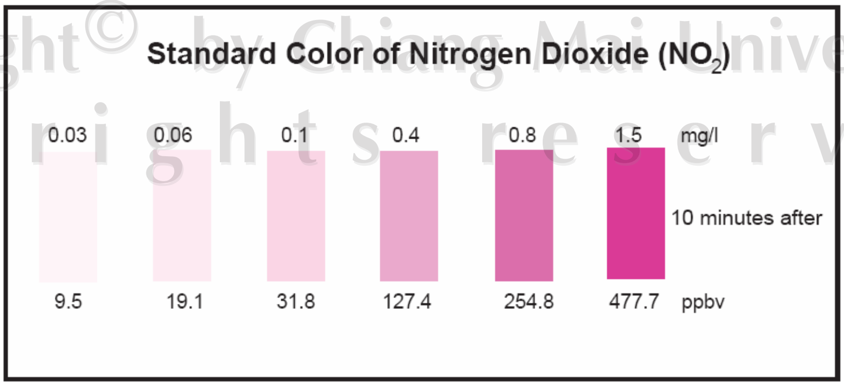

Figure 3.12 Standard color chart of nitrogen dioxide in mg/l and ppbv (based on 24 hour exposure)

3.5.2 Stability of test kit reagent

To produce test kit, stability of reagent is important. In this study stability of Saltzmann reagent and 20% TEA were tested.

A) Stability of Saltzmann reagent

Stability was measured based on absorbance of nitrite. Saltzmann reagent was prepared and kept under dried and dark conditions at room temperature. The experiment was carried by measurement an absorbance of mixed solution of nitrite standard and Saltzmann reagent every week within 4 weeks. The results showed that absorbance of the solution decreased with storage time (Table 3.13 and Figure 3.13). The absorbance was reduced about 10% since week 2 and remains the same within 4 weeks of the experiment. After 4 weeks, the Saltzmann reagent was obviously contaminated because a light purple color appeared. It can be concluded that Saltzman reagent can be used within 4 weeks under dry and dark condition at room temperature (20-27 ^{0}C).

Table 3.13 Stability study of Saltzmann reagent

Time (week)	**Mean absorbance (n=3)**	**% Decrease**
0	0.0663	100
1	0.0653	98
2	0.0605	91
3	0.0595	90
4	0.0604	91

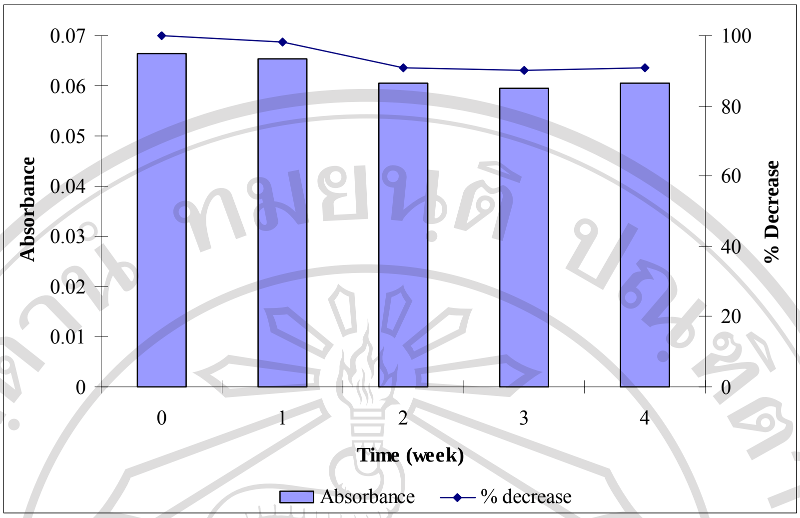

Figure 3.13 Stability of Saltzmann reagent at room temperature

B) Efficiency of 20%TEA

20%TEA was prepared and stored at dried and dark conditions at room temperature (20-27 ^{0}C). The solution has been tested in comparison with a fresh prepared-solution, by 24 hours exposed at the PCD monitoring station. The same test has been repeated every week within a month. The results are illustrated in Table 3.14 and Figure 3.14. It was found that nitrogen dioxide concentrations obtained from stored TEA solution was 11-25% less than those from fresh prepared solution. Therefore, the absorbing solution (20% TEA) must be freshly prepared.

Table 3.14 Concentration of NO_2 from storage 20% TEA absorbing at 20-27 °C

Time	Concentration of NO_2 (ppbv)		%Difference	PCD (ppbv)
	Storage	Fresh preparation		
1	16.9±1.5	20.6 ±0.9	17.9	21.2
2	15.4±2.1	20.6±1.8	25.2	20.5
3	18.2±2.5	20.5±2.5	11.2	22.3
4	16.4±1.1	19.6±1.7	16.3	18.2

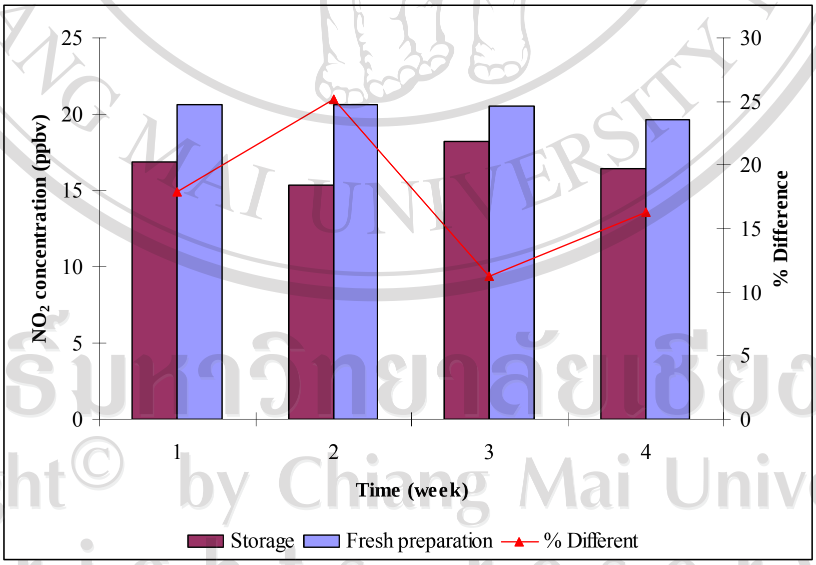

Figure 3.14 Efficiency of TEA in different time to storage

3.5.3 Testing of NO_2 test kit efficiency

Efficiency of the NO_2 test kit was tested by 24 hours exposure of passive sampling tube. Each tube was extracted and color was developed as detail in topics 2.4.1 and 2.4.2. Then the color chart was compared to the standard color of nitrogen dioxide to find out its concentration. In order to avoid any bias that might occur by the experiment, the concentration determined for each sample was then judged by five times of eye measurement. A mean NO_2 value obtained from the standard color chart was then compared to the value obtained from spectrophotometer and PCD monitoring station as shown in Table 3.15. It was found that NO_2 concentrations obtained from the test kit are well agreeable to the ones from another two measurements, which proves that test kit is reliable to be used for determining the nitrogen dioxide in ambient air. However, it could not be used to measure exact value as done by spectrophotometry or automatic sensor.

Table 3.15 Comparison of NO_2 concentration between NO_2 test kit, spectrophotometer and chemiluminescence (PCD)

Sampling date	**Concentration of NO_2 (ppbv)**		
	Test kit	**Spectrophotometry**	**Chemiluminescence**
7-8/11/2007	9.5-19.1	11.1	11.9
13-14/11/2007	19.1	13.2	15.8
15-16/11/2007	9.5-19.1	17.3	18.2
3-4/12/2007	19.1	20.6	21.2
10-11/12/2007	19.1	20.7	20.5
16-17/12/2007	19.1	20.4	22.3
25-26/12/2007	9.5-19.1	19.6	18.2

3.5.4 Reliability in estimation of nitrogen dioxide content from the standard color chart

After a standard color chart of nitrogen dioxide was produced, its efficiency was tested. Validation of the color chart has been performed using a test form as shown in Table 2.2. One hundred students in Chemistry Department, Faculty of Science, Chiang Mai University was randomly chosen as a representative of student's population in Faculty of Science (n=3,307). At 95% confidence, number of sample (n) at 10% error of population size equals 3,000 and 4,000 are 97 and 98, respectively (Appendix B). Questionnaire is a method of data collection by comparing sample color in a test tube with the standard color chart and match the nearest color indicate the measured value of the sample. When the developed color lies between two standard colors, nitrogen dioxide value will be reported in a range of these two colors. All answers responsed by the tester were analysed. Efficiency of NO_2 standard color chart tested with 100 persons is shown in Table 3.16 and Figure 3.15. The overall yielded encouraging facts 64.9%. However, there are some problems in the estimating nitrogen dioxide content by untrained and uninitiated, especially from 0.06, 0.20, 0.60 and 0.80 mg/l. This problem lessens with experience and training.

Cost of self-constructed NO_2 test kit 1 pack (20 sampling tubes) about 250 baht. This evaluation is only an accessory of test kit such as diffusion tube, chemical, shelter and color chart, it is not an evaluation of economic cost.

Table 3.16 Frequency distribution of nitrogen dioxide color chart efficiency (n=100)

No.	**Prepared NO_2 concentration (mg/l)**	**Readable concentration of nitrogen dioxide (mg/l)**											**Accuracy (%)**
		0.03	**0.04-0.06**	**0.06**	**0.06-0.10**	**0.10**	**0.10-0.40**	**0.40**	**0.40-0.80**	**0.80**	**0.80-1.50**	**1.50**	
1	0.03	93*	1	5				1					93.0
2	0.04	13	70*	17	-	-	-	-	-	-	-	-	70.0
3	0.06	-	52	48*	-	-	-	-	-	-	-	-	48.0
4	0.10	7	2	6	18	62*	2	3	-	-	-	-	62.0
5	0.20	-	3	14	7	13	44*	-	-	-	-	-	44.0
6	0.40	1	-	6	1	14	8	58*	-	12	-	-	58.0
7	0.60	-	-	-	-	-	2	1	53*	38	6	-	53.0
8	0.80	-	-	-	-	2	2	5	14	55*	11	11	55.0
9	1.00	-	-	-	-	-	-	-	-	2	77*	21	77.0
10	1.50	-	-	-	-	-	-	-	1	2	8	89*	89.0
Average (%)													**64.9**

The chosen value is marked with asterisk (*)

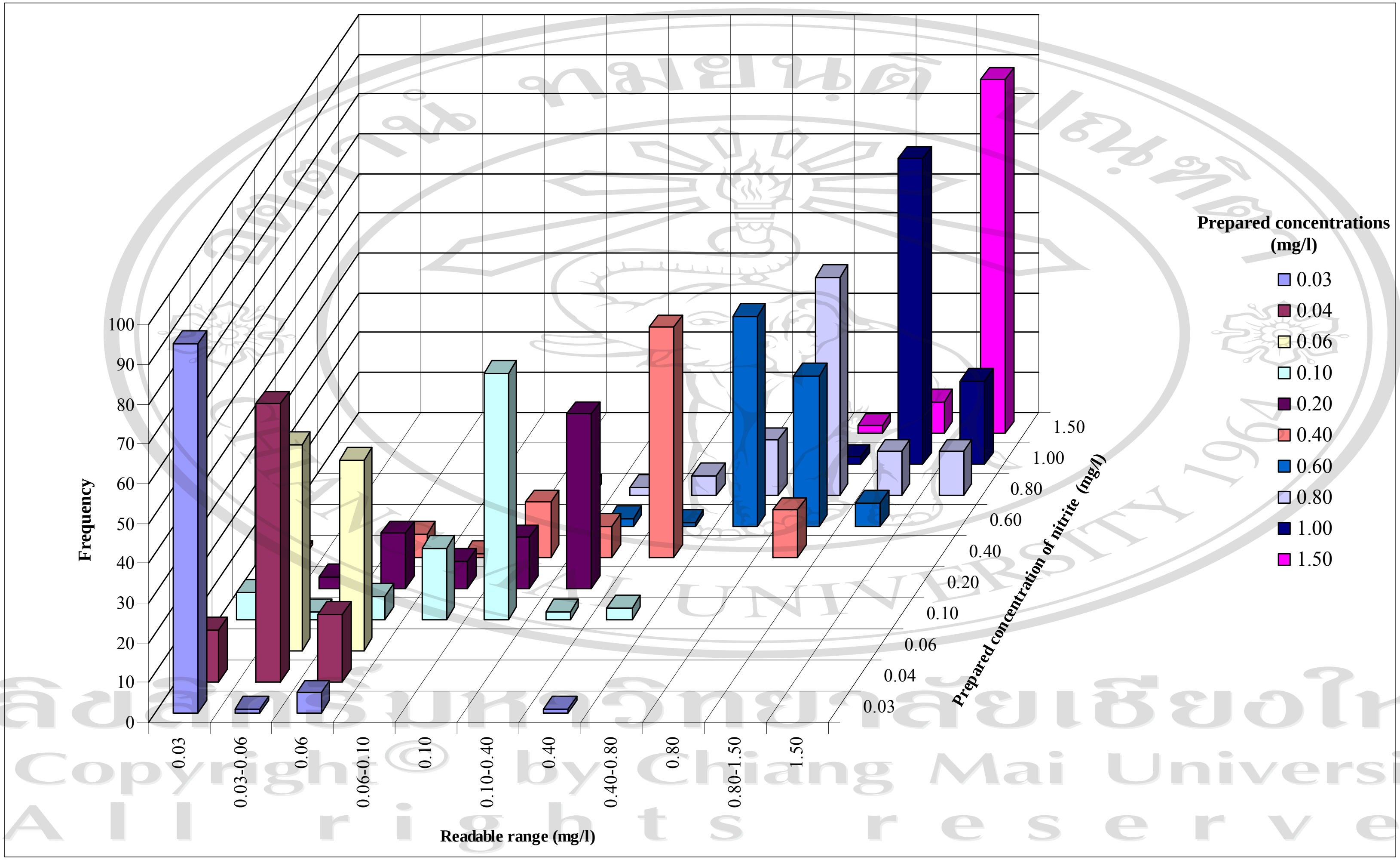

Figure 3.15 Efficiency of nitrogen dioxide color chart