# CHAPTER 3

# RESULTS AND DISCUSSION

The investigation of the effects of different factors on the complexation process involving in sulfur dioxide determination was done through the variations of concentration of color development reagent (pararosaniline), volume and reaction time of sulfamic acid**,** type and volume of formaldehyde, reaction time of color development respectively. The results of such investigation are about to be discussed in the following sections.

## 3.1 Optimization of the method for fabrication of a sulfur dioxide test kit

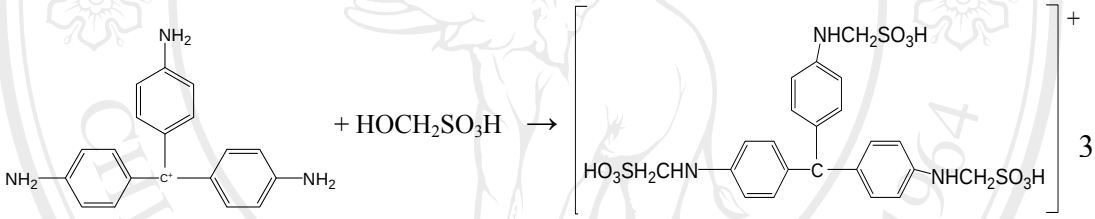
The standard US EPA method was chosen and applied for determination of $SO_2$ in ambient air by passive sampler. The method provided a clear observation to the color change of solution especially when the change of sulfite quantity is down to lower mg/l level. It is quite interesting to track down the color path occurring in this method. $SO_2$ present in the ambient air reacts with tetrachloromercurate (TCM) and forms a stable complex, dichlorosulfitomercurate (DSM), which is subsequently reacted with acid bleached pararosaniline dye and formaldehyde (HCHO) to develop an intensely color (West and Gaeke, 1956). The intensity color is measured spectrometrically at 550 nm, with in the Beer's law application range. As shown in equations 3.1-3.3.

$$[HgCl_4]^{-2} + SO_2 + H_2O \rightarrow [HgCl_2SO_3]^{-2} + 2H^+ + 2Cl^- \qquad 3.1$$

TCM was only used for trapping $SO_2$ in the case of determination by spectrometric system because TCM form stable complex with $SO_2$ in forms of $SO_3^{2-}$, which can completely develop color solution with reagent. The dichlosulfitomercurate (II); $[HgCl_2SO_3]^{-2}$ stabilizes the sulfur dioxide against stronger oxidants. Next, the stabilized medium is reacted with formaldehyde.

$$[HgCl_2SO_3]^{-2} + HCHO \rightarrow HOCH_2SO_3H \qquad 3.2$$

The formaldehyde adduct is reacted with pararosaniline hydrochloride to produce a red-purple dye.




3.3

pararosaniline methyl sulfonic acid

Nitrogen dioxide ($NO_2$) above 2 ppm can interfere, so $NO_2$ is reduced to nitrogen gas ($N_2$) by sulfamic acid ($H_2NSO_3H$). There are a number of potential interferences in this reaction, but most of these are eliminated by the addition of appropriate reagents. The nitrite ion formed from $NO_2$ is destroyed by reaction with sulfamic acid.

$$HOSO_2NH_2 + NO_2^- + H^+ \rightarrow N_2 + H_2SO_4 + H_2O \qquad 3.4$$

The use of EDTA in the absorber solution and phosphoric acid in the pararosaniline reagent solution serve to complex any metals present. However, mercury, which is part of TCM, is not formed complex which EDTA in this experiment because pH of the solution was adjusted to 3-5, which is not suitable for

Hg-EDTA complex formation (pH = 6 is required in this case) (Chaitiemwong, 1994). Among the various manuals monitoring system, the pararosaniline dye based colorimetric method has been adopted as a reference technique by the 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.

### 3.1.1. Optimized concentration of PRA for $SO_2$ determination

Optimization of color development for $SO_2$ determination has been tested based on reaction with pararosaniline reagent varied from 0.004 %v/v, 0.008 %v/v, 0.012 %v/v and 0.016 %v/v. The result is shown in Table 3.1 and Figures 3.1-3.2. Figure 3.1 illustrates absorbances of different concentrations of sulfite. It can be seen that at lower concentrations ($\leq$ 0.10 mg/l), slope of linear line is steeper than that obtained from higher sulfite concentration (0.02-0.08 mg/l). Therefore, calibration curve of each PRA ratio was plotted again and separated into 2 concentration ranges as shown in Figures 3.2. It was found that the 0.008 % v/v and 0.012 % v/v pararosaniline provided high sensitivities over the others. However, paired samples T-test at 95% confidence level (see Appendix B) showed significant difference between these two concentrations. Therefore 0.008% v/v PRA was selected because it provides high absorbance and use less reagent, which is in a long term environmental friendly.

**Table 3.1** Effects of pararosaniline concentrations on absorbance of sulfite

| Concentration of pararosaniline ( % v/v) | Net signal* (Absorbance unit) obtained from the standard sulfite (mg/l) | | | | | | | | Linear equation y =ax + b | $R^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 0.01 | 0.05 | 0.10 | 0.20 | 0.40 | 0.60 | 0.80 | | |
| 0.004% | 0.1065 | 0.1884 | 0.3076 | 0.4446 | 0.5506 | 0.7435 | 0.9361 | 1.0933 | y = 1.1527x + 0.2350 | 0.9515 |
| 0.008% | 0.2001 | 0.2753 | 0.4020 | 0.5624 | 0.7611 | 0.8852 | 1.0952 | 1.2873 | y = 1.2644x + 0.3422 | 0.9361 |
| 0.012% | 0.3117 | 0.3503 | 0.4526 | 0.6073 | 0.7363 | 0.8986 | 1.0814 | 1.2400 | y = 1.1142x + 0.4081 | 0.9530 |
| 0.016% | 0.3912 | 0.4017 | 0.4856 | 0.6095 | 0.7174 | 0.8804 | 1.0242 | 1.1410 | y = 0.9317x + 0.4548 | 0.9576 |

* Average of three replicate determinations

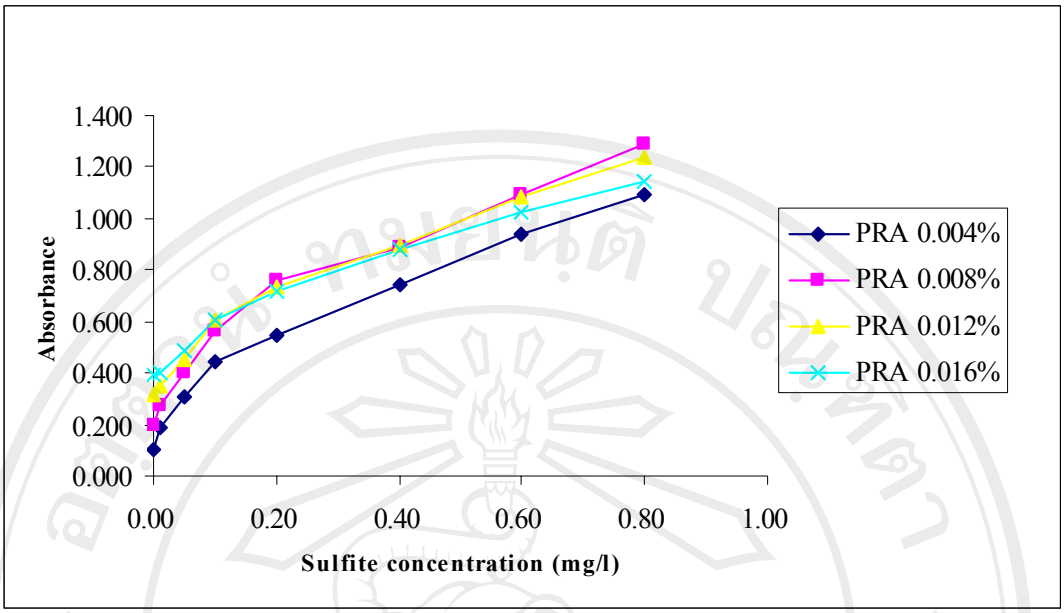



**Figure 3.1** Effects of pararosaniline concentrations on absorbance of sulfite

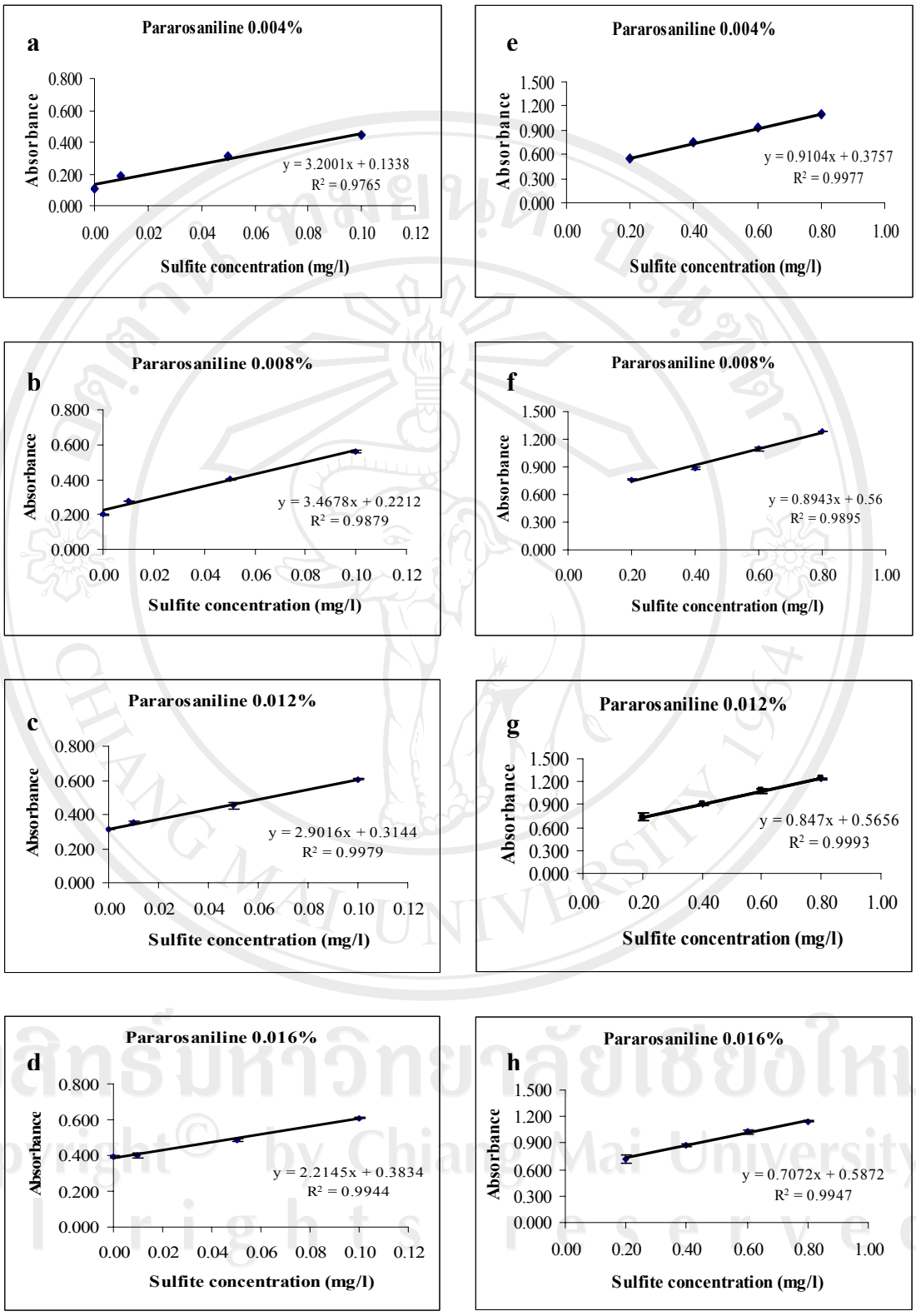



**Figure 3.2** Calibration curves of sulfite standards at different concentrations of pararosaniline; a-d. Sulfite concentration ≤ 0.10 mg/l, e-f. Sulfite concentration = 0.20-0.80 mg/l

### 3.1.2 Optimized volume of sulfamic acid

Sulfamic acid was used for decompose of nitrite, which might contaminate in the solution. Different volume of sulfamic acid varied from 25-400 µl was tested and the results come out that 50 µl and 100 µl provided high absorbance. In conclusion a volume of 100 µl was selected because it provides high absorbance and excess for getting rid of nitrogen dioxide. The result is shown in Table 3.2 and Figure 3.3.

**Table 3.2** Optimization volume of sulfamic acid

| **Volume of sulfamic acid (µl)** | **Average absorbance (n = 3) λ = 550 nm** | **SD** |
|---|---|---|
| 25 | 0.1462 | 0.0036 |
| 50 | 0.1622 | 0.0019 |
| 100 | 0.1611 | 0.0018 |
| 200 | 0.1347 | 0.0042 |
| 300 | 0.1261 | 0.0010 |
| 400 | 0.1195 | 0.0015 |

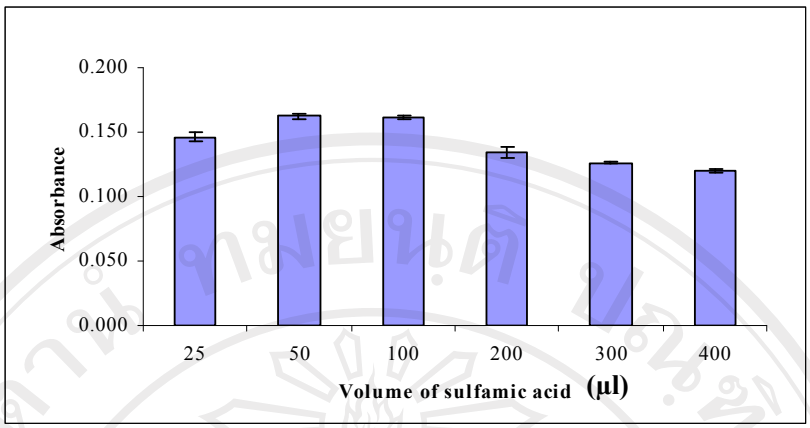



**Figure 3.3** Optimization volume of sulfamic acid

### 3.1.3 Reaction time of sulfamic acid

According to the procedure mentioned in a topic 2.4.3, sulfamic acid was added into the sulfite solution and left for 20 min. From the beginning and every 5 min, the solution was tested and measured by spectrophotometry at 550 nm. It was found that time did not have any effect on absorbance value. This means after adding sulfamic acid, a next step can be immediately carried out. The result is shown in Table 3.3 and Figure 3.4.

**Table 3.3** Reaction time of sulfamic acid

| Time (min) | Absorbance (n = 3) | SD |
|---|---|---|
| 0 | 0.1659 | 0.0011 |
| 5 | 0.1660 | 0.0010 |
| 10 | 0.1685 | 0.0012 |
| 15 | 0.1683 | 0.0010 |
| 20 | 0.1688 | 0.0013 |

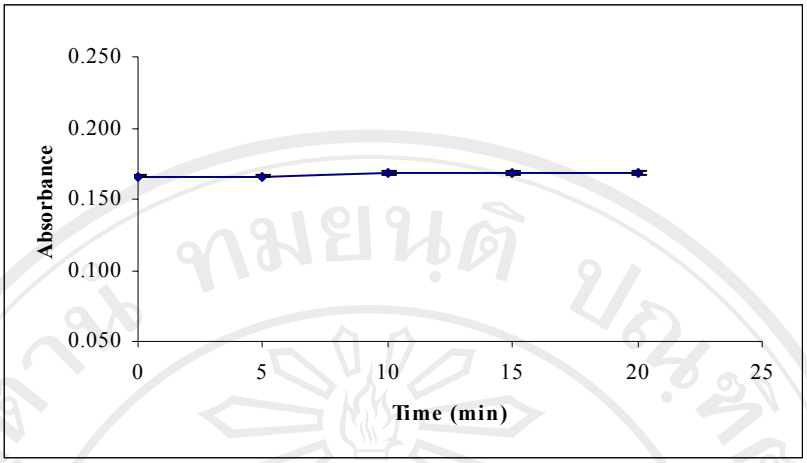



**Figure 3.4** Reaction time of sulfamic acid

### 3.1.4 Volume of formaldehyde

Formaldehyde was used for forming of color solution, therefore its volume varying from 100 to 500 µl was tested. The result is shown in Table 3.4 and Figure 3.5. It was found that 300 µl of formaldehyde provided the highest absorbance. So it can be concluded that this point was the optimum volume of formaldehyde solution.

**Table 3.4** Volume of formaldehyde and absorbance of sulfite solutions

| Volume of formaldehyde (µl) | Absorbance (n = 3) | SD |
|---|---|---|
| 100 | 0.1522 | 0.0057 |
| 200 | 0.1661 | 0.0024 |
| 300 | 0.1731 | 0.0025 |
| 400 | 0.1653 | 0.0024 |
| 500 | 0.1445 | 0.0041 |

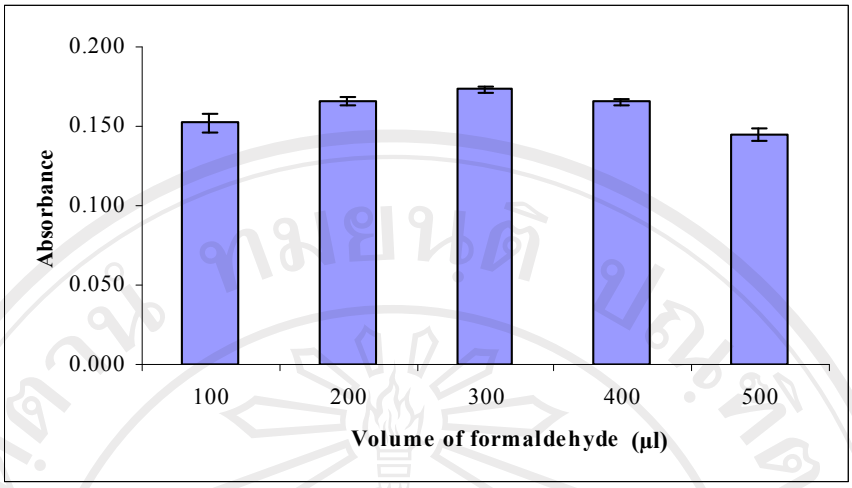



**Figure 3.5** Volume of formaldehyde

### 3.1.5 Testing of formaldehyde reagent

In order to find out whether there is any difference between formaldehyde with and without buffer system. The experiment was carried out and the result is shown in Table 3.5 and Figure 3.6. No difference was found between these two solutions. So that buffered formaldehyde was selected because it is more stable and can be kept for 6 months.

**Table 3.5** Comparison type of formaldehyde reagent

| Type of formaldehyde | Net signal* (Absorbance unit) obtained from the standard sulfite (mg/l) | | | | Linear equation y= ax + b | $R^2$ |
|---|---|---|---|---|---|---|
| | 0.05 | 0.10 | 0.50 | 1.00 | | |
| 0.2 % v/v formaldehyde solution | 0.0876 | 0.1752 | 0.7572 | 1.4639 | y = 1.4905x + 0.2350 | 0.9996 |
| buffered formaldehyde | 0.0876 | 0.1752 | 0.7572 | 1.4639 | y = 1.4432x + 0.2570 | 0.9998 |

* Average of three replicate determinations

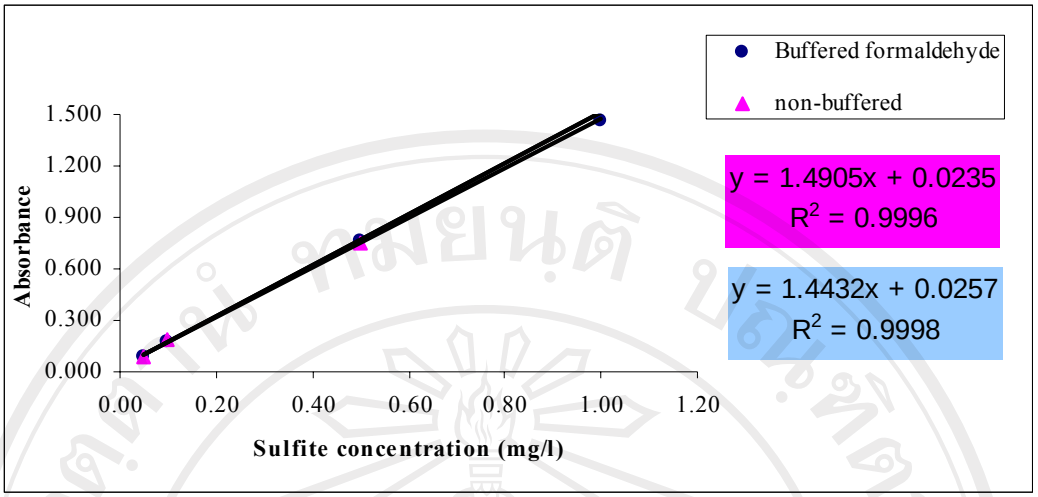



**Figure 3.6** Linear regression obtained from buffered and non-buffered formaldehyde reagents

### 3.1.6 Reaction time of color development

After adding pararosaniline to develop color of the solution, reaction time was observed. Absorbance of the solution was measured every 5 min until 25 min. The result is shown in Table 3.6 and Figure 3.7. It was found that the absorbance of the solution increased with time especially at the first 5 min and continuous to be slightly increased until 10 min. After that it slightly decreased until 25 min. Therefore 10 min reaction time was selected.

**Table 3.6** Reaction time of color development

| Time (min) | Absorbance (n = 3) | SD |
|---|---|---|
| 0 | 0.1242 | 0.0159 |
| 5 | 0.1739 | 0.0029 |
| 10 | 0.1885 | 0.0011 |
| 15 | 0.1854 | 0.0023 |
| 20 | 0.1787 | 0.0031 |
| 25 | 0.1707 | 0.0014 |

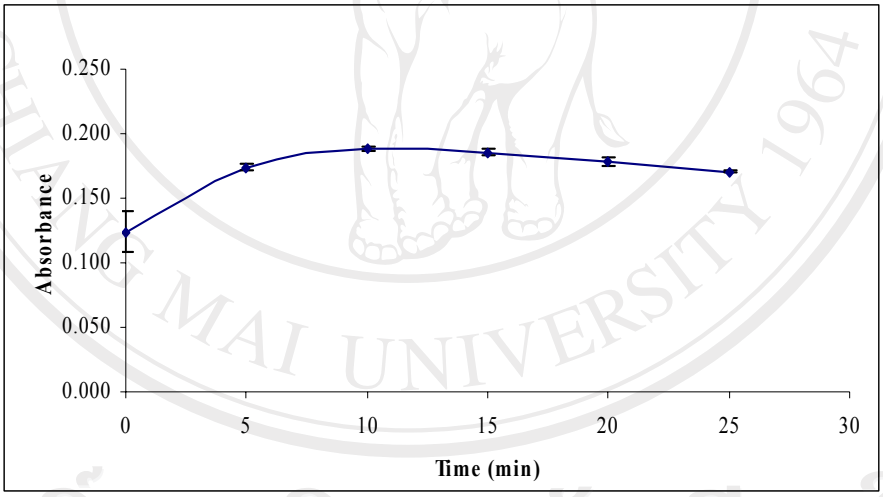



**Figure 3.7** Reaction time of color development

### 3.1.7 Optimum methods for $SO_2$ determination

The optimal composition of the reagent for constructing a sulfur dioxide test kit is shown in Figure 3.8.

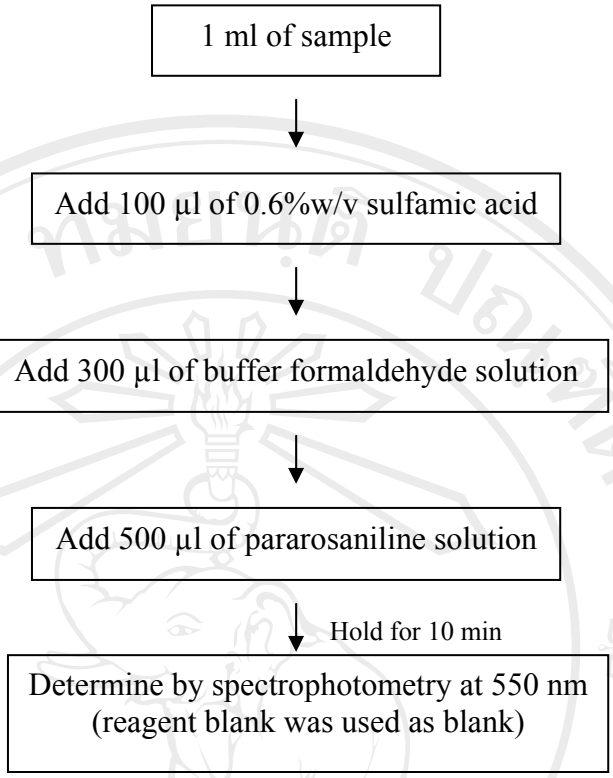



**Figure 3.8** Optimum methods for $SO_2$ determination

**3.2 Effect of the interferences**

The last parameter investigated was the effect of interferences on the color of solution. $NH_3$, HCl, $NO_2$ and $O_3$, which normally present in ambient air, were selected and tested in this study in form of $NH_4^+$, $Cl^-$, $NO_2^-$ and $NO_3^-$ (form $O_3$), respectively. Various concentrations of each interference including 0.01, 0.10 and 1.00 mg/l were added into the 0.10 mg/l sulfite solution. After that the modified US EPA method was applied and the solutions were measured by spectrophotometry. There is no difference found as illustrates in Table 3.7 and Figure 3.9. However there was no significant difference ($p > 0.05$) of $SO_2$ concentrations obtained from each interfering by Paired Samples T- Test at 95% confidence level (see Appendix B). Therefore the interfering not effect due to $NH_3$, HCl, $NO_2$ and $O_3$ in the determination of $SO_2$.

**Table 3.7** The interfering effect of sulfur dioxide

| $SO_3^{2-}$ : Interference (mg/l) | $NH_3$ (n=3) | | HCl (n=3) | | $O_3$ (n=3) | | $NO_2$ (n=3) | |
|---|---|---|---|---|---|---|---|---|
| | Abs. | Conc. | Abs. | Conc. | Abs. | Conc. | Abs. | Conc. |
| 0.10 : 0.00 | 0.1910 | 0.10 | 0.1910 | 0.10 | 0.1910 | 0.10 | 0.1910 | 0.10 |
| 0.10 : 0.01 | 0.1732 | 0.09 | 0.1885 | 0.10 | 0.1775 | 0.10 | 0.1829 | 0.10 |
| 0.10 : 0.10 | 0.1805 | 0.10 | 0.1945 | 0.11 | 0.1846 | 0.10 | 0.1875 | 0.10 |
| 0.10 : 1.00 | 0.1851 | 0.10 | 0.2066 | 0.11 | 0.1917 | 0.10 | 0.1925 | 0.10 |

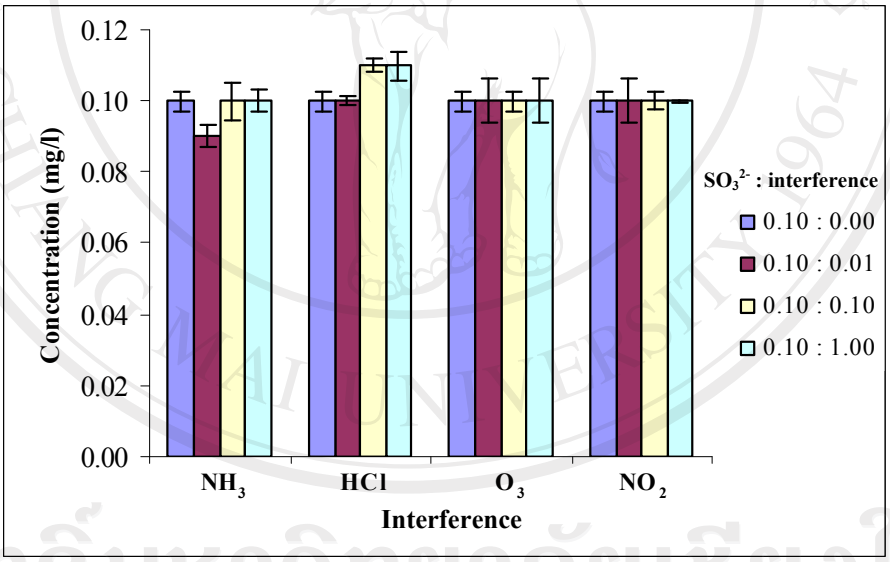



**Figure 3.9** The interfering effect of sulfur dioxide



## 3.3 Analytical Characteristics

### 3.3.1 Linearity range of sulfur dioxide

The standard US EPA method was applied for $SO_2$ determination by adding 1 ml of sulfite standard in tetrachloromercurate solution with 100 µl of

0.6% sulfamic acid, 300 µl of 0.2% formaldehyde solution and 500 µl of pararosaniline solution, respectively. A mixed solution was left for 10 min. Absorbance of standard solutions of sulfite and reagent blank were measured at 550 nm. Under the optimum conditions, the linear dynamic range (LDR) was obtained in the range of 0.002-1.200 mg/l. After that those concentrations were plotted against their absorbance as shown in Table 3.8 and Figure 3.10.

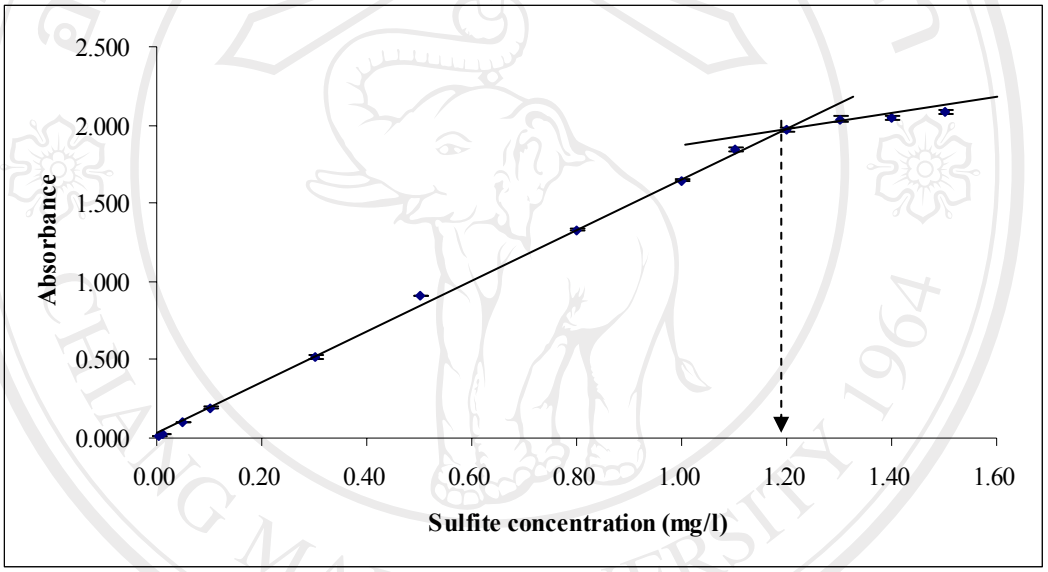



**Figure 3.10** Linear dynamic range of sulfite standard

**Table 3.8** Linear dynamic range of sulfite standard

| Concentration of sulfite solution (mg/l) | Absorbance | SD |
|---|---|---|
| 0.002 | 0.0127 | 0.0026 |
| 0.050 | 0.0964 | 0.0011 |
| 0.100 | 0.1945 | 0.0070 |
| 0.300 | 0.5143 | 0.0100 |
| 0.500 | 0.9082 | 0.0054 |
| 0.800 | 1.3318 | 0.0034 |
| 1.000 | 1.6433 | 0.0080 |
| 1.100 | 1.8424 | 0.0084 |
| 1.200 | 1.9696 | 0.0087 |
| 1.300 | 2.0383 | 0.0161 |
| 1.400 | 2.0487 | 0.0099 |
| 1.500 | 2.0848 | 0.0128 |

### 3.3.2 Calibration curve of sulfur dioxide

Using the optimal experimental parameters, linearity of calibration curve was investigated in the range of 0.006-0.50 mg/l of sulfur dioxide. The result was exhibited in Table 3.9 and Figure 3.11. Linear regression analysis of the sulfur dioxide in absorbance unit (Y) versus various sulfite ion concentrations in mg/l (X) yielded the following equation: $Y = 1.8145x - 0.0165$ ($r^2 = 0.9992$).

**Table 3.9** Absorbance of standard sulfite solution

| Sulfite concentration ( n = 3) (mg/l) | Absorbance |
|---|---|
| 0.006 | 0.0155 |
| 0.050 | 0.1073 |
| 0.100 | 0.2146 |
| 0.300 | 0.5568 |
| 0.500 | 0.9230 |

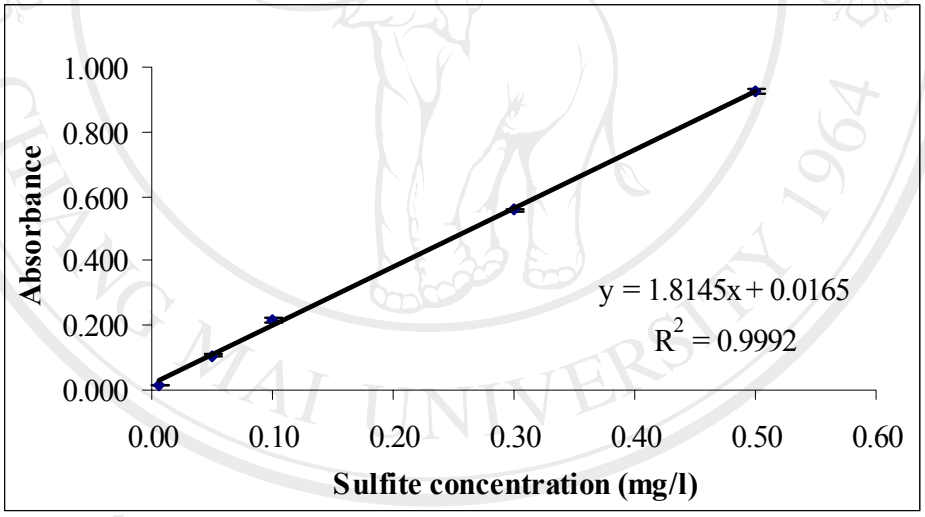



**Figure 3.11** Calibration curve of sulfite standard solution



### 3.3.3 Limit of detection and limit of quantification

The limit of detection (LOD) and limit of quantification (LOQ) were obtained by use of linearity curve of sulfite concentration with good correlation ($r^2$ = 0.9994). Ten measurement of 0.005 mg/l standard solution was done and absorbances obtained were calculated back into concentration. LOD and LOQ

were calculated by 3 times and 10 times of standard deviation (SD) obtained from those ten measured concentrations as shown in Table 3.10. LOD and LOQ were 0.002 and 0.006 mg/l, respectively.

**Table 3.10** LOD and LOQ of spectrophotometry

| Experiment number | Absorbance | Sulfite concentration (mg/l) |
|---|---|---|
| 1 | 0.0136 | 0.004 |
| 2 | 0.0128 | 0.004 |
| 3 | 0.0160 | 0.005 |
| 4 | 0.0151 | 0.005 |
| 5 | 0.0140 | 0.004 |
| 6 | 0.0148 | 0.005 |
| 7 | 0.0156 | 0.005 |
| 8 | 0.0146 | 0.004 |
| 9 | 0.0158 | 0.005 |
| 10 | 0.0131 | 0.004 |
| **Average** | - | **0.004** |
| **SD** | - | **0.0006** |
| **LOD (3xSD)** | - | **0.002** |
| **LOQ (10xSD)** | - | **0.006** |

### 3.3.4 Repeatability and reproducibility of method

The repeatability of the system was determined by repeating measurements of 0.1 mg/l sulfite solutions for 10 times. The reproducibility of the system was pursued by preparing 10 solutions of 0.1 mg/l sulfite solution followed by analysis in the same manner. The results obtained are summarized in Table 3.11. The repeatability and reproducibility of the method were reported in term of % RSD and the values were 1.24 and 3.95% respectively indicating that this method and device develop are very precise.

**Table 3.11** Repeatability and reproducibility of method for replicate determination of sulfite solution

| Experiment number | Analytical signal (Absorbance unit) | |
|---|---|---|
| | Repeatability | Reproducibility |
| 1 | 0.1894 | 0.1818 |
| 2 | 0.1857 | 0.1845 |
| 3 | 0.1863 | 0.1827 |
| 4 | 0.1865 | 0.1798 |
| 5 | 0.1824 | 0.1965 |
| 6 | 0.1867 | 0.1865 |
| 7 | 0.1862 | 0.1954 |
| 8 | 0.1853 | 0.1953 |
| 9 | 0.1818 | 0.1971 |
| 10 | 0.1827 | 0.1996 |
| **Average** | **0.1853** | **0.1899** |
| **SD** | **0.0023** | **0.0075** |
| **% RSD** | **1.24** | **3.95** |

### 3.3.5 Stability of Complex

With respect to the stability of complex, it was found that the absorbance was stable during 8-24 min at room temperature. Further increase in reaction time resulted slowly decreasing of absorbance values. The stability of color has been investigated and found that the solution was completely mixed at 8 min as shown in Table 3.12 and Figure 3.12.

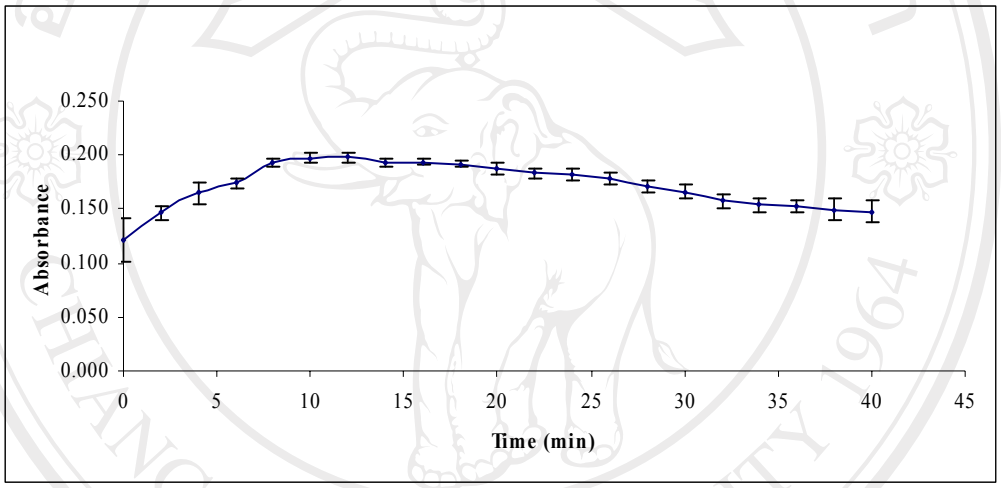



**Figure 3.12** Stability study at room temperature of sulfite solution at 0.1 mg/l

**Table 3.12** Stability study at room temperature of sulfite solution at 0.10 mg/l

| Time (min) | Absorbance (n = 3) | Concentrations (mg/l) |
|---|---|---|
| 0 | 0.1209 | 0.06 |
| 2 | 0.1463 | 0.08 |
| 4 | 0.1652 | 0.09 |
| 6 | 0.1745 | 0.09 |
| 8 | 0.1927 | 0.10 |
| 10 | 0.1978 | 0.10 |
| 12 | 0.1973 | 0.10 |
| 14 | 0.1928 | 0.10 |
| 16 | 0.1935 | 0.10 |
| 18 | 0.1916 | 0.10 |
| 20 | 0.1877 | 0.10 |
| 22 | 0.1834 | 0.10 |
| 24 | 0.1817 | 0.10 |
| 26 | 0.1784 | 0.09 |
| 28 | 0.1706 | 0.09 |
| 30 | 0.1660 | 0.09 |
| 32 | 0.1574 | 0.08 |
| 34 | 0.1539 | 0.08 |
| 36 | 0.1524 | 0.08 |
| 38 | 0.1497 | 0.08 |
| 40 | 0.1476 | 0.08 |

### 3.4 Development of passive sampler for determination of $SO_2$ in ambient air

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 tube was subtracted from blank tube to obtain the real value.

#### 3.4.1 Optimization of diffusion tube types

Types of diffusion tube were studied for the suitability of diffusion of gas from ambient air. The PS tube is transparent, while the PE and PP are less transparent. However, the properties of those three types are similar in term of water sorption rate, which is 0.01% for PE and PP and 0.06% for PS (http://clgc.rdi.ku.ac.th/article/es/plastic/recycle.html). The values indicated hydrophobic property. Four set of tube were been exposed at the sampling site for 3 days. From Table 3.13, PP diffusion tube (93 mm length and 14.8 mm i.d.) gave exactly the same concentrations of sulfur dioxide detected by fluorescence technique (0.5 ppbv). Therefore, the 93 mm PP tube was selected. However there was no significant difference of $SO_2$ concentrations obtained from each type testing by One-Way ANOVA (CRD test) at 95% confidence level (see Appendix B). Therefore all tube type tested can be used for $SO_2$ sampling. Their concentrations were compared with values obtained from fluorescence measurement of PCD monitoring station. Mean $SO_2$ concentrations and their max and min values are illustrated in Figure 3.13.

**Table 3.13** Types of diffusion tube and their percent difference for sulfur dioxide determination

| Types | Mean $SO_2$* (ppbv) | SD | %RSD | %Error |
|---|---|---|---|---|
| PP (56 mm L) | 0.32 | 0.0427 | 13.2 | 36.0 |
| PP (93 mm L) | 0.47 | 0.0426 | 9.1 | 6.0 |
| PS (98 mm L) | 0.39 | 0.0757 | 19.6 | 22.0 |
| PE (54 mm L) | 0.34 | 0.0654 | 19.4 | 32.0 |

**Note** Sulfur dioxide concentration of PCD monitoring station was 0.5 ppbv.
Median $SO_2$ concentration (3 days) on 31/ 03/ 07 – 02/ 04/ 07.
* Average of three replication

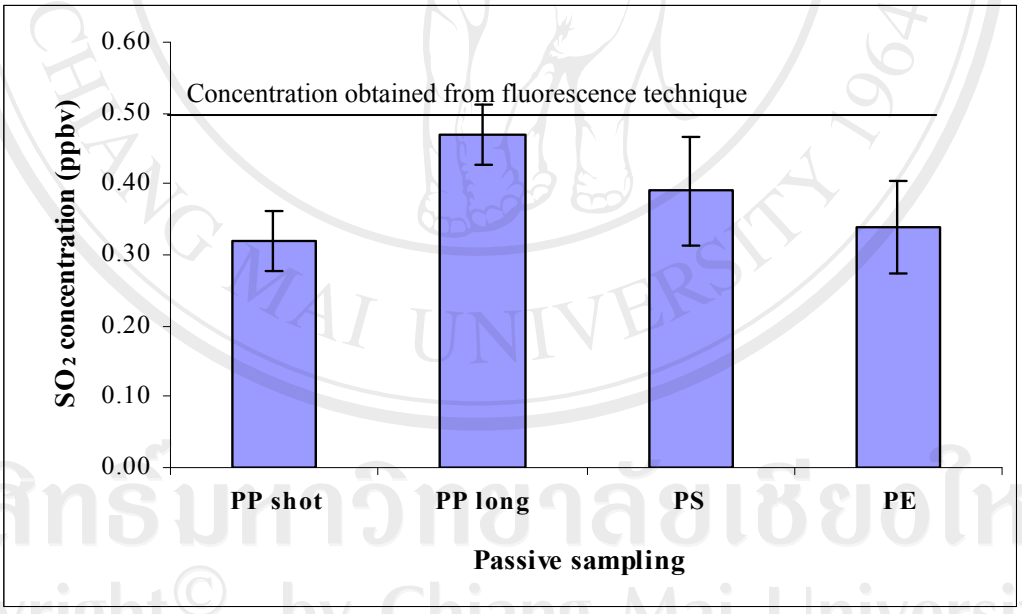



**Figure 3.13** Types of diffusion tube and compared with values from PCD monitoring station of sulfur dioxide

### 3.4.2 Testing of filtration of sulfite solution

The filtration was done by filtered sample solution through 0.45 μm cellulose filter with helping of glass syringe in order to get rid of contaminated particles prior to measurement with spectrophotometry at 550 nm. The result is shown in Table 3.14-3.15 and Figure 3.14. $SO_2$ concentrations obtained from filtered solutions were less than those from non-filtered solutions at every sampling duration (1, 3, 5 and 7 days starting from 29$^{th}$ March to 4$^{th}$ April 2007). Percent loss of $SO_2$ concentrations compared between filtrate and non filtrate was in a range of 4.4-18.2 % (Table 3.14). Moreover, comparison of $SO_2$ concentrations of filtered and non-filtered solutions using Paired samples T-test showed significant difference at 95% confidence level (see Appendix B).

$SO_2$ concentrations obtained from passive sampling and spectrophotometry were less than those from active sampling and fluorescent measurement within a range of 6.0-44.0 % as shown in Table 3.15. Considering of sampling period, 3 days sampling provided less percent difference of $SO_2$ concentrations with 18 % and 6 % of filtered and non-filtered solutions, respectively. Therefore, it can be concluded that 3 days sampling was an appropriate period for determination of $SO_2$ in ambient air and no filter process was required in sample preparation because no filtration provided less $SO_2$ loss (% difference) in comparison with $SO_2$ concentration obtained from fluorescence measurement.

**Table 3.14** $SO_2$ concentrations (ppbv) from filtrate and non filtrate process and percent loss

| $SO_2$ concentration | Sampling duration (days) | | | |
|---|---|---|---|---|
| | 1 (n=5) | 3 (n=5) | 5 (n=5) | 7 (n=5) |
| **No filtrate** | 0.45 | 0.47 | 0.34 | 0.44 |
| **filtrate** | 0.43 | 0.41 | 0.28 | 0.36 |
| **% loss from filtration** | 4.4 | 12.8 | 17.6 | 18.2 |

**Table 3.15** Filtered and non-filtered $SO_2$ concentrations from various sampling duration in comparison with fluorescent measurement

| $SO_2$ concentration | 1 days (n = 5) | | 3days (n = 5) | | 5 days (n = 5) | | 7 days (n = 5) | |
|---|---|---|---|---|---|---|---|---|
| | Filt | No filt | Filt | No filt | Filt | No filt | Filt | No filt |
| **Active Sampling and fluorescence (ppbv)** | 0.6 | | 0.5 | | 0.5 | | 0.6 | |
| **Mean (n=5) from passive sampler (ppbv)** | 0.43 | 0.45 | 0.41 | 0.47 | 0.28 | 0.34 | 0.36 | 0.44 |
| **SD of passive** | 0.10 | 0.09 | 0.06 | 0.04 | 0.05 | 0.04 | 0.04 | 0.04 |
| **%RSD** | 22.2 | 19.8 | 14.3 | 7.5 | 17.0 | 13.1 | 11.7 | 8.6 |
| **% Difference of active and passive** | 28.3 | 25.0 | 18.0 | **6.0** | 44.0 | 32.0 | 40.0 | 26.7 |

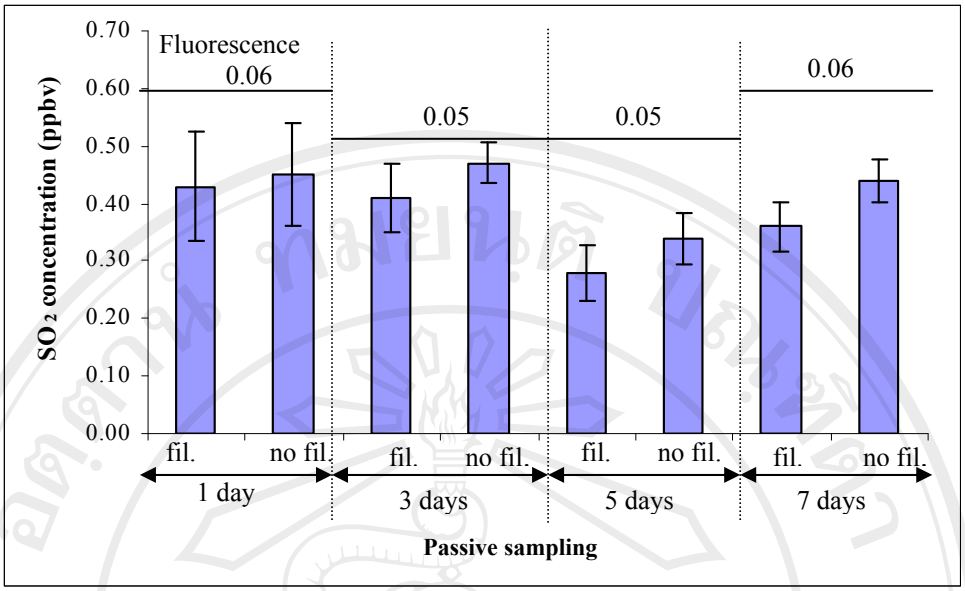



**Figure 3.14** Filtered and non-filtered $SO_2$ concentrations from various sampling duration in comparison with fluorescence measurement

### 3.4.3 Optimum sampling period of $SO_2$ in ambient air

$SO_2$ sampling duration was tested by exposure 7 sets (each set consist of 5 sampling tubes and 3 blank tubes) of diffusion samplers at the sampling site. The first set was collected at 24 hrs after exposure. After that every 24 hrs, one individual set was collected until the last set. The experiment has been complete within 7 days from 20 March to 26 April 2007. The result is shown in Table 3.16 and Figure 3.15. It was found that 3 days exposure gave the least percent difference (7.3%) of $SO_2$ concentration from passive and active sampling. Long sampling time affected to mass collected of the sampling due to stability and diffusion limits. The diffusion limit depends on the dimension of the sampler such as size of cross section (capacity of sorbent) which affect to rate of diffusion in long time exposure. Due to the capacity of sorbent and

diffusion length of the sampler were limited so that it reached the steady state at time 3 days. Then, even the samplers were continuously exposed, the rate of collection will continuously decrease after 3 days. Comparison of sampling period using One-Way ANOVA (CRD test) showed significant difference at 95% confidence level (see Appendix B). This means that 3 days exposure was appropriate for measurement of $SO_2$ in ambient air. This result is strongly agreed with the test kit of filtration process (3.4.2).

**Table 3.16** Sampling period and their percent difference for sulfur dioxide

| **$SO_2$ concentration** | **Sampling duration (days) (n = 5)** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **1 day** | **2 days** | **3 days** | **4 days** | **5 days** | **6 days** | **7 days** |
| **Mean from fluorescence (ppbv)** | 1.0 | 1.1 | 1.1 | 1.2 | 1.5 | 1.2 | 1.3 |
| **Mean from passive sampler (ppbv)** | 0.74 | 0.82 | 1.02 | 0.84 | 1.03 | 0.92 | 0.79 |
| **SD** | 0.12 | 0.07 | 0.06 | 0.08 | 0.12 | 0.13 | 0.15 |
| **% RSD** | 16.7 | 9.0 | 5.8 | 9.2 | 12.0 | 14.2 | 19.1 |
| **%Difference** | 26.0 | 25.4 | **7.3** | 30.0 | 31.3 | 23.3 | 39.2 |

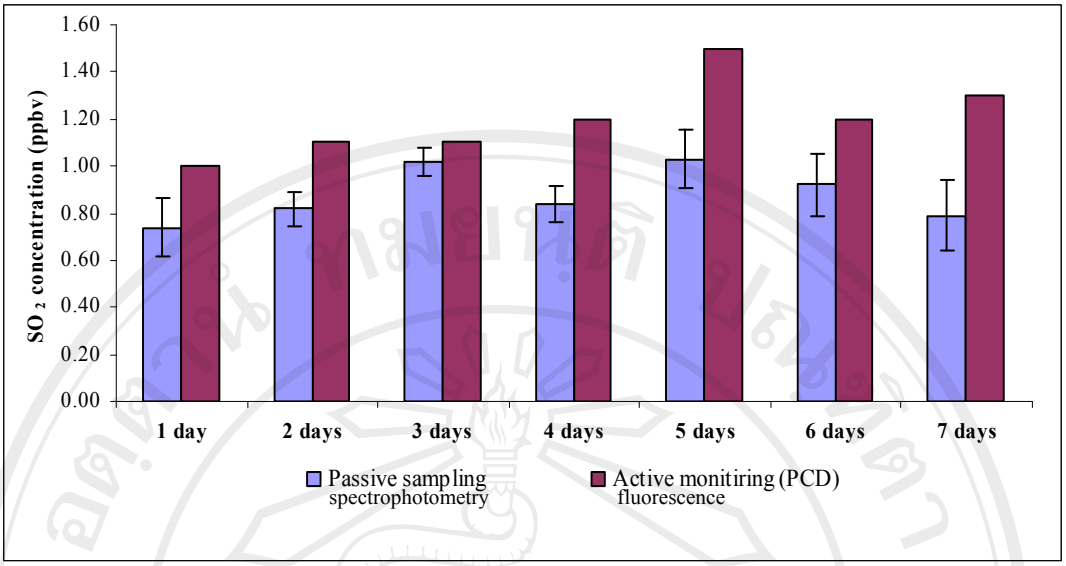



**Figure 3.15** Sampling period of sulfur dioxide in ambient air

### 3.5 Construction of $SO_2$ test kit and reliability testing

The $SO_2$ test kit was designed and constructed (Figure 3.16). 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 kit reagents was studied. The kit was tested by comparing with the PCD fluorescence technique. The questionnaire for survey research was tested. The results of such investigation are about to be discussed in the following sections.


**Figure 3.16** Sulfur dioxide test kit

### 3.5.1 Construction of sulfur dioxide standard color chart

According to the results obtained in earlier sections, the optimal composition of reagents to be used for determination of sulfur dioxide is 1 ml of standard sulfite in tetrachloromercurate added with 100 µl of 0.6%sulfamic acid, 300 µl of buffer formaldehyde solution and 500 µl of pararosaniline solution. The mixed solution was left for 10 min and $SO_3^{2-}$ specific colors were formed as shown in the Figure 3.17. It was found that the color can be categorized based on its visual distinguish ability among the different concentrations. The solution without any sulfite (0 mg/l) under the optimal condition was the original pale magenta color. Upon the presence of sulfite, the color of the solution was for magenta 0.006 mg/l sulfite whereas deep magenta was 0.1 mg/l $SO_3^{2-}$ solution. A distinguishable pale purple color also resulted was 0.2 mg/l $SO_3^{2-}$ solution but the 0.4 mg/l $SO_3^{2-}$ concentration produced purple color. The color of solution was deep purple for 0.8 mg/l. Finally, the

1.2 mg/l $SO_3^{2-}$ concentration was violet color. However, the concentration of sulfite was higher than 1.2 mg/l the color has a deep shade of violet. The standard reference color chart was constructed by Adobe Illustrator program, established the relationship between the amounts of sulfite standard solution with color chart. It can be divided into 6 categories as shown in the Figure 3.18. All these categories belong to the solution with different sulfite concentration levels. Unit conversions of $SO_2$ concentration from unit of part per million (ppm) was converted to part per billion by volume (ppbv) as shown in an appendix A (L = 0.071 mm, A = 0.000172 m, t = 259200 sec, D = 1.36 x $10^{-5}$ $m^2s^{-1}$(25 ◦C, 1 atm), molecular volume = 24.46 (25 ◦C,1 atm), Mw = 64).

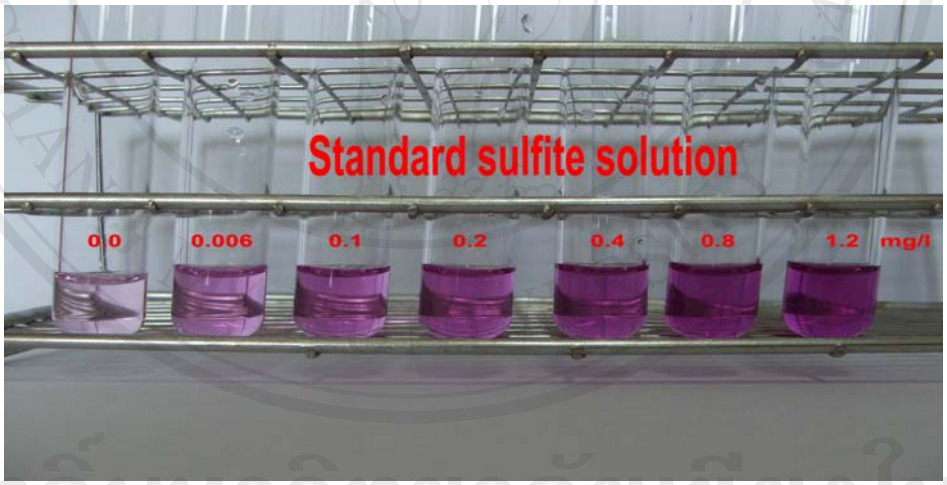



**Figure 3.17** Visual colors of sulfite solutions at different concentrations

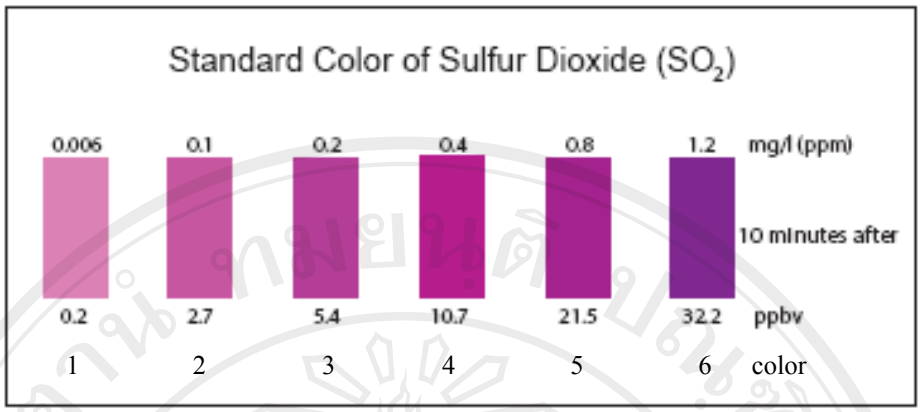



**Figure 3.18** Standard reference color chart of sulfur dioxide; 1 = magenta, 2 = deep magenta, 3 = pale purple, 4 = purple, 5 = deep purple and 6 = violet

### 3.5.2 Stability of test kit reagent

The stability of test kit reagents such as tetrachloromercurate, pararosaniline, sulfamic acid, and buffer formaldehyde were studied by measuring the absorbance of the color developed every week up to 16 weeks as shown in Table 3.17. It can be stored for at least 13 weeks at room temperature as shown in Figure 3.19 where % recoveries versus time (week) were presented.

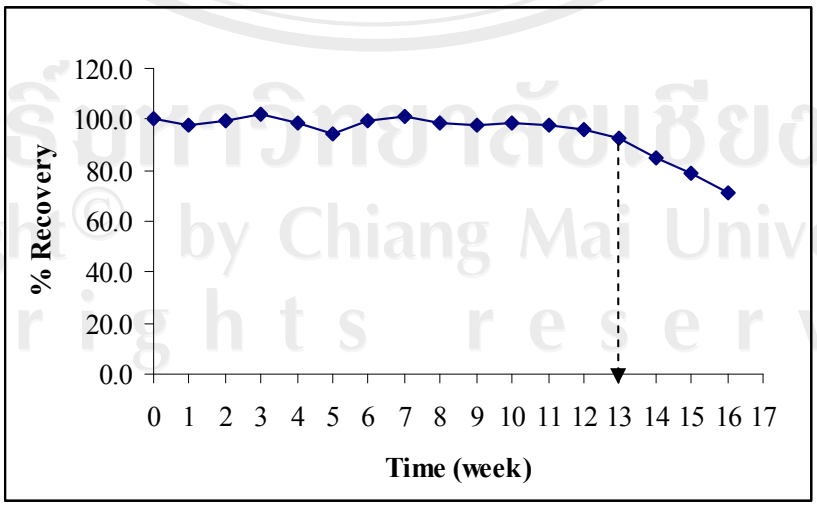



**Figure 3.19** Stability of test kit reagents

**Table 3.17** Stability study of test kit reagents

| Time (week) | Absorbance (n = 3) | Mean Concentrations (mg/l) | % Recovery |
|---|---|---|---|
| 0 | 0.2019 | 0.104 | 100 |
| 1 | 0.1978 | 0.101 | 98 |
| 2 | 0.2010 | 0.103 | 100 |
| 3 | 0.2056 | 0.106 | 102 |
| 4 | 0.1997 | 0.102 | 99 |
| 5 | 0.1906 | 0.097 | 94 |
| 6 | 0.2015 | 0.103 | 100 |
| 7 | 0.2038 | 0.105 | 101 |
| 8 | 0.1987 | 0.102 | 98 |
| 9 | 0.1973 | 0.101 | 98 |
| 10 | 0.1989 | 0.102 | 98 |
| 11 | 0.1976 | 0.101 | 98 |
| 12 | 0.1950 | 0.100 | 96 |
| 13 | 0.1872 | 0.095 | 92 |
| 14 | 0.1734 | 0.088 | 85 |
| 15 | 0.1618 | 0.082 | 79 |
| 16 | 0.1466 | 0.073 | 71 |

### 3.5.3 Determination of sulfur dioxide in air by $SO_2$ test kit in comparison with spectrophotometric method and fluorescent techniques

After the exposure, the color developed by each sample was compared to the standard color of sulfur dioxide chart 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 and its mean value was then compared to the value obtained by measuring with spectrophotometer and PCD monitoring station. It can be seen from the Table 3.18 that the results determined by the test kit are well agreeable to the ones from the spectrophotometric measurements which proves that the test kit is reliable to be used for determining the sulfur dioxide at low level in air sample. EPA's health-based national air quality standard for $SO_2$ is 0.03 ppm (measured on an annual arithmetic mean concentration) and 0.14 ppm (measured over 24 hours). Pollution Control Department air quality standard for $SO_2$ is 0.04 ppm or 0.1 $mg/m^3$ (1 year), 0.12 ppm or 0.30 $\mu g/m^3$ (24 hours) and 0.3 ppm or 780 $\mu g/m^3$ (1 hours).

**Table 3.18** Concentration of sulfur dioxide determined by sulfur dioxide test kit compared with the spectrophotrometric method and fluorescence

| Sampling date | Concentration of sulfur dioxide (ppbv) | | |
|---|---|---|---|
| | Spectrophotometry (n = 5) | Fluorescence | $SO_2$ Test kit (n = 5) |
| 10-12 September 2007 | 0.96 | 1.1 | 0.2 – 2.7 |
| 22-24 September 2007 | 0.87 | 1.0 | 0.2 – 2.7 |
| 28-30 September 2007 | 1.03 | 1.1 | 0.2 – 2.7 |

### 3.5.4 Survey questionnaires for reliability in estimation of $SO_2$ content

In survey questionnaires, the researcher randomly chose 100 students in Chemistry Department, Faculty of Science, Chiang Mai University as a representative of students 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 as shown Appendix C. Questionnaires is a method of data collection by compare the developed color in a glass tube with color in a standard color chart and match the nearest color indicates the measured value of the sample. When the developed color lies between 2 standard colors, $SO_2$ value will be reported in a range of these two colors. The answers the respondent makes are onto a permanent medium and brought into analysis. The result is shown in Table 3.19 and Figure 3.20. Analysis of questionnaires has yielded encouraging facts, which were 68.6 %, 44.3% and 68.7% for concentrations in a range 0.006-0.2, 0.3-0.6 and 0.8-1.2 mg/l, respectively. The overall yielded encouraging fact 62.0 %. However, there are some problems in estimating $SO_2$ content by the untrained and uninitiated, especially from 0.30, 0.40 and 0.6 mg/l. This problem lessens with experience and training.

**Table 3.19** Readable concentration of $SO_2$ from survey questionnaires of 100 students in Chemistry Department, Chiang Mai University

| Number of tube | Prepared $SO_2$ concentration (mg/l) | Readable concentration of $SO_2$ (mg/l) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.006 | 0.006-0.1 | 0.1 | 0.1-0.2 | 0.2 | 0.2-0.4 | 0.4 | 0.4-0.8 | 0.8 | 0.8-1.2 | 1.2 |
| 1 | 0.006 | 95* | 5 | - | - | - | - | - | - | - | - | - |
| 2 | 0.05 | 29 | 63* | 8 | - | - | - | - | - | - | - | - |
| 3 | 0.10 | 3 | 10 | 75* | 8 | 4 | - | - | - | - | - | - |
| 4 | 0.15 | - | - | 18 | 56* | 22 | 3 | 1 | - | - | - | - |
| 5 | 0.20 | - | - | 2 | 22 | 54* | 16 | 6 | - | - | - | - |
| 6 | 0.30 | - | - | - | - | 20 | 43* | 30 | 4 | 3 | - | - |
| 7 | 0.40 | - | - | - | - | 4 | 8 | 47* | 33 | 7 | 1 | - |
| 8 | 0.60 | - | - | - | - | - | - | 7 | 43* | 37 | 12 | 1 |
| 9 | 0.80 | - | - | - | - | - | - | - | 7 | 54* | 33 | 6 |
| 10 | 1.00 | - | - | - | - | - | - | - | 1 | 6 | 65* | 28 |
| 11 | 1.20 | - | - | - | - | - | - | - | - | 4 | 9 | 87* |

The highest chosen value is marked with asterisk

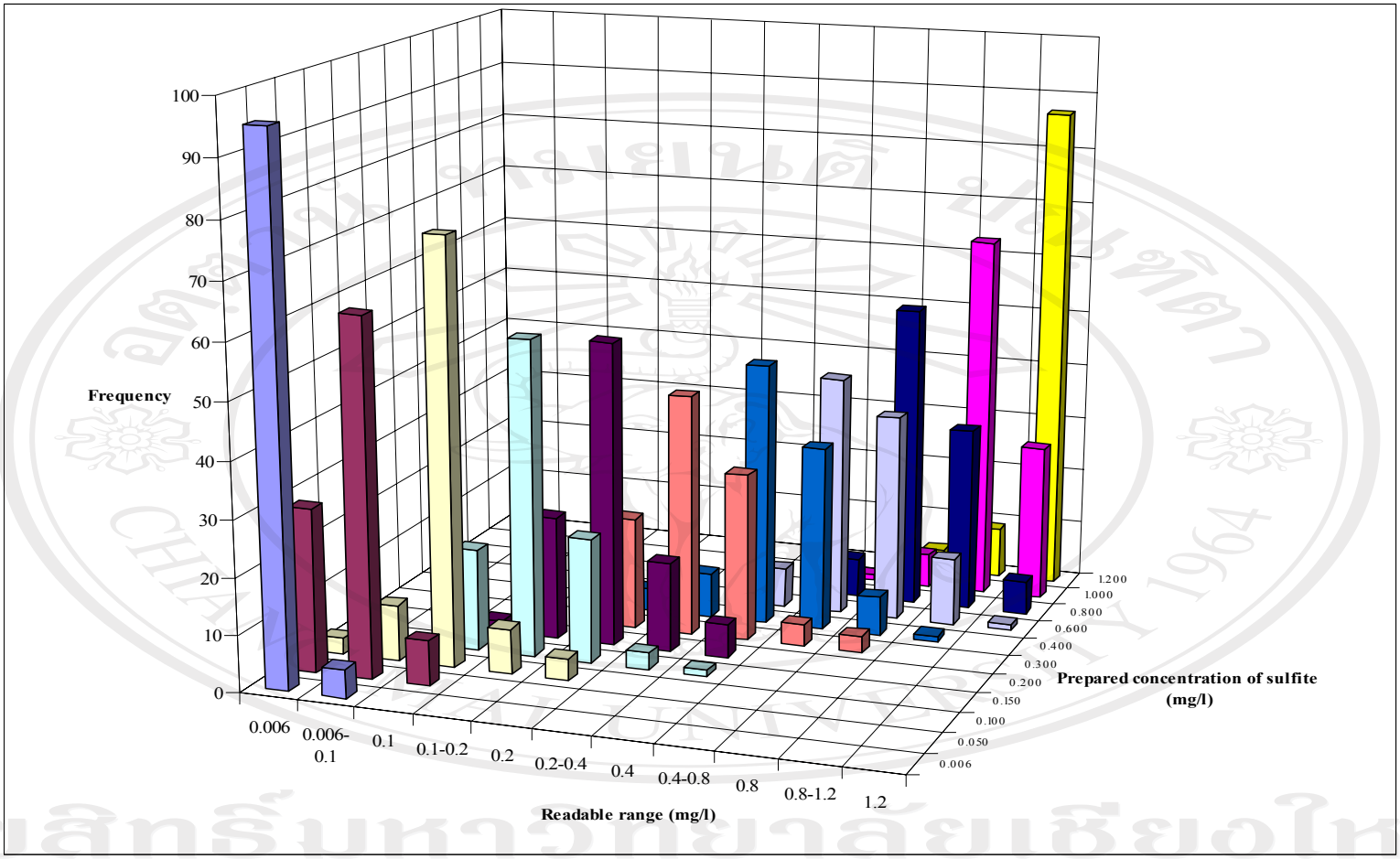



**Figure 3.20** Readable concentration of $SO_2$ from survey questionnaires of 100 students in Chemistry Department, Chiang Mai University. (Colors presented in this graph have no relation to sulfite concentration.)