CHAPTER 2

EXPERIMENTAL

2.1 Apparatus

1. Polyethylene tubes, DTU, Denmark
2. Polysyrene tubes, OV chemicals Co., Ltd., Thailand
3. Filter papers (Whatman no. 1, 6, 40 and glass fiber filter GF/A), Whatman International Ltd., England
4. Polypropylene boxes, Raaco, Denmark
5. Syringe filter, 0.45 μm cellulose acetate, Chrom Tech, Inc., England
6. Membrane filter, 0.45 μm cellulose acetate, Sartorius, Germany
7. Vacuum pump, Water associate, USA
8. Ultrasonic bath, Transsonic Digital S, Elma, USA
9. Ultrasonic bath, model 8891, Cole-Parmer Instrument Co., USA
10. Analytical balance, Sartorius Basic BA 210s, Germany

2.2 Chemicals

1. Triethanolamine ($C_6H_{15}NO_3$, 149.19), 99%, BDH Chemicals Ltd., England
2. Sodium iodide (NaI, 149.89), 99%, Carlo Erba, Italy
3. Sodium hydroxide (NaOH, 40.00), Lab scan, Ireland
4. Glycerin ($C_3H_8O_2$, 92.09), 99.5%, Carlo Erba, Italy
5. Potassium iodide (KI, 166), 99-105%, AJAX, Australia
6. Sodium arsenite ($NaAsO_2$, 129.90), 98%, Fisher, USA

7. Ethylene glycol ($HOCH_2$, 62.07), 95%, M&B, England
8. Methanol (CH_3OH, 32.04), 99.9%, Carlo Erba, Italy
9. Sodium carbonate (Na_2CO_3, 105.99), 99.7%, Carlo Erba, Italy
10. Sodium bicarbonate ($NaHCO_3$, 84.01), 99.5%, Merck, Germany
11. Sulfuric acid (H_2SO_4, 98.08, D=1.84 kg/l), 98.0%, BDH Chemicals Ltd., England
12. 1,2-di-(4-pyridyl)ethylene, Merck, Germany
13. 3-methyl-2-benzothiazolinone hydrazone hydrochloride (3-MBTH), Merck, Germany
14. Sodium nitrite ($NaNO_2$, 69.00), 99-100.5%, Merck, Germany
15. N-(1-Napthyl) ethylenediamine dihydrochloride ($C_{12}H_{14}N_2 \cdot 2HCl$, 259.20), purum, Fluka, Switzerland
16. Sulfanilamide ($C_6H_2N_2O_2S$, 172.21), >98%, purum, Fluka, Switzerland
17. Phosphoric acid (H_3PO_4, 98), 85%, Merck, Germany
18. Pyridyl-4 aldehyde, Aldrich, Germany
19. Potassium chloride (KCl, 74.55), Carlo Erba, Italy
20. Sodium chloride (NaCl, 58.44), Carlo Erba, Italy
21. Mercuric chloride ($HgCl_2$, 271.49), Carlo Erba, Italy
22. Nitrate standard solution (1000 ppm), Merck, Germany
23. Sulfate standard solution (1000 ppm), Merck, Germany
24. Sodium sulfite (Na_2SO_3, 126.02), 98%,Carlo Erba, Italy
25. Sulfamic acid (HSO_3NH_2, 97.08), Carlo Erba, Italy
26. Formaldehyde (HCHO, 30.02), BDH Chemicals Ltd., England

2.3 Instruments

1. Metrohm Ion Analysis, Switzerland
    - Anion separation column ; Metrosep A Supp 4-250
    - Anion guard column ; Metrosep A Supp 4/5 guard
    - Interface ; 762 IC interface
    - Detector ; 732 IC detector
    - Suppressor ; self generator suppressor
    - 752 unit pump for H_2SO_4 to suppressor
    - 709 IC pump for mobile phase
    - IC net 2.3 program
2. Spectrophotometer, Perkins Elmer Lambda 25

2.4 Passive sampler

2.4.1 Configuration of passive samplers

A passive sampler used in this work consists of a diffusion tube containing sorbent impregnated with absorbing solution. The diffusion tube is mounted vertically, the opened end upright, in the protective shielding to protect the effects of meteorologicals as shown in Fig 2.1.

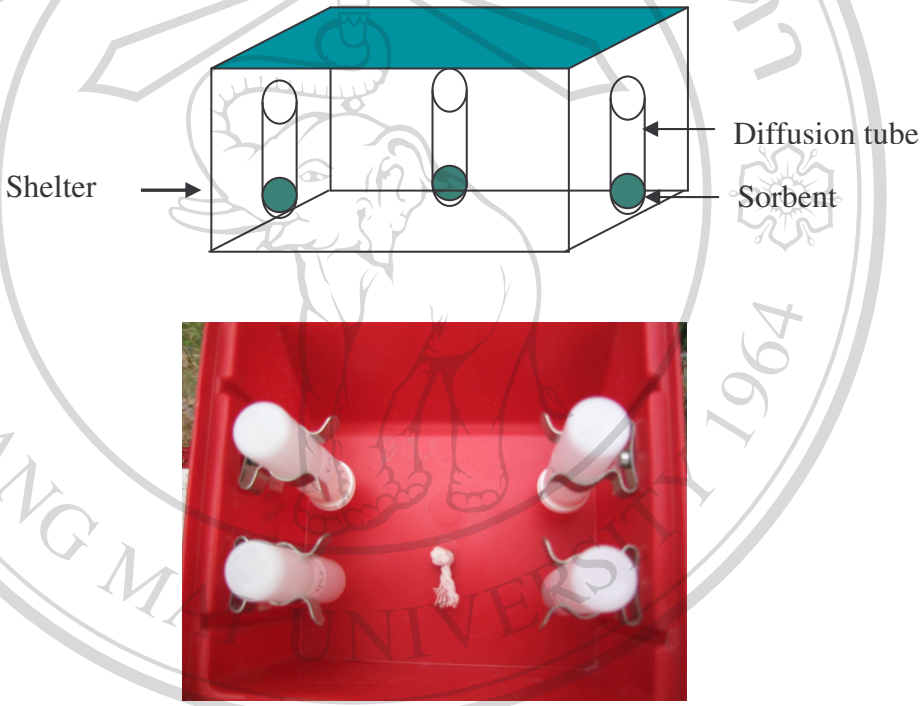

Fig 2.1 The configuration of passive sampler (a) and the gas diffusion pathway (b)

2.4.2 Methodology

A) Preparation of passive samplers

A-1) Diffusion tube

A diffusion tube has one opened end, which can be closed with cap. The diagram of the tube is shown in Fig 2.2.

To minimize background contamination, all the components of a diffusion tube were cleaned up by 30 minutes sonicating and rinsed twice with milli-Q water before drying at 60 ^{o}C overnight. The exposed tube can be reused after cleaning following the above instruction.

A-2) Sorbent

The sorbent used in this experiment was the filter paper because of its appropriate properties such as porosity and it was cost effective.

The paper was cut with a scissor in a circle with a same size of an inner diameter of the diffusion tube. The sorbents (cut filter paper) were cleaned up by 15 min sonicating in milli-Q water and 2 times rinsing. Then the sorbent was air-dried at 60^{o}C overnight. After cooling in desiccates, it was placed at the bottom of the tube. Preferably volume of a absorbing solutions was then added on the filter paper. The passive sampler must be capped and stored in a refrigerator until exposure.

B) Sampling procedure

Sampling is started by removal of the caps out. The samplers are exposed at the sampling site allowing unrestricted movement of air around

them. They were fixed by a clip to stake at about 1.5 meters above the ground. In each experiment, samplers are simultaneously exposed with unopened samplers being used as blanks. The accurately exposure time was recorded. The samplers and blanks were stored in a refrigerator prior to analysis to minimize background contamination.

C) Shipment

The exposed passive samplers for a period of time were collected and immediately closed with caps. The time of exposure was recorded. The samplers were kept in the airtight container along transportation and stored in refrigerator until analysis.

D) Extraction process

Extraction is an important step that should be optimized because it leads to under- or over-estimation of pollutants. Before extraction process, all of diffusion tubes were dipped in deionized water to remove the dirty or any contaminate on outside of tube.

Extraction conditions have been optimized by spiking known amount of standard solution onto the sorbent placed in diffusion tube. Both in terms of extraction techniques and time have been compared. The extraction temperature was controlled at about 25-29 ^{o}C to avoid the lost of products.

The extraction efficiency was calculated in term of percent recovery as shown in equation 2.1.

$$\%\text{Recovery} = \left(\frac{\text{Measured concentration}}{\text{Initial concentration}} \right) * 100 \qquad \text{.....(2.1)}$$

E) Sample preparation

After extraction process, the solution was filtered through 0.45 μm cellulose filter with helping of glass syringe in order to get rid of contaminated particles, which could disturb measurement.

F) Calculation of pollutant gases in ambient air

Concentrations of pollutant gas presented in ambient air were calculated from the value of gases found in diffusion tube following the Fick's law (equation 1.4). The unit of microgram per cubic meter ($\mu g/m^3$) was converted to part per billion volume (ppbv) as shown in an appendix A.

2.5 Development of Passive samplers

NO_2 was selected as the representative of target pollutant gases to indicate optimum conditions because its concentration in an ambient air was relatively high. The first absorbing solution used for this test was 20% Triethanolamine (TEA) because of its high efficiency (Carolyn, *et al*., 2000).

2.5.1 Comparison of diffusion tubes

Two types of diffusion tube including polyethylene (PE) and polystyrene (PS) were used for NO_2, SO_2 and O_3 sampling. Both types of tube have the polyethylene cap. They have the same length (5.40 cm), but different inner diameters as shown in Fig 2.2. Their efficiencies have been compared. The preparation of diffusion tube was described in section 2.4.2.

Glass fiber filter (GF/A) were used as the sorbent. It was cut in a circle to fit into the inner diameter of the diffusion tube. The diffusion tubes as well as the sorbent must be carefully cleaned before setting up the passive sampler. The sorbents was allowed to reach bottom of the tube and impregnated with 50 µl of 20% TEA. The passive sampler consisted of 5 samplers and 3 blanks. They were exposed as described in section 2.4.2 to collect NO_2 from indoor (in the laboratory) and outdoor at the monitoring station of Pollution Control Department (Chiang Mai Governmental Office Center).

After 1 week exposure all diffusion tubes were collected. An extraction was done by adding 4 ml of milli-Q water into the diffusion tubes and then sonicating for about 10 min. The extractant was filtered and determined for NO_2 concentration by IC.

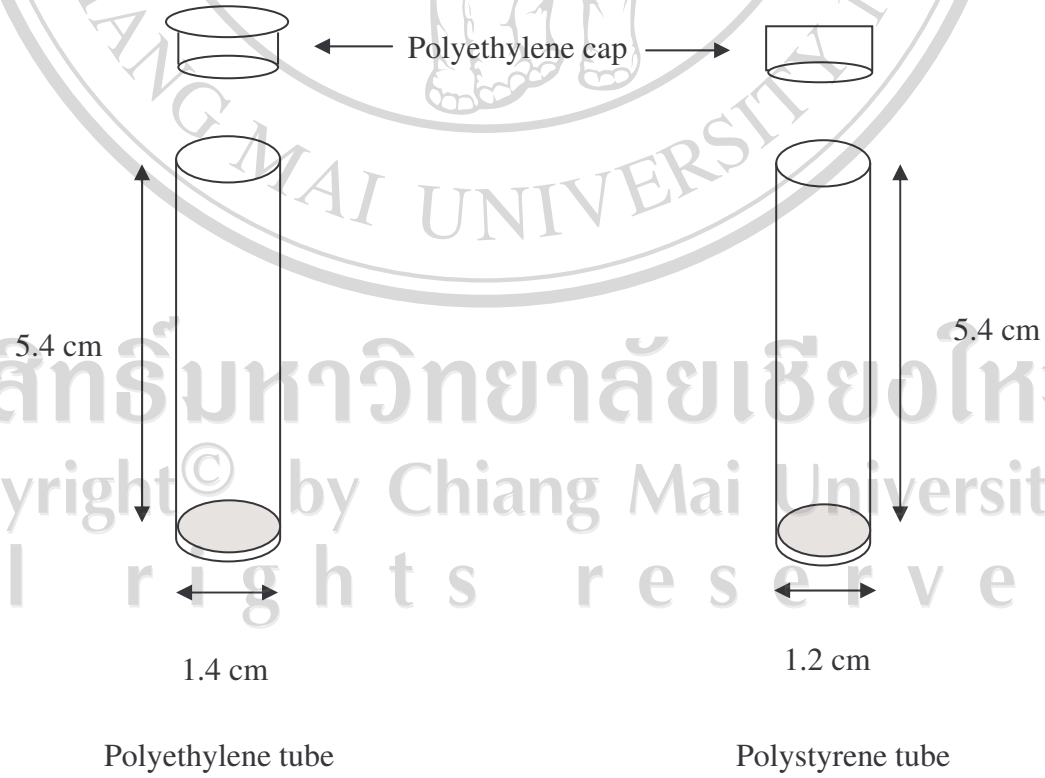

Fig 2.2 Diagram of diffusion tubes

2.5.2 Comparison of sorbent

Four types of sorbent including cellulose filter Whatman no.1, 6, 40 and glass fiber filter (GF/A) have been investigated to compare their absorptivities. The PE tube was used as a diffusion tube and 20% TEA was used as an absorbing solution. Sorbents were prepared as the method mentioned in section 2.4.2. After that each type of the sorbent was allowed to place inside at the bottom of 8 PE tubes (3 tubes were capped and set as blank, whereas another 5 tubes were uncapped and set as collecting samplers). All of sorbent were impregnated with 50 µl TEA. Then all of diffusion tubes were mound in the protective shielding by fixing the opened end upright and exposed for 1 week in the laboratory at a height about 1.70 meters above the ground.

After 1 week exposure all diffusion tubes were collected. The extraction was done by adding 4 ml of milli-Q water into the tubes and then sonicating for about 10 min. The extractant was filtered and determined NO_2 concentration by IC.

2.6 Analysis of NO_2, SO_2 and O_3 by ion chromatography (IC)

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.

2.6.1 Optimization of IC

The mobile phase composition and its flow rate have been optimized. The first mobile phase composition was 1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3.

The second was 2.0 mM $NaHCO_3$/2.4 mM Na_2CO_3 in 5% acetone. The maximum pressure of the separating column must not be higher than 12 Mpa and the maximum flow rate should not be over 2.0 ml/min. In this work, the mobile phase flow rate between 0.8 to 1.5 ml/min was tested. The optimum mobile phase and its flow rate were obtained based on the resolution (Rs) of Chloride (Cl^-) and nitrite (NO_2^-) peaks because they were very close to each others.

A) Preparation of mobile phase

A-1) ***1.7 mM $NaHCO_3$/1.8 mM Na_2CO_3***

Stock solution (170 mM $NaHCO_3$/180 mM Na_2CO_3) was prepared by dissolving 1.4282 g $NaHCO_3$ and 1.9078 g Na_2CO_3 in milli-Q water and diluting to 100 ml.

A-2) ***2.0 mM $NaHCO_3$/2.4 mM Na_2CO_3***

Stock solution (200 mM $NaHCO_3$/240 mM Na_2CO_3) was prepared by dissolving 1.6802 g $NaHCO_3$ and 2.5440 g Na_2CO_3 in milli-Q water and diluting to 100 ml.

Each mobile phase was then prepared by pipetting 10 ml of the above stock solution and diluting to 1 liter with milli-Q water. The solution was filtered through a 0.45 μm cellulose acetate membrane (Millipore) to remove micro-particles. The solution was degassed in an ultrasonic bath for 15 min every day before use in order to remove dissolved gases.

B) Preparation of 100 mM H_2SO_4 for suppressor

5.45 ml of concentration H_2SO_4 was pipetted into 1 liter volumetric flask which contained small amount of milli-Q water. The volume was then adjusted with milli-Q water.

2.6.2 Precision of ion chromatograph

A) Repeatability of ion chromatograph

The repeatability was the results of standard deviation of measurements repeated by the same analyst on the same instrument within a shot time period. The repeatability was checked by 6 times continuously injection of a 0.2 ppm mixed standard solution (NO_2^-, SO_4^{2-} and NO_3^-) into ion chromatographic system under the optimum conditions.

B) Reproducibility of ion chromatograph

The reproducibility was checked by injecting a 0.2 ppm mixed standard solution of NO_2^-, SO_4^{2-} and NO_3^- into the optimum conditions of ion chromatographic system for 3 continuous days. The results of the reproducibility were estimated by standard deviation and the related values.

2.7 Optimization of extraction process for NO_2, SO_2 and O_3 determination by ion chromatography

Extraction conditions have been optimized by spiking the 20 µl of each 100 ppm of NO_2^-, SO_4^{2-} and NO_3^- standard solution onto the sorbent (Whatman GF/A), which was placed in diffusion tube and then leaved in desiccater until dry. After that 4 ml of milli-Q water was then added. Both in term of technique

(comparing between using and non using ultrasonicator) and time consuming have been investigated. Concentrations of NO_2^-, SO_4^{2-} and NO_3^- after extraction were determined by IC. The extraction process for NO_2 was also applied for determination by spectrophotometry.

A calibration curve was made by plotting the different concentrations of NO_2^-, SO_4^{2-} and NO_3^- mixed standard solution versus their peak areas.

2.8 Detection limit (DL) of for analysis methods

2.8.1 Detection limit for ion chromatograph (applied from Taylor, 1987)

The detection limit was checked by injecting a 0.2 ppm mixed standard solution of NO_2^-, SO_4^{2-} and NO_3^- into ion chromatographic system with the optimum conditions. The detection limit was obtained from 3 times of standard deviation of measurements repeated 5 times by the same analyst on the same instrument.

2.8.2 Detection limit for spectrophotometer

The detection limit was obtained by the use of linearity curve. According to the IUPAC definition, DL is the amount or concentration (X) resulting in an analyte signal (measured value) Y.

$$Y = Y_B + 3S_B \quad \text{.....(2.2)}$$

where S_B is the blank signal standard deviation with the related blank signal mean value, Y_B.

Linear regression analysis used for validation of linearity is made under the assumption that the y-values are normally distributed around the regression line with a standard deviation $S_{y/x}$ (see Appendix B). Provided this assumption is valid, $S_{y/x}$ may therefore be used instead of S_B in the equation for calculation of DL. As estimate for Y_B may also be obtained from the regression line as the Y-axis intercept value. Interesting these values in equation 2.2 and combining with the linear equation Y = a+bX, yield:

$$DL = [a + (3*Sy/x - a)] / b = [3*Sy/x] / b \quad \ldots\ldots\ldots(2.3)$$

Where b is the slope and a is the intercept of regression line with the y-axis. If this approach to be used, the factor of curvature, n, for the regression line should be between 0.9-1.0. (Miller and Miller, 1988)

This method was also applied for ion chromatographic analysis system.

2.9 Determination of Nitrogen dioxide (NO_2)

2.9.1 Selection of absorbing solution

A) Preparation of absorbing solution

A-1) ***20% v/v Triehanolamine (TEA);*** 20 ml of TEA was accurately pipetted into 100 ml volumetric flask and adjusted to volume with milli-Q water.

A-2) ***12% TEA + 4% glycerin*****;** 12 ml TEA and 4 ml glycerin were accurately pipetted into 100 ml volumetric flask then diluted to volume with milli-Q water.

A-3) ***KI/NaAsO$_2$/ ethylene glycol/ NaOH in Methanol.*** 10 g Potassium iodide (KI), 1 g of sodium arsenite ($NaAsO_2$), 1 g sodium hydroxide (NaOH) and 5 g ethylene glycol were dissolved in 84 ml ethanol.

A-4) ***Methanolic NaI/ NaOH*****;** 3.95 g sodium iodide (NaI) and 0.44 g sodium hydroxide (NaOH) were dissolved in methanol and adjust to volume 50 ml.

B) Sampling

The PE tube and GF/A were used for setting up a passive sampler. The diagram of step of NO_2 determination is shown in Fig 2.4.

The 50 µl of absorbing solution was added onto sorbent. Each type of absorbing solution (section 2.9.1) consisted of 5 and 3 replicates for collecting samplers and blanks, respectively. They were exposed in the laboratory for 1 week.

C) Analysis of NO_2

After one week indoor exposure, NO_2 was extracted (section 2.7) and were then determined by IC and spectrophotometry.

The diagram of steps of selection absorbing solution for NO_2 is shown in Fig 2.3

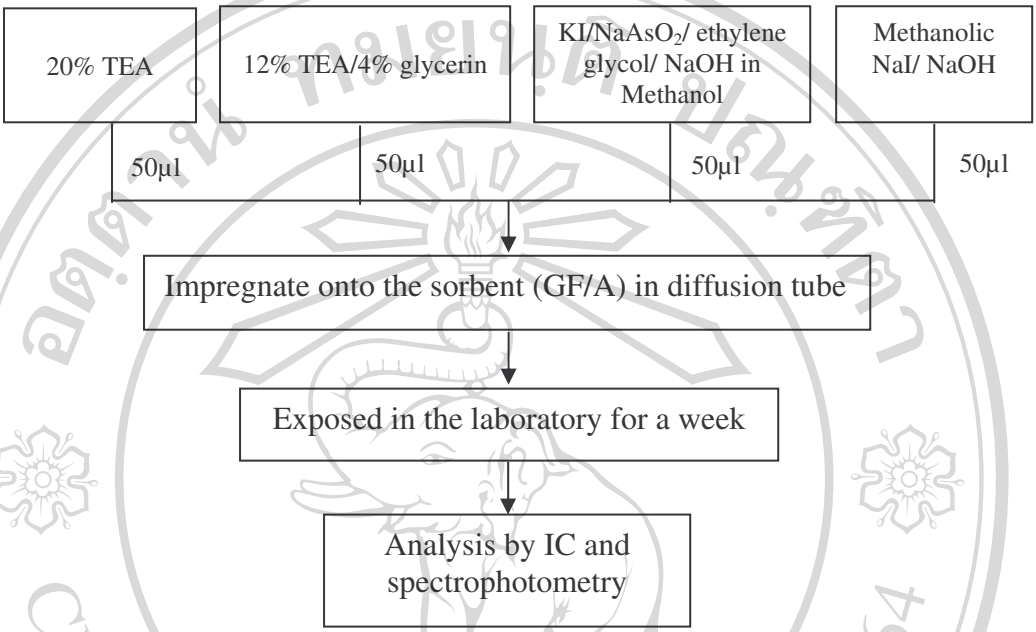

Fig 2.3 Diagram of steps of selection absorbing solution for NO_2

2.9.2 Determination of NO_2 by ion chromatography

NO_2 was determined by IC under the optimum conditions. The mobile phase was 1.7 mM $NaHCO_3$/ 1.8 mM Na_2CO_3/ with the flow rate of 1.0 ml/min. A calibration curve was made by plotting the different concentrations of NO_2^- standard solution diluted with milli-Q water versus the peak areas.

2.9.3 Determination of NO_2 by spectrophotometry

The Saltzmann reagent is prepared by adding 8 ml phosphoric acid to 500 ml milli-Q water. 8.0 g sulphanilamide and 0.2 g N-(1-Naphtyl) ethylenediamine dihydrochloride (NEDA) were dissolved with milli-Q water

and adjusted to 1 liter. The reagent was stored in a refrigerator till the time of analysis. Extractant and Saltzmann reagent (2:1) was read at 542 nm using a 1 cm optical path length cell after 10 minutes mixing. Before taking the measurement, spectrophotometer was zeroed against the reagent blank solution to avoid the interferences from impurities in reagents. The nitrite in solution diazotises the sulphanilamide and the diazonium salt formed couples with the NEDA to form a purple azodye.

A calibration curve is made using NO_2^- standard solution diluted with milli-Q water into different concentrations. Standard solutions are first measured as the same way as sample. All of standard solutions must be freshly prepared.

A calibration curve was made by plotting the different concentrations of NO_2^- standard solution versus the peak areas.

2.9.4 Study of sampling period for NO_2

Ranges of exposure were tested in order to compare the level of NO_2 detected. Exposure duration including 1,3,5 and 7 days was tested under the same conditions and locations. 3 respected to 5 replicates were used as blanks and collecting samplers in each exposure range.

The samplers were exposed at PCD monitoring site (Chiang Mai Governmental Office Center) and collected after the test duration of each set was completed. After that NO_2 was extracted and determined by IC.

2.10 Determination of Sulfur Dioxide (SO_2)

2.10.1 Selection of absorbing solution for determination by ion chromatography

A) Preparation of absorbing solution.

Four different absorbing solution were tested and compared.

A-1) ***20% Triethanolamin (TEA)*** see section 2.9.1.

A-2) ***12% TEA + 4% glycerin*** see section 2.9.1.

A-3) ***2 M Sodium carbonate (Na_2CO_3);*** 21.1980 g of Na_2CO_3 was dissolved in milli-Q water and adjusted to volume in volumetric flask 100 ml.

A-4) ***Methanolic NaOH*;** 0.5 g NaOH was dissolved in small amount of milli-Q water. Then this solution was diluted with methanol in 50 ml volumetric flask.

B) Sampling

A 50 µl of each absorbing solution was added onto glass fiber filter GF/A and placed in the PE tube. Each set consists of 3 and 5 replicates of blanks and collecting samplers, respectively. All of passive samplers were exposed in the laboratory for a week to determine indoor SO_2. After getting optimum absorbing solution, it was applied for trapping outdoor SO_2. Data obtained from IC analysis was compared with spectrophotometry and PCD data.

C) Analysis of SO_2

After 1 week exposure, SO_2 was extracted and determined by IC. Data obtained from IC were compared with spectrophotometry and PCD data.

The diagram of steps of selection absorbing solution for SO_2 is shown in Fig 2.4

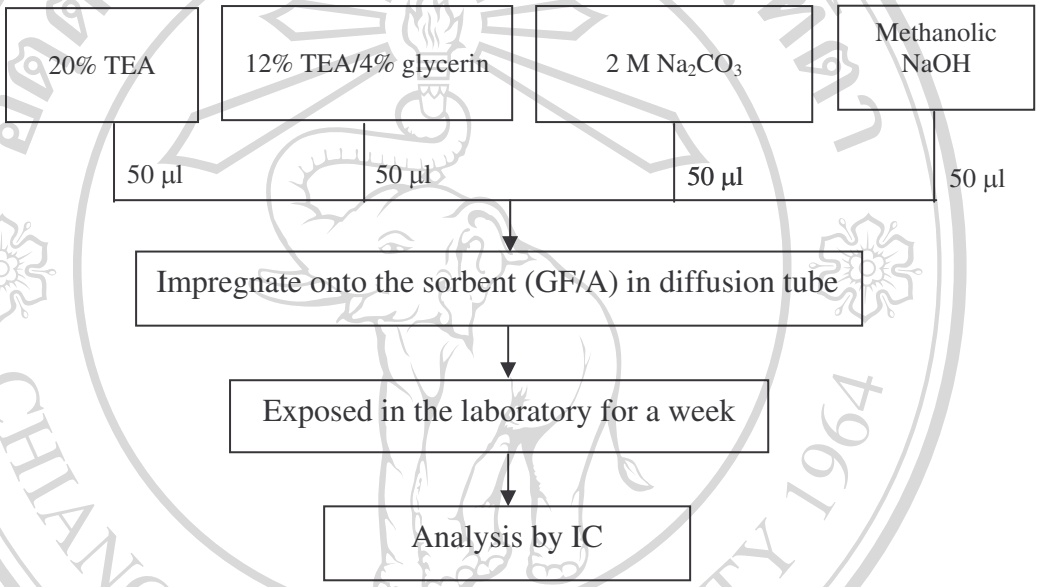

Fig 2.4 Diagram of steps of selection absorbing solution for SO_2

2.10.2 Determination of SO_2 by ion chromatography

SO_2 was determined by IC using the same conditions which as NO_2 determination. A calibration curve was made by plotting the different concentration of SO_4^{2-} standard solution diluted with milli-Q water versus the peak areas.

2.10.3 Optimization of absorbing solution for determination by spectrophotometry

Tetrachloromercurate (TCM; $HgCl_4$) was used for trapping SO_2 in an ambient air. The SO_2 presented in the ambient air reacts with TCM and forms 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 (U.S.Environmental Protection Agency; USEPA).

A) Preparation of absorbing solution.

Tetrachloromercurate (0.04 M Potassium tatracholomercurate) 1.086 g mercuric chloride, 0.0066 g EDTA and 0.6 g potassium chloride were dissolved in milli-Q water and adjusted volume to 100 ml in volumetric flask. The pH of this reagent should be between 3.0 and 5.0. (USEPA)

Note: Mercuric chloride is highly poisonous. If spilled on skin, flush with water immediately.

B) Sampling

The passive sampler consisted of PE tube (diffusion tube) and sorbent (Whatman GF/A). Each set consists of 3 blank tubes and 5 collecting tubes.

B-1) First exposure

To study the absorptivity of TCM as absorbing chemical, the passive samplers consisted of 3 blank tubes and 5 collecting tubes were exposed for a week in laboratory to determine indoor SO_2. The sorbent was impregnated with 50 µl of TCM. Trapped SO_2 was extracted and determined by spectrophotometry. The calibration curve was constructed from SO_3^{2-}

concentration against their absorbance (Abs). The stock standard solution of SO_3^{2-} was diluted with milli-Q water.

B-2) Second exposure

To study outdoor SO_2 absorptivity of TCM, the passive samplers consists of 3 blank tubes and 5 collecting tubes were exposed for a week at the PCD air quality monitoring site (Yupparaj Wittayalai School) to determine outdoor SO_2. The sorbent was impregnated with 50 µl of TCM. SO_2 was extracted and then determined by spectrophotometry. The calibration curve was prepared the same way as described in the first exposure.

B-3) Third exposure

To compare the efficiency of absorbing chemicals, the passive samplers were divided into 2 groups. The first group was 50 µl of 4 M TCM impregnated onto sorbent. In the second group, 2 ml of 4 M TCM was filled in diffusion tubes without the sorbent. Each group consisted of 3 sets for different exposure periods (1, 3 and 5 days). All of the passive samplers were exposed at the PCD monitoring site (Yupparaj Wittayalai School).

After exposure, SO_2 in the first group was extracted and then determined by spectrophotometry. The calibration curve was constructed from SO_3^{2-} concentration against their absorbance (Abs) by using milli-Q water as the diluting solution.

In the second group, it was found that the volume of absorbing solution was decreased after exposure. Therefore, absorbing solution in each tube was adjusted back to 2 ml with 4 M TCM. SO_2 was determined by

spectrophotometry with the same condition used in the first group. The calibration curve of the second group was constructed the same way as the first group but with different diluting solution (4 M TCM solution).

C. Analysis of SO_2

After 1 week exposure, SO_2 was extracted and determined by spectrophotometry.

2.10.4 Extraction process for SO_2 determination by spectrophotometry

The final product of absorbing solution and SO_2 was in form of SO_3^{2-}. Extraction conditions have been optimized by spiking a known amount (20 µl of 100 ppm) of SO_3^{2-} standard solutions which is representative of SO_2 onto each sorbent (Whatman GF/A), which was placed in the diffusion tube and leaved in the desiccater until dry. The extraction was done by adding 4 ml of milli-Q water into the diffusion tube. Both in term of technique (using and non using ultrasonicator) and time consuming have been investigated. SO_3^{2-} was measured by spectrophotometry after reacted with pararosaniline reagent at the appropriate conditions.

2.10.5 Determination of SO_2 by spectrophotometry

All reagents and analysis method used were prepared following the standard USEPA methods.

A) Preparation of reagent

***Stock pararosaniline (PRA) solution*;** 200 mg of pararosaniline hydrochloride (0.2% PRA) was dissolved in 100 ml of 1 M HCl. This stock reagent is a yellowish red.

***Pararosaniline reagent*;** 25 ml of 3 M phosphoric acid was added to 20 ml of PRA stock solution and diluted to 250 ml with milli-Q water in volumetric flask. The reagent is stable for about a month, but it has to be stored away from heat and light.

Sulfamic acid (0.6%); 0.6 g sulfamic acid was dissolved in 100 ml milli-Q water. Prepare fresh daily.

Formaldehyde (0.2%); 5 ml formaldehyde (36 to 38%) was dilute to 1000 ml with milli-Q water. Prepare fresh daily.

SO_3^{2-} ***Standard solution*;** Stock standard solutions (1000 ppm) were prepared by dissolving 1.02 g of Na_2SO_3 in the solution of 1 g/l ethylenediamine tetraacetic acid (EDTA) as a stabilising agent (Kass and Ivaska, 2001). Working standard solution of SO_2 were prepared by diluting stock standard solution of Na_2SO_3 with milli-Q water. The standard $NaSO_3$ must be freshly prepared.

B) Sample analysis

To 1 ml of extractant or standard solution, 0.1 ml of 0.6% sulfamic acid was added and allowed to react for 10 min. After that 0.2 ml of 0.2% formaldehyde solution and 0.5 ml of pararosaniline solution were added and left for at 30 minutes. During 30 minute, a temperature must be controlled to be between 20 to 30 ^{o}C. After that, the absorbance of the sample, standard

solution and reagent blank was measured between 30 and 60 minute at 550 nm with a 1 cm optical path length cell by using milli-Q water as blank. Milli-Q water is used as a reference instead of the reagent bank because of the sensitivity of the reagent to temperature.

2.10.6 Study of sampling period for SO_2

In this study, all of passive samplers were divided into three groups for 1,3,5 and 7 days exposure. Each group consists of 3 blanks and 5 collecting samplers.

All samplers were exposed at PCD monitoring site (Chiang Mai Governmental Office Center) for a desired period of time (1,3,5 and 7 days). After that SO_2 was extracted and then determined by ion chromatography.

2.11 Effect of glycerin for determination of NO_2 and SO_2

2.11.1 Preparation of absorbing solutions

According to the reason that TEA can absorb both NO_2 and SO_2, 20% TEA (Gair, *et al*., 1990) was used for absorbing these pollutant gases. Absorbing solutions were prepared in various conditions by adding glycerin varying from 2 to 10% and compared with non adding glycerin. 20 ml of TEA was added into 5 volumetric flasks of 100 ml volume. After that, 2, 4, 6, 8 and 10 ml of glycerin were added in the flask no 1-5, respectively in order to prepare 2, 4, 6, 8 and 10% glycerin in 20% TEA solution. The volume was adjusted to 100 ml with milli-Q water.

2.11.2 Sampling

50 µl 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 (3/4/05-9/4/05) at PCD monitoring site (Chiang Mai Governmental Office Center).

2.11.3 Analysis of NO_2 and SO_2

After 1 week exposure, all of passive samplers were extracted. NO_2 and SO_2 were then subsequently determined by IC under the optimum mobile phase (1.7 mM $NaHCO_3$/ 1.8 mM Na_2CO_3) with flow rate of 1 ml/min.

2.11.4 Preparation of standard curve

A calibration curve was prepared from mixed standard solution of NO_2^- and SO_4^{2-} diluted with milli-Q water into different concentrations (0.2-1.0 ppm).

2.12 Determination of ozone (O_3)

2.12.1 Selection of absorbing solution for O_3 determination by ion chromatography

A) Preparation of absorbing solution

***0.1% $NaNO_2$*;** 0.1 g of $NaNO_2$ was dissolved in milli-Q water and adjusted to volume 100 ml.

***0.1% $NaNO_2$/ 0.1% Na_2CO_3/ ethylene glycol*;** 0.1 g of $NaNO_2$ and 0.1 g of Na_2CO_3 were dissolved with milli-Q water. 1 ml of ethylene glycol was then added. The solution was adjusted to 100 ml in volumetric flask with milli-Q water.

B) Sampling

To compare the absorptivity, the passive sampler consisted of the diffusion tube (PE tube) and the sorbent (Whatman GF/A). the absorbing solution including 0.1% $NaNO_2$ and a mix of 0.1% $NaNO_2$/ 0.1% Na_2CO_3/ ethylene glycol in a volume of 50 µl were impregnated onto the sorbents. Each set of the absorbing solution consists of 5 collecting samples and 3 blanks, respectively. They were exposed in the laboratory for 1 week.

C) Analysis of O_3

After 1 week indoor exposure, the tubes were collected. O_3 was then extracted and then determined by IC in form of NO_3^-.

The diagram of steps of selection absorbing solution for O_3 is shown in Fig 2.5

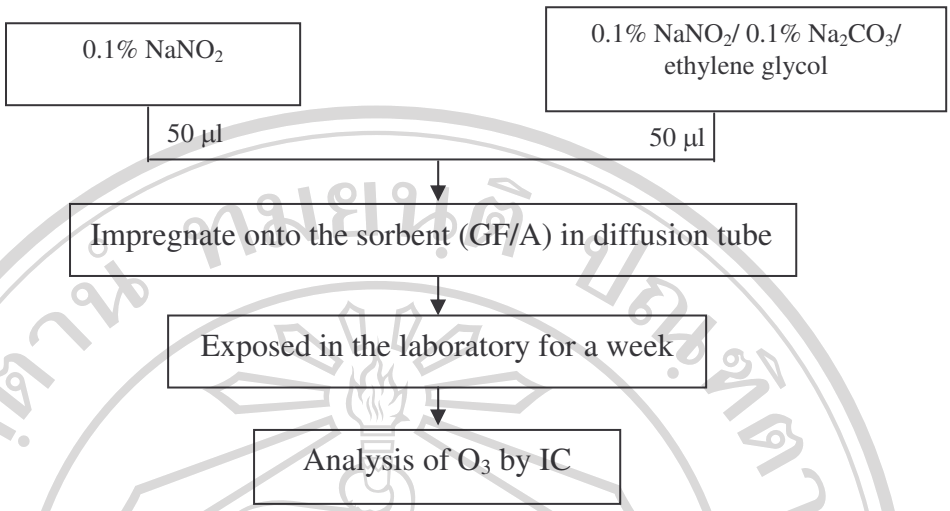

Fig 2.5 Diagram of steps of selection absorbing solution for O_3 determination by IC

2.12.2 Determination of O_3 by ion chromatography

O_3 concentration was determined by ion chromatographic system under the optimum condition. The mobile phase was 1.7 mM $NaHCO_3$/ 1.8 mM Na_2CO_3 with the flow rate of 1.0 ml/min. A calibration curve was made by plotting the different concentration of NO_3^- standard solution diluted with milli-Q water versus the peak area.

2.12.3 Selection of absorbing solution for O_3 determination by spectrophotometry

A) Preparation of absorbing solution

***0.1% DPE (1,2-di-(4-pyridyl)ethylen) in methanol*;** 0.1 g DPE was dissolved by methanol. Then, the total volume was adjusted to 100 ml in volumetric flask with MeOH.

***0.5% DPE (1,2-di-(4-pyridyl)ethylene) in glacial acetic acid*;** 0.5 g of DPE was dissolved in glacial acetic acid and make volume to 100 ml with glacial acetic acid.

It is recommended that fresh absorbing reagent should be prepared at lease every 2 weeks (Thomas and Daniel, 1966).

B) Sampling

A 50 μl of each absorbing solution was added onto the glass fiber filter (GF/A) contained in polyethylene tube. Each set consisted of 3 blanks and 5 collecting samples. All of passive samplers were exposed in the laboratory for a week to determine indoor O_3. After getting optimum absorbing solution, it was applied for trapping outdoor O_3.

C) Analysis of O_3

O_3 was extracted from the exposed diffusion tube and then determined by spectrophotometry.

The diagram of steps of selection absorbing solution for O_3 is shown in Fig 2.6.

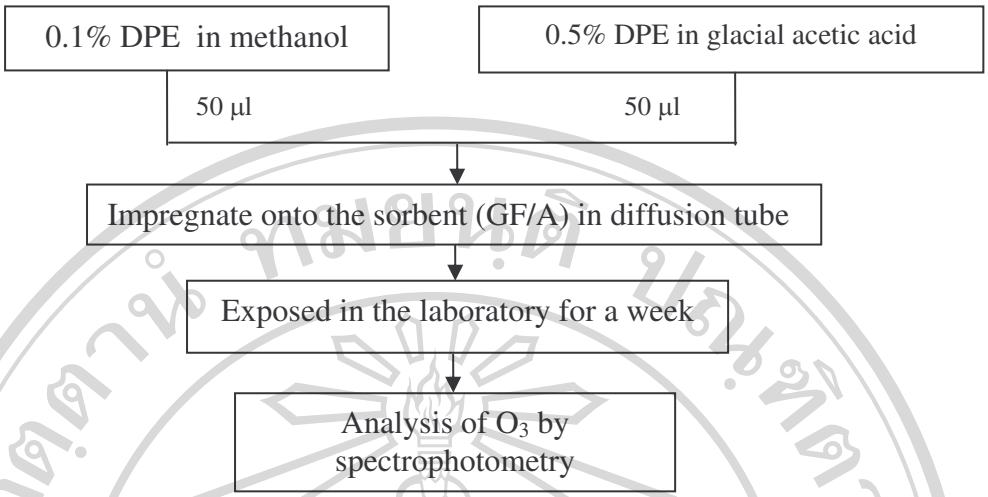

Fig 2.6 Diagram of steps of selection absorbing solution for O_3 determination by spectrophotometry

2.12.4 Extraction process for O_3 determination by spectrophotometry

The final products of the reaction between O_3 and the absorbing solution was pyridyl-4-aldehyde. Therefore, the extraction conditions have been optimized by spiking pyridyl-4-aldehyde standard solution onto the Whatman GF/A placed in diffusion tube. The concentration of pyridyl-4-aldehyde was determined by spectrophotometer after it was extracted with 2 ml of milli-Q water. Both in term of technique (using and non using of ultrasonicator) and time consuming have been investigated.

2.12.5 Determination of O_3 by spectrophotometry

The color-developing reagent used for O_3 determination by spectrophotometer was a 0.2% aqueous solution of 3-methyl-2-

benzothiazolinone hydrazone hydrochloride (3-MBTH). The reagent must be stored in a refrigerator till analysis (Thomas and Daniel, 1966).

The color-developing reagent was mixed with the extracted solution in a ratio of 1:1. After mixing at least 20 min at room temperature, the yellow color appeared and remained stable. The solution was measured at 432 nm against the mix solution of milli-Q water/reagent as blank.

The concentration of ozone in the absorbing solution was readily calculated from the absorbance-concentration curve. According to 1 μg of absorbing solution generates 2.75 μg of pyridyl-4-aldehyde. Therefore 1 ppm O_3 was generated by 2.75 ppm pyridyl-4-aldehyde. The standard curve of O_3 is made by dissolving pyridyl-4-aldehyde in milli-Q water at different concentrations. The color was developed color with the same method as the sample.

2.12.6 Outdoor ozone measurement

A) First exposure

The passive samplers (consisted of PE diffusion tube and glass fiber filter) were divided into 2 groups. In the first group trapped O_3 by using a mix of 50 μl of $NaNO_2$, Na_2CO_3 and ethylene glycol as the absorbing chemical. The second, group O_3 was trapped by using 50 μl of DPE / methanol as the absorbing chemical. Each group consists of 3 blanks and 5 collecting samples. All passive samplers were exposed at the PCD monitoring site (Chiang Mai Governmental Office Center) for 1 week (2 replicates of 15/5/05-21/5/05 and 26/5/05-1/6/05)

Trapped O_3 was extracted and determined by IC (first group) and spectrophotometry (second group).

B) Second exposure

The passive samplers were divided into 6 groups as shown in Table 2.1 and exposed at the PCD monitoring site (Chiang Mai Governmental Office Center) for 1 week (7/7/05-13/7/05). Each group consists of 3 blanks and 5 collecting samples.

Table 2.1 Outdoor O_3 measurement conditions

Set	Absorbing chemical	Protective shelter	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	

In the first three groups, 50 µl of $NaNO_2$ / Na_2CO_3 / ethylene glycol was used as an absorbing solution, while in the last three groups, 50 µl of DPE / methanol was used.

The first and the fourth groups were the original passive samplers, which consisted of glass fiber filter placed in the polyethylene tube mounded in the original protective shelter.

The second and the fifth groups were different from the first and fourth groups only they had extra protective shelter, which had more cover area than the primitive one as shown in Fig 2.7.

The third and the sixth groups were special from the second and fifth groups by wrapping the tubes were wrapped with the aluminum foil as shown in Fig 2.8 in order to protect them from light.

After 1 week exposure, the first three groups were extracted and determined by IC system whereas the last three groups ozone was extracted and determined by spectrophotometry.

Fig 2.7 The protective shelter

Fig 2.8 Diffusion tube with the aluminium foil

C) Third exposure

The propose of the third exposure was to measure ozone by using the modified passive sampler (foil-wrapped tube) and optimize the absorbing chemical for ozone determination by spectophotometry. The passive samplers were exposed at the PCD monitoring site (Yupparaj Wittayalai School) for 8 hr and 24 hr (22/9/05 and 4/10/05).

The passive samplers were divided into 3 sets. Each set consisted of 3 blanks and 5 collecting samples as shown in Table 2.2.

In the first set, 50 µl of a mix of $NaNO_2$, Na_2CO_3 and ethylene glycol was used as the absorbing solution. The tubes were exposed for 8 hr and 24 hr. ozone was extracted and determined by IC.

In the second set, 50 µl of DPE / MeOH was used as the absorbing solution. The tubes were exposed for 8 hr and 24 hr. Ozone was extracted and determined by spectrophotometry.

In the third set, 2 ml of DPE / MeOH was used as absorbing solution by directly filled into the diffusion tubes. No sorbent was used in this method. The tubes were exposed for 8 hr and 24 hr. After that the tubes were collected and brought to the lab. The solution in diffusion tubes was adjusted to 2 ml against with DPE / MeOH absorbing solution and ozone was determined by spectrophotometric method as described in section 2.12.5. The solution was measured at 432 nm against the mix solution of methanol and reagent as blank.

The calibration curve was prepared by diluting stock standard pyridine-4-aldehyde with the DPE / MeOH absorbing solution at difference concentrations.

Table 2.2 Measurement of ozone by using the modified passive sampler (foil-wrapped tube) and optimize the absorbing chemical

Set no.	Absorbing solution	Sampling period (hr)	Number of tubes		Determination technique
			Sampling	Blank	
1	50 µl of a mix of $NaNO_2$, Na_2CO_3 and ethylene glycol	8	5	3	IC
		24	5	3	
2	50 µl of DPE / MeOH	8	5	3	Spectrophotometry
		24	5	3	
3	2 ml of DPE / MeOH	8	5	3	Spectrophotometry
		24	5	3	

2.13 Application of passive samplers

The chosen passive samplers, which their components were tested as described in the previous sections, were applied for determination of NO_2, SO_2 and O_3 at three sampling sites in Chiang Mai City. The conditions of passive samplers are shown in Table 2.3.

Table 2.3 The conditions of passive samplers for determination of NO_2, SO_2 and O_3 at three sampling sites in Chiang Mai City

Pollutant gas	Absorbing solution	Sampling period (days)	Determination technique
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

Three sampling sites in Chiang Mai City were selected as shown in Table 2.4 and Fig 2.9 for validation of the optimized passive samplers.

Table 2.4 Description of sampling sites

Site	Location	Site description
A	Chiang Mai Governmental Office Center	Sub-urban site
B	Yupparaj Wittayalai School	Urban site
C	Mea-Hia Research Center, Chiang Mai University	Background site

Site A and B are the air quality monitoring site of the Pollution Control Department (PCD), Thailand. Site A is located in the direction of North-West from the city, there was a disturbance from road construction nearly the site. Site B is located inside the Chiang Mai City, surrounded by community including school, temples, governmental offices and business buildings etc. Site C is also one of the PCD's site. It is acid deposition monitoring station, where both wet and dry depositions have been monitored. Therefore, data obtained from this site can be compared. Site C was selected as the background site due to low human activities surrounded. It is located about 7 kilometers in a south-west direction of Chiang Mai city.

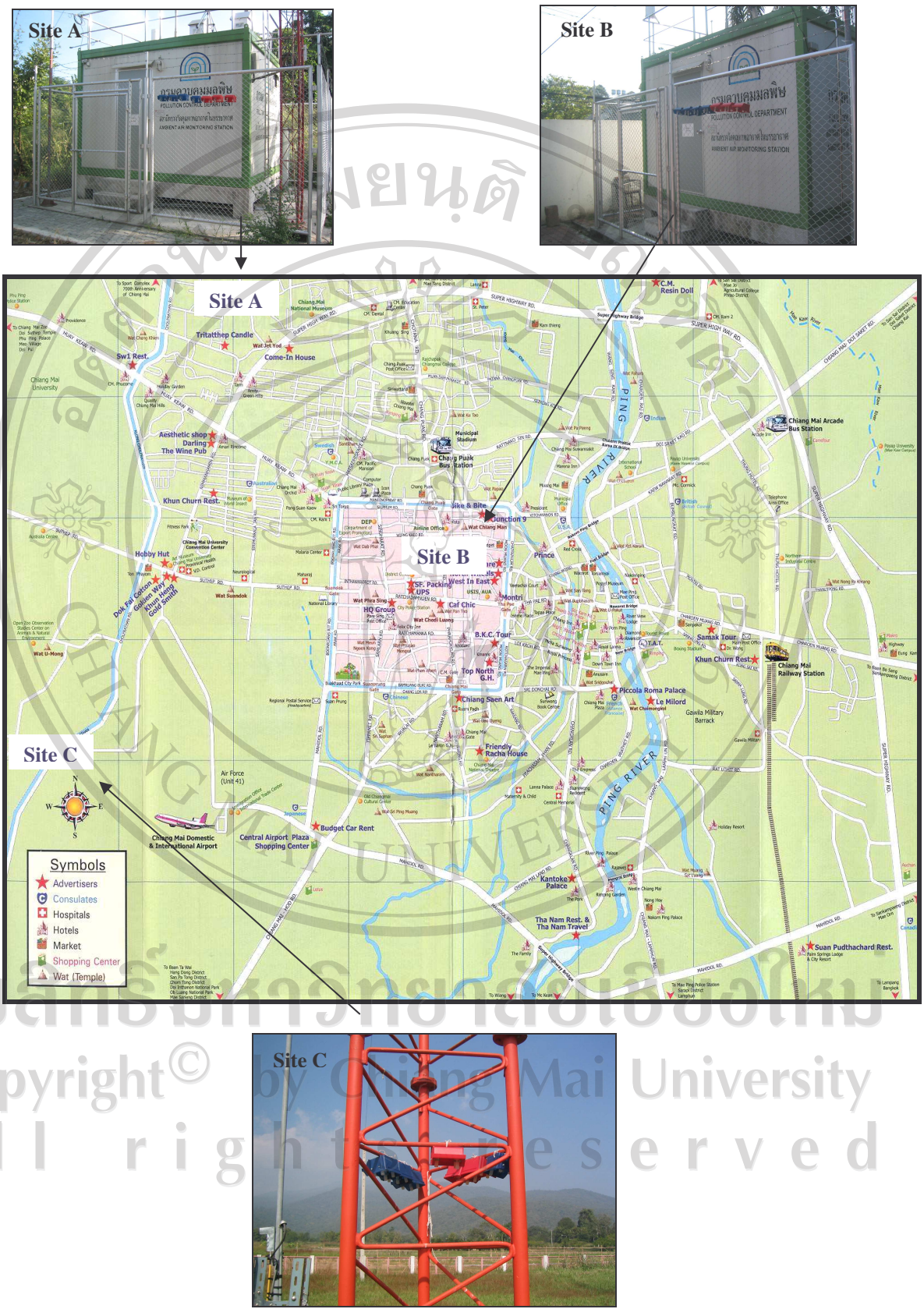

Fig 2.9 Map of the sampling site in Chiang Mai City

2.14 Validation of passive sampler

An accuracy of the results obtained from the passive sampler was evaluated by comparing with a standard active monitoring located at site A (Chiang Mai Governmental Office Center) and site B (Yupparaj Wittayalai School). The active monitoring data was obtained from the pollution control department (PCD) of Thailand.

Precision is expressed as the standard deviation (SD) and percentage relative standard deviation (%RSD), which is calculated by the equation 2.3 and 2.4 (Carl and Jo, 1993).

$$SD = [(x_i-x)^2/(n-1)]^{1/2} \quad \text{.....2.3}$$

$$\%RSD = [SD / \bar{x}] * 100 \quad \text{.....2.4}$$

Where x_i = individual value in data

$\bar{x}$ = mean of data

n = number of measurements

Precision of the passive sampling technique was checked by determining the replication of diffusion tubes both for samplers and field blanks.