CHAPTER 2

EXPERIMENTAL

2.1 Apparatus, Chemicals and Instruments

2.1.1 Appartus

1) Micropipettes : 100 µl, 1000 µl and 1 to 10 mL
2) Syringe filter, 0.45 µm cellulose acetate, Chrom Tech, U.S.A
3) 1000, 100, 50, 10 mL volumetric flask, Duran, Germany
4) 25 ml PP volumetric flask, Vit Lab, Germany
5) 250, 100, 50 mL beaker, Scott Duran, Germany
6) 1000 mL funnel, Alltech, Blegium
7) Stainless steel mesh filter support ring, Alltech, Blegium
8) 1000 mL GL-45 safety-coated glass bottle, Alltech, Blegium
9) Polypropylene tubes, NIPRO (Thailand) corp., Ltd., Thailand
10) GF/A filter papers, Whatman tnternational Ltd., England

2.1.2 Chemicals

1) Ammonium (NH_4^+) standard solution, 1000 ppm, Merck, Germany
2) Calcium (Ca^{2+}) standard solution, 1000 ppm, Merck, Germany
3) Magnesium (Mg^+) standard solution, 1000 ppm, Merck, Germany
4) Potassium (K^+) standard solution, 1000 ppm, Merck, Germany
5) Sodium (Na^+) standard solution, 1000 ppm, Merck, Germany
4) 99.5% Tartaric acid, Univar, Australia.
5) 98.0% Dipicolinic acid, Fluka, Germany.

6) Deionized water (conductivity < 0.15 mS/m), Chemistry Department, Chiang Mai University

7) Milli Q water, Chemistry Department, Chiang Mai University

2.1.3 Instruments

1) Ion Chromatograph, Model 2.733.0020, Metrohm, Switzerland, consist of
   - Cation guard column, Metrosep C 2 Guard.
   - Cation separation column, Metrosep C 2-150 (150x4.0mm).
   - A conductivity detector
   - Injection valve, Model C 2-2346DK
   - Interface, 771 interface
   - Pump, 752 unit pump for H_2SO_4 and H_2O to suppressor
   - Output, IC net 2.3 program

2) AIRmetrice MiniVol™ Portable Air sampler, consist of
   - Pump
   - Pre-separator and Cassette Filter Holder
   - Quartz filter, Whatman® 47 mm
   - Programmable 7 day Timer with battery back up
   - Sealed lead-acid batteries, 12 AH capacity (24-hr sampling duration)
   - 1 amp built in charger adapter
   - Digital manometer, model DIG1135

3) Analitical balance, MX5, Mettler Toledo, Switzerland

4) Analitical balance, AB304-S, Mettler Toledo, Switzerland

5) Ultrasonicator, Transonic Digital S, Elma, Germany

6) Ultrasonicator, Crest Tru-Sweep 690T, U.S.A

7) Conductivity meter, tetraCon® 325, inoLab, Germany

8) pH meter, 744, Metrohm, Switzerland

9) Vacuum pump, Rocker 300, Keika Ventures, U.S.A

10) Oven, Model 100-800, Memmert, Germany

11) Desiccator

2.2 Sampling method

2.2.1 Sampling site

PM_{10} samples were collected from 2 areas in Chiang Mai.(Figures 2.1 and 2.2.) The first sampling site was in the Yupparaj Wittayalai School (18° 47' 28.43''N, 98° 59' 24.26''E), represented urban air quality with high traffic (urban area). The sample concentrations were compared with values obtained from the Pollution Control Department (PCD) air quality monitor station at the same sampling duration. The latter site locates at Mae Hia Research Center (18 °45' 40.3''N, 98° 55' 54.3''E), Faculty of Agriculture, Chiang Mai University, representative of less pollution area with low anthropogenic activities (suburban area)

2.2.2 Sampling duration

PM_{10} samples were collected in dry season for 3 months (February – April 2009) and wet season for another 3 months (June – August 2009). Sampling frequency was twice a week in working day (Wednesday) and weekend day (Saturday). Samples were collected at the same time from the same site within a period of 24 hr intervals. The sampling duration is shown in Table 2.1.

Table 2.1 Sampling duration and number of samples

Sampling site	Station	Sampling duration	No. of PM_{10} samples
1	Yupparaj Wittayalai School	Dry season (February – April 2009)	22
		Wet season (June – August 2009)	25
2	Mae Hia Research Center	Dry season (March – April 2009)	12

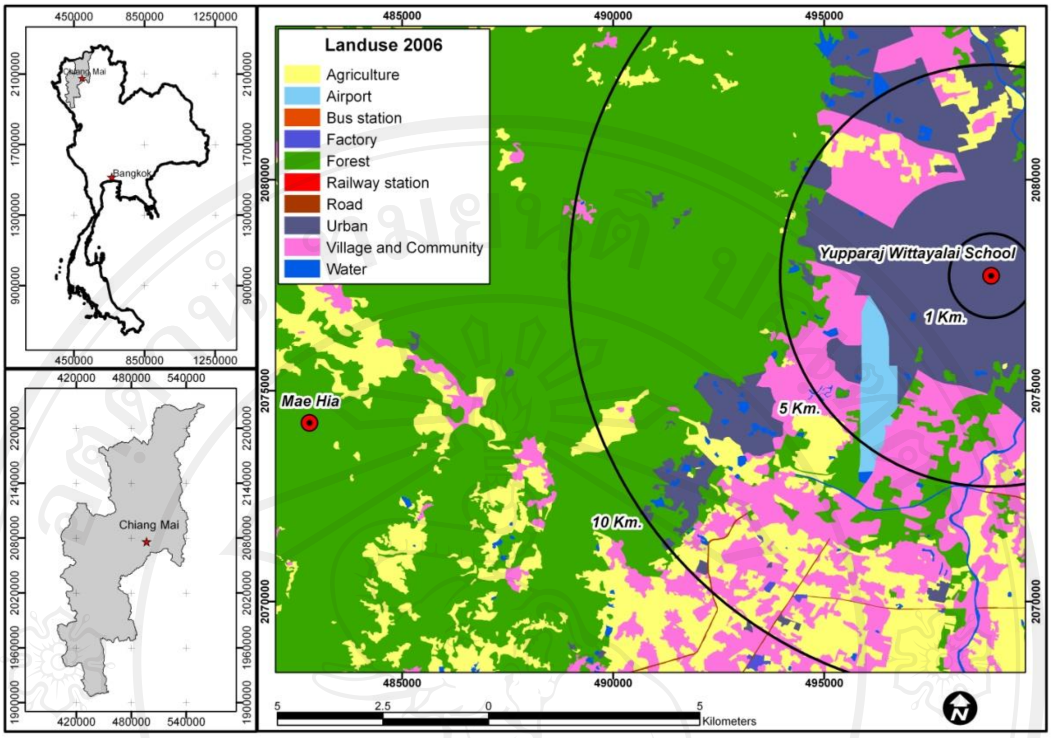
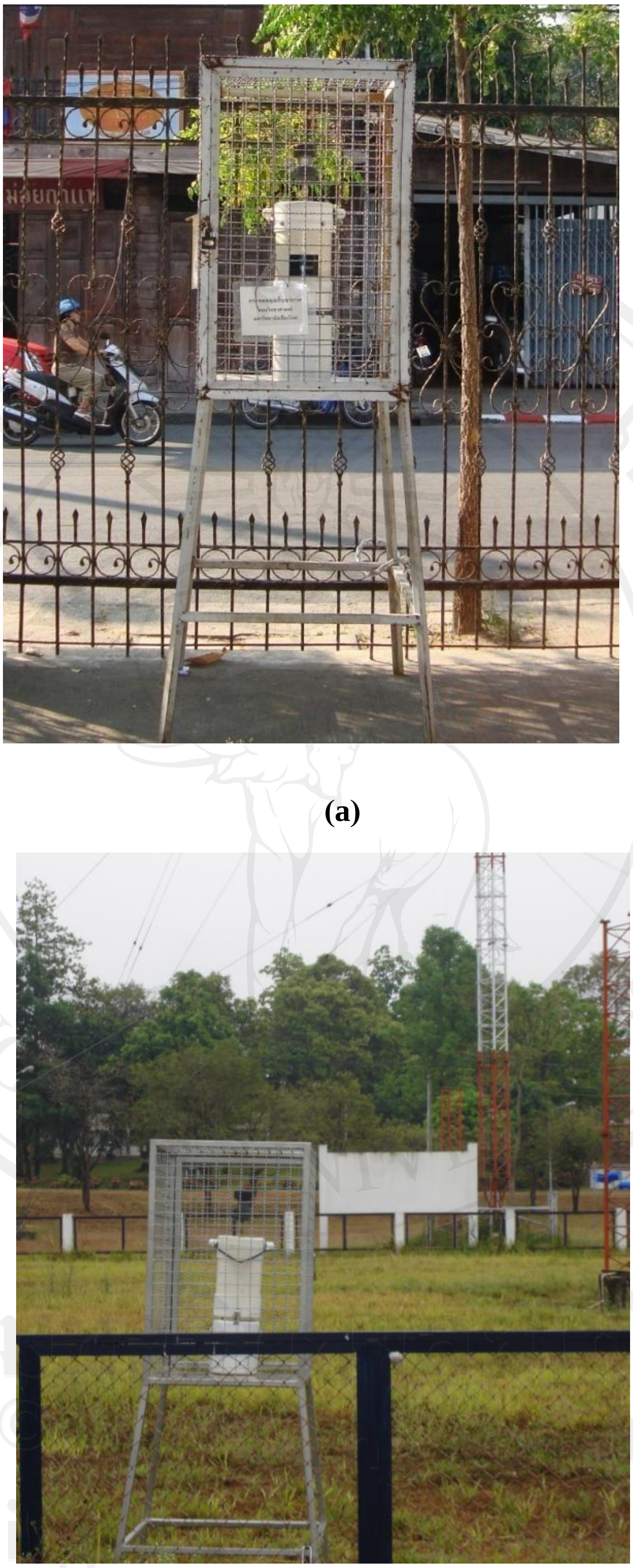


Figure 2.1 Land used profile of Yupparaj Wittayalai School (a)

and Mae Hia Research Center (b)



(a)

(b)

Figure 2.2 Sample collection at Yupparaj Wittayalai School (a) and Mea Hia Research Center (b)

2.3 Analytical characteristics

2.3.1 Repeatability and Reproducibility

The repeatability was the results of standard deviation of measurements repeated by the same analyzed on the same instrument within a short time period. Reproducibility was the closeness of agreement between independent results obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories and after different intervals of time) (IUPAC Compendium of Chemical Terminology, 1997).

The repeatability was checked by 5 time continuously injection of a 0.40 µg/mL mixed standard solution of cation (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) into ion chromatograph under the optimum conditions. The reproducibility was checked by injecting a 0.40 µg/mL mixed standard solution cation (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) into ion chromatograph under the optimum conditions for 5 days. The results of the reproducibility were estimated by standard deviation and the related values.

2.3.2 Limit of detection (LOD) and limit of quantification (LOQ)

In analytical chemistry, the LOD is the lowest concentration of the analyte that can be detected with a given degree of confidence. LOQ is a parameter for quantitative assays for low levels of compounds in the sample matrices and used particularly for determination products or low levels of active constituent in a product (Gibbons, 1996). The LOD was obtained from 3 time, while LOQ was obtained from 10 times of standard deviation from measurement of standard solution.

LOD and LOQ of Ion Chromatoghaph

The detection limit and limit of quantification was checked by injecting 7 times of the lowest concentration (0.1 µg/mL) of mixed cation standard (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) into ion chromatographic system under the optimum conditions.

2.4 Preparation of solutions for analysis of PM_{10}

2.4.1 Analysis of cations in PM_{10} samples

a) Calibration curve preparation

Before analysis of ion concentration, calibration curve for individual ion species with 5-8 points of standard concentrations was constructed. The commercial individual ion standard solution (1000 µg/mL) from Merck Company has been used for stock solution. Mixed cations (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) standard solution was prepared and diluted with deionized water to concentration of 10 µg/ml. The 10 µg/ml standard solution was used for preparation of working standard solutions (0.1, 0.2, 0.4, 0.8, 1, 2 and 4 µg/ml).

Mixed standard solutions were injected into IC columns under optimum conditions. The prepared standard concentration must cover the sample concentration. The working standard solutions were freshly prepared form mixed stock standard solution by dilution every analysis day. The important point, mixed standard was prepared in polypropylene volumetric flask to avoid ion exchange.

b) Preparation of mobile phase for caion analysis

The eluent solution for cation analysis was 4 mM Tartaric acid / 0.75 mM dipicolinic acid which prepared by 0.6000 g of tartaric acid and 0.1250 g of dipicolinic acid in deionized water before adjusted volume to 1000 mL in volumetric flask.

Because the system inlet line was very small, therefore air or small particles in eluents could block in the system, causing baseline noise and shortening the life-time of the column. Eluents were filtered by a filter holder set with a nylon membrane filter (pore size 0.45 µm) and degassed by vacuum and ultra-sonication prior to analysis.

2.5 Sampling of atmospheric PM_{10}

2.5.1 PM_{10} sampling

Steps of sample collection are described as follows,

a) The pre-exposed quartz filter (Ø 47 mm, Whatman In. Ltd, UK) was weighed by using six point microbalance weight scale. Each filter was weighed at least three times before and after sampling following the equilibration period. It was stored in desiccators before and after sampling for at least 24 hour.

b) Before the PM_{10} sampling started at each sampling site, the actual flow rate of the Minivol Portable Air Sampler was calibrated by measuring transfer standard pressure of manometer in inches of water at different rotameter indication in range of 4.0-6.5 l/min.

c) The MiniVol air sampler was placed 2 m above ground at each sampling site. A weighed filter was inserted into a pre-separator. 2 or 3 drops of grease solutions in hexane were dripped onto an impactor, in order to restrain unwanted PM sizes, whereas the selected size of sample was passed through the filter. Air was automatically pumped with a flow rate of 5 l/min through a particle size separator for 24 hr programmed by a time. Parameters including ambient temperature, barometric pressure, sampling date and time.

d) After 24 hr sampling, the filter was kept in a sealed plastic bag, then transferred into desiccators before post-exposure weight. PM_{10} concentration was reported in term of µg/m^3. The PM_{10} sample was kept under cool conditions in freezer waiting for extraction.

2.6 PM_{10} Sample extraction

2.6.1 Optimization of PM_{10} extraction conditions

Extraction condition of anions in PM_{10} samples using ultrasonication including extraction volume of Milli-Q water, temperature and time conditions were optimized.

The volume of an extracted solution (Milli-Q water) has been justified in order to find out the appropriate volume for anion extraction. Quartz filter was placed into 250 ml beaker, then 600 µL of 250 µg/mL mixed cation standard solution (Na^+, NH_4^+, K^+, Ca^{2+} and Mg^{2+}) was spiked onto pure quartz fiber filters and left for 15 minutes before extraction (n=10). 30 ml of Milli-Q water were added to the spiked filter paper in beaker. The beaker were closed and covered with paraffin film.

The filters were extracted using ultrasonicator for 30 minutes at full sonication power under room temperatures (25ºC). An extracted solution was filtered with a cellulose acetate membrane. Then the ionic species in the filters are analyzed by Ion Chromatography (IC). The extraction efficiency was calculated in term of percent recovery as shown in equation 2.1.

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

2.6.2 Extraction and analysis of PM_{10} samples

The quartz filter which contained PM_{10} samples and its laboratory blanks (unexposed filters) were extracted by 30 ml of Milli-Q water contained in 250 mL clean beakers, which were covered by paraffin film to reach an equilibrium condition. Then, it was sonicated in an ultrasonicator for 30 minutes full sonication power under room temperature (25ºC). After extraction process, the extracted solution was filtrated through cellulose acetate membrane (pore size 0.45 μm). Filtrated samples were stored in polyethylene bottles and kept in refrigerator at 4 °C waiting for analysis.

A Metrohm ion chromatograph was used for the determination of major cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}). The analysis conditions of ion chromatograph (IC) are detailed in Table 2.2

Table 2.2 Condition of ion chromatograph for cation

Analysis item	Condition
Mobile phase	4 mM Tartaric acid/0.75 mM Dipicolinic acid
Flow rate	1.0 ml/min
Injection loop	20.0 µL
Guard column	Metrosep C 2 Guard
Analysis column	Metrosep C 2-150 (4.0 x 150mm)
Particle size	7.0 µm
Suppressor	-
Detector	Conductivity
Temperature	35.0 °C

2.7 Data analysis

2.7.1 Chemical analysis

Comparison of PM_{10} concentrations at Yupparaj Wittayalai School obtained from this experiment and values of automatic active samplers of the Pollution Control Department (PCD) were analyzed by SPSS (Pair-Test). The correlation of PM_{10} and PM_{10} – bound ion concentrations were calculated by SPSS statistic program (Pearson Correlation).

2.7.2 Satellite data and trajectory analysis

Fire count maps, displaying the active burning hot spots, were derived from MODIS (Moderate Resolution Imaging Spectroradiometer) satellite images. The data were analysed using a standard MODIS MOD14 Fire and Thermal Anomalies Product algorithm (http://modis.gsfc.nasa.gov/data/dataprod/dataproducts.php?MOD_NUMBER=14). In addition, backward air mass trajectories were used to trace the origins and transport pathways of pollutants from the surrounding regions to the monitoring site. The 1-day backward air trajectories were obtained by the National Oceanic and Atmospheric Administration(NOAA) HYSPLIT Model (http://www.arl.noaa.gov/ready/hysplit4.html).