CHAPTER 2

METHODOLOGY

2.1 List of Apparatus

a) Analytical balance, Sartorius Basic BA 210s, Germany

b) Cellulose sheet, 40x40 cm., ADVANTEC No.590, Japan

c) Conductivity meter, Inolab, TetraCon 325, Germany

d) Filter holder set, Milipore, U.S.A.

e) Filter membrane, 0.45 µm nylon, diameter 47 mm, Sartorius, Germany

f) Filter membrane (F0), 0.8 µm Polytetrafluoro ethylene filter (PTFE), 47 mm. diameter, MFS,

g) Filter membrane (F1), 0.45 µm Polyamide filter, diameter 47 mm, Orange scientific,

h) Filter membrane (F2), 0.45 µm Cellulose filter, diameter 47 mm, ADVANTEC, Japan

i) Filter membrane (F3), 0.45 µm Cellulose filter, diameter 47 mm, ADVANTEC, Japan

j) Four-Stage open face filter holder, Nilu, Norway

k) Ion Chromatography DX-300, Dionex Corp, U.S.A., consisting of

  - A Rheodyne model 9126 injection valve

- Anion guard column, IonPac® AG4A, 4 mm.(4 x 50 mm.).
- Anion separation column, IonPac® AS4A, 4 mm.(4 x 250 mm.).
- Anion self regenerating suppressor-I
- Cation guard column, IonPac® CG12 (4 x 50 mm.).
- Cation separation column, IonPac® CS12 (2 x 250 mm.).
- Cation self regenerating suppressor-I
- A conductivity detector
- BDS, Barspec Data System, Barspec System,Inc., Israel

l) pH meter, Precisa, pH 900, Switzerland

m) Precipitation wet only collector, Acrochem Metrics, Inc., Model 301, U.S.A.

n) Micropipette, Eppendorf, Germany

o) Stainless steel syringe filter holder, Advantec MFS, Inc., U.S.A

p) Ultra-sonicator, Model 8891, Cole-Parmer Instrument Co., U. S.A.

q) Vacuum pump, Gast, U.S.A.

2.2 List of Chemicals

1) Chloride (Cl^-) standard solution 1000 ppm, Merck, Germany.
2) Nitrate (NO_3^-) standard solution 1000 ppm, Merck, Germany.
3) Sulfate (SO_4^{2-}) standard solution 1000 ppm, Merck, Germany.
4) Sodium (Na^+) standard solution 1000 ppm, Merck, Germany.
5) Ammonium (NH_4^+) standard solution 1000 ppm, Merck, Germany.
6) Potassium (K^+) standard solution 1000 ppm, Merck, Germany.
7) Magnesium (Mg^{2+}) standard solution 1000 ppm, Merck, Germany.
8) Calcium (Ca^{2+}) standard solution 1000 ppm, Merck, Germany.
9) 99.5% Sodium carbonate (Na_2CO_3), Merck, Germany.
10) 99.5% Sodium bicarbonate ($NaCO_3$), Merck, Germany.
11) 99% Methansulfonic acid (MSA), ACROS organics, Belgium.
12) 98% Glycerol, BDH, England
13) >99% Potassium carbonate (K_2CO_3), Fluka, Switzerland
14) 85% Phosphoric acid (H_3PO_4), Carlo ERBA, Italy
15) 30% Hydrogen peroxide (H_2O_2), Carlo ERBA, Italy
16) Helium gas, 99.99% (HP), TIG, Thailand.
17) Nitrogen gas, 99.99% (HP), TIG, Thailand.
18) Milli Q and Milli RX water (conductivity < 0.15 mS/m.), Chemistry Department, Chiang Mai University.

2.3 Sampling Site and Sampling Period

A sampling site is located at the Meteorological station in the area of Mea Hia Research Center, Chiang Mai University. The sampling site was classified by Acid Deposition Monitoring Network in East Asia (EANET) criteria as rural site. This station is locate at latitude 18° 45´ 40.3? N and longitude 98° 55´ 54.3? E. Its elevation is 334 meter above mean sea level. The monitoring period for both wet and dry depositions had been done within 12 months. The surrounding details of sampling site in different scales are shown in Table 2.1 and Figure 2.1 (See more detail in Appendix C).

Table 2.1 Surrounding of sampling site

Scale Type	Radian	Details
Onsite Scale	0-100 m	80% of Mae Hia Research Center are used for research purposes stock for students of Agriculture and Veterinary Faculties. The rest of the areas are used for the office building, parking lot, etc.
Local Scale	100 m – 10 km	Most of the areas are forest, communities and agricultural areas. Other land-use is airport, golf course, etc.
Regional Scale	10 – 50 km	The radian of this scale covers Chiang Mai city consisting of communities, universities, transportation station, airport, industrial estate, etc.

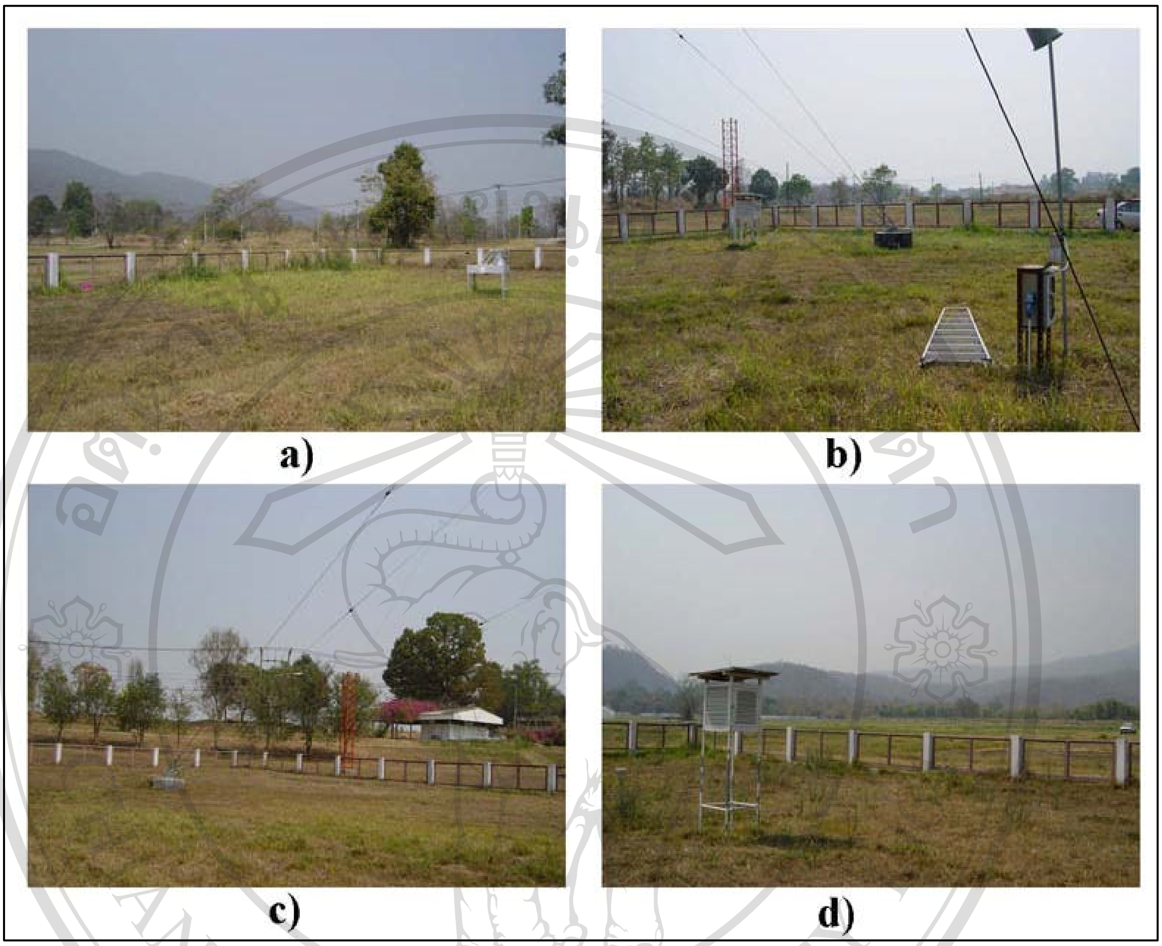

Figure 2.1 Surrounding of sampling site; a) North, b) South, c) East and d) West.

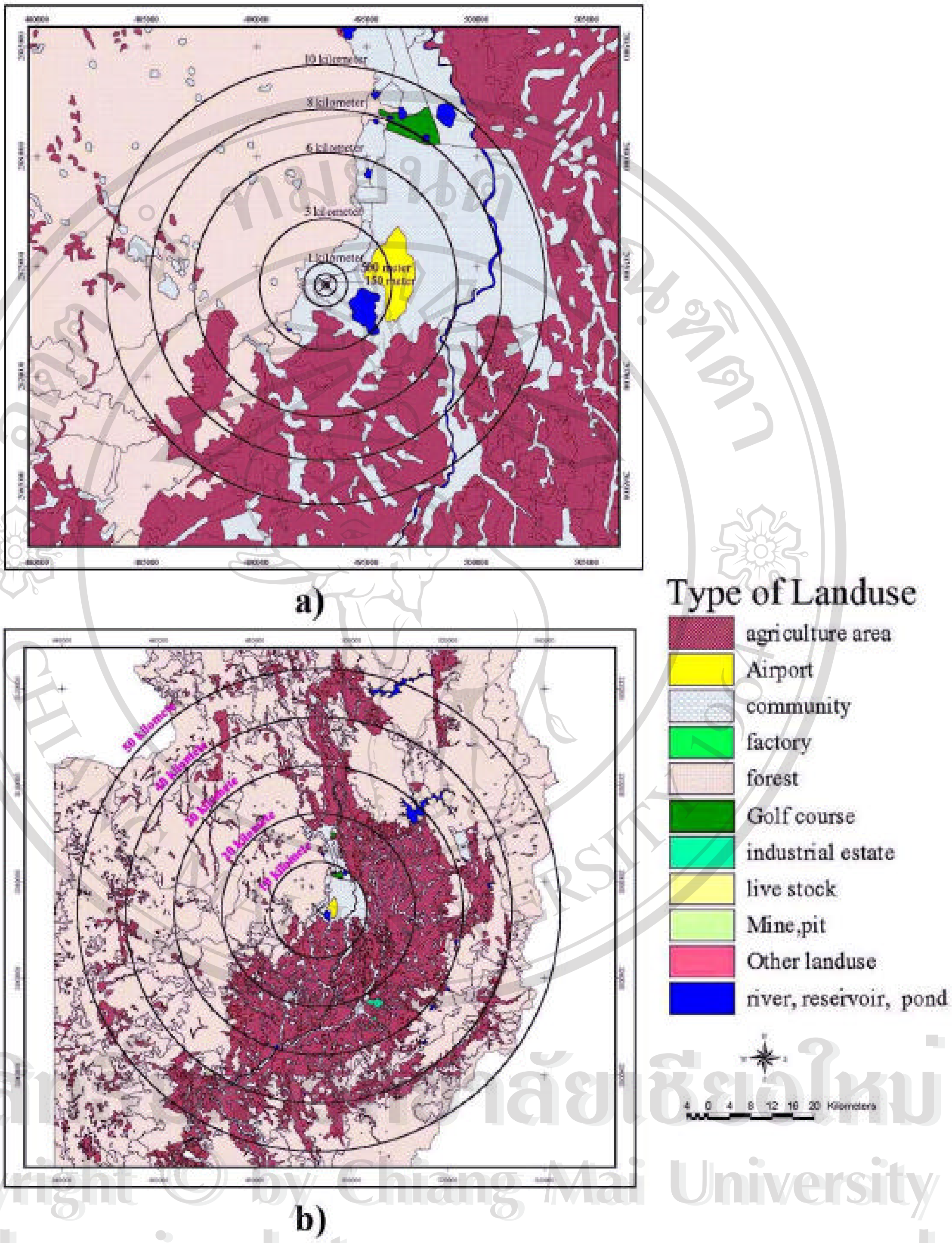

Figure 2.2 Type of land use around sampling site in the different scale, a) local scale (radian 100 m-10 km), b) regional scale (radian 10-50 km)

2.4 Wet Deposition

2.4.1 Samples Collection and Storage

Rain samples were collected on a daily basis by using the wet only collector with an automatic lid as shown in Figure 2.2. Sample recovery was made at 9.00 am local time. De-ionize water with conductivity < 0.15 mS/m was used for cleaning a sampling bucket after sample collection even in case of no rain. Sampling periods was 12 months started from 1 April, 2003 to 31 March, 2004.

The meteorological data during sampling period were also recorded. Rain gauge was used for measurement of precipitation amount in millimeter unit, air temperature and humidity were measured by air thermometer and hygrometer, respectively.

Collected rain samples were labeled and transferred to Air Pollution Monitoring Laboratory at Chiang Mai University. They were stored in refrigerator at 4 °C.

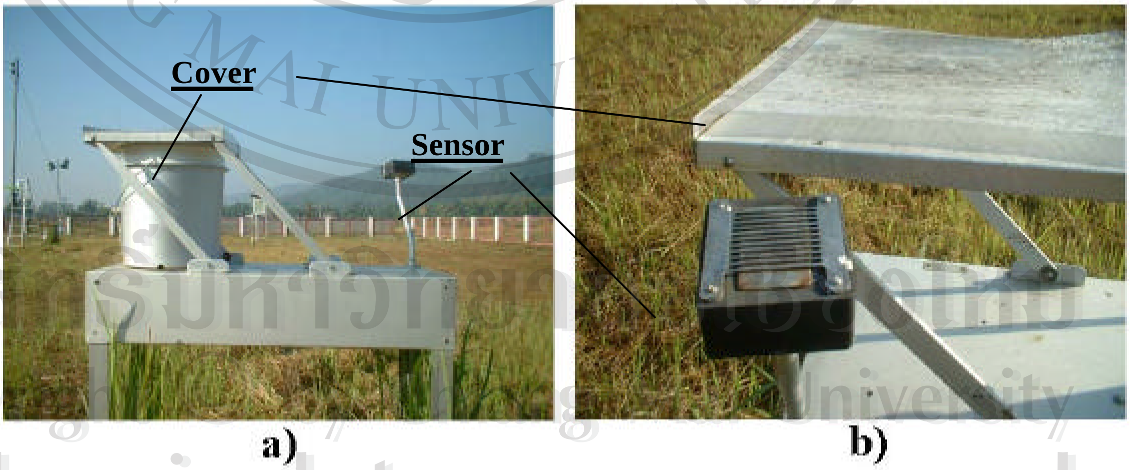

Figure 2.3 Precipitation collector instrument

2.5 Dry Deposition

2.5.1 Air Samples Collection

A dry deposition sample is proposed to measure the level of air pollution in atmosphere. The main pollutants such as SO_2, HNO_3, NH_3, HCl, and acid aerosols were collected by four-stage filter pack. It was operated by connect with sampling set, which controlled an inlet height and flow rate.

The inlet of air sampling holder should be set up at the height of about 3 meters above the ground. If there are any obstacles close to the monitoring site, this part should be set up higher than 3 meters. During sampling period, the diaphragm pump is recommended for stable flow rate. Flow rate at 1 L/min is recommended for weekly or biweekly sampling. For counting of air volume, mass flow meters that could monitor accumulated volumes was used in order to avoid the effect of the low atmospheric pressure at high altitude. The mass flow meter should be installed between filter holder and pump. Gas volume meters with flow rate meters (of float type) could be also acceptable. In this case, the flow rate meter and gas volume meters was set up consequently after the pump to measure flow rate and volume under the condition of atmospheric pressure.

Air volumes counted by mass flow meter or gas volume meters was used for calculation of ambient air concentration.

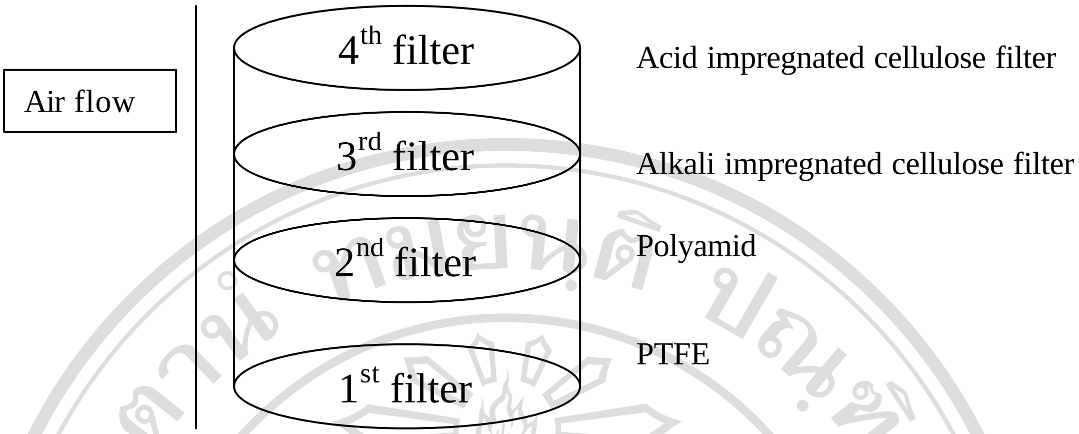

Figure 2.4 Schematic diagram of four-stage filter pack

The four-stage filter pack is composed of four filters in line with the air stream as shown in Figure 1.6. Aerosols were collected on the first filter while the gaseous substances such as SO_2, HNO_3, NH_3, HCl and NH_3 will pass though this filter. HNO_3, partial SO_2, HCl and NH_3 in air sample were collected by second filter. The remaining SO_2 and HCl were reacted with alkali impregnated substance on the third filter. Finally, the fourth filter with acid impregnated substance trapped the remaining NH_3 in air samples after passing through the first, second and third filters.

2.5.2 Preparation of four stage filter pack

Filters and impregnate solution were handled in the laboratory only under the clean conditions. Moreover they should not be exposed to air longer than necessary due to a possible uptake of gases by filters or solutions. Disposable plastic gloves and tweezers should always be used when handling filters.

Only a clean filter holder should be used to prevent excess contamination. The filters are mounted on the filter holder using clean plastic tweezers, taking into account the necessity to prevent the leak in the filter holder. Filters, especially impregnated one, should be always sealed up to avoid the contamination by unexpected ambient pollutants before and after the sampling time.

The first two layers of filter pack sampling set are not necessary to impregnate with any solution. By the way, the other two layer filters (F2, F3) are used for trapping excess acid particles.

a) Preparation of impregnate solution

Impregnate solutions were carefully prepared under the clean laboratory condition. Because the contamination was easily occurred and it will effected to the blank samples, therefore plastic gloves were used to handle in this step. All glasswears were washed by de-ionized water and dried in oven at 60 °C. After dried, cleaned glasswears were prevented from contamination by kept in plastic zip bag.

I) Alkaline impregnate solution (F2), 6% K_2CO_3 + 2% glycerin

Alkaline impregnated solution for third layer of four stage filter pack was the potassium carbonate solution. 30 g. K_2CO_3 and 11.5 ml of 87% glycerin were dissolved in 500 ml Milli Q water to make the solution.

II) Acid impregnated solution (F3), 5% H_3PO_4 + 2% glycerin

29.41 ml of H_3PO_4 and 11.5 ml of 87% glycerin were dissolved in 500 ml Milli Q water. It was used as acid impregnate solution.

b) Impregnation of filters

Impregnate solution was divided into three parts (100 ml each) in clean beakers. Then, six cellulose filters were soaked in 1st, 2nd and 3rd beaker, respectively using clean plastic tweezers. An excess alkaline solution on cellulose filters were absorbed by clean cellulose sheet (ADVANTEC No.590). After that, the alkaline impregnated filters were kept in a pes-tri dish and packed in a plastic zip bag to prevent from contamination. The diagram showimg the coating steps is show in Figure 2.3

2.5.3 Filter pack installation

Prepared filters packs were connected with a sampling set at the monitoring site which was connected and operated by flow meter and pump (Figure 2.5). Flow rate of air input was 1L/min. Detail of sampling such as time, ambient temperature were recorded before start the sampling. Operation of sampling was for 7 days a month continuously.

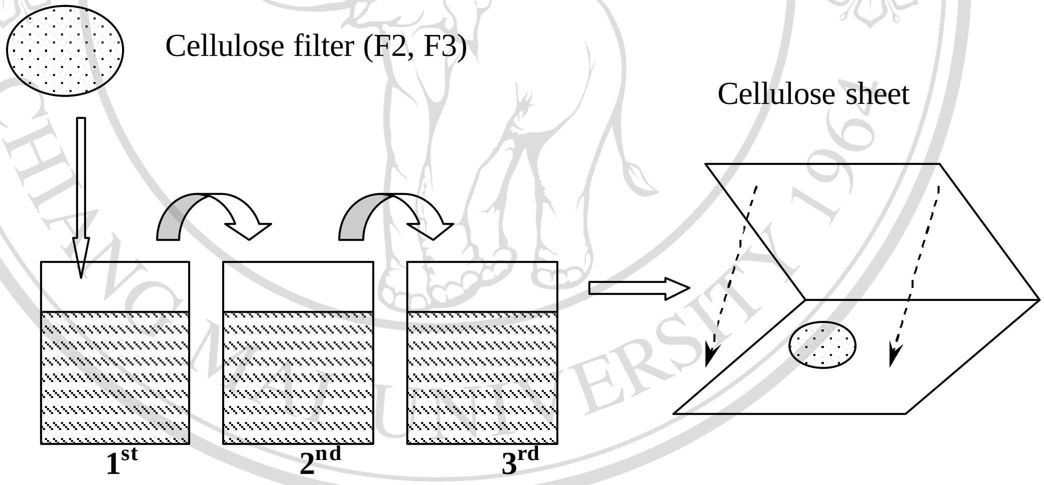

Figure 2.5 Impregnation of filter (F2 and F3)

2.5.4 Sample Collection

Pump flow rate and site condition were recorded before stop sampling. Filter pack holder set was disconnected out from the sampling set after turnned off the operation of pump. Then, the collected volume of air sample was recorded. The filter pack holder set was closed with plastic cap or para-film and stored in clean plastic zip bag to avoid absorption after stop sampling. The collected filter pack was transferred to laboratory and analysed as soon as possible.

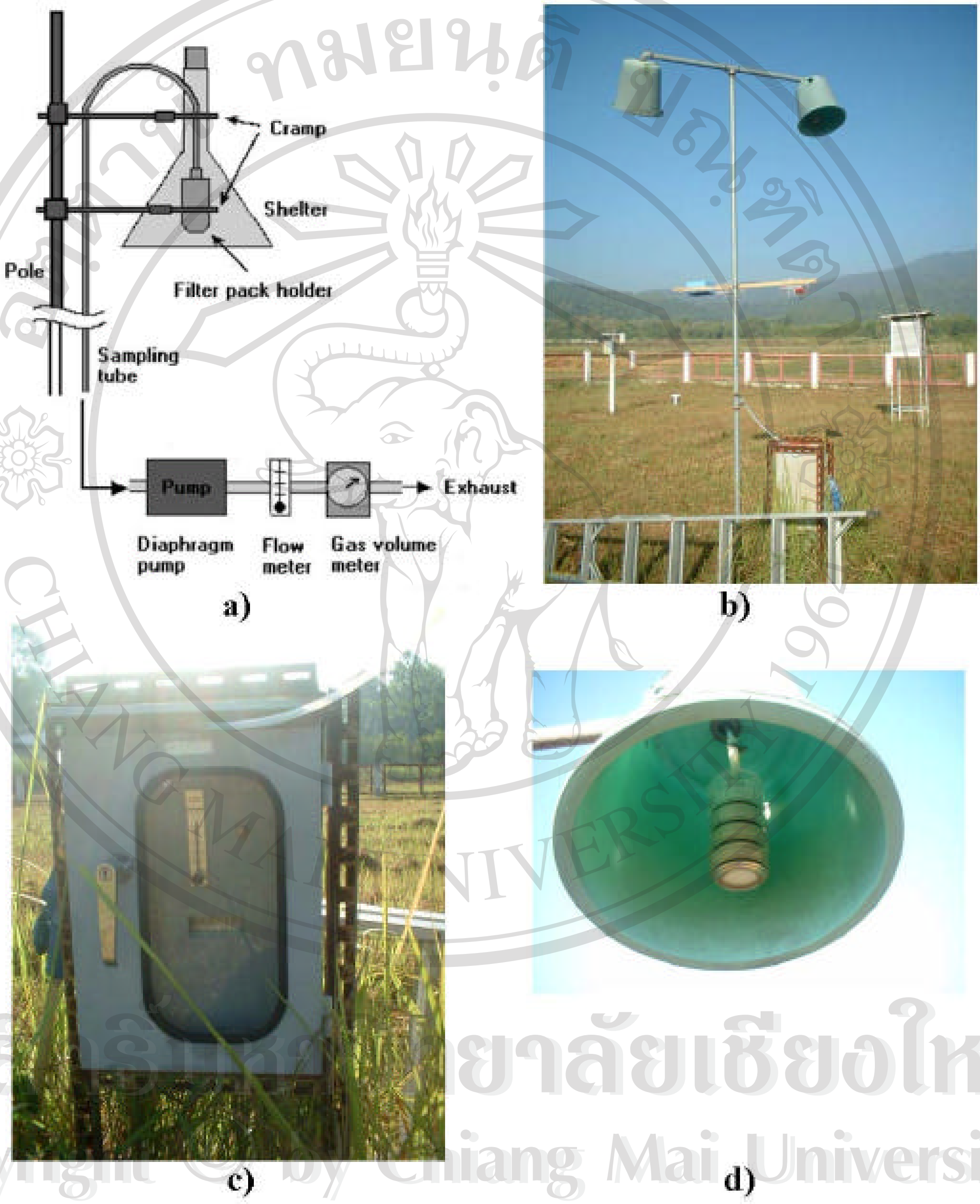

Figure 2.6 Filter pack sampling system and onsite condition

a) Schematic diagrams of filter pack sampling system
b) On-site Filter pack sampling set
c) Pump
d) Connection of filter pack set to sampling set

2.5.5 Sample extraction

Extraction processes of collected dry sampler were necessary in order to bring all analytes into liquid form. Each filter type required a specific solvent for a different proposes.

Collected PTFE (F0) and its laboratory blanks were extracted by 20 ml of de-ionize water contained in clean beakers, which were covered by para-film to reach an equilibrium condition. Then, it was sonicated in an ultrasonic bath for 30 minutes. After extraction process, insoluble matters were filtered out by cellulose acetate membrane (pore size 0.45 µm). Filtrated samples were stored in polyethylene bottles and kept in refrigerator at 4 °C. An extraction processes were also applied to use with other stage filters (F1, F2, and F3). The specification of extracted solution and collected species for each filter are shown in Table 2.2

Table 2.2 Extract solution for each filter sampler.

Stage	**Filter type**	**Collected species**	**Extraction solution**
1st(F0)	Polytetrafluoro ethylene (PTFE)	Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}	20 ml Milli Q water
2nd(F1)	Polyamide	Cl^-, NO_3^-, SO_4^{2-}, NH_4^+	20 ml 0.05% H_2O_2
3rd(F2)	Alkali impregnate filter; 6% K_2CO_3 + 2% glycerin	Cl^-, SO_4^{2-}	20 ml Milli Q water
4th(F3)	Acid impregnate filter; 5% H_3PO_4 + 2% glycerin	NH_4^+	20 ml Milli Q water

2.6 Analytical methods

Analytical work can be divided into analysis of wet and dry depositions. The wet deposition was referred to precipitation samples (rainfall and hail that falled during a monitoring period), while dry deposition was referred to air sample that was collected by four-stage filter pack sampling set.

2.6.1 Wet sample

An analytical procedure for precipitation analysis was started after weighting of rain sample weight. Electro-conductivity (EC) and pH of the samples were measured before filtration. After that, the samples were filtrate by stainless steel syringe filter holder with cellulose acetate posr size 0.45 μm and analyse by ion chromatography for anion and cation concentrations. The steps and methods of analysis are shown in Table 2.3 and Figure 2.6.

a) Electro conductivity

The Electro-Conductivity (EC) is the simply method to determine the total dissolved substances in solution. EC of the samples were measured by Inolab Model TetraCon 325. The measurement was expressed in the mS/m unit. During the measurement the temperature of water bath was controlled at 25 °C. The conductivity range of rain samples extends from <0.5-100 ms/cm.

Potassium chloride standard solutions were used to prepared the calibration curve. Its concentration was 0.01 ppm which gave the conductivity at 141.3 mS/m.

b) pH

The pH of a rain sample is determined electrometrically, using pH standard solutions with a glass electrode in combination with a reference electrode. Using instrument that has temperature compensation can control the temperature effect on electrometric pH measurement. A temperature of 25 °C is recommended for pH measurement.

Two buffer solutions were used to calibrate the pH instrument. Biphthalate and Phosphate solution were used for this propose. Their pH values were 4 and 7, respectively.

Table 2.3 Sampling and analysis of wet deposition

Parameter	Method	Remake
1. Amount of rain (report in millimeter unit.)	Rain gauge	Measure at least 0.1 mm.
2. Total amount of rain water (report in gram unit per day.)	Weight	Measure at least 0.1 g.
3. Electro-Conductivity	Conductivity cell	Measure at least 0.01 mS/m.
4. pH	Glass electrode	Measure at least 0.01 unit.
5. Anions (Cl^-, NO_3^-, SO_4^{2-})	Ion chromatography	Measure at least 0.1 µmol/L.
6. Cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+})	Ion chromatography	Measure at least 0.1 µmol/L.

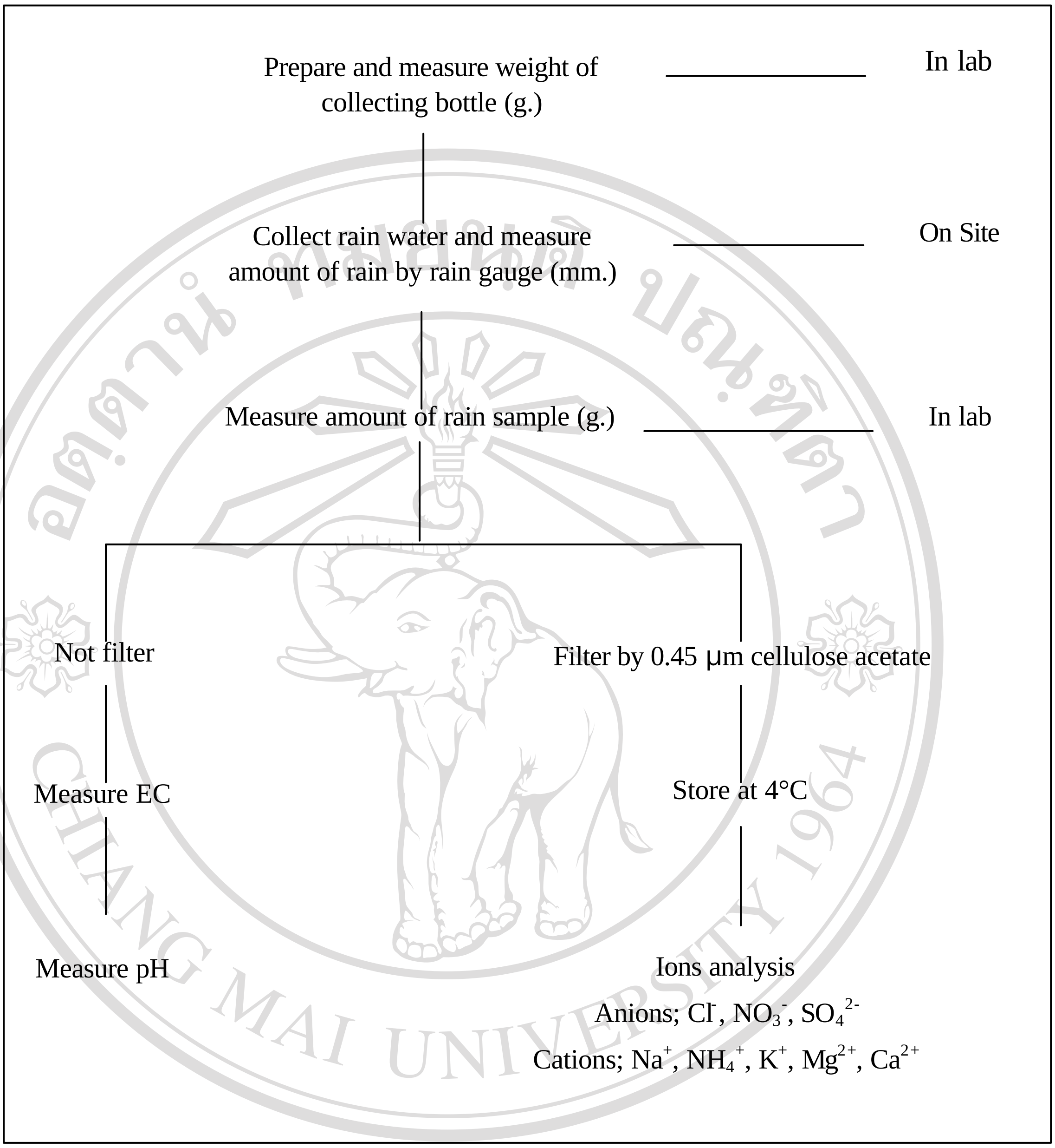

Figure 2.7 Analytical steps for all samples

c) Analysis of ion concentration

Samples were analysed both in term of qualitative and quantitative using Ion chromatograph (DX300). IonPac AS4A (4x250 mm) and IonPac CS12 (4x250 mm) column were used for anion and cation analysis, respectively. Analytes were anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). The analysis conditions for ion chromatography (IC) are concluded in Table 2.4

Table 2.4 IC conditions for anion and cation analysis.

Analysis item	Anion	Cation
Eluent (Mobile phase)	1.8mM Na_2CO_3 / 1.7 mM $NaHCO_3$	20 mM methansulfonic acid
Flow rate	1.5 ml/min	1.0 ml/min
Injection loop	25 µl	25 µl
Injection amount	100 µl	100 µl
Guard column	Anion guard column, IonPac® AG4A, 4 mm. (4 x 50 mm.).	Cation guard column, IonPac® CG12 (4 x 50 mm.).
Analysis column	Anion separation column, IonPac® AS4A, 4 mm. (4 x 250 mm.).	Cation separation column, IonPac® CS12 (2 x 250 mm.).
Suppressor	Anion self regenerating suppressor-I	Cation self regenerating suppressor-I
Detector	Conductivity	Conductivity

The calibration curve for individual ion with 5-7 points of standard concentration was set up.

I) Calibration Curve Preparation

The commercial individual ion standard solution (1000 ppm) from Merck Company has been used for stock solution. The stock solution of each ion was diluted to 100 ppm by Milli Q water. Then, 50 ml mixed anions standard solution was prepared by taking 10 ml of 100 ppm of individual stock solution in 50 ml volumetric flask and adjusted volume by Milli Q water. In the same way, 50 ml of mixed cations standard solution was prepared.

Various concentrations of mixed standard varied from 0.1 to 2.0 ppm wer prepared and injected into IC columns. The working standard solutions were freshly prepared from mix stock standard solution by dilution every analysis day. Then calibration curve of each ion was drawn by plotting peak response (PA) against ion concentration.

d) Anion Analysis

A mixture of 1.70 mM $NaHCO_3$ / 1.80 mM Na_2CO_3 solution was used as an eluent for IonPac AS4A (4x250 mm) column. The eluent stock solution was prepared by dissolved 1.4280 g sodium bicarbonate ($NaHCO_3$) and 1.9085 g sodium carbonate (Na_2CO_3) in milli Q water and diluted the resultant solution to 100 ml. This stock solution was then used to prepare a solution of 1.70 mM $NaHCO_3$ / 1.80 mM Na_2CO_3 by pipetting 10.0 ml of it into 1000 ml volumetric flask and adjusted volume by milli Q water.

The analysis conditions were mentioned in Table 2.4. A 100 µL of sample was injected to ion chromatography under the optimized condition. The run time per injection was 7 minutes.

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

e) Cation analysis

The eluent stock solution for cation system was 1.0 M methansulfonic acid, which prepared by 96.1 g of Metansulfonic acid concentration to 1000 ml by Milli Q water. The cation working eluent (Mobile Phase) was 20 mM methansulfonic acid which was diluted 20.0 ml of eluent stock solution to 1000 ml by milli Q water. A 100 ml of sample was injected to IC under optimized condition as shown in Table 2.4. The run time per injection was 10 minutes.

2.6.2 Dry sample

Extracted samples were measured by ion chromatograph using the same condition as wet samples. However, only ion concentrations were measured. Each layer of filter pack was analysed for different ion species. The first stage filter (PTFE; F0) was analysed for all ion species including Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}. The second stage filter (Polyamide; F1) was analysed for Cl^-, NO_3^-, SO_4^{2-}, NH_4^+. The alkali impregnated filter (F2) in third stage was analysed for Cl^-, SO_4^{2-}. The acid impregnated filter (F3) in the last layer was analysed for NH_4^+.