

CHAPTER 2

METHODOLOGY

2.1 Apparatus

- 2.1.1 0.45 μm Disposable syringe filter cellulose acetate, Chrom Tech, U.S.A.
- 2.1.2 1000, 100, 50, 10, 5 mL volumetric flask, Duran, Germany.
- 2.1.3 25 mL PP volumetric flask, Vit Lab, Germany.
- 2.1.4 400, 100, 50 mL beaker, Scott Duran, Germany.
- 2.1.5 10, 5 mL Transfer pipette, Witeg, Germany.

2.2 Chemicals

- 2.2.1 Chloride (Cl^-) standard solution 1000 ppm, Merck, Germany.
- 2.2.2 Nitrate (NO_3^-) standard solution 1000 ppm, Merck, Germany.
- 2.2.3 Sulfate (SO_4^{2-}) standard solution 1000 ppm, Merck, Germany.
- 2.2.4 Sodium (Na^+) standard solution 1000 ppm, Merck, Germany.
- 2.2.5 Ammonium (NH_4^+) standard solution 1000 ppm, Merck, Germany.
- 2.2.6 Potassium (K^+) standard solution 1000 ppm, Merck, Germany.
- 2.2.6 Calcium (Ca^{2+}) standard solution 1000 ppm, Merck, Germany.
- 2.2.7 Magnesium (Mg^{2+}) standard solution 1000 ppm, Merck, Germany.
- 2.2.8 99.9% Sodium carbonate (Na_2CO_3), Scharlau, Spain.
- 2.2.9 99.7% Sodium hydrogen carbonate (NaHCO_3), Scharlau, Spain.
- 2.2.10 99.5% Tartaric acid, Univar, Australia.
- 2.2.11 98.0% Dipicolinic acid, Fluka, Germany.
- 2.2.12 95-97% Sulfuric acid (H_2SO_4), Merck, Germany.

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

2.2.14 99.5% Thymol (2-Isopropyl-5-methy phenol), Labchem , Australia.

2.3 Instruments

2.3.1 Conductivity meter, tetraCon®325, inoLab, Germany.

2.3.2 Analytical balance, AB304-S, Mettler Toledo, Switzerland.

2.3.3 Micropipette, Eppendorf, Germany.

2.3.4 Wet-only collector, Model 301, Acrochem Metrics Inc., U.S.A.

2.3.5 Ultra-sonicator, T710DH, Elma, Germany.

2.3.6 pH meter, 744, Metrohm, Switzerland.

2.3.7 Vacuum pump, Rocker 300, Keika Ventures, U.S.A.

2.3.8 Oven, Model 100-800, Memmert, Germany.

2.3.9 Ion chromatograph, Model 2.733.0020, Metrohm, Switzerland, consist of

- a) Anion guard column, Metrosep A 4/5 Guard.
- b) Anion separation column, Metrosep A supp 4 (250x4.0mm).
- c) Cation guard column, Metrosep C 2 Guard.
- d) Cation separation column, Metrosep C 2-100 (100x4.0mm).
- e) Anion self-generating Suppressor.
- f) A conductivity detector.
- g) Injection valve, Model C 2-2346DK.
- h) Interface, 771 interface
- i) Pump, 752 unit pump for H₂SO₄ and H₂O to suppressor
- j) Output, IC net 2.3 program

2.4 Sampling Site and Sampling Period

A sampling site is located at Meteorological station in the area of Mea Hia Research Center, Chiang Mai University, Muang District, Chiang Mai Province which in an opening in a large open meadow close to the reservoir. This site was classified as rural site based on Acid Deposition Monitoring Network in East Asia (EANET) criteria which is located at latitude $18^{\circ} 45' 40.3''$ N and longitude $98^{\circ} 55' 54.3''$ E (Chirasathaworn, 2005). Its elevation is 334 meter above mean sea level. The sampling period for both wet and bulk depositions had been done during August 2005 to July 2006. The surrounding detail of sampling site in different scales is shown in Table 2.1 and Figure 2.1.

Table 2.1 Surrounding of sampling site (Chirasathaworn, 2005).

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 area are forest, communities and agricultural areas. Other land-use is air port, golf course, etc.
Regional Scale	10 - 50 km	The radian of this scale covers Chiang Mai city consisting of communities, universities, transportation station, air port, industrial estate, etc.

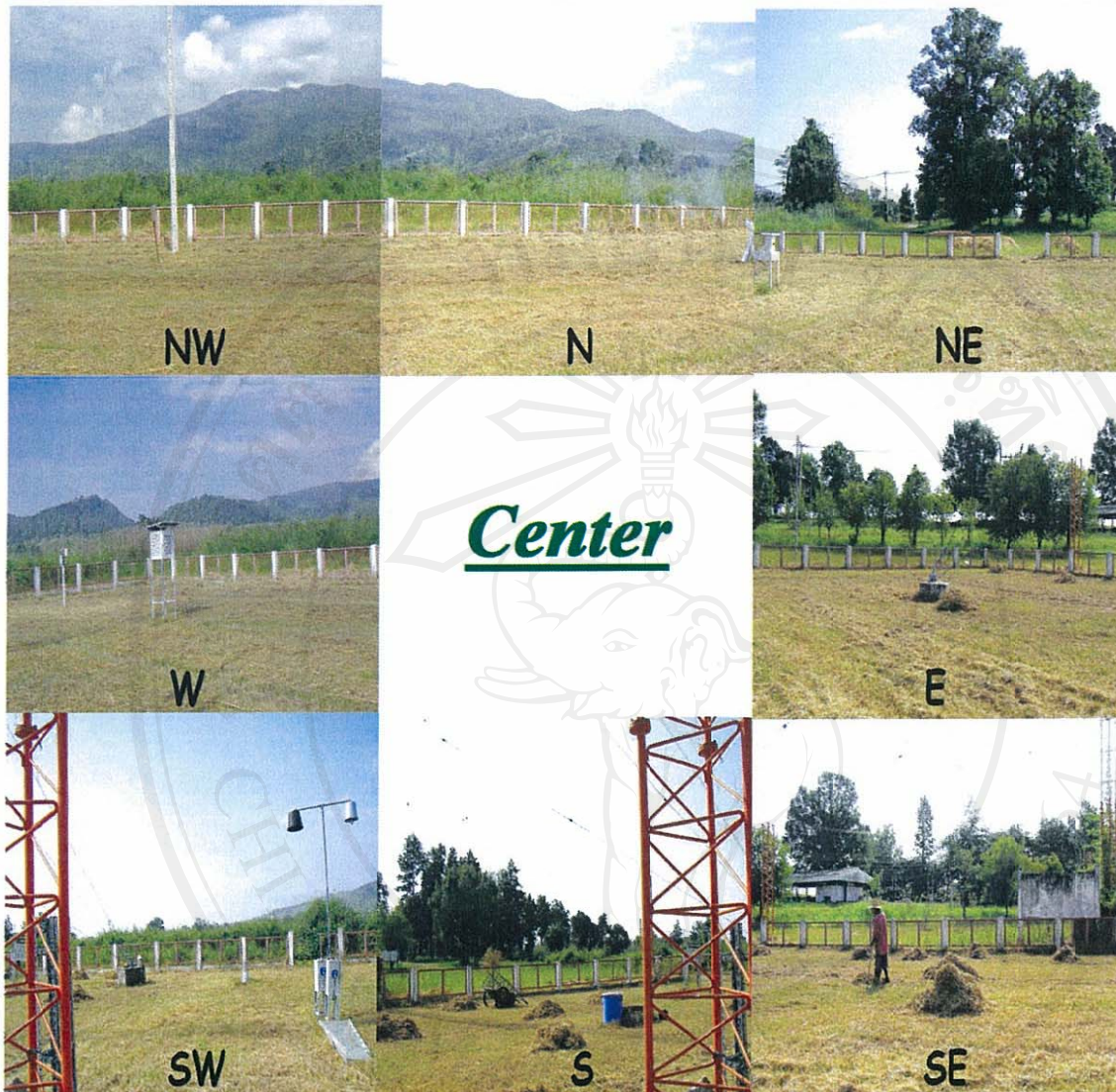


Figure 2.1 Surrounding of sampling site

2.5 Rainwater sampling

Rainwater samples were collected during August 2005 to July 2006 on a daily basis from both of the bulk and wet-only collectors and dispatched to the laboratory for analysis within a week. Sample recovery was made at 9.00 am local time. Bulk collector consist of polyethylene funnels with a diameter of 20 cm, a sharp-edged vertical rim and a slope of 45 degree, set at height of 120 cm above ground level. A

nylon wire mesh placed under the funnels prevented contamination by large particles and some insects. Funnel was supported by and drained into 4.5 L polyethylene bottle. The bottle is wrapped with aluminium foil to shield against light. After rain event, the bottle and funnel were removed and the new (washed) one was put in place. The bulk collector used in this research is shown in Figure 2.2

A scare crew was constructed and placed nearby the sampler for prevention of birds in the sampling site and reduction of into reduce bird dropping contamination by in the bulk collector. A scare crew is shown in Figure 2.3.



Figure 2.2 Self constructed bulk collector

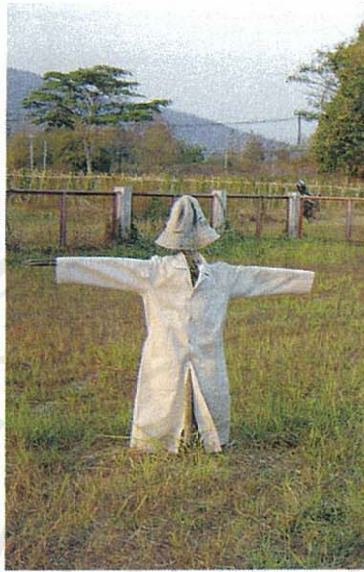


Figure 2.3 A scare crew at the sampling site

Wet-only precipitation was collected by automatic wet-only collector which consists off a bucket which has an orifice diameter of 29 cm, a lid and a sensor. This collector type set at height of 120 cm. Rainfall sensors immediately response to activate the opening of the lid. After rain event, the rainwater was transfer into a cleaned bottle and washed the old bucket with deionized water and put in place. Wet-only collector is shown in Figure 2.4. Rain gauge was used for measurement of precipitation amount in millimeter unit to compare the efficiency of rainwater collection.



Figure 2.4 Wet-only collector

2.6 Chemical analysis.

On arrival at the laboratory, the rainwater sample was weighted and after that it was divided into two parts. First part was for electro-conductivity (EC) and pH measurement under controlled temperature at 25 degree Celsius using conductivity (Figure 2.5 a) and pH meter (Figure 2.5 b), respectively. The second part of the sample was filtrated through 0.45 μm cellulose acetate filter paper and stored in the dark at 4 degree Celsius until ion analysis was performed, typically within a week after sampling.



(a)



(b)



(c)

Figure 2.5 Equipment/instrument used for analysis of chemical composition of rain samples (a) Conductometer, (b) pH meter, (c) Ion chromatograph

A Metrohm ion chromatograph (Figure 2.5 c) was used for the determination of major cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) and major anions (Cl^- , NO_3^- and SO_4^{2-}). Hydrogen ion (H^+) concentration was derived from pH value, while bicarbonate (HCO_3^-) concentration was calculated using the following equation;

$$[\text{HCO}_3^-] = 1.24 \times 10^{(\text{pH}-5.35)} \quad (2.1)$$

The analysis conditions of ion chromatograph (IC) are detailed in Table 2.2

Table 2.2 Conditions of ion chromatograph for anion and cation analysis

Analysis item	Anion	Cation
Mobile phase	1.8 mM Na ₂ CO ₃ /1.7 mM NaHCO ₃	4 mM Tartaric acid/0.75 mM Dipicolinic acid
Flow rate	1.00 mL/min	1.00 mL/min
Injection loop	20.0 µL	20.0 µL
Guard column	Metrosep A 4/5 Guard	Metrosep C 2 Guard
Analysis column	Metrosep A supp 4-250 (4.0 x 250mm)	Metrosep C 2-100 (4.0 x 100mm)
Particle size	9.0 µm	7.0 µm
Suppressor	Anion self-generating Suppressor with DI water/100mM H ₂ SO ₄	No
Detector	Conductivity	Conductivity
Temperature	35.0 °C	35.0 °C

2.7 Preparation of Calibration curve and eluent

2.7.1 Calibration curve preparation

Before analysis of ion concentrations, calibration curve for individual ion species with 5-6 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 anions standard solution 100 µg/mL was prepared by pipetting 5.0 mL of the stock solution of each anion transfer to 50.0 mL volumetric

flask and adjusted volume by deionized water. The same process was done for cations standard solution.

Working ranges of mixed standard solution were 0.1 – 1.0 and 0.2 – 1.0 $\mu\text{g/mL}$ for cations and anions, respectively. They are injected into IC columns under optimum conditions. In case that the concentration of ion in rainwater sample was higher than the range of calibration, higher standard concentration were prepared and injected to IC under the same concentration to cover the sample concentration. The working standard solutions were freshly prepared from mixed stock standard solution by dilution every analysis day. The important point, cation mixed standard was prepared in polypropylene volumetric flask to avoid ion exchange. Then calibration curve of each ion was drawn by plotting peak area against ion concentration.

2.7.2 Preparation of mobile phase for anion analysis

A mixture of 1.70 mM NaHCO_3 / 1.80 mM Na_2CO_3 solution was used as an eluent for Metrosep A supp 4-250 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 deionized water and diluted the resultant solution to 100.0 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 deionized water.

2.7.3 Preparation of mobile phase for cation analysis

The eluent solution for cation analysis was 4 mM Tartaric acid / 0.75 mM dipicolinic acid which prepared by weighted 0.6000 g of tartaric acid and 0.1250 g of

dipicolinic acid and dissolved in deionized water before adjusted volume to 1000 mL in volumetric flask.

Because the system inlet line was very small that air or small particles in eluents 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.

2.8 Accuracy of ion analysis by IC

2.8.1 Repeatability

The repeatability was the results of standard deviation of measurements repeated by the same analyst on the same instrument within a short time period. The repeatability was checked by 7 times continuously injection of a 0.4 ppm mixed standard solution of anions (Cl^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) into ion chromatograph under the optimum conditions.

2.8.2 Reproducibility

The reproducibility was checked by injecting a 0.4 ppm mixed standard solution anions (Cl^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) into ion chromatograph under the optimum conditions for 3 days. The results of the reproducibility were estimated by standard deviation and the related values.

2.9 Detection limit of IC (applied from Taylor, 1987)

Detection limit is commonly understood to be the smallest concentration that can measure with a particular technique. The detection limit was checked by injecting 7 times of the lowest concentration ($0.1 \mu\text{g/mL}$) of mixed cations standard (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) and the lowest concentration ($0.2 \mu\text{g/mL}$) of mixed anions standard (Cl^- , NO_3^- and SO_4^{2-}) into ion chromatographic system under 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.

2.10 Quality assurance and quality control for wet deposition monitoring

The artificial rainwater sample with a code number 052 from the Inter-laboratory comparison project 2005 under the Acid Deposition Monitoring Network in East Asia (EANET) (2005 Round Robin Analysis Survey) was analysed by IC under the same conditions with the real samples. The sample was first 100 times diluted by deionised water and then divided into 3 parts (A, B and C). Each part was injected 3 times to IC under the optimum conditions. The analytical result was used to calculate ion and conductivity balance in order to check the accuracy of analysis.

2.10.1 Cation and anion balance (R_1)

The principle of electro-neutrality in precipitation water requires that total anion equivalents must be equal to total cation equivalents. The ion balance values are controlled by required criteria as shown in Table 1.8. According to this principle, ion balance in a precipitation samples can be calculated by the following equation;

$$R_1 = [(C - A)/(C + A)] \times 100\% \quad (2.2)$$

Where C and A represents anion and cation equivalent, respectively

This is simplified from of the corresponding equation used by US EPA where the denominator is the average of the two sums.

$$A(\mu\text{eq/L}) = \sum C_{Ai} \times V_i \quad (2.3)$$

Where C_{Ai} is the concentration of i-th anion in $\mu\text{mol/L}$, V_i is the valence of the given ion.

$$C(\mu\text{eq/L}) = 10^{(6-\text{pH})}/1.008 + \sum C_{ci} \times V_i \quad (2.4)$$

Where C_{ci} is the concentration of i-th cation in $\mu\text{mol/L}$. If the unit mg/L is used, it should be converted as follows:

$$(\mu\text{mol/L}) = (\text{mg/L}) \times 1000 / M \quad (2.5)$$

Where the molecular weight (M) for cations and anions is given in Table 2.3

When pH is greater than 6 and R_1 is significantly greater than zero, bicarbonate (HCO_3^-) concentration should be included for the computation of R_1 and R_2 . When formic acid, acetic acid, or both are measured, formate and acetate ions should be considered in the evaluation of R_1 and R_2 . The concentrations ($\mu\text{eq/L}$) of these weak acids will be calculated from the dissociation constant, K_a and pH as follows:

$$\begin{aligned}
 [\text{HCO}_3^-] &= P_{\text{CO}_2} H_{\text{CO}_2} K_{a1} / [\text{H}^+] &&= (360 \times 10^{-6})(3.4 \times 10^{-2}) 10^{\text{pH}-6.35+6} \\
 &&&= 1.24 \times 10^{\text{pH}-5.35} \quad (2.6)
 \end{aligned}$$

$$\begin{aligned}
 [\text{HCOO}^-] &= [\text{HCOOH}] K_a / [\text{H}^+] &&= [\text{HCOOH}] \times 10^{\text{pH}-\text{p}K_a} \\
 &&&= [\text{HCOOH}] \times 10^{\text{pH}-3.55} \quad (2.7)
 \end{aligned}$$

$$\begin{aligned}
 [\text{CH}_3\text{COO}^-] &= [\text{CH}_3\text{COOH}] K_a / [\text{H}^+] &&= [\text{CH}_3\text{COOH}] \times 10^{\text{pH}-\text{p}K_a} \\
 &&&= [\text{CH}_3\text{COOH}] \times 10^{\text{pH}-4.56} \quad (2.8)
 \end{aligned}$$

Constants for HCO_3^- , HCOO^- and CH_3COO^- are included in Table 2.3.

Table 2.3 Basic constants of each ion (EANET, 2000)

Ion	Molecular weight (MW)	Molar conductivity (λ) S cm ² / mol
H ⁺	1.008	349.7
NH ₄ ⁺	18.04	73.5
Ca ²⁺	40.08	59.8 x 2
K ⁺	39.10	73.5
Mg ²⁺	24.31	53.3 x 2
Na ⁺	22.99	50.1
NO ₃ ⁻	62.01	71.5
SO ₄ ²⁻	96.06	80.0 x 2
Cl ⁻	35.45	76.3
HCO ₃ ⁻	61.02	44.5
HCOO ⁻	45.00	54.6
CH ₃ COO ⁻	59.10	40.9

Table 2.4 Required criteria for R_1 (EANET, 2000)

(C+A), $\mu\text{eq/L}$	R_1 , %
< 50	± 30
50-100	± 15
> 100	± 8

2.10.2 Electric conductivity balance (R_2)

For dilution solutions (e.g. below 10^{-3} M), the total conductivity can be calculated in mS/m from the molar concentrations and molar conductivity (at infinity dilution) of the individual ions. The calculation is as follows:

$$\Lambda_{\text{calc}} = \sum c_i \Lambda_i^0 \times 10^{-4} \quad (2.9)$$

Where Λ_{calc} denotes the calculated conductivity of the solution (in mS/m), C_i the ionic concentration of the i -th ion (in $\mu\text{mol/L}$), Λ_i^0 the molar conductivity (in $\text{S cm}^2/\text{mol}$) at infinite dilution and 25.0°C .

Thus

$$\Lambda_{\text{calc}} = \left\{ \begin{array}{l} 349.7 \times 10^{(6-pH)} + 80.0 \times 2c(\text{SO}_4^{2-}) + 71.5c(\text{NO}_3^-) + 76.3c(\text{Cl}^-) \\ + 73.5c(\text{NH}_4^+) + 50.1(\text{Na}^+) + 73.5c(\text{K}^+) + 59.8 \times 2c(\text{Ca}^{2+}) + 53.3 \times 2c(\text{Mg}^{2+}) \end{array} \right\} / 1000$$

Where $c(\dots)$ denotes the ionic concentrations in $\mu\text{mol/L}$ of the ion in parentheses and the constants are the molar conductivity of the individual ion at infinite dilution at 25°C (Table 2.3).

The calculation conductivity values can then be compared to the observed value for precipitation samples as the relation below;

$$R_2 = \left(\frac{\Lambda_{calc} - \Lambda_{meas}}{\Lambda_{calc} + \Lambda_{meas}} \right) \times 100\% \quad (2.10)$$

This is similar to the equation for the calculation of cation and anion balance.

The required comparison criteria of measured and calculated ionic and conductivities are expressed in Tables 2.4 and 2.5, respectively. If the required ionic and conductivity comparison criteria have not been met, the analysis should be repeated or a flag should be entered into the database indicating that the result did not meet the required criteria.

Table 2.5 Required criteria for R_2 (EANET, 2000)

Λ_{meas} , mS/m	R_2 , %
< 0.5	± 20
0.5-3	± 13
> 3	± 9