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 1000, 600, 400, 100, 50 mL beaker, Scott Duran, Germany.
- 2.1.5 10, 5 mL graduate pipette, Witeg, Germany.
- 2.1.6 10, 5 mL transfer pipette, Witeg, Germany.
- 2.1.7 1000 mL funnel, Alltech, Blegium.
- 2.1.8 In-line filter cap, Alltech, Blegium
- 2.1.9 Stainless steel mesh filter support ring, Alltech, Blegium
- 2.1.10 1000 mL GL-45 safety-coated glass bottle, Alltech, Blegium

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- 2.2.1 Chloride (Cl⁻) standard solution 1000 ppm, Merck, Germany.
- 2.2.2 Nitrate (NO₃⁻) standard solution 1000 ppm, Merck, Germany.
- 2.2.3 Sulfate (SO_4^{2-}) standard solution 1000 ppm, Merck, Germany.
- 2.2.4 Phosphate (PO₄³⁻) standard solution 1000 ppm, Merck, Germany.
- 2.2.5 Acetate (CH₃COO⁻) standard solution 1000 ppm, AccuSPEC, Canada.
- 2.2.6 Formate (HCOO⁻) standard solution 1000 ppm, AccuSPEC, Canada.

- 2.2.7 Sodium (Na⁺) standard solution 1000 ppm, Merck, Germany.
- 2.2.8 Ammonium (NH₄⁺) standard solution 1000 ppm, Merck, Germany.
- 2.2.9 Potassium (K⁺) standard solution 1000 ppm, Merck, Germany.
- 2.2.10 Calcium (Ca²⁺) standard solution 1000 ppm, Merck, Germany.
- 2.2.11 Magnesium (Mg²⁺) standard solution 1000 ppm, Merck, Germany.
- 2.2.12 99.9% Sodium carbonate (Na₂CO₃), Scharlau, Spain.
- 2.2.13 99.7% Sodium hydrogen carbonate (NaHCO₃), Scharlau, Spain.
- 2.2.14 99.5% Tartaric acid, Univar, Australia.
- 2.2.15 98.0% Dipicolinic acid, Fluka, Germany.
- 2.2.16 95-97% Sulfuric acid (H₂SO₄), Merck, Germany.
- 2.2.17 Deionized water (conductivity < 0.15 mS/m), Chemistry Department, Chiang Mai University.
- 2.2.18 Milli Q water, Chemistry Department, Chiang Mai University.
- 2.2.19 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 Analitical 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 Filter holder set, Milipore, U.S.A.
- 2.3.6 Filter membrane, 0.45 µm nylon, diameter 47 mm, Sartorius, Germany
- 2.3.7 Filter membrane (F0), 0.8 µm Polytetrafluoro ethylene filter (PTFE),

47 mm. diameter, MFS, Japan.

- 2.3.8 Filter membrane (F1), 0.45 μm Polyamide filter, diameter 47 mm,Orange Scientific, Japan.
- 2.3.9 Filter membrane (F2), 0.45 μm Cellulose filter, diameter 47 mm, ADVANTEC, Japan.
- 2.3.10 Filter membrane (F3), 0.45 µm Cellulose filter, diameter 47 mm,

ADVANTEC, Japan.

of

- 2.3.11 Four-Stage open face filter holder, Nilu, Norway.
- 2.3.12 Ultra-sonicator, T710DH, Elma, Germany.
- 2.3.13 pH meter, 744, Metrohm, Switzerland.
- 2.3.14 Vacuum pump, Rocker 300, Keika Ventures, U.S.A.
- 2.3.15 Oven, Model 100-800, Memmert, Germany.
- 2.3.16 Ion chromatograph, Model 2.733.0020, Metrohm, Switzerland, consist

a) Anion guard column, Metrosep A 4/5 Guard.

- b) Anion separation column, Metrosep A supp 5 (250x5.0mm).
- c) Cation guard column, Metrosep C 2 Guard.
- d) Cation separation column, Metrosep C 2-150 (150x4.0mm).

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 $\mathrm{H}_2\mathrm{SO}_4$ and $\mathrm{H}_2\mathrm{O}$ 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 Mae Hia Research Center, Chiang Mai University, Muang District, Chiang Mai Province (Figure 2.1) 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° 45' 40.3" N and longitude 98° 55' 54.3" E (Chirasathaworn, 2005). Its elevation is 334 meter above mean sea level. The surrounding detail of sampling site in different scales is shown in Table 2.1 and Figure 2.3. Figure 2.2 is a type of land use around sampling site in regional scale. The sampling period for both wet and dry depositions had been done within 16 months during September 2006 to December 2007. The sampling period has been divided into four periods (Wet I is September 2006 – October 2006, Dry I is November 2006 – April 2007, Wet II is May 2007 – October 2007, Dry II is November 2007 – April 2007).

	Scale Type	Radian	Details
	Onsite Scale	0 - 100 m	80% of Mae Hia Research Center are used for
â,	i anê	าเหาถึง	research purposes stock for students of
	Jand		Agriculture and Veterinary Faculties.
Co	Local Scale	100 m - 10 km	Most of the area are forest, communities and
	P715	Uy C	gricultural areas. Other land-use is airport, golf
Α	ll r	ight	course, etc. e s e r v e d
	Regional Scale	10 - 50 km	The radian of this scale covers Chiang Mai city
			consisting of communities, universities,
			transportation station, airport, industrial estate,
			etc.

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



Figure 2.2 Type of land use around sampling site in regional scale



Figure 2.3 Surrounding of sampling site

2.5 Wet deposition

2.5.1 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 2.4. 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. Before raining occurs should to put thymol about 1-5 g/time to preserve rain samples. Sampling periods was 16 months started from 1 September, 2006 to 31 December, 2007.

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 Environmental Chemistry Research Laboratory, Faculty of Science, Chiang Mai University. They were stored in refrigerator at 4 °C.



Figure 2.4 Precipitation collector instrument

2.6 Dry Deposition

2.6.1 Air Samples Collection

A dry deposition sample is proposed to measure the level of air pollution in atmosphere. The main pollutants such as SO₂, HNO₃, NH₃, 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 was set up at the height of about 3 meters above the ground. During sampling period, the diaphragm pump was set for stable flow rate (1 L/min). For measuring of air volume, mass flow meters were used in order to avoid the effect of the low atmospheric pressure at high altitude. The mass flow meter was installed between filter holder and pump. Gas volume meters with flow rate meters (of float type) were also acceptable. In this case, the flow rate meter and gas volume meter were set up consequently after the pump to measure flow rate and volume under the condition of atmospheric pressure (Chirasathaworn, 2005). Air volumes counted by mass flow meter or gas volume meters was used for calculation of ambient air concentration.

The four-stage filter pack is composed of four filters in line with the air stream as shown in Figure 2.5 Aerosols were collected on the first filter while the gaseous substances such as SO₂, HNO₃, NH₃ and HCl will pass though this filter. HNO₃, partial SO₂, HCl and NH₃ in air sample were collected by second filter. The remaining SO₂ and HCl were reacted with alkali impregnated substance on the third filter.Finally, the fourth filter with acid impregnated substance trapped the remaining NH₃ in air samples after passing through the first, second and third filters.



Figure 2.5 Schematic diagram of four-stage filter pack

2.6.2 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 (Chirasathaworn, 2005).

The first two layers (F0 and F1) of filter pack sampling set are not necessary to impregnate with any solution. By the way, the other two layer filters (F2 and 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 is easily occurred and it will effect to the blank samples, therefore plastic gloves were used to handle in this step. All glassware were washed by de-ionized water and dried in an oven at 60 °C. After dried, cleaned glass wears were prevented from contamination by kept in plastic zip bag.

I) Alkaline impregnate solution (F2), 6% K₂CO₃ + 2% glycerin

Alkaline impregnated solution for the third layer of a four stage filter pack was the potassium carbonate solution. $30 \text{ g } \text{K}_2\text{CO}_3$ 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% H₃PO₄ + 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, cellulose filters were soaked in 1st, 2nd and 3rd beaker, respectively using clean plastic tweezers. An excess alkaline (F2) and acid (F3) solution on cellulose filters were absorbed by clean cellulose sheet (ADVANTEC No.590). After that, the impregnated filters were kept in a pettri dish and packed in a plastic zip bag to prevent from contamination. The diagram showing the coating steps is illustrated in Figure 2.6.



Figure 2.6 Impregnation of filter (F2 and F3)

2.6.3 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 2.7). Flow rate of air input was 1 L/min. Detail of sampling such as time, ambient temperature were recorded. Operation of sampling was for 10 days continuously. Therefore, 3 samples per month were collected.

2.6.4 Sample Collection

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Flow rate of pump and site conditions were recorded before stop the sampling. Filter pack holder set was disconnected from the sampling set after turned off the operation of the 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.

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- Figure 2.7 Filter pack sampling system and onsite condition (Chirasathaworn, 2005)
- a) Schematic diagrams of filter pack sampling system
- b) On-site Filter pack sampling set
- c) Pump

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d) Connection of filter pack set to sampling set

2.6.5 Sample extraction

Extraction of collected filters 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 deionized 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 μ m). 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
		33 63	solution
1 st (F0)	Polytetrafluoro ethylene	NH4 ⁺ , Ca ²⁺ , K ⁺ , Mg ²⁺ ,	20 ml Milli-Q
	(PTFE)	Na ⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	water
$2^{nd}(F1)$	Polyamide	NH4 ⁺ , Cl ⁻ , NO3 ⁻ , SO4 ²⁻	20 ml 0.05% H ₂ O ₂
3 rd (F2)	Alkali impregnate filter;	Cl ⁻ , SO ₄ ²⁻	20 ml Milli-Q
onvrid	$6\% \text{ K}_2 \text{CO}_3 + 2\% \text{ glycerin}$	iang Mai U	water
4 th (F3)	Acid impregnate filter;		20 ml Milli-Q
	5% H ₃ PO ₄ + 2% glycerin	rese	water e u

2.7 Chemical analysis.

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.

2.7.1 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 filtered by stainless steel syringe filter holder with cellulose acetate pore size 0.45 mm and analysed by ion chromatography for anion and cation concentrations. The methods of analysis are shown in Table 2.3.

Parameter	Method	Remake
1. Amount of rain (mm)	Rain gauge	Detection level 0.1 mm.
2. Total amount of rain water	Weight	Detection level 0.1 g.
(gram/day)	U	a ? '
3. Electro-Conductivity	Conductivity cell	Detection level 0.01 mS/m.
4. pH	Glass electrode	Detection level 0.01 unit.
5.Anions(HCOO ⁻ , CH ₃ COO ⁻ , Cl ⁻ , NO ₃ ⁻ , PO ₄ ³⁻ and SO ₄ ²⁻)	Ion chromatography	Detection level 0.1 µmol/L.
6. Cations(Na ⁺ , NH ₄ ⁺ , K ⁺ , Ca ²⁺ and Mg ²⁺)	Ion chromatography	Detection level 0.1 µmol/L.

Table 2.3 Sampling and analysis of wet deposition

a) Electro-conductivity

The Electro-Conductivity (EC) is the simply method to determine the total dissolved inorganic substances in solution. EC of the samples were measured by Inolab Model TetraCon 325 (Figure 2.8a). The measurement was expressed in mS/cm unit. During the measurement temperature of water bath was controlled at 25 °C. Potassium chloride (KCl) standard solutions were used to prepare calibration curve of conductivity. At 0.01 ppm KCl concentration, the conductivity should be obtained 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. In this work, Metrohm pH meter (Figure 2.8b) was used. 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.



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Figure 2.8 Equipment/instrument used for analysis of chemical composition of rain samples (a) Conductometer inoLab/tetraCon®325, (b) pH meter Metrohm/model 744, (c) Ion chromatograph Metrohm/model 2.733.0020

c) Analysis of ion concentration

A Metrohm ion chromatograph (Figure 2.8 c) was used for the determination of major cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) and major anions (HCOO⁻, CH₃COO⁻, Cl⁻, NO₃⁻ and SO₄²⁻). Hydrogen ion (H⁺) concentration was derived from pH value, while bicarbonate (HCO₃⁻) concentration was calculated using the following equation; $[HCO₃⁻] = 1.24 \times 10^{(pH-5.35)}$ (2.1)

The analysis conditions of ion chromatograph (IC) are detailed in Table 2.3

Analysis item	Anions	Cations	
Mobile phase	1.8 mM Na ₂ CO ₃ /1.7 mM NaHCO ₃	4 mM Tartaric	
â/0.75		mM	
Dipicolinic â		21	
Flow rate	0.70 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 5-250	Metrosep C 2-150	
	(5.0 x 250mm)	(4.0 x 150mm)	
Particle size	9.0 μm	7.0 μm	
Suppressor	Anion self-generating suppressor		
	with DI water/100mM H ₂ SO ₄	\rightarrow //	
Detector	Conductivity	Conductivity	
Temperature	35.0 °C	35.0 °C	

 Table 2.4 Conditions of ion chromatograph for anion and cation analysis

2.7.2 Dry sample **1918**1888888

Extracted samples were measured by ion chromatograph using the same conditions as analysis of 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 NH₄⁺, Ca²⁺, K⁺, Mg²⁺, Na⁺, Cl⁻, NO₃⁻, and SO₄²⁻. The second stage filter (Polyamide; F1) was analysed for NH₄⁺, Cl⁻, NO₃⁻, and SO₄²⁻. The alkali impregnated filter (F2) in third stage was

analysed for Cl⁻ and SO₄²⁻. The acid impregnated filter (F3) in the last layer was analysed for NH_4^+ .

2.8 Preparation of Calibration curve and eluent

2.8.1 Calibration curve preparation

Before analysis of ion concentrations, calibration curve for individual ion species with 5-8 points of standard concentrations was constructed. The commercial individual ion standard solution (1000 μ g/mL) from Merck Company has been used for stock solution. Mixed anions standard solution 100 μ g/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 precess was done for cations standard solution.

Working ranges of mixed standard solution were $0.1 - 10.0 \mu$ g/mL for cations and anions. They were 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 conditions to cover the sample concentration. The working standard solutions were freshly prepared form 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.

2.8.2 Preparation of mobile phase for anion analysis

A mixture of 1.70 mM NaHCO₃ / 1.80 mM Na₂CO₃ solution was used as an eluent for Metrosep A supp 5-250 column. The eluent stock solution was prepared by dissolved 1.4280 g sodium bicarbonate (NaHCO₃) 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 NaHCO₃ / 1.80 mM Na₂CO₃ by pipetting 10.0 mL of it into 1000 mL volumetric flask and adjusted volume by milli Q water.

2.8.3 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 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 0.45μ m) and degassed by vacuum and ultra-sonication prior to analysis.

2.9 Accuracy of ion analysis by IC

2.9.1 Repeatability

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 7 times continuously injection of a 0.4 ppm mixed standard solution of anions (HCOO⁻, CH₃COO⁻, Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) into ion chromatograph under the optimum conditions.

2.9.2 Reproducibility

The reproducibility was checked by injecting a 0.4 ppm mixed standard solution anions (HCOO⁻, CH₃COO⁻, Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻) and cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) into ion chromatograph under the optimum conditions for 3 days. The results of the reproducibility were estimated by standard deviation and the related values.

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

Detection limit is commonly understood to be the smallest concentration that can be measured with a particular technique. The detection limit was checked by injecting 7 times of the lowest concentration (0.1 μ g/mL) of mixed cation standard (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) and the lowest concentration (0.2 μ g/mL) of mixed anion standard (HCOO⁻, CH₃COO⁻, Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻) 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.

2.11 Quality assurance and quality control for wet deposition monitoring

The artificial rainwater sample with a code number 061 (high concentration) and 062 (low concentration) from the Inter-laboratory comparison project 2006 under the Acid Deposition Monitoring Network in East Asia (EANET) 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.

2.11.1 Cation and anion balance (R₁)

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. According to this principle, ion balance in a precipitation samples can be calculated by the following equation;

$$R_{1} = [(C - A)/(C + A)] \times 100\%$$
(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.

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

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

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

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

$$(\mu mol/L) = (mg/L) \times 1000 / M$$
 (2.5)

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

When pH is grater than 6 and R1 is significantly greater than zero, bicarbonate (HCO_3^-) concentration should be included for the computation of R₁ and R₂. When formic acid, acetic acid, or both are measured, formate and acetate ions should be considered in the evaluation of R₁ and R₂. The concentrations (µeq/L) of these weak acids will be calculated from the discussion constant, K_a and pH as follows:

$$\begin{bmatrix} HCO_{3}^{-} \end{bmatrix} = P_{CO_{2}}H_{CO_{2}}K_{a1} / \begin{bmatrix} H^{+} \end{bmatrix} = (360 \times 10^{-6})(3.4 \times 10^{-2})10^{pH-6.35+6}$$
$$= 1.24 \times 10^{pH-5.35}$$
(2.6)

 $[HCOOH] \times 10^{pH-pKa}$

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Constants for
$$HCO_3$$
, $HCOO$ and CH_3COO are included in Table

Table 2.5 Basic constants of each ion (EANET, 2000)

 $[HCOO^{-}] = [HCOOH] Ka / [H^{+}]$

 $= [HCOOH] \times 10^{pH-3.55}$ (2.7) $= [CH_3COOH] \times 10^{pH-pKa}$ (2.8)

 $[CH_3COO^{-}] = [CH_3COOH] Ka / [H^{+}]$

tants for
$$HCO_3^-$$
, $HCOO^-$ and CH_3COO^- are included in Table 2.

$$= [CH_3COOH] \times 10^{pH-4.30}$$

O₃⁻, HCOO⁻ and CH₃COO⁻ are included in Table 2.4.

$$D_3^-$$
, HCOO⁻ and CH₃COO⁻ are included in Table 2.

IonMolecular weight (MW)Molar conductivity (
$$\lambda$$
)
S cm² / molH⁺1.008349.7NH₄⁺18.0473.5Ca²⁺40.0859.8 x 2K⁺39.1073.5Mg²⁺24.3153.3 x 2Na⁺22.9950.1NO₃62.0171.5SO₄²⁻96.0680.0 x 2Cl⁻35.4576.3HCO₃⁻61.0244.5HCOO⁻45.0054.6CH₃COO⁻59.1040.9

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2.11.2 Electric conductivity balance (R₂)

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:

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

Where Λ_{calc} denotes the calculated conductivity of the solution (in mS/m), Ci the ionic concentration of the i-th ion (in µmol/L), Λ_i^0 the molar conductivity (in S cm²/mol) at infinite dilution and 25.0 °C.

Thus

$$\Lambda calc = \begin{cases} 349.7 \times 10^{(6-pH)} + 80.0 \times 2c(SO_4^{2-}) + 71.5c(NO_3^{-}) + 76.3c(Cl^{-}) \\ + 73.5c(NH_4^{+}) + 50.1(Na^{+}) + 73.5c(K^{+}) + 59.8 \times 2c(Ca^{2+}) + 53.3 \times 2c(Mg^{2+}) \end{cases} / 1000$$

Where c (...) denotes the ionic concentrations in μ 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 2.4).

The calculation conductivity values can then be compared to the observed value for precipitation samples as the relation below; $R_{2} = \left((\Lambda_{calc} - \Lambda_{meas}) / (\Lambda_{calc} + \Lambda_{meas}) \right) \times 100\%$ (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 2.5 and 2.6, 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 resulted did 0783 not meet the required criteria.

Table 2.6 Required criteria for R₂ (EANET, 2000)

S	$\Lambda_{\rm meas},{ m mS/m}$		R ₂ , %	
	< 0.5	Juliu Martin	<u>+</u> 20	
STA	0.5-3	t a A	±13	
305	>3	- Culton	<u>+</u> 9	

Quality assurance and quality control for dry deposition monitoring 2.12

Filter samples from the Inter-laboratory comparison project 2006 under the Acid Deposition Monitoring Network in East Asia (EANET) were analysed by IC in term of 3 parameters: chloride ion, sulfate ion (from the sample filters impregnated by K₂CO₃) and ammonium ion (from the sample filters impregnated by H₃PO₄) in the extracted solution. The details of samples are shown in Table 2.7.

In the case of samples No.061d-1, No.062d-1, No.063d-1, 20 ml H₂O₂ solution (0.05%-v/v) were poured into a beaker and ultrasonicated for 20 minutes. Samples No.061d-2, No.062d-2, No.063d-2, were handeled in the same way as the 1st series sample, only DI water was used instead of H₂O₂. The insoluble matters were filtered out of the extracted solutions using a membrane filter (pore size 0.45 μ m), which previously well washed by deionized water more than 100 ml. The sample

tubes were sealed and kept in the refrigerator. Samples analysis was carried out as soon as possible after extraction by IC under the same conditions with the real samples.

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Name	Details	Container	Number	Note
			of samples	
No.061d-1	Alkali-Impregnated	Polyethylene	3 replicates	Known amount of salts
9.	filter (small amount)	centrifuging	(a,b,c)	were put on the filter
67	(Juliu	tube	L	impregnated by K ₂ CO ₃
No.061d-2	Acid-Impregnated	Polyethylene	3 replicates	Known amount of salts
502	filter (small amount)	centrifuging	(a,b,c)	were put on the filter
202		tube		impregnated by H ₃ PO ₄
No.062d-1	Alkali-Impregnated	Polyethylene	3 replicates	Known amount of salts
	filter (small amount)	centrifuging	(a,b,c)	were put on the filter
		tube		impregnated by K ₂ CO ₃
No.062d-2	Acid-Impregnated	Polyethylene	3 replicates	Known amount of salts
× ×	filter (small amount)	centrifuging	(a,b,c)	were put on the filter
		tube	25'/	impregnated by H ₃ PO ₄
No.063d-1	Alkali-Impregnated	Polyethylene	3 replicates	The filter was
	filter (small amount)	centrifuging	(a,b,c)	impregnated by H ₃ PO ₄
	٢	tube	_	0
No.063d-2	Acid-Impregnated	Polyethylene	3 replicates	The filter was
quant	filter (small amount)	centrifuging	(a,b,c)	impregnated by K ₂ CO ₃
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 Table 2.7 Details of sample filters