Chapter III

Methodology

The investigation of sulfate aerosol and its acidity was conducted from 8th to 23rd in January 1996. The concentration of SO_2, sulfate, ozone, catalysts and meteorological data from two communities near Mae Moh Power Plant, Lampang Province were measured. Various sampling and analysis techniques have been used to determine the relevant parameters. The meteorological, SO_2 and O_3 concentrations were provided by Pollution Control Department (PCD) and Electricity Generating Authority of Thailand (EGAT) from continuous measurement apparatus as indicated in table 3-1.

Table 3-1 Sampling and Analysis Methods

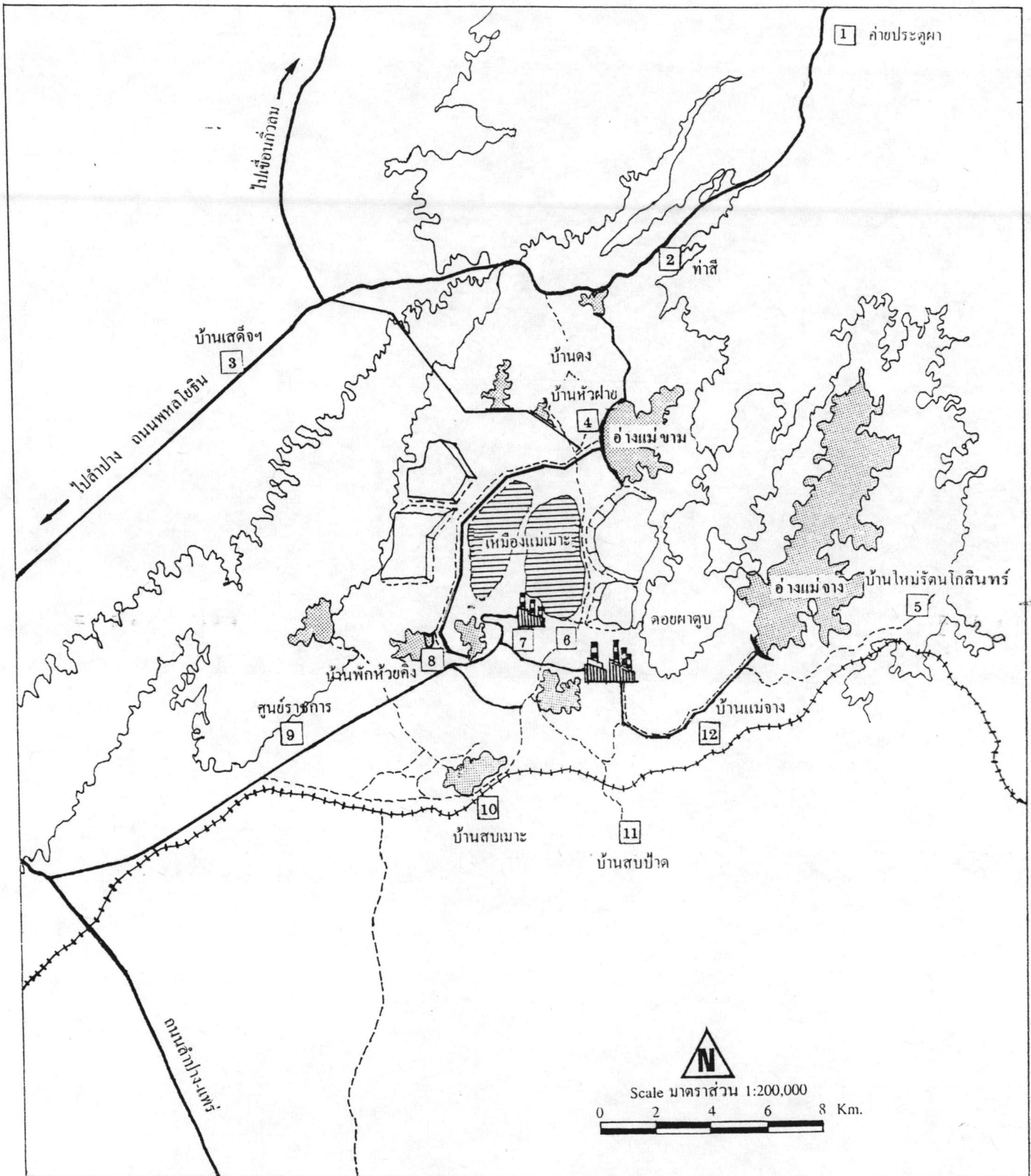| Parameter	Sampling	Analysis
Atmospheric Data :-		
Sulfur Dioxide (SO_2)[@]	Fluorescence Analysis	Fluorescence Analysis
Sulfate (SO_4^{2-})	Annular Denuder System	Ion Chromatography
Ozone (O_3)[@]	Chemiluminescense	Chemiluminescense
Hydrogen Ion (H^+)	Annular Denuder System	pH Analysis
Ammonia (NH_3)	Annular Denuder System	Colorimetry
Heavy Metal (Fe, Mn, V)	High-Volume Air Sampler	Atomic Absorption Spectroscopy
Meteorological Data :-		
Solar Radiation[@]	Pyranometer $(\lambda = 280\text{-}2800 \text{ nm})$	-
Net Radiation[©]	Eppley Pyranometer	-
Wind Speed[©]	Anemometer	-
Wind Direction[©]	Wind Vane	-

Remark: [@] Data were provided by PCD.
       [©] Data were provided by EGAT.

3.1 Criteria for Site Selection

The study of sulfate aerosol and its acidity was taken place at Ban Sob Pat and Ban Tha Si where the distance from the Power Plant are about 8 and 13 kilometers, respectively as shown in figure 3-1. The criteria for these sampling sites selection were as below:
- The two sampling sites locate approximately downwind and upwind positions from the Power Plant under the northeastern wind which is the prevailing wind during wintertime period.

MAE MOH AIR QUALITY MONITORING STATIONS NETWORK

1 ค่ายประตูผา

ไปเขื่อนกิ่วลม

2 ท่าสี

บ้านเสด็จฯ

3

บ้านดง

บ้านห้วยฝาย

ไปลำปาง ถนนพหลโยธิน

4 อ่างแม่ขาม

เหมืองแม่เมาะ

อ่างแม่จาง บ้านใหม่รัตนโกสินทร์

ดอยผาดูบ

5

7 6

8

บ้านพักห้วยคิง

บ้านแม่จาง

12

ศูนย์ราชการ

9

10

11

บ้านสบเมาะ

บ้านสบป้าด

ถนนเข้าปางม่วง

N

Scale มาตราส่วน 1:200,000

0   2   4   6   8 Km.

Mae Moh Air Quality monitoring Stations		Monitoring Parameters
1. Pratupha Army Camp	10. Ban Sob Moh	Continuous SO₂ , NO₂, TSP

Mae Moh Air Quality monitoring Stations:
1. Pratupha Army Camp
2. Ban tha Si
3. Ban Sadet
4. Ban Hua Fai
5. Ban Mai Ratanakosin
6. Metrorological Main Station
7. EGAT House Ban Ko-O
8. EGAT Housing Ban Huai King
9. Mae Moh Goverment Center
10. Ban Sob Moh
11. Ban Sob pat
12. Ban Mae Chang
13. Mae Moh Plantation
14. Substation 2
15. Old Power Plant EGAT Housing
16. Ban Phalad
17. Ban Hua Sua

Monitoring Parameters
Continuous SO₂ , NO₂, TSP
☐ Station No. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10,11 .12
Metrorological Tower
☐ Station No. 1, 3, 4, 5, 6, 7, 8, 9, 10, 11,12,14
Integrated SO₂, NO₂, TSP
O Station No. 15
Dustfall and Sulfation
O Station No. 6, 13, 14, 16, 17

Figure 3-1 Sampling Site and Mae Moh Air Quality Monitoring Stations Network.

- The statistic of SO_2 measurements from PCD and EGAT continuous SO_2 monitoring data indicate that Ban Sob Pat has the highest SO_2 levels, especially during wintertime period.

- Equipment limitations and electrical power requirements limited the available site, but both of the selected sampling sites are within the villages having the similar socio-economic patterns.

3.2 Criteria for Sampling Period

This investigation was conducted from January 8th-23rd, 1996 (during the wintertime due to the climatological condition of Thailand). By considering data from the solar radiation which indicate that the surface soil (heat gain) can obtain the sunlight at about 8.00-9.00 and be dropped at about 17.00. Samples were collected twice per day (09.00-17.00 and 17.00-09.00) which represented daytime and nighttime period. Appendix C show the diurnal patterns of solar radiation and net radiation during the sampling time.

3.3 Sulfate aerosol

3.3.1 Sampling

Sulfate aerosol is collected by the annular denuder system (ADS) which consists of an inlet with an impactor or cyclone preseparator designed to eliminate all particles with a DP_{50} of 2.5 μm or greater, an annular denuder to remove ammonia, and a filter for collecting the aerosol. The system was operated by drawing air through the elutriator-accelerator jet assembly, an impactor frit and coupler assembly, passed denuders to remove nitric acid and ammonia, then into a single-stage filter assembly, respectively. The single-stage filter assembly contains a 47-mm Teflon® filter supported by a stainless steel screen. The filter is a 2 μm pore-size Teflon® membrane filter, Zefluor (Gelman Sciences). The Teflon® filter collects the fine aerosol. The pump unit maintains a flow of 10 L/m, and a timer allows programmed start and end times. ADS samples have run each day for 8 hours (17.00-09.00) and 16 hours (09.00-17.00) for 15-day periods. Figure 3-2 illustrates a two-stage annular denuder system assembled. Figure 3-3 shows the field sampling box with the two-stage annular denuder and pump-timer system.

3.3.2 Analysis

The ADS assembly is removed subsequently between each run from its field housing, its ends capped, and it is brought back to the laboratory. In the laboratory, the assembly pieces are uncoupled and capped. The denuder tube is not extracted. The Teflon® filter is unloaded from the filter assembly in an ammonia free atmosphere and either immediately extracted or stored in a ammonia free container for later extraction. A glove-box, lined with citric acid soaked paper, is used to maintain an ammonia free atmosphere.
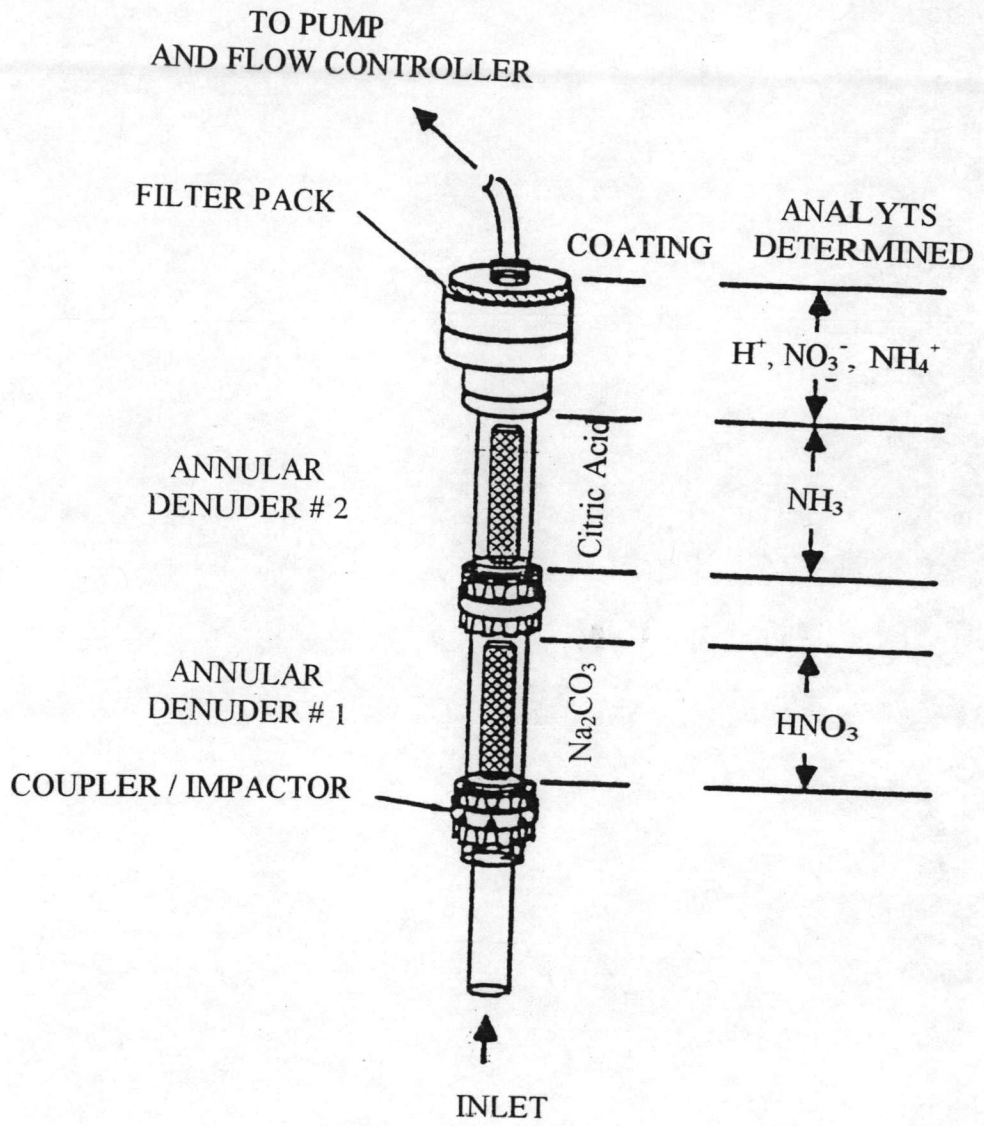
Figure 3-2 Annular Denuder System (ADS) with Coupler/Impactor Assembly
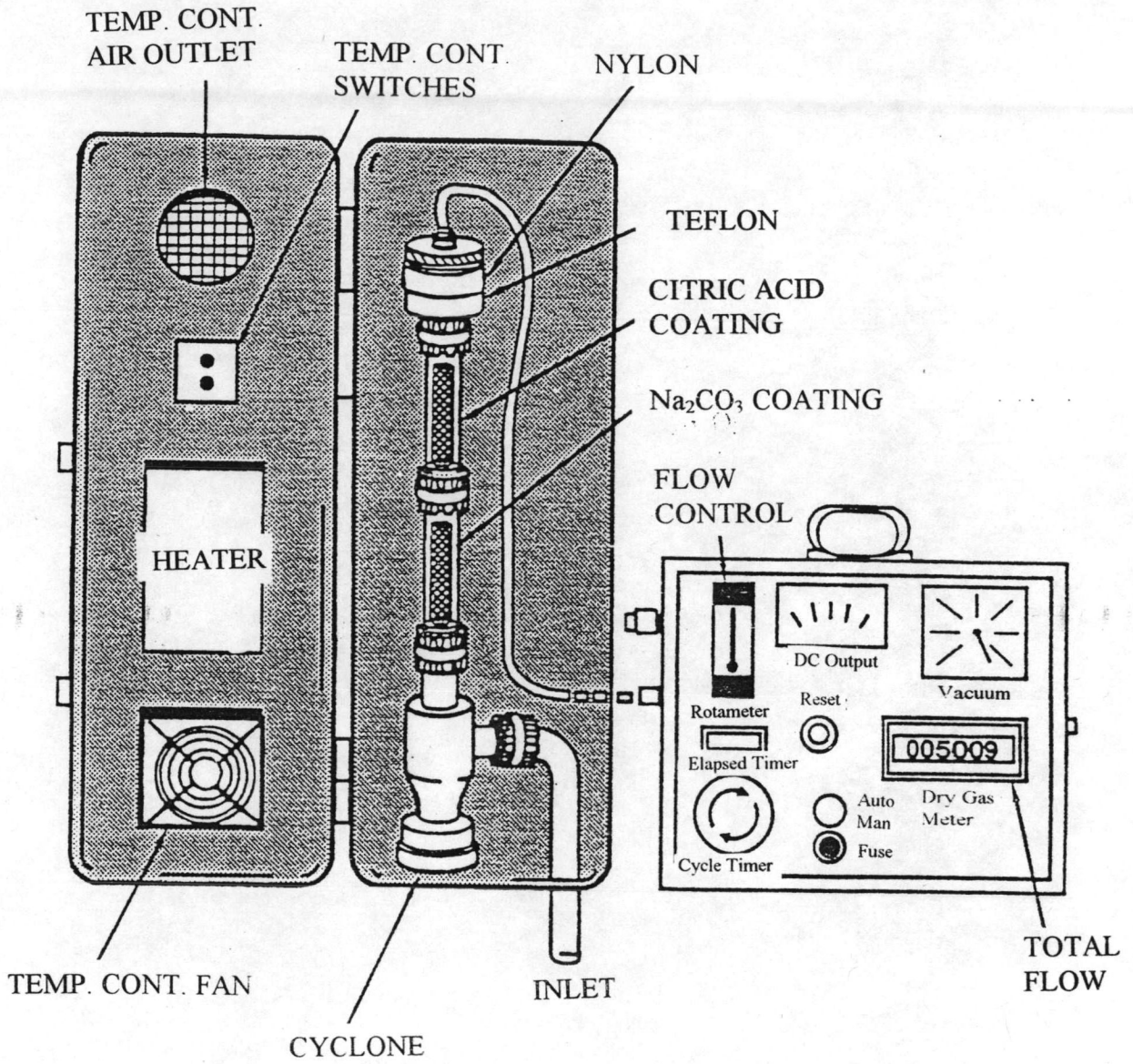
Figure 3-3 Annular Denuder System in Field Sampling Box with Pump-Timer System

To extract the Teflon® filter, it is placed in an extraction vessel, particle-laden side down. The filter is soaked with 200 μL of methanol, then extracted with 6.0 mL of extraction solution (ES) (20 mL of 2M KCl, 10 mL of 0.01N HClO₄ mix well with 980 mL of DDW). The extraction vessel is put in an ultrasonic bath for 20 minutes. The extraction solution is then decanted into a container. The sample handling and analytical protocals have been summarized in figure 3-4.
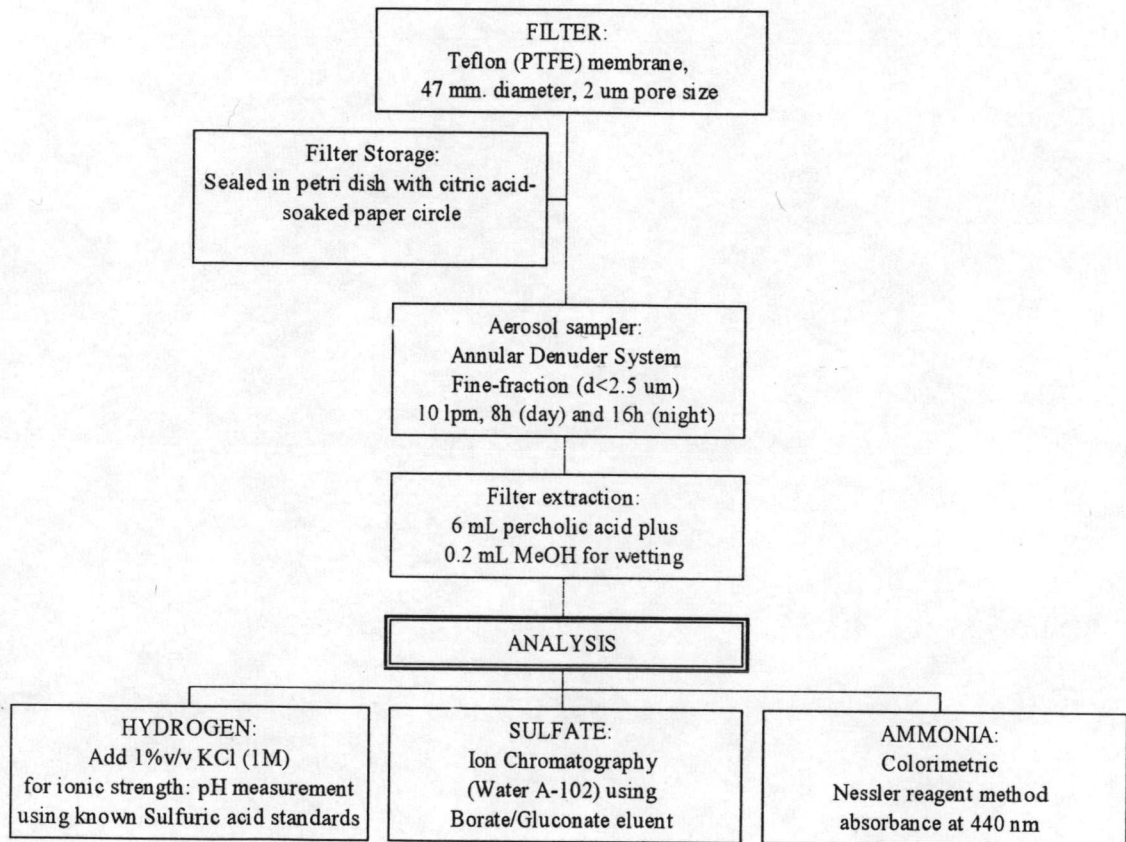
Figure 3-4 Sample handling and analytical protocols

Acidity (H⁺) determinations is conducted by pH measurements of 1 mL of the extracted filter solution in polystylene vials. Filter acidities are calculated from standards made with sulfuric acid. The standards range from 0 to 150 μg equivalent of strong acid aerosol concentration. A pH meter is used to measure the pH of the filter extract. The perchloric acid was used to systematically shift the extract's pH down to an acidic domain where weak acids, especially dissolved CO_2 would not buffer the solution. A spike of KCl was added to each pH aliquot (yielding 10^{-2} M) to eliminate an ionic strength bias. For each batch of filter extracts, a calibration curve is calculated using the mean pH of each standard reading taken before and after the batch.

The ammonia (NH_3) concentration is determined by using the colorimetric Nessler reagent method. From reading the absorbance of the yellow-brown solution which produced by Nessler reagent at 440 nm and comparing it with a standard curve. The sulfate concentrations are quantified by ion chromatography (Water Ion Analysis Method # A-102 with IC-PAK A HC Column) using Borate/Gluconate eluent. The concentrations of ions in the sample extracts were collected for blank filter levels. After the analysis completed, the atmospheric species concentration were calculated to obtain the final concentration of each species. Appendix A showed the atmospheric species concentration calculations. To each the calculation of ionic balances and sulfate aerosol speciation, all concentrations are given in nanoequivalents per cubic meter of air volume unit (neq/m^3). Therefore 1 neq/m^3 unit was equivalent to the concentrations of $H^+(H_2SO_4)$ and SO_4^{2-} as 0.049 and 0.048 $\mu g/m^3$ respectively.

3.4 Heavy Metals

3.4.1 Sampling

Total suspended particulates (TSP) were collected on a 8 in. x 10 in. glass fiber filter of 0.3 μm pore size with an efficiency of collection more than 95 percent by the High Volume Air Samplers (Wedding & Associates, Inc. serial # 1040940879UTSB). TSP was collected at the same duration time with the aerosol sampling time. After sampling was completed, the filter were weighted again. The weight difference of the filter before and after sampling was the total suspended particulates weight. Heavy metals are analyzed from the hot extraction the filter using 3M HNO_3 and then analyzed by atomic absorption spectrometry.

3.4.2 Analysis

Iron, manganese and vanadium (Fe, Mn and V) content of the samples are analyzed by atomic absorption spectrometry using an air-acetelene (air-C_2H_2) flame for Fe and Mn with wavelength 248.3 and 279.5 nm (detection limit = 0.02 and 0.01 ppm) while V values obtained by using N_2O-C_2H_2 flame with wavelength 318.4 nm (detection limit = 0.2 ppm).

3.5 Sulfur Dioxide

The florescence SO_2 analyzer performs a continuous dry gas analysis for sulfur dioxide (SO_2). Its operation is based on UV fluorescence. This method is designated as an Equivalent Method (EQSA-0779-039) as defined in CFR 40, Part 53, by the U.S. EPA. The method measures sulfur dioxide concentrations on the principle of ultraviolet radiant excitation resulting in fluorescence of the SO_2 molecule. SO_2 molecules are irradiated by light in the far-ultraviolet at 214 nm and florescences with a secondary emission in the 300-350 nm region. This secondary emission yields a light output that is proportional to the concentration of sulfur dioxide molecules present.

The sample gas is continuously drawn into a cylindrical Teflon-coated reaction cell at near ambient pressures. The atmospheric gas is excited by UV light at wavelength 214 nm. The fluorescent secondary emission of the SO_2 molecules present in the gas is measured by a photo-multiplier tube (PMT). The filtered UV light passes through a collimating lens that focuses the light energy at the center of the cell. The PMT is optically tuned to measure the fluorescent emission and outputs the signal through an amplifier to a synchronous demodulator. Simultaneously, the UV light source intensity is measured by a reference photo-detector tube located directly across the reaction cell from the lamp. The mixer board electronics then uses this signal to compensate for any variation in the UV light source. The signal is filtered through a 55-second electronic time constant and divided for the output voltage of choice. The DC voltage output is seperated and buffered for interface to recorders and data acquisition systems.

3.6 Ozone

Determination of ozone in the atmosphere is obtained by using Gas-Phase Chemiluminescense Instrument. The method is based on the gas phase chemiluminescense reaction of ozone with ethylene to produce an excited species that emits light in the visible range. The reaction is rapid and specific takes place in a chamber that has a light transparent end-face couple to a photomultiplier tube. The resulting signal produced by the photomultiplier tube is proportional to ozone concentration. The signal is further amplified and either read directly on a recorder or converted into a digital display, depending upon the construction of the specific instrument. Chemiluminescense instruments are available with several measurement ranges within the same instrument. Generally, these are 0 to 40, 0 to 400, and 0 to 4,000 µg ozone/m^3 (0 to 0.02, 0 to 0.2, and 0 to 2 ppm, respectively, by volume).

3.7 Solar and Net Radiation

The radiations are measured by using the pyranometer (Eppley Precision Infared Radiometer Model PIR), which its development intended for the measurement of (unidirectional) incoming or outgoing long-wave terrestrial radiation. For the measurement of long-wave radiation in general, and for the isolation of this flux from the solar short-wave radiation in daytime, the glass hemisphere system has been replaced by a hemisphere of silicone (30 mm diameter), which is cemented into a removable collar (with an O-ring seal) on the instrument case. On the inner surface of this envelope is a vacuum-deposited interference filter. The composite envelope transmission exhibits a sharp transition between about 3 and 4 µm from complete opaqueness to maximum transparency, and (apart from the normal waviness associated with such interference patterns) a general transmittance of about 0.50 decreasing, with increasing wavelength, to 0.30-0.40 around 50 µm. Tests have demonstrated that this coated hemisphere does not exhibit significant transmission of sunlight; absorption and re-emission effects are small and have been determined.

A thermistor-battery-resistance circuit (in addition to that employed for temperature compensation of radiometer response) is incorporated to precisely compensate for detector temperature. The basis of this innovationis that since the signal out of the pyranometer (when used for the measurement of infrared radiation) is representative of net radiation flux at the receiver surface,

$$R_{net} = (R_{in} - R_{out})$$

where: R_{net} = net radiation
R_{in} = heat gain (solar radiation)
R_{out} = heat loss

then R_{in} can be directly measured if the portion of the signal dur to R_{out} can be removed.

$$R_{in} = R_{net} + R_{out}$$