

1. Introduction

1. To monitor dry deposition, one must either measure the dry deposition directly or measure air concentrations and calculate dry deposition by inferential methods. In most situations, however, it is not feasible to apply direct measurement methodologies as routine monitoring.
2. Therefore, “Commencement of concentration monitoring using any available measurement technology at as many sites as feasible” is placed as “Step 1” of the step-wise approaches for dry deposition monitoring in “Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET”¹⁾ (hereinafter referred to as the “Strategy Paper”)
3. It is described in the Strategy Paper that the purposes of dry deposition monitoring are (i) to provide data for the evaluation of total acid deposition on soil, vegetation etc. for the assessment of the adverse effects on specified ecosystems, and (ii) to provide data for the evaluation of the regional budget of sulfur and nitrogen with the aid of modeling and that for these purposes the concerned chemicals are primarily, gaseous SO₂, NO₂, O₃, HNO₃, NH₃, and the particulate SO₄²⁻, NO₃⁻, NH₄⁺ and Ca²⁺.
4. Measurements of air concentration are available to use any of automatic real-time monitoring instruments, filter packs, denuders, or passive samplers.
5. Among these methods, filter packs have been adopted in the dry deposition monitoring programs in North America and Europe, namely CASTNet (US), CAPMoN (Canada) and EMEP²⁾ (Europe).
6. One of advantages of filter packs is that they can monitor many parameters at relatively low cost. Especially “four-stage filter pack” method can monitor all of the above-mentioned concerned chemicals except NO₂ and O₃, at the same time.
7. During the preparatory phase of EANET, five countries carried out four-stage filter pack monitoring mostly based on the method recommended by the JICA Group Training Course³⁾. (The results were described in the “Report on the Acid Deposition Monitoring of EANET during the Preparatory Phase”.⁴⁾)

8. This technical document shows a recommended method of four-stage filter pack for dry deposition monitoring of EANET. The method and procedure described here are generally derived from the developments and experiences of various research programs in North America, Europe and Japan. This manual will be reviewed and revised as appropriate, taking into account the latest scientific information and experiences accumulated in East Asia.

2. Fundamental items

9. Fundamental items concerning monitoring on dry deposition were described in the Guidelines for Acid Deposition Monitoring in East Asia⁵⁾ (hereinafter referred to as the “Guidelines”) that was adopted at The Second Interim Scientific Advisory Group Meeting of EANET.
10. Monitoring sites should be selected in accordance with the criteria for deposition monitoring site described in the Guidelines.
11. The Guidelines expect weekly data and accept daily data on the filter pack monitoring. According to the Strategy Paper, the sampling period of air concentrations could be longer than one day, e.g., a week.
12. Filter pack method is available for the measurement of SO₂, HNO₃, HCl, NH₃, and particulate component (SO₄²⁻, NO₃⁻, Cl⁻, Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺). The four-stage filter pack method can measure all of these parameters at the same time.
13. It should be emphasized that the filter pack method is not completely precise measurement of the above chemicals because of artifacts on the filter pack. For example, volatilization of particulate NH₄NO₃ and NH₄Cl on a filter could be occurred during sampling period. However, the artifacts could be reduced taking into account its specification. The results of previous studies⁶⁻⁸⁾ show by means of evidence that the filter pack method is generally available in spite of the artifacts.

3. Four-stage filter pack method

3.1. Principle

14. The four-stage filter pack is composed of four filters in line with the air stream as shown in Fig. 1. Aerosols are collected on the first filter (made of PTFE; polytetrafluoro-ethylene), and then the gaseous substances such as SO_2 , HNO_3 , HCl , NH_3 will pass through this filter. The second filter (made of polyamide) collects all HNO_3 and parts of SO_2 , HCl and NH_3 in the sampling air. The other parts of SO_2 and HCl react with alkali substance on the third filter (made of cellulose). NH_3 passes through the first, second and third filters and reacts with acid substance on the fourth filter (made of cellulose). The reactions on filters are summarized in Table 1.

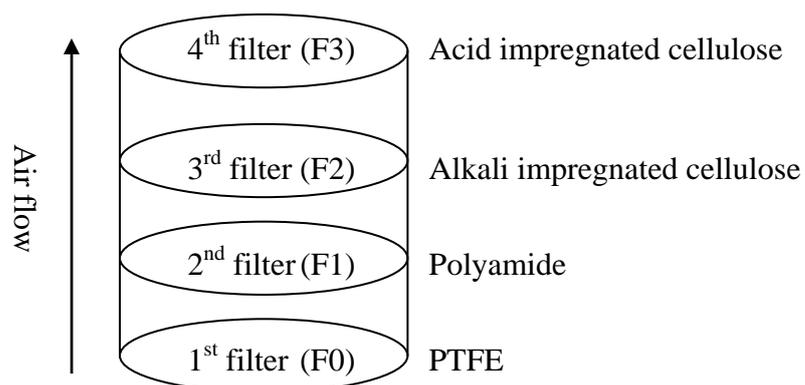


Fig. 1 Schematic diagram of the four-stage filter pack

Table 1 Reactions on filters in four-stage filter pack

| Stage | Reaction | Collected specie |
|-------------------------|---|---|
| 1 st (F0) | Filtration | aerosols |
| 2 nd (F1) | Adsorption | HNO_3 , partial SO_2 , partial HCl |
| | Neutralization by collected acid gases | partial NH_3 |
| 3 rd (F2) | Neutralization by alkali impregnated cellulose filter | SO_2 , HCl |
| 4 th (F3) | Neutralization by acid impregnated cellulose filter | NH_3 |

3.2. Preparation of filter pack

15. Filters and extraction solutions should be only handled in the laboratory. Moreover they should not be exposed to air longer than necessary due to a possible uptake of gasses by filters or solutions. Disposable plastic gloves and tweezers should always be used when handling filters.

3.2.1. Specification of filter

16. PTFE filter (T080A047A by ADVANTEC, pore size: 0.8 μ m, diameter: 47mm) is recommended as the first filter (F0). Polyamide filter (ULTIPOR N66 by PALL, pore size: 0.45 μ m, diameter: 47mm) is recommended as the second filter (F1). The third filter (F2) is made from a filter (51A by ADVANTEC, diameter: 47mm) impregnated with a solution formed by mixing 6% K₂CO₃ + 2% glycerin in pure water. The fourth filter (F3) is made from a filter (51A by ADVANTEC, diameter: 47mm) impregnated with a solution formed by mixing 5% phosphoric acid + 2% glycerin in pure water.

Table 2 Specifications of the four filters

| Stage | Specification of filter | Collected specie |
|-------------------------|--|--|
| 1 st (F0) | PTFE filter, T080A047A / ADVANTEC (pore size: 0.8 μ m, diameter: 47mm) | aerosol |
| 2 nd (F1) | Polyamide filter, ULTIPOR N66 / PALL (pore size: 0.45 μ m, diameter: 47mm) | HNO ₃ , SO ₂ , HCl, NH ₃ |
| 3 rd (F2) | Impregnated filter, 51A / ADVANTEC (diameter: 47mm) Solution: 6% K ₂ CO ₃ + 2% glycerin | SO ₂ , HCl |
| 4 th (F3) | Impregnated filter, 51A / ADVANTEC (diameter: 47mm) Solution: 5% phosphoric acid + 2% glycerin | NH ₃ |

3.2.2. Procedures of preparations of filter pack

17. Recommended procedure of preparation of alkali impregnated filter is described as follows:

- 1) prepare the mix solution (6% K_2CO_3 + 2% glycerin);
 - prepare three 500mL beakers;
 - weight 30g of K_2CO_3 and 10g of glycerin in each 500mL beaker;
 - pour into deionized water (less than 0.15mS/m) to each beaker and adjust to 500g;
 - mark the numbers (No.1, No.2 and No.3) of the beakers for distinction;
 - dunk cellulose filters into No.1 beaker and stir them with a glass stick;
- 2) pull up a filter from the No.1 beaker using plastic tweezers; dunk it in the No.2 beaker for the rinse;
- 3) pull up the filter from the No.2 beaker using plastic tweezers; dunk it in the No.3 beaker for the rinse;
- 4) pull up the filter from the No.3 beaker using plastic tweezers, and put the filter between two sheets of large cellulose sheet (ADOVANTEC No.590) to absorb extra water from the impregnated filter;
- 5) keep the impregnated filter in a clean plastic filter case and seal it in a polyethylene bag with marking " K_2CO_3 ";
- 6) Back to 2).

18. Recommended procedure of preparation of acid impregnated filter is described as follows:

- 7) prepare the mix solution (5% H_3PO_4 + 2% glycerin);
 - prepare three 500mL beakers;
 - weight 29.4g of H_3PO_4 and 10g of glycerin in three 500ml beakers;
 - pour deionized water (less than 0.15mS/m) into each beaker and adjust to 500g;
 - mark the numbers (No.1, No.2 and No.3) of the beakers for distinction;
 - dunk cellulose filters into No.1 beaker and stir them with a glass stick;
- 8) pull up a filter from the No.1 beaker using plastic tweezers; dunk it in the No.2 beaker for the rinse;
- 9) pull up the filter from the No.2 beaker using plastic tweezers; dunk it in the No.3 beaker for the rinse;

- 10) pull up the filter from the No.3 beaker using plastic tweezers, and put the filter between two sheets of large cellulose sheet (ADOVANTEC No.590) to absorb extra water from the impregnated filter;
 - 11) keep the impregnated filter in a clean plastic filter case and seal it in a polyethylene bag with marking “H₃PO₄”;
 - 12) Back to 2).
19. The four-stage filter holder by NILU is recommended. A clean filter holder should be used to prevent excess contamination. The PTFE, the polyamide, the alkali impregnated and the acid impregnated filters are mounted on F0, F1, F2, F3 stages of the filter holder using clean plastic tweezers respectively, taking into account preventing the leak in the filter holder. The filter pack holders should be tightened using the exclusive torque to avoid leak after assembly.
20. Filters especially impregnated filters should be always sealed up to avoid the contamination by ambient pollutants, except the sampling time. The mounted filter holder should be capped by an exclusive cap and then sealed in a polyethylene bag. And furthermore, an aluminum-coated bag should seal it up. While the sealed mounted holder is transported to a monitoring site, it should be kept in a transportation box.

3.3. Sampling

21. The schematic diagram of filter pack sampling is given in Fig. 2. The side of the air intake (1st stage) should face the ground surface as shown in Fig. 2. The sampling system should be assembled taking into account the order of equipments though the pass of sampling air as shown in Fig. 2. The inlet of sampling air should be set up from 5 to 10 meters above the ground. It should be around 3 meters higher than the height of the buildings if the inlet is on the buildings. It is also important to avoid leaks though the pass of sampling air.

3.3.1. Sampling period

22. Sampling should be done through continuous suction for a week. If it is difficult to exchange filter holders every week in remote sites, continuous suction for

biweekly is also acceptable.

3.3.2. Flow rate

23. A flow rate at 1 liter/min is recommended for weekly or biweekly sampling. If it is difficult to detect concentrations in remote sites, flow rates could be increased to 2 liter/min.

3.3.3. Sampling procedure

24. Recommended sampling procedure at that site are described as follows:

[Start]

- 13) read the counter in the volume meter and record the value in the sampling notebook;
- 14) dismount the exclusive cap from the new unexposed filter pack and mount it in the sampling system;
- 15) switch on the pump and record the time and the flow rate in the sampling notebook;

[Stop]

- 16) record the flow rate in the sampling notebook;
 - 17) switch off the pump and record the time in the sampling notebook;
 - 18) dismount the filter pack holder from the sampling system and cap it using a exclusive cap and then seal it in a polyethylene bag.
 - 19) keep the sealed holder in the transportation box
 - 20) read the counter in the volume meter and record the value in the sampling notebook.
25. In the laboratory, it is recommended that the sample filters are dismounted from the holder and are kept in clean plastic filter cases separately with description of sample number. Moreover the each case should be sealed by a polyethylene bag one by one, and furthermore, an aluminum-coated bag should seal them up. And then it should be kept in the refrigerator.

3.3.4. Maintenance

26. Maintenance should be performed in accordance with their instructions for field instruments such as pumps, flow meters and gas volume meters. Calibration of the flow meters and the gas volume meters should be done at least once every year.

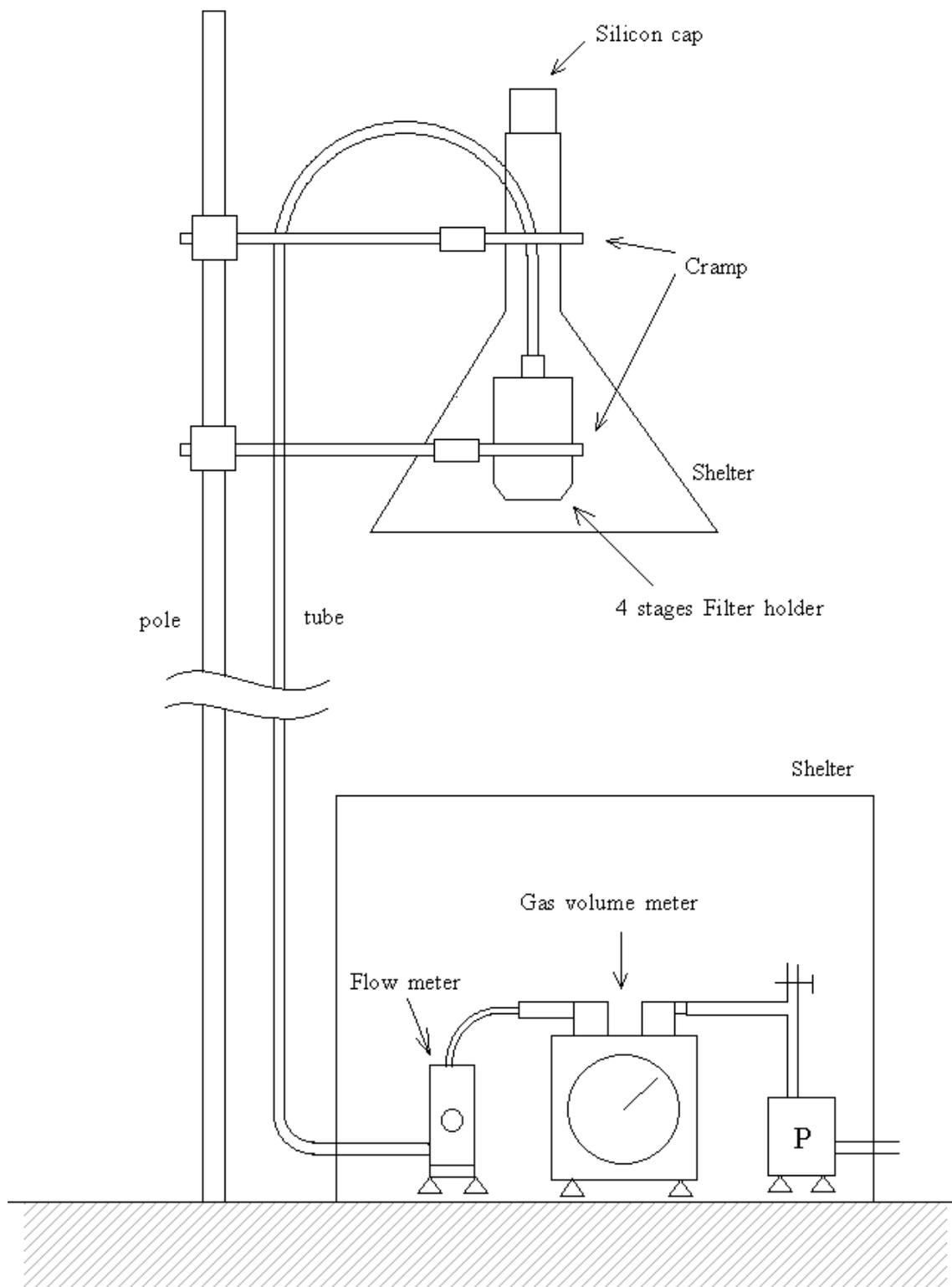


Fig. 2 Schematic diagram of filter pack sampling

3.4. Extraction and chemical analysis

27. Extractions of sample filters and chemical analysis should be carried out as soon as possible after sampling. Extractions and chemical analysis of blank filters that are kept in a laboratory should be carried out at the same time.

3.4.1. Procedure of extraction

28. Recommended extraction procedure is described as follows:

- 21) prepare 50ml polypropylene test tubes with caps;
- 22) dunk polypropylene test tubes into the diluted laboratory detergent overnight and then wash them by water (first) and deionized water (second), after that, dry them in clean air;
- 23) describe the sample identification on each test tube such as F0 filter with sample number, F0 filter blank, F1 filter with sample number, F1 filter blank and so on;
- 24) put the sample filters into their test tube;
- 25) in the case of F0, F1, F3 stage samples, pour 20mL deionized water into the tubes; in the case of F2 stage sample (alkali impregnated stage), pour 20mL H₂O₂ solution (0.05%-v/v) into the tubes;
- 26) shake the sample tubes during 20 minutes for their extractions using a shaker or an ultrasonic bath;
- 27) pick up the filters from the extracted solutions in the tubes and cap the tubes using exclusive caps;
- 28) filter out the insoluble matters in the extracted solutions using a membrane filter (pore size 0.45µm) which is well washed by deionized water;
- 29) keep the sample tubes in the refrigerator.

3.4.2. Chemical analysis

29. Chemical analysis should be carried out after the extractions as soon as possible. Based on the principle described in the chapter 3.1, the parameters that are requested to analyze are shown in Table 3.
30. Ion chromatography is recommended to analyze the above-mentioned parameters.

The analytical method should be followed by the “Technical Documents for Wet deposition Monitoring in East Asia”, especially the chapter 4.4 and 4.5 of the document.

Table 3 Analyzed parameters of the four stages

| Stage | Species | Solvent |
|-------|---|-----------------------------------|
| F0 | SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} | 20mL Water |
| F1 | SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ | 20mL Water |
| F2 | SO_4^{2-} , Cl^- | 20mL 0.05% H_2O_2 |
| F3 | NH_4^+ | 20mL Water |

31. After the chemical analysis of the extracted solutions from impregnated filters, especially F2 and F3 filters, the injector of the ion chromatograph is contaminated by K_2CO_3 or phosphoric acid that are impregnated in the filters. The contamination should be removed completely by deionized water at the last of the chemical analysis.

3.4.3. Treatment of blank

32. A blank value should be determined by median of 5 blank values. The median value is available for samples obtained in a month as the blank. Chemical analysis of samples and blanks should be done every one month in a lump.
33. Normally the blank values should be sufficiently low. If high blank values are found, a problem has to be identified and solved, e.g. by inspection of the routine in the laboratory.

3.5. Calculation of results

34. The concentrations of the parameters in the air is basically given by:

$$C_{\text{Air}} = \alpha * \text{net } C_{\text{Sol}} * V_{\text{Sol}} / V_{\text{Air}} \quad (\alpha = 10^3 / M);$$

C_{Air} : concentration in the air (nmol/m³),

net C_{Sol} : net concentration in the solution (mg/l),

V_{Sol} : volume of the solution (ml),

V_{Air} : volume of the sampled air corrected at 20 °C (m³),

M : molecular weight.

35. The net C_{Sol} should be calculated by:

$$\text{net } C_{\text{Sol}} = C_{\text{Sol, Sample}} - C_{\text{Sol, Blank}} ;$$

$C_{\text{Sol, Sample}}$: concentration in the solution from the sample filter,

$C_{\text{Sol, Blank}}$: concentration in the solution from the blank filter.

36. V_{Air} should be corrected at 20 °C using the data of temperature obtained at the same site or near the site as follows:

$$V_{\text{Air}} = V_{\text{Air, Sample}} * (20 + 273) / (T + 273) ;$$

$V_{\text{Air, Sample}}$: uncorrected volume of the sample air,

T : averaged temperature during the sampling period (°C).

37. The calculations should be carried out, taking into account the principle of the four-stage filter pack method described in the chapter 5.1. Specification of the calculation for each parameter is summarized in Table 4.

Table 4 Specification of the calculation for each parameter

| Specie | M | Equation |
|-------------------------------|--|--|
| SO ₄ ²⁻ | 96.06 | $C_{Air} = \alpha * \text{net } C_{Sol, F0} * V_{Sol} / V_{Air}$ |
| NO ₃ ⁻ | 62.01 | |
| Cl ⁻ | 35.45 | |
| Na ⁺ | 22.99 | |
| K ⁺ | 39.10 | |
| NH ₄ ⁺ | 18.04 | |
| Ca ²⁺ | 40.08 | |
| Mg ²⁺ | 24.31 | |
| SO ₂ | 96.06 (SO ₄ ²⁻) | $C_{Air} = \alpha * (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F2}) * V_{Sol} / V_{Air}$ |
| HNO ₃ | 62.01 (NO ₃ ⁻) | $C_{Air} = \alpha * \text{net } C_{Sol, F1} * V_{Sol} / V_{Air}$ |
| HCl | 35.45 (Cl ⁻) | $C_{Air} = \alpha * (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F2}) * V_{Sol} / V_{Air}$ |
| NH ₃ | 18.04 (NH ₄ ⁺) | $C_{Air} = \alpha * (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F3}) * V_{Sol} / V_{Air}$ |

#1 $\alpha = 10^3 / M$

#2 net C_{Sol, F1} means the net C_{Sol} of the F1 sample filter

38. Calculation of chemical analysis results should be carried out carefully, because the measurement parameters have their own equations to convert ambient concentrations.
39. When a blank value is higher than the sample value, the data should be regarded as non-detected data (N.D.).
40. When samples seem to be obviously contaminated, the data should be treated as unrecorded data.

4. Data reporting

41. The data reporting format (Dry) that is shown in Table 5 should be used for the reporting data measured by the filter pack method. Data of a calendar year should be reported to Network Center by the end of July in the next year.

5. References

- 1) Interim Scientific Advisory Group and Task Force on Dry Deposition Monitoring of EANET, 1999. Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET
- 2) EMEP manual for sampling and chemical analysis, EMEP/CCC-Report 1/95
- 3) Matsumoto M., Monitoring of Dry Deposition, Textbook for JICA group training course.
- 4) Interim Scientific Advisory Group of EANET, 2000. Report on the Acid Deposition Monitoring of EANET during the Preparatory Phase – Its Results, Major Constraints and Ways to Overcome Them -.
- 5) Interim Scientific Advisory Group of EANET, 2000. Guidelines for Acid Deposition Monitoring in East Asia.
- 6) Sickles, J.E.II, Hodson, L.L., Vorburger, L.M., 1999. Evaluation of the filter pack for long-duration sampling of ambient air, Atmospheric Environment **33**, 2187-2202.
- 7) Eatough, N.L., Mcgregor, S., Lewis, E.A., Eatough, D.J., Huang, A.A., Ellis, E.C., 1988. Comparison of six denuder methods and a filter psck for the collection of ambient HNO₃ (g), HNO₂ (g), and SO₂ in the 1985 NSMC study, Atmospheric Environment **22**, 1601-1618.
- 8) Hastie, D.R., Schiff, H.I., Whelpdale, W.H., Peterson, R.E., Zoller, W.H., Anderson, D.L., Church T.M., 1988. Description and intercomparison of techniques to measure N and S compounds in the Western Atlantic Ocean Experiment, Atmospheric Environment **22**, 2393-2399.

Table 5

Form (Dry) Results of air concentration analysis (Filter Pack)

Site name: _____ **Site Classification:** _____

Name of Laboratory: _____ **Name of reporter:** _____

Unit: nmol/m³

| Sample No. | Sampling period | | | | Gas | | | | Particle | | | | | | | |
|------------|-----------------|------|------|------|-----------------|------------------|-----|-----------------|-------------------------------|------------------------------|-----------------|------------------------------|-----------------|----------------|------------------|------------------|
| | Start | | End | | SO ₂ | HNO ₃ | HCl | NH ₃ | SO ₄ ²⁻ | NO ₃ ⁻ | Cl ⁻ | NH ₄ ⁺ | Na ⁺ | K ⁺ | Mg ²⁺ | Ca ²⁺ |
| | Date | Time | Date | Time | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |

Artifact of filter pack method

Artifacts of HNO₃, NH₃ and HCl on filters could be happened during samplings. The mechanisms are based on the reactions as follows:

(1) Artifacts of HNO₃,

- ① $\text{NH}_4\text{NO}_3 (\text{P}) \rightarrow \text{NH}_3 (\text{G}) + \text{HNO}_3 (\text{G}),$
- ② $\text{NH}_4\text{NO}_3 (\text{P}) + \text{H}_2\text{SO}_4 (\text{P}) \rightarrow \text{NH}_4\text{SO}_4 (\text{P}) + \text{HNO}_3 (\text{G}),$
- ③ $\text{NaNO}_3 (\text{P}) + \text{H}_2\text{SO}_4 (\text{P}) \rightarrow \text{NaHSO}_4 (\text{P}) + \text{HNO}_3 (\text{G}),$
- ④ $\text{NaCl} (\text{P}) + \text{HNO}_3 (\text{G}) \rightarrow \text{NaNO}_3 (\text{P}) + \text{HCl} (\text{G});$

(2) Artifacts of NH₃,

- ① $\text{NH}_4\text{NO}_3 (\text{P}) \rightarrow \text{NH}_3 (\text{G}) + \text{HNO}_3 (\text{G}),$
- ② $\text{NH}_4\text{Cl} (\text{P}) \rightarrow \text{NH}_3 (\text{G}) + \text{HCl} (\text{G}),$
- ③ $\text{H}_2\text{SO}_4 (\text{P}) + \text{NH}_3 (\text{G}) \rightarrow \text{NH}_4\text{HSO}_4 (\text{P}),$
- ④ $\text{NH}_4\text{HSO}_4 (\text{P}) + \text{NH}_3 (\text{G}) \rightarrow (\text{NH}_4)_2\text{SO}_4 (\text{P});$

(3) Artifacts of HCl,

- ① $\text{NaCl} (\text{P}) + \text{HNO}_3 (\text{G}) \rightarrow \text{HCl} (\text{G}) + \text{NaNO}_3 (\text{P}),$
- ② $2\text{NaCl} (\text{P}) + \text{H}_2\text{SO}_4 (\text{P}) \rightarrow 2\text{HCl} (\text{G}) + \text{Na}_2\text{SO}_4 (\text{P}),$
- ③ $\text{NH}_4\text{Cl} (\text{P}) \rightarrow \text{HCl} (\text{G}) + \text{NH}_3 (\text{G}).$

(P) and (G) mean “particle” and “gas”, respectively.

Photos



NILU filter holder (4 stage, open face)



Mounting a filter on a stage



Tightening a stage by an exclusive torque for NILU holder



Sealed filter case



Sealed filter holder