Technical Document for Filter Pack Method in East Asia

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1. Introduction

To monitor dry deposition, one must either measure the dry deposition directly or measure air concentrations with following calculation of dry deposition fluxes by inferential methods. However, the application of the direct measurement methodologies for routine monitoring is not feasible for the most of situations. Therefore, "Commencement of concentration monitoring using any available measurement technology at as many sites as feasible" is pointed out as "Step 1" of the step-wise approaches for dry deposition monitoring described in the Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET¹⁾ (hereinafter referred to as the "Strategy Paper") which was developed by the Task Force on Dry Deposition Monitoring of the Acid Deposition Monitoring Network in East Asia (EANET) (hereinafter referred to as the "Task Force").

The QA/QC Program for the Air Concentration Monitoring in East Asia²⁾ (hereinafter referred to as the "QA/QC Program") was endorsed at the First Session of Scientific Advisory Committee (SAC1) held in November 2001. The QA/QC Program deals with "the first priority chemical species*", which are defined in the Strategy Paper, measured by automatic monitors. As for the second priority chemical species*, the QA/QC Program describes that "Since more discussions are needed at the Task Force concerning QA/QC activities for other air concentration monitoring, such as filter packs, denuders, and passive samplers for the second priority chemicals, the QA/QC activities for these methods will be integrated in this program in the future, taking account of the progress of the discussions at the Task Force."

* The Strategy Paper defines the priority chemical species as follows: First priority: SO₂, O₃, NO, NO₂ (urban), and particulate mass concentration, Second Priority: NO₂ (rural and remote), HNO₃, NH₃, particulate component (SO₄²⁻, NO₃-, NH₄+, and Ca²⁺).

Among the air concentration monitoring methods, filter packs have been adopted for the dry deposition monitoring programs in North America and Europe, namely, CASTNet (US), CAPMoN (Canada) and EMEP ³⁾ (Europe). Japan, especially Japan Environmental Laboratories Association (JELA), and Republic of Korea also have experiences to carry out monitoring using the filter pack methods for longtime. Malaysia, Mongolia, Philippines Russia and Vietnam have been carrying out the air concentration monitoring using the JELA four-stage filter pack method since the

preparatory phase of EANET.

In line with the suggestion of the QA/QC Program and in response to request by the EANET participant countries using filter packs, this document has been developed as a reference for the method. A preliminary draft of the technical document was developed by the Secretariat of the Task Force (the Network Center for EANET) and then distributed among the members of the Task Force in September 2002. The preliminary draft was also introduced at the Third Senior Technical Managers' Meeting of EANET (STM3) held on 2-4 October 2002 in Niigata, Japan. Based on the comments from the Task Force and at STM3, a revised version (November 2002 version) was prepared and introduced at SAC2 held on 25-27 November 2002 in Bangkok, Thailand. After that, a revised draft (April 2003 version) was prepared based on the comments at SAC2 and further investigations on filter pack methods and then distributed among the members of the Task Force. Taking into account the comments on the revised draft by the Task Force members and information exchange at STM4 held on 1-3 October 2003, the final draft was prepared and submitted to SAC3 held on 24-26 November 2003 in Pattaya, Thailand. This document was finally endorsed by SAC3.

This document describes basic matters for the filter pack method of EANET. In addition, more detailed explanation for the JELA four-stage method is attached to this document for information as Appendix 1, because the most of EANET participating countries (eight ones in 2002) use this method.

The method explained in this Technical Document has been developed based on its examinations, for example, in Europe and northern North America, and in East Asia. It is emphasized that there are still uncertainties to apply in middle latitudes. This document should be reviewed and revised as appropriate, taking into account the latest scientific information and experiences accumulated in East Asia.

2. Fundamental items

2.1 Monitoring sites

Monitoring sites should be selected in accordance with the criteria for deposition monitoring site described in the Guidelines for Acid Deposition Monitoring in East Asia⁴⁾ (hereinafter referred to as the "Guidelines") that was adopted at the Second Interim Scientific Advisory Group Meeting of EANET in March 2000. It is recommended in the Guidelines that the dry deposition monitoring should be done at the same site used for wet deposition monitoring.

2.2 Monitoring frequency

The Guidelines describes that weekly data are expected and daily data are also accepted in the case of ion concentrations to be measured by filter pack. According to the Strategy Paper, the sampling period of air concentrations could be longer than one day, e.g., a week. The monitoring frequency of the filter pack method should follow these descriptions fundamentally. If weekly sampling is difficult to be carried out, biweekly sampling could also be acceptable. It is desirable that the sampling is carried out through a year continuously. If it is difficult, adequate sampling duration in every month should be determined, taking into account the situation in respective countries.

2.3 Artifacts of filter pack

It should be emphasized that filter pack method does not ensure completely precise measurement due to possibility of artifact problems. For example, volatilization of particulate NH₄NO₃ and NH₄Cl after collected on a filter, caused by increase of temperature during sampling period, could be occurred. The volatilized compounds are collected as gases such as NH₃, HNO₃ and HCl on following filters. In addition, high humidity might cause a reduction of gas concentration measured by filter pack method due to trapping of gases by condensed water in the filter pack. Previous studies⁵⁾, however, provided some evidences that the artifacts are not so significant. Some considerable artifacts are listed in Appendix 2.

3. Specifications of filters

3.1 Filters for aerosol sampling

Aerosols are collected at the fist stage. The first stage filter is mounted in front of the other filters collecting gases. The material of the aerosol filter should not absorb acid and alkali gases and should have acceptable efficiency to collect sub-micron particles. For this purpose, Teflon (PTFE; polytetrafluoro-ethylene) filters are preferred. Recommended filters are as follows:

- ➤ ADVANTEC T080A047A
- ➤ Gelman Zefluor

3.2 Filters for nitric acid sampling

The second stage filter is designated to collect nitric acid. Nitric acid passes through the first stage and is caught on the second filter in principle. In order to collect nitric acid separately from other nitrogen oxides, Nylon (polyamide) filters are preferred. Recommended filters are as follows:

- PALL ULTIPOR
- > Gelman Nylasorb

It has to be taken notice that the second polyamide filter collects partial sulfur dioxide, hydrochloric acid and ammonia as along with nitric acid from the sampling air.

3.3 Filters for sulfur dioxide and hydrochloric acid samplings

The remaining sulfur dioxide and hydrochloric acid that pass through the second stage will be collected on the third stage. The remaining sulfur dioxide and hydrochloric acid react with alkali substance on the filter mounted on the third stage. For this purpose, cellulose filters impregnated by potassium carbonate are preferred. Recommended filters are as follows:

- ➤ ADVANTEC 51A
- ➤ Whatman 41

For the calculations of ambient concentrations, the amounts of sulfur dioxide, hydrochloric acid, and ammonia collected by the second filter have to be added to those collected by the alkali-impregnated filters.

3.4 Filters for ammonia sampling

The remaining ammonia that passes through the second and third stages will be collected on the fourth stage (Case1). In the case that sulfur dioxide and hydrochloric acid are not sampled by the filter pack (when filters for acidic gases samplings are not used), the remaining ammonia that passes through the second will be collected on the third stage (Case2). The remaining ammonia reacts with acid substance on the filter mounted on the stage (third or fourth). The filters are preferable to be impregnated by phosphoric acid. In Case1, cellulose filters, which are same as the third stage filter, could be utilized. For the calculation of ambient concentration, the amount of ammonia collected by the second filter has to be added to that collected by the acid-impregnated filters.

The specifications are summarized in Table 1.

Table 1 Specifications of filters

Stage	Specifications of filters	Reaction	Collected species
First	Teflon (PTFE) filter	Filtration	Aerosol
Second	Nylon (Polyamide) filter	Adsorption	HNO ₃ Partial SO ₂ , HCl
		Neutralization by collected acid gases	Partial NH ₃
Third	Case 1: Cellulose filter impregnated by K ₂ CO ₃	Neutralization by alkali impregnated on the filter	SO ₂ , HCl
	Case 2: Cellulose filter impregnated by phosphoric acid	Neutralization by acid impregnated on the filter	NH ₃
Fourth (Case 1 only)	Filter impregnated by phosphoric acid	Neutralization by acid impregnated on the filter	NH ₃

4. Sampling

4.1 Sampling height

The inlet of air sampling holder should be set up at the height of about 3 meters above the ground. In the case of any close obstacles in the surround of the monitoring site such as forest trees, the inlet should be set up higher than 3 meters above the ground, if possible over the top of the obstacles (above tree canopies).

4.2 Sampling system

Diaphragm pump is recommended for stable flow rates during the sampling. For counting of air volume, mass flow meters that could monitor accumulated volumes are recommended. Especially at the sites located in high altitude mountain, the mass flow meters should be adopted to avoid the effect of the lower atmospheric pressure. 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 meters and gas volume meters should be set up consequently after the pump to measure flow rates and volumes under the condition of atmospheric pressure.

4.3 Flow rate

The flow rate of 1 liter/min is recommended for weekly or biweekly sampling. If it would be difficult to detect concentrations in remote sites, flow rates could be increased up to 2 liter/min. Typical flow rate for daily sampling is around 15 liter/min. If specific devices are utilized for removing large particles in the inlets such as impacter, the exact flow rates depend on the devices. Open-face inlet should be recommended in the case of weekly or biweekly sampling, because there are no standard devices for the range of flow rates from 1 to 2 liter/min. Air volumes counted by mass flow meters or gas volume meters should be used for calculation of ambient air concentration.

5. Operation in laboratory

5.1 Preparation of filter pack

Filters and extraction solutions should be 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 or after the sampling time.

5.2 Extraction and chemical analysis

Extractions of sample filters and chemical analysis should be carried out every month. Extractions and chemical analysis of blank filters stored in a laboratory should be carried out at the same time. For the extractions, the sample shakings should be done by using a shaker or an ultrasonic bath during 20 minutes. Chemical analysis should be carried out each month in a lump but as soon as possible after the extractions. Analyzed species and solvent for each stage are shown in Table 2.

Table 2 Analyzed species and solvent for each stage filter

Stage	Species	Solvent
First	SO ₄ ²⁻ , NO ₃ -, Cl ⁻ , NH ₄ ⁺ , Na ⁺ , K ⁺ , Ca ²⁺ ,	Deionized water
	Mg^{2+}	
Second	SO ₄ ²⁻ , NO ₃ -, Cl ⁻ , NH ₄ ⁺	Deionized water
Third	Case1: SO ₄ ²⁻ , Cl ⁻	$0.05\%H_{2}O_{2}$
	Case2: NH ₄ ⁺	Deionized water
Fourth	NH ₄ ⁺	Deionized water
(Case 1 only)		

Ion chromatography (IC) is recommended for analysis of the above-mentioned chemical components. The analytical method should follow the procedures described by "Technical Documents for Wet deposition Monitoring in East Asia", especially in chapters 4.4 and 4.5 of that document.

5.3 Treatment of blank

A blank value should be determined as median of 5 analytical results of blank filters. One median value is available as the blank value for sample sets obtained for one month. Chemical analysis of samples and blanks should be done each month in a lump.

6. Calculation of results and data reporting

6.1 Determinations of concentrations

The concentrations of a compound in air are basically determined as follows:

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

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, 1 atm (m³),

M: molecular weight.

The net C_{Sol} should be calculated by:

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

C_{Sol. Sample}: concentration in the solution from the sample filter,

C_{Sol. Blank}: median concentration in the solutions from the blank filters.

Network Center for EANET could provide a calculation program (Excel file) following the equations upon requests.

When a blank value is detected as higher than the sample value, the corresponded data should be regarded as non-detected data (N.D.). If samples seem to be obviously contaminated, the data should be treated as unrecorded data. If sampling processes are stopped by any accident during sampling periods (for example; shutdown of electricity), the samples obtained in these periods should be rejected, because filter packs absorb gases like passive samplers when they are in the breaks.

6.2 Data reporting

The data reporting format (Dry) presented in Table 3 should be used for the reporting of data measured by the filter pack method. Report on data sets for a calendar year as a whole should be submitted to Network Center by the end of June in the next year.

Table 3

Form (Dry)	Results of air concentration analysis (Filter Pack)
Site name:	Site Classification:
Name of Laboratory:	Name of reporter:

Unit: nmol/m³

Sample	Sampling period			Gas			Particle												
No.	Sta	Start		nd so		End		SO. UNO.	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	302		1\П3	304		NO ₃	CI	МП4	Na	K	Mig	Ca			

References

- Interim Scientific Advisory Group and Task Force on Dry Deposition Monitoring of EANET, Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET (1999)
- 2) Scientific Advisory Committee and Task Force on Dry Deposition Monitoring of EANET, QA/QC Program for the Air Concentration Monitoring in East Asia (2001)
- 3) EMEP manual for sampling and chemical analysis, EMEP/CCC-Report 1/95, http://www.nilu.no/projects/ccc/manual/index.html
- 4) Interim Scientific Advisory Group of EANET, Guidelines for Acid Deposition Monitoring in East Asia (2000)
- 5) Sickles, J.E.II, Hodson, L.L., Vorburger, L.M., Evaluation of the filter pack for long-duration sampling of ambient air, Atmospheric Environment **33**, 2187-2202 (1999)
- 6) Interim Scientific Advisory Group of EANET, Technical Documents for Wet deposition Monitoring in East Asia (2000)

Procedures of the four-stage filter pack method

This appendix explains the procedures of the four-stage filter pack method developed by Japan, especially Japan Environmental Laboratories Association (JELA)

1. Principle

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 (F0: made of PTFE), while the gaseous substances such as SO₂, HNO₃, HCl, NH₃ will pass though this filter. The second filter (F1: made of polyamide) collects all HNO₃ and partial SO₂, HCl and NH₃ from the sampling air. The remaining SO₂ and HCl react with alkali substance on the third filter (F2: made of cellulose). The remaining NH₃ reacts with acid substance on the fourth filter (F3: made of cellulose) after passing through the first, second and third filters.

Aerosols are collected on the aerosol filter (F0) mounted in front of the other filters (F1, F2 and F3) collecting gases. The material of the aerosol filter should not absorb acid and alkali gases and should have acceptable efficiency to collect sub-micron particle because sulfate aerosols are mostly of the fraction below 1 μm. For this purpose, Teflon (PTFE; polytetrafluoro-ethylene) filters are preferred.

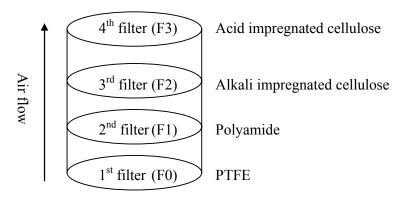


Fig. 1 Schematic diagram of the four-stage filter pack

2. Preparation of filter pack

PTFE filter (pore size: $0.8\mu m$, diameter: 47mm) is recommended as the first filter (F0). Polyamide filter (pore size: $0.45\mu m$, diameter: 47mm) is recommended as the second filter (F1). The third filter (F2) is recommended to be cellulose filter (diameter: 47mm) impregnated with a solution prepared by mixing $6\% \ K_2CO_3 + 2\%$ glycerin in pure water. The fourth filter (F3) is made of cellulose filter (diameter: 47mm) impregnated with a solution of mixed 5% phosphoric acid +2% glycerin in pure water.

Recommended preparation procedure of alkali impregnated filter (F2) is described as following steps:

- 1) prepare the mix solution (6% $K_2CO_3 + 2\%$ glycerin);
 - prepare three 500mL beakers;
 - weight 30g of K₂CO₃ 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;
- 2) dunk cellulose filters into No.1 beaker and stir them with a glass stick;
- 3) pull up a filter from the No.1 beaker using plastic tweezers; dunk it in the No.2 beaker for the rinse;
- 4) pull up the filter from the No.2 beaker using plastic tweezers; dunk it in the No.3 beaker for the rinse;
- 5) pull up the filter from the No.3 beaker using plastic tweezers, and put the filter between two sheets of large cellulose sheet (ADVANTEC No.590) to absorb extra water from the impregnated filter;
- 6) keep the impregnated filter into a clean plastic filter case and seal it in a polyethylene bag with marking "K₂CO₃";
- 7) Back to step 2) for next filter. But maximum 20 sheets could be prepared by one solution.

Recommended procedure of preparation of acid impregnated filter (F3) is described as following steps:

- 1) prepare the mix solution (5% $H_3PO_4 + 2\%$ glycerin);
 - prepare three 500mL beakers;
 - weight 29.4g of H₃PO₄ and 10g of glycerin in each 500ml beaker;

- 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;
- 2) dunk cellulose filters into No.1 beaker and stir them with a glass stick;
- 3) pull up a filter from the No.1 beaker using plastic tweezers; dunk it in the No.2 beaker for the rinse;
- 4) pull up the filter from the No.2 beaker using plastic tweezers; dunk it in the No.3 beaker for the rinse;
- 5) pull up the filter from the No.3 beaker using plastic tweezers, and put the filter between two sheets of large cellulose sheet (ADVANTEC No.590) to absorb extra water from the impregnated filter;
- 6) keep the impregnated filter into a clean plastic filter case and seal it in a polyethylene bag with marking "H₃PO₄";
- 7) Back to step 2) for next filter. But maximum 20 sheets could be prepared by one solution.

The four-stage filter holder developed by NILU (Norwegian Institute for Air Research) is utilized. Only 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 respectively using clean plastic tweezers, taking into account the necessity to prevent the leak in the filter holder. The filter pack holders should be tightened using the exclusive torque to avoid leak after assembly.

Filters, especially impregnated one, should be always sealed up to avoid the contamination by unexpected ambient pollutants before or after the sampling time. The mounted filter holder should be capped by an exclusive cap, and then a leak of air through stage connections should be checked using a flow meter with a pump.

After leak checking, the mounted filter holder should be sealed into a polyethylene bag. And an aluminum-coated bag should be used to seal it up further. The sealed mounted holder should be kept in a transportation box during their deliverance to a monitoring site.

3. Sampling

Sampling system is presented in Fig. 2.

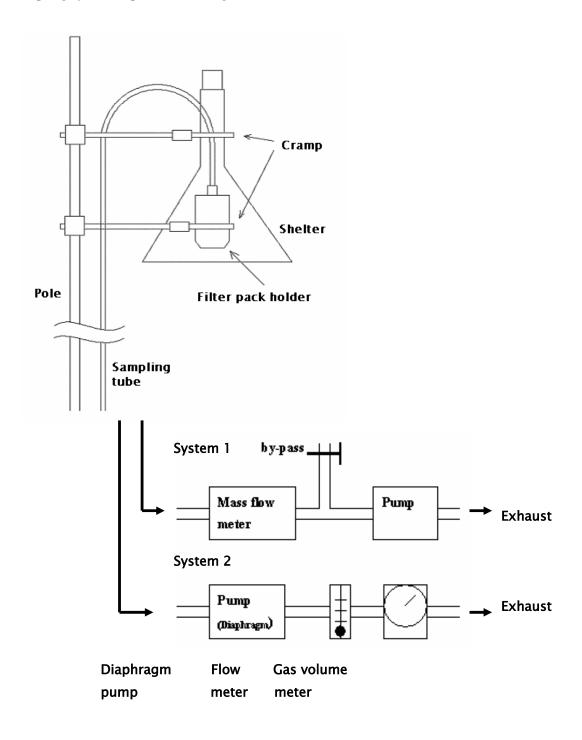


Fig. 2 Schematic diagram of filter pack sampling system

Recommended sampling procedure at monitoring site is described as follows:

[Start]

- 1) read the registered value of the volume meter counter and record it in the sampling notebook;
- 2) remove the exclusive cap from the new unexposed filter pack and mount the holder in the sampling system;
- 3) switch the pump on and record the time and the flow rate in the sampling notebook;

[Stop]

- 4) record the flow rate in the sampling notebook;
- 5) switch the pump off and record the time in the sampling notebook;
- 6) dismount the filter pack holder from the sampling system, put the exclusive cap on and then seal it into a polyethylene bag and an aluminum-coated bag;
- 7) keep the sealed holder in the transportation box;
- 8) read the value of volume meter counter and record it in the sampling notebook.

Sample filters are recommended to be dismounted from the holder in the laboratory and be kept separately in clean plastic filter cases with description of sample number. Each of the filter cases should be sealed one by one into a polyethylene bag. Furthermore, they should be placed into aluminum-coated bag. After the sealing they should be kept in the refrigerator.

Maintenance of equipment should be performed in accordance with their instructions for operation of 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 using the national standard method.

4. Extraction and chemical analysis

Recommended extraction procedure is described as follows:

- 1) prepare polypropylene test tubes (50ml) with caps;
- 2) dunk polypropylene test tubes into the diluted laboratory detergent for overnight and then wash them by water (at the first) and deionized water (at the second), and dry them in clean air;
- 3) mark 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;
- 4) put the sample filters into correspondent test tube;
- 5) 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 $20mL\ H_2O_2$ solution (0.05%-v/v) into the tubes;
- 6) shake the sample tubes during 20 minutes for their extractions using a shaker or an ultrasonic bath;
- 7) pick up the filters from the extracted solutions in the tubes and cover the tubes using exclusive caps;
- 8) filter the insoluble matters out of the extracted solutions using a membrane filter (pore size 0.45μm) previously well washed by deionized water;
- 9) keep the sample tubes in the refrigerator.

If sufficient detection of the chemical species by IC is difficult for samples from sites with low air concentrations, the air flow rates could be increased to 2 liter/min (see paragraph 26). If the detection would be still difficult in spite of increasing the air flow rate, the solvent volume might be set less than 20mL but to be enough for analyzing.

5. Determinations of concentrations

Regarding the determinations of concentrations, the equations are summarized in Table 1.

Table 1 Equations for determinations of concentrations

Specie	M	Equation
SO ₄ ²⁻	96.06	
NO ₃ -	62.01	
Cl	35.45	
Na ⁺	22.99	$C_{Air} = \alpha * net C_{Sol, F0} * V_{Sol} / V_{Air}$
K ⁺	39.10	
NH ₄ ⁺	18.04	
Ca ²⁺	40.08	
Mg^{2+}	24.31	
SO2	96.06 (SO ₄ ² -)	$C_{Air} = \alpha * (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F2}) * V_{Sol} / V_{Air}$
HNO3	62.01 (NO ₃ ⁻)	$C_{Air} = \alpha * net C_{Sol, F1} * V_{Sol} / V_{Air}$
HCl	35.45 (Cl ⁻)	$C_{Air} = \alpha * (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F2}) * V_{Sol} / V_{Air}$
NH3	18.04 (NH ₄ ⁺)	$C_{Air} = \alpha * (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F3}) * V_{Sol} / V_{Air}$

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

#3 see "6.1 Calculation of results" in this text.

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

6. Photo

Some photos demonstrate filter pack kit and important operations.





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

Artifact of filter pack method

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

- (1) Artifacts of HNO₃,
 - ① $NH_4NO_3(P) \rightarrow NH_3(G) + \underline{HNO_3(G)}$
 - ② $NH_4NO_3(P) + H_2SO_4(P) \rightarrow NH_4SO_4(P) + \underline{HNO_3(G)}$
 - 3 NaNO₃ (P) + H₂SO₄ (P) \rightarrow NaHSO₄ (P) + <u>HNO₃ (G)</u>,
 - 4 NaCl (P) + $\underline{\text{HNO}_3(G)} \rightarrow \text{NaNO}_3(P) + \text{HCl}(G);$
- (2) Artifacts of NH₃,
 - ① $NH_4NO_3(P) \rightarrow \underline{NH_3(G)} + HNO_3(G)$,
 - ② $NH_4Cl(P) \rightarrow NH_3(G) + HCl(G)$,
 - \bigcirc H₂SO₄ (P) + NH₃ (G) \rightarrow NH₄HSO₄ (P),
 - 4 NH₄HSO₄ (P) + NH₃ (G) → (NH₄)₂SO₄ (P);
- (3) Artifacts of HCl,
 - ① NaCl (P) + HNO₃ (G) \rightarrow HCl (G) + NaNO₃ (P),
 - ② $2NaCl(P) + H_2SO_4(P) \rightarrow 2HCl(G) + Na_2SO_4(P)$,
 - ③ $NH_4Cl(P) \rightarrow \underline{HCl(G)} + NH_3(G)$.

(P) and (G) mean "particle" and "gas", respectively.

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