

The Fourth Senior Technical Managers' Meeting
of the Acid Deposition Monitoring Network
in East Asia
1-3 October 2003, Niigata, Japan

Review of Existing QA/QC Activities on Filter Pack Method

The Network Center

1. Introduction

As part of the QA/QC activities of EANET, the Network Center (NC) has implemented inter-laboratory comparison projects on wet deposition since 1998, on soil since 1999 and on inland aquatic environment since 2000.

As for dry deposition monitoring for EANET, Technical Manual and QA/QC Program have not been developed and inter-laboratory comparison project has not been implemented either.

At the Second Session of the Scientific Advisory Committee (SAC2) held on 25-27 November 2002, however, it was suggested that NC should provide a plan and related guidelines for the inter-laboratory comparison on dry deposition (air concentration monitoring) taking the experience of EMEP and other networks into account.

In response to the suggestion, NC has collected information on existing QA/QC activities, especially on inter-laboratory comparison projects for filter pack methods of related networks.

Air concentrations could be measured by automatic real-time monitoring instruments, filter packs, denuders, passive samplers, etc. The review, however, has focused on filter pack method because many participating countries (9 countries in 2002) adopted this method.

This document summarizes the information that NC has got from EMEP (Europe) and CASTNet (US).

2. QA/QC activities in EMEP

EMEP, Co-operative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe, has 36 different laboratories in European countries. They are performing chemical analysis of air and precipitation samples. Since the measurement program is based on individual national network, the participating laboratories apply different sampling and analytical methods.

In order to improve the data comparability and to get a picture of the different laboratories' performance, inter-laboratory comparisons are organized by the Chemical

Coordinating Center (CCC) at the Norwegian Institute for Air Research (NILU). So far 20 inter-comparisons have been arranged. Flow chart of 20th inter-comparison is shown in Figure 1.

At the 17th inter-comparison (1999), the program is as follows.

- 1) Major components (pH, Conductivity, SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) in precipitation,
- 2) SO_2 in absorbing solution (for H_2O_2 absorption solution method),
- 3) NO_2 in absorbing solution (for filter sampling and iodide absorption method),
- 4) SO_2 on impregnated filter (for filter sampling), and
- 5) SO_4^{2-} in airborne particle (for filter sampling).

In these program, 4) and 5) is concerning to filter pack method. In 4), five KOH-impregnated filter samples (including one unidentified blank) for determination of SO_2 were distributed to participating laboratories. Specification of filter is cellulose (Whatman 40). 4 sample filters were added different amounts of H_2SO_4 . Sample value was calculated after subtracting blank value.

Meanwhile in 5), five cellulose filters (Whatman 40) for determination of SO_4^{2-} by wet chemical method were prepared. Different amounts of H_2SO_4 solution had been added on these filters. The amount of SO_4^{2-} on the filters distributed were divided into two groups called “low” and “high” since some laboratories use low-volume sampling (1-3.5 m^3) and some use medium-volume (10-50 m^3).

At the end of the 90's, CCC mentioned the future inter-laboratory comparison to improve as follows.

- SO_4^{2-} in particles is extracted from the aerosol filter in the same extraction as NO_3^- and NH_4^+ , and in similar way as are HNO_3 and NH_3 from impregnated filter. A good performance for both SO_4^{2-} in air and precipitation therefore indicates that the extraction is well done even for the other components.
- For NH_3 , there is in addition a potential contamination problem with the acid impregnated filters.
- Future laboratory comparisons are expected to contain filter samples of NO_3^- and NH_4^+ .

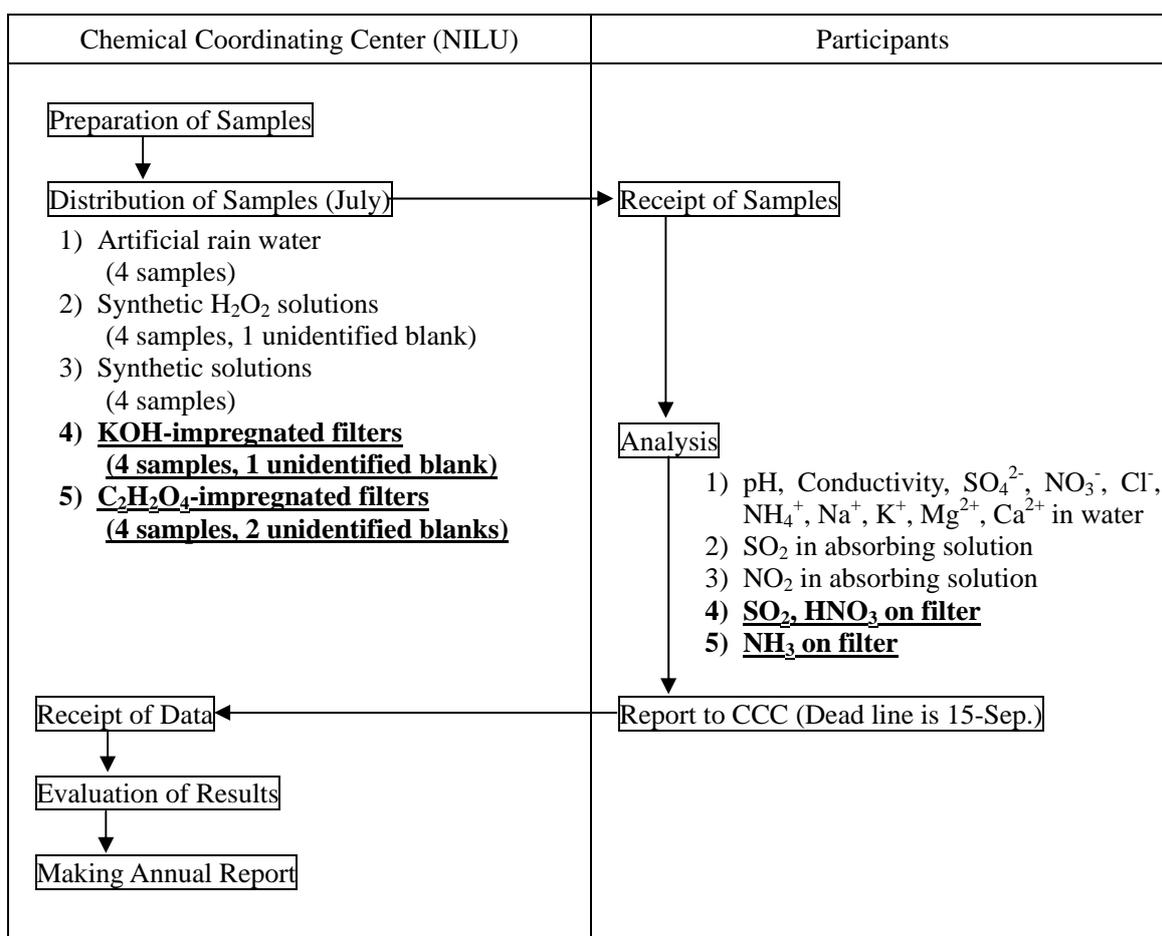
From 19th inter-comparison (2001), the program was revised as follows.

- 1) Major components (pH, Conductivity, SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Mg^{2+} ,

- Ca²⁺) in precipitation,
- 2) SO₂ in absorbing solution (H₂O₂ absorption solution method),
 - 3) NO₂ in absorbing solution (for filter sampling and iodide absorption method),
 - 4) SO₂ and HNO₃ on impregnated filter (for filter sampling), and
 - 5) NH₃ on impregnated filter (for filter sampling).

In these program, determination of HNO₃ was added in 4), and 5) was revised to determination of NH₃ on C₂H₂O₄-impregnated filter. In 5), 6 sample filters (including 2 unidentified blanks) were prepared. Cellulose filter (Whatman 40) was impregnated by oxalic acid, and 4 filters had been added different amounts of ammonium salt solution. Sample value was calculated after subtracting averaged blank value.

Figure 1 Flow Chart of 20th Inter-Laboratory Comparison in EMEP (2002)



Expected value of KOH and C₂H₂O₄ impregnated filters for determination of SO₂, HNO₃ and NH₃ at 19th and 20th inter-comparisons are shown in Table 1.

Table 1 Expected Value of Impregnated Filters

(Unit: $\mu\text{g}/\text{Filter}$)

		KOH-impregnated filter		C ₂ H ₂ O ₄ -impregnated filter
		SO ₂ (as SO ₄ ²⁻)	HNO ₃ (as NO ₃ ⁻)	NH ₃ (as NH ₄ ⁺)
19 th (2001)	1	54.11	173.88	7.73
	2	72.14	188.37	10.31
	3	126.25	57.96	41.25
	4	168.34	50.72	46.40
20 th (2002)	1	60.12	152.15	9.66
	2	66.12	137.66	12.90
	3	156.30	57.97	43.83
	4	192.36	43.47	48.99

Note:

The amount of SO₂, HNO₃, and NH₃ on the distributed filters corresponds to air concentrations when 25 m³ is sampled are as follows.

SO ₂	1.44-5.12 $\mu\text{g}/\text{m}^3$	(0.54-1.92 ppb)
HNO ₃	1.76-7.53 $\mu\text{g}/\text{m}^3$	(0.67-2.92 ppb)
NH ₃	0.31-1.95 $\mu\text{g}/\text{m}^3$	(0.41-2.62 ppb)

3. QA/QC Activities in CASTNet

USEPA established the Clean Air Status and Trends Network (CASTNet) in cooperation with the National Oceanic Atmospheric Administration (NOAA) in 1990. CASTNet has 85 monitoring sites, and Harding ESE, as prime contractor, is responsible for network operations and QA activities.

CASTNet have not been arranged any inter-laboratory comparison program because of adopting center laboratory. The center laboratory, Harding ESE, participates to inter-laboratory comparison studies by the ECAN National Water Research Institute (NWRI) National Laboratory for Environmental Testing (NLET) and United States Geological Survey (USGS) for SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, pH, and specific conductance. The ECAN study is conducted every six months and USGS study is conducted biweekly.

For reference, the method of inspection and acceptance of each filter in CASTNet is introduced in Appendix 1.

Appendix 1

Inspection and Acceptance of Filters in CASTNet

- (1) Teflon and Nylon filters require no preparation for use in filter packs.
- (2) Whatman filters must be impregnated with K_2CO_3 to collect SO_2 .
- (3) Prior to being loaded into the filter packs, each lot of Teflon, nylon, and Whatman filters are analyzed to ensure that background contamination from the manufacturing and impregnation processes is within acceptable limits.
- (4) Acceptance testing is done on each box of Teflon and nylon filters prior to preparation of the filter packs.
 - Five filters (5%) from each box of 100 are extracted and analyzed.
 - If any of the five filters show nitrate or sulfate contamination above the detection limit (Table A), the box is rejected and not use in filter packing.
 - Whatman filters are acceptance tested after the impregnation procedure.
 - Each set of impregnated filters is assigned an impregnation date. The impregnation date is considered the Whatman lot number.
 - Acceptance testing is performed on 2% of the Whatman filters contained in each lot. (The number of filters in a lot may range from 200 to 800 filters depending upon the demand.)
 - The acceptance test samples are prepared, extracted and analyzed.
 - A Whatman filter lot is considered acceptable if no more than one acceptance sample shows sulfate contamination above $3.83 \mu\text{g}$ (equivalent to an approximate ambient concentration of $0.7 \mu\text{g}/\text{m}^3$ as SO_2).

Table A Teflon, Nylon, and Whatman Filters Acceptance Criteria

Filter Media	Acceptance Criteria (μg)	
	SO_4^{2-}	NO_3^- -N
Teflon	< 1.00	< 0.200
Nylon	< 1.00	< 0.200
Impregnated Whatman	< 3.83*	N/A

* Batch is acceptable with one filter > 3.83 μg