

EANET

The Network Center for the Acid Deposition Monitoring Network in East Asia

**Report of the Inter-laboratory
Comparison Project 2005 on
Dry Deposition
(Filter Pack Method)**

1st Attempt

November 2006
Acid Deposition and Oxidant Research Center

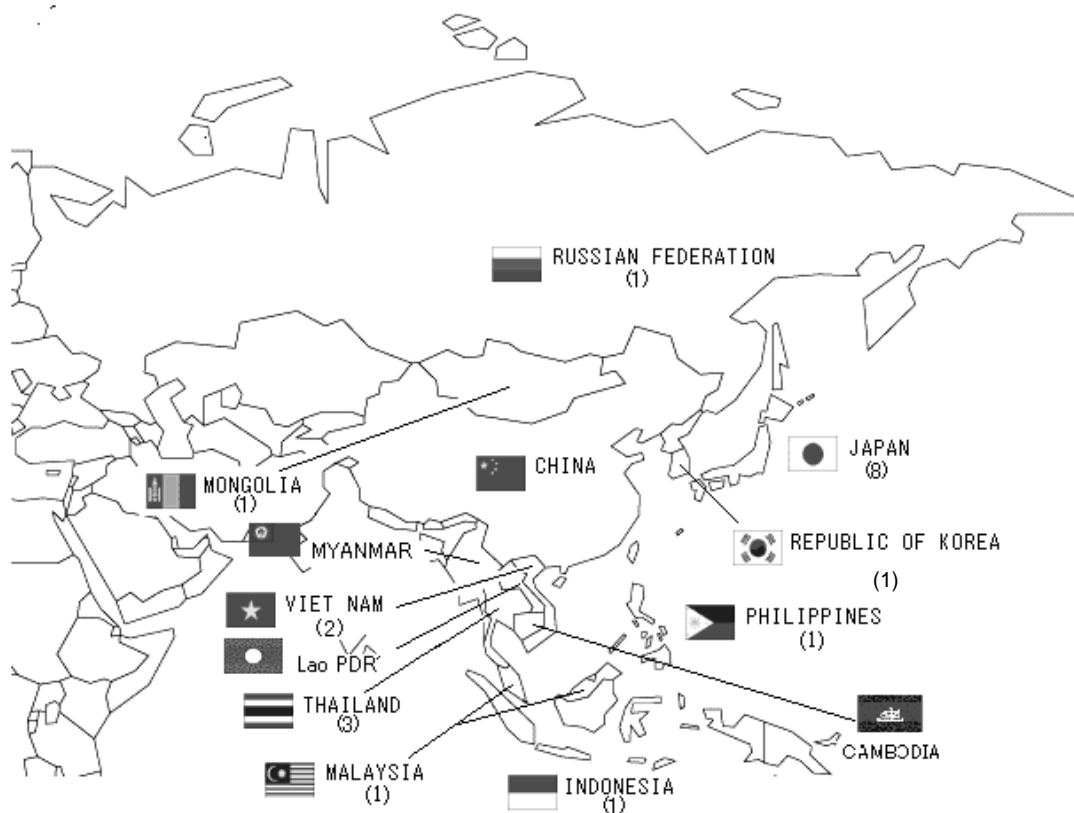
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1. Introduction

This inter-laboratory comparison project (round robin analysis survey of uniformly prepared impregnated filter samples and blank filters) was conducted among the analytical laboratories in participating countries of the Acid Deposition Monitoring Network in East Asia (EANET), based on the Quality Assurance / Quality Control (QA/QC) Program of EANET. The purposes of this project are, through the evaluation of analytical results, analytical equipment and its operating condition and other practices, (i) to recognize the analytical precision and accuracy of the measurement in each participating laboratory, and give an opportunity to improve the quality of the analysis on dry deposition monitoring (filter pack method), and (ii) to improve reliability of analytical data through the assessment of suitable analytical methods and techniques.

Impregnated filters which contain three ions, SO_4^{2-} , Cl^- , and NH_4^+ , were prepared and distributed by the Network Center (NC) in November, 2005. Most of the participating laboratories join this activity and submitted their analytical results to NC. Obtained results for the amount of SO_4^{2-} , Cl^- , and NH_4^+ on the distributed filters were compared with the prepared values and statistically treated. List of the participating laboratories, individual analytical results with their laboratory's short name, and various statistical parameters are summarized in this report.



* Figure in parenthesis shows the number of laboratories of each country (19 laboratories from 9 countries)

Fig.1 Participating laboratories in 2005

2. Procedure

2.1. Participating Laboratories

Nineteen laboratories in charge of chemical analysis in 9 countries of EANET participated in this first attempt. The Network Center (NC) shipped the sample filters to all of these laboratories in 9 countries, and almost all of them submitted their analytical results to NC. The names of the participating laboratories are presented in *APPENDIX 1*.

2.2. Dispatched Sample Filters

Sample filters, on which small and large amount of salts (ions) were impregnated, were prepared and distributed to the laboratories as well as blank filters. The details of the sample filters are described in Table 1. The information on the analytical precision and accuracy on the individual parameters were summarized through the statistical treatment of the submitted analytical results from each participating laboratory.

Table 1 Outline of distributed filter samples

Name	Details	Container	Number of filters	Note
No.051-1	Alkali-Impregnated filter (small amount)	Polyethylene centrifuging tube	3 (a, b, c)	Known amount of salts are put on the filter impregnated by K_2CO_3
No.051-2	Acid-Impregnated filter (small amount)	Polyethylene centrifuging tube	3 (a, b, c)	Known amount of salts are put on the filter impregnated by H_3PO_4
No.052-1	Alkali-Impregnated filter (large amount)	Polyethylene centrifuging tube	3 (a, b, c)	Known amount of salts are put on the filter impregnated by K_2CO_3
No.052-2	Acid-Impregnated filter (large amount)	Polyethylene centrifuging tube	3 (a, b, c)	Known amount of salts are put on the filter impregnated by H_3PO_4
No.053-1	Alkali-Impregnated filter (blank)	Polyethylene centrifuging tube	3 (a, b, c)	The filter impregnated by K_2CO_3
No.053-2	Acid-Impregnated filter (blank)	Polyethylene centrifuging tube	3 (a, b, c)	The filter impregnated by H_3PO_4

2.3. Analytical Parameters

All participating laboratories were expected to analyze the sample filters and submit the results as the net amount of three kinds of contained salts, Sulfate, Chloride and Ammonium, in the units of microgram (μg).

2.4 Analytical Procedure

The recommended procedures for sampling and analysis on filter pack method are described in EANET Document, "Technical Document for Filter Pack Method in EAST Asia" (NC, 2003). Each sample filter was put in a centrifuging tube and distributed to the participating laboratories. Thus, extracting solvent could be poured directly into the centrifuging tube and then the extract operation could be carried out.

Extraction procedure was carried out according to the following procedures;

- (1) In the case of Sample No.051-1, No.052-1, No.053-1, pour exactly 20 mL H_2O_2 solution (0.05%-v/v) into the centrifuging tube, then shake or vibrate the tubes during 20 minutes for extractions using shaker or ultrasonic bath.
- (2) In the case of Sample No.051-2, No.052-2, No.053-2, pour exactly 20 mL deionized water into the centrifuging tube, then shake or vibrate the tubes during 20 minutes for the extractions using shaker or ultrasonic bath.
- (3) Filter the insoluble matters out of the extracted solutions using a membrane filter (pore size $0.45\mu\text{m}$) previously well washed by pure water (more than 100mL).

Note 1) Put a name on each sample tube and keep them in the refrigerator.

Note 2) Carry out the analysis as soon as possible after the extraction process.

Participating laboratories were expected to use the same analytical methods. Analytical methods specified in the Technical Document are described in Table 2.

Table 2 Analytical methods specified in the Technical Document

Parameter	Analytical method
SO_4^{2-}	Ion Chromatography
Cl^-	Spectrophotometry
NH_4^+	Ion Chromatography Spectrophotometry (Indophenol Blue)

2.5. Submission of the results

It was requested that the results were reported as **the net amount** of each salt contained in sample filters. The net amount can be determined by:

$$M_{\text{sol}} = C_{\text{sol}} \times V_{\text{sol}} \quad (1)$$

where M_{sol} : the net amount of each component in the extracting solution (μg);
 C_{sol} : concentration of each component in the extracting solution (mg/L);
 V_{sol} : volume of the extracting solution (mL).

The net values of absolute amount should be calculated by:

$$\text{net } M_{\text{sol}} = M_{\text{sol, Sample}} - M_{\text{sol, Blank}} \quad (2)$$

where $M_{\text{sol, Sample}}$: the net amount (μg) of each component in the extracting solution from the sample filters, No.051-1, No.051-2, No.052-1 and No.052-2;
 $M_{\text{sol, Blank}}$: the averaged net amount (μg) in the extracting solutions from the blank filters, No.053-1 and No.053-2.

3. Results

The Network Center (NC) distributed the sample filters to 19 laboratories in the participating countries of EANET, and received the data on analytical results. Outline of the submitted results are summarized in Table 3. Statistics such as Average, Minimum (Min.), Maximum (Max.), Standard deviation (S.D.) and Number of data (N) were calculated for each analyzed ion. Outlying result which was apart from the average greater than a factor of 3 of S.D. was not included for this statistical calculation. As shown in Table 3, averages of submitted results were fairly well agreed with the prepared values within a range from -8.1% (SO_4^{2-}) to -1.8% (Cl^-) for Sample No.051 (small amount), and from -4.5% (Cl^-) to 0.9% (NH_4^+) for Sample No.052 (large amount). But there were a few laboratories of which submitted results were clearly different from prepared values.

The Data Quality Objectives (DQOs) of EANET was specified as $\pm 15\%$ for every constituent by the QA/QC program in EANET. In this report, detected values of three filters (a, b, c) were averaged every Sample No. and the averaged values were compared with the prepared values with taking the DQOs into account. The flag "E" was put to the result of which accuracy exceeded DQOs by a factor of 2 ($\pm 15\% \sim \pm 30\%$), and the flag "X" was put to the data of which accuracy exceeded DQOs more than a factor of 2 ($< -30\%$ or $> 30\%$).

$$\text{Accuracy (\%)} = (\text{Obtained result} - \text{Prepared value}) / \text{Prepared value} * 100 \quad (3)$$

Flag E: $-30\% \leq \text{Accuracy} < -15\%$ or $15\% < \text{Accuracy} \leq 30\%$

Flag X: $\text{Accuracy} < -30\%$ or $30\% < \text{Accuracy}$

Table 3 Summary of analytical results of the sample filters
(Reported data after removing outliers)

Constituents	Prepared* (Vp)	Average (Va)	$\Delta V/Vp$ * (%)	S.D.	Number	Min.	Max.
<i>Sample No.051 (Small)</i>							
SO ₄ ²⁻ (μg)	25.0	23.0	-8.1	3.25	19	17.8	31.6
Cl ⁻ (μg)	2.80	2.80	-1.8	0.91	18	1.28	5.20
NH ₄ ⁺ (μg)	5.30	5.08	-4.2	0.54	18	3.35	6.02
<i>Sample No.052 (Large)</i>							
SO ₄ ²⁻ (μg)	70.0	67.9	-3.0	5.62	19	53.4	77.6
Cl ⁻ (μg)	30.0	28.6	-4.5	2.61	17	23.1	32.0
NH ₄ ⁺ (μg)	20.0	20.2	0.9	2.48	19	14.7	24.9

* Prepared: Prepared values which were expected to be extracted from each filter

* ΔV : Average (Va) - Prepared (Vp)

The results were evaluated by the comparison analyses of i) Concentration dependence between Sample No.051 (small amount) and No.052 (large amount); ii) Individual parameters; iii) Circumstances of analysis in each participating laboratory. The evaluation of results on both of Sample No.051 and No.052 is presented in “3.1. Comparison by Sample”. The evaluation of results for each constituent is presented in “3.2. Analytical Parameters”. And the evaluation of results by the circumstances of analysis such as analytical method used, experience of personnel, and other analytical condition is presented in “3.3. Circumstances of Sample Analysis”.

3.1. Comparison by Sample

Sample of small amount

For Sample No.051 (small amount), 10 analytical data in 56 submitted results exceeded the DQOs ($\pm 15\%$) by a factor of 2 ($\pm 30\%$) and were flagged by "E". Also 5 analytical data exceeded the DQOs more than a factor of 2 and were flagged by "X". Amount of flagged data was 15 and the ratio of the flagged data was about 26.8 percents in total for Sample No.051 (Fig.2). Result of SO_4^{2-} has no flags of "X". (Table 4 and 5)

Table 4 Number of flagged data for Sample No.051 (small amount)

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	5	5	0	10
Flag X *	0	3	2	5
Data within DQOs	14	10	17	41
Ratio of Flagged (%)	26.3	44.4	10.5	26.8

* E : Value exceeded the DQO by a factor of 2

* X : Value exceeded the DQO more than a factor of 2

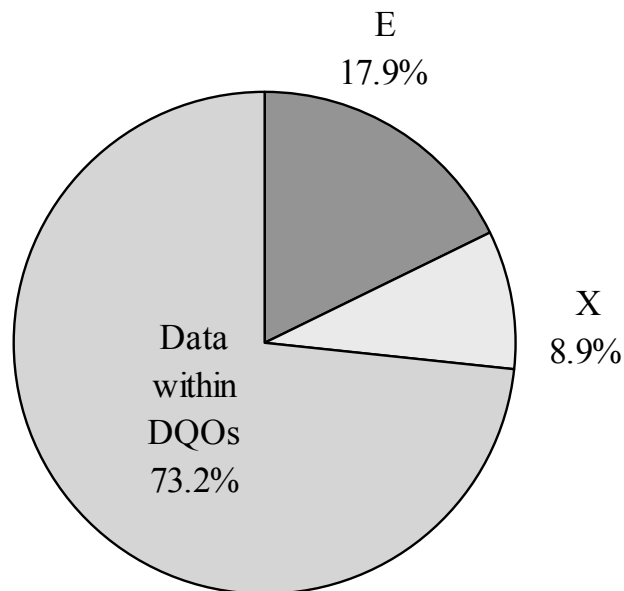


Fig.2 Percentage of flagged data for Sample No.051 (small amount)

Table 5 Averaged analytical results of Sample No.051 (small amount)

Lab. Code		SO ₄ ²⁻ (µg)		Cl ⁻ (µg)		NH ₄ ⁺ (µg)
ID02	E	19.5	X	5.20		4.67
JP01		22.2	E	2.28		5.08
JP02		24.6		2.63		5.30
JP03		23.5		2.50		5.27
JP04		25.3		2.76		5.05
JP05	E	17.8	X	1.28		5.70
JP06		24.5	E	3.57		5.33
JP07		23.8		2.39		5.08
JP08		22.8		2.51		5.12
KR01		26.5		2.69		4.73
MY01		22.9		2.80		4.89
MN01		25.7	E	2.00		5.47
PH01		22.1		3.13	X	3.35
RU01	E	18.4		-		5.24
TH01		21.9		2.72	X	7.65
TH02		21.9	E	2.26		4.88
TH03		23.1		2.89		6.02
VN01	E	18.4	E	2.22		5.10
VN02	E	31.6	X	4.60		5.43

(Note) E: Value exceeded the DQO (±15%) by a factor of 2

X: Value exceeded the DQO (±15%) more than a factor of 2

Sample of large amount

For Sample No.052 (large amount), 10 analytical data in 56 submitted results exceeded the DQOs ($\pm 15\%$) by a factor of 2 ($\pm 30\%$) and were flagged by "E". Also 1 analytical data exceeded the DQOs more than a factor of 2 and were flagged by "X". Amount of flagged data was 11 and the ratio of the flagged data was about 19.6 percents in total for Sample No.052 (Fig.3). Results of SO_4^{2-} and NH_4^+ have no flags of "X". (Table 6 and 7)

Table 6 Number of flagged data for Sample No.052 (large amount)

	SO_4^{2-}	Cl^-	NH_4^+	Total
Flag E *	2	4	4	10
Flag X *	0	1	0	1
Data within DQOs	17	13	15	45
Ratio of Flagged (%)	10.5	27.8	21.1	19.6

* E : Value exceeded the DQO by a factor of 2

* X : Value exceeded the DQO more than a factor of 2

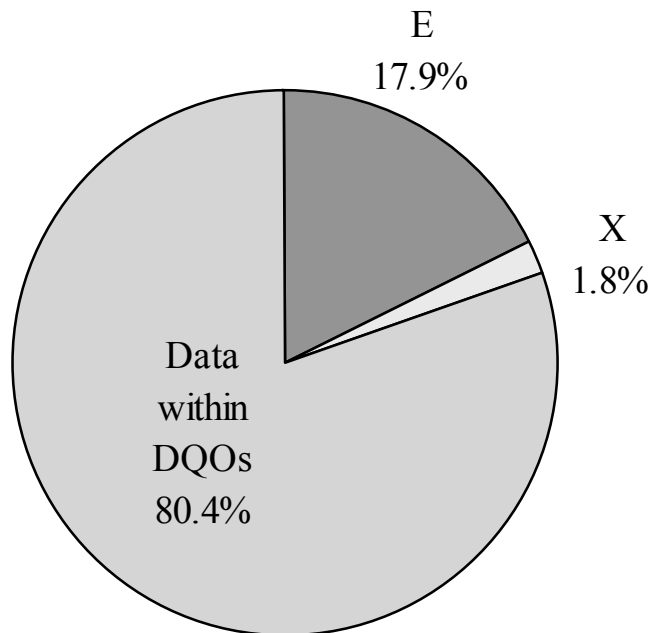


Fig.3 Percentage of flagged data for Sample No.052 (large amount)

Table 7 Averaged analytical results of Sample No.052 (large amount)

Lab. Code	SO ₄ ²⁻ (µg)	Cl ⁻ (µg)	NH ₄ ⁺ (µg)
ID02	65.5	X 13.1	19.6
JP01	69.2	28.1	20.1
JP02	70.6	29.4	19.9
JP03	68.2	29.1	20.3
JP04	70.9	31.2	20.0
JP05	69.3	E 24.5	21.2
JP06	61.6	E 24.1	19.4
JP07	67.7	29.3	17.7
JP08	67.4	29.2	20.2
KR01	68.2	30.5	17.2
MY01	70.3	30.4	19.6
MN01	72.3	E 25.1	E 24.9
PH01	68.8	31.2	21.9
RU01	75.2	-	20.8
TH01	66.6	30.5	E 24.9
TH02	70.1	29.1	17.6
TH03	77.6	32.0	E 23.1
VN01	E 53.4	29.0	20.7
VN02	E 57.3	E 25.2	E 14.7

(Note) E: Value exceeded the DQO (±15%) by a factor of 2

X: Value exceeded the DQO (±15%) more than a factor of 2

Sample of blank

Sample No.053 (No.053-1 and No.053-2) was supplied for the implementation of blank analysis. Obtained results are summarized in Table 8. Medians of SO_4^{2-} , Cl^- and NH_4^+ were 0.07 μg , 0.90 μg , and 0.37 μg , respectively. Blank values were detected in wide range including 0 μg . Table 9 shows the ratio of blank value to analytical result. Reverse mesh indicates that there was a flag for Sample No.051 or 052. Although the blank values were relatively higher, flags were not appeared at some laboratories. As a result, a clear relationship between the blank values and the flagged data was not found.

Table 8 Analytical results of Sample No.053 (blank)

Lab. Code	SO_4^{2-} (μg)	Cl^- (μg)	NH_4^+ (μg)
ID02	0.80	0.60	0.80
JP01	0.07	0.44	0.13
JP02	0.00	0.78	0.42
JP03	0.00	0.57	0.08
JP04	1.45	3.69	0.64
JP05	0.00	0.00	0.37
JP06	0.00	0.95	0.29
JP07	0.00	0.94	0.28
JP08	0.00	0.48	0.42
KR01	0.00	9.57	24.2
MY01	0.11	0.71	0.39
MN01	3.13	2.40	0.00
PH01	1.54	1.46	0.00
RU01	7.10	-	0.74
TH01	0.13	0.72	0.61
TH02	0.09	1.33	0.82
TH03	0.95	0.86	0.09
VN01	0.00	1.95	0.18
VN02	0.00	5.00	0.00
Average	0.81	1.80	1.60
Median	0.07	0.90	0.37
Minimum	0.00	0.00	0.00
Maximum	7.10	9.57	24.2
Standard deviation	1.73	2.31	5.48

Table 9 The ratio of blank to analytical results ($V_{\text{blank}}/V_{\text{result}}$)

Lab. Code	Small amount			Large amount		
	SO ₄ ²⁻ (μg)	Cl ⁻ (μg)	NH ₄ ⁺ (μg)	SO ₄ ²⁻ (μg)	Cl ⁻ (μg)	NH ₄ ⁺ (μg)
ID02	0.04	0.12	0.17	0.01	0.05	0.04
JP01	0.00	0.19	0.03	0.00	0.02	0.01
JP02	0.00	0.30	0.08	0.00	0.03	0.02
JP03	0.00	0.23	0.02	0.00	0.02	0.00
JP04	0.06	1.34	0.72	0.02	0.12	0.18
JP05	0.00	0.00	0.06	0.00	0.00	0.02
JP06	0.00	0.27	0.05	0.00	0.04	0.01
JP07	0.00	0.39	0.06	0.00	0.03	0.02
JP08	0.00	0.19	0.08	0.00	0.02	0.02
KR01	0.00	3.56	5.12	0.00	0.31	1.41
MY01	0.00	0.25	0.08	0.00	0.02	0.02
MN01	0.12	1.20	0.00	0.04	0.10	0.00
PH01	0.07	0.47	0.00	0.02	0.05	0.00
RU01	0.39	-	0.14	0.09	-	0.04
TH01	0.01	0.26	0.08	0.00	0.02	0.02
TH02	0.00	0.59	0.17	0.00	0.05	0.05
TH03	0.04	0.30	0.01	0.01	0.03	0.00
VN01	0.00	0.88	0.04	0.00	0.07	0.01
VN02	0.00	1.09	0.00	0.00	0.20	0.00

■ : Flagged data of "E" for Sample No.051 or No.052

■ : Flagged data of "X" for Sample No.051 or No.052

3.2 Analytical Parameters

The general overviews of the results were presented below in Figures and Tables for each analytical parameter (SO₄²⁻, Cl⁻ and NH₄⁺). The results received from each laboratory were normalized by prepared values to evaluate their deviation. The numbers of flagged data were also shown in tables for each analytical parameter.

SO₄²⁻ (Sulfate)

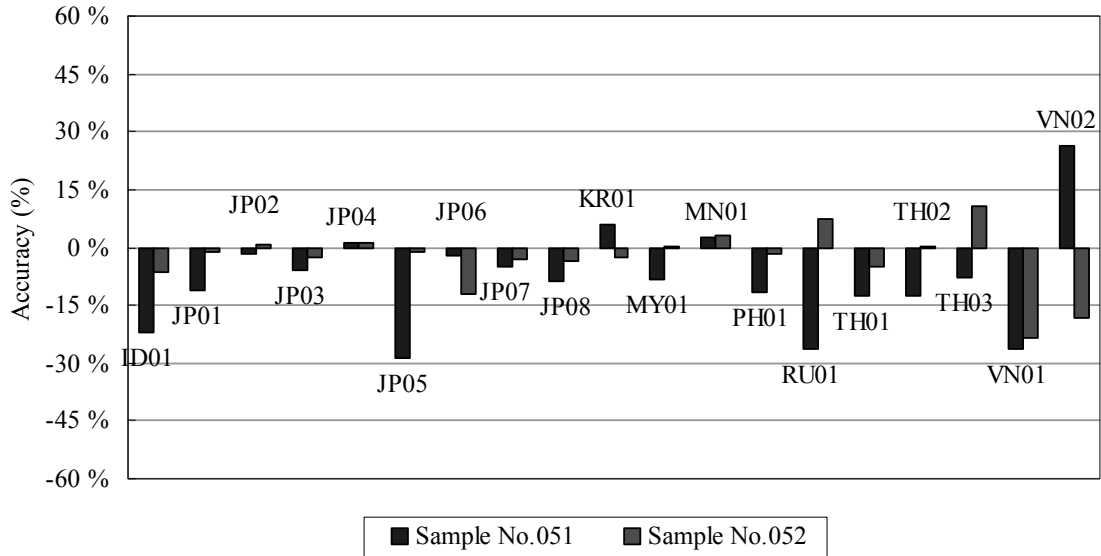


Fig.4 Distribution of SO₄²⁻ data normalized by prepared value

Table 10 Analytical method and flagged data of SO₄²⁻

<i>Analytical Method</i>			
Ion Chromatography	19/19		
<i>Flagged Data</i>			
	Flag E	Flag X	Flagged (%)
Sample No.051	5	0	26.3
Sample No.052	2	0	10.5

All of the participating laboratories used Ion Chromatography for the determination of SO₄²⁻. “E” flags appeared at 5 laboratories for Sample No.051 and at 2 laboratories for Sample No. 052. On the other hand, “X” flag did not appear for both samples. Most of flagged data were lower than the prepared value.

Cl⁻ (Chloride)

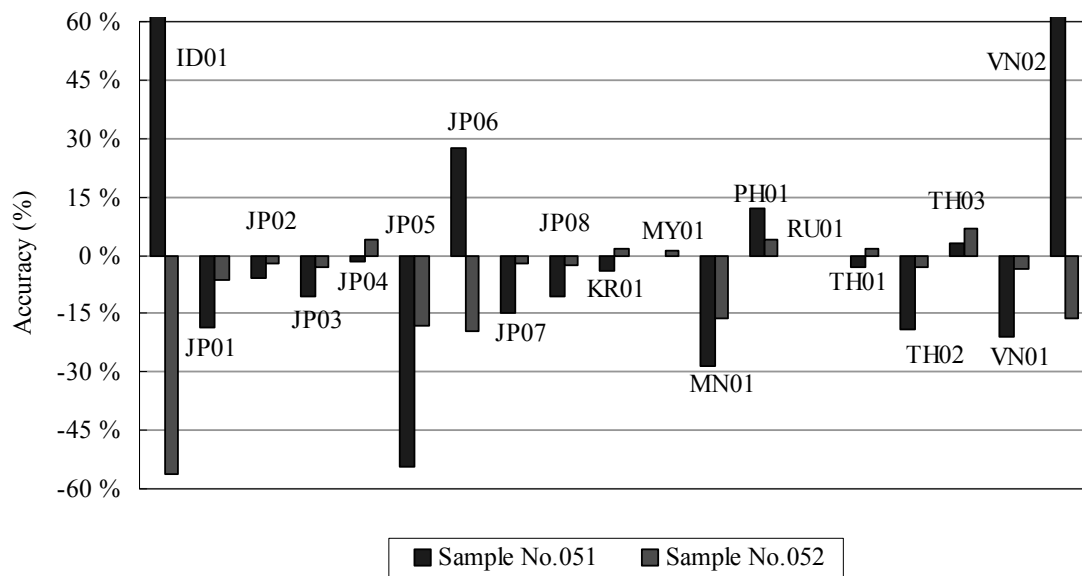


Fig.5 Distribution of Cl⁻ data normalized by prepared value

Table 11 Analytical method and flagged data of Cl⁻

<u>Analytical Method</u>			
Ion Chromatography	18/18		
<u>Flagged Data</u>			
	Flag E	Flag X	Flagged (%)
Sample No.051	5	3	44.4
Sample No.052	4	1	27.8

As same with the analysis of SO₄²⁻, all laboratories used Ion Chromatography for the determination of Cl⁻. Results of ID01, JP05, MN01 and VN02 had the flagged data for both of samples. Particularly those of ID01 had “X” flag for both of samples. The data of ID01 and VN02 exceeded “prepared value” more than 60% for Sample No.051. The ratio of the flagged data for Sample No.051, which had small amount, was larger than that for Sample No.052 which had large amount.

NH₄⁺ (Ammonium)

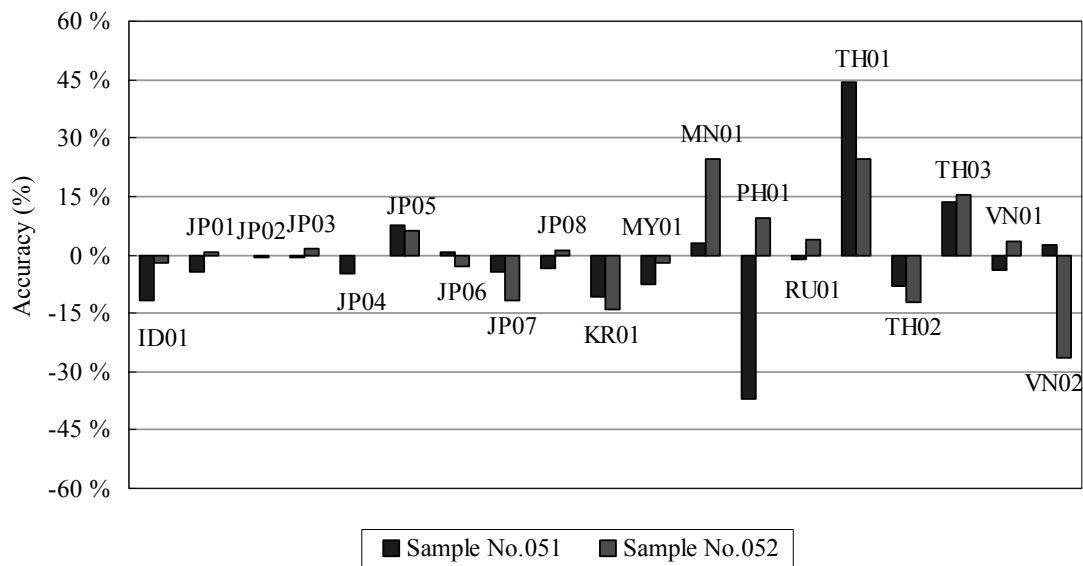


Fig.6 Distribution of NH₄⁺ data normalized by prepared value

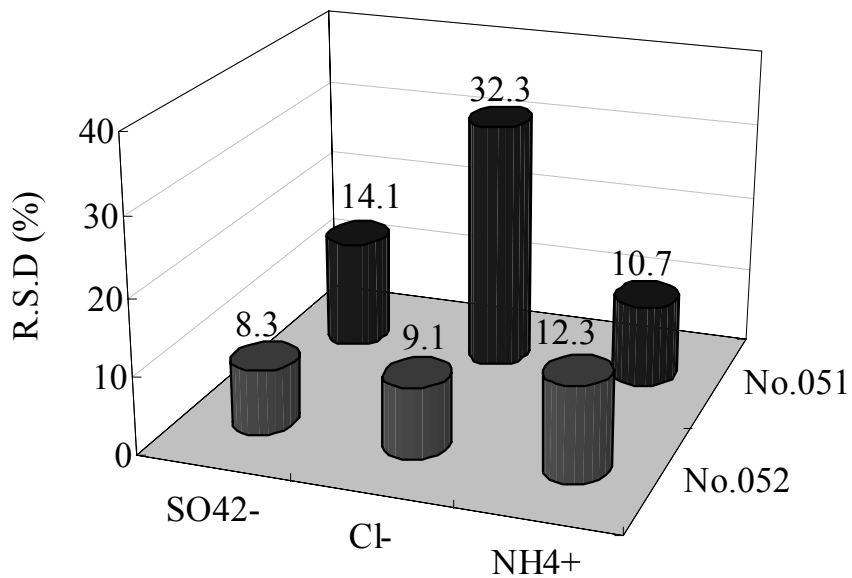
Table 12 Analytical method and flagged data of NH₄⁺

<u>Analytical Method</u>			
Ion Chromatography			17/19
Spectrometry (Indophenol blue)			1/19
Spectrometry			1/19
<u>Flagged Data</u>			
	Flag E	Flag X	Flagged (%)
Sample No.051	0	2	10.5
Sample No.052	4	0	21.1

18 laboratories used recommended analytical method of EANET for the determination of NH₄⁺; 16 laboratories used Ion Chromatography and 1 laboratory used Indophenol Spectrophotometry. 1 laboratory used Spectrophotometry other than Indophenol blue method. There were no “E” flags for Sample No.051 and no “X” flag for Sample No.052. Differ from the results of SO₄²⁻ and Cl⁻, the ratio of the flagged data for Sample No.051, which had small amount, was lower than that for Sample No.052 which had large amount.

Relative Standard Deviation (R.S.D)

The values of the relative standard deviation (R.S.D) for the results of Sample No.051 and No.052 are shown in the figure 7. The values of R.S.D for Sample No.051 were larger than those for Sample No.052 except NH_4^+ . Especially, R.S.D. of Cl^- for Sample No.051 showed relatively higher value compared with the others.



$$\text{R.S.D (\%)} = (\text{Standard deviation} / \text{Average}) * 100$$

(Reported data after removing the outliers)

Fig.7 Relative standard deviation of each constituent data

3.3 Circumstance of Sample Analysis

Methods Used

As shown in Table 13, most of participating laboratories used recommended methods of EANET. All laboratories used Ion Chromatography for the determination of anions. As for determination of NH_4^+ , 17 of 19 laboratories used Ion Chromatography and 1 laboratory used Indophenol Spectrophotometry. However, 1 laboratory used the Spectrophotometry other than Indophenol blue method.

Table 13 Analytical methods used for sample analysis

Lab. Code	$\text{SO}_4^{2-}, \text{Cl}^-$	NH_4^+
ID01		Ion Chromatography
JP01		Ion Chromatography
JP02		Ion Chromatography
JP03		Ion Chromatography
JP04		Ion Chromatography
JP05		Ion Chromatography
JP06		Ion Chromatography
JP07		Ion Chromatography
JP08		Ion Chromatography
KR01		Ion Chromatography
MY01		Ion Chromatography
MN01		Ion Chromatography
PH01	Ion Chromatography	Indophenol Spectrophotometry
RU01	Ion Chromatography	Spectrophotometry
TH01		Ion Chromatography
TH02		Ion Chromatography
TH03		Ion Chromatography
VN01		Ion Chromatography
VN02		Ion Chromatography

Years of experience for staff in charge

According to the information about “years of experience for staff in charge” obtained through this project, clear evidence for improvement of data quality was not found. The average of the years of experience was 5.7 years, and this project was the first experience for the staff of JP03, JP07, MY01 and TH02 to conduct the analysis of filter pack samples. Years of experience for staff in charge are summarized in Table 14. Reverse mesh in Table 14 indicates that there was a flag for Sample No.051 and/or 052. Reverse mesh with dark color indicate flagged data in both of Sample No.051 and No.052.

Table 14 Years of experience (unit: year)

Lab. Code	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺
ID01	2	2	2
JP01	21	21	21
JP02	6	6	6
JP03	1	1	1
JP04	10	10	10
JP05	2	2	2
JP06	2	2	2
JP07	1	1	1
JP08	0.8	0.8	0.8
KR01	3	3	3
MY01	1	1	2
MN01	8	8	8
PH01	4.5	4.5	4.5
RU01	15	15	15
TH01	9	9	9
TH02	0	0	0
TH03	3	3	3
VN01	11	11	11
VN02	2	2	2

(Note) Reverse mesh: Flagged data in Sample No.051 and/or No.052 (Dark color: Flagged data in both of Sample No.051 and No.052)

The number of flagged data in laboratories

In the results of Sample No.051 and 052, the total number of flagged data was 26 (E: 20, X: 6) among the whole of 112 values. The attribution of flagged data in each laboratory was presented in Figure 8. The number of laboratories with good results without flagged data was 6 (33%). The number of laboratories that submitted data with less than 2 flagged values were 11 (61%) in this attempt. There was one laboratory which had 5 flagged data. The analytical procedures in this laboratory should be reconsidered as well as quality of standard solutions, and so on.

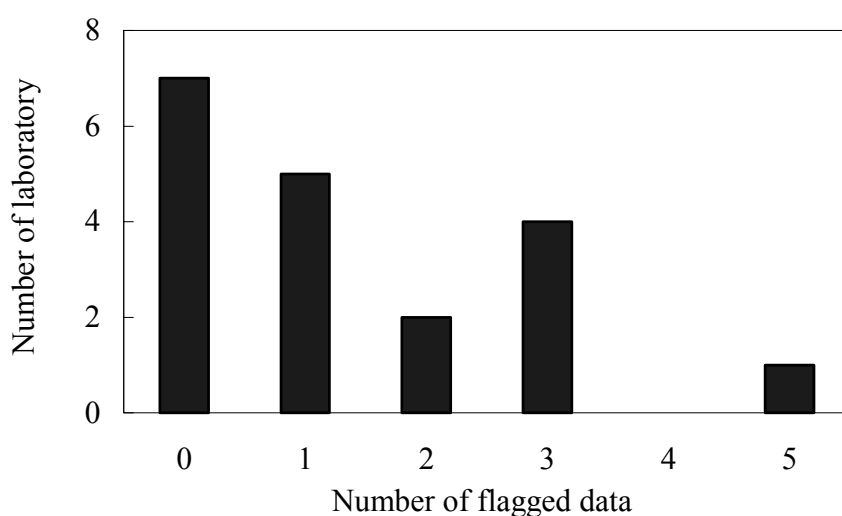


Fig.8 Distribution of laboratories with the number of flagged data

Calibration standard solution

Table 15 shows the lowest (except to zero) and highest concentrations of the calibration standard solution for the analytical methods used in each laboratory, and also shows the prepared values in the unit of $\mu\text{mol/L}$. The concentrations of the standard solution in some laboratories were not in the appropriate range for the sample analysis. Flagged data mainly appeared for the laboratories of which the standard solution was not in the appropriate range. A thick character in Table 15 indicates that the value of standard solution is less than the prepared value of small amount or more than the prepared value of large amount.

Table 15 Ranges of the calibration standard solution in each laboratory

Lab. Code	SO ₄ ²⁻ (μmol/L)		Cl ⁻ (μmol/L)		NH ₄ ⁺ (μmol/L)	
	Lowest	Highest	Lowest	Highest	Lowest	Highest
ID02	5.21	52.1	5.63	141	22.2	111
JP01	1	208	1	565	0.5	558
JP02	5.21	208	14.1	564	2.77	111
JP03	5.21	104	2.82	56.4	5.54	111
JP04	5.2	104	5.64	141	5.54	111
JP05	1.06	40.4	2.87	110	6.01	108
JP06	2.61	26.0	7.08	70.8	5.57	55.6
JP07	1.04	77.9	5.65	282	2.89	144
JP08	0.21	104	0.56	56.4	0.55	111
KR01	5.21	52.1	14.1	141	22.2	273
MY01	1.04	62.5	1.41	113	2.77	55.4
MN01	5.1	125	9.3	170	11.1	111
PH01	0.5	208	1.07	564	28.8	109
RU01	5.21	104	8.06	161	5.56	111
TH02	0.1	10.4	0.28	28.2	0.55	55.4
TH03	5.21	31.2	14.1	84.6	5.54	166
TH05	0.25	20.7	0.2	56.6	10.7	55.2
VN01	2.08	104	2.82	141	5.54	277
VN02	10	50	10	50	10	50
Sample No.051	13.0		3.95		14.7	
Sample No.052		36.4		42.3		55.4

(Note) Thick character: Concentration of standard solution was not appropriate.

Reverse mesh: Flagged data in Sample No.051 and/or No.052 (Dark color:

Flagged data in both of Sample No.051 and No.052)

4. Reference

- 1) Guidelines for Acid Deposition Monitoring in East Asia
March 2000 adopted at:
The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia.
- 2) Technical Documents for Wet Deposition Monitoring in East Asia
 - > Technical Manual for Wet Deposition Monitoring in East Asia
 - > Quality Assurance / Quality Control (QA/QC) Program for the Preparatory-Phase Wet Deposition Monitoring in East Asia, March 2000 adopted at:
The Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia.
- 3) Technical Documents for Filter Pack Method in East Asia
November 2003 adopted at:
The Third Session of the Scientific Advisory Committee (SAC3)

Contact Information

Please address all inquiries, comments and suggestions about this report to:

Acid Deposition and Oxidant Research Center (ADORC)

1182, Sowa, Niigata-shi, 950-2144, Japan

Tel: +81 25-263-0550

Fax: +81 25-263-0567

E-mail: eanetdata@adorc.gr.jp

URL: <http://www.eanet.cc>

Contact persons:

Name	Department & E-mail address
Mr. Shinji NAKAYAMA (EANET QA/QC Manager)	Dept. Head, Data Management Department E-mail: nakayama@adorc.gr.jp
Dr. Tatsuya SAKURAI	Researcher, Data Management Department E-mail: sakurai@adorc.gr.jp
Dr. Tsuyoshi OHIZUMI	Dept. Head, Atmospheric Research Department E-mail: ohizumi@adorc.gr.jp

Appendix 1 Participating laboratories

<u>Countries / Laboratories</u>	<u>Code</u>
<u>1. INDONESIA</u>	
1) Environmental Management Center (PUSARPEDAL)	(ID01)
<u>2. JAPAN</u>	
2) Hokkaido Institute of Environmental Sciences	(JP01)
3) Niigata Prefectural Institute of Public Health and Environmental Sciences	(JP02)
4) Nagano Environmental Conservation Research Institute	(JP03)
5) Gifu Prefectural Institute of Health and Environmental Science	(JP04)
6) Toyogiken Co., Ltd.	(JP05)
7) Shimane Prefectural Institute of Public Health and Environmental Science	(JP06)
8) Okinawa Prefectural Institute of Health and Environment	(JP07)
9) Acid Deposition and Oxidant Research Center (ADORC)	(JP08)
<u>3. MALAYSIA</u>	
10) Department of Chemistry	(MY01)
<u>4. MONGOLIA</u>	
11) Central Laboratory of Environmental Monitoring	(MN01)
<u>5. PHILIPPINES</u>	
12) Environmental Management Bureau (EMB)	(PH01)
<u>6. REPUBLIC OF KOREA</u>	
13) National Institute of Environmental Research (NIER)	(KR01)
<u>7. RUSSIA</u>	
14) Limnological Institute, Russian Academy of Sciences/Siberian Branch	(RU01)
<u>8. THAILAND</u>	
15) Pollution Control Department (PCD)	(TH01)
16) King Mongkut's University of Technology Thonburi	(TH02)
17) Chiang Mai University (CMU)	(TH03)
<u>9. VIET NAM</u>	
18) Center for Environmental research, Institute of Meteorology and Hydrology	(VN01)
19) Mid-central Regional Hydro Meteorological Center	(VN02)

Appendix 2 Statistics summary by raw data submitted

Analytical results of Sample No.051 (small amount)

Lab. ID	SO ₄ ²⁻ (µg)	Cl ⁻ (µg)	NH ₄ ⁺ (µg)
ID02	19.5	5.20	4.67
JP01	22.2	2.28	5.08
JP02	24.6	2.63	5.30
JP03	23.5	2.50	5.27
JP04	25.3	2.76	5.05
JP05	17.8	1.28	5.70
JP06	24.5	3.57	5.33
JP07	23.8	2.39	5.08
JP08	22.8	2.51	5.12
KR01	26.5	2.69	4.73
MY01	22.9	2.80	4.89
MN01	25.7	2.00	5.47
PH01	22.1	3.13	3.35
RU01	18.4	-	5.24
TH02	21.9	2.72	7.65
TH03	21.9	2.26	4.88
TH05	23.1	2.89	6.02
VN01	18.4	2.22	5.10
VN02	31.6	4.60	5.43
Prepared value	25.0	2.80	5.30
Number of data	19	18	19
Average	23.0	2.80	5.23
Minimum	17.8	1.28	3.35
Maximum	31.6	5.20	7.65
Standard deviation	3.25	0.91	0.79

Analytical results of Sample No.052 (large amount)

Lab. ID	SO ₄ ²⁻ (μg)	Cl ⁻ (μg)	NH ₄ ⁺ (μg)
ID02	65.5	13.1	19.6
JP01	69.2	28.1	20.1
JP02	70.6	29.4	19.9
JP03	68.2	29.1	20.3
JP04	70.9	31.2	20.0
JP05	69.3	24.5	21.2
JP06	61.6	24.1	19.4
JP07	67.7	29.3	17.7
JP08	67.4	29.2	20.2
KR01	68.2	30.5	17.2
MY01	70.3	30.4	19.6
MN01	72.3	25.1	24.9
PH01	68.8	31.2	21.9
RU01	75.2	-	20.8
TH02	66.6	30.5	24.9
TH03	70.1	29.1	17.6
TH05	77.6	32.0	23.1
VN01	53.4	29.0	20.7
VN02	57.3	25.2	14.7
Prepared value	70.0	30.0	20.0
Number of data	19	18	19
Average	67.9	27.8	20.2
Minimum	53.4	13.1	14.7
Maximum	77.6	32.0	24.9
Standard deviation	5.62	4.40	2.48

Appendix 3 Implementation manual in 2005

Implementation Manual of Quality Assurance/ Quality Control Project for Filter Pack Method under the Acid Deposition Monitoring Network in East Asia (EANET)(2005)

1. Purpose

This inter-laboratory comparison project is conducted to improve the accuracy of dry deposition monitoring among the laboratories in EANET countries. The purpose of this project is (1) to recognize the precision of analytical equipment and the performance of its operator with obtaining information on an accuracy of measurements in each participating laboratory and give an opportunity to improve the quality of the analysis on acid deposition monitoring and (2) to find the merits and demerits of analytical method and improve reliability of analytical data through the assessment of analytical procedures.

2. Method

(1) Participating laboratories

Laboratories in charge of chemical analysis for filter pack method of dry deposition monitoring in the participating countries of EANET.

(2) Activities

Six kinds of sample filters putting into centrifuging tubes (hereafter “samples”) are distributed to the abovementioned laboratories. The information on the analytical precision and accuracy of individual parameters can be obtained through the statistical treatment of submitted analytical results.

(3) Analytical Parameters

All participating laboratories shall measure samples and submit the data on 3 parameters: chloride ion (Cl^-), sulfate ion (SO_4^{2-}) (from the sample filters impregnated by K_2CO_3), ammonium ion (NH_4^+) (from the sample filters impregnated by H_3PO_4) in the extracted solution.

3. Outline of samples

Table1. Outline of sample filters

Name	Kind of samples	Container	Number of samples	Note
No.051-1	Alkali-Impregnated filter (low concentration)	Polyethylene centrifuging tube	3 (a, b, c)	Necessary salts are put on the filter impregnated by K_2CO_3 (F2)
No.051-2	Acid-Impregnated filter (low concentration)	Polyethylene centrifuging tube	3 (a, b, c)	Necessary salts are put on the filter impregnated by H_3PO_4 (F3)
No.052-1	Alkali-Impregnated filter (high concentration)	Polyethylene centrifuging tube	3 (a, b, c)	Necessary salts are put on the filter impregnated by K_2CO_3 (F2)
No.052-2	Acid-Impregnated filter (high concentration)	Polyethylene centrifuging tube	3 (a, b, c)	Necessary salts are put on the filter impregnated by H_3PO_4 (F3)
No.053-1	Alkali-Impregnated filter (blank)	Polyethylene centrifuging tube	3 (a, b, c)	The filter impregnated by K_2CO_3 (F2)
No.053-2	Acid-Impregnated filter (blank)	Polyethylene centrifuging tube	3 (a, b, c)	The filter impregnated by H_3PO_4 (F3)

4. Analysis

(1) Outline of analytical procedure

Pour directly extracting solvent into centrifuging tube and then carry out the extract operation. Don't take filter out from centrifuging tube throughout this procedure. Analysis has to be conducted within 3 months after distribution of samples.

See reference "Technical Document for Filter Pack Method in EAST Asia" (NC, 2003) about detail of operation.

(2) Extraction procedure

- a) **In the case of Sample No.051-1, No.052-1, No.053-1**, pour exactly 20 mL H_2O_2 solution (0.05%-v/v) into the centrifuging tube, then shake the sample tubes during 20 minutes for extractions using shaker or ultrasonic bath.
- b) **In the case of Sample No.051-2, No.052-2, No.053-2**, pour exactly 20 mL **deionized water** into the centrifuging tube, then shake the sample tubes during 20 minutes for the extractions using shaker or ultrasonic bath.
- c) Filter the insoluble matters out of the extracted solutions using a membrane filter (pore size $0.45\mu\text{m}$) previously well washed by purified water (more than 100 mL).

Note 1) Seal the sample tubes and keep them in the refrigerator.

Note 2) Carry out the analysis as soon as possible after extraction.

(3) Analytical method

Use the same analytical methods and data checking procedures for this inter-laboratory comparison project as described in the “Technical Manual for Wet Deposition Monitoring in East Asia, March 2000” adopted at The Second Interim Scientific Advisory Group Meeting of EANET (hereafter the “Technical manual”) and “Quality Assurance and Quality Control (QA/QC) Program for Wet Deposition Monitoring in East Asia March 2000” adopted at The Second Interim Scientific Advisory Group Meeting of EANET (hereafter the “QA/QC program”). Analytical methods described in the Technical manual and the QA/QC program are introduced in table 2.

Table2. Analytical methods suggested by Technical Documents

Parameter	Analytical method
SO_4^{2-} Cl^-	Ion Chromatography (preferably with suppressor)
NH_4^+	Ion Chromatography or Spectrophotometry (Indophenol blue)

(4) Submission of the result

It is requested that results are reported as **the net values of absolute amount** in samples. Absolute amount in samples is determined as follows:

$$M_{\text{sol}} = C_{\text{sol}} \times V_{\text{sol}} \quad (1)$$

M_{sol} : absolute amount of each component in the extracting solution (μg)

C_{sol} : concentration of each component in the extracting solution (mg/L)

V_{sol} : volume of the extracting solution (mL)

The net values of absolute amount should be calculated by:

$$\text{net } M_{\text{sol}} = M_{\text{sol, Sample}} - M_{\text{sol, Blank}} \quad (2)$$

$M_{\text{sol, Sample}}$: absolute amount of each component in the extracting solution from the sample filter(No.051-1, No.051-2, No.052-1, No.052-2) (μg)

$M_{\text{sol, Blank}}$: average absolute amount in the extracting solutions from the blank filters(No.053-1, No.053-2) (μg).

5. Calibration

For the analysis of anion and cation, a calibration curve will be derived from at least 5 working standard solutions (Std0, Std1, Std2, Std3, Std4) including the solution which concentration of each ion is “0” (Std0). And the determination of ions has to be proceeded between Std0 and Std4.

6. Preparation of the report

Complete the attached reporting format [1] to [5], with considering the following issues.

[Report format [1]]

1. Fill the name of the organization and the person which have conducted the analysis of the sample, in the column of “Organization/ analyst”. In the case that several persons carried out the analysis, fill in the name of the every person.
2. Fill the absolute amount of parameter in extracting solution (M_{sol}) as three significant digits after rounding the forth digits number of the data in the correspondent column of “Data”.
3. Calculate the average value as arithmetic mean value and fill the mean value as three significant digits after rounding the forth digits number of the data in the column of “Mean” of Table 1.
4. Calculate the net values of absolute amount using the equation (2) and fill them in the column of “ $M_{\text{sol, Sample}}$ ” of table 2
5. Calculate the average value as arithmetic mean value and fill the average value as three significant digits after rounding the forth digits number of the data in the column of “Mean” of Table 2.
6. Fill the standard deviation of the results calculated by following equation with three significant digits in the column of “Standard Deviation” of Table 2.

$$\text{Standard Deviation} = \left[\sum_{i=1}^3 (X_i - X)^2 / (3-1) \right]^{1/2}$$

X_i : Individual datum, X : Average ($X = \sum X_i / 3$), 3 means the number of measurements.

Note: Procedures from “3” to “6” are conducted automatically by Excel calculation.

[Report format [2]]

7. Fill the name of the organization and the person who have conducted the analysis of the sample, in the column of "Organization/ analyst". In the case that several persons carried out the analysis, fill in the name of the every person.
8. Fill the concentrations of ions in the standard solutions in the correspondent column of "Standard Solution".

[Report format [3]-[5]]

9. Fill the name of the organization which have practically analyzed the sample, in the column of "Person in charge of measurement/calculation". In the case that several persons carried out the analysis, fill in the name of the every person.
10. Fill the years of experience on chemical analysis as the business of the person, in the column of "Years of experience for chemical analysis".
11. Fill the period of experience on acid deposition analysis as the business of the person, in the column of "Years of experience for chemical analysis of acid deposition".
12. Fill the date of extraction of sample in the column of "Start date of analysis", and fill the date of finishing sample analysis of individual parameter in the column of "Finish date of analysis".
13. Complete other position in Report format [3]-[5].

8. Submission of the report

Submission materials are as follows.

(i) Summary of results (Report [1])

by both Electronic file in the disk and Printing

(ii) Concentration of standard solution(SO_4^{2-} , Cl^- , NH_4^+) (Report [2])

by both Electronic file in the disk and Printing

(iii) Reports of items (SO_4^{2-} , Cl^- , NH_4^+) (Report [3] – [5])

by both Electronic file in the disk and Printing

(iv) The copies of the set of calibration curves (SO_4^{2-} , Cl^- , NH_4^+)

by Printings

(v) The copy of the analysis chart for Std1 (SO_4^{2-} , Cl^- , NH_4^+)

by Printings

(vi) One copy of analysis charts of the Sample No.052-1 and No.052-2 (SO_4^{2-} , Cl^- , NH_4^+) by Printings

9. Deadline of the report submission

February 28, 2006 (It should be submitted to **NC through the national QA/QC manager**)