

**Quality Assurance/Quality Control (QA/QC)
Program
for
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**

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The QA/QC programs were developed and adopted at the First Interim Scientific Advisory Group (ISAG) Meeting in October 1998, mainly based on the Monitoring Guidelines and Technical Manuals for Acid Deposition Monitoring in East Asia, adopted at the Expert Meetings (1993-1997). It included some modifications, taking into account the progress after the Technical Manuals had been adopted.

Considering the latest scientific and technical information and experiences accumulated during the preparatory-phase activities of the Acid Deposition Monitoring Network in east Asia (EANET), the Monitoring Guidelines and Technical Manuals for Wet Deposition Monitoring, Soil and Vegetation Monitoring, and Monitoring for Inland Aquatic Environment were revised at the Second ISAG Meeting in Jakarta in March 2000. Accordingly, the QA/QC programs as well as the Data Reporting Procedures and Formats were also revised at the same time to maintain consistency with these technical documents.

The participating countries of EANET are expected to make efforts for implementing their QA/QC activities in accordance with these QA/QC programs, taking into account the situation in respective countries. Based on the experiences of the participating countries as well as the progress in scientific and technical information, these QA/QC programs will be reviewed and revised where necessary.

1. Objectives

1.1. Objectives of QA/QC programs

Considering the significance of possible future problems regarding acid deposition, it becomes increasingly important to obtain accurate and precise data on acid deposition. With this recognition, many countries of the world have already initiated their acid deposition monitoring programs. However, informed decisions cannot be made on the basis of unreliable data, and therefore certain levels of data quality should be assured. A monitoring system without adequate QA/QC runs the risk of not being able to control the quality of data, and not being able to assure accuracy and precision. QA/QC has thus become essential part of all measurement systems in general, and acid deposition monitoring in particular, because it requires especially high international comparability of data.

For uses of acid deposition data in recent years, such as assessment of spatial distributions and temporal trends, research on acid deposition related processes and impacts on aquatic and terrestrial ecosystems, and the development and evaluation of long-range transport and transmission models, it is especially important that measured data satisfy specified levels of reliability with necessary information on measurement methods.

The objectives of this QA/QC program are to obtain reliable data that can be comparable among the countries of the East Asian region, as well as with other networks by ensuring data accuracy, precision, representativeness and completeness in acid deposition monitoring.

1.2. Definitions

Quality control is defined as "the routine use of procedures designed to achieve and maintain a specified level of quality for a measurement system". Quality Assurance is

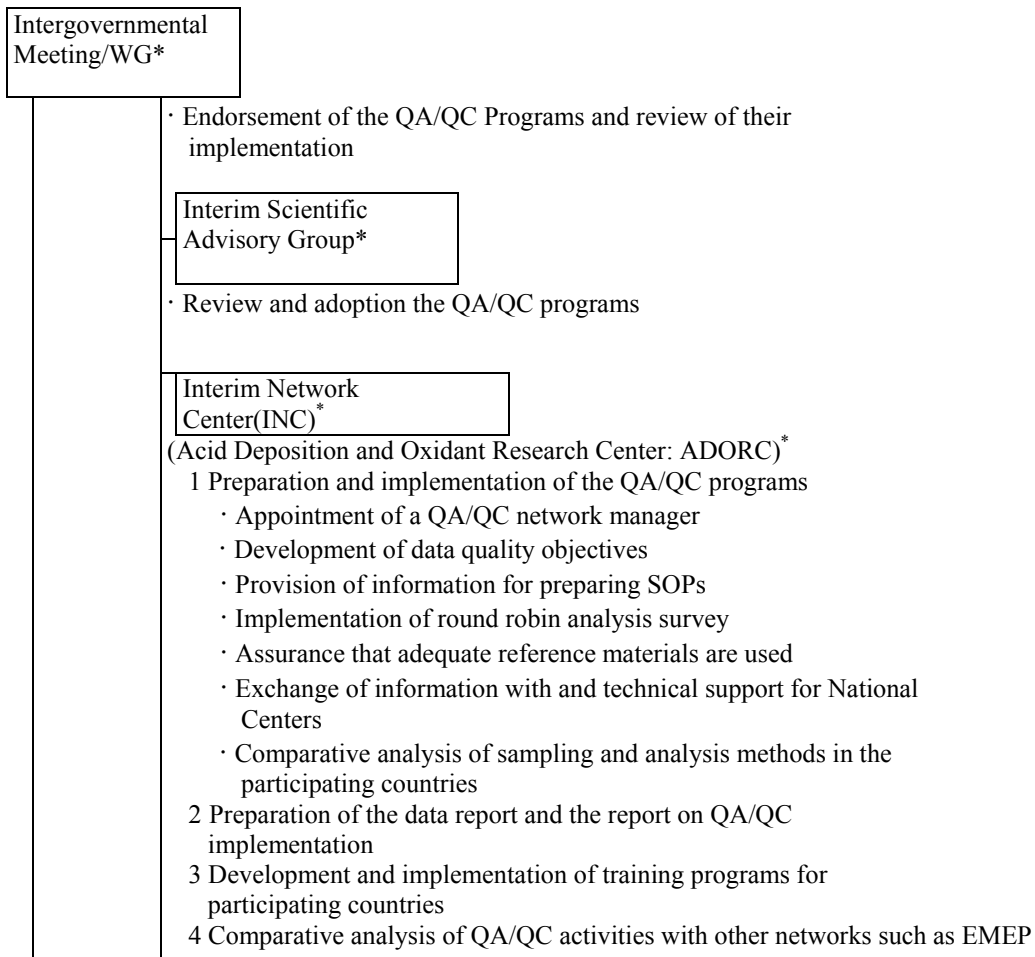
defined as "a set of coordinated actions such as plans, specifications, and policies used to assure that a measurement program can be quantifiable and produce data of known quality".

According to the United States Environmental Protection Agency, the difference between quality control and quality assurance is the following: quality control is a "system of activities to provide a quality product" and quality assurance is a "system of activities to provide assurance that the quality control system is performing adequately. In other words, quality assurance is quality control for quality control".

To assure specific data quality, QC activities should be implemented for all the steps of the measurement activities, from sample collection to data reporting. The QA/QC programs should include QA/QC activities for all the components of the measurement/analysis systems, i.e. the field (sampling sites), laboratory, data management and data reporting processes. All QA/QC activities should be documented.

2. Roles of relevant entities

The roles of relevant entities of QA/QC activities during the preparatory phase are shown in Figure 1.



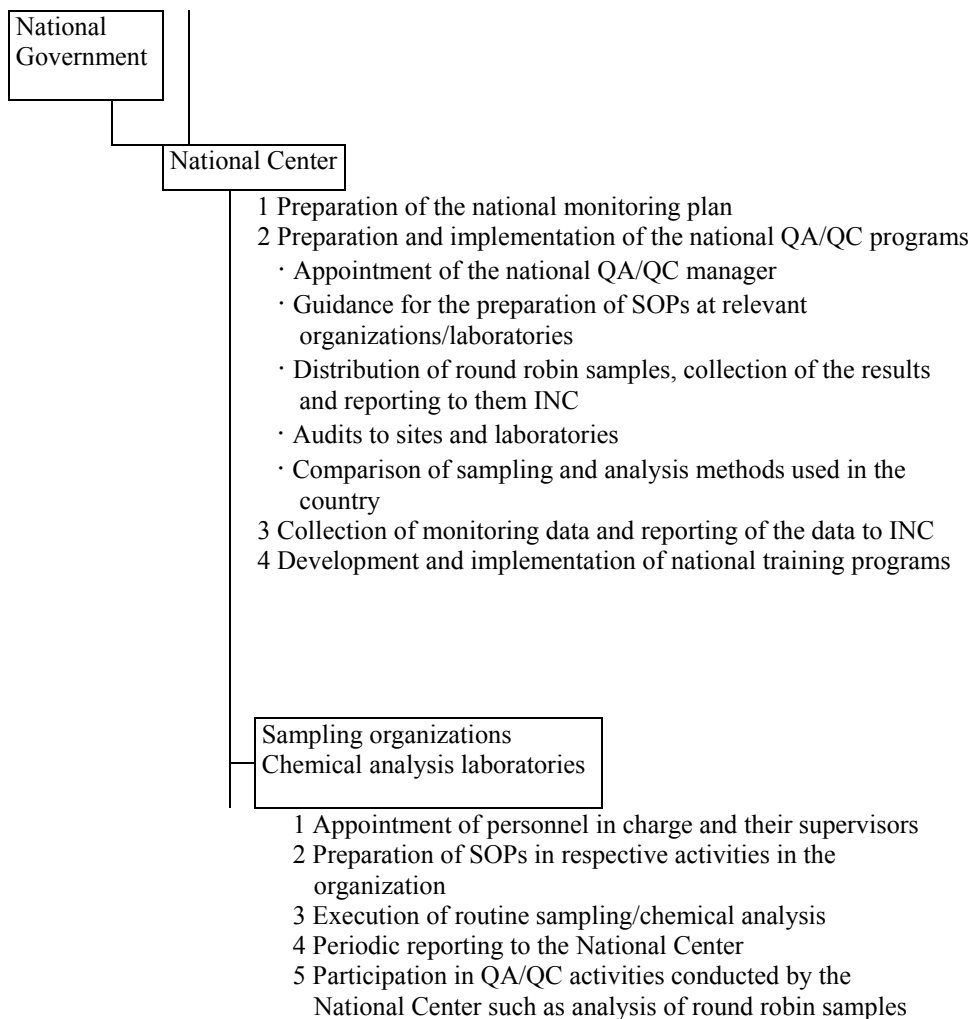


Figure 1 Roles of Relevant Entities

Note (*): The name and organization will be changed as appropriate after the formal establishment of EANET.

3. Fundamental matters regarding the QA/QC programs

These QA/QC programs cover all QA/QC activities, including the activities of INC, the National Centers and the sampling/chemical analysis organizations. The National Centers and the sampling/chemical analysis organizations need to execute various QA/QC activities, including development of national QA/QC programs and SOPs, according to the above mentioned roles (2.). In these processes, the following fundamental matters should be taken into account.

3.1. Development of national QA/QC programs

Each participating country should develop and revise as appropriate, its own QA/QC programs, taking into consideration national conditions. The items to be covered in the national QA/QC program are listed in Appendix 1.

3.2. Clear assignment of responsibility

In the National Center, the national QA/QC manager should be appointed. In the sampling and/or chemical analysis organizations, personnel in charge of data management and reporting and their supervisors should be appointed; their names should be reported to the National Center.

3.3. Standard operating procedures (SOPs)

SOPs are the procedures used in all the processes of the monitoring system, i.e. in the field, laboratory, and data management areas. SOPs provide a method to ensure that all personnel follow the same procedures to avoid variance of data quality between personnel in charge, and that they conduct their works with good understanding of QA/QC. Each sampling and chemical analysis organization (laboratory) should make effort to prepare SOPs that meet the actual conditions of respective organizations, taking account of the Technical Manuals and the national QA/QC programs. In preparing SOPs, it is important that they are sufficiently specific and easy to understand, and that they should be reviewed and updated on the basis of latest information and circumstances. Appendix 2 presents major items that should be included in SOPs for wet deposition monitoring.

3.4. Data quality objectives(DQOs)

The required data quality objective(DQO) values can be different, depending on the objectives of programs. The DQO values define the desirable levels of accuracy, precision and completeness required by the program.

The required DQO values in EANET for wet deposition monitoring are defined in Table 1. QA/QC activities mentioned in chapters 4 through 10 are needed to achieve such DQO values. The participating countries are expected to make efforts to meet these DQOs.

Table 1 Data quality objective values in wet deposition monitoring**a) Required accuracy, precision, precipitation and completeness (unit:%)**

Accuracy ¹⁾	Precision ²⁾	Precipitation ³⁾	Completeness ⁴⁾
±15%	15%	>90%	>80%

1) Accuracy (A) is calculated by the following formula:

$$A = [(certified\ values) - (analytical\ values)] * 100 / (certified\ values)$$

2) Precision (S_i) is calculated by the following formula:

$$S_i = (\sum d_i^2 / 2N_i)^{1/2} * 100 / A_v$$

where d_i and A_v denote, the difference between the duplicate analyses and mean, respectively (see Appendix 3 2.3), and N_i is the number of sample pairs in the reporting period.

3) Precipitation (P) is calculated by the following formula, monthly or seasonally to the extent possible, and at least annually:

$$P = (\text{amount of precipitation measured by the collector}) * 100 / (\text{amount of precipitation measured by standard raingage})$$

4) The percentage of the total amount of the precipitation that is associated with valid samples during each given period (%TP). Please refer to Section 7.4 for details.

b) Detection limits and determination limits

(both determined as specified in Appendix 3; unit $\mu\text{mol/L}$)

Items	Detection limits	Determination limits
SO_4^{2-}	0.3	1.0
NO_3^-	0.5	1.5
Cl^-	0.5	1.5
NH_4^+	0.8	3.0
Na^+	0.3	1.0
K^+	0.3	1.0
Ca^{2+}	0.2	0.6
Mg^{2+}	0.3	1.0
pH	Replicate measurement of RM should agree to within ± 0.05 pH value of RM.	
EC	Replicate measurement of deionized water (EC: less than 0.15 mS/m) should agree to within ± 0.02 mS/m	

RM: Reference material prepared as a laboratory working standard for acid rain analysis.

4. Sampling sites

4.1. Sampling sites

More than one site should be selected that is clearly defined as either urban, rural or remote. Rural or remote sites are recommended. It is desirable to monitor major air pollutants and ion concentrations of aerosols at the site in parallel with wet deposition measurements.

4.2. Classification of sampling sites

EANET monitoring sites are classified into two basic categories, namely deposition monitoring sites and ecological survey sites. Deposition monitoring sites are sampling sites to collect fundamental data on the temporal and spatial distribution of acid deposition, and are further classified into three sub-categories: remote sites, rural sites, and urban sites for the objectives of the monitoring. Ecological survey sites are those to provide basic data for assessing the effects of acidification on terrestrial ecosystems, and further

classified into two sub-categories: basic survey sites, and ecosystem analysis sites. All sites in each country should be classified according to these categories. Regarding the deposition monitoring sites, at least one or more remote or rural sites should be established in a country participating in the EANET activities. The detailed explanation of these categories are described in chapter 2.2 of the Monitoring Guidelines.

4. 3. Site selection for rural and remote sites

Selection of sampling sites is a critical factor in the monitoring of wet deposition. Therefore, sampling sites should be located in areas suitable for the purpose of the Network, and should properly represent the area in question. Site selection criteria specifically applied for wet deposition monitoring sites are described in Chapter 2.1 of the Technical Manual for Wet Deposition Monitoring.

4.4. Documentation of conditions around sampling sites

All monitoring sites should essentially satisfy the siting criteria. If there are some differences from the criteria, they should be documented and evaluated. Any significant change around sampling sites should be promptly reported to INC through the National Center.

4. 5. Site performance audit

A site performance audit for a precipitation monitoring network should be made at least once a year by the National Center. This audit provides field training and exchange of information. A site performance audit should also include items such as operation checks of samplers, sample handling and data reporting and so on. The National Center should prepare the SOP for site audits. The results of each audit should be documented and stored at the National Center.

5. Collection and handling of samples

5. 1. Collector

The amount of wet deposition can not be measured directly, but can be calculated by multiplying the concentrations of chemical species in precipitation by the amount of precipitation. The concentrations of wet-only samples should be measured; the most appropriate collector for this purpose is a wet-only sampler.

The persons in charge of collecting samples will report the manufacturer, model name, manufacture date and other necessary information of the sampler and standard rain gauge to the National Center and INC through each organization in charge of collecting samples.

Each organization in charge of collecting samples must keep instrument manuals available. The persons in charge should take them when they go to the sampling sites.

5.2. Monitoring frequency

The sampling frequency is the length of time that a sample collection vessel is connected with a collector. For deposition monitoring sites, that is for an urban, rural or remote site,

wet deposition samples should be collected every 24 hours (daily) or every precipitation event. If a collection bucket is used, it should be changed every day, whether precipitation occurred or not. Daily sampling is more recommended than event sampling since site operators often have difficulty determining the start and end time of precipitation events, and since operators are seldom available to collect samples at times of the day and night. However, when samples are collected by event bases considering the relationship with meteorological conditions, the definition of event, that is the interval of two precipitation events, should clearly be decided and reported to network center. The start and end time of events should also be reported with the data.

Where analysis of daily samples is not practical, combining daily samples for a weekly (7 days) composite or sampling for an week can be acceptable only when the integrity of sample composition can be maintained, for instance, by refrigerating and/or adding biocide to samples.

5. 3. Registration of the person in charge of collecting samples and their supervisors

Each organization in charge of collecting samples will appoint a person in charge of collecting samples and their supervisors. The persons who collect samples should be well trained. The persons who collects samples at each site and their supervisors should be registered to the National Center. The name of the person who collects each sample should be recorded in the on-site record table.

5. 4. Operational check

The instruments used for sampling are a rain gauge, precipitation collector and rainfall sensor. The following points should be checked and recorded before sampling.

- a) The conductivity of deionized water used in cleaning is less than 0.15mS m^{-1} ($1.5\mu\text{S cm}^{-1}$).
- b) Operation of precipitation auto collector should be checked on the following item:
 - Proper rainfall sensor response and operation of opening lid is checked.
 - Proper rainfall sensor heating ;
 - Mechanical operation of the collector; and
 - The cleanliness of collecting funnel and collecting vessels.

A field blank test should be undertaken monthly to obtain the information whether there is contamination on the collector, leading tubes and/or sampling bottles or not. After the sample is collected from the sampler, the funnel should be cleaned by using such as wet Kim Wipe. Then, 100 ml deionized water should be added to the collector and collected in the same manner as the usual sample collection, and sent to the analytical laboratory for the determination of all the monitored chemical species. The remaining deionized water should also be sent to the laboratory for analysis. If the concentration of the chemical species in the field blank is obviously higher than the usual field blank values and/or those measured immediately after exchange of tubes, the funnel should be cleaned and/or tubes should be replaced.

- c) Check of standard rain gauge operation

Standard rain gauge maintenance and inspection should be undertaken, based on the regulations established in each country, including heater on/off (in the case that both snow and rain are measured), removal of dust and garbage, and balance calibration.

5. 5. Handling and transportation of samples

Samples should be handled with disposable plastic gloves. Transportation of samples from sampling sites to chemical analysis laboratories must be done in cooler boxes filled in freezer packs or by cool delivery service. However, when biocide is used for sample preservation, the cooling of samples is not required.

5. 6. On-site inspection

Together with on-site audit, operation of sampling instruments, the cleanliness of sampling instruments and vessels, on-site sample handling and data documentation should be inspected by the National Center. The National Center should prepare SOPs for on-site inspection. The inspection results should be recorded and stored.

5. 7. Parallel measurement

In order to evaluate analytical precision and collection precision of sampling instruments in the whole Network, it would be informative to deploy more than 2 sets of instruments at the same site for parallel measurement. Using these results, it would be possible to determine the precision of samplers used in each country.

Since it is difficult to collect the samples for parallel measurement at typical sites, this test may be undertaken systematically by INC and/or National Centers.

5. 8. Meteorological Measurement

Wind direction/speed, temperature, humidity, precipitation amount and solar radiation in relation to wet deposition should be measured at the nearest meteorological station in accordance with the measurement frequencies and methods of the meteorological monitoring system of each country. The height of precipitation amount measurement is recommended to be from 1.0 to 1.5 m above the ground surface, same as that for the precipitation chemistry collector and the precipitation sensor.

6. Measurement and analysis

6. 1. Measurement parameters

pH, electric conductivity (EC) and concentrations of ionic species (SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) should be measured as required parameters.

In the case when failure to attain ion balance by measuring the major ions is recognized to be systematic, some additional ions relevant to the ion balance, such as fluoride, bicarbonate, nitrite and organic acids, are recommended to be identified and measured, as appropriate, although such measurements are not mandatory.

Heavy metals, phosphate, aluminum and organic compounds may be measured for the characterization of precipitation.

6.2. Fundamental measurement and analysis matters

Freedom from contamination of the apparatus, materials and reagents used for measurement and analysis must be confirmed beforehand; blank values of target substances should be as low as possible. Measurement and analysis should be conducted by persons who are well trained. To maintain high analytical quality, SOPs must be prepared for the management of apparatus, materials and reagents.

6.3. Laboratory audit

Laboratory audits should be carried out together with sampling site audits or separately by the National Center with similar frequencies. The laboratory audit consists of inspection and advice on sample handling, capacities of instruments, preparation and implementation of SOPs, and other QA/QC activities and their records. The audit results should be recorded and stored.

Other details on measurement and analysis of samples are mentioned in Appendix 3.

7. Data control

7.1. Introduction

There are three purposes concerning quality assurance of data control.

- 1) Assure that all sample data will be stored in databases in an adequate manner.
- 2) Mark with flags the data whose accuracy and representation are doubted.
- 3) Recognize and describe samples that were measured without standard methods, i.e. with contamination, instrument trouble, bulk sampling, etc.

Quality assurance and quality control in data control should be carried out in analysis organizations, National Centers, and the Interim Network Center, individually.

7.2. Data check in analysis organizations

7.2.1. Treatment of abnormal and unrecorded data

When the sensitivity of instruments is not stable, when the results of duplicate analyses or re-measurements are significantly different, or when the ratio of a theoretical value to that for determined data in ion balances and electrical conductivity is significantly different from 1, measurement should be repeated since reliability is low. When samples seem to be obviously contaminated, these data should be treated as unrecorded data.

These problems will waste much labor, time, and expense. In addition, abnormal or unrecorded data can corrupt research results. So, careful checks are needed to avoid data of inadequate quality. When abnormal or unrecorded data appear, the process should be carefully reviewed to prevent the occurrence of the same problem in the future.

7.2.2. Judgment of valid data

All measured data should be checked for ion balance by calculating R_1 and R_2 values. If necessary, re-measurement should be carried out and the adequacy of data should be checked. If the concentration or standard deviation of concentration of an ion differs greatly from the long term average concentrations or standard deviations of concentrations, respectively, during a given period, then this is cause for concern and should be carefully considered.

a) Calculation of ion balance (R_1)

- (1) Total anion (A) equivalent concentration ($\mu\text{eq/L}$) is calculated by summing the concentrations of all anions (C: $\mu\text{mol/L}$).

$$A (\mu\text{eq/L}) = \sum n C_{Ai} (\mu\text{mol L}^{-1}) = 2C (\text{SO}_4^{2-}) + C (\text{NO}_3^-) + C (\text{Cl}^-)$$

n, C_{Ai} : electric charge of ion and concentration ($\mu\text{mol/L}$) in anion 'i'.

- (2) Total cation (C) equivalent concentration ($\mu\text{eq/L}$) is calculated by summing the concentrations of all cations (C: $\mu\text{mol/L}$).

$$C (\mu\text{eq/L}) = \sum n C_{Ci} (\mu\text{mol/L}) = 10^{(6-\text{pH})} + C (\text{NH}_4^+) + C (\text{Na}^+) + C (\text{K}^+) + 2C (\text{Ca}^{2+}) + 2C (\text{Mg}^{2+})$$

n, C_{Ci} : electric charge of ion and concentration ($\mu\text{mol/L}$) in cation 'i'.

- (3) Calculation of ion balance (R_1)

$$R_1 = 100 \times (C-A) / (C+A) \quad (\%)$$

- (4) R_1 , which is calculated using the above equation, should be compared with standard values in Table 2. Re-measurement, check with standard samples, or inspection of standard curves are necessary, or the flags which indicate unsatisfied data should be marked in the database, when R_1 is not in the range.

When pH is greater than 6 and R_1 is significantly greater than zero, bicarbonate (HCO_3^-) concentration should be evaluated to compute R_1 and R_2 again to include bicarbonate contribution. When formic acid, acetic acid, or both are measured, formate and acetate ions should be considered in the evaluation of R_1 and R_2 . The concentrations ($\mu\text{eq/L}$) of these weak acids will be calculated from the dissociation constant, K_a and pH as follows:

$$[\text{HCO}_3^-] = \text{PCO}_2 \text{H}_2\text{CO}_3 \text{Ka}_1 / [\text{H}^+] = (360 \times 10^{-6})(3.4 \times 10^{-2}) 10^{(\text{pH}-6.35)} + 6$$

$$= 1.24 \times 10^{(\text{pH}-5.35)}$$

$$[\text{HCOO}^-] = [\text{HCOOH}] \text{Ka} / [\text{H}^+] = [\text{HCOOH}] \times 10^{(\text{pH}-\text{pKa})} = [\text{HCOOH}] \times 10^{(\text{pH}-3.55)}$$

$$[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}] \text{Ka} / [\text{H}^+] = [\text{CH}_3\text{COOH}] \times 10^{\text{pH}-\text{pKa}}$$

$$= [\text{CH}_3\text{COOH}] \times 10^{(\text{pH}-4.56)}$$

Atmospheric concentration of CO_2 in equilibrium with precipitation samples is assumed to be 360 ppm. Dissociation constants in terms of pKa for carbonic, formic, and acetic acids are 6.35, 3.55, and 4.56, respectively. In some sites, fluoride (F^-) and/or nitrite (NO_2^-) may contribute to a significant fraction of the major anions, which subsequently requires

calculations of R_1 and R_2 that include these anions.

Table 2 Allowable ranges for R_1 in different concentrations

(C + A) ($\mu\text{eq/L}$)	R_1 (%)
<50	± 30
50-100	± 15
>100	± 8

The flags should be marked as follows.

- 999 Missing measurement, reason not specified.
- 899 Measurement not defined, reason not specified.
- 783 Low precipitation, concentration unknown.
- 782 Low precipitation, value is obtained from diluted sample
(EANET original flags)
- 781 Below detection limit.
- 701 Less accurate than usual, reason not specified .
- 699 Mechanical problem, reason not specified.
- 599 Contamination not specified.

(Reference) Technical Manual for Monitoring Wet Deposition (for EANET)

Table 3 Basic constants

Ion	Molecular Weight (M)	Molar Conductivity (λ), $\text{S cm}^2/\text{mol}$
H^+	1.008	349.7
NH_4^+	18.04	73.5
Ca^{2+}	40.08	59.8×2
K^+	39.10	73.5
Mg^{2+}	24.31	53.3×2
Na^+	22.99	50.1
NO_3^-	62.01	71.5
SO_4^{2-}	96.06	80.0×2
Cl^-	35.45	76.3
HCO_3^-	61.02	44.5
HCOO^-	45.0	54.6
CH_3COO^-	59.1	40.9
F^-	19.00	55.5
Br^-	79.90	78.2
NO_2^-	46.01	71.8
PO_4^{3-}	94.97	69.0×3

Kagaku Binran, p. II-460-461. 3rd Ed., 1984, Maruzen, Tokyo.

b) Comparison between calculations and measurement in electrical conductivity (R_2)

(1) Total electric conductivity (Λ_{calc}) should be calculated as follows;

$$\Lambda_{calc} \text{ (mS/m)} = \{349.7 \times 10^{(6-pH)} + 80.0 \times 2C(\text{SO}_4^{2-}) + 71.5 C(\text{NO}_3^-) + 76.3 C(\text{Cl}^-) + 73.5 C(\text{NH}_4^+) + 50.1 C(\text{Na}^+) + 73.5 C(\text{K}^+) + 59.8 \times 2C(\text{Ca}^{2+}) + 53.3 \times 2C(\text{Mg}^{2+})\} / 10000$$

C: Molar concentration ($\mu\text{mol/L}$) of ions in the parenthesis, each constant value is molar conductivity at 25°C (see Table 3).

(2) Ratio (R_2) of calculations to measurements (Λ_{meas}) in electric conductivity should be calculated as follows;

$$R_2 = 100 \times (\Lambda_{calc} - \Lambda_{meas}) / (\Lambda_{calc} + \Lambda_{meas}) \quad (\%)$$

(3) R_2 , which is calculated using the above equation, should be compared with standard values in Table 4. Re-measurement, check with standard samples, or inspection of standard curves are necessary, or the flag which indicates unsatisfactory data should be marked in the database, when R_2 is not in the range.

Table 4 Allowable ranges for R_2 in different concentration

Λ_{meas} (mS/m)	R_2 (%)
<0.5	± 20
0.5 - 3	± 13
>3	± 9

(1 mS/m = 10 $\mu\text{S/cm}$)

The flags should be marked as follows.

999	Missing measurement, reason not specified.
899	Measurement not defined, reason not specified.
783	Low precipitation, concentration unknown.
782	Low precipitation, value is obtained from diluted sample (EANET original flags)
781	Below detection limit.
701	Less accurate than usual, reason not specified .
699	Mechanical problem, reason not specified.
599	Contamination not specified.
477	Inconsistency between measured and estimated conductivity.

When the concentration of ion is shown as (mg/L), it should be changed to equivalent concentration ($\mu\text{eq/L}$) as follows:

$$\mu\text{eq/L} = \text{mg/L} \times (1000 / \text{equivalent weight})$$

thus the total of anions and cations are shown as follows:

$$A(\mu\text{eq/L}) = \{C(\text{SO}_4^{2-})/48.03 + C(\text{NO}_3^-)/62.01 + C(\text{Cl}^-)/35.5\} \times 1000$$

$$C(\mu\text{eq/L}) = 10^{(6-pH)} + \{C(\text{NH}_4^+)/18.04 + C(\text{Na}^+)/22.99 + C(\text{K}^+)/39.10 + C(\text{Ca}^{2+})/20.04 + C(\text{Mg}^{2+})/12.16\} \times 1000$$

7.3. Evaluation of sampling sites

Although the above 10 items are analyzed for a precipitation sample at a site, it is necessary to assess whether or not these data meet the objectives of measurement. The evaluation criteria include regional representativeness of the site, judgment of valid samples and completeness of measurement. Evaluation of sampling sites should be carried out for each season and each year. Evaluation of site representativeness should be carried out by the National Center.

7.4. Evaluation of data completeness in measurement period

Completeness of data is defined as the proportion of valid data in a given monitoring period. Completeness of data of precipitation samples can be evaluated by four audit methods as follows. In this QA/QC program, %TP (the percentage of valid samples among the total precipitation in a given period (i.e. quantity of precipitation having available analysis)) should be used.

- (1) % Precipitation Coverage Length (%PCL): the percentage of measurement periods in a period.
- (2) % Total Precipitation (%TP): the percentage of valid sample amount out of the total precipitation in a given period.
- (3) % Valid Sample Length (%VSL): the percentage of period holding valid sample in a given period.
- (4) % Valid Sample with Measured Precipitation (%VSMP): the percentage of precipitation samples having valid analyses.

The target of data completeness is different whether the objective period is a year or a season. In this QA/QC program, >80% is adopted as the target value, with reference to WMO Regional Station level in the whole year.

8. Data reporting

Each organization responsible for field sampling and each analytical laboratory should record, control and store the following information.

8.1. Information on sites

Effort should be made to obtain the following information.

- (1) Sampling sites (location, site classification, measurement items, etc.)
- (2) A situation around the site at the on-site scale (buildings, trees, parking lots, roads, circumstance and land use around the sampling site, etc.)
- (3) A situation around the site on local scale (major roads, traffic, aviation, navigation, farming, major stationary emission sources, surrounding cities, population, etc.)
- (4) A situation around the site on regional scale (large stationary emission sources, main roads, cities, population, etc.)

8.2. Matters related to collection of samples

- (1) Sample collection instruments (pictures of instrument and design diagrams, model, name, manufacturer, manufactured date, etc.)
- (2) Conditions of each sample collection (detailed information about sampling site, sampling date, temperature, wind direction, wind speed, etc.)
- (3) Records of the on-site measurements (field blank data, sample volume, standard gauge precipitation depth reading, etc.)
- (4) Sample type (snow, rain, freezing rain, etc.) and contamination (noticeable suspended particulates, bird droppings, insects)
- (5) Sample history (shipping frequency, packing procedures, etc.)

8.3. Matters related to analytical procedures

- (1) Calibration and measurement procedures for analytical instruments
- (2) Miscellaneous other values required to obtain measurements

8.4. Local quality control activities

Each organization responsible for the field sampling and each analytical laboratory will record the following information and will store them with the data:

- (1) Performance of all procedures prescribed in SOPs
- (2) Routine instrument check and maintenance, record of instrument adjustment (calibration of instruments)
- (3) Names of producers and traceability of standard materials etc., institution of measurement conditions of analytical instruments and its results
- (4) Results of analysis of lowest detection limits and lowest determination limits
- (5) Sensitive variability of analytical instruments
- (6) Duplicate analysis and repeat analysis
- (7) Evaluation of cation and anion balance and conductivity difference
- (8) Evaluation of precipitation data (representativeness, validation of precipitation samples, completeness)
- (9) Results of site performance audit / inspection

9. QA/QC implemented by the (Interim) Network Center

9.1. Management of overall network QA/QC activities and preparation of reports on the network QA/QC activities

INC should appoint a network manager, who is responsible for managing overall network QA/QC programs and will provide appropriate guidance and advice to the participating countries based on this QA/QC program. INC should prepare reports on the results of round robin analysis, duplicate analysis and parallel analysis, comparison of sampling, and analytical methods etc. and QA/QC levels with other relevant networks.

9.2. Technical support for National Centers

INC should provide technical support, as appropriate, to each National Center in order to attain such objectives as follows:

- (1) INC should review QA/QC activities carried out by each National Center to ensure that the measurements are carried out and reported with the expected precision and

- accuracy and that all measurements activities are accurately documented and stored.
- (2) INC should, where appropriate, recommend changes that would improve the accuracy, precision, and completeness of the measurements.
 - (3) INC should provide useful information in order that the organizations responsible for the field sampling and analytical laboratories in each country can prepare SOPs.

9.3 Round robin analysis

To review the accuracy of chemical analysis, INC should send to all chemical analysis laboratories artificial precipitation inter-calibration samples once a year through each National Center, evaluate statistically the results of the analysis of the samples, and prepare reports about the results.

The results of these intercalibrations should be used to study and find solutions to existing laboratory problems and improve the quality of laboratory analyses.

9.4. Comparative analysis of sampling methods and chemical analysis methods

INC should compare the precision and accuracy of the field sampling and laboratory measurements, based on parallel precipitation measurements and duplicate sample analysis and grasp the overall precision and accuracy of wet deposition monitoring of the network.

9.5. Comparative analysis of the precision and accuracy between this Network and other networks

Based on items 9.3 and 9.4 above, INC should assess and compare the measurement methodology and quality assurance data of this Network with other relevant international and domestic networks, and submit reports to the Interim Scientific Advisory Group.

9.6. Assurance that adequate reference materials are used

INC should assure the adequacy of reference materials to be used by the laboratories of the network.

10. Training programs

It is necessary to improve knowledge and expertise related to wet deposition monitoring. Therefore, INC and the others should carry out technical training for personnel responsible for the implementation of the monitoring activities in each National Center and for leading technicians in national or local governments in East Asian countries.

10. 1. Training on Monitoring Guidelines etc.

Based on the results of the 2nd Meeting of the Interim Scientific Advisory Group and the 4th Meeting of the Working Group held in March 2000, training for personnel responsible for implementation of the monitoring activities in each National Center should be carried out to disseminate the details of the Monitoring Guidelines and Technical Manuals, revised QA/QC programs, and Data Reporting Procedures and Formats adopted by these meetings.

10. 2. Technical training on monitoring methodologies

In Fiscal 1997, the Japan International Cooperation Agency (JICA) started a training course on "Monitoring and Control Technology of Acid Deposition" in Hyogo Prefecture in Japan for 9 leading technicians from national or local governments in East Asia. From FY 1998, JICA has been carrying out this training course in close collaboration and coordination with the training programs prepared by the INC.

10. 3. Training by the National Center in each participating country

The National Center in each participating country should take the lead to prepare a national training program in each year, and implement training on sampling and chemical analysis methodologies. The National Center should also provide guidance for the preparation and implementation of SOPs to national sampling organizations and chemical analysis laboratories.

Appendix 1

Items to be covered in the national QA/QC program

1. Objectives
2. Definition and importance of the QA/QC programs
3. Application and roles of relevant entities
 - 3.1. Application
 - 3.2. Roles of relevant entities
4. Fundamental matters in the QA/QC program
 - 4.1. Clear assignment of responsibility
 - 4.2. Preparation of standard operating procedures
 - 4.3. Outline of sampling and chemical analysis methods
 - 4.4. Data quality objectives
5. Sampling sites
 - 5.1. Criteria on selection of sampling sites
 - 5.2. Documentation on site conditions
 - 5.3. Assessment and documentation of representativeness
 - 5.4. Site audit
6. Collection and handling of samples
 - 6.1. Criteria for sampling apparatus
 - 6.2. Operation check of samplers
 - 6.3. Handling and transportation of samples
 - 6.4. On-site inspection
 - 6.5. Parallel sampling
7. Measurement and chemical analysis of samples
 - 7.1. Standard materials and standard solutions
 - 7.2. Storage and pretreatment of samples
 - 7.3. Adjustment of instruments
 - 7.4. Fluctuation of instruments
 - 7.5. Calculation of detection limits and determination limits
 - 7.6. Duplicate and repeated analysis
 - 7.7. Ion balance check
 - 7.8. Comparison of calculated and measured conductivity
8. Data management
 - 8.1. Data check at laboratories
 - 8.2. Treatment of extraordinary data, and data validation
 - 8.4. Assessment of data quality by the National Center
 - 8.5. Assessment of adequacy of sampling sites, and completeness by the National Center

9. Data reporting
 - 9.1. Site information
 - 9.2. Sample collection
 - 9.3. Chemical analysis
 - 9.4. QA/QC activities
10. Training programs

Appendix 2

Major items to be included in SOPs in wet deposition monitoring

Standard operating procedures (SOPs) should be prepared for all elements of operation starting from sampling through data reporting, in accordance with the wet deposition monitoring manual to minimize differences of precision by different analysts. It is important to ensure that SOPs be complied with in actual operations. Even if samplers or analytical instruments conform to the monitoring manual, their manufacturers and/or types may be different in different sampling organizations or analytical laboratories. Therefore, SOPs should be prepared, taking into account the actual condition of each organization/laboratory. Individual SOPs should clearly describe scope of application, designation of operational staff and their supervisors, and reporting formats and so on. In the following table, the fundamental items are listed regarding individual SOPs on wet deposition monitoring. The additions and/or deletions may be needed, taking into account the actual condition of each laboratory in preparing SOPs.

1. Sampling
 - 1.1. Appointment of sampling staff and their supervisors
 - 1.2. Check of possible changes around the sampling sites
 - 1) Local situation(new construction of emission and contamination sources etc.)
 - 2) On-site situation
 - 1.3. Check of sampling instruments apparatus
 - 1) Appearance of sampler(check for corrosion etc.)
 - 2) Operation of sampler(rain sensor, moving of lid, documentation of repair of sampler)
 - 3) Collection efficiency (comparison with standard rain gauge)
 - 4) Cleaning of sampling parts
 - 1.4. Sampling methods
 - 1) Sampler(involving the documentation of check and maintenance)
 - 2) Sampling interval(sampling dates)
 - 3) Change of sample vessels
 - 4) Addition of biocide
2. Sample transportation and storage
 - 2.1. Transportation of samples
 - 2.2. Sample storage
 - 1) On-site storage
 - 2) Laboratory storage
3. Measurement and chemical analysis
 - 3.1. Appointment of analysis staff and their supervisors for each item
 - 3.2. Development of training plan
 - 3.3. Deionized water
 - 1) Daily maintenance
 - 2) Documentation of maintenance
 - 3.4. Measurement by instruments
 - 1) Measuring conditions of instruments
 - 2) Calibration
 - 3) Performance tests (sensitivity, stability, interference and its removal, documentation)

- of repair)
- 4) Calculation of lowest detection limits and lowest determination limits
- 5) Documentation of maintenance
- 3.5. Operating procedures for measurements
 - 1) Preparation of calibration curves
 - 2) Measurement/analysis of samples
 - 3) Repeated measurements/analyses
 - 4) Check of sensitivity fluctuation
- 3.6. Treatment of measurement results
 - 1) Calculation of concentrations
 - 2) Measurement of sensitivity fluctuation
 - 3) Repeat measurements/analyses
 - 4) Calculation of ion balances
 - 5) Comparison of measured and calculated conductivity
- 4. Quality assurance and quality control
 - 4.1. Evaluation of sample collection
 - 1) Comparison of precipitation amount with standard rain gauge
 - 2) Evaluation of ion balance
 - 3) Evaluation of conductivities
 - 4.2. Evaluation of reliability
 - 1) Evaluation of sensitivity fluctuations
 - 2) Evaluation of repeated measurements/analyses
 - 3) Evaluation of field blanks
 - 4) Comparison between measured data and lowest detection and determination limits
 - 4.3. Evaluation of results
 - 1) Representativeness of sampling sites
 - 2) Evaluation of sample validity
 - 3) Evaluation of completeness for the sampling period
 - 4) Determination of total precision
- 5. Management of sampling instruments, laboratory, measurement/analysis instruments and reagent/glassware
 - 5.1. Management of sampling instruments
 - 1) Appointment of management staff and their supervisors
 - 2) Documentation of names of manufacturers, types, manufacture dates and operation methods
 - 3) Daily and regular maintenance and inspection methods (including troubleshooting, parts supply and recording)
 - 5.2. Laboratory management
 - 1) Appointment of management staff and their supervisors
 - 2) Daily and regular maintenance and inspection methods (including items and recording format)
 - 5.3. Management of measurement/analysis instruments
 - 1) Appointment of responsible staff for each instrument, and overall measurement
 - 2) Documentation of names of manufacturers, types, manufacture dates and operation methods
 - 3) Daily and regular maintenance and inspection methods (including troubleshooting, parts supply and recording)
 - 5.4. Management of reagents, standard materials, etc.

- 1) Appointment of management staff and their supervisors
 - 2) Receiving and disposal of reagents (recording format of dates, manufacturer names, dealers, purity, degree of standard and valid period)
- 5.5. Management of glassware and polyethylene vessels
- 1) Appointment of management staff and their supervisors
 - 2) Cleaning methods
 - 3) Storage
 - 4) Confirmation of cleanliness
6. External audit
- 1) Check of sampling sites
 - 2) Measurement of field blank values
 - 3) Operation check of samplers
 - 4) Evaluation of the results of quality control
 - 5) Evaluation of the measured results

Appendix 3

QA/QC on measurements and analyses of samples

1. Measurement and analysis of samples

1.1. Deionized water

Water with a conductivity less than 1 0.15mS/m is acceptable for measurements, analyses, dilution of precipitation samples and cleaning.

1.2. Certified materials and certified samples

The measurements are evaluated by comparison of measured results of collected samples and certified materials. In order to assure the reliability of measurements, the certified solutions and certified materials that were certified for traceability should be used as much as possible.

For the analytical instruments, there are the US National Institute of Standards and Technology SRM etc. as the Certified Reference Materials (CRMs), certified in concentration. But since they are too expensive for daily use for instruments, it is convenient to use simulated rainwater as the working standard in the laboratories.

1.3. Pretreatment of samples at analytical laboratory

Sample amount, conductivity and pH should be measured as soon as possible after sample arrival, and checking agreement of samples and sample list. After conductivity and pH measurement, all samples should be filtered with clean membrane filters (pore size:0.45µm). Filters should be well washed and be free from contamination. After filtration, samples should be refrigerated at 4 °C.

Effort should be made to start analysis of the other parameters within a week of sample arrival in the laboratory and to complete the data sets by measuring EC, pH and all other chemical parameters.

The ionic constituents can be measured after dilution with deionized water if the quantity of samples are fairly small or if the samples are of high concentration, that is over the usual analytical range. In this case, the dilution flag must be marked in the reports, and the purity of water should be checked before dilution. But diluted samples are not to be used in measurement of pH and conductivity.

When a sample amount is very small, the order of measurement priority is as follows: Take an aliquot (e.g. 5ml) and dilute with deionized water to an appropriate amount, (1) determine sulfate, nitrate and chloride ions, by ion chromatography, then (2) ammonium ion, sodium, potassium, calcium and magnesium ions by ion chromatography when a cation column is available. If not, (2) ammonium ion by spectrophotometry, (3) sodium, calcium, magnesium and potassium by atomic absorption spectrometry. Flow chart of sampling and measurement of samples in concerning with sample amount are shown in Fig.1.

Another use of sample dilution is to reduce the concentration of those analyses exceeding the range of the analytical technique. In this case, an aliquot of sample (e.g., 10 ml) is taken in volumetric flask and deionized water is added to a certain amount (50 or 100 ml). It is also important to measure the ions analyzed in the deionized water used.

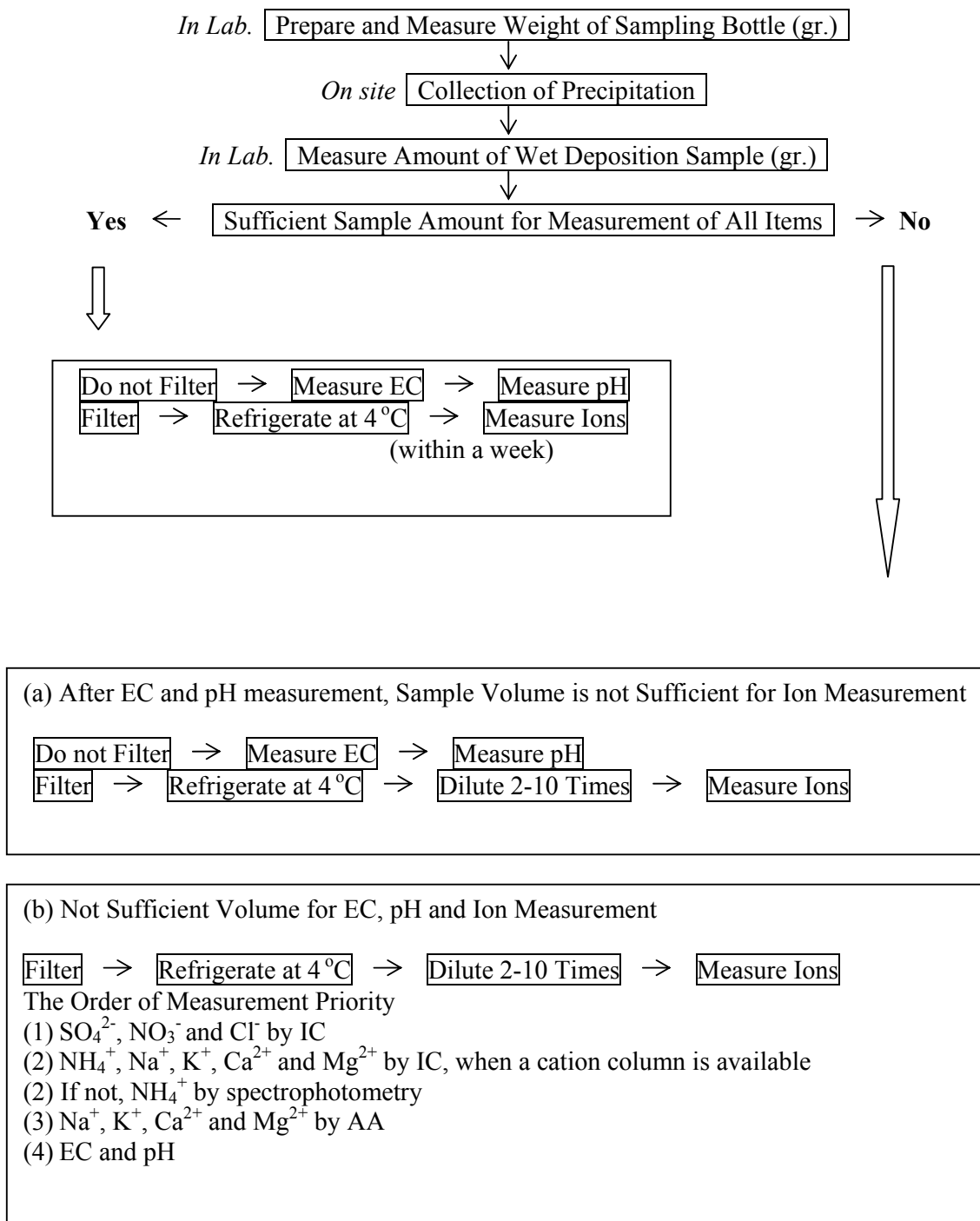


Fig. 1 Flow chart of sampling and chemical analysis of wet deposition

1.4. Adjustment of analytical instruments

Each of the analytical instruments must be calibrated when they are used, and they should be adjusted as appropriate.

a) pH meter

The pH recommended to be measured at 25 °C. The vessel which was filled with certified solution should be soaked in a temperature-controlled water bath; after calibration of the pH meter, tests of reproducibility and linearity are to be carried out to assure reliable measurement. It should be confirmed that the attached thermometer can also be reliable by comparison with a certified thermometer. It should be confirmed that the water bath can control the temperature fluctuation in the water bath to within the allowable range (In form 0 of JIS, it is ± 0.2 °C; in form I ± 0.5 °C). If a temperature controlled water bath is not available, use of water bath without temperature control but containing at least 5 L of water may be considered. It recommended to measure the concentrations of a series of hydrochloric acid solutions made with pH values in the range of 4.0~5.0 in approximately once a month, and confirm that the measurement results are within a stated range.

b) Electric conductivity meter(EC meter)

The conductivity recommended to be measured at 25 °C. It should be confirmed before the measurement that reliable data can be obtained with the calibration of the EC meter in a temperature-controlled water bath, with tests of reproducibility and linearity. It should also be confirmed that the attached thermometer can be reliable by comparison with a certified thermometer, and it should be confirmed that the constant-temperature water bath can control the temperature fluctuation in the water bath to within the standard (25 °C). If a temperature controlled water bath is not available, use of water bath without temperature control but containing at least 5 L of water may be considered.

c) Ion chromatograph

After setting up the components of working eluent and conditions of flux, and regulating the conditions under which target ions can be separated well, it should be then confirmed that the response is stable and the prescribed sensitivity is achieved.

d) Atomic absorption spectrometer

After setting up conditions of the current of the midair cathode lamp, the height of the burner, the fluxes of fuel gas and combustion-supporting gas, measuring the wavelength and slit range, it should be confirmed that the response is stable and that the prescribed sensitivity is achieved. If there is a possibility of optical interference, then corrections must be made to achieve sufficient reliability.

e) Spectrophotometer

Regarding target ions, it should be confirmed that the absorption is stable and the prescribed sensitivity is achieved. If there is a possibility of optical interference, then

corrections must be made to achieve sufficient reliability.

2. Evaluation of reliability

2.1 Sensitivity fluctuation of analytical instruments

While numerous samples are measured, measurements should be continued after confirming that the sensitivity fluctuation is within the prescribed range.

a) pH meter

More than once in every 20 samples, reference materials should be measured 3 times to confirm that their values are within ± 0.05 . If the sensitivity fluctuates over this range, the reasons should be found and removed, and then the reference material should be measured again.

b) Electric conductivity meter (EC meter)

More than once in every 20 samples, a reference material should be measured 3 times to confirm that the sensitivity fluctuation is within ± 0.2 mS/m with the sensitivity measured in making a calibration curve. If the sensitivity fluctuates over this range, the samples should be measured again after removing the cause of the fluctuation.

c) Ion chromatograph

A new calibration should be performed not more than 30-sample measurement. Reference materials should be measured after the calibration. It should also be done once or twice before the next calibration. Control charts should be applied for the measurement of the reference materials. Standard solutions and reference solutions must be prepared from different stock solutions in order to be independent. If the results of the control solutions are outside 3 standard deviations, or 15 % from the expected value, the reasons should be found and corrections made, and reference solution measured again.

If the retention time changes slowly while the separator column is deteriorating, then adequate actions could be taken as appropriate. If it changes significantly in a relatively short time, the reasons should be found and removed, then the reference material must be measured again.

d) Atomic absorption spectrometer

A new calibration should be performed not more than 30-sample measurement. Reference materials should be measured after the calibration. It should also be done once or twice before the next calibration. Control charts should be applied for the measurement of the reference materials. Standard solutions and reference solutions must be prepared from different stock solutions in order to be independent. If the results of the control solutions are outside 3 standard deviations, or 15 % from the expected value, the reasons should be found and corrections made, and reference solution measured again.

e) Spectrophotometer

A new calibration should be performed not more than 30-sample measurement. Reference materials should be measured after the calibration. It should also be done once or twice before the next calibration. Control charts should be applied for the measurement of the reference materials. Standard solutions and reference solutions must be prepared from different stock solutions in order to be independent. If the results of the control solutions are outside 3 standard deviations, or 15 % from the expected value, the reasons should be found and corrections made, and reference solution measured again.

2.2. Analyses of Not Detected and Lowest Determination Limit

In determining the detection and determination limits for the respective methods (Ion chromatography, Spectrophotometry, Atomic absorption spectrometry) used in measuring the concentrations of several ions in wet deposition samples, a standard solution with concentration near the lower determination limit should be measured 5 times. In this case, a standard deviation(s) is calculated as follows: 3 times this value is defined as Not Detected, and 10 times this value is defined as the Lowest Determination Limit (the unit of s is the same as that used for the concentration in rainwater).

$$\begin{aligned}\text{Not Detected} &= 3 s \text{ (}\mu\text{mol/L)} \\ \text{Lowest Determination Limit} &= 10 s \text{ (}\mu\text{mol/L)}\end{aligned}$$

Because the Lowest Determination Limit is different among analytical instruments that we are using and analytical conditions vary, LDL should be determined whenever analytical conditions are established or changed. It should be confirmed that LDL is below the DQO values described in Table 1 b) of main text 3.4.

2.3. Duplicate sample analysis

To estimate the contribution of analytical variability, duplicate sample analyses should be performed on about 5% of routinely analyzed samples. Samples containing a large quantity of precipitation should be divided, one half being analyzed immediately after the routine analysis, and the other half being refrigerated at about 4 °C to be analyzed within a week.

Precision (S_i) is calculated by the following formula:

$$S_i = (\sum d_i^2 / 2N_i)^{1/2} * 100 / A_v$$

where d_i and A_v denote, the difference between the duplicate analyses and mean, respectively, and N_i is the number of sample pairs in the reporting period. Analytical precision is then defined and reported as the standard deviation between the two analyses by the following equation. When the precision is larger than 15%, it must be analyzed again and the nearer to their values are used as analyses.

2.4. Certification of cation and anion balance

The principle of electroneutrality in precipitation water requires that the total of anion equivalents is equal to the total of cation equivalents, and the proportion of them is 1. For calculating cation and anion balance the following equation should be used:

$$R_1 = 100 \times (C - A) / (C + A) \text{ (\%)}$$

Here A and C represent the totals of equivalent concentrations ($\mu\text{eq/L}$) of anions and

cations, and they are given as follows:

$$A(\mu\text{eq/L}) = \sum nC_{A_i}$$

$$C(\mu\text{eq/L}) = 10^{(6-\text{pH})} + \sum nC_{C_i}$$

In the equations, C_{A_i} and C_{C_i} are the concentrations ($\mu\text{mol/L}$) of the i -th anion and cation, respectively, and n is the valence.

Calculations of ionic balance of precipitation (R_1) must satisfy the following criteria: R_1 is $\pm 30\%$ while $(C+A)$ is less than $50 \mu\text{eq/L}$, $\pm 15\%$ while $(C+A)$ is $50\sim 100 \mu\text{eq/L}$, and $\pm 8\%$ while $(C+A)$ is more than $100 \mu\text{eq/L}$ (reference Table 1).

If the required criteria are not met, the analysis should be repeated or a flag should be marked in the database indicating that the results did not meet the required criteria. When pH is greater than 6 and R_1 is significantly greater than zero, bicarbonate (HCO_3^-) concentration should be evaluated to compute R_1 and R_2 again including bicarbonate contribution. When formic acid, acetic acid, or both are measured, formate and acetate ions should be considered in the evaluation of R_1 and R_2 . The concentrations ($\mu\text{eq/L}$) of these weak acids will be calculated from the dissociation constant K_a and pH as follows:

$$[\text{HCO}_3^-] = \text{PCO}_2 \text{H}_2\text{CO}_3 K_{a1} / [\text{H}^+] = (360 \times 10^{-6})(3.4 \times 10^{-2}) 10^{(\text{pH} - 6.35)} + 6$$

$$= 1.24 \times 10^{(\text{pH} - 5.35)}$$

$$[\text{HCOO}^-] = [\text{HCOOH}] K_a / [\text{H}^+] = [\text{HCOOH}] \times 10^{\text{pH} - \text{p}K_a} = [\text{HCOOH}] \times 10^{(\text{pH} - 3.55)}$$

$$[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}] K_a / [\text{H}^+] = [\text{CH}_3\text{COOH}] \times 10^{(\text{pH} - \text{p}K_a)}$$

$$= [\text{CH}_3\text{COOH}] \times 10^{(\text{pH} - 4.56)}$$

Atmospheric concentration of CO_2 in equilibrium with precipitation samples is assumed to be 360 ppm. Dissociation constants in terms of $\text{p}K_a$ for carbonic, formic, and acetic acids are 6.35, 3.55, and 4.56, respectively. At some sites, fluoride (F^-) and/or nitrite (NO_2^-) may contribute to a significant fraction of the major anions, which subsequently requires calculations of R_1 and R_2 that include these anions.

2. 5. Comparison of calculation and measurement of the total conductivity

For dilute solutions (e. g. below 10^{-3} M), the total conductivity can be calculated in mS/m from the molar concentrations and molar conductivities (at infinite dilution) of the individual ions. The calculation is as follows:

$$\Lambda_{\text{calc}} = \sum c_i \Lambda_i^0 \times 10^{-4}$$

where Λ_{calc} denotes the calculated conductivity of the solution (in mS/m), c_i the ionic concentration of the i -th ion (in $\mu\text{mol/L}$), Λ_i^0 the molar conductivity (in $\text{S cm}^2/\text{mol}$) at infinite dilution and 25°C .

Thus

$$\Lambda_{\text{calc}} = \{349.7 \times 10^{(6-\text{pH})} + 80.0 \times 2c(\text{SO}_4^{2-}) + 71.5 c(\text{NO}_3^-) + 76.3 c(\text{Cl}^-) + 73.5 c(\text{NH}_4^+) + 50.1 c(\text{Na}^+) + 73.5 c(\text{K}^+) + 59.8 \times 2c(\text{Ca}^{2+}) + 53.3 \times 2c(\text{Mg}^{2+})\} / 10000$$

where $c()$ denotes the ionic concentrations in $\mu\text{mol/L}$ of the ion in parentheses and the constants are the molar conductivity of the individual ion at infinite dilution at 25°C (see Table 2).

The calculated conductivity values can then be compared to the observed values for precipitation samples by the relation

$$R_2 = ((\Lambda_{\text{calc}} - \Lambda_{\text{meas}}) / (\Lambda_{\text{calc}} + \Lambda_{\text{meas}})) \times 100 \%$$

This is similar to the equation for the calculation of cation and anion balance.

It is necessary that comparison of chemical analyses and calculations of conductivity (R_2) satisfies the criteria. The criteria are, similar to R_1 , different in different concentrations (reference Table 3). If the required criteria have not been met, the analysis should be repeated or a flag should be marked in the database indicating that the results did not meet the required criteria.

Table 1 Allowable ranges for R_1 in different concentrations

(C + A) ($\mu\text{eq/L}$)	R_1 (%)
<50	± 30
50-100	± 15
>100	± 8

Table2 Basic constants

Ion	Molecular Weight (M)	Molar Conductivity (λ), S cm ² /mol
H ⁺	1.008	349.7
NH ₄ ⁺	18.04	73.5
Ca ²⁺	40.08	59.8 x 2
K ⁺	39.10	73.5
Mg ²⁺	24.31	53.3 x 2
Na ⁺	22.99	50.1
NO ₃ ⁻	62.01	71.5
SO ₄ ²⁻	96.06	80.0 x 2
Cl ⁻	35.45	76.3
HCO ₃ ⁻	61.02	44.5
HCOO ⁻	45.0	54.6
CH ₃ COO ⁻	59.1	40.9
F ⁻	19.00	55.5
Br ⁻	79.90	78.2
NO ₂ ⁻	47.01	72.8
PO ₄ ³⁻	94.97	69.0 x 3

Kagaku Binran, p. II-460-461. 3rd Ed., 1984, Maruzen, Tokyo.

Table 3 Allowable ranges for R₂ in different concentration

Ameas (mS/m)	R ₂ (%)
<0.5	± 20
0.5 - 3	± 13
>3	± 9