Technical Manual
for
Wet Deposition Monitoring in East Asia -2010

Endorsed by
Scientific Advisory Committee of EANET at its Tenth Session

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The first manual, "Technical Manual for Wet Deposition Monitoring in East Asia", was developed in March 2000 under the adoption at the Second Interim Scientific Advisory Group Meeting of Acid Deposition Monitoring Network in East Asia. This manual, "Technical Manual for Wet Deposition Monitoring in East Asia -2010", was prepared as a revised version of the first manual under the discussion in the Expert Group on Revision of Technical Manual on Wet Deposition Monitoring and endorsed in the Tenth Session of the Scientific Advisory Committee on Acid Deposition Monitoring Network in East Asia held in 2010.

1. Introduction

1.1 Background

The Acid Deposition Monitoring Network in East Asia is dedicated to creating a common understanding of the status of the acid deposition among countries and organizations of the East Asia region, and to providing scientific inputs to assessment of acid deposition for decision making at various levels aimed at preventing adverse impacts of acid deposition in the region.   One of the goals of this network is to provide high-quality data and other information on the chemistry of wet deposition for all parts of East Asia.   Wet deposition comprises a significant fraction of the deposition to ecosystems.   Precipitation chemistry measurements provide information on the exchange of trace materials between the atmosphere and the earth's surface.

The Guidelines for Monitoring Acid Deposition in the East Asia Region were adopted on 23 March 1995 by The Expert Meeting.   In order to extend the guidelines, the technical manual for wet deposition monitoring was also adopted by The Expert Meeting on 4 February 1997.   The manual outlines the most appropriate wet deposition monitoring techniques in terms of siting, sampling, shipping, chemical analysis, QA/QC, and data reporting available at that time.

The 1st Intergovernmental Meeting of the ten member counties of EANET, China, Indonesia, Japan, Malaysia, Mongolia, the Philippines, Republic of Korea, Russia, Thailand and Vietnam took place on March 20, 1998 at Yokohama, Japan where the member countries officially agreed to form EANET and to start implementation of the Network in April, 1998.   All members agreed to amend their protocols as a first step in an ongoing effort to comply with the EANET guidelines and technical manuals as set out in the document titled "Implementation of Preparatory-phase Activities (EANET/IG/1/6 re., March 20, 1998)".   Subsequently the Guidelines and the Technical Manuals were reviewed and adopted at the 2nd Interim Scientific Advisory Group Meeting.

The technical manuals are to be reviewed and updated in a timely and appropriate fashion, in accordance with advances in science and technology.   The member countries are required to make reasonable efforts to improve their monitoring systems by making effective use of the guidelines and technical manuals.

1.2 Objectives of wet deposition monitoring

The wet deposition data set is intended to provide an observational basis for the evaluation of long-range transport of pollutants and the validation of deposition models. The data also allows for impact assessments of terrestrial ecosystems and urban infrastructure. The integrated body of measurements is designed to be shared with other acid deposition monitoring networks allowing for regional and global collaborations and to provide policy makers with the scientific facts required for formulating emission control strategies aimed at controlling acid precursors.

1.3 Outline of the manual for monitoring wet deposition

This technical manual addresses siting, sampling, chemical analysis, data reporting, quality assurance and quality control. For the majority of the methods, the necessary quality assurance is facilitated by a combination of simple and robust sampling techniques, sampling equipment with effective and complete technical manuals and the chemical analyses of simulated control samples. Techniques and methods that have been found effective within EMEP, NADP, CAPMoN and WMO have been developed and adapted by EANET.

This technical manual has adopted the molar unit for the reasons outlined below.
  a) Molar units are convenient when chemical conversions in the environment are considered.
  b) Molar concentration is precisely and easily converted to equivalent concentration whereas mass concentration could lose some significant digits when converted to equivalent concentration.
  c) Some quantities such as (Base cation)/Al ratio are usually expressed in molar ratio because valence of metals is not always clear for environmental samples.
  d) Molar concentration is an SI unit.

2. Planning

2.1 Monitoring sites

The siting of monitoring sites plays a critical role in the quality and type of data

resulting from a wet deposition sampling program. A sampling site should be representative of the area of interest and suitable for the intended monitoring program. Collocation of wet deposition sampling with dry deposition monitoring should be a consideration as is the availability of nearby meteorological data.

EANET monitoring sites are classified into two categories: deposition monitoring sites and ecological survey sites, both with subcategories: Deposition Monitoring sites are intended to monitor the temporal and spatial distribution of acid deposition whereas the Ecological Survey sites produce data which is used to assess potential impacts of acid deposition on terrestrial ecosystems. All the sites are to be classified as one of the following five types:

- a) Deposition monitoring sites
  - i. Urban sites
  - ii. Rural sites
  - iii. Remote sites
- b) Ecological survey sites
  - i. Basic survey sites
  - ii. Ecosystem analysis sites

Care must be taken to ensure that all five types of sites represent the region of interest in terms of natural and anthropogenic emissions, and topographic features. Meteorological conditions, including annual precipitation amounts and prevailing wind directions, should be taken into account. To ensure local meteorological influences are minimized, monitoring should not be sited on mountain tops, within mountain passes, valleys or basins. In general, they should not be near natural sources such as volcanoes unless the focus of that effort is to monitor their influences on precipitation chemistry.

Each country should establish at least one remote or rural site.

(1) Remote Sites

Remote sites should be representative of the EANET region of interest and should meet the following criteria.

- a) No significant changes in land-use practices are expected within a reasonable distance of the site for decades.

b) Major populations and industrial centers, major highways and airports do not impact the site and if possible location on islands, in mountain ranges and major forest reserves is desirable.

c) The effects of major natural phenomena including volcanic eruptions, forest fires and dust storms are not frequently experienced.

d) No sources should impact the site such as gravel roads, tilled agricultural fields, grazing land and pastures.

e) The local air shed needs to be entirely free of the influence of local pollution sources and contain only diluted vestiges of chemical species transported from long distant sources (at least 30-50 kilometers away).

(2) Rural sites

Rural sites should be representative of the EANET region of interest and should meet the following criteria.

a) Sites should be located in areas sufficiently far away from population and industrial centers so that the effects of large local sources of air pollution seldom impact the site.

b) No sources should impact the site such as gravel roads, tilled agricultural fields, grazing land and pastures.

2.1.1 Minimum distances to emission and contamination sources

a) Remote and ecological sites should have no large pollution sources within 50 km distance from the site: cities, thermal power plants, major motorway.

b) Rural sites should be at least 20 km distant from large pollution sources.

c) Remote and rural sites should be at least 500 m from main roads (more than 500 vehicles per day).

2.1.2 Local criteria

The criteria for locating collectors in rural sites, remote sites, and sites in ecological area are as follows.

a) The collector should be in an open, flat, grassy area far enough from trees, hills, and other obstructions to avoid adverse effects on sampling.

b) No obstructions should be within a few meters of the collector, and no object

should shade the collector.

c) The horizontal distance between a large obstruction and the collector should be at least twice the obstruction's height, or the top of an obstruction as viewed from the collector should be less than 30° above the horizon.

d) The collector should be a minimum off 100 m from local emission and contamination sources such as waste disposal sites, incinerators, parking lots, open storage of agricultural products, and domestic heating.

e) The collector and rain gauge (and dry deposition collector) should be in the same immediate area but no closer than 2 meters. A line drawn between the rain gauge and the wet deposition collector should be perpendicular to the prevailing wind direct (specifically during seasons where precipitation events are common).

2.1.3 Site relocation

Local influences and site characteristics can change with time influencing the precipitation chemistry of the samples collected. The characteristics of each site should be reviewed regularly and if serious siting criteria issued are detected an assessment is required to determine if on-sites changes can be made to improve sample representativeness or whether the site should be relocated. If necessary the collector should be relocated to another site which meets the siting criteria for the purpose of continuing to collect proper samples representing the area of interest.

Should it be necessary to move a site, it is recommended that duplicate sampling between the original and new locations using identical instrumentation and protocols take place for a period of at least one-year. It is important that sufficient data be collected to determine whether a bias between sites exists. Such changes could have an impact on the perceived trends in an area. A detailed analysis of the two data sets should be completed and any bias that is detected should be well documented.

2.2 Monitoring frequency and measurement parameters

2.2.1   Monitoring frequency

EANET recommends that samples should be integrated over a continuous 24 hour period.   Alternately collection can also be on an event basis which means samples are

only collect when a precipitation event occurs. Event sampling can be operationally inefficient as site operators often find it difficult to determine the start and end of a precipitation event and are not necessarily available at all times of the day. If a collection bucket is used, the bucket must be changed or at least cleaned daily regardless of whether a precipitation event has occurred. The sampling start time for daily samples should be at 0900 local time.

When the chemical analysis of daily samples is not practical, integrating (combining) daily samples for one week (7 days) is an acceptable option only when the integrity of sample composition would be maintained, by refrigeration and/or adding biocide.

2.2.2 Measurement parameter

(1) Precipitation chemistry parameters

The required analytical suite for precipitation samples is pH, electric conductivity (EC) and the concentration of major ions: SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}.

Depending on the chemical composition of the precipitation, the ion and conductivity balance may not meet your network's data quality objectives (based on major ions). If your criteria are not met in a systematic manner, consideration should be given to adding additional chemical analysis of additional ions including hydrogen carbonate (HCO_3^-), nitrite (NO_2^-), fluoride (F^-), bromide (Br^-), phosphate (PO_4^{3-}), and organic ions ($HCOO^-$, CH_3COO^-, and $(COO^-)_2$).

The chemical determination of heavy metals, aluminum, mercury, and organic compounds will aid in the characterization of precipitation.

(2) Meteorological measurements

It is recommended that monitoring sites incorporate collocated meteorological measurements including wind direction/speed, temperature, humidity, precipitation amount and solar radiation. Meteorological data can also be acquired from the nearest standard meteorological station (meeting the requirements of the national weather service). Local meteorological data is very useful when dealing with the interpretation of unusual precipitation events.

3. Sampling

3.1 Precipitation sampling

3.1.1   Facilities at the site

Precipitation samples normally have low concentrations of ionic species and are very susceptible to contamination.   Subsequently the handling of the samples is critical and every effort needs to be taken to preserve their chemical integrity until the samples are analyzed and the data finalized.

A hut should be provided immediately adjacent to the wet only sampler to support sample collection and associated measurements.   The sample collector and the hut should be separated from each other by at least 50 m and consideration should be given to protecting the equipment against vandalism by installing security measures such as a fence.

A reliable source of electrical power is essential to ensure that collectors operate continuously and precipitation events are detected and sampled.

The hut should be equipped with:
   a)   electric power;
   b)   refrigerator;
   c)   sink;
   d)   water supply;
   e)   pure water (conductivity < 0.15 mS m^{-1});
        If pure water is neither available at the site nor purchasable locally, it should be supplied by the analytical laboratory.
   f)   two types of electronic balances (one type: max. weight 15 kg, min. weight 1 g and the other: max. 100 g, min. 0.1 mg);
   g)   data logger;
   h)   personal computer;
   i)   telephone; and
   j)   tables and chairs.

The field measuring instruments should be equipped with:

a)   an automatic wet-only precipitation chemistry collector;

b)   a standard rain/snow gauge; and

Keep in mind that the rain gauge and the wet-only precipitation collector required at all sites, serve different functions.   The rain gauge measures the amount of precipitation.   The automatic precipitation collector collects samples for chemical analysis.   The two devices are not interchangeable.

c)   meteorological instruments (temperature, wind direction, wind speed, humidity and solar radiation).

Meteorological instruments should be connected to a data logger or a computer.

3.1.2 Sample collection system

Wet-only samples collected by an automated wet-only collector are required but collectors that collect distinct wet and dry samples may be used.

EANET does not require that the wet-only collector in use be the same type for all countries and subsequently the details associated with the technical operations of the samplers can not be considered here.   The operation of each collector should be done in accordance with the operation manual of each collector for each country.   Several different types are already in use in some countries, but the older collectors that cannot meet the following conditions should be replaced by an automatic precipitation collector that does meet the following four requirements.

(1) Collecting funnel

A sampling opening of a standard size is needed to ensure conformity among samplers in a country or region.   Collecting funnels should be made of an inert material ensuring that major ions are not leeched into or out of the samples during collection. Polyethylene or Teflon or Teflon-coatings have been found to be effective with polyethylene being the most cost efficient.   Teflon or silicone should be used to connect funnels and buckets.   To ensure inertness of materials all collecting materials, especially flexible tubing should be replaced yearly.

(2) Open-close lid

The wet sample should be shielded from contamination by dry deposition and the lid

should alternatively cover the bucket when a wet precipitation sample is not being collected. A motor driven lid controlled by a sensor as described in c) is required. The most important function of the lid is to seal the collection vessel during dry periods, preventing contamination by atmospheric gases and aerosols, and to minimize sample evaporation. Achieving tight seals is usually accomplished by mounting a flexible gasket covered with a Teflon sheet on the underside of the lid. For the maintenance and cleaning of the funnel, the sampler lid should open manually. Lids on the collectors used in snowy regions should have stainless steel or Teflon-coated, peaked, roofs mounted on the top of the lid. The peak prevents snow accumulation on the lid and reduces the blowing of snow into the collection vessel as the lid opens.

(3) Precipitation sensor

It is essential that the lid covering the collector container or funnel opens automatically within one minute of the onset of precipitation and closes promptly at the end of the precipitation event. When the grid and plate of the sensor are shorted by a drop of water, the lid motor is activated, lifting the lid from the container or funnel. The sensor should be designed to detect at least 0.05 mm h^{-1} rainfall intensity and 0.5 mm rain drop diameter, independent of wind direction. The sensor needs to be designed to prevent fog and dew from activating the collector, as well as to melt snow (allowing it to be detected), and to evaporate residual precipitation immediately after the event (thereby allowing the collector to close). The height of the sensor should be the same as that of the bucket or funnel. If required, in order to protect the detection surface from birds' droppings, some needles should be put up around the sensor.

(4) Sample container

The collector bucket or funnel with bottle should be chemically inert for the purpose of collecting and determining the trace level concentrations of major ions in acid precipitation. The height of the collection bucket or funnel should be 1.0 to 1.5 m above the ground. The volume of containers should be determined by considering the daily maximum precipitation amounts at a site over the previous ten years. Information on the height from the ground of the funnel and/or bucket of the precipitation chemistry collector, sensor and standard rain gauge should be reported with all data.

3.2 Snow sampling

Snow characteristics vary from region to region and can be dramatically different at the same location on different days. The collection of a representative snow sample can be challenging. Detecting precipitation in the form of light dry snow using electronic shorting sensors is much less efficient and reliable than when detecting rain.

Strong winds will impact the collection efficiency of any sampling container:
  a) Collected snow can blow out of the sampling container during periods of strong winds stiff winds
  b) Blowing surface snow can activate the sensor and result in the collection of a non-representative sample
  c) Snow can blow across the container opening and result in a reduced catch
  d) At times wet snow can collect more efficiently in the container than it would to a flat surface.

There is no universally accepted protocol or standard collector available which addresses the complexities of sampling snow and ice. Networks normally adapt their existing samplers to improve snow collection using one or more the following measures:
  a) Heating the collector lid, body surface and instrument box or interior of the sampler can help ensure that snow does not build up on the sampler itself and that the moving parts stay sufficiently warm to ensure they continue to operate properly during extreme cold events.
  b) The sensor should be heated sufficiently to ensure that ice and snow melt on contact resulting in the sensor working effectively without danger of accumulation and malfunction.
  c) The funnel should be heated to 4-5 ^{o}C to ensure the entire accumulation is sampled. Care should be taken to ensure that the funnel is not overheated as this can cause excessive evaporation and loss of sample.
  d) Collection efficiency can be improved by attaching a wind shield device to the collector to minimize the effect of wind on the sampling of snow (*e.g.*, Nipher Shield).
  e) To avoid the possibility of excessive evaporation of sample caused by a heated funnel in extremely cold regions, an open polyethylene cylindrical container of 20-50 cm diameter should be used. The height of this container should be at least

twice the diameter to prevent "blow-out" of snow.   This snow collector should be equipped with a wind-shielded and heated precipitation sensor or an infrared/optical snow sensor.

Each network should carefully examine the characteristics of snow in their region before embarking on changes to their existing sampler.

3.3 Measurement of precipitation amount

Each sampling site must be equipped with a standard precipitation gauge which has been approved by the appropriate national weather service or its equivalent for each country.   Standard precipitation gauges generally measure precipitation amount more efficiently and accurately than precipitation chemistry collectors:
   a) The standard gauges or their equivalents should be operated in parallel with the precipitation chemistry collector.
   b) The precipitation gauge should be mounted 1.0 to 1.5 m above the ground surface.   That height should be the same as the precipitation chemistry collector and the precipitation sensor.

The major environmental factors governing gauge under catch are:
   a) wind speed;
   b) vertical wind profile at the point of measurement;
   c) falling velocity of the precipitation; and
   d) distortion of the wind flow and drop/snowflake trajectories around the gauge.

Wind speed is the most critical of the four factors and is the single most important factor contributing to under catch in gauges, especially for snow.   The installation of a wind shield around a precipitation gauges reduces the wind speed at the gauge orifice, thereby increasing the gauge collection efficiency.   Many types of wind shields are in use: Alter Shield, Nipher Shield, Tretyakov Shield, Wyoming Shield and USSR Dual Fence Shield.   Shields are most effective in snowy regions and can be used to improve the efficiency of precipitation gauges, precipitation chemistry collectors and precipitation sensors.   Care should be taken to minimize the possibility of contamination of precipitation samples caused by the shield.

The primary tool used for the determination of precipitation amount should always be

the rain gauge. In the event that the dedicated gauge is not available, the precipitation amount can be calculated from the weight of collected precipitation sample. Taking the diameter of the collection device (funnel or container into consideration) and the density of rain (approximately 1.0 g mL^{-1} at 20 ^{o}C), the weight of the sample in grams will be equal its volume in mLs and the depth of precipitation can then be determined. Each site should have a weighing balance for this purposely with a capacity of 15 kg and a precision of at least 1 g. It is also recommended that each site routinely weigh all precipitation samples and include that information for quality assurance purposes. The use of a graduated funnel to determine volume is not recommended due to the high possibility of sample contamination.

3.4 Sample preservation

a) Precipitation chemistry samples are always at risk of degradation. Degradation can happen during field sample collection, shipment to the laboratory and during laboratory storage and analysis. Sample preservation techniques normally do not completely stop degradation. The best practice is minimize sample handling, shipping and storage times.

b) Refrigeration is the recommended sample preservation technique. Ideally samples should be refrigerated during collection, while awaiting shipment on-site, during shipping and in the laboratory before analysis.

c) If refrigeration cannot be used as the sample preservation technique, biocides should be used. Biocide can be effective in preventing microbial uptake and conversion of organic acids such as formic and acetic acid in regions where they are contained in rain water. It is recommended that Thymol (2-isopropyl-5-methyl phenol) be used. Thymol is a solid under normal ambient temperatures and should be loaded at the rate of 400 mg to a 1000 mL sample bottle prior to each sample collection. When Thymol is used ammonium ion should be measured by ion chromatography rather than Spectrophotometry (Indophenol blue).

4. Site operation

4.1 Sampling schedule for on-site operation

Each site should have an operation schedule for on-site tasks that meets the requirements of the national network. This schedule should include a minimum of sampling dates and times and supply specific dates for all preventative maintenance requirements. Each network should have Standard Operation Procedures (SOPs) and an up-to-date printed copy of the SOP should be available for the operators at each site (see Appendix 1).

4.2 Site operation check sheets

Check the consumables and tools for site operation.
    a) The keys for the individual monitoring station
    b) Sample bottles to replace
    c) Recording device (*e.g.*, memory card of precipitation amounts)
    d) Supplies (*e.g.*, pure water (If the water is not available at the site, the analytical laboratory should provide the site operators before a travel to the site.))
    e) Record sheets including the sample history form
    f) Still or video cameras
    g) Mobile phones (site operator will be able to communicate with the laboratory to solve problems just in case. E-mails and photo images will be effective and convenient to send messages for troubles.)
    h) Tools including clean globes, wiper, and cleaning goods
    i) Maintenance tools for continuous monitoring devices

The checking sheet should be updated on an annual basis.

4.3 Checking the site condition

Inspections of the condition of all areas of the sampling site should be undertaken on a regular schedule. Inspections should be initiated immediately after severe meteorological events like typhoons, lightning, and heavy storms and if there is suspicion of vandalism. The schedule for completion and submission of this check sheet should be included in the operation schedule referred to in section 4.1. The check list should include but not be limited to changes resulting from:
    a) animals (field mice, birds);
    b) insects (ants, bees, and spiders);
    c) vegetation (leaves and seeds of plants);

d) other materials (soil, dust, sea salt, garbage);

e) obstructions impacting the collector;

The site operator should ensure the lid of the collector is kept clear of obstacles and the lid opens and closes correctly. This includes obstructions caused by cold and snow.

f) electrical power failures; and

It can be accompanied by power surges which can impact the performance of instruments. Documentation of the power failure (date and time of failure) should be completed allowing for the evaluation of instrument performance and interpretation of data.

g) temperature and humidity controls.

The sampling building and refrigeration units should be maintained within pre-established limits. Those temperature limits should be clearly stated on the check sheet.

4.4 On-site sample collection

a) Clean plastic gloves should always be worn when handling samples. If the gloves are not appropriate or not available, operators should ensure that their hands have been washed and take care not to introduce any contamination.

b) The status of the precipitation sample collector should be checked each time a sample is collected. It should be confirmed that the precipitation sensor, sampling container lid, sample flow path and refrigeration (if present) are all in the proper configuration and working correctly.

c) After the sample is collected and before the sample container is replaced all components of the sampling train should be cleaned:

i. The funnel used on the collector should be rinsed with pure water and wiped periodically with a clean disposable material such as a Kimwipe.

ii. The inner surface of the sample flow train (path) should be rinsed with pure water. Ensure that the complete area between the funnel and the sample container are rinsed. If pure water is not produced or available on site it should be supplied by the responsible laboratory.

iii. If components such as the collection funnel need to be dried quickly, methanol or ethanol can be used.

d) The sample volume should be gravimetrically determined (weighed) on-site before the sample is transported to the laboratory to ensure that possible

contamination and spillage can be accounted for during shipping:

    i. The use of a measuring (graduated) cylinder should be avoided as this practice significantly increases the possibility of contamination.

    ii. If a graduated measuring cylinder is used, the sample must be divided into two fractions. The first fraction is measured and discarded, essentially acting as a rinse of the cylinder.

    iii. The weight of the fractions including the discard should be noted on the sample history form.

e) The on-site standard rain gauge should be read and the amount recorded immediately before or after the sample is collected. The gauge should be read regardless of whether a precipitation chemistry sample was observed in the sampling container.

f) All samples should be carefully examined for contamination and observations documented. Visible contamination such as leaves and insects should be removed by the operator with clean tweezers while wearing clean gloves.

g) Samples should be maintained at $4^{o}C$ to retard the degradation of organic compounds as well ammonium and nitrate ions. The sample should be maintained at $4^{o}C$ during storage and while being shipped to the analytical laboratory. Biocide is an option.

h) Samples exceeding 200 mL are split into to two aliquots of 100 mL each and the excess sample is discarded.

i) Twenty-four hour integrated samples (daily) should be shipped to the laboratory weekly or every second week. Seven day integrated samples (weekly) should be shipped a minimum of once each month.

4.5 Checking and maintenance of routine instruments and record devices

Each network and operating agency should establish written standard operating procedures for site operations detailing day to day maintenance of the precipitation chemistry collectors and standard gauges. The procedures should focus on the operational requirements (including the requirements from section 4.4) associated with:

    a) performance of the rain sensor;
    b) proper mechanical operation of the funnel or container lid;
    c) cleaning of the collection funnel and sampling train;
    d) standard rain gauge; and
    e) replacement of the memory card for recording precipitation amount.

Replacement should be done during each site visit. The recorded data should be checked on-site to ensure that the data record is complete and to potential ongoing data loss. Data transferred or taken to the laboratory should be checked immediately to ensure any problems are immediately addressed.

Rain and snow gauges should be inspected biannually

a) Each gauge should be disassembled and the internal funnel and wind shield visually inspected.

b) The anti-freezing system should be checked and charged with fresh anti-freezing liquid.

c) More frequent inspections are required immediately following events such as dust storms. Sites which are impacted by the "Asian dust season." require more frequent maintenance and the instruments should be inspected and overhauled after these periods to ensure they continue to meet specifications.

d) Every instrument at the site should have an operation manual which includes a trouble-shooting procedure.

4.6 Field blanks

Each network should have a field blank program. Field blanks will reveal potential sample contamination issues which are often caused by instrument issues and operator errors. Each field blank should consist of an active and control sample:

a) 100mL of pure water should be poured into the collection funnel and allowed to pass through the sampling train imitating an active sample.

b) The resulting sample should be handled in the same manner as a normal precipitation sample.

    i. If conductivity is normally measured on site it should be done immediately.

    ii. If the site does not have a conductivity meter one should be taken to the site when field blanks are scheduled.

    iii. If the sampling train is determined to contaminated, clean the system and repeat the conductivity check.

    iv. If the sampling train does not improve when cleaned and rinsed it should be replaced as soon as possible.

c) The control sample consists of approximately 100mL of pure water poured directly into a clean sample bottle.

d) Both the active and control bottle are labeled and shipped to the laboratory with the normal precipitation samples.

e) The analytical results from the field blanks should be assessed to determine if there are any contamination issues associated with sampling train.

f) The field blank data should be reported in the same way as sample data in Table 11, (p.93-95), named as FB-1,2,.........,n.

4.7 On-site sample documentation

On-site documentation specific to each sample is critical for ensuring effective data quality.   Each site should be equipped with a means to consistently report site and sample conditions and each operator should routinely record that information.   The laboratory should ensure that a proper reporting format consistent with each site and network's needs is used.   The information should be further recorded on the standard EANET sample history form.

The specific format of the sample history should take into consideration any meteorology and dry deposition measurements which are associated with the wet deposition measurement site.   A simple and concise format will minimize operator errors and ensure that the information supplied is clear and concise.   The sample history form should include but not necessarily be limited to:

a) site name or unique identifier;
b) sample identification number;
c) start and ending dates for each sampling period;
d) start and end times for each sampling period;
   i.   start and end time of the precipitation event, if possible
e) sample volume or weight: including collection vessel weight;
f) standard gauge precipitation depth reading;
g) sample type (snow, rain, freezing rain, mixed, hail, fog, mist);
h) sample contaminants specified on the site (*e.g.,* visible air-borne particles, bird droppings, insects, soil dust, leaf pieces);
i) instrument condition;
   i.   operating correctly/incorrectly,
   ii. cleaned yes or no

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      iii. unusual circumstances,

      iv. problems,

      v. observations

j) condition of buildings;

      i. unusual circumstances,

      ii. problems,

      iii. observations

k) site conditions;

      i. agricultural, construction, or industrial operations,

      ii. vehicular activity,

      iii. construction machine activity including the removing snow cover

l) weather condition during the sampling (*e.g.,* typhoon, lightning, heavy storms);

m) status of on-site supplies (*e.g.,* transporting vessels, pure water, freezer packs);

n) next scheduled site visit;

o) name of on-site operator;

p) site operator comments (*e.g.,* unusual circumstances, problems, observations); and

q) actions items for the site operation (*e.g.,* repair, renewals).

The sample history form should accompany the samples to the analytical laboratory and a copy should be retained at the sampling site as a backup or as a reference.

4.8 Sample shipment to chemical analysis laboratory

All samples collected should be shipped on each site visit.

a) Secondary sample transfer should be avoided at the field site to prevent contamination and spillage.

b) The bottles used to store and transport the samples must be chemically inert and strong enough to resist breakage and leakage. The clean shipping bottles should be supplied by the central analytical laboratory in each country.

c) Sample collection bottle caps must be tightly sealed to prevent leaks.

d) Consideration should be given to enclosing the sample bottles in bags during transport.

e) It is very important that the samples not be exposed to the high temperature during shipping. The most common methods for satisfying the above restrictions are:

     i. minimizing the shipping time (*e.g.,* by using overnight transportation services); and

    ii. cooling the samples during transport (*e.g.,* by using insulated shipping containers with freezer packs).

Recorder charts should be submitted to the laboratory along with the samples and sample history forms even if the data is electronically submitted.

5. Laboratory preservation

5.1 Introduction

This section will describe considerations for preparing the sample vessel from both a field and laboratory perspective. Effective communications between the laboratory and the field site will help determine the most effective approach.

The cleanliness and handling of the sampler collection vessel are important aspects of sample quality.   It is recommended that the sample vessel be maintained and cleaned under controlled conditions. Some sites may not have the infrastructure and pure water available that are required to ensure clean sampling vessels are used to collect each sample.   There are issues associated with cleaning the vessel on-site as well as transporting it to a central facility.

5.2 Cleaning and preparation of the sample collection vessel

The collection vessels (buckets and bottles) must be cleaned before the start of each sampling period.   The most effective approach would be to clean the vessels at each field site.   On-site preparation removes transportation issues such as delays, contamination, damage and cost.

When rinsing the vessel with sufficient amount of pure water and drying it under clean conditions are not possible these tasks should be performed in the laboratory. Logistics will dictate how often a sample vessel is shipped to the laboratory for thorough cleaning.

Thorough cleaning of buckets and bottles in the laboratory require soaking for 48 hours in laboratory detergent and then rinsing with potable water followed by doubly distilled or pure water.   The final bucket rinse should undergo an electric conductivity check (<0.15 mS m^{-1}) to ensure the vessel meets EANET standards.

5.3   Transport of the collection vessel to the collector

Each vessel should undergo a leak check before being prepared for shipment to sampling site.   The collection vessel must be capped and/or enclosed in plastic bags for transport to the precipitation collector.

References (Chapter 1-5)

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6.   Chemical Analysis

6.1   Introduction

The chemical analysis of the precipitation samples is a critical step in the determination of the wet precipitation component of the total atmospheric acid deposition within EANET.   The concentrations of the chemical constituents of precipitation are frequently low and can challenge the technical limits of the laboratory's analytical instrumentation.   It is critically important that each laboratory have detailed SOPs with strict QA/QC procedures (see Appendix 1). The laboratory SOPs should cover all details from glassware cleaning and calibration standard preparation to instrument analysis techniques.

EANET requires each laboratory to determine electric conductivity, pH, and the concentration of major ions including sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium ions (Ca^{2+}) for each precipitation samples. The concentrations of these ions are often near the detection limit of commercially available instrumentation. Analytical methodology and associated instrumentation need to be selected taking the detection limits into consideration. All EANET laboratories should be selecting analytical methods and equipment in a manner that ensures consistently high data quality. Consideration should be given to the followings.

a) Confidence in data quality is significantly improved when Standard Reference Materials (SRMs) are included in the analytical sample stream. SRMs are commercially available for known concentrations of major ions (*e.g.*, NIST SRM 2694, Simulated Rainfall), or can be provided by the Network Center of EANET.

b) A duplicate sample analysis program is also recommended (1 in every 10 or 1 in every 20 samples).

c) Ion balance (R1) is an effective tool and reviewing the ion balance for each sample will improve the overall data quality. Failure to meet the laboratories ion balance quality objects should result in the re-analysis of the sample in question. When a systematic imbalance between cation and anion sums at individual sites or within the network is apparent, consideration should be given to adding additional ions to the sample analysis to resolve the imbalance. The potential candidate ions include: hydrogen carbonate (HCO_3^-), fluoride (F^-), bromide (Br^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), and organic ions like formate ($HCOO^-$), acetate (CH_3COO^-), and oxalate ions ($(COO^-)_2$. Specifically, imbalance for high pH samples may be due to unmeasured HCO_3^- which composes a significant fraction of the anion sum. Ionic species such as aluminum, mercury, and heavy metals could be significant components of precipitation chemistry in some regions. If this is the case the analysis should be extended to those species on a routine basis.

d) Similar consideration should be given to conductivity balance (R2) as with ion balance.

e) Potential analytical methods are summarized in Table 1.

Table 1   Analytical techniques used in the analysis of ions in precipitation

Analyte	Analytical Techniques
Electric conductivity	Conductivity cell
pH	Glass electrode
Chloride, Nitrate, Sulfate,	Ion chromatography, Spectrophotometry
Ammonium	Ion chromatography, Spectrophotometry (Indophenol blue)*
Sodium, Potassium, Calcium, Magnesium ions	Ion chromatography, Atomic absorption/ Emission spectrometry
Hydrogencarbonate	Ion chromatography, Alkalinity method, HPLC
Nitrite, Fluoride, Phosphate	Ion chromatography, Spectrophotometry
Organic Acids	Ion chromatography
Heavy Metals, Aluminum	Atomic absorption spectrometry with graphite furnace, ICP, ICP/MS
Mercury	Atomic absorption spectrometry with graphite furnace, ICP, ICP/MS, Mercury analyzer with a gold trap

* An alternate analysis method should be used if thymol has been used as a biocide during sample collection.

6.2 Quality of chemicals and water

The quality of chemical reagents and water are very important for chemical analysis. Contaminates in the water and reagents used to make stock solutions will impact how those solutions are used.   High purity chemicals and ultra-pure water should be used to prevent possible contamination.   It is important that all reagents and materials be tested and apparatus checked before they are used to analyze samples.

6.2.1 Purity of chemicals

a)   All chemicals used should be a minimum of reagent grade.   All reagents must be of recognized analytical grade and conform to the specifications of the international standards on analytical reagents such as the American Chemical Society (ACS).   For example:

Chemicals used to prepare an Ion Chromatography eluent solution

Cation: Sulfuric acid 96% M = 96.06 g mol^{-1}

Merck ultra pure grade

Anion: Potassium Hydroxide Cartridge

Archemica International Co.,Ltd,

Commercial standard stock solutions should be traceable to a SRM from international standard bureaus such as the U.S. National Institute of Standards and Technology (NIST)

b) Standard stock solutions used for cation and anion analysis should be high purity and traceable. The chemical grade and traceability must be documented by the manufacturer.

6.2.2 Purity of water

A reliable and consistent source of water, free from contaminates is essential for laboratory analytical chemistry work. The minimum grade of water (referred to as pure water for the purposes of this manual) used in the laboratory for analytical work should have a conductivity of less than 0.15 mS m^{-1}. Many analytical applications require water that is Ultra-pure. IC is particularity susceptible to the use of contaminated water and can easily have a negative impact on eluent, working standards used in the preparation of calibration curves and all system blank checks. Ultra-pure water is defined as having a resistance greater or equal to 18.2 MΩ cm^{-1} (conductivity of 0.055 μS cm^{-1}). Purified laboratory water should meet or exceed the standard set out by the American Society for Testing and Materials (ASTM) of U.S. specification D1193, Type II (14.4).

Laboratory pure or ultra- pure water samples should be routinely analyzed by each analytical method in use in the laboratory and all relevant contaminates routinely charted and reported. Spikes or increases in target compounds require immediate investigation and likely replacement of water purification components.

Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and intra-laboratory quality control check solutions.

As mentioned above "pure water" in this document is defined purified water where the electric conductivity is less than 0.15 mS m^{-1}.   The degree of the purification increases as follows: (1) distillation after deionization, (2) deionization after distillation, (3) deionization after deionization and distillation where detailed techniques of distillation and deionization are different from the degree of purification.   It should be noted that the water purification for dissolved-organic-compound analysis should not end with ion-exchange process.

6.2.3 Laboratory sample handling

The concentrations of target analytes in wet deposition samples are normally low and often near the detection limit of the analytical equipment.   Laboratories must take extraordinary care with these samples to preserve the integrity of samples once they arrive at the laboratory facility.   Laboratory facilities must be free from external sources of contamination:

   a) Laboratory windows should be kept closed at all times and any air leaks sealed to minimize the introduction of external sources of gases and particulates that may contaminate the samples.

   b) Samples should always be capped or covered prior to analysis.

   c) The room temperature of the laboratory should constant. It should be within ±3 °C to minimize Ion chromatography baseline drift and detector response.

   d) Chemical analyses should be completed as soon as possible.   Each laboratory should set a deadline for analyses. Normally samples must be analyzed in 7-10 days.

   e) Samples should be refrigerated at all times and aliquots removed for analyses. The dissolution of particulate materials and the presence of microbial activity will affect the stability of ionic species in wet deposition samples.   This instability generally results in increased concentration of magnesium, calcium, sodium, and potassium and decreased ammonium concentrations.   Refrigeration will retard but not prevent changes in the concentration of these species.   Filtration is effective at stabilizing magnesium, calcium, sodium, and potassium concentrations that are influenced by the dissolution of alkaline particulate matter.

*Priority of chemical analysis

When samples reach the laboratory the sample collection document (Refer to Section

4.7) accompanying each sample should be reviewed carefully to understand the general history of the sample.   Samples must be collated with the shipping list, and priority of analysis assigned.

The flow chart in Figure 1 outlines the process which is required to determine whether samples have sufficient volume to be handled in a routine manner by the laboratory.

```
┌─────────────────────────────────────┐
│              In Lab                  │
│   Prepare clean sampling bottles and │
│      measure weight of the bottles.  │
└─────────────────────────────────────┘
                  │
                  ▼
┌─────────────────────────────────────┐
│             On Site                  │
│  Collect precipitation sample and    │
│  record amount from                  │
│  the standard rain gauge.            │
└─────────────────────────────────────┘
                  │
                  ▼
┌─────────────────────────────────────┐
│              In Lab                  │
│  Weigh the wet deposition sample (g) │
└─────────────────────────────────────┘
                  │
                  ▼
┌─────────────────────────────────────┐
│   Sufficient sample amount for       │
│   measurement of all items           │
└─────────────────────────────────────┘
```

Yes   **No**

Do not filter →Measure EC→Determine pH

Filtrate→Refrigerate at 4°C→Measure ions

(a) After EC and pH measurement, remaining sample volume
    is not sufficient for ions analysis

Do not filter→Measure EC→Measure pH

Filter→Refrigerate at 4°C→Dilute 2-10 times→Measure ions

(b) Not sufficient volume for EC, pH and ion measurement

Filter→Refrigerate→Dilute 2-10 times→Measure ions

The order of measurement priority
    (1) SO_4^{2-}, NO_3^- and Cl^- by IC
    (2) NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+} by IC, when a cation column is available
    (3) If not, NH_4^+ by spectrophotometry
   (4) Na^+, K^+, Ca^{2+} and Mg^{2+} by AAS

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

Priority of analysis is normally based on sample volume (determined in Figure 1, Yes or

No).   If the sample volume is sufficient, electric conductivity, and pH should be determined and then the sample should be filtered using a clean 0.45 μm-pore membrane filter as described below:

a) Each of the filters is carefully pre-cleaned with pure water prior use to reduce contaminants contained in the filter.   The filtrate is then discarded.

b) One to two milliliters of the sample is passed through the filter to ensure that the remaining water from step one is removed.   The filtrate is then discarded.

c) A predetermined amount of sample is then passed through the filter and the filtrate is sealed and stored at 4 °C for chemical analysis.

When sample volume is insufficient for routine handling or when the concentration of an analyte exceeds the range acceptable for the laboratory method (higher than the quantification limit), the sample should be diluted with pure water prior to analysis (or re-analysis).   Any contaminates in the water used to dilute the sample could impact the concentration of the analytes and the purity of water must be evaluated before the dilution.   Analytical results from diluted samples must be flagged when the data is reported.

For the analysis of insufficient amount sample EANET recommends the procedure shown in Figure 1.   An aliquot (*e.g.,* 5mL) is diluted with pure water to an appropriate (pre-determined) amount and then:

a) determine sulfate, nitrate and chloride ions, by ion chromatography;

b) determine ammonium, sodium, potassium, calcium and magnesium ions by ion chromatography when a cation column is available; or

c) ammonium ion by spectrophotometry; and

d) sodium, calcium, magnesium and potassium by atomic absorption spectrometry.

Never determine electric conductivity and pH on diluted samples.

As mentioned above, sample dilution can be used to reduce the concentration of the analtyes exceeding the range of the analytical technique as the followings.

a. An aliquot of sample (*e.g.*, 10 mL) is taken in calibrated volumetric flask.

b. Pure water is added.   The amount is dependent on the size of the volumetric flask (e.g. 40 mL is added to a 10 mL sample when using a 50 mL volumetric).

c. The quality of the pure water used to dilute the sample should be evaluated in advance and taken into consideration.

d. Sample dilution can be accomplished gravimetrically.

i. weigh a clean bottle and tare (zero) the analytical balance.
ii. add the small volume sample into the clean bottle and record the weight (the density of rain water and pure water is approximately 1.0 g mL^{-1} at 20 ^{o}C).
iii. add a sufficient amount of pure water to accomplish the required dilution. The dilution factor can be determined using the original sample weight and the final weight.

*Cleaning of laboratory plastic ware and glass ware

Cleaning of the laboratory ware, sample storage bottle, and sample handling container used for instrumental analysis plays a critical role in the quality control of the chemical analysis. Sample storage and handling containers can be made from plastic and glass and can be used for short term storage, sample dilution or as sample handing containers which are part of the laboratory's analytical instrument auto-samplers. All glass and plastic ware must be ultra-clean. Both the interior and exterior must be cleaned:

a) When there is any possibility that any items may have been contaminated with any type of materials, they should be rinsed with diluted nitric acid and then rinsed with pure water. Care must be taken not to contaminate the laboratory with nitric acid or any other cleaning material.

b) They should be cleaned with commercially available special purpose laboratory detergent. Detergent intended for home use can be used but it is not recommended.

c) A soft sponge type scrubbing brush could be applied to plastic ware or containers to avoid damaging the surface as the damaged surfaces could collect debris and retain some rinsing water.

d) Once the ware, bottle, and container are cleaned with detergent they should be repeatedly rinsed with tap water followed by a minimum of two rinses with pure water.

e) They should be dried in a clean laboratory at room temperature and should never be wiped or pre-dried with any material. The drying time can be reduced by rinsing with reagent grade ethyl alcohol but this method is not recommended.

f) Sample storage bottles should be filled with pure water and left overnight before drying and use.

g) A subset of cleaned bottles should act as a control and an aliquot of pure water stored in the bottles should be analyzed before they are used.

6.3 Electric conductivity

6.3.1 Background

The determination of electric conductivity is a basic analytical procedure. Conductivity provides information that is very helpful in:

    a) assessing electro-neutrality;
    b) estimating ionic concentration levels of samples;
    c) for overall data quality; and
    d) an important quick check of reagent water quality.

The precision and accuracy of this type of measurement are strongly dependent upon operator expertise and the age of conductivity cell used (Noguchi et al., 1997).

The electric conductivity of a solution is the reciprocal value of its resistance and can be directly measured by using a conductivity bridge with a measuring cell.   The conductivity varies with the solution temperature and is proportional to the concentration and the species of free ions present in the solution.   Since the electric conductivity also depends on the electrode areas and heir spacing, the measuring apparatus must be calibrated to obtain the cell constant or to adjust the instrument.   A KC1 solution of a known concentration and electric conductivity is used for calibration.

Electric conductivity is expressed in units of mS m^{-1} after correction to 25 ^{o}C.   The common range of electric conductivity for precipitation samples is from <0.5 to 100 mS m^{-1}.

If the sample volume is too small for the entire chemical analysis, the aliquot after conductivity measurement can be utilized for pH determination.   Don't measure conductivity after pH determination to avoid error caused by salt contamination from pH electrode.

6.3.2 Apparatus and equipment

    a) The conductivity-bridge and cell system must have a sufficiently broad working range of at least 0.1-100 mS m^{-1}.   The precision and accuracy of the

conductivity meter must be within ±0.5 % and ±1 % of the determination range, respectively.

b) Platinum conductivity cell

c) Thermometer

d) A water bath of 25°C temperature is recommended. When using a constant temperature bath it is important to check the bath temperature. If the electric conductivity meter has a temperature correction function it is important to confirm manually that the system is working correctly. If a temperature-controlled water bath is not available keep the temperature constant by using a water bath containing at least 5 L of water.

e) A plastic or glass ware vessel appropriately sized to accommodate the diameter of the cell is used.

6.3.3 Reagent solutions and consumable materials

a) Stock standard solution A, 0.1 M -KC1 - 7.456 g of pre-dried (2 h at 105 $^{\circ}$C) KC1 dissolved in pure water, and diluted to 1000 mL at 25 $^{\circ}$C with pure water.

b) Stock standard solution B, 0.01 M -KC1 -10 mL of 0.1M -KC1, dilute to the mark of 100 mL at 25 $^{\circ}$C with pure water.

The conductivity solutions must be freshly prepared for each set of analysis. If the preparation of fresh solutions isn't possible, single use high concentration stock solutions can be stored in a small volume air-tight test container and refrigerated until diluted for use.

6.3.4 Calibration

Calibration of the electric conductivity meter should be done with standard solutions of three different concentrations: 0.0001M-, 0.0005M-, and 0.001M- KC1 solutions. The solutions of these concentrations are prepared by diluting a 0.01 M-KCl stock solution with pure water. The purity of the pure water must be confirmed by measuring its electric conductivity. The electric conductivity of the KCl solutions of known concentrations (Table 2) must be plotted as a function of the KCl concentration confirms linearity of the concentration range from which the concentrations of the samples can be read.

The storage solution is drained out of the cell and rinsed with pure water before calibration.   The purity of "pure water" and potential contaminations of the cell will be evaluated by measuring electric conductivity of freshly purified water.   If the cell constant changes the electric conductivity measurement of the pure water and standard series should be repeated until the cell constant is stable.

Table 2   Electric conductivity of KC1 solution at 25 $^\circ$C

Concentration (M)	Electric conductivity (mS m^{-1})
0.0001	1.494
0.0005	7.390
0.001	14.700

An example of an electric conductivity meter calibration procedure SOP is described below.

(1) Preparation
   a.   Rinse the conductivity cell with fresh pure water.
   b.   Turn on the conductivity meter. The conductivity meter should read less than 0.05 mS m^{-1}.

(2) Calibration

   a. Raise the conductivity cell from the pure water and rinse the cell with pure water. Ensure the hole in the cell is well rinsed.
   b. Dip the cell in the span-solution (0.001M KCl: 14.7 mS m^{-1}) contained in a small vessel. Dip and lift the cell several times in the span-solution to ensure it is effectively rinsed.
   c. Discard the span-solution and refill the container with fresh span-solution.   Dip the cell in the span-solution. Ensure you re-seal the span solution bottle.
   d. Leave the system until the solution temperature is 25 $^\circ$C.   Raise and dip the cell several times.
   e. Record the temperature of the span solution.
   f. Select the unit of mS m^{-1} on the electric conductivity meter.   Record the conductivity in the correct numerical format.
   g. Rinse the cell with a stream of pure water from a squeeze bottle or rinse the cell by moving it up and down in a beaker filled with a sufficient amount of pure

water.

h. Confirm the conductivity of the rinse water reads less than 0.05 mS m^{-1}. Repeat step 7 until the cell reads less than 0.05 mS m^{-1}. Repeat steps 2 to 8 for all standards.

i. Ensure the cell remains in the beaker full of fresh pure water until you start measuring the conductivity of the samples.

6.3.5 Measurement procedure

The laboratory should follow the directions set out by the manufacturer of conductivity cell that is being used. The meter that the conductivity cell is connected to is normally designed to take measurements at 25 ^{o}C.   A temperature-controlled water bath can be used to ensure the sample being tested is maintained at the reference temperature.   If a constant temperature water bath is not used, the temperature of the samples and standards should be the same or close as possible.   Record the temperature reading of each sample and standard immediately after the electric conductivity measurement reading is recorded.

To ensure that there is no carry over or contamination between samples, the conductivity cell must be repeatedly rinsed with pure water after each measurement aliquot.   After rinsing, the remaining pure water is removed by shaking the cell.   If the cell will not to be immediately used ensure it is immersed in pure water ready for the next measurement.

When a sample volume is sufficient for conventional electric conductivity measurement, a portion of the sample is poured into a vessel and used to rinse the cell immediately before the conductivity measurement of the sample.   The same solution may be used as a rinse for the pH cell before the pH determination for that sample.

The electric conductivity should be determined to at least 0.01 mS m^{-1}.   If the temperature of the cell is different from 25 ^{o}C, the measurement should be corrected to 25 ^{o}C (Table 3).

Table 3   Electric conductivity of 0.0005M KC1

Temperature (^{o}C)	Electric conductivity (mS m^{-1})
20	6.68

21	6.82
22	6.95
23	7.10
24	7.24
25	7.39
26	7.54
27	7.69
28	7.84

6.3.6 Calculation

Electric conductivity is expressed as a measurement at 25 ^{o}C.   When the measurement is made at different temperatures, the data must be corrected to 25 ^{o}C.   Most types of electric conductivity meters have a temperature-correction function.   If a correction function is not provided, the correction should be made with correction coefficients provided by the manufacturer for the type of cell and the instrument used.

6.3.7 Quality control

Measured electric conductivity can be compared to the electric conductivity calculated from ion concentration results.   Each laboratory should establish data quality objectives for conductivity that can be used for quality control purposes.   Measurement and charting of intra-laboratory control solutions and SRM's should be part of the routine analytical procedures.   Participation in Inter-laboratory comparisons and duplicate analysis are effective measures for controlling data quality of electric conductivity.   Detailed Quality Control procedures are described in Chapter 7.

6.4 pH measurement

6.4.1 Background

pH is commonly used to represent precipitation acidity but plays a limited role in the evaluation of precipitation chemistry.   While pH uses simple equipment and is not technically challenging it is difficult to apply the same high data quality objects to this measurement as are used for other precipitation chemistry analytes.   The precision and accuracy of the pH measurement are dependent on many factors including the aging of

the electrode and the experience of the operator and challenged by its logarithmic scale.
（Noguchi et al., 1997）.

pH's logarithmic scale reflect changes from pH3.0 to pH7.5 corresponding with concentration of hydrogen ion, H^+ decreases from 1000 μmol L^{-1} to <0.1 μmol L^{-1}. The pH is defined as the free acidity in the form of its negative logarithm: pH = -log $[H^+]$, where $[H^+]$ is the concentration of free hydrogen ion with the unit of mol L^{-1}. The pH is determined electrometrically by using a standard pH meter with a glass $[H^+]$ electrode in combination with a reference electrode. The glass electrode potential varies as the activity of H^+ ion in solution.

Within EANET pH is reported at 25 ^{o}C. pH is strongly dependent on temperature. Temperature dependent discrepancies can be avoided by applying the temperature compensation function that is provided with most types of pH meters. When a temperature control system is not available, the potential errors could be minimized by measuring both the pH standard solutions and samples at a common temperature. The temperature for the measurement should be clearly documented.

6.4.2 Apparatus and equipment

pH meters are commercially available with varying specifications and options.
   a) A pH meter should have both an intercept and slope adjustment and should be capable of measuring to ±0.01 pH unit.
   b) Combination electrodes with both measuring and reference functions are preferable since they require less sample volume.
      i. One electrode should be a measuring glass electrode sensitive to hydrogen ions.
      ii. The second will be a reference electrode and is often composed of calomel or silver/silver chloride; other reference electrodes can also be used if a constant potential is provided.
   c) When not in use the pH electrode should be stored in an appropriate solution: a 7.4-mS m^{-1} KCl standard solution, 0.1 mM sulfuric acid, or the filling solution for the pH electrode. While pure water can be used for short periods it is not recommended as the electrode can be seriously damaged by algae growth common in warm climates. The electrode should be repeatedly rinsed with pure water prior to use.

One of the major problems that occur with pH measurements is the aging of the electrode:

a) Reference solutions, with a known pH and electric conductivity similar to precipitation samples should be used for checking the viability of the pH electrode.

b) Reference solutions should be refrigerated when not in use and replaced when solution pH or electric conductivity are seen to have changed:

    i. If the pH of the reference sample has changed from the previous measurement by more than 0.10 pH unit but electric conductivity has not changed, the electrode should be checked.

    ii. The measured value should be within ±0.02 pH units of the expected value. If large differences are observed, a new solution must be prepared from a concentrated calibration solution (commercially available standard reference materials). If electrode performance is still inadequate, the electrode must be replaced.

    iii. If possible, check the pH calibration with a series of dilute mineral acids (e.g., pH 4.0, 4.2, 4.4, 4.6, 4.8, 5.0 with HCl) once a month is recommended. For the preparation of these solutions, dilute 10, 6.3, 4.0, 2.5, 1.6, and 1.0 mL of 10^{-3} mol L^{-1} HCl solution to 100 mL with pure water, respectively.

6.4.3 Reagent solutions and consumable materials

Traceable commercially available primary standard buffer solutions:

a) pH 4.01 buffer solution
b) pH 6.86 buffer solution
c) pH 9.18 buffer solution

6.4.4 Calibration

The pH meter should be calibrated using a minimum of two points in the expected pH range before the measurement of each set of samples. pH 4.01 and 6.86 buffer solutions are normally used with precipitation chemistry samples (pH value of rain is normally in the range of 3.0 - 7.5).

a. In preparation for the calibration of the pH meter and electrode, charge the electrode with a filling solution supplied by the manufacturer and then rinse it carefully with pure water.

b. Using the pH 6.86 solution, set the intercept of the pH response by adjusting the standardization knob

c. Use the pH 4.01 solution to adjust the slope control of the pH response and the temperature function control.

d. Ensure the measured pH is within ±0.02 pH unit of the buffer value.

e. Rinse the electrode thoroughly with pure water after each calibration. It is very important to rinse thoroughly because precipitation samples are much more dilute than buffer solutions. Poor rinsing often causes errors. pH values should only be measured after the excess amounts of standard buffer solution are removed. Another option would be to use special low-ionic strength buffers and ionic strength adjustment solutions.

Confirmation of electromotive force value can be effective to evaluate the condition of the pH electrode.

An example of SOP for calibration procedures of a pH meter is described as below.

(1) Preparation

a. Remove the side cap (or sleeve) from the fill-hole of the electrode.
b. Rinse the electrode with fresh pure water.

(2) Calibration

a. Raise the electrode from the pure water.
b. Put the electrode into a small bottle filled in the pH6.86 solution.
   i. Dip and lift the electrode several times to rinse the electrode with the solution.
   ii. Discard the rinse solution and refill the small bottle with fresh pH6.86 solution.
c. Place the electrode back in the bottle and leave for one minute.
d. Ensure the meter is set to pH.
e. Initiate the calibration point by pressing the CAL button.

f.   Confirm the calibration.

g.   Select the "mv" channel and measure electromotive force. Confirm that the meter reads near "0 mv".

h.   Select pH.

i.   Raise the electrode and rinse it with pure water, especially the pin hole.

j.   Secure the working solution of pH 6.86 solution by closing the cap of the small bottle.

k.   Repeat steps (b.) to (f.) using the pH 4.01 buffer solution.

l.   Select the "mv" channel and measure electromotive force. Change the electrode or perform preventative maintenance of the electrode if the change in electromotive force value (from pH 6.86) is less than160 mv.

m.   Select pH.

n.   Raise the electrode and rinse it with pure water, especially pin hole.

o.   Secure the working solution of pH 4.01 solution by closing the cap of the small bottle.

p.   Insert the electrode is into the small bottle containing the pH6.86 buffer solution.

   i. Dip and lift the electrode several times to rinse the electrode with the solution.

   ii. Discard the rinse solution and refill the small bottle with fresh pH6.86 solution.

   iii. Dip and lift the electrode several times to rinse the electrode with the solution.

q.   Allow the meter to stabilize for one minute.   Confirm that pH value has not changed (*e.g.*, 6.86).

r.   Re-start again from (e.) if the pH value changed.

s.   Ensure the meter is set to pH.

t.   Initiate the calibration point by pressing the CAL button.

u.   Confirm the calibration.

v.   Select the "mv" channel and measure electromotive force. The electromotive force value and water temperature should be record.

w.   Select the meter channel back to pH.

x.   Raise the electrode and rinse it with pure water, especially the pin hole.

y.   Secure the working solution of pH 6.86 solution by closing the cap of the small bottle.

z.   Leave the electrode in the beaker full of fresh pure water until the pH

measurement of samples.

Note)
Plastic bottles should be used for dispensed standard buffer solutions because the electrode has to be dipped and lifted several times in the solution. Glass electrodes may break easily when glass vessels are used.

6.4.5   Measurement procedure

a. Calibrate the pH meter according to the procedure outlined in the previous section.
b. Place sufficient sample solution in a clean plastic or glass vessel to ensure that the sensing elements of the electrode are immersed.
c. Ensure the samples are kept at 25 ^{o}C in a water bath or ensure that the temperature of samples is the same as the temperature of standard buffer solutions. Record the temperature of all measurements not made using a constant temperature bath.
d. Rinse the electrode with excess amounts of each sample.
e. Wipe drops off the electrode with filter paper.
f. Immerse the electrode in the sample vessel and swirl the sample gently for a few seconds.
g. Allow the electrode to equilibrate for a few minutes and measure the pH of the sample until a constant value is obtained. Record the pH value and the temperature of the sample.

6.4.6   Calculation

The hydrogen ion concentration can be calculated using the following equation.

$$H^+ (\mu mol\ L^{-1}) = 10^{\ (6 - pH)}$$

6.4.7   Quality Control

The quality of measured pH can be assessed by:
   a) checking the condition of the electrode by measuring electromotive force (normally designated as mv on your pH meter);

The difference in electromotive force between pH 7 and pH 4 should be approximately 170 mv. When the difference of electromotive force value is lower 160mv the electrode should be changed or refurbished (change the solution etc.).

b) comparing electric conductivity and pH (especially in low pH and low conductivity samples);

The electric conductivity of hydrogen ion is calculated using the following equation.

$$\Lambda_{H+} = 349.7 \times 10^{(6-pH)}$$

The minimum molar conductivity Λ ($mS\ m^{-1}$) calculated using the H^+ concentration should be:

e.g.,   pH3: $\Lambda > 35 mS\ m^{-1}$ pH3.5: $\Lambda > 11.1\ mS\ m^{-1}$

pH4: $\Lambda > 3.5\ mS\ m^{-1}$ pH4.5: $\Lambda > 1.1\ mS\ m^{-1}$

c) reviewing ion and conductivity balances;

Please refer to section 7.2.6.

d) obtaining SRM and determining the pH of those references;

e) participation in Inter-laboratory comparison studies; and

f) performing and assessing duplicate sample analysis.

6.5 Anion determination by ion chromatography

6.5.1 Background

Ion chromatography is widely used to analyze anions in precipitation. Sulfate, nitrate, and chloride in precipitation separate on an ion exchange column due to the different affinities of the ions for the exchange material. The material commonly used for anion separation is a polymer coated with quaternary ammonium active sites. After separation, the anions pass through a strong acid cation exchange column (suppressor column) which exchanges all cations for H^+ ions by using an electrolytic suppresser. Chloride, nitrate and sulfate are detected as acids by a conductivity detector. Both isocratic and gradient methods are available for Ion Chromatographic analyses. A typical chromatogram from an isochractic analysis is shown in Fig. 2.

Any anions with a retention times similar to the target anions could co-elute and interfere. For example use of the anion-analysis column series IonPac anion guard

AG12A and separator column AS12A results in the nitrite (NO_2^-) ion eluting after the chloride (Cl^-) which elutes after the fluoride (F^-).   See Figure 2).

The ranges of measured anion concentrations in precipitation and their recommended minimum detectable amounts are shown in Table 4.

Table 4 Measured anion concentration in precipitation and recommended Minimum Detectable Amount (MDA)

| Anion	Range ($\mu mol\ L^{-1}$)	MDA ($\mu mol\ L^{-1}$)
SO_4^{2-}	<1 – 200	1
NO_3^-	<2 – 300	1
Cl^-	<1 – 1000	1
HCO_3^-	<50-1000	25
NO_2^-	<0.2 – 10	0.2
PO_4^{3-}	<0.1 – 3	0.1
F^-	<1 – 30	1
Br^-	<0.1 – 6	0.1
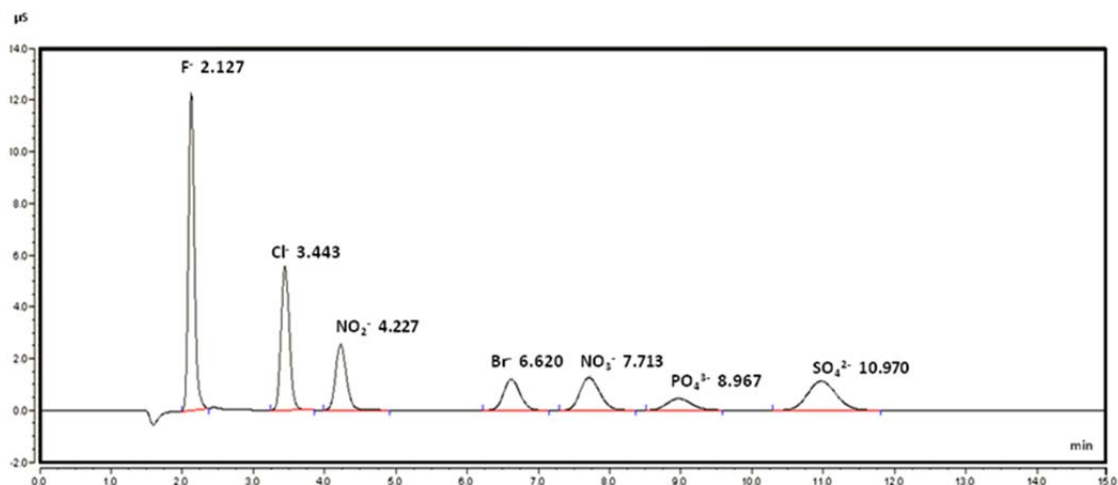
Fig. 2 Typical chromatogram of anions

6.5.2 Apparatus and equipment

a) Ion chromatography system (example 1: Dx500, example 2: ICS-2000) with a conductivity detector.   The Dx500 does not have an eluent generation (EG)

system. The ICS-2000 has an eluent generator that produces eluent from a concentrate contained in a cartridge.

b) Anion guard and separator columns: (example 1: IonPac anion guard AG14A with anion separator AS14A or AG4A-SC with AS4A-SC, example 2: IonPac AG17 with AS17)

c) Anion suppressor: (example 1: ASRS-II, example 2: ASRS-300)

d) Integrator or associated integration software for consistent interpretation of chromatographs

6.5.3 Reagent solutions and consumable materials

Calibration procedures for instruments are addressed with two examples.

(1) Example 1: Dx500 with no eluent generator

a) Concentrated eluent/stock solution: 0.40 M-Na_2CO_3/0.17 M-$NaHCO_3$:
   i. Dissolve 42.4 g Na_2CO_3 and 14.3 g $NaHCO_3$ in 1 liter of pure water.
   ii. Concentrated eluent 10mL aliquots may be kept refrigerated up to six months in air tight test tubes.

b) Working eluent: 4.0 mM-Na_2CO_3/ 1.7 mM-$NaHCO_3$ - :
   i. Dilute 40mL of concentrated eluent/stock solution (4 test tubes) to 4 liters with pure water.

c) Chemical suppressor regenerant solution: 50 mM-H_2SO_4.
   Dilute previously prepared 5M-H_2SO_4 accordingly. If an anion self-regenerating suppressor (ASRS) is employed in the recycle mode for chemical suppression, regenerant is not required, use eluent only.

d) Auto suppressors used in external water mode only require pure water. This method greatly extends the life of the suppressor. The suppressor normally requires 200-300 mA.

e) Concentrated mixed stock standard solutions are prepared from a 1000 mg L^{-1} of each chemical species (these solutions are commercially available, otherwise prepare from mixed high purity reagents). All ionic species may be prepared in the same calibrated volumetric flask creating one concentrated solution with all chemical species -$e.g.$, SO_4^{2-} & Cl^-: 200 mg L^{-1}, NO_3^-: 100 mg L^{-1}, F^- : 50mg L^{-1}

f) High concentrated standard solutions are prepared from the concentrated mixed stock standard solution by diluting with pure water.

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g) Working standard solutions are prepared from each high concentration standard solution by diluting with pure water.   Five standard solutions are normally required.   The lowest concentration standard solution can be used for the test of precision (*e.g*., LWL calculation).

h) If a set of analysis runs for a specific sample, pure water should be injected as a blank before the first injection of another sample or after injecting high concentration samples.   Concentration levels are easily estimated with conductivity measurements.

i) When a sample aliquot is to be transferred to a vessel, the vessel should be rinsed in advance with the solution to be measured.   A specific vessel is used repeatedly for a standard solution only on the day.

j) Using a series of analyses of the calibration standards mentioned above, produce a calibration curve on the milligram per liter concentration scale, mg L^{-1}.   One should note that the calibration curve is made to four significant figures throughout the analysis.   The numerical values thus obtained for ionic sample concentrations should be finally converted to those on the micromole per liter, μmol L^{-1}, to three significant figures by rounding the four significant figures in the mass units.

Note)

Since commercially available standard solutions have gravimetrical unit, it is convenient to prepare the standard solution series using gravimetrical units. Conversion from gravimetric units to molar units should be made at the final stage of concentration determination.   Detailed procedure for data reporting should be followed. See Chapter 8.

(2) Example 2: ICS-2000 Eluent Generation with Gradient System

a) Regent Free Ion Chromatography (RFIC) systems use eluent in a cartridge filled with concentrated KOH.   The system uses automated Eluent Generation(ER).

b) Set the flow rate to 1.0mL min^{-1}.   Start the eluent concentration at 5.0 mM-KOH.   Increase the concentration to 70mM-KOH for 17 minutes using the gradient system.   The exponential gradient rate is better than the isocratic rate because the peaks of SO_4^{2-}, NO_3^-, Cl^- and other anion (F^-, NO_2^-, PO_4^{3-} etc.) can be easily separated.

c) Pure water is used with EG systems to automatically dilute the concentrated

eluent in the cartridge into a working eluent solution.   The current setting for the chemical suppressor is approximately 150 mA when the operator is using 4mm columns.

d)   See example 1 for chemical suppressor and standard preparation details.

6.5.4   Measurement procedure

(1) Example 1: Dx500

(a) Setup and Preparation using Prepared Eluent

The eluent and stock eluent solutions containers must be emptied and cleaned before each use.   The eluent is prepared using pure high quality reagents.   Fresh dilution of a stock eluent solution is acceptable if the stock solution has been kept sealed and refrigerated since preparation.

If the stock solution was stored in a 10mL test tube, prepare a clean 2000mL volumetric flask by adding about 1600mL pure water.   Put the stock eluent aliquot into the flask and rinse the remaining eluent from the storage test tube with pure water at least three times. Fill the flask to 2000mL with pure water.

When carbonate and/or bicarbonate eluent concentration is high it is not uncommon to have problems with bubbles being generated in the eluent resulting in an unstable baseline.   To reduce this problem, degas the eluent with helium at a low flow rate. *e.g.*, 100 mL min^{-1}.

To purge the pump of bubbles prime the pump for 5 minutes.   A plastic syringe will be required to manually flush the pump with eluent and remove all of the bubbles.   The baseline should be monitored for a few hours after priming and startup.   After a stable baseline is achieved, pure water should be injected least 3 times and the resulting chromatograms checked to ensure that the system is working correctly.

A high current setting for the suppressor may be required for higher eluent settings. Keep in mind that the high current will shorten the life of the suppressor.   Refer to the manufacturer's manual and device brochures for appropriate suppressor current for varying eluent concentrations. In the case of 4.0 mM-Na_2CO_3/ 1.7 mM-$NaHCO_3$ eluent,

the recommended current is approximately 100mA.

If an automatic sampler is installed, the tubing system and the needle should be verified to be free from contamination. The supply of pure water used to rinse the sampler must also be free of contamination. One means of confirming that the rinse water meets minimum standards can be accomplished by measuring the electric conductivity of the pure water in a small beaker.

(b) Calibration and sample analysis

    a. Standards and samples are introduced into the ion chromatograph through a loop injector system.   The sample loop is usually 50 to 100 μL.

    b. The injection of calibration standards should start at the highest concentration standard, followed by standards with decreasing concentrations to prevent erroneous high values for the first sample injected after the calibration series.

    c. Each set of samples analyzed requires the analysis of a minimum of five standard solutions. Inject the calibration standards first. Pure water should be also analyzed following the standards to act as a system blank and to ensure there is no carry over from the standards. The user may determine carry over effect by examining the pure water chromatogram for contamination between the standard series and the first subsequent sample injection.   If there is little effect on sample analysis, injecting standard solution from lower to higher concentration may be acceptable.

    d. When an auto sampler is available, the vials should be rinsed with excess amounts of the sample that will be used in the vial.   When a manual syringe injection system is used the sample syringe should be also rinsed using excess amounts of the appropriate sample.

    e. Turn on the auto sampler switch to start analyzing samples.   Inject precipitation sample solution in the same manner as standard solutions.

    f. The system is checked by analyzing standard solutions of the high level concentration at least once a day. Laboratories should consider additional QC samples.

    g. When a sample concentration is higher than that of the highest standard solution, the sample is diluted and measured again.

    h. Pure water should be analyzed to clean and check the system path after high concentration samples (identified by their) high conductivity and after a change of

sample type (different site, rain or fog, etc.).

(2) Example 2 ICS-2000

(a) Setup and Preparation using a RFIC Eluent Generation

The eluent is prepared using a KOH-cartridge and pure water.   The eluent container is filled with freshly prepared pure water.   Pure water used for the auto-sampler rinse is kept in a separate 4-liter container.

Pure water must not be allowed to flow inside the column path without concentrated eluent because the pure water will not allow the ions to elute.

First prime the pump for 5 minutes.   A plastic syringe will be required to manually flush the pump with eluent and remove all of the bubbles.   The baseline should be monitored for a few hours after priming and startup.   After a stable baseline is achieved, pure water should be injected at least 3 times and those chromatograms checked to ensure the system is working properly.

A high current setting for the suppressor may be required for higher eluent settings however the high current will shorten the life of the suppressor.   Refer to the manufacturer manual and device brochures for recommended suppressor current setting according to the eluent concentration.

If an auto sampler is installed, the tubing system and the needle should be confirmed to be free from contamination.   The pure water supply used to rinse the system must also be free of contamination.   The purity of the water can be verified by measuring its electric conductivity in a small beaker.

(b) Calibration and sample analysis

See Example 1.

6.5.5   Calculation

Ion Chromatography software can be used to integrate the chromatograms however the

signal value (*e.g.*, peak area) should be confirmed for all data. If possible, the calculation of concentration should be also carried out using alternate calculation software (*e.g.*, Excel). This procedure is effective for finding some errors, peak misinterpretation, and baseline drift.

Data files should be named using unique identifiers such as the date. The file format should be the same in all cases to provide a convenient pattern for data searches. Example: "anion091002" is anion data, 2nd October 2009.

Calibration curves should be made using the standard peak areas or conductivity signals before and after every 30 samples. The calibration curve should be either a linear or quadratic fit. If the pure water signal or conductivity is high the IC maintenance (including check of contamination in sampling needle and injection valve) and subsequent reanalysis of samples should be carried out.

*Baseline Correction

a) Define the start and end points for all peaks of interest. When two peaks are connected (overlap) two types of baselines may be selected. A common baseline is applied to two peaks or the small peak is defined as a shoulder or rider peak. See Fig.3.
b) Consult the operation manual the manufacturer provided.
c) Subtract the pure water blank when a syringe filter has been used.
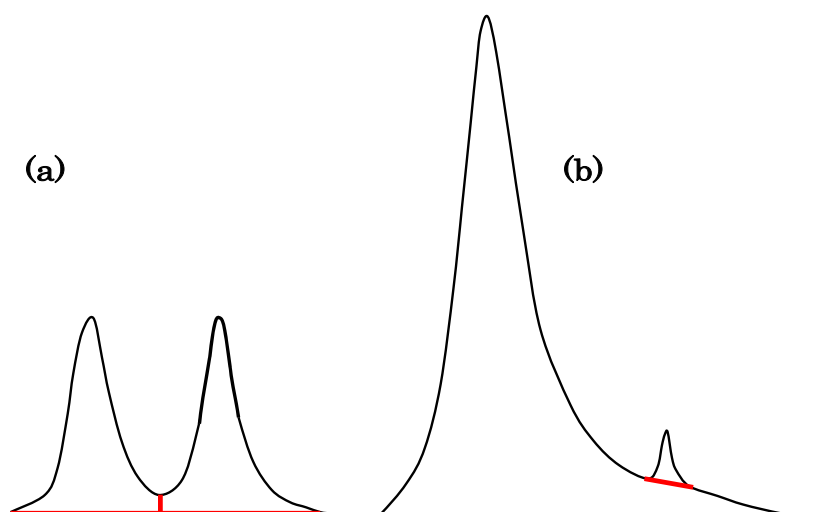

Fig. 3 Examples of baseline correction on Ion Chromatography

Other operations should be referred to the attached manual of the instrument. When a filter is applied to the syringe, the blank for pure water should be subtracted. .

6.5.6 Quality control

Quality of measured anion concentration can be controlled by the ion balance and conductivity balance check by using all mandatory ions concentrations. Periodic measurement of SRM, participation in Inter-laboratory comparison studies, and duplicate analysis are also effective for controlling data quality. Detailed procedures are described in Chapter 7.

The results of QC checks associated with ion balance or conductivity balance may be poor and result in outliers. Chemical re-analysis of the sample should be performed. If the reanalysis does not improve the ion balance or conductivity balance, the cause should be discussed and reported.

The major causes are:
    a) unmeasured peak (organic acid etc.);
    b) hydrogen carbonate ion (High pH, high concentration of Ca^{2+});
    c) low accuracy (Electric conductivity <0.2mS m^{-1}); and
    d) others.

In the case of (a) and (b), components should be analysis by the method described in the following section.

Variation of the retention time of peak is affected by the variation of eluent concentration often caused by incomplete mixing of the eluent during preparation. Shortening of retention times may be caused by aging of the columns. The signal value (peak area) of a standard solution may be affected by contamination of the flow path. The retention time and the signal value of a standard solution should be confirmed by comparing the signal value or area with that obtained in the previous analytical run.

The adsorption of anion components resulting in decreasing peak area can occur in the sampling needle, tube or injection valve.

6.6   Hydrogen Carbonate determination method

6.6.1   Background

High pH samples are often characterized by high concentration of Ca^{2+} and poor ion balance.   In some cases, the poor ion balances could be improved by the addition of hydrogen carbonate, HCO_3^- concentrations in the calculation.

Hydrogen carbonate determination was evaluated as a means to improve unacceptable ion balances.   The concentration was initially estimated based on the equilibrium between atmospheric CO_2 and dissolved hydrogen carbonate using the following equation: $[HCO_3^-]$ (neq mL^{-1}) = $1.24 \times 10^{(pH-5.35)}$ (JME, 2001; EANET, 2000a).   Using equilibrium resulted in an estimated concentration of hydrogen carbonate smaller than the imbalance (Noguchi and Hara, 2004).   Subsequently a HCO_3^- ion measurement method recommended and is described in this section.

There are a number of methods, including gradient ion chromatography, potassium chloride titration, combustion-infrared absorption photometry, and HPLC equipped with a specially developed separation column, that have been used for hydrogen carbonate determination.   EANET recommends the alkalinity method given that it is already in use for inland aquatic monitoring and most EANET laboratories have suitable methods as well as the equipment and expertise.   A gradient ion chromatography method is also acceptable as an optional.

Hydrogen carbonate is determined using a titration method of where the sample is titrated with sulfuric acid until pH 4.8 is achieved. This is commonly applied to water quality studies (EANET, 2000b).   A volume of more than 30mL of a sample needs to be available for analysis after the routine determinations are completed.   The sample is titrated with a sulfuric acid (0.005 mol L^{-1}) aqueous solution.   The concentration of HCO_3^- is calculated with the equation:

$$[HCO_3^-] = 2f*a/V + [H^+] - 15.85(V + a)/V$$

Where:
$[HCO_3^-]$ is hydrogen carbonate ion concentration (nmol mL^{-1});

f = the concentration of the added sulfuric acid (nmol mL^{-1})

a = the volume of the added sulfuric acid (mL);

V = the sample volume (mL);

[H^{+}] = the initial hydrogen ion concentration (nmol mL^{-1})

(Noguchi and Hara, 2004).

6.6.2   Apparatus and equipment

(1) Alkalinity method

    a) pH meter (See Section 6.4).

    b) Titrator or Titration devices (Magnetic stirrer, Burette 10mL, with precision lower than 0.05mL).

(2) Gradient ion chromatography method

Gradient ion chromatography method needs special equipment (*e.g.*, ICS-2000, Eluent generator system).

    a) Gradient ion chromatograph (*e.g.*, ICS-2000) with an electric conductivity detector.

    b) Anion separator column (*e.g.*, IonPac AG17 + AS17)

    c) Anion suppressor column (*e.g.*, ASRS-2)

    d) An integrator is recommended to process the chromatograms.

6.6.3   Reagent solutions and consumable materials

(1) Alkalinity method

    a) Stock solution, 0.01 M-sulfuric acid (commercially available is preferred, else prepare from concentrated solution with appropriate grade of purity)

    b) Titration solution, 0.002-0.005 M-sulfuric acid –dilute the stock solution as appropriate.

    c) Standard solution, 0.01 M-Na$_2$CO$_3$, sulfuric acid (0.005 mol L^{-1}) aqueous solution.

(2) Gradient ion chromatography method

a) The standard curve is prepared with a $NaHCO_3$ solution.

b) Air free conditions are required for analysis.

c) Fresh pure water is essential.

d) A blank check is required.

6.6.4 Measurement procedure

(1) Alkalinity method

a. Prepare:
   i. 50mL beaker;
   ii. pH6.86 and pH4.01 standard buffer solution;
   iii. sulfuric acid (0.005 mol L^{-1}) aqueous solution; and
   iv. titration devices.

b. Calibrate the pH meter using pH 4.01 and 6.86 buffer solutions.

c. Fill the burette with the titration solution.

d. Place a sufficient volume of sample (20-50 mL) in a clean glass vessel to cover the sensing elements of the electrode.

e. Rinse an electrode with pure water and wipe drops off electrode with filter paper. Immerse it in the sample vessel and gently swirl by magnetic stirrer.

f. Allow the electrode to equilibrate and measure the pH until a constant value is obtained. Record the constant pH value.

g. Titrate the sample with titration solution to the end-point of pH 4.8. Mix the sample constantly using a magnetic stirrer. Near pH 5.5, the titration solution should be added carefully drop by drop. Record the volume of added titration solution.

h. In order to have a precise volume of the added titration solution, the following steps should be taken:

   -Titrate every 0.1mL of the sulfuric acid (0.005 mol L^{-1}) aqueous solution and stir and measure pH.

   -Record value of titrated volume of the sulfuric acid (0.005 mol L^{-1}) aqueous solution when the pH value is just over pH4.8.

   - Titrated volume of the sulfuric acid = a_1mL

   - pH vales just over pH4.8= pH_1

i. Record the titrated volume of the sulfuric acid (0.005 mol L-1) aqueous solution and pH values just under pH4.8.

- Titrated volume of the sulfuric acid: a_2mL
- pH vales just under pH4.8: pH_2

(2) Gradient ion chromatography method

See Section 6.5.4, Example2.

Please ensure that bicarbonate removal devices have been removed from the IC prior to starting hydrogen carbonate analyses .

6.6.5   Calculation

(1) Alkalinity method

When $H_1 = 10^{(6-pH1)}$ and $H_2 = 10^{(6-pH2)}$,

$$a = a_1 + (a_2-a_1)/(H_2-H_1) \times (15.85-H_1)$$

$$[HCO_3^-] = 2f*a/V + [H^+] - 15.85(V + a)/V$$

where $[HCO_3^-]$: hydrogen carbonate ion concentration (μmol L^{-1})

   f: the concentration of the added sulfuric acid (μmol L^{-1});

   a: the volume of the added sulfuric acid (mL);

   V : the sample volume (mL);

   $[H^+]$: the initial hydrogen ion concentration (μmol L^{-1})

(2) Gradient ion chromatography method

See Section 6.5.5, Example2.

6.6.6   Quality control

High concentrations of HCO_3^- found in outlier samples (R_1) is normally derived from $CaCO_3$ found in soil dust.   In the case of Japanese precipitation samples affected by Asian dust, the concentration of HCO_3^- is approx. 80% of Ca^{2+} concentration (Noguchi and Hara, 2004).   The HCO_3^- concentration is normally smaller than the Ca^{2+} concentration but other ions have to be considered according to the composition of

precipitation components.

6.7 Fluoride determination method

6.7.1 Background

Fluoride species are emitted into the atmosphere from sources which include manufacturing facilities using fluoride compounds for alumina-electrolysis, fluorine-apatite processing, fluorine-compound glazing facilities.   If this kind of source is located in the vicinity of monitoring station, the collected sample would be affected by hydrogen fluoride, HF and fluoride ion concentration should be determined to evaluate the contribution of HF to the sample acidity.   If the anions are measured by ion chromatography, the fluoride ion can also be detected in the same chromatogram and determined in the same manner as the other anions.   A typical chromatogram from an isocratic analysis is shown in Fig. 2.

6.7.2 Apparatus and equipment

See Section 6.5.2.

When using chromatographic methods to determine the concentration of F^-, chloride and organic ions interfere and distort the F^- peak .   This issue is easily resolved when a gradient system with an eluent generator is used.

6.7.3 Reagent solutions and consumable materials

See Section 6.5.3.

Use of an eluent with a lowered concentration level and a decreased flow rate could enable the separation of the F^- peak from interfering peaks.   One should note that SO_4^{2-} and PO_4^{3-} ions would be trapped in the analytical column if the concentration level of the eluent is too low to elute these ions.   These ions will be removed from the column by switching to the standard eluent employed in the analysis of the major ions.   The standard stock and calibration solutions for F^- are prepared as a standard solution as F^- does not interfere with analysis of the other ions.

6.7.4 Measurement procedure

See Section 6.5.4.

6.7.5 Calculation

See Section 6.5.5.

6.7.6 Quality control

See Section 6.5.6.

Fluoride is sometimes difficult to determine because the fluoride peak appears shortly after the water dip. This species is significantly and is detected in the chromatogram frequently when the sample contains some seawater or sea salt which is associated with fluoride. Usually, however, the fluoride concentration is not sufficiently high as to influence the ion balance in terms of R_1.

6.8 Bromide determination method

6.8.1 Background

Little bromine is extracted from seawater, which contains only about 64.6 mg/kg. Much of the bromine output was used in the production of ethylene dibromide, a lead scavenger used in making gasoline antiknock compounds. Lead in gasoline, however, has been drastically reduced, due to environmental considerations. Bromine is also used in making fumigants, flameproofing agents, water purification compounds, dyes, medicinal, sanitizers, inorganic bromides for photography, etc. If those sources were identified in the vicinity of monitoring site, bromide would be measured for collected samples.

6.8.2 Apparatus and equipment

See Section 6.5.2

6.8.3 Reagent solutions and consumable materials

See Section 6.5.3

In some cases described also in 6.7.3, application of an eluent of a lower concentration level and a decreased flow rate could enable the separation of the Br- peak from interfering peaks.

6.8.4 Measurement procedure

See Section 6.5.4

6.8.5 Calculation

See Section 6.5.5

6.8.6 Quality control

See Section 6.5.6

6.9 Nitrite determination method

6.9.1 Background

Nitrite is not often found in precipitation samples under aerobic condition. Nitrite may result during storage as a result of microbe activity when precipitation samples contain significant amounts of organic materials (organic nitrogen etc.).   Nitrite may form during the winter when there are high concentrations of HONO and NO_2 in the atmosphere.   A typical chromatogram from an isocratic analysis is shown in Fig. 2.

NO_2^- can be measured using IC methods in the same manner as other major anions.

6.9.2 Apparatus and equipment

See Section 6.5.2.

NO_2^- can elute close to Cl^- under isocratic conditions. Interference issues can be easily resolved when IC gradient methods are employed.

6.9.3 Reagent solutions and consumable materials

See Section 6.5.3.

In some cases NO_2^- can be separated from Cl^- (described also in 6.7.3) by using a lower concentration eluent and a decreased flow rate. One should note that SO_4^{2-} and PO_4^{3-} ions would be trapped in the analytical column if the concentration level of the eluent is too low to elute these ions. These ions will be removed from the column by switching by to the standard eluent employed in the analysis of the major anions. Standard stock and calibration solution for NO_2^- need to be prepared individually because NO_2^- may be impact the concentration of NO_3^-. Nitrate ion concentrations should be checked in the NO_2^- standard solutions to determine if any conversion to NO_3^- has occurred.

6.9.4 Measurement procedure

See Section 6.5.4.

6.9.5 Calculation

See Section 6.5.5.

6.9.6 Quality control

See Section 6.5.6.

6.10 Phosphate determination method

6.10.1 Background

Phosphate is not normally found in precipitation samples. Phosphate may be present when the precipitation sample is contaminated with materials such as bird dropping or if there are sources in the area near the sampler. PO_4^{3-} can be directly measured by IC in

the same manner as major anion measurement. A typical chromatogram from an isocratic analysis is shown in Fig. 2.

6.10.2 Apparatus and equipment

See Section 6.5.2.

6.10.3 Reagent solutions and consumable materials

See Section 6.5.3.

A lower concentration eluent and a decreased flow rate could enable the separation of the PO_4^{3-} peak from interfering peaks. See section 6.5.3

PO_4^{3-} standard stock and calibration solution should be prepared individually. Decreased NO_3^- peaks have been observed when both NO_3^- and PO_4^{3-} are in the same standards.

6.10.4 Measurement procedure

See Section 6.5.4.

6.10.5 Calculation

See Section 6.5.5.

6.10.6 Quality control

See Section 6.5.6.

6.11 Organic acids determination method

6.11.1 Background

Acid rain is an acknowledged environmental concern. Due to the complex nature of this issue, it is important that both natural as well as anthropogenic contributions to

precipitation acidity be examined. According to the Annual Report of the National Acid Precipitation Assessment Program (1983), organic acids can play an important role in determining the free acidity of rainwater. Research by Keene and Galloway (1984) has shown that organic acids contributed 16% of the volume weighted free acidity in samples from central Virginia. In addition, they hypothesized that up to 35% of the free acidity in samples from the National Atmospheric Deposition Program (NADP) was attributable to organic acids.

Ion chromatography has been widely used in recent years to analyze for organic acids in food as well as in precipitation. The target organic acids that should considered within EANET are formate, acetate, proprionate and pyruvate. Organic anions in precipitation samples separate on an ion exchange column because of their different affinities for the exchange material. After separation, the anions pass through a strong acid cation exchange column (suppressor column) which exchanges all cations for H^+ ions or electric suppressor. Organic anions are detected as acids by the electric conductivity detector. The ion chromatograph is calibrated with standard solutions containing known concentrations of the anions of interest. Calibration curves are constructed from which the concentration of each analyte in the unknown sample is determined.

Five calibration solutions are needed to generate a suitable calibration curve. The lowest calibration solution should contain the analyte(s) of interest at a concentration slightly greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of the analyte in wet deposition. Ensure the remaining solutions are prepared in a manner such that they are evenly distributed throughout the concentration range. Prepare all calibration standards by diluting the commercially available 1000 mg L^{-1} stock standards. Use glass or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. Organic acid standards are prepared daily using 0.10 mg L^{-1} or less of each organic acid and stored at room temperature in high density polyethylene or polypropylene containers.

Tropical precipitation contains a variety of organic ions. If organic ions are not included in the analytical suite, the ion balance may not meet the ion balance criteria. If organic ions and common inorganic ions are to be determined simultaneously an IC with a gradient system will be needed to ensure there is sufficient ion resolution.

6.11.2   Apparatus and equipment

a) Ion chromatograph (*e.g.,* DIONEX ICS 3000) with a electric conductivity detector

b) Anion separator column (*e.g.,* AS 17-C 4x250 mm Analytical, AG 17-C 4x50 mm Guard)

c) Anion suppressor (*e.g.,* As RS – ULTRA II – 4 mm (ASRS 300 4 mm))

d) Auto Sampler

6.11.3   Analytical conditions

a) Mobile Phase: Eluent Cartridge Potassium Hydroxide, Pure Water

b) Flow Rate: 1.5 mL/min

c) Sample loop: 50 μL

d) Mobile Phase Run Sample at 1 mM

e) Trap Column: ATC-HC 9x75 mm

f) Anion Trap Column: CR-ATC Continuously Regenerated

6.11.4   Reagent solutions and consumable materials

a) Concentrated eluent, KOH cartridge generated by an "Eluent generator system".

b) Eluent concentration is increased from 1.0 mM-KOH to 60 mM-KOH with flow rate 1.5 mL/min (*e.g.,* 1-8 min.: 1.0 mM, 8-28 min: 1-30 mM, 28-38 min: 30-60 mM, 45-50 min: 60-1.0mM).

c) Pure water should be employed for the regenerant for a high concentration eluent .   The electric current applied to the suppressor is usually 200-300 mA.

d) Concentrated mixed stock standard solutions are prepared using 1000 mg L^{-1} solutions for each chemical species. (commercially available, otherwise prepare from mixed reagents of high purity)

e) High concentrated standard solutions are prepared from the concentrated mixed stock standard solution by diluting with pure water.

f) Working standard solutions are prepared from each high concentration standard solution by diluting with pure water. Five standard solutions are normally used. The lowest concentration standard solution can be used for the test of precision (*e.g.,* LWL calculation, and so on).

g) High concentration standards should be determined once a day if necessary. When the concentration level is significantly higher than samples, the standard is analyzed one more time after being diluted.

h) If a set of analysis runs for a specific sample, pure water should be injected as a blank before the first injection of another sample or after injecting high concentration samples. Concentration levels are easily estimated with conductivity measurements.

i) When a sample aliquot is to be transferred to a vessel, the vessel should be rinsed in advance with the solution to be measured. A specific vessel is used repeatedly for a standard solution only on the day of analysis not over multiple days.

6.11.5   Measurement procedure

See Section 6.5.4. Example2.

6.11.6   Calculation

See Section 6.5.5.

6.11.7   Quality control

See Section 6.5.6.

An isocratic method can be used to determine the concentration of organic-acids. It may be necessary to run two separate isocratic methods to resolve the organic-acids. The gradient method is strongly recommended if it is available and organic acids are not easily determined in a single isocratic chromatographic run .

6.12   Cation determination by ion chromatography

6.12.1   Background

Ion chromatography is widely used to determine the concentration of major cations in precipitation. The principle is the same as anion determination but with different column materials and a different suppressor column. Cation separation is achieved

using the active surfaces found on cation exchange resins.

Using the appropriate cation exchange columns, sodium, ammonium, potassium, calcium and magnesium ions can be detected using an electric conductivity detector under isocratic conditions (example 1: CG14 + CS14 with CSRS-II recycle suppressor, example 2: CG16 + CS16 with CSRS-300 recycle suppressor).

Any cations with a retention time similar to that of the other cations could interfere. For example, in samples with high concentration of Na^+, the peak of NH_4^+ becomes asymmetrical and often causes a significant error. In this case, measurement using more dilute eluent could improve the separation of peaks, or gradient methods may be used.

A typical chromatogram from an isocratic analysis is shown in Fig. 4.

The ranges of measured cation concentrations in precipitation and recommended minimum detectable amounts are given in Table 5.

Table 5 Measured cation concentration in precipitation and recommended Minimum Detectable Amount (MDA)

| Cation	Range ($\mu mol\ L^{-1}$)	MDA ($\mu mol\ L^{-1}$)
Na^+	<2 – 900	1
NH_4^+	<3 – 1000	1
K^+	<1 – 100	0.3
Ca^{2+}	<0.5 – 300	0.2
Mg^{2+}	<1 - 200	0.4
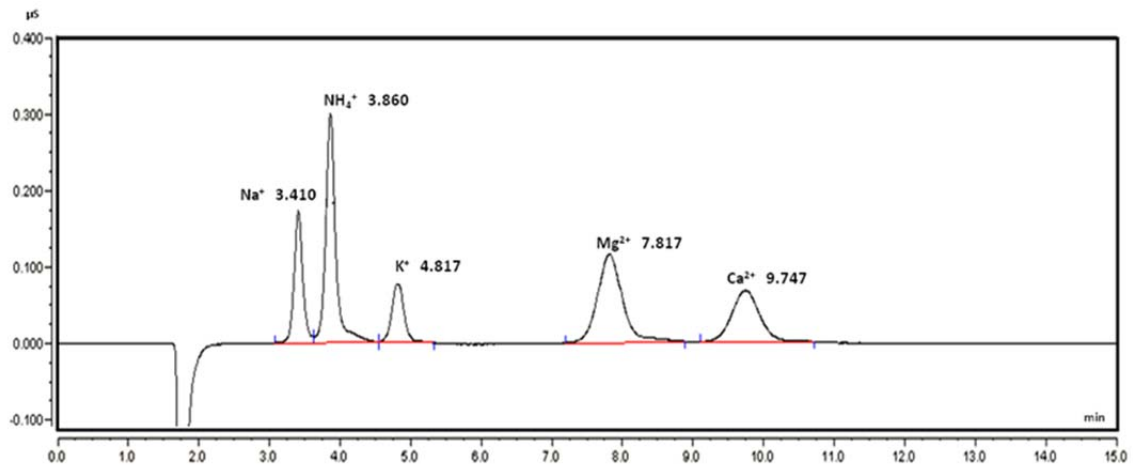
Fig.4 Typical chromatogram of cations

6.12.2 Apparatus and equipment

a) Ion chromatograph (example 1: DX-500, example 2: ICS-2000) with a electric conductivity detector

b) Cation separator column (example 1: CG14 + CS14, example 2: CG16 + CS16)

c) An integrator is recommended to process the chromatograms.

6.12.3 Reagent solutions and consumable materials

(1) Example 1: Dx500 - Isocratic Setup with manually prepared Eluent

a) Commercially available concentrated eluent (methane sulfonate: $2M\text{-}CH_3SO_3H$) should be divided into a set of 10 mL-aliquots sealed in a test tube and refrigerated up to six month before use.   Each aliquot is for a single use and the remaining aliquots will continue to be in the initial condition without any deterioration.   Any concentrated eluent aliquot has been stored at room temperature or under daylight condition should be discarded and not used.   This eluent would have been contaminated, degraded, or concentrated during storage.

b) Working eluent 10mM- CH_3SO_3H - dilute 20 mL of concentrated Eluent (2 test tubes) to 4 liters with pure water.

c) Two different suppressor modes are available: eluent and pure water is applied for the recycle and external modes respectively.   A suppressor will last longer

    in the external mode.

d)   Concentrated mixed stock standard solutions are prepared from a 1000 mg L^{-1} solution for each chemical species. (often commercially available, otherwise prepare from mixed reagents of high purity) -*e.g.,* Na$^+$: 200 mg L^{-1}, NH$_4^+$&Ca^{2+}: 100 mg L^{-1}, K$^+$&Mg^{2+}: 50 mg L^{-1}

e)   High concentrated standard solutions are prepared from the concentrated mixed stock standard solution by diluting 2, 4, 10 times of mixed stock solution with pure water (*e.g.*, 100 mg L^{-1}, 40 mg L^{-1}, 20 mg L^{-1}-Na$^+$).

f)   Working standard solutions are prepared from each high concentration standard solution by diluting 10 and 100 times with pure water (*e.g.*, 10 mg L^{-1}, 4 mg L^{-1}, 2 mg L^{-1}, 1 mg L^{-1}, 0.4 mg L^{-1}, 0.2 mg L^{-1}-Na$^+$). Normally used 5 standard solution (*e.g.*, 10 mg L^{-1}, 4 mg L^{-1}, 2 mg L^{-1}, 1 mg L^{-1}, 0.4 mg L^{-1}-Na$^+$). Lowest concentration standard solution can be used for the test of precision (*e.g.*, LWL calculation, etc.).

(2) Example 2:   ICS-2000 - Gradient Setup with RFIC Eluent Generator

a.   Concentrated eluent, CH$_3$SO$_3$H cartridge generated by "Eluent generator system".

b.   The working concentration of CH$_3$SO$_3$H starts from 10 mM, and the concentration should be linearly increased up to 40 mM in 25 minutes.

c.   For eluent regeneration and extended suppressor life the eternal mode is strongly recommended. Suppressor current is approximately 100mA.

d.   See example l.

6.12.4 Measurement procedure

(1) Example   1: Dx500

(a) Preparation

The eluent tanks should be drained and rinsed with pure water before each use. Prepare the eluent as per section 6.12.3 (Reagent solution and consumable materials Example 1).   If using a concentrate, transfer the refrigerated aliquot to approximately 1600mL pure water in a 2L volumetric flask. Rinse the test tube with pure water several times to ensure an accurate final concentration.   Note that MSA is extremely viscous

and extensive rinsing may be required. Fill the flask to the mark. Mix well by repeated inversion.

Apply an appropriate current to the suppressor as per the instrument manual. The current for cation analysis using MSA usually starts at 50mA. Higher currents will deteriorate the suppressor faster. After the baseline is well stabilized confirm the stability by repeated injections of pure water.

If an automatic sampler is installed, the tubing system and the needle should be verified free from contamination. The rinse pure water supply must also be free of contamination. The confirmation may easily be obtained by measuring electric conductivity of the pure water in a small beaker.

(b) Calibration curve

    a. Standards and samples are injected through a loop injector system. The sample loop is usually 50 to 100 μL

    b. The injection should start from the highest concentration standard, followed by standards with decreasing concentrations to prevent erroneous high values for the first sample injected after the calibration series.

    c. Start analysis by injecting a minimum of five standard solutions. Pure water should be also analyzed following the standards to check the system blank. The user may determine carry over effect by examining the pure water chromatogram for contamination between the standard series and the first subsequent sample injection. If there is little effect on sample analysis, injecting standard solution from lower to higher concentration may be acceptable.

    d. Arrange standard solutions every thirty samples in the automatic sampling unit. Also arrange a pure water sample as a blank in the unit. Prepare a calibration curve with standard solutions covering the full concentration range of the automatically injected samples.

    e. When an auto sampler is available, the vials should be rinsed with excess amounts of sample. When a manual syringe injection system is used the sample syringe should be also rinsed using excess amounts of sample.

    f. Turn on the auto sampler switch to start analyzing samples. Inject precipitation sample solution in the same manner as standard solutions.

    g. The system is checked by analyzing standard solutions of the high level

concentration at least once a day.　When a sample concentration is higher than that of the standard solution, the sample is diluted and measured again.

h.　Pure water should be analyzed to clean and check the system path after high concentration samples identified by high conductivity and after a change of sample series (different site, rain or fog, and so on).

(2) Example　2: ICS-2000

(a) Preparation

Prepare the eluent using a concentrated methanesulfonic acid cartridge and pure water. The eluent container is filled with freshly prepared pure water.　Pure water is also used for the auto-sampler rinse in a separate 4-liter container.

Pure water must not be allowed to flow inside the column path without concentrated eluent because the pure water will not allow the ions to elute.

The regenerant is also purged with compressed air.

(b) Calibration curve and sample analysis

See example l.

6.12.5　Calculation

Ion Chromatography software can be used to integrate the chromatograms however the signal value (*e.g.*, peak area) should be confirmed for all data.　If possible, the calculation of concentration should also be done by using alternate calculation software (*e.g.*, Excel).　This is an effective procedure for finding some errors such as peak misinterpretation and baseline drift

Data files should be named using unique identifiers such as the date.　The file format should be the same in all cases to provide a convenient pattern for data searches. Example: "anion091002" is anion data, 2nd October 2009.

Calibration curves should be made using the standard peak areas or conductivity signals

before and after every 30 samples. The calibration curve should be either least-mean square method for first or second order regression. Calculate the sample concentrations with the calibration.

When one sample blank is significantly high, subtract this quantity from the calibrated value or reanalyze the sample blank with care after ensuring the integrity of the injection and automatic sampling units. If the pure water signal or conductivity is high the IC should be maintained including contamination checks the sampling needle and injection valve. Subsequent reanalysis of samples should be carried out.

Calibration of the baseline:
    a. Define the start and end points for all peaks of interest.
    b. Consult the operation manual the manufacturer provided.
    c. Subtract the pure water blank when a syringe filter is used.

6.12.6 Quality control

Quality of measured cation concentration can be controlled by the ion balance and conductivity balance check by using all mandatory ions concentrations. Periodic measurement of SRM, participation to Inter-laboratory comparison project, and duplicate analysis are also effective for controlling data quality of cation concentration. Detailed procedure is described in Chapter 7.

Poor ion balance and conductivity balance checks may occur. When R_1, R_2 or both do not meet the standard, these samples should be subjected to reanalysis and the new set of the measurements should be evaluated again with the previous results. If the reanalysis does not solve the problem, the most probable reason(s) is to be noted in a comment section for that sample in the data report. Imbalance is frequently associated with the following factors:
    a) chromatographic interference suggested by additional peaks due to organic acids or unknown compounds;
    b) significant contribution of unanalyzed HCO_3^- ion suggested by low pH and a high concentration of Ca^{2+}; and
    c) very low accuracy and precision associated with low concentration levels of the sample with low electric conductivity, less than 0.2mS m^{-1}.

If some other reason(s) is recognized, the description should be provided with the in the comment section, otherwise comment 'unknown'.

It should be noted that the retention times of the ion chromatogram vary with a number of factors; 1) the concentration level of the eluent, 2) the aging of the analytical column, 3) a contaminated series of the standard solution, 4) contaminated flow-line due to the memory of the previous sample or contaminant accumulation.

The laboratory chemist must initiate an investigation to evaluate the variations of retention times and the reproducibility of the standard series to detect and resolve potential problems of the analytical system as early as possible.   Experiences imply that the cation analysis system could frequently produce overestimated measurements attributable to accumulated contaminants on the inside of the flow line.

The retention time varies with the eluent concentration and the degree of the column aging whereas the peak response of each ion in the standard solution is affected by the degradation of the standard solutions and the flow line.   Monitor the chromatographic system to confirm the stability of the analysis system by comparing the previous results in terms of retention times and the peak responses of the ionic species of different concentration levels in the standard series.

6.13   Ammonium ion determination by spectrophotometry

6.13.1   Background

Ammonium ion is predominately determined with automated or manual systems based on phenolate.   A water bath regulated to $50^{o}C$ is strongly recommended to speed up the reaction time and facilitate analysis.

The recommended minimum detectable amount of NH_4^+ with this method is 2 μmol L^{-1} and the determination range is 2-110 μmol L^{-1}.   This range can be extended by diluting samples.

The analytical sample is easily contaminated with ammonia gas, NH_3, from ambient air. Most laboratories have sufficient ammonia in the background air to easily contaminate precipitation samples.   The sample test tubes have to be closed throughout the analysis

except when the reagents are added. All sample tubes used for the method must be washed with pure water and a small portion of the sample of interest. This technique requires some experience and skills above and beyond that normally afforded the bench technician. Practical training with a qualified chemist is recommended for high quality measurements.

6.13.2 Apparatus and equipment

(1) Manual spectrophotometric method

    a) Spectrophotometer with a 630 nm setting
    b) Heating bath ($50^{o}C$)
    c) Glass test tubes with ground-in stoppers

(2) Automated spectrophotometric method

    a) Automated spectrophotometry (*e.g.,* BL-TEC K.K. Autoanalyzer)

6.13.3 Reagent solutions and consumable materials

(1) Manual spectrophotometric method

    a) Stock standard solution 5.54 mmol L^{-1} - dissolve 0.2965 g NH_4Cl (dried at $105^{o}C$) in pure water and dilute to 1000 mL.
    b) Alkaline phenol: 3.5 g of sodium hydroxide (NaOH) + 8.5 mL phenol + 0.04g sodium nitroprusside in 100 mL pure water; refrigerate the solution at $4\,^{o}C$ for a period not exceeding 1 week; prepare freshly on a weekly basis.
    c) Sodium hypochlorite (NaClO) solution - dilute 250 mL of 5.25 % NaClO to 500 mL with pure water.
    d) Buffer solution: Dissolve 18g CyDTA ($C_{14}H_{22}N_2O_8$ H_2O) , 5g NaOH, and 5g Na_2CO_3 in pure water and dilute to 1000mL with pure water with a resulting pH of 10; prepare fresh weekly.

One should note that the color development is affected by the solution pH. The buffer solution might affect measurements, and buffer solutions apply only if necessary.

(2) Automated spectrophotometric method

According to the operating manual:

Example (*e.g.,* BL-TEC K.K. Autoanalyzer)

a) Stock standard solution (5.54 mmol L^{-1}): dissolve 0.2965 g NH_4Cl (dried at 105 ^{o}C) in pure water and dilute to 1000 mL.

b) Buffer solution: dissolve 18g CyDTA ($C_{14}H_{22}N_2O_8$ H_2O), 5g NaOH, and 5g Na_2CO_3 in pure water and dilute to 1000 mL by pure water while controlling the pH to 10; prepare fresh weekly.

c) Sodium nitroprusside solution: dissolve 0.6g sodium nitroprusside in pure water and dilute to 1000 mL; prepare fresh weekly.

d) Mixed solution: mix buffer solution with sodium nitroprusside solution in the rate of 4 : 1 and add 1ml of 15% $CH_3(CH_2)_{11}OSO_3Na$ solution to 100 mL of mixed solution; prepare fresh daily.

e) Alkaline phenol solution: dissolve 47.5 g phenol and 19 g NaOH in pure water and dilute to 500 mL by pure water; prepare fresh weekly.

f) NaClO solution: effective chlorine concentration is more than 1.5%; prepare fresh daily and store in a colored bottle.

6.13.4   Measurement procedure

(1) Manual spectrophotometric method

a. The spectrophotometer should be on for 30 minutes before the measurement operation to ensure it has reached the required operating temperature.

b. Pour 5 mL of sample into the test tube. Add 15 mL of pure water, 0.5 mL of alkaline phenol solution, and 0.5 mL of sodium hypochlorite solution; close the test tube with the glass stopper.   In the case of low concentration-level samples, use the 20 mL sample for the analysis without adding pure water.

c. Set the heating bath to 50 ^{o}C, leave the sample in the heating bath for 2 hours and measure the sample with the spectrophotometer at 630 nm

d. Always analyze a reagent blank solution.

(2) Automated spectrophotometric method

a. Three reagents are added in proportion with different flow rates regulated by tubing of differing bore size: Mixed solution; 0.641 mL min^{-1}, Alkaline phenol solution; 0.381 mL min^{-1}, NaClO solution; 0.151 mL min^{-1}.

b. Select a wavelength of 630 nm for the optical filter.

c. Confirm the stabilized baseline.

d. Inject an aliquot of standard solution of the highest concentration in the series and inject the blank pure water twice in succession.

e. Confirm the square-shaped peaks. Confirm that there is no interference of the highest concentration standard with the following pure water peak. Confirm sufficient reproducibility (*e.g.,* within 3%) of the two successive pure water peaks. If the three requirements are not fulfilled, rinse the tubing system with care or replace the tubing in order to satisfy all three conditions.

6.13.5　Calculation

Whereas the systems offer highly sensitive analysis, the dynamic range does not extend into the high range. High concentration samples must be diluted. Automated dilution is provided with some automated spectrophotometric instruments. Divide the analytical samples into two groups, high and low concentration groups, before proceeding to the measurement operation.

(1) Manual spectrophotometric method（0.05-1.0 mg L^{-1}）

a. Five calibration solutions, 0.2, 0.4, 0.6, 0.8, 1.0 mg L^{-1}, and one zero standard (blank, normally pure water) are needed to generate a suitable calibration curve with the least-mean-square regression analysis.

b. Analyze the standard solutions before and after the samples. When more samples are to be analyzed than in an average run, analyze the highest standard periodically to confirm that peak response has not deteriorated.

c. In the linear regression analysis of the standard series, some high concentration standards may deviate downward from a linear regression line, in which case appropriately dilute the high concentration to attain the linearity for further analysis.

(2) Automated spectrophotometric method

a. a., b., and c. are same as (1)

b. In most cases, the calibration curve will be generated automatically with the software attached to the analytical system.   Even in this case, confirm that the peak outputs and linearity of the calibration solutions are all within the usual variations.

6.13.6   Quality control

Quality of measured ammonium ion concentration can be controlled by the ion balance and conductivity balance check by using all mandatory ions concentrations.   Periodic measurement of SRM, participation in Inter-laboratory comparison studies, and duplicate analysis are effective for controlling the data quality of ammonium ion concentration.   Detailed procedure is described in Chapter 7.

In manual and automated spectrophotometric methods, no pretreatment is needed for precipitation samples in terms of interfering species and the sample pH. If some precipitation occurs in samples, coagulation sedimentation treatment or steam distillation should be applied for the pretreatment of samples as needed.

It should be noted that the absorbance reading could be underestimated if the addition of NaClO is delayed or the available chlorine amount is insufficient.

6.14   Metal determination by atomic absorption/emission spectrometry

6.14.1   Background

Atomic absorption spectrometry is a simple and rapid procedure that can be used to determine Na^+, K^+, Ca^{2+} and Mg^{2+} in precipitation.   Detection limits, sensitivity, and optimum range vary depending on the manufacturer and the atomic absorption spectrophotometer model.

The low concentration of Na^+, K^+, Ca^{2+} and Mg^{2+} in precipitation requires using very sensitive procedures (see Table 6).   In flame atomic absorption spectrometry these metals are atomized directly in a flame.   A light beam from a lamp, whose cathode contains a specific metal, first passes through the flame containing the atomized sample and then enters a monochromator whose detector measures the current caused by the

absorption of light. Since the wavelength of the light absorbed is characteristic for individual metals, the light energy absorbed by the flame is proportional to the metal concentration in the sample measured.

Table 6   Range of measured metal concentrations and recommended Minimum Detectable Amounts (MDA)

Metal	Range (μmol L^{-1})	MDA (μmol L^{-1})
Na$^+$	0.4 – 90	0.4
K$^+$	1 – 30	1
Ca^{2+}	0.2 – 80	0.2
Mg^{2+}	0.2 – 20	0.2

MDA is defined as S/N=2

6.14.2   Apparatus and equipment

a) Atomic absorption (and/or emission) spectrophotometer
   Single- or dual-channel, single- or double-beam instrument having monochromator; photomultiplier detector; adjustable slit; a wavelength range of 190 to 800 nm; a slot burner system, power supply and amplifier; and a suitable recorder or computer

b) Hollow cathode lamps for Na, K, Ca and Mg
   Either single- or multi-element lamps are allowed to use for the analysis. For the determination of Na and K, flame atomic emission measurement can also be used, when the instruments is equipped for it.

c) Compressed gases and pressure-reducing valves
   Two cylinders of acetylene are necessary; the air may be supplied from a laboratory compressor (with a cleaning unit) or a cylinder of compressed air.

6.14.3   Reagent solutions and consumable materials

a) Standard solution: Commercially available 1000mg L^{-1} solution for Na, K, Ca and Mg.

b) Cesium chloride solution: for example 5 g-Cs L^{-1}

c) Lanthanum nitrate solution: for example 0.5g-La L^{-1}

6.14.4   Measurement procedure

Because of the many differences between atomic absorption spectrophotometers detailed instructions cannot be formulated; the analyst should follow the manufacturer's operating instructions for each instrument.   In general, operations are as follows:

    a. Switch on the analyzer

    b. Align the light source for maximum response

    c. Ignite the flame

    d. Allow the instrument to warm up (at least 15 minutes)

    e. Reset the wavelength

    f. Optimize and adjust the nebulization rate for maximum response

    g. Adjust the burner position for maximum response

    h. Prepare a full calibration curve and analyze one standard after every 20 samples

Table 7 gives examples of the operating conditions for each metal determined by atomic absorption /emission spectrometry with an air/acetylene slot burner.

Table 7   Atomic absorption (AA)/emission (AE) spectrometry of metals

	Na	K	Ca	Mg
Mode	AA or AE	AA or AE	AA	AA
fuel and flame condition	Air-acetylene Stoichiometric	air-acetylene stoichiometric	air-acetylene rich flame	air-acetylene stoichiometric
Analytical line (nm)	589.6	766.5	422.7	285.2

In the atomic absorption spectroscopy method for sodium and potassium, positive interference is caused for either species when the other concentration is significantly higher in the sample.   The extent of the interference will level off with a certain amount of the interfering species.   The interference level may be reduced by adding cesium chloride to the concentration of 1000 mg-Cs L^{-1}.

In the analysis of calcium and magnesium ions, lanthanum nitrate is added to eliminate interfering components including silicate and aluminum.

6.14.5   Calibration

    a.   Prepare a stock standard solution from high purity chemicals (preferably

metals) using pure water and HNO_3 (concentrated spectrograde purity) at a concentration of 1000 mg of metal L^{-1}. Commercially available standard solutions may be used.

b. Prepare a blank (use pure water and nitric acid- and/or lanthanum nitrate or strontium chloride solution) and six calibration standard solutions by diluting the stock metal solution to various concentrations in appropriate ranges for each set of analyzed samples.   The same stock nitric acid-and/or - lanthanum nitrate solution must be added to both the samples and the calibration solutions.

6.14.6   Quality control

The quality of the measured metal concentration can be controlled by the ion balance and conductivity balance check by using all mandatory ions concentrations.   Periodic measurement of SRM, participation in Inter-laboratory comparison studies, and duplicate analysis are also effective for controlling the data quality of metal concentration.   The detailed procedure is described in Chapter 7.

References (Chapter 6)

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7. QA/QC

The data are controlled by the personnel in charge of the laboratory (PCL), the national QA/QC managers (NAM) in each participating country and the network QA/QC manager (NEM).

The PCL has to collect the measurement data and other information that should be reported to NAM of each participating country.   A NAM is the personnel in charge of QA/QC activities in each country.   He/she has to control the data from PCL. The National Center has to report the monitoring data to the Network Center.   The NEM has to set up the validated database.   The validated data should be disclosed not only among the EANET regions but also outside EANET.

PCL: Personnel in Charge of Laboratory
NAM: NAtional Manager
NEM: NEtwork Manager

PCL Collects measurement data and other information	Reports →	NAM In charge of QA/QC activities in each country, controlling data from PCL	Reports →	NEM Sets up validated database to be disclosed within and outside EANET
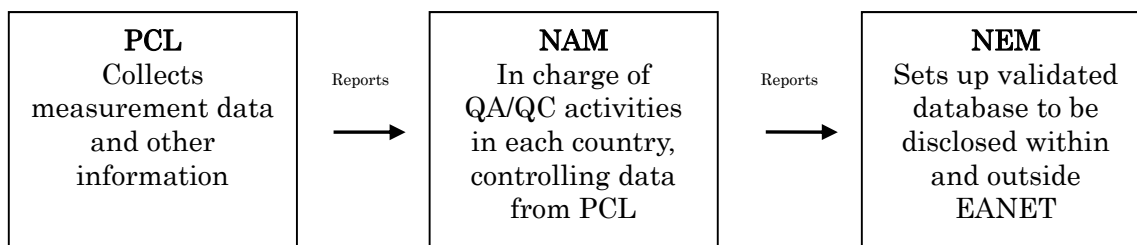
7.1 Classification of data

Data are classified into two types: 1) data to be controlled and reported by PCL to NEM through NAM, 2) data to be controlled by NAM. Later data should be reported to NEM by a request.

7.1.1 Reporting data

The data to be reported by PCL to NEM through NAM are grouped into two types: 1) information about sites, sampling, shipping, laboratory operation, chemical analysis,

etc., 2) measurement results of precipitation chemistry including precipitation amounts, calculated index. Remarks and notes (flag) also compose major parts of the measurement results.

(1) Information about sites, sampling, shipping, laboratory operation, chemical analysis:

❀ Name of country and site (Code of country and site)
❀ Name of NAM
❀ Name of laboratory and PCL (Code of laboratory)
❀ Information of site (on -site scale, local scale, regional scale)
❀ Information of sampling condition (precipitation chemistry collector, rain gauge, meteorological parameter and measurement devices)
❀ Information of sample history (shipping frequency, packing procedure, laboratory operation, etc.)
❀ Chemical analysis condition (Control Chart)

(2) Measurement results

❀ Name of country and site (Code of country and site)
❀ Name of NAM
❀ Name of laboratory and PCL (Code of laboratory)
❀ Sample number (Code consist of country code, site code, year, month and number)
❀ Start and end of date and time of sampling
❀ End of date of chemical analysis
❀ SO_4^{2-}, NO_3^-, Cl^- concentrations (μmol L^{-1})
❀ NH_4^+, Na^+, K^+, Ca^2, Mg^{2+} concentrations (μmol L^{-1})
❀ Other ions concentrations (non-mandatory items)
❀ Electric conductivity (mS m^{-1})
❀ pH (0.01 pH unit)
❀ R_1: cation and anion balance (for definition and calculation, see Section 7.2.2.)
❀ R_2: conductivity balance (see Section 7.2.2.)
❀ Amount of sample solution (0.1 g unit)
❀ Amount of precipitation (data from meteorological instruments or reported data)
❀ Note (Flag): any other information

7.1.2 Controlled data by individual country

The data to be controlled by an individual country (NAM) are: 1) the information which affects air pollution situation such as meteorological data, climate, climate vegetation and life style, 2) the information which affects measurement accuracy such as condition of chemical analysis instruments and laboratory conditions. These data should be reported as requested or required.

(1) Information on the situation of air pollution

❋   Meteorological data

❋   Climate (rainy and dry season, season of sand storm, volcanic condition, etc.)

❋   Vegetation (the type of tree, season of pollen dispersion, etc.)

❋   Life style (agricultural operation, biomass burning, etc.)

(2) Information on the precision of measurement results

❋   Condition of analytical instrument, (calibration curve, water temperature of each sample during analysis, etc.)

❋   Laboratory condition (instrument list and etc.)

7.2 Data checking

Data checking or validation is based upon:
・experience with the data from earlier measurements;
・relations between chemical components in air and precipitation;
・knowledge about spatial variation;
・knowledge about temporal variation; and
・comparisons between measurements and estimates from theory or models.

Records of old data can be used to create simple statistics including percentiles, mean values and standard deviations. Log-transformed data are often preferred. These statistics can be used in connection with control chart or in other comparisons of new data with aggregation of the old ones.

Relations between various chemical components (including ion balances and conductivity balances), relationship between sea salt components, and relationship

between constituents from neighboring stations and time-series plots are useful.

7.2.1 Statistical test

The statistical tests compare new measurements with data already stored in the database. The tests are carried out to identify possible outliners and results which may be wrong. They can be based upon assumption about the data distributions.

Each precipitation component may be compared with earlier data using the lognormal distribution. Data which is not within the four times the standard deviations range, should be checked by comparison with other components, concentrations obtained on earlier and later days, and concentrations from neighboring sites.

7.2.2 Ion balance and conductivity balance check

(1) Cation and anion balance (R_1)

The principle of electroneutrality in precipitation requires that the total anion equivalents equal the total cation equivalents. According to this principle, ion balance in a precipitation sample should be checked by the method described below:

For evaluating cation and anion balance, the following equation should be used in the present monitoring:

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

where C and A represents anion and cation equivalents (μeq L^{-1}), respectively.

This is simplified from of the corresponding equation used by US EPA where the denominator is the average of the two sums.
(EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. V: Precipitation Measurement Systems. EPA/600/R-94/038E US EPA Office of Research and Development, Washington, DC 20460, April 1994)

$$A \ (\mu eq \ L^{-1}) = \Sigma \ C_{Ai} \text{ x } V_i$$

where C_{Ai} is the concentration of i-th anion in $\mu mol\ L^{-1}$, V_i is the valence of the given ion.

$$C\ (\mu eq\ L^{-1}) = 10^{(6-pH)} + \Sigma\ C_{Ci}\ x\ V_i$$

where C_{Ci} is the concentration of i-th cation in $\mu mol\ L^{-1}$. If the unit $mg\ L^{-1}$ is used, it should be converted as follows:

$$(\mu mol\ L^{-1}) = (mg\ L^{-1})\ x\ 1000/M$$

where the molecular weight (M) for cations and anions is given in Table 8.

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 ($\mu eq/L$) of these weak acids will be calculated from the dissociation constant, Ka and pH as follows:

$$[HCOO^-] = [HCOOH]K_a/[H^+] = [HCOOH]\ x\ 10^{pH-pKa} = [HCOOH]\ x\ 10^{pH-3.55}$$
$$[CH_3COO^-] = [CH_3COOH]K_a/[H^+] = [CH_3COOH]\ x\ 10^{pH-pKa}$$
$$= [CH_3COOH]\ x\ 10^{pH-4.56}$$

Constants for $HCOO^-$, and CH_3COO^- are included in Table 8.

Dissociation constants in terms of pKa for formic, acetic, and oxalic acids are 3.55, 4.56, and 3.81 (2nd step), respectively.

When ion chromatography is used for organic acid analysis, concentration of organic acid is determined by sample pH and output of ion chromatography (C_{IC} ($\mu eq\ L^{-1}$)). In the case of formate, C_{IC} corresponds to the sum of concentration, $[HCOO^-]+[HCOOH]$, so that $[HCOO^-]$ concentration in the sample can be calculated by using the following equation.

$$[HCOO^-] = C_{IC}\ /\ (1+10^{3.55-pH})$$

At some sites, the concentration of fluoride (F^-), bromide (Br^-), and nitrite (NO_2^-) ions are significant and their concentrations should be included for the calculations of R_1 and R_2. Constants for F^-, Br^-, and NO_2^- are given also in Table 8.

If the required criteria shown in Table 9 have not been met, the analysis should be repeated or a flag should be entered into the database indicating that the results did not meet the required criteria.

Table 8   Basic constants

Ion	Molecular Weight (M)	Molar Conductivity (λ), $S\ cm^2\ mol^{-1}$
H^+	1.008	349.7
NH_4^+	18.04	73.5
Ca^{2+}	40.08	59.5 ×2
K^+	39.10	73.5
Mg^{2+}	24.31	53.0×2
Na^+	22.99	50.1
NO_3^-	62.01	71.4
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	55.4
Br^-	79.90	78.1
NO_2^-	46.01	71.8
PO_4^{3-}	94.97	92.8×3

W. H. Haynes (Edition-in-Chief) (2011) CRC Handbook of Chemistry and Physics, Ed 92nd, 5-77, 78, CRC Press.

Table 9   Required criteria for R_1

(C + A), $\mu eq\ L^{-1}$	R_1, %
<50	±30
50-100	±15
>100	±8

(2) Comparison between calculated and measurement in electric conductivity (R_2)

For dilute solutions (e.g. below 10^{-3} M), the total electric conductivity can be calculated in mS m^{-1} from the molar concentrations and molar conductivity (at infinite dilution) of the individual ions.   The observed electric conductivity values should be checked by the method described below, comparing to the calculated electric conductivity values for precipitation samples.

$$\Lambda\text{calc} = \Sigma\, c_i\, \Lambda_i{}^0 \times 10^{-4}$$

where Λcalc denotes the calculated electric conductivity of the solution (in mS m^{-1}), c_i the ionic concentration of the i-th ion (in μmol L^{-1}), $\Lambda_i{}^0$ the molar conductivity (in S cm^2 mol^{-1}) at infinite dilution and 25 ^{o}C.
Thus

$$\Lambda\text{calc} = \{349.7\ x10^{(6-pH)} + 80.0 \times 2c(SO_4{}^{2-}) + 71.4\ c(NO_3{}^-) + 76.3\ c(Cl^-) + 73.5\ c(NH_4{}^+)$$
$$+\ 50.1\ c(Na^+) + 73.5\ c(K^+) + 59.5 \times 2c(Ca^{2+}) + 53.0 \times 2c(Mg^{2+})\}/10000$$

where c( ) denotes the ionic concentrations in μmol L^{-1} of the ion in parentheses and the constants are the molar conductivity of the individual ion at infinite dilution at 25 ^{o}C (see Table 8).

The calculated electric 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.

If the required electric conductivity comparison criteria shown in Table 10 have not been met, the analysis should be repeated or a flag should be entered into the database indicating that the results did not meet the required criteria.

Table 10   Required criteria for R_2

Λmeas, mS m^{-1}	R_2, %
<0.5	± 20

0.5 – 3	± 13
>3	± 9

7.2.3 Data completeness

Completeness of data is defined as the proportion of valid data in a given monitoring period. Data completeness should be evaluated in terms of the rainfall amount ratio determined by ratio of the precipitation chemistry collector to the rain gauge.

The following value of index of data completeness should be reported. Two kinds of data completeness measures are used, Percent Precipitation Coverage Length (%PCL) and Percent Total Precipitation (%TP).

・%PCL   Percent Precipitation Coverage Length is the percent of the summary period for which information on whether or not precipitation occurred is available. If precipitation is known to have occurred during a particular sampling period but no measurement of the amount is available, then no knowledge of precipitation is assumed. Total precipitation depth (TP) is the amount of precipitation occurring during the period of precipitation coverage. This data completeness measure does not include any consideration of the availability of the varied precipitation chemistry sample.

・%TP   Percent Total Precipitation is the per cent of the total precipitation data measured during the summary period that is associated with valid samples.

Data completeness objectives can be different depending on the interval (i.e. period is a year or a season).

7.2.4 Analytical precision

The precision of the laboratory chemical analyses for precipitation samples should be tested by the method described in the section 9.4.2 and the results should be reported to the National Center.

7.3 Data flags

Data flags are used as an indicator of the quality of the information for data users. Data flags and/or data comments are useful as they clearly indicate whether data is valid or invalid. The function of the flags and comments is to ensure that the user has full knowledge of the data validity, and of the conditions which produce that level of validity. The user can then select the data most appropriate to his/her application with a high level of confidence.

7.4 Data validation

Monitoring data should be validated within the analytical organization (analytical laboratory) first. If the concentration or standard deviation of the concentration of an ion differs greatly from the historical long term average concentrations or the values or standard deviations of concentrations or values, respectively, during a given period, then the analytical result should be carefully reviewed and assessed.

Suspect samples should be re-analyzed and the quality of the resulting data should be assessed using ion balance (R_1) and the comparison between its calculated and measured electric conductivity (R_2).

Data validated in the laboratories are sent to the National Center and checked by NAM. Each country is expected to organize an expert group which is responsible for data validation. Data are sent to Network Center after the domestic data validation processes in each participating country is completed. NEM is responsible examining the monitoring situation for each National Center and for reviewing the data taking into consideration the guidelines established by the international expert group for data validation. The Network Center prepares a validated data draft report which is submitted to the Scientific Advisory Committee for adoption.

7.5 Inter-laboratory comparison program

All EANET laboratories are expected to participate in inter-laboratory comparison studies run by the Network Center. Inter-laboratory comparison samples are to be sent to each laboratory once each a year. The samples are to be analyzed and returned to the National Center within the prescribed time interval where the results will undergo statistical analysis and evaluation. A report will be prepared and returned to all participating laboratories.

The results of the EANET National Center inter-laboratory program are to be used to identify problems and find solutions which will improve the quality of laboratory analyses.

7.6 Meta data

Information about sites, sampling, shipping, and laboratory operation have same importance as precipitation chemistry including precipitation amounts, calculated index. Since those data will provide large effectiveness in data analysis such as temporal trends and special distribution, they should be stored carefully and compiled in Network Center.

8. Data Reporting

8.1 Data reporting form

Data reporting forms should be used to report site conditions (on site, local scale, and regional scale), sampling conditions, sample history, chemical analysis conditions and measurement results (precipitation chemistry including precipitation amounts, calculated index, flags and data completeness).   Network Center staff responsible for the measurements are also responsible for ensuring that all data elements are properly entered into the appropriate databases.   Data should be submitted to the center annually.

Each data form requires both the name and code of country and site, the name of NAM, the name and code of laboratory and the name of the PCL.

8.1.1 Information about sites, sampling, shipping, and laboratory operation

(1)   Site condition
When reporting changes in conditions in the immediate vicinity of a monitoring site ensure that the site Name and Code are given first.   The category of a site is determined by the siting criteria.   Each site is allowed only one class.

Any change in the immediate environment of the site should be reported every year,

even if the original site selection criteria are not affected.

- Describe any potential sources in the area of the collector which could potentially contaminate the samples. Ensure that you report on the conditions for all three scales; on-site, local and regional are included.

- A map for each of the three scales needs to be sent to the Network Center with the both the location of the potential contamination sources and meteorological sites clearly marked.

a)   On-site scale: within 100m of the collector (Fig. 5)

List the locations of the collector, rain gauge, and meteorological parameter measurement devices. Trees, overhead wires, buildings, and other physical obstacles should be described. Ground cover, slope, and farmlands etc., are important factors that need to be documented. Pictures of the collector and its surroundings should be attached

b)   Local scale: 100m-10km radius of collector (Fig. 6)

Storage of agricultural products, fuels, vehicles, parking lots, maintenance yards, feed lots, dairy barns or a large concentration of animals should be described and marked on the local scale map. Urban areas should be noted and information such as population included.

c)   Regional scale: 50km radius of collector (Fig. 7)

All stationary and mobile emission sources described and the types of chemicals and the amount emitted documented. Urban areas with population greater than 10,000 should be included. Meteorological stations should marked and sponsoring agencies noted along with the parameters measured.

(2)   Sampling condition

a)   Precipitation chemistry collector

Report the following: (i) model and manufacturer of the collector along with pictures of collector and design diagrams, (ii) funnel diameter (iii) materials/composition of the funnel material, underside of lid, tubing, filters and filter holder, storage bottles, (iv) chemical used as biocide and (v) planned start and end times of sample collection.

b) Rain gauge and meteorological parameter measurement devices

Model and manufacturer of all instruments should be reported together with diagrams or pictures.

(3) Sample history

Information on sample history plays an important role in sample handling from the time the sample was collected to the completion of the chemical analysis.

a) Shipping

Report: shipping frequency and packing procedure for all collected samples.

b) Laboratory operation

Report: sample preparation procedure, chemical analysis frequency, range of laboratory room temperature.

8.1.2 Chemical analysis

Each Chemical Analysis Method and all Control Charts should be reported as the laboratory QA/QC data for each sampling station. The following items are to be included.

(1) SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+:

Method, Instrument Name and Type, Detection limit.

Performance: calibration curve (5 points), ions content in the pure water (when a dilution process is included), data resulting from the analysis of standard reference materials (commercial SRM), data from duplicate or triplicate sample analysis (preferably every 10 to 20 samples), detection limit.

(2) Electric conductivity:

Instrument Name and Type

Performance: calibration curve for KC1 solutions (2 or 3 points) and pure water used, data obtained from analysis of standard reference materials (commercial SRM), temperature of samples and standard solutions, data from duplicate or triplicate sample analysis (preferably every 10 to 20 samples).

(3) pH:

Instrument Name and Type,

Performance: data obtained from standard reference material solutions (commercial SRM), temperature of sample and standard solutions, data from duplicate or triplicate samples (preferably one out of every 10 to 20 samples).

Describe the methods and performance indicators on the reporting form for all chemical species analyzed.

8.1.3 Measurement results and flags

The reporting form should include sampling conditions, precipitation amounts, date the chemical analysis was completed, concentration of components and all flags.   Refer to Table 11 for an example of a form.

Each national center must keep all raw data for future reference.

The EMEP flag protocol was used to develop the sample flags used in EANET. EANET plans to unify the systems in the future an effort to simplify the exchange of data between networks. The following items are to be included on the EANET reporting form:

❉   Sample number (Code consist of country code, site code, year, month and number)
❉   Start and end of date and time of sampling
       If a unique code name is used for each sample solution it is recoded followed by the DATE the sample was collected. Check that it is the same as the one on the sample information form.
        [Unit: yyyy/mm/dd   hh:mm, e.g. 2010/01/31   09:00]

❉   End of date of chemical analysis
        [Unit: yyyy/mm/dd, e.g. 2010/02/09]

❉ SO_4^{2-}, NO_3^-, Cl^- ,NH_4^+, Na^+, K^+ , Ca^2, Mg^{2+} concentrations
        Each laboratory analysis may use units such as mg L^{-1}, the report type is converted into the molarity, it is reported.
        [Unit: μmol L^{-1}, Format: ####.#, e.g.,. 121.2]

Flags：

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.

❋　Electric conductivity

[Unit: mS m^{-1}, Format: ##.##, e.g.,. 3.25]

Flags：

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.

❋　pH

[Unit: pH unit, Format: ##.##, e.g.,. 4.25]

Flags：

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.

❋　R_1: Cation and anion balance (for definition and calculation, see Section 7.2.2)

[Unit: ％, Format: ####.#, e.g.,. 1030.0]

Flags :

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.

478　　Inconsistency discovered through ion balance calculation.

※　R_2: Comparison between calculated and measured in electric conductivity (see Section 7.2.2)

[Unit: ％, Format: ####.#, e.g.,. 931.0]

Flags :

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 electric conductivity.

※　Amount of sample solution

[Unit: g, Format: #####.#, e.g.,. 3020.0]

Flags :

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)

701　　Less accurate than usual, reason not specified.

699　　Mechanical problem, reason not specified.

※　Amount of precipitation (data from meteorological instruments or reported data)

[Unit: mm , Format: ####.#, e.g.,.   320.5]

Flags：

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)

701   Less accurate than usual, reason not specified.

699   Mechanical problem, reason not specified.

*Note: any other information

Improvement in data handling and data reporting will be implemented as dictated by operational requirements and monitoring activities.

References (Chapter 7-8)

Vet, Robert J. (1991), "The Handbook of Environmental Chemistry", Volume 2, Part F, EMEP (1996) EMEP Manual for sampling and chemical analysis.

Krognes, T., Gunstrom, T. O. and Schaug, J. (1995) Air Quality Databases at NILU.

WMO GAW No. 85 Chemical Analysis of Precipitation for GAW: Laboratory Analytical Methods and Sample Collection Standards.

W. H. Haynes (Edition-in-Chief) (2011) CRC Handbook of Chemistry and Physics, Ed 92nd, 5-77, 78, CRC Press.

Items	North direction (NW-NE)	East direction (NE-SE)	South direction (SE-SW)	West direction (SW-NW)
Existence of trees, poles, buildings, and height of them				
Existence of incinerators, domestic heating, parking lots, storage of fuel, agricultural products, daily farm, and livestock				
Slope degree of the site	$^{\circ}$ - $^{\circ}$	$^{\circ}$ - $^{\circ}$	$^{\circ}$ - $^{\circ}$	$^{\circ}$ - $^{\circ}$
Surface condition of the site	(%)	(%)	(%)	(%)
Existence of a forest, river, lake, marsh, farm or fields				
Existence of roads, and their traffic densities*				

On site scale (within 150m: a sketch map should be attached)

*Describe roads with more than <u>100 vehicles/day</u> for <u>remote sites</u>, and roads with more than <u>1,000 vehicles/day</u> for <u>urban</u> and <u>rural sites</u>.

On-site Scale (within 150m)
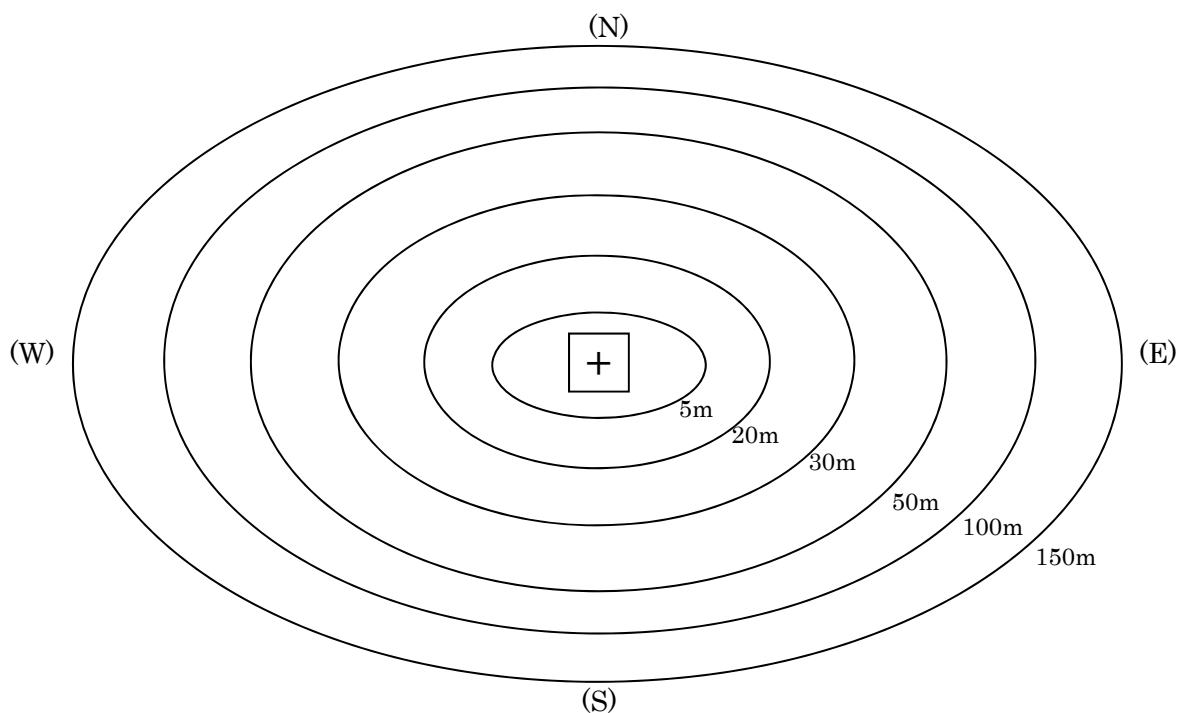
Site Name :

Fig. 5 Outline of monitoring site (On site scale)

Items	North direction (NW-NE)	East direction (NE-SE)	South direction (SE-SW)	West direction (SW-NW)
Information on trunk roads, expressways, and their traffic densities (with more than 5,000 vehicles/day)				
Information on airports and railways				
Information on major emission sources such as large industries, and power plants and their fuel consumptions and so on				
Information on houses/settlements with more than 5,000 persons, and their population				
Descriptive information around the site such as topography and meteorological condition				

Local scale (150m - 10km: a sketch map should be attached)
(For an urban site, at least information of area within 150m-1km from the site is expected)

Local Scale (150m – 10km)
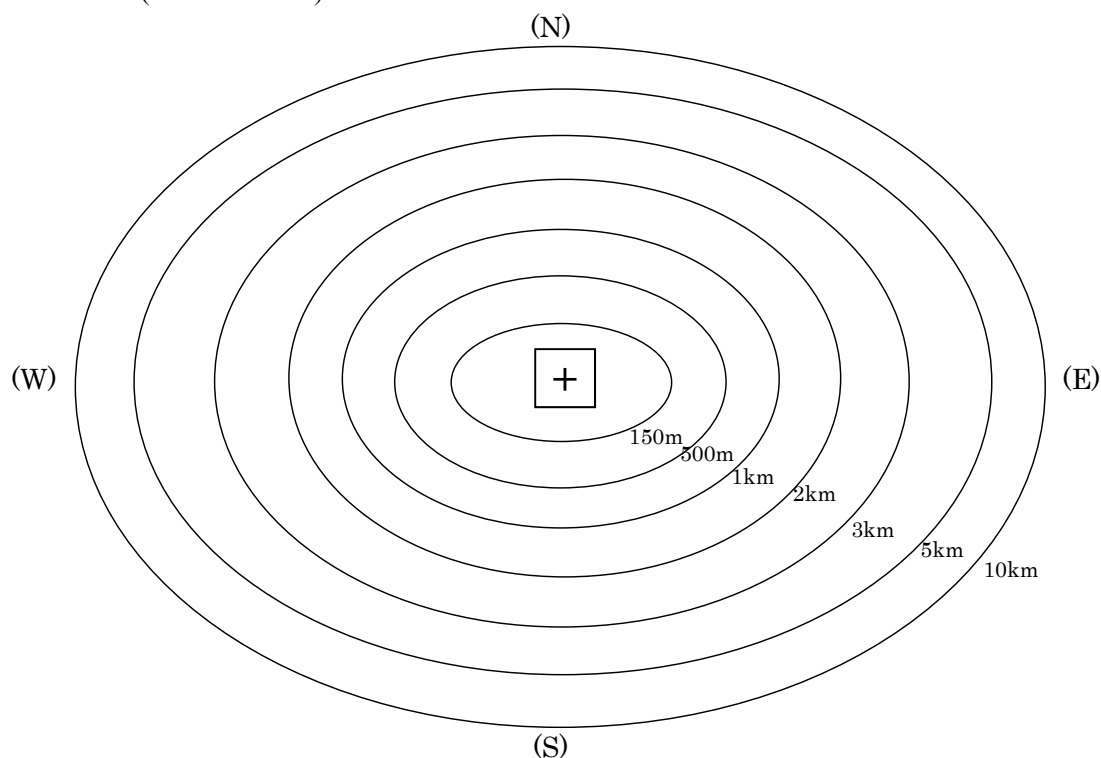
Site Name :

Fig. 6 Outline of monitoring site (Local scale)

Items	North direction (NW-NE)	East direction (NE-SE)	South direction (SE-SW)	West direction (SW-NW)
Existence of main stationary air pollution sources*				
Existence of trunk roads with more than <u>10,000 vehicles/day</u>, and their traffic densities				
Existence of cities with the population more than <u>10,000 persons</u>				

Regional scale (10km - 50km:a sketch map should be attached)

*: For <u>rural site</u>, description should be made on huge emission sources larger than <u>10,000tons/y</u> and other major pollution sources.

Regional Scale（10km -50km）
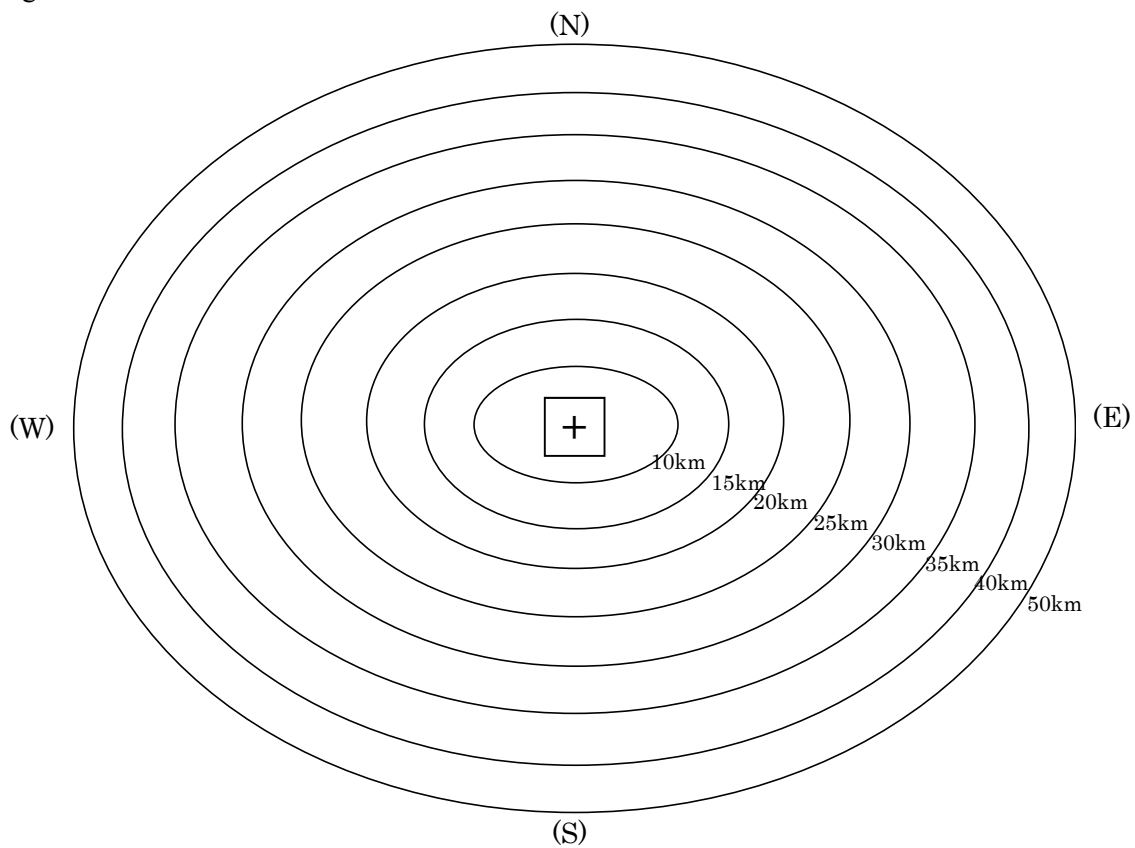
Site Name :

Fig. 7 Outline of monitoring site (Regional scale)

Table 11-1 Data reporting form (Anions)

Form(Wet A) No.1   **Results of wet deposition analysis (Anion)**

Site name :

Funnel diameter : _____ (mm)

Name of Laboratory :

Name of reporter : _____

Sample No.	Sampling period					SO_4^{2-} umol/l			NO_3^- umol/l			Cl^- umol/l										Date of analysis	Note
	Start			End																			
	Date	Time		Date	Time	flg1	flg2	flg3	flg1	flg2	flg3	flg1	flg2	flg3	flg1	flg2	flg3	flg1	flg2	flg3	flg1	flg2	flg3		

Table 11-2 Data reporting form (Cations)

Form(Wet A) No.2   **Results of wet deposition analysis(Cation)**

Site name :

Name of Laboratory :

Funnel diameter _____ (mm)

Name of reporter :

Sample No.	Sampling period						NH4+ umol/l				Na+ umol/l				K+ umol/l				Ca2+ umol/l				Mg2+ umol/l				Date of analysis	Note
	Start		End					flg1	flg2	flg3			flg1	flg2	flg3		flg1	flg2	flg3		flg1	flg2	flg3		flg1	flg2	flg3		
	Date	Time	Date	Time																									

Table 11-3 Data reporting form (EC, pH, R1, R2, and Precipitation)

Form(Wet A) No.3   **Results of wet deposition analysis(EC, pH, R1 ,R2, Precipitation)**

Site name :

Name of Laboratory :

Funnel diameter :＿＿＿＿＿ (mm)

Name of reporter :＿＿＿＿＿

Method Code   1: Rain Gauge   2: Calculation by sample amount   3: others

| Sample No. | Sampling period | | | | | | EC mS/m | | | | pH | | | | R1 | | | | R2 | | | | Amount of sample g | | | | Amount of precipitation mm | Method Code | | | | Date of analysis | Note |
| | Start | | | End | | | | flg1 | flg2 | flg3 | | flg1 | flg2 | flg3 | | flg1 | flg2 | flg3 | | flg1 | flg2 | flg3 | | flg1 | flg2 | flg3 | | | flg1 | flg2 | flg3 | | |
	Date	Time		Date	Time																													

9. Overall QA/QC

9.1 Introduction

Quality assurance and quality control (QA/QC) plays a key role for wet deposition monitoring.   Carefully designed and executed quality assured operating systems will produce data with a high degree of accuracy, precision, completeness, comparability and representativeness.

Quality control and quality assurance play an important role in all types of environmental monitoring.   The differences between quality control and quality assurance are described in Vet (1991).   Quality control is defined as the procedures followed to ensure that the analytical system is 'in control'.   Quality assurance is defined as the procedures used to ensure that the quality control procedures are effective. The difference between QA and QC when viewed in the context of an analytical laboratory is often made by considering quality control to be focused on internal laboratory operations and quality assurance to be independent of quality control and external to the laboratory (Vet, 1991).   In a more general context quality control is applied to the monitoring and laboratory systems before and during measurements whereas quality assurance focuses on the data and the effectiveness of the procedures after completion.

Measurements should follow the established standard methods.   Errors are made and accidents happen and when they do the details of the incidents must be recorded as those details are important components of each data record.   Data users must be fully informed as to the suitability of the data for their intended use.   It is essential that the quality of the conclusions from the data analysis should be consistent with the known data quality.

Both scientific and administrative data users have become increasingly concerned about the impact of data quality on the validity of the wet deposition data used and ultimately the interpretations and conclusions associated with their research.

The QA/QC procedures in this chapter were developed by utilizing the most relevant and up-to-date components of the operation manuals from the major international wet deposition monitoring networks and integrating those protocols to best reflect EANET's

needs .

9.2 Data quality objectives (DQOs)

Data quality objective (DQO) values are based on the objectives of each program and can be different among programs. The DQO values define the desirable levels of accuracy, precision and completeness required by the program.

EANET DQO values for wet deposition monitoring are defined in Table 12. QA/QC activities outlined in this chapter are required to ensure the DQO values are attained. The participating countries are expected to make every effort to meet the DQOs.

Table 12 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 using the following formula:

   A = [(certified values)-(analytical values)] x 100 / (certified values)

2) Precision (Si) is calculated using the following formula:

   $Si = (\Sigma di^2/2Ni)^{1/2} \times 100/Av$
   where di and Av denote the difference between the duplicate analyses and mean, respectively (see Section 9.4.2), and Ni is the number of sample pairs in the reporting period.

3) Precipitation (P) is calculated by using the following formula (monthly, seasonally or annually. All network are requested to prove at least annual values):

   P = (amount of precipitation measured by the collector) x 100
      /(amount of precipitation measured by standard rain gage)

4) To determine the percentage of the total amount of the precipitation that is associated with valid samples during each given period (%TP) refer to Section 7.2.3.

b) **Detection limits and determination limits**

   (both determined as specified in Section 9.4.2; unit $\mu mol \ L^{-1}$)

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 within ±0.05pH units	
EC	Replicate measurement of pure water (EC: less than 0.15 mS m^{-1}) should agree within ±0.02mS m^{-1}	

RM: Reference material prepared as the laboratory working standard for precipitation analysis

9.3 Standard operating procedures (SOPs)

SOPs are written procedures used in all the processes of the monitoring system, i.e. in the field, laboratory and for data management. SOPs provide a method designed to ensure that all personnel follow the same procedures in an identical manner minimizing the variance of data quality between individuals ensuring each person conducts their works with a scientifically sound understanding of QA/QC. Each of the sampling and chemical analysis organizations or laboratories should ensure that SOPs they prepare meet the requirements of their respective organizations and that SOPs comply with the Technical Manuals and the national QA/QC programs. SOPs need to be straight forward and sufficiently clear to ensure that beginners can perform the tasks in an effective manner. SOPs are to be updated in a timely manner and should take into consideration changes in technology and advances in science. Essential components of wet deposition SOPs are outlined in Appendix 1.

9.4   Data quality assessment

The assurance of the precision and accuracy of the field sampling and laboratory measurements is the principal target of the quality assessment of precipitation data. In general, precipitation data generation is a process of sample collection, sample handling sample storage and laboratory chemical analysis. The precision and accuracy of the precipitation measurements is dependent on all of those processes.

9.4.1 Sampling precision

In order to effectively determine sampling precision each organization must undertake a duplicate sampling program with collocated precipitation collectors at an operational monitoring site. Sampling must be undertaken using identical procedures for collection, handling, shipping, and storage for each set of duplicate samples. To ensure all aspects

of the measurement program are under control regular reviews by experts are required. Reviews require site visits and re-training of the site operators on a periodic basis to ensure the site operations are following the SOPs.

9.4.2 Quality control of laboratory measurements

Precision and accuracy are an integral part of laboratory quality control.   Ensuring that precision and accuracy meet the DQOs is an important step in the validation of chemical analyses of wet deposition samples and ensuring the quality control standards are sufficiently maintained.

(1) Analytical precision

To estimate the analytical variability, duplicate analysis of a sample should be determined a minimum of 1 in every 20 samples.   Large volume samples should be divided into two aliquots, one half for immediate routine analysis and the other should be immediately refrigerated and stored at $4^{o}C$ and analyzed in less than 7 days as part of another analytical run.   Analytical precision is defined as the standard deviation between the two analyses:

$$Si = (\Sigma di^{2}/2Ni)^{1/2}$$

where di denotes the difference between the two measurements, and Ni is the number of the sample pairs for the duplicate analysis in the reporting period.   The factor, 2, is included in the denominator to account for the random error associated with both measurements.

(2) Accuracy of chemical analysis

The accuracy of analytical measurements is evaluated by analyzing simulated precipitation samples referred to as inter-laboratory comparison samples.   Within EANET the inter-laboratory comparison samples are prepared using reagent grade chemicals supplied to all analytical laboratories by the Network Center on an annual basis.   Analytical performance is evaluated using the data from the chemical determination of the inter-laboratory comparison samples.   Statistical analysis and control charting of the results is helpful in identifying deficiencies and finding solutions to analytical issues and will result in an improvement of data quality.

(3) Definition of " Detection limit" and "Determination limit"

The measurement is not always addressed by a definite number.   For example some

analytes may be "not detected" or "below determination limit". In order to define these parameters, a standard solution is prepared at concentration levels near determination limit of the analytical method. Analyze the above standard solution five times to determine the standard deviation (s.d.). The "Detection limit" and "Determination limit" are defined as three and ten times of the standard deviation, respectively.

Detection limit = 3 (s.d.)

Determination limit = 10 (s.d.)

The numerical figures for these measures may differ considerably depending upon experimental conditions including the types of instruments, the instrumental history, and operator experience. For this reason, the standard deviation should be determined whenever the analytical conditions are changed.

9.5 Site performance audit

The National Center should carry out an annual technical audit for each site to ensure that the on-site criteria are being met and to provide an opportunity for a detailed review of the site including the condition of the infrastructure and status of the instrumentation. Such site visits encourage communication between the National Center and site operators facilitating problem solving, technical upgrades and training. A site performance audit should include the following steps:

(1) Operation check of wet-only automatic collector
   a) 1-2 drops of pure water is applied by the auditor to the precipitation sensor. The collector is qualified if the lid successfully moves from the dry-side collector to the wet-side collector within a few seconds. Clean the sensor if necessary to ensure the lid responds promptly to precipitation events.
   b) The bottom of the collector lid needs to be examined to ensure it is clean and without defects which might result in a poor seal.
   c) The wet-side funnel surface should be clean and without defects.
   d) Several minutes after the wet-side collector is opened, check the heating of the sensor with hand.
   e) Ensure the lid closes within the correct time interval.

(2) Procedure check for container cleaning
   a) The site operator may be responsible for the cleaning and maintenance of all

types of vessels including the bottles for sample shipping and storage. The auditor needs to determine what vessels are prepared and cleaned by the operator and ensure all protocols are covered.

b) The operator is required to demonstrate how all vessels' are cleaned.

c) The auditor and operator are to have a face-to-face discussion with each other on the steps required to eliminate potential contamination of the samples.

d) The pure water must be checked to ensure its electric conductivity is less than 0.15 mS m^{-1}.

(3) Review of site operations and data documentation

a) The auditor must observe the site operator while he performs his routine tasks including sample handling, instrumental operation, and data reporting.

b) The auditor should ensure that SOPS and site check sheets are on-site

c) After the routine tasks are completed the auditor should interview the operator to ensure the details of the instrumentation and the operations are understood. A face-to-face review of the monitoring techniques with the operator will serve as a means of on-site training. The training should cover all aspects but have an emphasis on the tasks that need improvement .

(4) A site audit report should be prepared by the auditor.

9.6 Laboratory audit

Laboratory operations should also be audited by the National Center with similar frequencies to the site and sampling audit. Focus is placed on sample handling, capability of the instrumentation, the SOPs, and all QA/QC activities and their records and the log book.

The audit practice should be clearly reported and stored for further discussion and long-term evaluations of the QA/QC of the long-term monitoring operation.

9.7 Preliminary quality assurance of data sets

Monitoring data should be assessed at predetermined intervals. Accuracy, precision, representativeness, completeness, and comparability are to be quantitatively evaluated and the overall data quality evaluated in terms of the scores representing the quality of

the criteria.

The accuracy and precision of the measurements will be assessed on the basis of chemical analysis performance. Evaluations of site representativeness will be based on the site evaluation report using the three different scale maps and the site audit reports. Comparability for the chemical analysis is evaluated by the analysis of common simulate or actual precipitation samples. Comparability of sample collection will be quantified based on collocated sampling results. The data from collocated sampling should be carefully reviewed to ensure all measurements are equivalent and without logistical and operational errors.

Data completeness for the precipitation amount measurement should be evaluated in terms of the ratio of the rainfall amount in the sample collector to that in the rain gauge. Data completeness for ionic concentration measurements is determined by the fraction of valid data in a certain monitoring period where valid samples are associated with acceptable measurements in terms of ion balance and conductivity check, R_1 and R_2.

The data report should be provided with the outputs of chemical analysis and with verbal descriptions, flag codes, and operators' remarks on every aspect of the monitoring procedures. Audit personnel and network staff are encouraged to submit suggestions and proposals to the national center after reviewing the reports.

9.8   External quality assurance program

EANET will maintain an external quality assurance program designed to:

- verify that the measurements are being carried out and reported with the expected precision and accuracy and that all measurements activities are accurately documented;
- identify sources of variability and recommend changes and controls that would improve the accuracy, precision, and completeness of the measurements;
- certify the measurement contractor's assessment of precision and accuracy;
- assess and compare the measurement methodology and quality assurance data of this network to other international and domestic networks.

EANET's external audit program is intended to identify problems and recommend

solutions intended to improve the monitoring program by improving the practical techniques and practices.

9.9 Training

International and national training programs of the monitoring techniques should be provided. Details of the training program will be addressed in a separate document.

References (Chapter 9)

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Vet, Robert J. (1991) "The Handbook of Environmental Chemistry", Volume 2, Part F, Ed. O. Hutziger, Springer-Verlag Berlin Heidelberg 1991.
WMO GAW No.85 Chemical Analysis of Precipitation for GAW: Laboratory Analytical Methods and Sample Collection Standards.

Appendix 1

Major items to be included in SOPs in wet deposition monitoring

Standard operating procedures (SOPs) should cover all aspects of wet deposition monitoring from sampling through data reporting, in accordance with the wet deposition monitoring manual to minimize potential biases introduced by different operators and analysts.   It is important to ensure that SOPs be written to reflect the actual operational details.   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.   SOPs should be customized for each organization/laboratory. Individual SOPs should clearly describe the scope of application, designation of operational staff, their supervisors, and reporting formats etc.   The following table includes the essential components for wet deposition monitoring SOPs.   Additions and/or deletions to the table may be needed to ensure the individual SOPs apply to each organization.

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 (including 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. Training plan
  3.3. Pure 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 detection limits and 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 electric 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 stuff 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 2

List of useful websites

EANET plays a role to clarify acid deposition in East Asian region as one of the continental scale acid deposition monitoring networks in the world.   Information of the networks other than EANET is available in the following websites.

- EMEP (The Cooperative Programme for Monitoring and Evaluation of the Long range Transmission of Air Pollutants in Europe): http://www.emep.int/

- NADP (National Atmospheric Deposition Network in USA): http://nadp.sws.uiuc.edu/

- WMO (World Meteorological Organization - Global Atmosphere Watch) : http://www.wmo.int/pages/prog/arep/gaw/precip_chem.html

- CAPMoN (Canadian Air and Precipitation Monitoring Network): http://www.ec.gc.ca/rs-mn/

Appendix 3

EMEP flag system

(Norwegian Institute for Air Research, EMEP manual for sampling and chemical analysis, Section 6.4 (2001))

1. Data flags

Several flags have in the past been used to give information about the quality of the data stored in the data base. These flags are revised and are currently under evaluation. The new data flag system contain the old flags, and it will be extended at need.

Some EMEP sites are located at the coast and are from time to time highly exposed to sea salt particles. This will of course affect several components in precipitation which should be flagged in the data base. In particular the "excess sulphate" in precipitation, which will be the difference between two large numbers, may have a high uncertainty and should be flagged.

The person responsible for the data reporting in each participating country is the data originator (DO). The DO will have access to NILU's external computer and will take care of the future data transfer to the central data base at the CCC.

Flags are sorted according to severity. Flags above 250 indicate an exception that has invalidated or reduced the quality of the data element.

Flags below 250 indicate that the element is valid, even if it may fail simple validation tests. The value may for example be extreme, but has been tested and found correct.

The flag 100 is used to indicate that a value is valid even if an exception in the 999-250 range has also been flagged. In this case the 100 flag must appear before the other flags. In all other cases, the most severe flag should appear first if more than one flag is needed.

All flags are grouped in two categories: V (valid measurement) or I (invalid measurement).

1.1 Group 9: Missing

When a measurement is missing and no particular information is available, we cannot assign any numerical value to the measurement (no substitution value is applicable). The measurement value must have been replaced with the transfer file missing flag. For all flags in this group, the measurement is irrecoverably lost, and no substitution value may be computed or estimated. The DO assigns one of the following flags in the flag variable (in addition to setting the transfer file missing flag):

Flag Mnemonic	V/I	Description
999 MMU	I	Missing measurement, unspecified reason
990 MSN	I	Precipitation not measured due to snow-fall. Needed for historic data, should not be needed for new data
980 MZS	I	Missing due to calibration or zero/span check

1.2 Group 8: Undefined

In some cases a measurement may not be performed because the parameter to be measured is not defined. As mentioned above, the concentration of pollutants in precipitation is undefined when there is zero precipitation. In this situation the measurement is not missing, and the data availability

is not reduced. It is not possible to compute or estimate a substitution value for a measurement that is undefined. The DO assigns one of the following flags:

Flag Mnemonic	V/I	Description
899 UUS	I	Measurement undefined, unspecified reason
890 UNP	I	Concentration in precipitation undefined, no precipitation

1.3 Group 7: Value unknown

This group of flags is assigned by the DO when the exact numerical value is unknown, but significant additional information is available. This situation exists when a measurement is below the detection limit of the instrument or method, or is considered to be less accurate than normal.

For many data users it is important to know that the value is low, even if a numerical value is not available. Some users may also need to use or create a substitution value. The substitution value may be based on the detection limit (if reported), or on some other estimate. Statisticians have described methods for using the distribution function of all reported values to estimate the average of the values that fall below the detection limit.

Flag Mnemonic	V/I	Description
799 MUE	I	Measurement missing (unspecified reason), data element contains estimated value
784 LPE	I	Low precipitation, concentration estimated
783 LPU	I	Low precipitation, concentration unknown
781 BDL	V	Value below detection limit, data element contains detection limit
780 BDE	V	Value below detection limit, data element contains estimated value.
771 ARL	V	Value above range, data element contains upper range limit
770 ARE	V	Value above range, data element contains estimated value
750 ALK	I	H+ not measured in alkaline sample
701 LAU	I	Less accurate than usual, unspecified reason. (Used only with old data, for new data see groups 6 and 5)

1.4 Group 6: Mechanical problem

This group of flags is assigned by the DO when a measurement value is less accurate than normal due to severe weather or instrument malfunction. The measured value is reported, but should be excluded from use when strict quality control is required.

Flag Mnemonic	V/I	Description
699 LMU	I	Mechanical problem, unspecified reason
679 LUM	V	Unspecified meteorological condition
678 LHU	V	Hurricane
677 LAI	I	Icing or hoar frost in the intake
659 LSA	I	Unspecified sampling anomaly
658 LSV	I	Too small air volume
657 LPO	V	Precipitation collector overflow. Heavy rain shower (squall)
656 LWB	V	Wet-only collector failure, operated as bulk collector
655 LMI	V	Two samples mixed due to late servicing of sampler. Estimated value created by averaging
654 LLS	V	Sampling period longer than normal, observed values reported
653 LSH	V	Sampling period shorter than normal, observed values reported
649 LTP	V	Temporary power fail has affected sampler operation

1.5 Group 5: Chemical problem

This group of flags is assigned by the DO when a measurement value is less accurate than normal due to some kind of chemical contamination of the sample. The measured value is reported, but should be excluded from use when strict quality control is required.

Flag Mnemonic	V/I	Description
599 LUC	I	Unspecified contamination or local influence
593 LNC	I	Industrial contamination
591 LAC	I	Agricultural contamination
578 LSS	I	Large sea salt contribution (ratio between marine and excess sulphate is larger than 2.0). Used for old data only. For newer data use 451/450.
568 LSC	I	Calcium invalid due to sand contamination
567 LIC	I	pH, NH4 and K invalid due to insect contamination
566 LBC	I	pH, NH4 and K invalid due to bird droppings
565 LPC	I	K invalid due to pollen and/or leaf contamination
558 SCV	V	Sand contamination, but considered valid
557 LIV	V	Insect contamination, but considered valid
556 LBV	V	Bird droppings, but considered valid
555 LPV	V	Pollen and/or leaf contamination, but considered valid
549 LCH	I	Impure chemicals
540 LSI	I	Spectral interference in laboratory analysis
532 LHB	V	Data less accurate than normal due to high field blank value
531 LLR	V	Low recovery, analysis inaccurate
521 LBA	V	Bactericide was added to sample for storage under warm climate. Considered valid

1.6 Group 4: Extreme or inconsistent values

This group of flags is assigned by the DO after evaluation of the credibility of the measured values. If a measured value is extremely high or low, it may in many cases be suspected to be wrong based on statistics alone. In a conservative presentation of the data set such elements should be excluded.

Some measurements are found to be inconsistent with other measurements or with computed parameters (ion balance, conductivity, etc.). As above, such measurements may be used with caution, but should be excluded from use when strict quality control is required.

Flag Mnemonic	V/I	Description
499 INU	V	Inconsistent with another unspecified measurement
478 IBA	I	Invalid due to inconsistency discovered through ion balance calculations
477 ICO	I	Invalid due to inconsistency between measured and estimated conductivity
476 IBV	V	Inconsistency discovered through ion balance calculations, but considered valid
475 COV	V	Inconsistency between measured and estimated conductivity, but considered valid
460 ISC	I	Contamination suspected
459 EUE	I	Extreme value, unspecified error
458 EXH	V	Extremely high value, outside four times standard deviation in a lognormal distribution
457 EXL	V	Extremely low value, outside four times standard deviation in a lognormal distribution

456 IDO	I	Invalidated by data originator
451 SSI	I	Invalid due to large sea salt contribution
450 SSV	V	Considerable sea salt contribution, but considered valid

1.7 Group 3

This group of flags (flags 301-399) is presently not defined.

1.8 Group 2: Exception flags assigned by the database co-ordinator

This group of flags is reserved for use by the database co-ordinator. The flags in this group are identical to group 4 above. They are only assigned by the database co-ordinator if an inconsistency is found, and the data originator has not previously flagged the condition.

Flag Mnemonic	V/I	Description
299 CNU	V	Inconsistent with another unspecified measurement
278 CBA	I	Invalid due to inconsistency discovered through ion balance calculations
277 CCO	I	Invalid due to inconsistency between measured and estimated conductivity
276 CIV	V	Inconsistency discovered through ion balance calculations, but considered valid
275 CCV	V	Inconsistency between measured and estimated conductivity, but considered valid
260 CSC	I	Contamination suspected
259 CUE	I	Unspecified error expected
258 CXH	V	Extremely high value, outside four times standard deviation in a log-normal distribution
257 CXL	V	Extremely low value, outside four times standard deviation in a log-normal distribution
251 CSI	I	Invalid due to large sea salt contribution
250 CSV	V	Considerable sea salt contribution, but considered valid
249 QDT	V	Apparent typing error corrected. Valid measurement
211 QDI	V	Irregular data checked and accepted by database co-ordinator. Valid measurement
210 QDE	V	Episode data checked and accepted by database co-ordinator. Valid measurement

1.9 Group 1: Exception flags for accepted, irregular data

Flag Mnemonic	V/I	Description
147 QOD	V	Below theoretical detection limit or formal Q/A limit, but a value has been measured and reported and is considered valid
120 QOR	V	Sample reanalysed with similar results. Valid measurement
111 QOI	V	Irregular data checked and accepted by data originator. Valid measurement
110 QOE	V	Episode data checked and accepted by data originator. Valid measurement
100 QOU	V	Checked by data originator. Valid measurement

1.10 Group 0

This group of flags (flags 001-099) is presently not defined. The "flag" value 0 is not an error condition flag. It must be assigned to the flag variable for all measurements that are of normal quality. In this manner the DO confirm that the data element is valid (with no known exception that

should have been flagged).