

**Technical Manual
for
Wet Deposition Monitoring in East Asia**

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of

Acid Deposition Monitoring Network in East Asia

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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 useful 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 chemical composition of wet deposition from all parts of East Asia. Wet deposition is responsible for 30-50 % of deposition fluxes 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 wet deposition monitoring techniques in terms of siting, sampling and shipping, chemical analysis, QA/QC, and data reporting of wet deposition, taking into consideration currently available technical manuals from other international wet deposition monitoring networks.

From April 1998, the preparatory-phase activities of the Acid Deposition Monitoring Network in East Asia (EANET) started, based on the decision of the Intergovernmental Meeting on EANET, held in March 1998 in Yokohama, Japan. Ten countries in East Asia, namely, China, Indonesia, Japan, Malaysia, Mongolia, the Philippines, Republic of Korea, Russia, Thailand and Vietnam, participated in the preparatory-phase activities. During the preparatory-phase, the participating countries made effort to comply with these guidelines and the technical manual to the extent possible.

In accordance with the relevant provisions of the "Implementation of Preparatory-phase Activities (EANET/IG/1/6 re., March 20, 1998)" adopted by the First Intergovernmental Meeting, the 2nd Interim Scientific Advisory Group Meeting reviewed and adopted the Guidelines and the Technical Manuals, taking into account the preparatory-phase activities and the latest scientific/technical information.

Documents titled the “Quality Assurance/Quality Control Programs for EANET Activities”, and the “Data Reporting Procedures and Formats” are the integral parts of the guidelines and the technical manuals as the complementary parts of acid deposition monitoring activities.

The technical manuals will be reviewed and updated in a timely and appropriate fashion, in keeping with advances in scientific/technical information understanding. It is desirable that the countries in East Asia endeavor to improve monitoring systems for acid deposition by making effective use of these guidelines and technical manuals.

1.2. Objectives of acid deposition monitoring

Monitoring data obtained from comprehensive observations based on this manual can be utilized not only evaluating long-range transport and deposition models, but also for assessing impacts of acid deposition on terrestrial ecosystems and urban structures. In the future, it is expected that such monitoring will provide the basis for cooperative studies with other acid deposition monitoring networks, and will contribute to the formulation of proposal to governments for control of the emission sources of acid substances.

1.3. Outline of the manual for monitoring wet deposition

In this technical manual, standard suggested items concerning, sampling methodology, analytical methods, data control and data reporting, and quality assurance and quality control aspects on wet deposition monitoring in EANET are described. For the majority of the methods, the necessary quality assurance is facilitated by a combination of simple and robust sampling techniques with well-described sampling equipment, and use of synthetic control samples for the chemical analyses. The methods and procedures are generally derived from the development and experience gained within Acid Deposition Monitoring Networks of JEA, EMEP, NADP, WMO and various research programs.

Throughout this technical manual, the molar unit is adopted for reasons 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. Fundamental items concerning monitoring on wet deposition

2.1. Monitoring sites

Selection of sampling sites is a critical factor in the monitoring of wet deposition. Therefore, sampling sites should be located in areas suitable for the purpose of the survey, and should properly represent the area in question. In addition, coordination is required with dry deposition monitoring, and the closest meteorological station.

EANET monitoring sites are classified into two basic categories, namely deposition monitoring sites and ecological survey sites. Deposition monitoring sites are sampling sites to collect fundamental data on the temporal and spatial distribution of acid deposition, and are further classified into three sub-categories: remote sites, rural sites, and urban sites for the objectives of the monitoring. Ecological survey sites are those to provide basic data for assessing the effects of acidification on terrestrial ecosystems, and further classified into two sub-categories: basic survey sites, and ecosystem analysis sites. All sites in each country should be classified according to these categories. Regarding the deposition monitoring sites, at least one or more remote or rural sites should be established in a country participating in the EANET activities.

2.1.1. Siting the sampling equipment

Sampling sites should be selected in places where land use in the vicinity of the sites proposed is likely to remain in almost the same condition for several decades. The selection of a site, and the proper location of the collector, is also important in order to ensure that the precipitation samples represent the area in question. In selecting the sites, consideration of the topographic features and land use types around a site, and meteorological conditions such as annual precipitation amounts and prevailing wind directions, should be taken into account. Sites should not be located in areas dominated by local meteorological conditions, such as mountaintops, cols, coastal sites which receive local wind effects, and valleys and basins which are subject to the formation of

stagnant air. In general, they should not be located around strong natural sources.

In selecting sites, consideration must be given to the emission sources surrounding the proposed site. The EMEP guidelines recommend that when the major part of the emissions influencing the air quality in an area are situated outside that area, selection of the site involves mainly considerations of the effects of the immediate surroundings and emissions within the nearest 20 km. They should not be located in areas dominated by local emission and contamination sources. Coastal areas which receive sea spray, volcanic areas and hot spring resorts which receive geothermal emissions, gravel roads, farmyards and tilled agricultural fields which receive windblown soil dust, and grazing land and pasture which receive ammonia are not recommended. In particular, ammonia is a special problem since the emissions are mainly linked with animal husbandry and agricultural activities.

In selecting a site, consideration of the field operation of instruments should also be required. Supply of electricity with stable voltage is necessary for continuous operations of wet-only collector. They should not be located in areas with frequent power breakdowns. A solar cell system should be available for sampling sites remote from power transmission lines. Each participant should have a preventive maintenance plan which covers all instruments used in the domestic network. Counterplans for vandalism should also be considered.

2.1.2. Minimum distance to emission and contamination sources

The guidelines establish a regulation for the minimum distances to emission and contamination sources.

- a. Regions within 50 km of large pollution sources such as cities, thermal power plants, major motorways should be excluded as remote sites and sites in ecological areas.
- b. Regions within 20 km of large pollution sources should be excluded as rural sites.
- c. Regions within 500 m of main roads (more than 500 vehicles/day) should be excluded as remote sites and rural sites.

These were based on guidelines from European and North American monitoring programmes with a mind to East Asian conditions. The distances given in this manual

should be taken only as indicative. An appraisal of local emission influences on air and precipitation chemistry must be made on the basis of considerations of meteorological and topographic conditions at the site.

2.1.3. Local criteria

Ideal criteria for placement of collectors in rural sites, remote sites, and sites in ecological area as follows.

- a. An open, flat, grassy area far enough from trees, hills, and other obstructions to avoid effects on sampling . No objects should be within a few meters of the collector, and no object should shade the collector.
- b. The horizontal distance between a large obstruction and the collector should be at least twice the obstruction height, or the top of an obstruction as viewed from the collector should be less than 30 °C above the horizon.
- c. The collector should be free from local emission and contamination sources such as waste disposal sites, incinerators, parking lots, open storage of agricultural products, and domestic heating. Regions within 100 m of these emission and contamination sources should be excluded
- d. The horizontal distance between collector and rain gauge (and dry deposition collector) should be greater than 2 meters. The rain gauge and the wet deposition collector should cross the direction of the prevailing wind during precipitation events.

2.2. Monitoring frequency and measurement parameters

2.2.1. Monitoring frequency

Samples should be collected every 24 hours in principle. Collection can also be conducted for each precipitation event, but this is operationally inconvenient because site operators often find difficulty in determining the start and end of precipitation events, and because operators are not easily available to collect samples at all times of day and night. If a collection bucket is used, it should be changed every day-whether precipitation occurred or not. The starting time of a day should be at 0900 local time as a general rule. If a refrigerator is not in use, biocide should be used for preserving the samples.

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

2.2.2. Measurement parameters

a) Precipitation chemistry parameters

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

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

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

b) Meteorological measurements

Wind direction/speed, temperature, humidity, precipitation amount and solar radiation in relation to wet deposition should be measured on-site or at the nearest meteorological station in accordance with the measurement frequencies and methods of the meteorological monitoring system of each country.

2.3. Laboratory treatment of samples

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

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

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

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

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

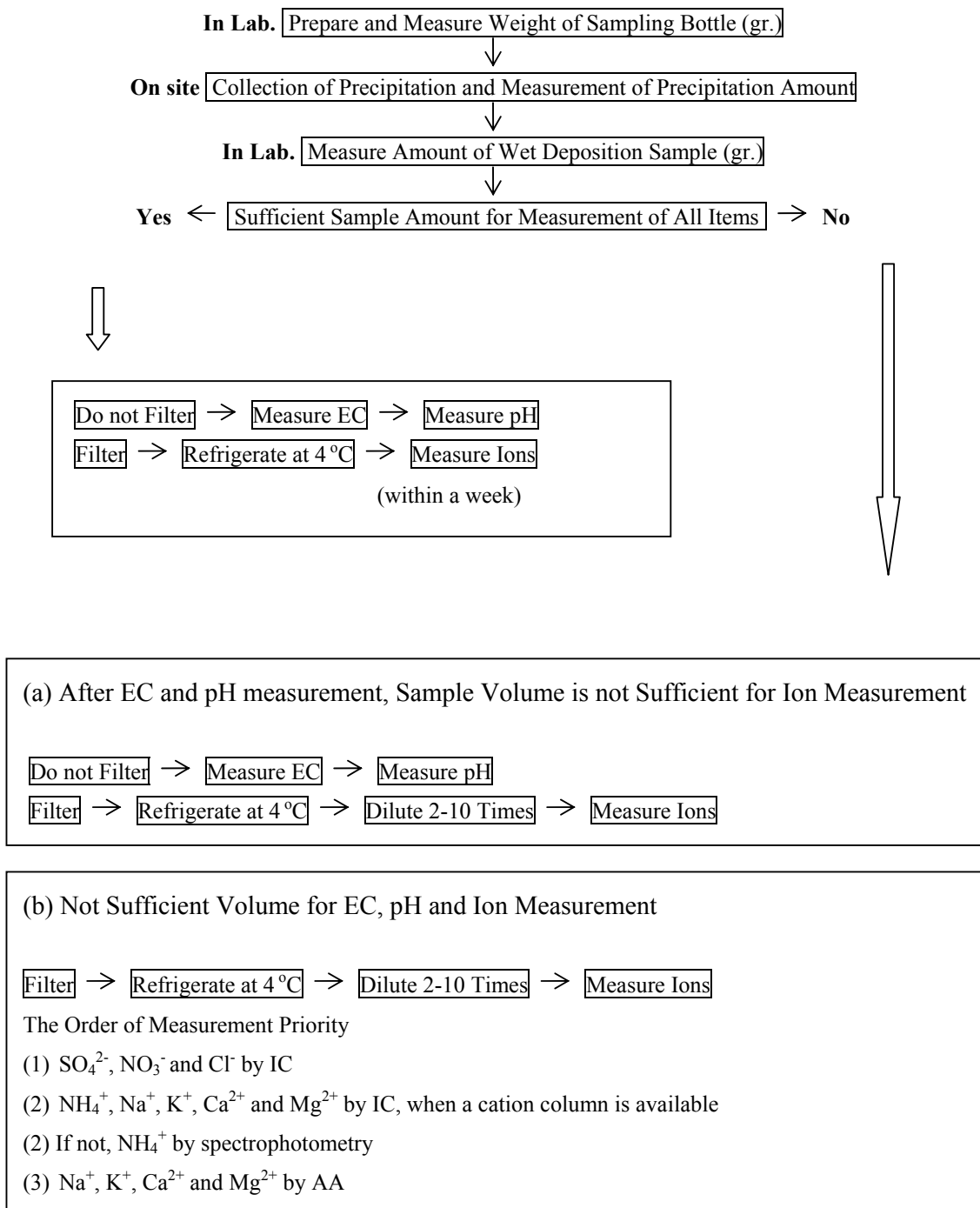


Fig. 1 Flow chart of sampling and chemical analysis of wet deposition

3. Wet deposition sampling methods

3.1. Collection of samples

3.1.1. Facilities at the site

Precipitation samples have low ionic concentrations and are thus very susceptible to contamination. The primary aims for field sampling are to maximize sample collection and to handle samples in a way that preserves their integrity. In principle, there should be a person responsible for the sampling. The site should have an operation shelter or hut and field measuring instruments. The latter should be separated from the former by more than 50m. All these facilities should be fenced for security. Supply of electricity is necessary for the operation of precipitation chemistry collectors. The operation shelter should be equipped with electric power, a refrigerator, sink, water supply, deionized water supply (less than 0.15 mS/m), two types of electronic balance (one type: max. weight:15 kg, min. weight 1 g and another:max.100 g, min. 0.1 mg), a data logger, a personal computer, telephone, working tables and chairs. As field measuring instruments, an automatic precipitation chemistry collector, a standard rain/snow gauge, and other meteorological instruments for measurement of temperature, wind direction and wind speed. All these instruments should be connected to the data logger or the computer. The rain gauge and the precipitation collector 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.

If the deionized water cannot be produced at the site or purchased, it should be supplied by the analytical laboratory. The amount of collected precipitation for each sample is recommended to be measured with the balance when the rain gauge is not available. Since the density of rain water is approximately 1.0 g/ml at 20 °C, the weight of the sample can be taken to equal its volume. The measurement of the precipitation sample volume by a graduated vessel increases the possibility of sample contamination, so the use of a balance is recommended. For daily or weekly sampling, the balance should have a capacity of 15 kg and a precision of at least 1 g. Graduated vessels are not recommended.

3.1.2. Sample collection instruments

All collected samples referred to here are "wet-only" samples. The most appropriate device is a wet-only collector. However, also acceptable are wet/dry versions which are composed of two collection buckets, one for collection of precipitation during the wet period and the other for collection of dry fallout during the dry period. The automatic precipitation collector basically consists of a collecting bucket or funnel, a lid that can be opened and closed, a precipitation sensor, and a sample container. A lid alternatively covers the bucket not in use. Because the collectors do not need to be of the same type, the technical details of collector operation can not be considered here. The operation of each collector should be done in accordance with the manual of each collector. Several different types are already in use in various countries, but the older collectors that cannot meet the following conditions should be replaced:

- the collector container or funnel opens automatically within 1 minute of the onset of precipitation and closes promptly at the end of the precipitation event.
- the wet sample should be shielded from contamination by dry deposition
- the collector bucket or funnel with bottle should be chemically inert to major constituents in acid precipitation
- the height of the collection bucket or funnel should be 1.0 to 1.5 m from the ground

The first two criteria will be covered by installing a precipitation sensor and a motor-driven tight fitting lid for the automatic collector. When the grid and plate of the sensor are shorted by a drop of water, the motor is activated, lifting the lid from the container or funnel. The sensor should have a minimum detection capability of 0.05 mm/h rainfall intensity and of 0.5 mm raindrop diameter, regardless of its direction. The sensor also should be heated 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 after events end (thereby allowing the collector to close). The height of the sensor should be as 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. The most important function of the lid is to seal the collection vessel during dry periods, preventing contamination by atmospheric gases and aerosols, and minimizing sample evaporation. Achieving good 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 lid should be able to be opened manually. Collectors used in snowy regions should have stainless steel or Teflon-coated, peaked, roofs mounted on the top of the lid. This prevents snow accumulation on the lid and blowing into the collection vessel when it opens.

To ensure inertness to major constituents in precipitation, polyethylene or Teflon or Teflon-coating should be in use for collecting funnels or buckets. Teflon or silicone should be in use for tubes which connect containers with the collecting funnels. To maintain inertness to major constituents in precipitation, tubes should be replaced once a year. For containers, for lower cost, durability, and availability, polyethylene should be generally employed. The capacity of containers should be determined by considering daily maximum precipitation amounts in the past ten years at the site.

3.1.3. Measurement of precipitation amount

Precipitation amount should be measured and/or recorded at the sampling site with each country's standard precipitation gauge or its equivalent. Standard precipitation gauges generally measure precipitation amount more efficiently and accurately than precipitation chemistry collectors. For this reason, they should be operated in parallel with the precipitation chemistry collector. The height of precipitation amount measurement is recommended to be from 1.0 to 1.5 m above the ground surface, same as that for the precipitation chemistry collector and the precipitation sensor.

The major environmental factors governing gauge undercatch are windspeed, the vertical wind profile at the point of measurement, the fall velocity of the precipitation, and the distortion of the wind flow and drop/snowflake trajectories around the gauge. In these factors, wind speed is the most important one that influences gauge undercatch, especially for snow. For these reason, information on the height of funnel of precipitation chemistry collector and that of rain gauge from ground level should be included in the reporting.

The method of reducing wind effects on gauge catch is by using wind shields around the gauges. The shields reduce the wind speed at the gauge orifice, thereby increasing the gauge collection efficiency. There are many types of wind shields in use, such as the Alter Shield, Nipher Shield, Tretyakov Shield, Wyoming Shield and U.S.S.R. Dual Fence Shield. In snowy countries, wind shields should be installed around gauges, precipitation chemistry collectors and precipitation sensors, but one should be careful to avoid contamination caused by the shield.

3.1.4. Snow sampling

The sampling of snow is difficult, because of the difficulty of detection of light dry snow by the electronic shorting sensor, blowing out of collected snow from the container or funnel by high winds and catch by wind and/or varying of the cross section of the collector caused by a heavy snow event. Since the characteristics of snow change from region to region, no standard snow chemistry collector has been developed at present. One collector is the same as the automatic precipitation chemistry collector, but improved for the use of snowy regions. The collector lid, body surface, inner part, sensor and funnel are heated to avoid the troubles caused by freezing and covering by snow. The heating temperature of the funnel should be 4-5 °C, and due attention should be paid in order to minimize the loss of sampled water by evaporation. It is also desirable to attach a wind shield device to the collector to minimize the effect of wind on the sampling of snow (e.g., Nipher Shield). But this collector presumably is unsuitable to extremely cold regions, because evaporation of water may cause serious error. In such a cold region, instead of the heated funnel, an open polyethylene cylindrical container of diameter 20-30 cm should be used as the collection vessel on a wet-only or wet/dry collector. 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 infrared rays snow sensor. But, since the characteristics of snow vary according to such factors as snowfall condition and density of snow sample, each situation must be examined individually before standardizing.

3.1.5. Use of biocides

If refrigeration cannot be used as sample preservation, biocides should be used to prevent microbial uptake and conversion of organic acids such as formic and acetic acid in regions where they are contained in rainwater. Thymol (2-isopropyl-5-methyl phenol) is

recommended because it is a solid and hence non-volatile at ordinary temperature. Thymol should be added at the rate of 400 mg to a 1000 ml sample bottle prior to the bottle being loaded into the collector, not only on a 7-days but also on a 24-hours basis. When Thymol is used in sample collection, ammonium ion should be measured by ion chromatography. Spectrophotometry (Indophenol blue) is not recommended.

3.2. Sample handling and shipping

3.2.1. Cleaning and preparation of collection vessel

The cleaning of collection vessels (buckets, funnel, bottles) before each sampling is necessary. Cleaning should be done at each field site. This has the advantage of saving the trouble of transporting large buckets across long distances, subjecting them to damage, delays and high transport costs. Buckets and bottles should be cleaned after leaching in laboratory detergent for 48 hours with water and doubly distilled or deionized water, followed by conductivity checks on the rinse waters (<0.2 mS/m). The funnel used on the collector should be washed well with deionized water and wiped with clean paper such as Kim wipe periodically.

3.2.2. Transport of the collection vessel to the collector

After checking leak-proof of collection vessels, they should be capped and/or enclosed in plastic bags for transport to the precipitation collector.

3.2.3. Removal and replacement of sample at the collector

The collection vessel should be capped (and/or bagged) and removed from the collector. Operators should be wearing disposable plastic gloves whenever handling the collection vessel.

3.2.4. Transportation of sample to the sample handling area

Sample spillage and contamination should be avoided by keeping the collection vessel capped and/or enclosed in bags during transport. Due to concern over potential sample contamination and spillage, sample transfer should be avoided at the field site.

3.2.5. On-site measurements

On-site measurements are recommended for sample volume by reading standard gauge depth (precipitation amount).

- Sample volume is recommended to be measured gravimetrically before transport to laboratory particularly when the rain gauge is not available. In that case, gravimetric measurements are easier to make and less prone to contamination and spillage. At each site, an electric balance with a 15 kg-capacity and with a minimum reading at least 1 g should be available as mentioned before. Gravimetric measurements should be quality controlled by checking a known weight before weighing the sample, or an automatic adjustable precision balance should be used. Volumetric measurements using graduated cylinders are not recommended because of the high potential for sample contamination and spillage.
- If a standard recording gauge is in use, reading should normally be taken within a few minutes of sample collection. Measurements must be made for every sampling period whether precipitation chemistry samples are collected or not.

3.2.6. Field blank

Field blank should be evaluated monthly. After samples are collected from the collector and the funnel and tubes are washed, 100 ml deionised water is added to the collector and collected in the same manner as usual sample collection and then sent to the analytical laboratory for the determination of all the chemical species. The remaining deionized water should also be sent to the laboratory for analysis. If the concentration of the chemical species in the field blank is obviously higher than the usual field blank values and/or those measured immediately after exchange of tubes, the funnel should be cleaned and/or tubes should be replaced.

The data of the field blank should be reported in the same way as sample data in Table 8, (p.47-49), named as FB-1,2,.....,n.

3.2.7. On-site sample preservation

In case of significant visible contamination including leaves and/or insects, filtration with a clean filter is recommended. Filters should be free from contamination.

Biologically active microorganisms are known to induce changes in the concentration of ammonium, nitrate, and organic acids in precipitation samples. To avoid this effect refrigeration should be done after measurement of sample volume, if a biocide is not in use. Samples should be refrigerated at 4 °C before shipment to the analytical laboratory. If sample volume is more than 200 ml, the part of the sample in excess of 200 ml can be discharged. The sample should be stored in 100 ml polyethylene bottles in duplicate. The samples should be shipped to the analytical laboratory weekly or biweekly if samples collected every 24 hours, or monthly if samples collected weekly.

3.2.8. Sample documentation

All precipitation samples collected at a site should be identified with the following information on the sample label and data form. This information should be recorded on preprinted forms often called sample history forms or field observer report forms. The format and content of the forms used in this network are shown elsewhere. The following quantitative and qualitative information should be recorded in a form.

- site name
- sample identification number
- sample start date, start time, end date, end time
 - (- precipitation start time and end time)
 - (- sample volume or weight (including collection vessel weight))
- standard gauge precipitation depth reading
- sample type (snow, rain, freezing rain, mixed, hail)
- sample contamination (noticeable suspended particulates, bird droppings, insects)
- instrument condition (operating correctly/incorrectly)
- site conditions (agricultural, industrial, or vehicular activity)
- operator remarks (unusual circumstances, problems, observations)
- supply requirements (transporting vessels, deionized water, freezer packs)
- operator's name or initials.

The sample history form should accompany the samples to the analytical laboratory.

3.2.9. Routine instrument checking and maintenance

Standard operating procedures at each site include routine checks and maintenance of the precipitation chemistry collectors and standard gauges, etc. Typical operations include:

- checking for proper sensor response and heating
- checking for satisfactory hood movement, and
- cleaning of the collection funnel and standard rain gauge funnel.

Semi-annual maintenance is normally required on standard gauges that measure both snow and rain, e.g. installing/removing internal funnel and wind shield, and charging with antifreeze or oil.

Trouble-shooting manuals should be available with each instrument at each site.

3.2.10. Sample shipment

The bottles used to store and transport the samples must be strong enough to resist breakage and leakage, while keeping the samples chemically stable. The most common methods of achieving the latter are (a) minimizing the shipping time (e.g. by using overnight transportation services) and (b) cooling the samples during transport (e.g. by using insulated shipping containers with freezer packs). The clean shipping bottles should be supplied by the central analytical laboratory in each country.

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4. Analytical methods

4.1. Introduction

It is important to choose suitable analytical procedures in order to obtain acceptable chemical data. Analytical procedures for precipitation analysis are frequently at the detection limits of analytical methods and instruments used, so that careful and sensitive analytical procedures have to be carried out. Therefore, analytical laboratories for precipitation chemistry should be equipped adequately to generate and to report analytical data of the highest quality. Samples arriving at laboratory should be kept in a refrigerator and used for analysis as soon as possible.

Sample solutions received at a laboratory must be well documented at the sampling sites. When a sample amount is very small, the order of measurement priority is as follows: Take an aliquot (e.g. 5ml) and dilute with deionized water to an appropriate amount, (1) determine sulfate (SO_4^{2-}), nitrate (NO_3^-) and chloride ions (Cl^-), by ion chromatography, then (2) ammonium ion (NH_4^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium ions (Mg^{2+}) by ion chromatography when a cation column is available. If not, (2) ammonium ion by spectrophotometry, (3) sodium, calcium, magnesium and potassium by atomic absorption spectrometry. If the remaining solution is enough for conductivity and pH measurement, measure them in this order.

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

For QA/QC of the analytical procedure, it is recommended to use standard reference materials (SRMs) of known concentrations of ions. SRMs can be commercially available (e.g. NIST SRM 2694, Simulated Rainfall), or can be provided by the central laboratory. It is also recommended to do duplicate analysis for every 10 or 20 of samples measured.

The following parameters should be analyzed as required parameters in precipitation samples in the analytical laboratory: conductivity, pH, sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-), ammonium (NH_4^+), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}).

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

Heavy metals, phosphate, aluminum and organic compounds may be measured for the characterization of precipitation. Procedures suggested for rainwater analysis are specified in Table 1. The analytical methods detailed here are typical for precipitation samples analyzed on instrumentation commonly available in many laboratories at the time of writing. These methods will require modification and revision if new or different analytical systems are employed, or if sample composition is unusual.

Table 1 Procedures Suggested for Rainwater Major Constituent Analysis

Analysis	Instrumental Method
Electric Conductivity	Conductivity Cell
pH	Glass electrode (preferably with the Electrode of non-leak inner cell)
Chloride, Nitrate, Sulfate, Nitrite, Fluoride, Phosphate	Ion Chromatography (preferably with suppressor) Spectrophotometry
Ammonium	Ion Chromatography Spectrophotometry (Indophenol blue)*
Sodium, Potassium, Calcium, Magnesium Ions	Ion Chromatography Atomic Absorption/ Emission Spectrometry
Heavy Metals, Aluminum Mercury	Atomic Absorption Spectrometry with Graphite Furnace, ICP Emission Spectrometry, ICP/MS, Mercury Analyzer With a Gold Trap
Organic Acids	Ion Chromatography

*Not recommended if the biocide, thymol, is used in sample collection.

4.2. Electric conductivity

4.2.1. Background

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

Conductivity is measured and expressed in units of mS/m and corrected to 25 °C. The conductivity range of precipitation samples extends from <0.5 - 100 mS/cm.

In case of the sample amount is very small, the aliquot which is used for conductivity measurement can be used for pH determination. If this is done, the conductivity has to be measured before the pH to avoid any possible error due to salt contamination from the pH electrode.

4.2.2. Apparatus

- a. The conductivity bridge and cell must have a measurement range of 0.1-100mS/m. The precision of the conductivity meter has to be within $\pm 0.5\%$ of the range and have an accuracy of $\pm 1\%$ of the range.
- b. Platinum conductivity cell
- c. Thermometer
- d. Water bath of 25 °C temperature is recommended. If a temperature controlled water bath is not available, use of water bath without temperature control but containing at least 5 L of water may be considered.
- e. Plastic or glass vessel corresponding to the diameter of the cell used

4.2.3. Reagent solution

- a. Stock solution A, 0.1 M -KCl - 7.456g of predried (2h at 105 °C) KCl dissolved in deionized water, and diluted to 1000 ml at 25 °C with deionized water.

- b. Stock solution B, 0.01 M -KCl -10 ml of 0.1M -KCl, dilute to the mark of 100 ml at 25 °C with deionized water.

4.2.4. Calibration

Calibration for conductivity measurement is multipoint. With each set of precipitation samples, a set of 0.0001M-, 0.0005M-, and 0.001M- KCl solutions should be prepared from 0.01 M- KCl stock solution by dilution with deionized water. The conductivity of the deionized water should also be measured. The specific conductivity of known KCl solutions (Table 2) should be expressed in a graph. The sample conductivity can then be read directly from this plot of measured conductivity vs. the specific conductivity.

Table 2 Conductivity of KCl solution at 25 °C

Concentration	Conductivity
M	mS/m
0.0001	1.494
0.0005	7.390
0.001	14.700

4.2.5. Measurement procedure

The manufacturer's directions for operation of the instrument should be followed. The samples and the standard solutions are recommended to be measured at 25 °C in a water bath if available. The cell must be rinsed thoroughly with deionized water between measuring each sample and excess water should be shaken off. The conductivity cell must be kept clean. The measured value should be expressed to 0.01 mS/m. If the temperature of the sample is not 25 °C, correct the measured value to 25 °C (Table 3).

Table 3 Conductivity of 0.0005M KCl

Temperature	Conductivity
°C	mS/m
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

4.3. pH measurement

4.3.1. Background

The pH of precipitation varies between 3.0 and 7.5 pH units (the concentration of hydrogen ion varies from $<0.1 \mu\text{mol/l}$ to $1000 \mu\text{mol/l}$). The pH of a precipitation sample is related to the free acid activity as the negative logarithm of the hydrogen ion concentration by the equation

$$\text{pH} = -\log(\text{H}^+)$$

where (H^+) is the activity or concentration of free hydrogen ions. The pH of a precipitation sample is determined electrometrically, 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.

The temperature effect on electrometric pH measurements can be controlled by using instruments that have temperature compensation. A temperature of 25°C is recommended for pH measurement.

4.3.2. Apparatus

pH meters are commercially available with different specifications and options. A pH meter should have both an intercept and slope adjustment and should be capable of measuring to ± 0.01 pH unit. Two electrodes should be used with the pH meter. A measuring glass electrode is sensitive to hydrogen ions. The reference electrode can be calomel, or silver/silver chloride; other reference electrodes can also be used as long as they have a constant potential. Combination electrodes with both measuring and reference functions are preferable since they require less of the sample to be used.

pH electrodes should be stored in deionized water (when the room temperature is above 25 °C, it is not recommended to keep an electrode in deionized water for a long time, because electrodes are prone to be attacked by photosynthetic algae), in a 7.4-mS/m KCl standard, in 10^{-4} M acid (H_2SO_4) solution or in filling solution. Prior to use, the pH electrode should be thoroughly rinsed with deionized water.

One of the chief problems that occurs with pH measurements is the aging of the electrode. Reference solutions, which have a known pH and conductivity similar to those of the precipitation samples, should be used for checking the pH electrode. These solutions should be stored under refrigeration and replaced when solution pH or conductivity are seen to have changed. If the pH of the reference sample has changed from the previous measurement by more than 0.10 pH unit but conductivity has not changed, the electrode should be checked. The measured pH value is recommended to agree within ± 0.02 pH unit of the expected value. If large differences are observed, a new solution is prepared from a concentrated calibration solution (commercially available standard reference materials). If performance is still inadequate, the electrode must be replaced. If possible, checking pH calibration with a series of dilute mineral acids (ex. pH 4.0, 4.2, 4.4, 4.6, 4.8, 5.0 with HCl) once in a month, is recommended to obtain good pH values. 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 HCl solution to 100 ml with deionized water, respectively.

4.3.3. Reagents and solutions

A commercially available primary standard buffer solution with a pH of 4.01(4.0) and 6.86 (7.0) should be used, having guaranteed traceability.

4.3.4. Calibration of pH meter

The pH meter should be calibrated before and after each set of precipitation samples at a minimum of two points in the expected pH range. As most precipitation samples have a pH value in the range of 3.0 - 7.5, pH 4.0 and 7.0 buffer solutions are therefore used.

Before calibration, fill the electrode with a filling solution supplied by the manufacturer and then rinse it carefully with deionized water. Use the pH 6.86 (7.0) buffer solution to set the intercept of the pH response with the standardization knob, and then use the pH 4.01 (4.0) buffer to adjust the slope control of the pH response and the temperature function control. Check the measured pH to be within ± 0.02 pH unit of the buffer value. Rinse the electrode thoroughly with deionized water after each calibration. It is very important to rinse thoroughly because precipitation samples are much more dilute than buffer solutions, thus incomplete rinses often cause errors. Use of special low-ionic strength buffers and ionic strength adjustment solution is recommended.

4.3.5. Measurement procedure

- a. Calibrate the pH meter according to the procedure outlined in the previous chapter.
- b. Place the sample solution in a clean plastic or glass vessel to cover the sensing elements of the electrode. Maintenance of the samples at 25°C in a water bath is recommended. If a temperature controlled water bath is not available, use of water bath without temperature control but containing at least 5 L of water may be considered.
- c. Rinse and wipe drops off the electrode with filter paper, immerse it in the sample vessel and swirl the sample gently for a few seconds.
- d. 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 (preferably to 0.01 unit) and the temperature of the sample.

4.4. Anion determination by ion chromatography

4.4.1. Background

Ion chromatography has been widely used in recent years to analyze anions in precipitation. Sulfate, nitrate, and chloride in precipitation are separated on an ion exchange column because of their different affinities 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 or an electric 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 isochratic analysis of a precipitation sample containing chloride, nitrate, and sulfate is shown in Figure 2.

Any anions with a retention time similar to that of the main anions could interfere. For example, when NO_2^- exists, it elutes just after Cl^- , which causes the peak to be asymmetric.

The ranges of measured anion concentrations in precipitation and recommended detection limits are given in Table 4.

Table 4 Measured Anion Concentration in Precipitation and Recommended Minimum Detectable Amount (MDA)

Anion	Range ($\mu\text{mol/l}$)	MDA ($\mu\text{mol/l}$)
SO_4^{2-}	<1 - 200	1
NO_3^-	<2 - 300	1
Cl^-	<1 - 1000	1
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

4.4.2. Apparatus

- a. Ion chromatograph (example 1: YEW 7000, example 2:DX500) with a

conductivity detector

- b. Anion separator column (example 1: ICS-A13, example 2: IonPac AG4A-SC or AS11 + AS4A-SC)
- c. Anion suppressor column (example 1: HPS-SA-1, example 2:ASRS-1)
- d. An integrator is recommended to process the chromatograms.

4.4.3. Reagents and solutions (Isochratic methods)

Example 1

- a. Concentrated eluent, 0.4M- Na_2CO_3 /0.4M- NaHCO_3 - dissolve 84.79g Na_2CO_3 and 67.24g NaHCO_3 in 2 liters of hot deionized water.
- b. Working eluent 4mM- Na_2CO_3 / 4mM- NaHCO_3 , - dilute 40 ml of concentrated eluent to 4 liters with deionized water.
- c. Regenerant, 15 mM- H_2SO_4 - dilute previously prepared 1.5M- H_2SO_4 accordingly,
- d. Mixed stock solution -10.4 mmol/l SO_4^{2-} , 16.1 mmol/l NO_3^- , and 28.2 mmol/l Cl^- (often commercially available, otherwise prepare from reagents of high purity)
- e. Standard solution A – dilute 5 (or 2) ml of mixed stock solution to 500 (or 200) ml with deionized water (104 $\mu\text{mol/l}$ SO_4^{2-} , 161 $\mu\text{mol/l}$ NO_3^- , and 282 $\mu\text{mol/l}$ Cl^-).
- f. Working standard solutions are prepared from standard solutions by diluting 20, 10 and 2 ml of standard solution to 200 ml with deionized water prior to every measurement.

Example 2

- a. Concentrated eluent, 0.18M- Na_2CO_3 /0.17M- NaHCO_3 -dissolve 19.6g Na_2CO_3 and 14.28g NaHCO_3 in 1 liters of hot deionized water.
- b. Working eluent 1.8mM- Na_2CO_3 / 1.7mM- NaHCO_3 - dilute 40 ml of concentrated eluent to 4 liters with deionized water.
- c. Regenerant, 50 mM- H_2SO_4 - dilute previously prepared 5M- H_2SO_4 accordingly.
- d., e., f., same as example 1.

4.4.4. Measurement procedures

Example 1

- a. Prepare new eluent and regenerator solutions (if required).
- b. Set up the chromatograph for most sensitive range
- c. Begin to pump the eluent and regenerant (if required) through the columns.

Condition instrument for at least 30 minutes.

- d. Inject standard solutions through the loop injector (50 or 100 μ l) and start analysis. It is preferable that calibration curve will be constructed from at least 5 working standard solutions
- e. 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. In the case that there is little affect on sample analysis, for example, if injecting deionized water between the standard series and the first subsequent samples injection, injecting standard solution from lower to higher concentration could be acceptable.
- f. Inject precipitation sample solution in the same manner as standard solutions.

(when an auto sampler is available)

- d. Fill the auto sampler with standards and samples.
- e. Turn on the auto sampler to start analyzing samples.

4.5. Metal cation determination by ion chromatography

4.5.1. Background

Besides anion analyses, ion chromatography has also been widely used in recent years to analyze cations in precipitation. The principle is the same as that of anion determination except that different column materials are used and that the suppressor column is often omitted. The material commonly used for cation separation is a cation exchange resin with active surface. Suppressor columns are used (example 2:DX500), or sometimes not used (example 1: YEW7000). Sodium, ammonium, potassium, calcium and magnesium ions are detected by a conductivity detector, without changing the eluent when certain columns (example 1: ICS-C25 or C45, example 2: CG14 + CS14 with CSRS-1 recycle suppressor) are used. In other columns (example 1: ICS-C15) monovalent cations (Na^+ , NH_4^+ , K^+) are determined using an eluent and then divalent cations (Mg^{2+} and Ca^{2+}) are determined using another eluent.(Figures 3)

Any cations with a retention time similar to that of the main 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.

The ranges of measured cation concentrations in precipitation and recommended detection limits are given in Table 5.

Table 5 Measured Cation Concentration in Precipitation and Recommended Minimum Detectable Amount (MDA)

Cation	Range ($\mu\text{mol/l}$)	MDA ($\mu\text{mol/l}$)
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

4.5.2. Apparatus

- Ion chromatograph (example 1: YEW 7000, example 2: DX100) with a conductivity detector
- Cation separator column (example 1: ICS-C25, example 2: CG14 + CS14)
- An integrator is recommended to process the chromatograms.

4.5.3. Reagents and solutions (Isochratic methods)

Example 1

- Concentrated eluent, 1 M-Tartaric Acid
- Working eluent, 5mM-Tartaric Acid / 1 mM-2,6 PDCA (2,6-Pyridinedicarboxylic acid), -Add 0.167g of 2,6 PDCA to 5 ml of concentrated eluent and make up with deionized water to 1 l.
- Mixed stock solution (a mixture of 1000 mg/l of each chemical species)
- Standard solution A
- Working standard solution

Example 2

- Concentrated eluent, commercial methane sulfonate (reagent grade)
- Working eluent, 10 mM methane sulfonate- dilute 0.65 ml of concentrated eluent in 1 l deionized water
- , d. f., the same as example 1

4.5.4. Measurement procedure

- a. Prepare new eluent and regenerator solutions.
- b. Set up the chromatograph for the most sensitive range
- c. Begin to pump the eluent through the columns. Condition instrument for at least 30 minutes.
- d. Inject standard solutions through the loop injector (50 or 100 μl) and start analysis. It is preferable that calibration curve will be constructed from at least 5 working standard solutions
- e. Turn on the auto sampler switch to start analyzing samples. 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. In the case that there is little affect on sample analysis, for example, if injecting deionized water between the standard series and the first subsequent samples injection, injecting standard solution from lower to higher concentration could be acceptable.
- f. Inject precipitation sample solution in the same manner as standard solutions.
(when an auto sampler is available)
- d. Fill the auto sampler with standards and samples.
- e. Turn on the auto sampler to start analyzing samples.

4.6. Ammonium ion determination by spectrophotometry

4.6.1. Background

For measuring ammonium in wet deposition samples, automated or manual spectrophotometric determination with phenate is used. A sample is mixed with alkaline phenol and hypochlorite to form an indophenol blue complex. A 50 °C controlled temperature heating bath is used to increase the rate of color formation. The transmitted light energy (630 nm wavelength) measured through the sample is a function of the concentration of ammonium ion in the sample.

The detection limit of this method is 2 $\mu\text{mol/l}$ and the concentration range is 2-110 $\mu\text{mol/l}$ as NH_4^+ . This range can be extended by sample dilution. The test tubes have to be closed throughout the analysis. Elevated concentrations of ammonium in the laboratory air will result in a positive interference. Wash sample cups with deionized water immediately

prior to use and rinse cups again with portion of the standard or sample to be analyzed. It is worth noting that this method requires more skill and training to get good data compared with other instrumental analyses.

4.6.2. Apparatus

- Spectrophotometer with a 630 nm setting
- Heating bath (50 °C)
- Glass test tubes with ground-in stoppers

4.6.3. Reagents and solutions

- Stock solution 5.54 mmol/l - dissolve 0.2965 g NH_4Cl (dried at 105 °C) in deionized water and dilute to 1000 ml.
- Alkaline phenol: 3.5 g of sodium hydroxide (NaOH) + 8.5 ml phenol + 0.04g sodium nitroprusside in 100 ml deionized water; refrigerate the solution at 4 °C for a period not exceeding 1 week; prepare fresh weekly
- Sodium hypochlorite (NaOCl) solution - dilute 250 ml of 5.25 % NaOCl to 500 ml with deionized water

4.6.4. Measurement procedure

- a. The spectrophotometer should be on for 30 minutes before proceeding
- b. Put the 5 ml of sample in the test tube, add 15 ml of deionized water, 0.5 ml of alkaline phenol solution, and 0.5 ml of sodium hypochlorite solution; close the test tube with glass stopper
- c. Set the heating bath to 50 °C, leave the sample in the heating bath for 2 hours and measure the sample with the spectrophotometer at 630 nm

4.7. Metal determination by atomic absorption/emission spectrometry

4.7.1. 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 (Fig. 4). 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 Limits of Detection

Metal	Range ($\mu\text{mol/l}$)	Detection Limit ($\mu\text{mol/l}$)
Na^+	0.4 - 90	0.4
K^+	1 - 30	1
Ca^{2+}	0.2 - 80	0.2
Mg^{2+}	0.2 - 20	0.2

Detection Limit is defined as $S/N=2$

4.7.2. Apparatus

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 PC (Figure 4)

b. Hollow cathode lamps for Na, K, Ca and Mg.

Single-element lamps and multi-element lamps can be used. For the determination of Na and K, flame atomic emission measurement can also be used, when the instrument has devices for it.

c. Compressed gases and pressure-reducing valves -

Two cylinders of clear acetylene are necessary; the air may be supplied from a laboratory compressor (with a cleaning unit) or a cylinder of compressed air.

4.7.3. Calibration

- a. Prepare stock standard solution from high purity chemicals (preferably metals) using deionized water and HNO₃ (conc. spectrograde purity) at a concentration of 1000 mg of metal/l. Commercially available standard solutions may be used.
- b. Prepare a blank (use deionized water and nitric acid- and/or lanthanum nitrate 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 must be added to both the samples and the calibration solutions.

4.7.4. 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 the particular 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

Mode	Na	K	Ca	Mg
	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

Addition of lanthanum nitrate solution is effective to eliminate the interference of co-existing anions and of unequal ionization ratio in the flame between the sample and standard solutions. It is important to add the correct amount of lanthanum solution so that the lanthanum concentration in both the samples and the working standard solutions are similar.

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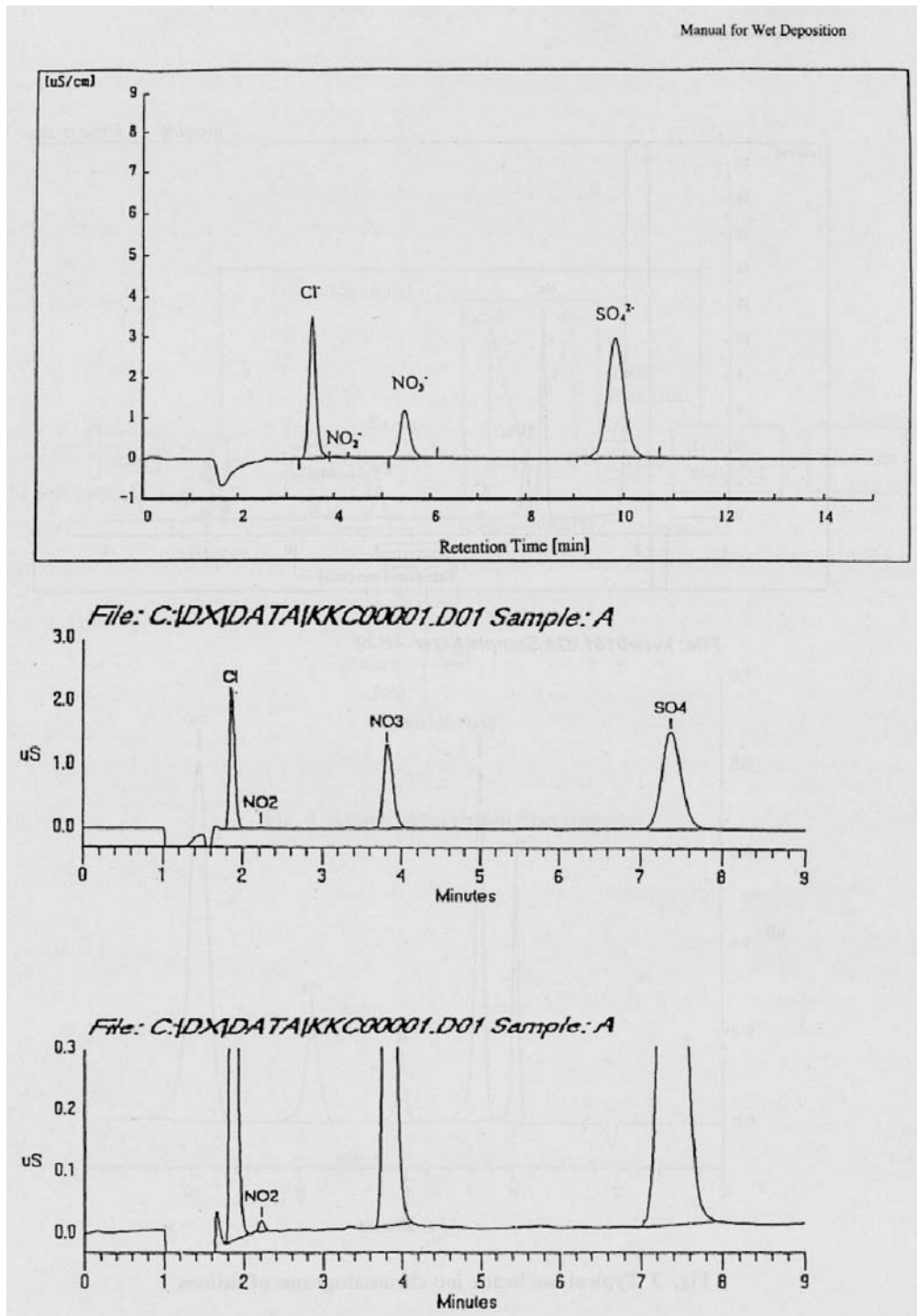


Fig. 2 Typical isochratic ion chromatograms of anions

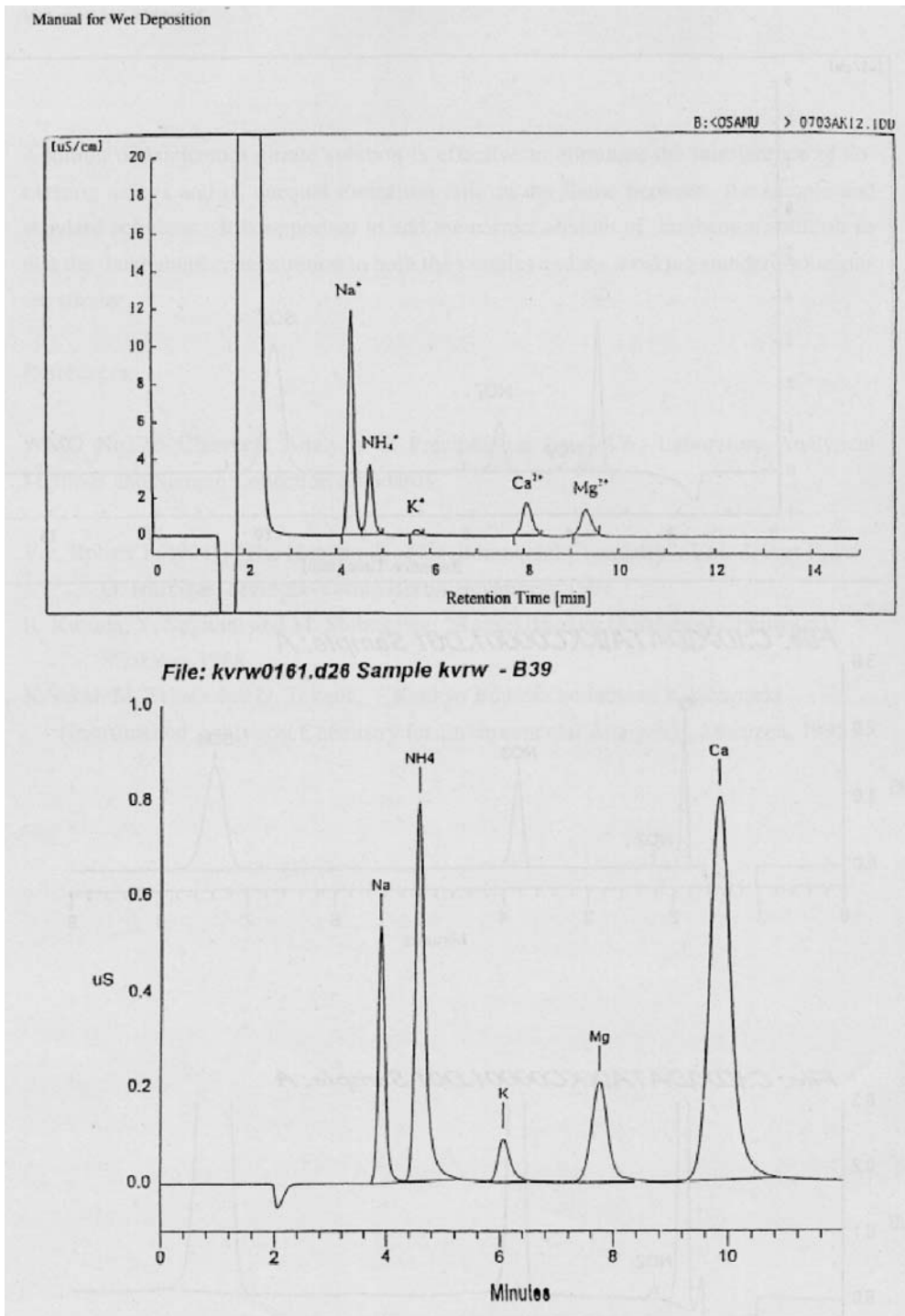


Fig. 3 Typical isochratic ion chromatograms of cations

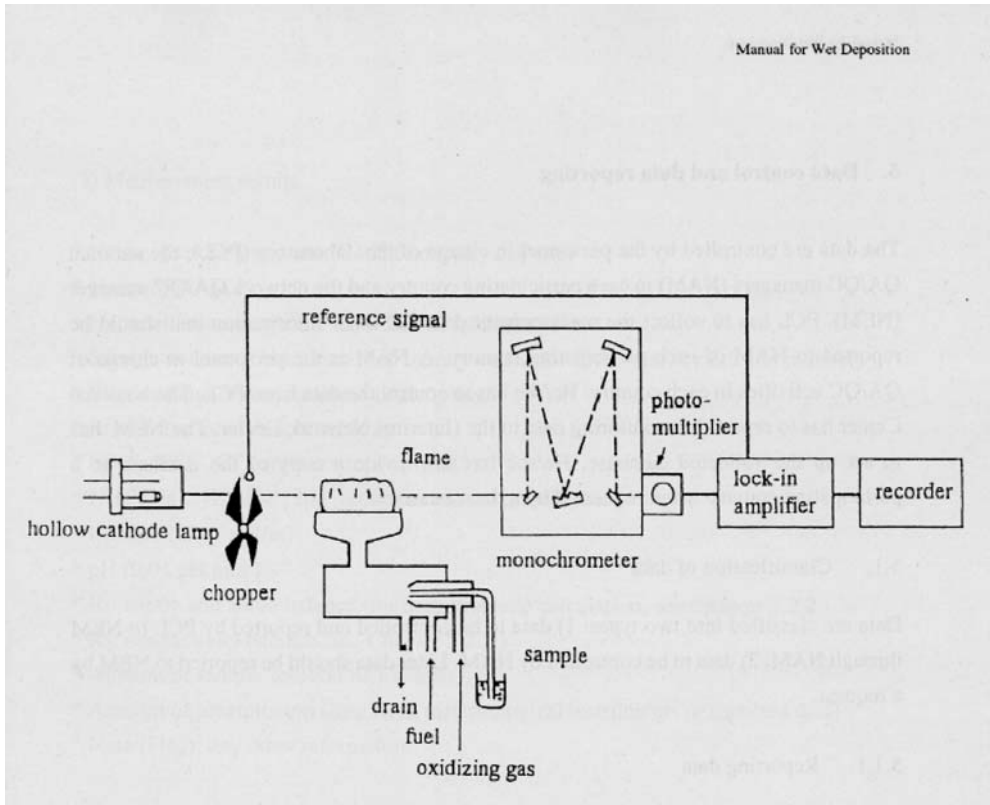


Fig. 4 Atomic Absorption Spectrometer

5. Data control and data reporting

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). 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 (Interim) Network Center. The NEM has to set up the validated database. He/she has to provide a copy of the database to a participating country when requested by a the country.

5.1. 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.

5.1.1. Reporting data

The data to be reported to 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 ($\mu\text{mol/l}$)
- * NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} concentrations ($\mu\text{mol/l}$)
- * Conductivity (mS/m)
- * pH (0.01 pH unit)
- * R_1 : cation and anion balance (for definition and calculation, see Chapter 5.2.2.)
- * R_2 : conductivity balance (see Chapter 5.2.2.)
- * Amount of sample solution (0.1 g unit)
- * Amount of precipitation (data from meteorological instruments or reported data)
- * Note (Flag): any other information

5.1.2. Controlled data by individual country

The data to be controlled by 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, laboratory conditions. These data should be reported when there is a demand.

(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.)

5.2. 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,
- 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. .

5.2.1. Statistical tests

The statistical tests compare new measurements with data already stored in the database. The tests are carried out to identify possible outliers 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.

5.2.2. Ion balance and conductivity balance check

The principle of electroneutrality in precipitation water requires that total anion

equivalents equal total cation equivalents. According to this principle, ion balance in a precipitation sample should be checked by the method described in 6.2.2.

For dilute solutions (e. g. below 10^{-3} M), the total conductivity can be calculated in mS/m from the molar concentrations and molar conductivity (at infinite dilution) of the individual ions. The observed conductivity values should be checked by the method described in 6.2.2, comparing to the calculated conductivity values for precipitation samples.

5.2.3. Data completeness

Data completeness should be evaluated in terms of the rainfall amount ratio of that by precipitation chemistry collector to rain gauge. Data completeness describes the fraction of valid data in a certain monitoring period. The following value of index of data completeness should be reported.

Two kinds of data completeness measures are used, that is per cent precipitation coverage length (%PCL) and per cent total precipitation (%TP).

- %PCL Per cent precipitation coverage length is the per cent 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 Per cent total precipitation is the per cent of the total precipitation data measured during the summary period that is associated with valid samples.

5.2.4. Analytical precision

The precision of laboratory chemical analyses of precipitation samples should be tested and be reported by the method described on 6.2.2.

5.3. Data flags

To indicate quality information to data users, data flags and/or data comments are useful; they will indicate whether a 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 conditions which produce that level of validity. Thereby, the user can select the data most appropriate to his/her application.

In near future, data flags and/or data quality comments will be implemented in EANET in a manner consistent with those used by EMEP, as shown in Appendix. For the time being, several flags should be utilized, as described in 5.4.3.

5.4. Data reporting form

Data reporting forms may be used for the reporting site condition (on site, local scale, regional scale), sampling condition, sample history, chemical analysis condition and measurement results (precipitation chemistry including precipitation amounts, calculated index, flags and data completeness). Staff in the Interim Network Center responsible for the measurements will have responsibility for ensuring that all data elements are properly entered into the appropriate databases. Data should be submitted to the center once every year .

The followings should be described on every data form: name of country and site (code of country and site), name of NAM, name of laboratory (code of laboratory) and name of PCL.

5.4.1. Information about sites, sampling, shipping, laboratory operation

(1) Site condition

Any change in the immediate environment of the site should be reported every year, even if the site selection criteria remain satisfied.

Name and code of each site should be given first. The category of a site should be determined by consideration of the siting criteria. No site is included in more than one class.

The area around the collector should be described in terms of potential sources of contamination of samples on three different scales. Maps of the site and potential contamination sources should be provided to the Interim Network Center . An example of such a report is taken from NAtChem, Canada (Fig.5 and Table 9). The required site information is described in 1.1, and 1.2 should be updated annually.

- On-site scale

Description of the on-site scale is given for the area within a radius of 100m from collector. Locations of collector, and rain gauge, and meteorological parameter measurement devices should be given. Trees, overhead wires, buildings, and other physical obstacles should be also described. Ground cover and slope, and farmlands etc., are also important factors. Pictures of the collector and its surroundings should be attached.

- Local scale

Surface storage of agricultural products, fuels, vehicles, parking lots, or maintenance yards and feed lots, dairy barns or a large concentration of animals within a radius of 100m-10km should be described. Urban areas will be also described with population.

- Regional scale

Both stationary and mobile emission sources within 50 km should be described with emitted chemical species and emission intensities. Urban areas with population greater than 10,000 should be described. Meteorological stations should be described on the map with available information.

(2) Sampling condition

- Precipitation chemistry collector

The following should be reported: model and manufacturer of the collector, funnel diameter, materials of funnel, underside of lid, tubing, filter and filter holder, storage bottles, and chemical used as biocide. Start and end times of sample collection in the sampling plan should be reported.

Pictures of collector and design diagrams should be attached.

- Rain gauge and meteorological parameter measurement devices

Model and manufacturer should be reported together with figures or pictures.

(3) Sample history

Sample history plays an important role in sample handling from collection to chemical analysis. An example is taken from CAPMoN (Fig. 6)

- Shipping

Shipping frequency and packing procedure for collected samples should be also reported.

- Laboratory operation

The following should be reported: sample preparation procedure, plan of chemical analysis frequency, range of laboratory room temperature.

5.4.2. Chemical analysis

The chemical analysis methods and control chart should be reported as the laboratory QA/QC data for each sampling station. The following items are included in the form.

SO_4^{2-} : Method applied, instrument name and type, detection limit

Performance: calibration curve (5 points), sulfate content in the deionized water (when a dilution process is included), data obtained from analysis of standard solution (commercial SRM) of known sulfate value, data from duplicate or triplicate analysis of samples (preferably every 10 to 20 samples), detection limit and recovery of spiked sample (if available).

NO_3^- : Method applied, instrument name and type, detection limit

Performance: calibration curve (5 points), nitrate content in the deionized water (when dilution process is involved), data obtained from analysis of standard solution (commercial SRM) of known nitrate value, data from duplicate or triplicate analysis of samples (preferably every 10 to 20 samples), detection limit, recovery of spiked sample (if available).

Cl^- : Method applied, instrument name and type, detection limit

Performance: calibration curve (5 points), chloride content in the deionized water (when dilution process is involved), data obtained from analysis of standard

solution(commercial SRM) of known chloride value, data from duplicate or triplicate analysis of samples(preferably every 10 to 20 samples) , detection limit, recovery of spiked sample (if available).

NH_4^+ : Method applied, instrument name and type, detection limit

Performance: calibration curve (5 points), ammonium content in the deionized water(when dilution process is involved), data obtained from analysis of standard solution(commercial SRM) of known ammonium value, data from duplicate or triplicate analysis of samples(preferably every 10 to 20 samples) , detection limit, recovery of spiked sample (if available).

Ca^{2+} : Method applied, instrument name and type, detection limit, additives (e.g. Lanthanum solution.)

Performance: calibration curve (5 points), calcium content in the deionized water(when dilution process is involved), data obtained from analysis of standard solution(commercial SRM) of known calcium value, data from duplicate or triplicate analysis of samples(preferably every 10 to 20 samples) , detection limit, recovery of spiked sample (if available).

Mg^{2+} : Method applied, instrument name and type, detection limit, additives

Performance: calibration curve (5 points), magnesium content in the deionized water(when dilution process is involved), data obtained from analysis of standard solution(commercial SRM) of known magnesium value, data from duplicate or triplicate analysis of samples(preferably every 10 to 20 samples) , detection limit, recovery of spiked sample (if available).

Na^+ : Method applied, instrument name and type, detection limit, additives

Performance: calibration curve (5 points), sodium content in the deionized water(when dilution process is involved), data obtained from analysis of standard solution(commercial SRM) of known sodium value, data from duplicate or triplicate analysis of samples(preferably every 10 to 20 samples) , detection limit, recovery of spiked sample (if available).

K^+ : Method applied, instrument name and type, detection limit, additives

Performance: calibration curve (5 points), potassium content in the deionized water (when dilution process is involved), data obtained from analysis of standard

solution (commercial SRM) of known potassium value, data from duplicate or triplicate analysis of samples (preferably every 10 to 20 samples), detection limit, recovery of spiked sample (if available).

Conductivity: Instrument name and type

Performance: calibration curve for KCl solutions (2 or 3 points) and deionized water used, data obtained from analysis of standard solution (commercial SRM) of known Conductivity value, temperature of sample and standard solutions, data from duplicate or triplicate samples (preferably every 10 to 20 samples).

pH: Instrument name and type

Performance: data obtained from with standard solution (commercial SRM) of known pH value, temperature of sample and standard solutions, data from duplicate or triplicate samples (preferably every 10 to 20 samples).

When other chemical species are reported in the form, describe the methods and performance.

5.4.3. Measurement results and flags

Sample chemistry should be reported with the data quality (flags). The reporting form should include sampling conditions, precipitation amounts, date of completion of chemical analysis, concentration of components and flags for each component. An example of Form is shown in Table 8. Each national center should keep all the raw data for future reference.

The following items are included in the form.

* Sample number (Code consist of country code, site code, year, month and number)

* Start and end of date and time of sampling

When a code name for each sample solution is adopted put this here and then,

DATE (date of the sample collection, check that it should be the same as the one on the sample information form).

[Unit: yyyy/mm/dd hh:mm, ex. 2000/01/31 09:00]

* End of date of chemical analysis

[Unit: yyyy/mm/dd, ex. 2000/02/09]

* SO_4^{2-} , NO_3^- , Cl^- concentrations

Though the analysis may use units such as mg/L, the report type is converted into the molarity, it is reported.

[Unit: $\mu\text{mol/l}$, Format: #####.#, ex. 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.

* NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} concentrations

Though the analysis may use units such as mg/L, the report type is converted into the molarity, it is reported.

[Unit: $\mu\text{mol/l}$, Format: #####.#, ex. 23.2]

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.

*Conductivity

[Unit: mS/m , Format: ##.##, ex. 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: ##.##, ex. 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.

* R₁: cation and anion balance (for definition and calculation, see Chapter 5.2.2.)

[Unit: %, Format: #####.#, ex. 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.

*R₂: conductivity difference (see Chapter 5.2.2.)

[Unit: %, Format: #####.#, ex. 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 conductivity.

* Amount of sample solution

[Unit: g, Format: #####.#, ex. 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: #####.#, ex. 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

Further details of data handling and data reporting will be established on the basis of preliminary monitoring activities.

References

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

Krognest, 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.

Table 8(2)

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

Site name : _____

Funnel diameter : _____ (mm)

Name of Laboratory : _____

Name of reporter : _____

Sample No.	Sampling period				NH ₄ ⁺ μmol/l	flg1	flg2	flg3	Na ⁺ μmol/l	flg1	flg2	flg3	K ⁺ μmol/l	flg1	flg2	flg3	Ca ²⁺ μmol/l	flg1	flg2	flg3	Mg ²⁺ μmol/l	flg1	flg2	flg3	flg1	flg2	flg3	Date of analysis	Note			
	Start		End																													
	Date	Time	Date	Time																												

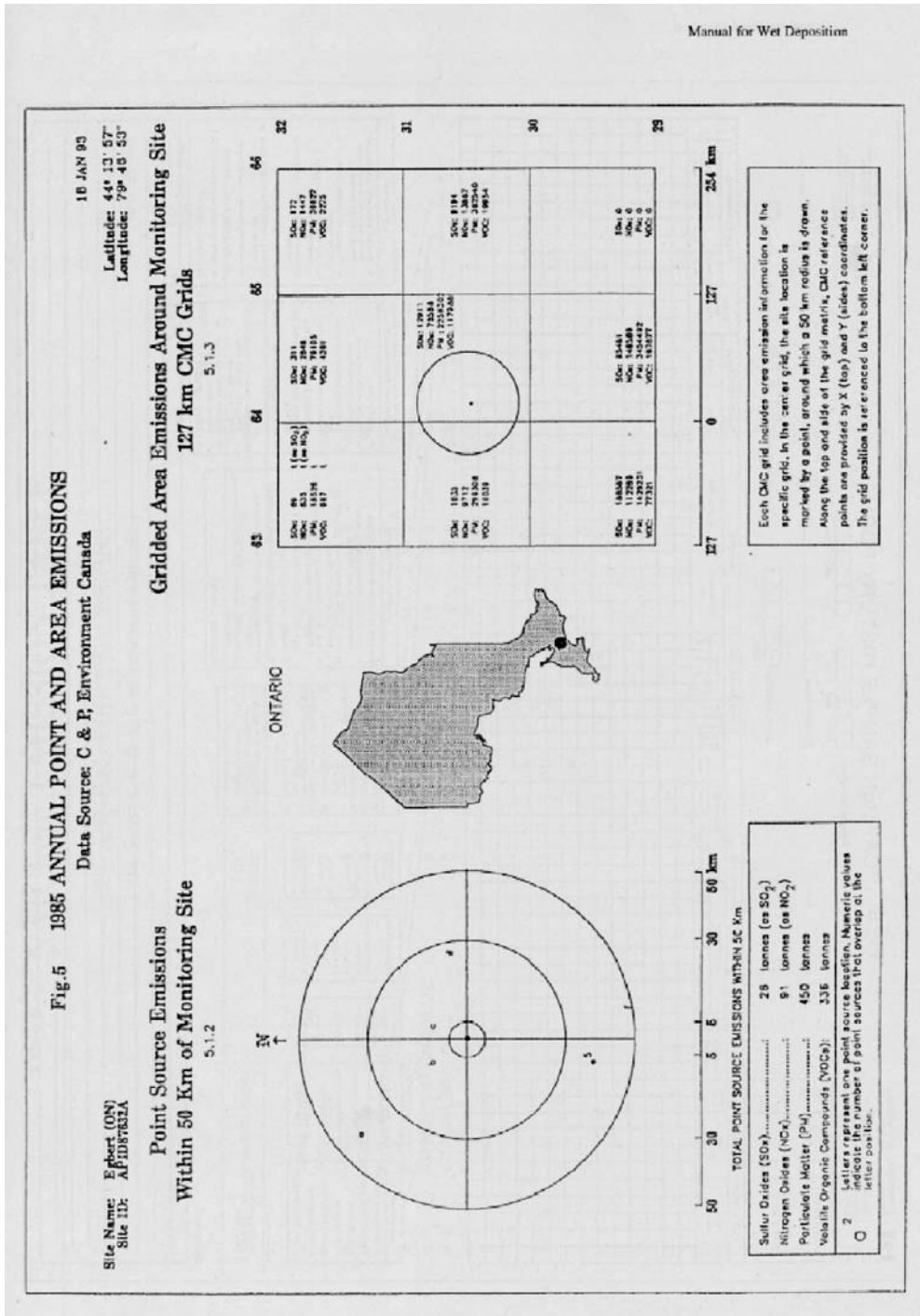


Fig.5

Table 9 NatChem EMISSION TABLE

1985 ANNUAL POINT EMISSIONS
Data Source: C & P, Environment Canada

12 OCT 92

Site Name: Egbert (ON)
Site Id: CAPM87632A

Latitude: 44° 13' 57"
Longitude: 79° 48' 53"
Page Number: 1 of 1.

Ref #	Industry Name	SOx Tonnes	NOx Tonnes	VOC Tonnes	PM Tonnes	Distance Km	Direction	Product
a	TOWN OF COLLINGWOOD	17	43	170	170	40.7	NW	
b	INDUSMIN	0	6	0	1	13.9	NNW	
c	MOLSON	1	21	41	122	14.3	NNE	
d	INDUSMIN	0	3	0	3	27.4	ENE	
e	ALCAN EXTRUSIONS	0	4	125	0	38.9	SSW	
e 2	BATRONICS INC.	0	5	0	16	38.9	SSW	
e 3	BATCLIFF'S OF CANADA LTD.	8	2	0	114	38.9	SSW	
e 4	STERLING DRUG CO.	0	3	0	0	38.9	SSW	
e 5	YORK COUNTY HOSPITAL	0	4	0	0	38.9	SSW	
f	CARPENTER E.R. CO.	0	0	0	24	49.6	SSE	
Totals:		26	91	336	450			

Table 9

6. Quality assurance /quality control

6.1. Introduction

Quality assurance and quality control (QA/QC) plays a key role of wet deposition monitoring. Measurements of wet deposition, when obtained with carefully designed and executed quality assured operating systems, will produce data of high accuracy, precision, completeness, comparability and representative.

Quality control and quality assurance play an important role in all types of monitoring. Although they sound alike, they are actually different and their differences are addressed in Vet(1991). Quality control will be defined as procedures to ensure that the analytical system is 'in control' while quality assurance is defined as procedures to ensure that the quality control procedures are effective. Differences between QA and QC is often made by considering quality control to laboratory operations and quality assurance to be external (Vet, 1991). In other words, quality control will be applied to the monitoring system before and during the measurements whereas quality assurance will be important after the measurement.

Measurements should as much as possible follow closely the standard methods. It is, however, not always possible to follow the standard methods throughout the measurements. Accidents will occur. Therefore, all aspects of measurement, including all problems encountered, should be recorded and reported as an important part of each data record. The point is to document what was done and how it was done before and during the measurements, so that data users are fully informed as to the suitability of the data for any intended use. It is essential that the quality of the conclusions from the data analysis should be consistent with known data quality.

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

In this chapter, QA/QC procedures are addressed after considering corresponding operation manuals of major international monitoring networks of wet deposition.

6.2. 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 and storage, and laboratory chemical analysis. The precision and accuracy of precipitation monitoring is then composed as the sum of the precision and accuracy of individual processes.

6.2.1. Sampling precision

Sampling precision should be established by duplicate sampling with collocated precipitation collectors at the measuring station employing identical collection, handling, and storage procedures for all duplicated samples from the station. Periodic visits to the station by experts and training of observers are required to ensure that all collection procedures are being followed and that no major physical change has taken place at the site.

6.2.2. Quality control of laboratory measurements

Assessment of the precision, accuracy, and validation of laboratory chemical analyses of precipitation samples are required to ensure maintenance of the quality control standards for precipitation analysis in the chemical laboratory.

a. Analytical precision

To estimate the contribution of analytical variability, duplicate sample analysis should be performed on about 5% of routinely analyzed samples. Samples containing a large quantity of precipitation should be divided, one half being analyzed immediately after the routine analysis, and the other half being refrigerated at about 4°C to be analyzed within a week. Analytical precision is then defined and reported as the standard deviation between the two analysis. The analytical precision is defined as

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

where d_i denotes the difference between the two analysis, and N_i is the number of sample

pairs in the reporting period. An additional factor of 2 is included in the denominator to take into account the random error associated with both measurements.

b. Accuracy of chemical analysis

Artificial “precipitation” inter-calibration samples should be sent to all chemical laboratories yearly from a reference laboratory. The accuracy of chemical analysis would be determined from results of the analysis of inter-calibration samples of these artificial precipitation. The results of these inter-calibrations should be used to study and find solutions to existing laboratory problems and to improve the quality of laboratory analyses.

c. Cation and anion balance

The principle of electroneutrality in precipitation water requires that total anion equivalents equal total cation equivalents.

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

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

Where C and A represents anion and cation equivalents, 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: Precision Measurement Systems. EPA/600/R-94/038E US EPA Office of Research and Development, Washington, DC 20460, April 1994)

$$A(\mu\text{eq/L}) = \sum C_{A_i} \cdot V_i$$

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

$$C(\mu\text{eq/L}) = 10^{(6-\text{pH})} / 1.008 + \sum C_{C_i} \cdot V_i$$

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

$$(\mu\text{mol/L}) = (\text{mg/L}) \times 1000/M$$

where the molecular weight (M) for cations and anions is given in Table 10.

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

$$\begin{aligned} [\text{HCO}_3^-] &= P_{\text{CO}_2} \text{HCO}_2 K_{a1} / [\text{H}^+] = (360 \times 10^{-6}) (3.4 \times 10^{-2}) 10^{\text{pH}-6.35+6} \\ &= 1.24 \times 10^{\text{pH}-5.35} \end{aligned}$$

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

$$\begin{aligned} [\text{CH}_3\text{COO}^-] &= [\text{CH}_3\text{COOH}] K_a / [\text{H}^+] = [\text{CH}_3\text{COOH}] \times 10^{\text{pH}-\text{p}K_a} \\ &= [\text{CH}_3\text{COOH}] \times 10^{\text{pH}-4.56} \end{aligned}$$

Constants for HCO_3^- , HCOO^- , and CH_3COO^- are included in Table 10.

Air concentration of CO_2 in equilibrium with precipitation samples is assumed to be 360 ppm. Dissociation constants in terms of pKa for carbonic, formic, and acetic acids are 6.35, 3.55, and 4.56, respectively.

In some sites, 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 10.

The required ion balances of precipitation analyses are given in Table 11. If the required criteria 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 Basic constants

Ion	Molecular Weight (M)	Molar Conductivity (λ), S cm ² /mol
H ⁺	1.008	349.7
NH ₄ ⁺	18.04	73.5
Ca ²⁺	40.08	59.8 x 2
K ⁺	39.10	73.5
Mg ²⁺	24.31	53.3 x 2
Na ⁺	22.99	50.1
NO ₃ ⁻	62.01	71.5
SO ₄ ²⁻	96.06	80.0 x 2
Cl ⁻	35.45	76.3
HCO ₃ ⁻	61.02	44.5
HCOO ⁻	45.0	54.6
CH ₃ COO ⁻	59.1	40.9
F ⁻	19.00	55.5
Br ⁻	79.90	78.2
NO ₂ ⁻	46.01	71.8
PO ₄ ³⁻	94.97	69.0 x 3

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

Table 11 Required criteria for R₁

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

d. Comparison between calculated and measurement in electric conductivity

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

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

where Λ_{calc} denotes the calculated conductivity of the solution (in mS/m), c_i the ionic

concentration of the i-th ion (in $\mu\text{mol/L}$), Λ_i^0 the molar conductivity (in $\text{S cm}^2/\text{mol}$) at infinite dilution and 25°C .

Thus

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

where $c()$ denotes the ionic concentrations in $\mu\text{mol/L}$ of the ion in parentheses and the constants are the molar conductivity of the individual ion at infinite dilution at 25°C (see Table 10).

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

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

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

The required comparison criteria of measured and calculated conductivities are expressed in Table 13. If the required conductivity comparison criteria 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 12 Required criteria for R_2

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

6.3. Site performance audit

A site performance audit for a precipitation monitoring network should be made at least once a year. This audit provides field training and exchange of information. A detailed protocol for a site performance audit will be developed later. A site performance audit should include the following steps:

a. Check of operation of wet-only automatic collector

To check sampling operation, the auditor should add 1-2 drops of deionized water to the precipitation sample sensor. The collector is judged to be operating normally if, within a few seconds, the lid covering the wet bucket moves out. If the wet bucket is open, the cleanliness of the bucket should be checked. After the wet bucket has been open for several minutes, the auditor should touch the sensor plate to check that it is heating. If necessary, the moisture may be removed from the sensor plate by blowing across the plate. The sensor plate then dries more quickly and the lid should cover the bucket again.

b. Check of procedure for container cleaning

The auditor should check the container cleaning procedure performed by a responsible person, and the availability of containers on-site. The auditor should also check the quality of deionized water at the site (electric conductivity < 0.15 mS /m).

c. Review of site procedures and data documentation

The auditor should observe site personnel performing all the routine site operation duties. This should include review of sample handling, of instrumentation procedures, and of data reporting. After observing sample handling, the auditor should then interview the site personnel to gather detailed information on the operation of the sampling device, sample treatment, water supply, and data recording. The interview should also be used to assess operator training.

6.4. Preliminary quality assurance of obtained data sets

The data should be assessed in terms of accuracy, precision, representativeness, completeness, and comparability. These elements will be quantitatively evaluated and the overall data quality will then be evaluated.

Accuracy and precision will be assessed in connection with evaluation of chemical analysis practices, and site representativeness can be evaluated on the basis of reports on the site description as well as site audit. Comparability will be assessed by collocated sampling with different type of collectors and intercomparison study of common precipitation samples.

Data completeness should be evaluated in terms of the ratio of rainfall collected by the precipitation chemistry collector to that collected by the standard rain gauge. Data completeness describes the fraction of valid data in a certain monitoring period. Valid samples are defined as acceptable in terms of ion balance and conductivity check measures, R1 and R2. A tentative target value of this data completeness is 80 %.

In addition to the results of chemical analysis, comments and flags should be compiled in order to assess monitoring techniques. On this basis, some suggestions for improving data quality should be submitted.

6.5. External quality assurance program

During Acid Deposition Monitoring in East Asia, an external quality assurance program will be implemented to:

- verify that the measurements are being carried out and reported with the expected precision and accuracy and that all measurement 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; and
- assess and compare the measurement methodology and quality assurance data of this network to other international and domestic networks.

Further details of this program will be established on the basis of preliminary monitoring activities.

6.6. Training

Overseas and local technical training should be provided. Details of the training will be given in a separate document.

References

Chemical Society of Japan (1984) Kagaku Benran (Handbook of Chemistry), 3rd ed., Maruzen, Tokyo.

Eaton, W. C. (1990) External Quality Assurance Audits of the Utility Acid Precipitation Study Program (UAPSP), UAPSP 119 Contract U101-2.

Summers, P. W. , private communications.

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) Flag system

The database shall contain data that have been calibrated, scaled and quality controlled by personnel in charge in a laboratory (PCL). As long as a measured value is available for all elements in a time series, matters are simple. But in real life, the required information is not always available:

- A measurement may be missing because something went wrong. The problems range from human error to instrument breakdowns to bird-droppings in the buckets, the possibilities are innumerable.
- In many cases a measured value is available, but the accuracy may have been reduced by some problem.
- When there has been no precipitation, concentrations of compounds in the precipitation are undefined. Also other situations exist where a measurement precipitation value is undefined. In statistical evaluations this should not be confused with missing measurements.
- When a parameter is below the detection limit of the instrument, no numerical value is available, but we know the value is low. Such information may be significant to many users of the data set.

It is not practical to register and report every detail of things that go wrong. A selected set of information should be registered to serve the following main objectives:

- To create (in some cases to salvage) a series of measurements with the highest data availability possible in spite of unavoidable irregularities.
- To provide the data user with possibility to include or exclude less reliable data elements, depending on his requirements. (Please note that it is the responsibility of the data user to ensure that his programs treat flagged data elements correctly.)
- To facilitate statistical treatment of failure modes, for subsequent method improvements (in near future).

A flag is related directly to a single data element. It is generated by the data originator, and is coded into a flag element that has a numerical value from 0 to +1 (stored in the numflag column of the measurement value table). A flag value of zero means that no flag exists for the corresponding data element. By setting the flag value to zero, the PCL confirms that the data element is valid (with no known exception that should have been flagged).

Each flag may be represented either by three digit number (001 to 999). The flag values are sorted so that the most serious (least recoverable condition) is given the highest numerical value. If more than one flag is used, the most serious must always be given first. This allows for evaluation of the seriousness of the condition by one simple arithmetical test. It would have been far more complicated to test for a large number of specific flag values. Each numerical flag is a three digit string (xxx, yyy, zzz, etc). The flag stored in the numflag column is a real value in the format 0.xxxyyyzzz. This allows a maximum of three conditions to be flagged simultaneously in one string variable. For example, flag is input with 0.678657478, when the sample is affected by typhoon, and when overflow and ionic balance are outside specification [typhoon: 678, overflow :657 and ionic balance standard the outside: 478].

(2) List of flags used in the EMEP database

(For the time being, these flags are not utilized in EANET.)

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.

Group 9: Missing flags

- 999 Missing measurement, unspecified reason
- 990 Precipitation not measured due to snow-fall. Needed for historic data, should not be needed for new data
- 980 Missing due to calibration or zero/span check *

Group 8: Flags for undefined data elements

- 899 Measurement undefined, unspecified reason
- 890 Concentration in precipitation undefined, no precipitation

Group 7: Flags used when the value is unknown

- 799 Measurement missing (unspecified reason), data element contains estimated value
- 784 Low precipitation, concentration estimated

- 783 Low precipitation, concentration unknown
- 781 Value below detection limit, data element contains detection limit
- 780 Value below detection limit, data element contains estimated value. Also used for aggregates that is uncertain since many input elements were below the detection limit
- 771 Value above range, data element contains upper range limit
- 770 Value above range, data element contains estimated value
- 750 H⁺ not measured in alkaline sample
- 701 Less accurate than usual, unspecified reason. (Used only with old data, for new data see groups 6 and 5)

Group 6: Mechanical problem

- 699 Mechanical problem, unspecified reason
- 679 Unspecified meteorological condition
- 678 Hurricane
- 677 Icing or hoar frost in the intake *
- 659 Unspecified sampling anomaly
- 658 Too small air volume *
- 657 Precipitation collector overflow. Heavy rain shower (squall)
- 656 Wet-only collector failure, operated as bulk collector
- 655 Two samples mixed due to late servicing of collector. Estimated value created by averaging
- 654 Sampling period longer than normal, observed values reported
- 653 Sampling period shorter than normal, observed values reported
- 649 Temporary power fail has affected collector operation

Group 5: Chemical problem

- 599 Unspecified contamination or local influence
- 593 Industrial contamination
- 591 Agricultural contamination
- 578 Large sea salt contribution (ratio between marine and excess sulphate is larger than 2.0)
- 568 Sand contamination
- 567 Insect contamination
- 566 Bird droppings
- 565 Pollen and/or leaf contamination
- 549 Impure chemicals
- 540 Spectron interference in laboratory analysis
- 532 Data less accurate than normal due to high field blank value

- 531 Low recovery, analysis inaccurate
- 521 Bactericide was added to sample for storage under warm climate

Group 4: Extreme or inconsistent values

- 499 Inconsistent with another unspecified measurement
- 478 Inconsistency discovered through ion balance calculations
- 477 Inconsistency between measured and estimated conductivity
- 460 Contamination suspected
- 459 Extreme value, unspecified error
- 458 Extremely high value, outside four times standard deviation in a lognormal distribution
- 457 Extremely low value, outside four times standard deviation in a lognormal distribution

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

(The database co-ordinator (DC) in EMEP: The NEM in EANET)

- 299 Inconsistent with another unspecified measurement
- 278 Inconsistency discovered through ion balance calculations
- 277 Inconsistency between measured and estimated conductivity
- 260 Contamination suspected
- 259 Unspecified error expected
- 258 Extremely high value, outside four times standard deviation in a log-normal distribution
- 257 Extremely low value, outside four times standard deviation in a log-normal distribution
- 249 Apparent typing error corrected
- 211 Irregular data checked and accepted by database co-ordinator
- 210 Episode data checked and accepted by database co-ordinator

Group 1: Exception flags for accepted, irregular data

- 147 Below theoretical detection limit or formal Q/A limit, but a value has been measured and reported
- 120 Sample reanalysed with similar results
- 111 Irregular data checked and accepted by data originator
- 110 Episode data checked and accepted by data originator
- 100 Qualified by data originator

(*: Flag for air pollution sampling)

(3) Flag under consideration

The following flags have to be discussed to the database co-ordinator in EMEP.

782 Low precipitation, concentration estimated from analysis of diluted sample.

678 Hurricane or typhoon .

676 Squall.

675 Sand storm.

674 Biomass burning (e.g. forest fire).

673 Volcano

564 Algal growth in sample.

399 Use of precipitation amounts data at nearby meteorological station.

349 Use of calculated precipitation amounts by sample volume.

(Under line: Flags under consideration as the EANET original flags.)