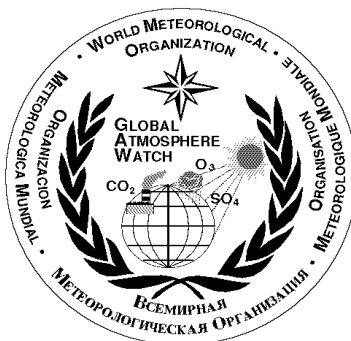# WORLD METEOROLOGICAL ORGANIZATION
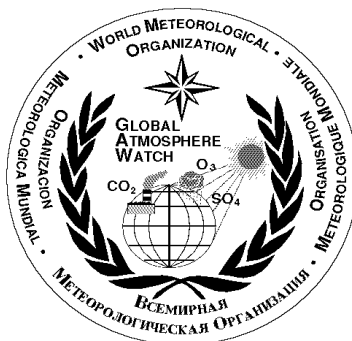# GLOBAL ATMOSPHERE WATCH

No. 160

MANUAL FOR THE

GAW PRECIPITATION CHEMISTRY

PROGRAMME

Guidelines, Data Quality Objectives and Standard Operating Procedures

November 2004

(Amended October 2015)

WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

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MANUAL FOR THE
GAW PRECIPITATION CHEMISTRY
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Guidelines, Data Quality Objectives and Standard Operating Procedures

Edited by Mary A. Allan

Prepared by

GAW Precipitation Chemistry Science Advisory Group

World Meteorological Organization

NOTE

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ACKNOWLEDGMENT

GLOSSARY

ABBREVIATIONS

AAS	atomic absorption spectrometry
ac	alternating current
AC	automated colorimetry
ACS	American Chemical Society
AES	atomic emission spectrometry
BDL	below detection limit
Ca^{2+}	calcium ion
$CaCO_3$	calcium carbonate
$CaSO_4$	calcium sulphate
CAPMoN	Canadian Air and Precipitation Monitoring Network
$CHCl_3$	Trichloromethane, also known as chloroform
CH_3COO^-	acetate ion
CH_3COOH	acetic acid
Cl^-	chloride ion
CoV	coefficient of variation
CRM	certified reference material
CsCl	caesium chloride
csv	comma separated value (computer file structure)
dc	direct current
DI	deionised
DL	detection limit
DQO	data quality objective
EANET	East Asia Acid Deposition Monitoring Network
EDL	electrode discharge lamp
EMEP	Cooperative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe
F^-	fluoride ion
ftp	file transfer protocol
GAW	Global Atmosphere Watch Programme
GAW-PC	Global Atmosphere Watch Precipitation Chemistry Programme
GFAA	graphite furnace atomic absorption spectrometry
H^+	hydrogen ion
HCl	hydrochloric acid
HCO_3^-	hydrogen carbonate ion, also known as bicarbonate ion
$HCOO^-$	formate ion
HCOOH	formic acid
HDPE	high density polyethylene
HNO_3	nitric acid
H_2O	water
HPICE-ASI	high performance ion exclusion chromatography
H_2SO_4	sulphuric acid
IC	ion chromatography
ICP-AES	inductively coupled plasma - atomic emission spectrometry
ICP-MS	inductively coupled plasma - mass spectrometry
IEC	ion exclusion chromatography
ISC	ion suppressor column
ISO	International Organization for Standardization
K^+	potassium ion

KCl	potassium chloride
KNO_3	potassium nitrate
La_2O_3	lanthanum oxide
Mg^{2+}	magnesium ion
MgO	magnesium oxide
$MgSO_4$	magnesium sulphate
Na^+	sodium ion
NaCl	sodium chloride
Na_2CO_3	sodium carbonate
NADP	National Atmospheric Deposition Programme (in USA)
$NaCH_3COO$	sodium acetate
NaHCOO	sodium formate
$NaHCO_3$	sodium hydrogen carbonate, also known as sodium bicarbonate
$NaNO_3$	sodium nitrate
Na_2SO_4	sodium sulphate
NCDC	National Climatic Data Centre (in USA)
NH_3	ammonia
NH_4^+	ammonium ion
NH_4Cl	ammonium chloride
NH_4NO_3	ammonium nitrate
NILU	Norsk institutt for luftforskning (Norwegian Institute for Air Research)
NIST	National Institute for Standards and Technology (in USA)
NMHS	National Meteorological and Hydrological Service
NO_2^-	nitrite ion
NO_3^-	nitrate ion
NSS sulphate	non-sea salt sulphate
pH	a measure of the acidity of a solution, defined as the negative log of the hydrogen ion concentration (given in moles per litre): $pH = -\log_{10} [H^+]$
PO_4^{3-}	phosphate ion (orthophosphate)
POPs	persistent organic pollutants
QA	quality assurance
QAPjP	Quality Assurance Project Plan
QA/SAC	Quality Assurance - Science Activity Centre
QC	quality control
SD	standard deviation
SHF	sample history form
SO_3^{2-}	sulfite ion
SO_4^{2-}	sulphate ion
SOP	standard operating procedure
UNEP	United Nations Environment Programme
USA	United States of America
UTC	coordinated universal time
UV	ultraviolet
WDC	World Data Centre
WDCPC	World Data Centre for Precipitation Chemistry
WMO	World Meteorological Organization

UNITS

˚C	degrees Celsius, also known as degrees Centigrade
cm	centimetre
d	day
g	gram
$g\ m^{-2}\ y^{-1}$	gram per square metre per year
h	hour
kg	kilogram
$kg\ ha^{-1}\ y^{-1}$	kilogram per hectare per year
km	kilometre
L	litre
m	metre
M	molar [molarity is a unit of concentration defined as the number of moles of solute per litre of solution]
mM	millimolar
mg	milligram
$mg\ L^{-1}$	milligram per litre
min	minute
mL	millilitre
mm	millimetre
mol	a chemical quantity containing 6.02×10^{23} atoms or molecules
$m\ s^{-1}$	metre per second
N	normal [normality is a unit of concentration defined as the number of gram equivalent weights of solute per litre of solution]
pH	unit of acidity defined as: $pH = -\log_{10}[H^+]$
pK_a	equilibrium constant for weak acids defined as $pK_a = -\log_{10}(K_a)$ where K_a denotes the dissociation constant of interest (often referred to as the dissociation constant in the case of weak acids and bases)
t	metric tonne (10^6 g)
y	year
μ	micro (10^{-6})
$μe\ L^{-1}$	microequivalent per litre
μm	micron, micrometre (10^{-6} m)
$μmol\ L^{-1}$	micromole per litre
$μS\ cm^{-1}$	micro Siemens per centimetre [a unit commonly used for measuring electric conductivity]

DEFINITION OF TERMS

accuracy

The degree of agreement between an observed value and an accepted reference value. Accuracy includes both random and systematic error.

aliquot

A representative portion of the whole.

analyte

The substance, in a chemical analysis, whose concentration is to be measured.

audit

A systematic evaluation to determine the operational quality of some managerial or operational function or activity.

bias

A persistent positive or negative deviation of the measured value from the true value. In practice, it is expressed as the difference between the value obtained from analysis of a homogenous sample and the reference value:

Bias = Measured mean value – reference value

blank sample

A sample prepared by using deionised water or a chemical matrix (reagent) and processed so as to measure artefacts in the measurement (sampling and analysis) system.

blind sample

A sample submitted for analysis with a composition and identity that is known to the submitter but is unknown to the analyst. The blind sample is used to test the analyst's or laboratory's proficiency in the execution of the measurement process.

bulk sample

A sample that has been exposed continuously to the atmosphere for the entire sampling period. This occurs when the sample container is left uncovered between periods of precipitation during a sampling period, allowing some unknown amount of dry deposition to enter the sample. Since the dry deposition process is affected by wind speed, temperature, vegetation, surface type and other variables, the bulk sample container does not receive dry deposition that is representative of dry deposition received in the site environment. Therefore it is not possible to accurately estimate dry deposition as the difference between a bulk deposition measurement and an independent wet deposition measurement.

calibration check solution

A synthetic or real precipitation sample with known ion concentrations, which is analysed in each analytical run to give an independent check of the analytical performance.

certified value

The reported numerical quantity that appears on a certificate for a property of a reference material.

chain of custody

An unbroken trail of accountability that ensures the physical security of samples, data, and records.

collocated sampler

Two or more precipitation chemistry collectors located within 30 meters of one another for the purpose of evaluating the precision of sample collection.

comparability	A measure of the degree to which methods and data sets can be represented as similar.
completeness	The amount of valid data obtained, compared to the planned amount (i.e., number of rain samples collected versus number of rain samples that occurred), usually expressed as a percentage.
control chart	A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control (Taylor, 1987).
data quality objectives	(DQOs) The stated objectives of a measurement programme for the quality of its measurements and resulting data. DQOs are described in measurable terms (i.e., accuracy, precision, completeness, representativeness and comparability), and QA plans and QC procedures are created so that they test whether or not DQOs are met.
deionised water blank	A blank sample that is measured to test for contamination in the deionised water supply at the laboratory or field site. Freshly produced deionised water should have a conductivity of 0.05 μS cm^{-1} or less. An acceptable value for aged deionised water is less than 1.5 μS cm^{-1}.
detection limit (DL)	The minimum concentration of an analyte that can be reported with 99 percent confidence (or some other predetermined confidence level) that the value is above zero. If any analyte concentration is less than the minimum concentration defined as the DL, then that analyte concentration is considered to be no different than a zero concentration. Such an analyte concentration is called a below detection limit concentration, or BDL.
dry deposition (DD)	There are two meanings of the term. First, DD is a process of the transfer of any species to the underlying surface due to direct contact on the "air-surface" border. DD includes atmospheric turbulent diffusion, adsorption, absorption, impaction and gravitational settling. Condensation of water vapour on a surface is another DD process, resulting in the formation of dew or frost. The DD process is continuous even during precipitation. The DD process is affected by type of underlying surface (e.g., soil, rock, water, plant species) and surface conditions (e.g., wetness, leaf area, stomatal opening). Second, DD is the mass of material taken up by the underlying surface (over unit of area during unit of time).
duplicate	Consisting of, or existing in two identical samples or analyses.
field blank	A blank sample added to a precipitation sample container (bucket, bag, or funnel, bottle and connecting tubes) after the container has been installed in the precipitation chemistry sampler, at the end of a sampling period when no precipitation has occurred. A field blank is used to assess artefacts in the measurement (sampling and analysis system).
interquartile range	The interquartile range is a robust scale estimator, equal to the difference between the upper and lower quartiles (25th and 75th percentiles). For a normal population, the standard deviation can be estimated by dividing the interquartile range by 1.34898.
Kimwipes[TM]	A trade name for a tissue used for cleaning sampler containers, laboratory instruments and other surfaces.

Kleenex^{TM}   A trade name for a tissue used for cleaning sampler containers, laboratory instruments and other surfaces.

Modified Median Absolute Difference (M.MAD)
A measure of overall network precision defined as:

$$M.MAD = \frac{1}{0.6745} Median(\,|\,x_i - Median(x_i)\,|\,)$$

where: x_i = the variable of interest

Percent Precipitation Coverage Length (%PCL)
The percent of the summary period (e.g., month, season, year) for which information is available on whether precipitation occurred or not.

Percent Total Precipitation (%TP)
The completeness of precipitation depth associated with valid chemical analysis and valid sample collection.

precipitation sample container blank
A sample prepared by adding deionised water to a precipitation sample container after the container has been cleaned but prior to exposure. This blank is used to assess the container cleaning process.

precision   The degree of agreement of repeated measurements of a homogenous sample by a specific measurement procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation of the sample set. *Overall Precision* is the precision of the complete precipitation chemistry measurement system including the field and laboratory components

quality assurance (QA)   An integrated system of activities involving planning, quality control, reporting, and remedial action to ensure that measurements, data, products or services meet defined standards of quality.

Quality Assurance/Science Activity Centre (QA/SAC)
A set of international centres, established by the WMO and operated in the framework of the GAW Programme to collect and distribute environmental data. QA/SAC America is based in Albany, New York, USA and is responsible for the collection and distribution of the GAW-PC data.

quality control (QC)   The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of the users. The aim is to provide quality that is satisfactory, adequate, dependable and economical.

reference material   A material, one or more properties of which are sufficiently well established to be used for the calibration of an instrument, for the assessment of a measurement method, or for assigning values to materials.

replicate measurement   The measurement of the variable of interest, performed on two or more representative samples. Replicate analysis is used to assess analytical precision.

representativeness
: The degree to which data accurately and precisely represent a characteristic in the population, e.g., spatial or temporal representativeness.

spike
: A known mass of an analyte, added to a sample and used to determine recovery efficiency or for other quality control purposes.

split sample
: Two or more separate portions of the same sample treated identically throughout the laboratory analytical procedure. Analyses of laboratory split samples are beneficial when assessing precision associated with laboratory procedures.

standard deviation
: The standard deviation is a measure of spread of a normal distribution equal to the following:

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

where: x = each individual value
$\bar{x}$ = the mean of all values
n = the number of values

standard operating procedure (SOP)
: A written set of procedures that details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and that is accepted as the method for performing certain routine or repetitive tasks.

traceability
: The ability to trace the history, application, or location of an entity by means of recorded identifications. For the purpose of calibration, traceability relates measuring equipment to national or international standards, primary standards, basic physical constants or properties, or reference materials. For the purpose of data collection, it relates calculations and data generated throughout the project back to the requirements for the quality of the project.

verification
: The process by which a sample, measurement method, or unit is systematically determined to meet specified performance criteria.

wet deposition (WD)
: There are two meanings of the term. First, WD is a process of scavenging of any gases and/or particles from the atmosphere by liquid (i.e., water droplets) and solid (i.e., ice crystals) phases. The process involves removal of any species by droplets/ice crystals within clouds (i.e., in-cloud scavenging), and by falling drops/snowflakes (i.e., below-cloud scavenging). Second, WD is the mass of material deposited from the atmosphere to the underlying surface in precipitation (over unit of area during unit of time).

1.   INTRODUCTION

This is a manual for the Global Atmosphere Watch Precipitation Chemistry (GAW-PC) Programme. Where possible, it describes standard operating procedures and otherwise provides guidance on methods and procedures. Chapter 1 describes the background and objectives of the programme, its future plans, points of contact, and outlines subsequent chapters in this document.

1.1   Background

Acid deposition has been identified as a major environmental problem in Europe and eastern North America since the 1960s and 1970s. Concerns focused on the adverse effects of acid rain on the environment, including acidification of fresh waters and terrestrial ecosystems, eutrophication of coastal waters, and forest damage. The main cause of this human-induced environmental problem has been the emission of sulphur and nitrogen compounds into the atmosphere from sources in such economic sectors as energy production, transport, industry and agriculture. The primary driving force for studying acid deposition is to better understand the atmospheric transport and deposition of various pollutants and their effects on the environment so that nations, singly and/or collectively, can make informed decisions about controlling emissions.

Measurements of the chemical composition of precipitation have been made for many years in various regions of the world with varying degrees of success. In general, more measurement sites and more sophisticated research programmes have been implemented in regions where acid deposition has been identified as a major environmental concern. In other regions, the number of measurement sites has been low and the measurement quality very often uneven. Inconsistencies in instrumentation and sampling protocols around the world continue and have made international data comparisons and atmospheric modelling efforts difficult. In addition, economic development and population growth in developing countries in Asia, South America and Africa, as well as land use and climate changes, have made these regions vulnerable to atmospheric deposition of pollutants.

In June 1989, the World Meteorological Organization (WMO) established the Global Atmospheric Watch (GAW) Programme to address the lack of coordination among the research and monitoring networks. The goal of the GAW Programme was, and continues to be, to monitor the long-term evolution of the atmospheric composition and properties on global and regional scales in order to assess this contribution to climate change and other environmental issues. Several programmes, including the former Background Air Pollution Monitoring Network (BAPMoN) were combined to form the GAW. The GAW Programme coordinates global monitoring of aerosols, ozone, greenhouse gases, ultraviolet radiation, selected reactive gases and precipitation chemistry.

The focus of this report is the global precipitation chemistry network comprised of more than 200 stations, most of which are in Europe and North America (Figure 1.1). The number of precipitation measurement sites in South America, Africa and in many parts of Asia remains extremely low.

The data are presently archived at the GAW World Data Centre for Precipitation Chemistry (WDCPC), located with the Quality Assurance/Science Activity Centre (QA/SAC) at the State University of New York in Albany, New York, USA. The co-location of the WDCPC and the QA/SAC makes it easier for the data to be quality assured and archived in a timely and effective manner. GAW data from the 1970's onward have been quality assured to the extent possible given the lack of quality control information. There is greater confidence in the post-1988 data. New data are being submitted continuously and once data quality has been assured and appropriate flags attached, the data are archived and available for distribution. World Wide Web sites have been established to facilitate timely data submission and data access.
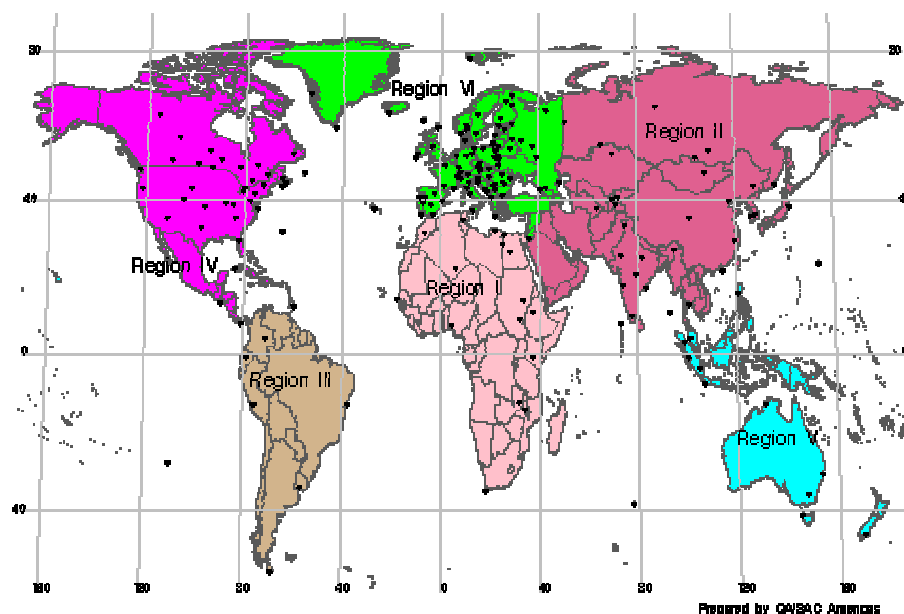
Figure 1.1: Active GAW Precipitation Chemistry Programme stations, as of September 2003.

For general information on the GAW Precipitation Chemistry Programme, visit the GAW website or contact the Chief, Environment Division, AREP:
http://www.wmo.ch/web/arep/gaw/gaw_home.html
LBarrie@.wmo.int

For information on WDCPC and on ordering GAW Precipitation Chemistry Programme data, visit website:
http://www.qasac-americas.org

Or send a fax: +1 518 437 8768   or +1 518 437 8758

Or contact:
WMO Quality Assurance – Science Activity Centre for Precipitation and Aerosol Chemistry
Attention: WMO/GAW Data Manager
Atmospheric Science Research Centre
251 Fuller Road
Albany, New York 12203
USA

For GAW station information (e.g., site descriptions, measurement programs and available data, and contact people), visit the GAW Station Information System (GAWSIS) website:
http://www.empa.ch/gaw/gawsis/   **[This is a website in progress]**

See Chapter 5 for information on GAW precipitation chemistry data submittal

1.2   GAW Precipitation Chemistry Programme Objectives

The objectives of the GAW Precipitation Chemistry Programme are:

- To assure the harmonization of measurements conducted globally by various regional and national programmes
- To enable quantification of patterns and trends in the composition of atmospheric precipitation at global and regional scales
- To improve the understanding of biogeochemical cycles of major chemical species
- To facilitate global assessments of acid deposition and to investigate long-range transport from major source areas
- To provide the data needed for evaluating effects of acid deposition on major ecosystems, for example, coastal and sensitive areas, and for developing control measures.

To address the first objective and to improve the quality of global data, the GAW Precipitation Chemistry Programme has undertaken to revise its standard operating procedures including all on-site, laboratory, data management and quality assurance aspects of the measurement system. The new procedures documented and presented in the following chapters are for major ions in precipitation.

Major ions and measurements covered in this manual

Sulphate	Chloride	Calcium	Conductivity
Nitrate	Sodium	Magnesium	
Ammonium	Potassium	pH	

Other provisional measurements include

Alkalinity
Organic Acids

1.2.1   Data Quality Objectives

The cornerstone for establishing and maintaining the quality of any measurement programme is through the use of *Data Quality Objectives* (DQOs). DQOs are statements of the overall level of uncertainty that a programme will accept in its data.

The Data Quality Objectives for the GAW Precipitation Chemistry Programme are presented in Table 1.1.   Decades of experience in measuring and statistically analyzing precipitation chemistry have helped to develop the form and value of these DQOs. **It is the responsibility of each and every participating organization to review these DQOs and adjust their GAW precipitation chemistry measurement programme to meet or exceed the DQOs.** Further discussion of DQOs is found in Chapter 6.   A detailed description of how the DQOs were established and how participating organizations can calculate their own data quality indicators for comparison to the DQOs is given in Appendix A.

Measurement Parameter	Detection Limits	Precision Overall	Precision Laboratory	Inter-Network Bias Overall	Inter-Network Bias Laboratory	Calibration Levels	Completeness
pH (pH units)	*	± 0.1 pH unit at pH > 5 ± 0.03 pH unit at pH < 5	± 0.04 pH unit at pH > 5 ± 0.02 pH unit at pH < 5	±0.24 pH unit at pH > 5 ±0.12 pH unit at pH < 5	± 0.07 pH unit	4.0 & 7.0 low ionic strength reference solutions	90 %PCL[1] 70 %TP[2]
Conductivity ($\mu S\ cm^{-1}$)	± 2	*	*	*	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Acidity/ Alkalinity ($\mu mole\ L^{-1}$)	*	*	*	*	± 25%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
SO_4^{2-} ($mg\ L^{-1}$)	0.06	0.06	0.03	± 0.42	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
NO_3^- ($mg\ L^{-1}$)	0.09	0.06	0.03	± 0.36	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Cl^- ($mg\ L^{-1}$)	0.04	0.02	0.02	± 0.05	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
NH_4^+ ($mg\ L^{-1}$)	0.02	0.02	0.01	± 0.08	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Ca^{++} ($mg\ L^{-1}$)	0.02	0.02	0.01	± 0.05	± 15%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Mg^{++} ($mg\ L^{-1}$)	0.01	0.01	0.01	± 0.02	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Na^+ ($mg\ L^{-1}$)	0.02	0.01	0.01	± 0.03	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
K^+ ($mg\ L^{-1}$)	0.02	0.01	0.01	± 0.02	± 20%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Formate (($mg\ L^{-1}$)	*	*	*	*	*	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Acetate ($mg\ L^{-1}$)	*	*	*	*	*	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Standard Gauge Precipitation Depth (mm)	0.2	0.1 daily 0.3 weekly	n/a n/a	± 5% for rain ± 15% for snow ± 10% rain+snow	n/a n/a	In a range between the 2nd & 98th percentile depth values	95 %PCL - annual 90 %PCL - quarterly
Sample Depth (mm)	0.2	0.1 daily 0.3 weekly	n/a n/a	± 5% for rain ± 15% for snow ± 10% rain+snow	n/a n/a	In a range between the 2nd & 98th percentile depth values	90 %PCL[1] 70 %TP[2]

* -- Not Available   n/a -- Not Applicable

1) %PCL is Percent Precipitation Coverage Length (see Sections 6.10.3 and A.7 for detailed explanation).

2) %TP is the Percent Total Precipitation (see Section 6.10.3 and A.7 for detailed explanation).

1.3 Future Directions

It is recognized that GAW must produce strict data acceptance criteria, clear procedures, and effective feedback for nations and stations making precipitation chemistry measurements in connection with qualified meteorological measurements. Such steps will ensure an adequate base of reliable information on which to conduct research and make policy decisions.

In accordance with the procedures outlined in this document, the GAW intends to upgrade the Precipitation Chemistry Programme by taking steps to harmonize measurement and quality assurance (QA) procedures used in the various regional and national deposition monitoring programmes, keeping in mind the investments already in place in those programmes. The development of this manual is seen as a first step in that process. Additionally:

- An expanded GAW Laboratory Intercomparison Programme has been designed to address differences in regional precipitation chemistry and is to be administered twice annually.
- Training programmes are to be developed for nations and/or laboratories with substandard performances and for those just entering the GAW measurement programme.

The principal focus of the GAW continues to be on major ions in precipitation for the foreseeable future. The GAW recognizes the growing global concern with regard to atmospheric deposition of heavy metals and persistent organic pollutants (POPs). In addition, the GAW will conduct an assessment of the requirement for dry deposition (atmosphere-surface exchange) measurements at selected precipitation chemistry stations. Such assessments will be published and used to determined whether additional measurements should be incorporated into the GAW programme.

There is a great deal of concern worldwide about the air quality within urban areas, where the large majority of the world's population resides. The primary concerns within the urban environment are on the effects of air pollution on human health and welfare. The inclusion of urban sites within the GAW Precipitation Chemistry Programme has been discussed. While at this time the objectives for the programme are for long term *global* and *regional* monitoring, the future may see the inclusion of urban monitoring, with specific urban objectives identified. For this reason, urban sites are mentioned briefly in some of the following chapters.

Despite obvious achievements of the GAW precipitation chemistry and deposition activities, some problems, as mentioned above, remain to be solved. The harmonization of global data and the accomplishment of GAW Precipitation Chemistry Programme goals will take many years to attain.

1.4 This Document

This manual describes the most recent operational objectives, station siting requirements, field and laboratory operating procedures, data management, and quality assurance of the GAW Precipitation Chemistry Programme. The chapters are designed with the intent of promoting the use of up-to-date measurement methods, high level quality assurance and quality control procedures, proven instrumentation, and highly consistent laboratory techniques. A **Glossary** defines abbreviations, units of measure, and common terms used within the report. **References** are included in each chapter. **Appendices** provide detailed materials related to specific chapters and are an integral part of this manual. The manual is organized as follows:

1. **Introduction**
   - GAW background
   - GAW Precipitation Chemistry Programme objectives
   - Future directions
   -
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- Site documentation

3. Field Protocols
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- Data quality assurance
- Data analysis
- Data archiving and distribution

6. Quality Assurance and Quality Control
- The objectives of QA/QC
- Data Quality Objectives
- Overarching aspects of QA/QC for siting, field, laboratory and data

APPENDIX A. A Description of How the GAW Precipitation Chemistry Programme Data Quality Objectives Were Established and Recommended Calculations for Data Quality Assessment

APPENDIX B. GAW Precipitation Chemistry Programme Site Description Form

APPENDIX C. Preparing Control Solutions

APPENDIX D. Sources for Certified Reference Materials

APPENDIX E. Flagging Precipitation Results with Poor Ion Balances as Valid or Invalid: A Proposed Approach from EMEP

APPENDIX F. Guidelines for Submission of GAW Precipitation Chemistry Data to QA/SAC Americas

APPENDIX G. Laboratory and Station Registration Forms for the GAW Precipitation Chemistry Programme.

APPENDIX H. The WDCPC Non Sea Salt Sulphate Correction Algorithm.

In this document, the term National Meteorological and Hydrological Service (NMHS) is identified as a country's participating agency within the GAW Precipitation Chemistry Programme. The use of term NMHS may also refer to another agency or organization that has been designated as the responsible GAW participant. Each NMHS is responsible for making this document available to its field, laboratory and data management personnel, and for translating this report into its official state language, if necessary.

2. SITING

This chapter describes the global and regional sites that currently make up the GAW Precipitation Chemistry Programme, and states the criteria and specifications that should be used in locating these sites. Guidelines for precipitation chemistry sampler and rain/snow gauge placement at the site are given, and required site documentation is shown.

2.1   General Considerations

Site characteristics can seriously impact the quality of sampled precipitation. As a result, site selection is a critical part of a monitoring network's design.

The GAW Programme has established guidelines for monitoring on a regional and global basis. The GAW Precipitation Chemistry Programme has further refined the guidelines for siting to monitor precipitation chemistry. While specific siting criteria can be at times difficult to meet, there is some latitude for countries in selecting sites. If a site that is part of an existing network is to be designated as a GAW precipitation chemistry site, it must be carefully assessed as to how well it meets the siting criteria in this chapter. If the desire is to locate a new station, then the siting criteria can be used to select the best possible site.

2.2   Categories of Stations

In the GAW Programme, there are two categories of monitoring stations, where a wide range of measurements may be taken, including precipitation:

- *Global stations* provide measurements needed to address atmospheric environmental issues of global scale, such as climate change, stratospheric ozone depletion, tropospheric ozone increases and changes in the oxidizing capacity of the atmosphere. A global station is considered remote, with low (background) levels of pollutants, representative of a large atmospheric regime.
- *Regional stations* provide measurements primarily to help assess regional aspects of global atmospheric environmental issues, such as acidic wet and dry deposition, long range transport of pollutants, biogeochemical cycles, exchange of pollutants between the atmosphere and the sea, biomass burning, biogenic sources and sinks of greenhouse gases and others. A regional station is considered less remote than a global station, with medium levels of pollutants, representative of the surrounding few hundreds of kilometres.

A *contributing partner station* is one that is not a Global or Regional GAW Programme station but it contributes data to a GAW World Data Centre. Contributing partner stations are being defined at the time of this manual's writing and will be described in a future GAW report.

2.3   Network Density

The current guideline for GAW network density is that there should be a minimum of one global station per principle climatic zone and per major biome (e.g., Bailey, 1989 and Bailey and Hogg, 1986). This has not yet been achieved. For regional stations, the density should allow regional aspects of global environmental issues and environmental problems of interest to the regions or country(ies) concerned to be adequately addressed.

2.4   Siting Criteria for GAW Stations

The GAW Programme established siting criteria for its global and regional monitoring stations (WMO GAW Report No. 99) that apply to the broad suite of measurement components (i.e., not just to precipitation chemistry measurements). These siting criteria have been established despite the difficulty of finding locations where suitable conditions are met often enough and evenly enough through the year and on a long-term basis.

In principle, and depending on the measurement component:

1) Global stations preferably should be located in remote (if possible pristine) areas where:

   a) no significant changes in land-use practices are expected for at least 50 years within a reasonable distance (30-50 km) in all directions from the stations; away from major populations and industrial centres, away from major highways and airports; if possible on islands, mountain ranges and major forest reserves;
   b) effects of major natural phenomena such as volcanic eruptions, forest fires and dust storms are not frequently experienced;
   c) it can be reasonably assumed that the ambient air at the station is entirely free of the influence of local pollution sources, nearly free of the influence of regional pollution sources at least 60% of the time evenly distributed over the year, and contains only diluted vestiges of chemical species carried to the site by the long-range transport from sources located at least 30-50 kilometres away;
   d) a full programme of surface meteorological observations is carried out.

2) Regional stations should be located:

   a) in rural areas, at any rate sufficiently far away from population and industrial centres, so that the effect of local sources of air pollution is absent at the station most of the year;
   b) on, or close to meteorological/climatological stations making surface and rawindsonde observations.

For both station types, particular care must be taken that each station represents the region of interest in terms of the natural and anthropogenic emissions, and topographic features.

Other siting considerations include: availability and interest of scientists, existence of a suitable infrastructure, relevance to national and/or regional issues and objectives (especially in developing countries) and the long-term commitment of all parties involved, including laboratories.

GAW global stations are considered as research centres and are expected to monitor all or most of the variables of the GAW measurement programme listed in the WMO GAW Report No. 99, whereas regional stations have a more flexible observational programme. Global stations also serve as reference stations for regional stations. **Stations are expected to operate for at least ten years.**

2.4.1   Siting Guidelines for GAW Precipitation Chemistry Programme Stations

Sites chosen for precipitation sampling should be representative of larger areas. Areas immediately outside of urban and industrial areas are to be avoided. To aid in site identification, Table 2.1 gives the minimum distance that a station should be from various emissions sources.

The distances given in Table 2.1 are guidelines only. It is recommended that an appraisal of the influence of local emissions on the air and precipitation chemistry at a site be made during the site selection process. Such an appraisal should consider meteorological and topographic conditions, along with estimated emissions from the activities mentioned in Table 2.1.

Sites must be representative with respect to their exposures to air masses. The ideal is a well-exposed site in a flat or moderately undulating terrain. If valleys cannot be avoided, the site should be located on the side of the valley above the most pronounced nighttime inversion layer. Coastal sites with pronounced diurnal wind variations due to land-sea breeze effects are also not recommended. Since vegetation is a sink for many air pollutants, it is important to avoid situations where precipitation sheltering by vegetation (e.g., a stand of trees) results in lowered precipitation amounts or sample concentrations when the wind is blowing from a particular direction. In general, sampling sites should not be located around strong natural sources of interfering species, such as geothermal areas,

volcanoes, and areas subject to excessive windblown dust. Sea spray contamination should be avoided by locating the sampler sufficiently inland from the coastline.

Specific attention should be directed to industrial operations and suburban/urban area related sources. Large industrial operations such as power plants, chemical plants and manufacturing facilities should be at least 50 km away from the sampler, preferably further. If the emission sources are located in the general upwind direction (i.e., the mean annual west-east flow in most cases) from the sampler, then its distance should be increased to 100 km. This same criterion also applies to suburban/urban areas whose population approximates 25,000 people. For larger population centres (i.e., greater than 100,000) the sampler should be no closer than 100 km. This distance is doubled to 200 km, if the population is upwind of the sampler. Beyond 100 to 200 km both industrial and urban sources are generally assumed to blend in sufficiently with the air mass characteristics of the region. In highly populated continental regions (e.g., NE United States, portions of western Europe, SE China) it may not be possible to meet all distance guidelines for regional stations.

2.4.2 On-Site Requirements

The site should be accessible in both summer and winter and have a low risk of vandalism. Placement of the precipitation chemistry sampler and standard precipitation gauge should conform as nearly as possible to the following:

1) Install the sampler and gauge over undisturbed land. Naturally vegetated, level areas are preferred, but grassed areas and slopes up to ±15% are acceptable. Sudden changes in slope within 30 metres of the sampler should be avoided. Ground cover should surround the sampler for a distance of approximately 30 metres. In farm areas, a vegetated buffer strip must surround the sampler for at least 30 metres.

2) Maintain the height of vegetation at the site to less than approximately 0.5 metres and no higher than half the height of the precipitation chemistry sampler or gauge (measured from the ground to the sampling orifice).

3) Ensure that structures do not project onto the sampler or gauge at an angle greater than 45 degrees from the horizontal (30 degrees is considered optimal, but 45 degrees is the highest angle acceptable). Therefore, as shown in Figure 2.1, the distance from the sampler to the object must be at least equal to the height of the object and preferably twice the height of the object. Residential dwellings are to be twice their height away from the sampler (30 degrees) and should be no closer than 30 metres from the sampler when they are in the prevailing upwind direction. Anemometer towers, poles and overhead wires are considered to be structures and must meet these on-site requirements.
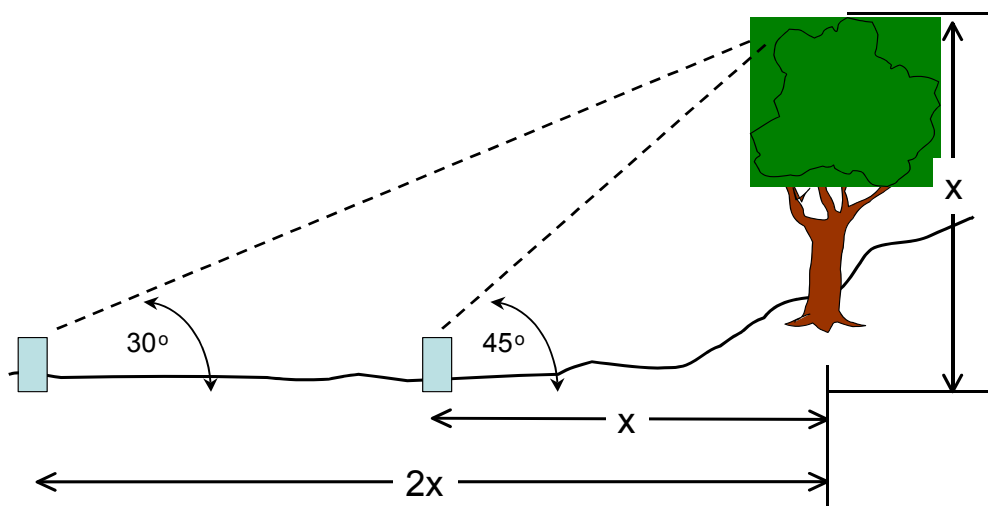
Figure 2.1: How to locate sampler and gauge away from nearby objects.

Table 2.1: Minimum-Distance Guidelines for GAW Precipitation Chemistry Stations.

Potential Interference	Minimum Distance to Site (km) Global	Regional	Examples, Notes and Local Considerations
SO$_2$ or NO$_x$ Point Source			If emission sources (such as power plants, refineries,
>100 tonnes per year	50	20	chemical plants, smelters or other major industrial facilities)
>1000 tonnes per year	100	50	are located in the general upwind direction from the collector,
Major Industrial Complex	150	50	then the regional distances indicated should be doubled.
Town, population 1,000-10,000	25	10	Future population growth and associated land development
Town, population 10,000-25,000	50	20	should be considered carefully, especially for towns and
City, population 25,000-100,000	100	50	villages near a station. If population centres are located in
City, population >100,000	200	100	the general upwind direction from the collector, then the regional distances indicated should be doubled.
Major highway, airport, railway, shipping lane, harbour	25	5	Moving sources of pollution, such as air, ground, or water traffic or the medium on which they traverse (e.g., runway, taxiway, road, tracks, or navigable river), should not be within 500 metres of the collector.
Secondary road, heavily travelled	5	1	The local road network around the site is of particular
Secondary road, lightly travelled	1	0.5	concern. Traffic volume and type as well as road surface will largely determine the impact at the site.
Feedlot operations	50	2	Acceptable distances will vary greatly depending on size of the operation. Even small concentrations of animals should be housed no closer than 500 metres. If the feedlot, dairy barn or animal waste pile can be smelled at the collector, it is too close.
Intensive agricultural activities	10	2	Surface storage of agricultural products, fuels, vehicles or other source materials should be kept at least 500 metres from the collector.
Limited agricultural activities	1	0.4	Storage of small amounts of agricultural products, fuels, or other source materials should be kept at least 200 metres from the collector and well sealed.
Parking lot or large paved area	0.5	0.2	On-site parking lots and maintenance yards also need to be kept at least 300 metres from the collector.
Building with fuel combustion	1	0.4	
Sewage treatment plant	20	2	
Active volcano, fumarole, etc.	100	20	Geothermal sites including geysers and springs may have significant emissions and should be avoided.
Natural salt, dust, alkali sources	2	2	Windswept materials from salt and alkali flats as well as sea spray from coastlines can contaminate samples.
Tree line, building	0.05	0.05	

4) To reduce wind turbulence, do not enclose the base of the sampler. Any object over 1 metre high that is capable of deflecting wind should not be located within 5 metres of the sampler.

5) Install the precipitation gauge 5 to 30 metres from the precipitation chemistry sampler in accordance with National Meteorological and Hydrological Service (NMHS) standards. In general, the gauge mouth should be located no higher than the sampler orifice and, for some gauges, placement should be as close to the ground surface as possible (but high enough to avoid ground splash).

6) In areas where more than 20% of annual precipitation is in the form of snow, equip the gauge with a suitable wind shield. **It is recommended that the wind shield be installed by a meteorological expert**.

7) In areas having an accumulation of over 0.5 metres of snow per year, the sampler and gauge may be raised off the ground on a platform (or platforms). Platforms should be no higher than the maximum anticipated snow pack. Equip the sampler with a properly counterweighted snow roof in areas where snow is 10% or more of the annual precipitation depth. If installed, leave the roof on year-round.

8) Install fencing, if needed, to reduce vandalism or encroachment by animals. An open mesh, galvanized chain link fence is recommended. The placement of the fence must meet requirements in items 3) and 4), above.

See Chapter 3 for a detailed discussion of site facilities and operation of precipitation samplers and gauges. Bigelow (1984) and Dossett and Bowersox (2001) provide examples of siting manuals.

It is recommended, but not required, that the precipitation station be located at a standard meteorological station (GAW or other), if that station successfully meets the siting requirements stated in this chapter. This enhances the value of the precipitation chemistry data by making other collocated meteorological parameters available for data interpretation. Meteorological data are especially useful when unusual precipitation measurements are reported.

2.5   Site Documentation

Each station (or its designated agency or NMHS) is required to maintain written descriptions of the site (on regional, local, and on-site scales) and a history of all changes made to the station. The following items will aid NMHSs in tracking site changes and evaluating if siting criteria and site requirements are being met:

1) The GAW Precipitation Chemistry Programme Site Description Form (Appendix B).
2) Regional, local, and on-site sketches.
3) Colour or black and white photographs of the site showing the area surrounding the sampler in 8 directions at 45 degree intervals (i.e., photos taken facing N, NE, E, SE, S, SW, W, NW). The pictures should be taken at a distance of 5 to 7 metres from the sampler, with the sampler and rain gauge showing in the foreground. Clearly label the back of each photo as to the site, date, and direction.
4) A map of the region, preferably a topographic map (1:24,000 scale or similar), with the station location identified with a circled X. Include adjoining map(s) if the site is near the map border.

Station personnel should keep a copy of the documentation for their own records and to use for periodic evaluation of the site.

Information about the GAW ground-based stations is available from the GAW Station Information System (GAWSIS), an initiative by the QA/SAC Switzerland in collaboration with the WMO Secretariat, the GAW World Data Centres and other GAW representatives. The goal of GAWSIS is to provide the GAW community and other interested people with an up-to-date, searchable data base of site descriptions, contact people, measurement programmes and available data. The GAWSIS website is now in use at:

http://www.empa.ch/gaw/gawsis/

Information on any new sites or closed sites should be reported to the WDCPC and to GAWSIS.

NOTE: At this time, the WDCPC is not maintaining an archive of the GAW precipitation chemistry site documentation (i.e., photos, site histories, site quality assurance information, site maps, etc.). It is the responsibility of each GAW Precipitation Chemistry Programme participant to make their site documentation available to interested data users, via the Internet, if possible.

2.6 On-Going Site Evaluation and Siting Changes

Ideally, each site should be inspected by network personnel every year and independently audited every 5 years (Martini and Mohnen, 1994). Any changes to the site should be documented and corrected forms and maps (as described in the preceding section) should be maintained by the NMHS. This includes changes at regional and local scales as well as at the site. Examples of changes which should be documented include: a new industrial complex being constructed many kilometres away; urban and suburban growth near to the site; new agricultural activity being initiated adjacent to the site; and new (interfering) instrument towers being placed near the precipitation sampler or gauge at the site. Where changes are deemed to have invalidated the chemical and spatial representativeness of the site: 1) changes must be made to bring the site back into compliance (if possible), 2) the site must be eliminated as a GAW site, or 3) the site must be reclassified as to the representativeness of its data (e.g., from a global to a regional site).

Changes in site location must be documented so that data users have the ability to determine if measurement changes correlate with physical changes at the site.

1) All site moves greater than 30 metres from the original location require new site sketches, and pictures. A new map is required only if the site moves off the old map.
2) If the station equipment is moved more than 1 kilometre, it is considered to be a new site. A new station ID number will be assigned to the site by the WDCPC. New station coordinates and start dates must be provided (refer to Chapter 5 for data submittal).
3) The reason(s) for the site change should be described in writing.

The documentation of all site changes is to be kept by the GAW Precipitation Chemistry Programme participant (i.e., the NMHS or its designate), and made available to interested data users upon request. Information on site changes or closures should be reported to the WDCPC and GAWSIS.

2.7   References

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3.   FIELD PROTOCOLS

This chapter presents methods for measuring wet deposition in the GAW-PC Programme.   It discusses sample collection, handling, documentation and shipping procedures. Methods for measuring fog or cloud water and not addressed within the current programme. Since wet deposition is calculated as the product of the concentration of a chemical and the amount of precipitation, two different field instruments are used. Precipitation chemistry measurements are made using a wet-only precipitation sampler designed to be open only during precipitation. Precipitation amount is measured using a standard precipitation gauge designed to maximize collection efficiency for rain and snow with no consideration of the chemistry.

3.1   Essential Components of Field Measurements

The following points summarize the essential components of all GAW precipitation chemistry field measurements:

- Assign the responsibility for field operations to a single person. This person will ensure that facilities are equipped properly, supplies are available, equipment operates according to specifications, and standard operating procedures are followed. (Section 3.2)
- Every site must have a clean shelter or laboratory where samples can be weighed and where other observations and sample handling activities can be performed. Samples are weighed to measure sample size, not transferred to a graduated cylinder or similar container to measure volume. (Section 3.2.1)
- Equip every site with a precipitation chemistry sampler for collecting samples for chemical analysis. The primary goal is to collect wet-only deposition using an automated wet-only precipitation chemistry sampler; however, the GAW Precipitation Chemistry Programme recognizes there are local conditions under which this may not be possible. (Section 3.2.1.1)
- Equip every site with a standard precipitation gauge for measuring the precipitation amount. The NMHS or designated responsible agency should select the most accurate and representative gauge for the range of meteorological conditions encountered at each site. (Section 3.2.1.2)
- Collect samples daily at 0900 local time. Where the cost of site visits and analytical services makes daily sampling impractical, a multi-day sampling period, up to a maximum of 7 days (i.e., weekly sampling) is recommended. Weekly sampling that commences at 0900 local time on Tuesday is the 7-day sampling period of choice.   The GAW Precipitation Chemistry Programme strongly discourages sampling periods longer than 7 days. (Section 3.2.2)
- Minimize sample handling, keep storage times short, ship samples rapidly to the analytical laboratory, and analyze samples promptly. Consider sample preservation practices where NMHS objectives require accurate measurements of labile species, such as organic acids. (Section 3.2.3)
- Clean all surfaces that precipitation samples may contact (e.g., funnels, bottles, tubing, buckets, etc.), preferably at a single central facility. Use reagent-grade deionised water (conductivity <0.5 μS cm^{-1}). Test the cleanliness of precipitation sample containers by ensuring that the conductivity of the final rinse does not exceed 1.5 μS cm^{-1}. (Section 3.3.1)
- Conduct tests of the cleanliness of sample collection and handling procedures (i.e., field blanks) at least once per month. Report the results of these and other QA/QC tests to the WDCPC on an annual basis. (Section 3.3.2.3)
- For every sample, measure the sample volume, gravimetrically. Also measure the standard precipitation gauge amount following standard NMHS protocols.   Field chemistry measurements are not among the standard set of measurements archived at the WDCPC and are not recommended. (Section 3.4)
- Record information about every sample on a sample history form that documents quantitative information and observations by the site operator. (Section 3.5)

3.2   Sample Collection

Precipitation samples are characterized by low ionic concentrations and are very susceptible to contamination. The goal of field sampling is to collect representative samples for chemical analysis and handle samples in a way that preserves their chemical integrity. In principle, this is best accomplished by assigning a single person the responsibility for sample collection.

Field Components

Automated wet-only precipitation chemistry sampler

Standard meteorological rain/snow gauge

A shelter or field laboratory equipped with
      Electric power
      Temperature control
      Refrigerator
      Sink
      Deionised water supply ($<1.0\ \mu S\ cm^{-1}$)
      Electronic scale or triple-beam balance
      Tables or laboratory benches and chairs
Optional
      pH meter
      Data logger
      Personal computer
      Telephone
Required if sample containers are cleaned at field site
      Conductivity meter
      Deionised water purification system

3.2.1   Site Facilities

The GAW Precipitation Chemistry Programme recommends that each site have a shelter or laboratory where field measurements can be performed. This facility should be more than 50 m from the field instruments. The shelter should be equipped with electric power, temperature control, a refrigerator, a sink, a deionised water supply (conductivity $<1.0\ \mu S\ cm^{-1}$), an electronic scale or balance (capacity of 15 kg and sensitivity of 1 g), tables or laboratory benches, and chairs. If deionised water cannot be produced at the operations shelter, it may be supplied by the analytical laboratory and delivered in clean, tightly sealed, polyethylene containers. Use of a graduated cylinder or other volumetric container for measuring sample volumes is strongly discouraged, because of the contamination potential from the container itself. Instead, volumes should be measured by weighing the samples and converting weights to volumes (density ~1.0 g L^{-1}). Optional equipment for the operations shelter includes a data logger for recording field measurements, a personal computer, and a telephone.

The primary goal is to measure wet-only deposition, although the GAW Precipitation Chemistry Programme recognizes there are local conditions under which that may not be possible (see Section 3.2.1.1). Collecting wet-only deposition means opening a sampling container only when precipitation occurs.   To do this, every site should be equipped with a wet-only precipitation sampler. Accompanying this sampler, each site must operate a rain/snow gauge that is the NMHS standard for precipitation chemistry network operations. As previously mentioned, both the collector and gauge are required because of their different functions. Electricity to power the field instruments may be supplied by alternating current (ac) from an electrical utility company or direct current (dc) from a battery or solar array.

It is desirable for the field site to be located at a standard meteorological station (Section 2.4.2) or to have measurements of temperature, wind direction, and wind speed at a standard height, as long as no GAW-PC siting criteria are violated. Use of commercial meteorological instrumentation requires strict adherence to manufacturers' specifications, as well as periodic calibration checks. Their installation and field operation is not covered in this document.

3.2.1.1 Precipitation Chemistry Samplers

As mentioned previously, the primary goal is to measure the chemistry of wet-only deposition. A precipitation chemistry sampler with the following design and operational features can meet this goal:

1) The sampler is automated to collect wet-only deposition samples.
2) The sensitivity of the sampler to open during precipitation and close during dry periods is either set by the manufacturer or adjusted for local conditions in accordance with standard operating procedures.
3) The precipitation sample container (e.g., a bucket or funnel-and-bottle) and all surfaces that the precipitation sample contacts must be chemically inert for the constituents measured.
4) The sampler must seal and protect the sample from contamination during dry periods.
5) The height of the opening through which precipitation enters the sampler (i.e., the collection orifice) must be 1 to 1.5 m above ground, except for areas that receive high snowfall accumulations, where the sampler may be raised onto a platform above the snow (see Section 2.4.2 for guidance).

The GAW Precipitation Chemistry Programme does not endorse the use of specific precipitation chemistry samplers, but defers to each NMHS to select a sampler that meets the above conditions and is best suited to the environment in which it will be used. NMHS personnel who require information on acceptable precipitation samplers should contact the WMO Secretariat or the QA/SAC for recommendations. (See Chapter 1 for contact information.) Table 3.1 offers detailed specifications that can serve as a guide for evaluating sampler performance.

A typical, automated, wet-only deposition sampler has the following components: a precipitation sample container (funnel-and-bottle, bucket, etc.), a lid that opens and closes over the sample container orifice, a precipitation sensor, a motorized drive mechanism with associated electronic controls, and a support structure to house the components. Precipitation sample containers should have sufficient volume to hold all precipitation collected during the sampling period. A system that can be activated manually for testing, cleaning, and routine maintenance is recommended. A modular design that allows removal of individual components, such as the sensor, facilitates rapid repair with a minimum of tools and expertise.

The precipitation sample should come in contact only with the precipitation sample container and, depending on the sampler design, the funnel, tubing, etc., that direct the sample into this container. It is essential that all surfaces contacting the sample be chemically inert so that major inorganic constituents neither adsorb to nor desorb from these surfaces. Tests have shown that polyethylene, polypropylene, and Teflon^{TM} (or a Teflon^{TM}-coating) are satisfactory materials. Glass and metal containers are not good materials for measuring major ions and must be avoided, as they are prone to both positive and negative artefacts for cations.

A sensor detects precipitation and sends an electronic signal, activating a motorized drive that uncovers the sample container orifice. When precipitation ends, the lid seals the sample container orifice. Typically, sensors are heated to prevent false openings due to dew or rime ice and to melt snow or ice. This requires optimal temperature control. A sensor that is too hot evaporates precipitation too rapidly and disrupts airflow, interfering with the fall of snowflakes and tiny droplets approaching sensor surfaces. For a comprehensive evaluation of sensor performance, see Winkler (1993) and Vet (1991). Droplet size, precipitation type and intensity, temperature, wind speed, and sensor shape and orientation all affect sensor response. Avoid sensors lacking adequate sensitivity (consult Winkler for examples). To preclude repeated cycling of the lid during periods of light

precipitation, some samplers delay closure for one or two minutes after the last precipitation is detected. The duration of the delay must be balanced against the requirement to minimize sample exposure to dry deposition. In a network of sites, it is important to standardize sensor performance according to NMHS policies.

Table 3.1: Automated Wet-Only Precipitation Chemistry Sampler Performance Characteristics.

Range	Unattended (no user intervention) collection of precipitation samples of 0.05 to 25 cm liquid equivalent depth
Sensitivity and false positive operation	Opens within 5 seconds of the onset of precipitation of any type or rate. Closes within 120 seconds of the cessation of precipitation. Does not open in the absence of precipitation
Accuracy: sample volume in relation to standard precipitation gauge amount	+0% to -20% for liquid equivalent depths of 0.05 to 0.25 cm of precipitation and +0% to -10% for liquid equivalent depths >0.25 cm of precipitation, except for snow*
Real time recording	Records opening and closing within 5 minutes of a polled request and provides a report on the status of important functional components (e.g., sensor)
Operating temperature range	-45ºC to +50ºC
Operating wind limit	Sample container opens and closes properly, 15 m s^{-1} steady, 25 m s^{-1} gust
Reliability, maintainability, availability	Periodic maintenance interval ≥90 days, mean time between failures >500 days, and mean time to repair or maintain ≤60 minutes
Electrical Power	Powered by ac line power (with optional 12-volt dc battery operation during line current interruptions) or powered by 12-volt dc battery with solar panel recharge
Height	Precipitation sampler orifice and sensor are 1.0 to 1.5 m above surface and can be adjusted readily to maintain 1.0 m height above accumulated snow
Precipitation sample container	All sample container surfaces (funnel, bottle, tubing etc.) contacted by precipitation are chemically inert for the constituents measured; capacity should be adequate to hold all precipitation from the sampling period
Precipitation sample container orifice	A lid must seal the orifice against evaporation or gas and particle intrusion during dry weather
Contamination from splash	Splash from instrument surfaces must not enter the collection orifice

* Goodison et al., 1998

During dry weather, it is essential that the sample container orifice remain covered and tightly sealed. This limits evaporation, ensures that no gas exchange occurs between the sample and the atmosphere, and prevents aerosols and other airborne contaminants from entering the container. A chemically inert compressible pad or gasket should be mounted on the underside of the lid to ensure that the lid tightly seals the sample container orifice.

Nothing should interfere with the free fall of precipitation into the sampler, and the sampler design should prevent splash, rebounding snowflakes, and ice pellets from entering or exiting the container. Special adaptations may be required in regions where snow may accumulate on sampler surfaces. One way to prevent snow from blowing from the cover into the sampler is to mount a stainless steel or Teflon^{TM}-coated, peaked roof atop the cover. These adaptations should only be implemented if consistent with standard operating procedures. The instrument manufacturer's guidelines or experiences of other networks may help if adaptations are needed.

Under limited situations, it may be possible to adopt a sampling strategy that does not use an automated wet-only precipitation sampler.

- One alternative is to collect samples using a manual wet-only sampler. Uncontaminated, manual wet-only sampling requires round-the-clock availability of field observers alert to weather conditions, so that they can uncover clean sample containers just before the

onset of precipitation and cover samples when precipitation ceases. Data from a manual wet-only deposition sampler are acceptable, if the observer verifies that the samples were exposed only during precipitation. This should be done on the sample history form (see section 3.5). NOTE: When submitting manual wet-only data to the WDCPC, select 'Manual_Wet_Only' for the Sampling_Type field of the #SAMPLE_PROTOCOL metadata structure. This will allow the WDCPC to properly flag the data. See Chapter 5 for details about data submission and format.

- Another alternative is to collect samples using a bulk (i.e., continuously open) sampler, although the GAW Precipitation Chemistry Programme strongly discourages this option. Data from a bulk sampler are acceptable where the NMHS verifies that bulk samples are collected in locations sufficiently remote from pollution and local dust (coarse particle) sources so that contamination from dry deposition is negligible. Even in these settings, the bulk sample containers must be changed daily. The WDCPC will identify these data as bulk data and will attach a warning that states, "These data may be biased by an unknown amount due to sample exposure during dry weather." If a NMHS has data that quantify these biases and will make these data available on request, the WDCPC will append the following statements to the warning: "Data are available that estimate the size of these biases. Contact the WDCPC for more information."

3.2.1.2 Precipitation Depth Measurements

The GAW Precipitation Chemistry Programme requires every site to measure precipitation depths using the NMHS-designated standard precipitation gauge or its equivalent. Manual gauges are preferred. Precipitation depths are used to calculate the mass of a chemical deposited by precipitation on an area of earth surface (i.e., the wet deposition flux or loading). Standard precipitation gauges are designed to be the most accurate and representative means of measuring precipitation depths. Thus, each site must operate a precipitation gauge in parallel with its precipitation chemistry sampler. Precipitation chemistry sampler volumes are used to calculate wet deposition fluxes only when the standard gauge fails or is temporarily out of service. The data record should document such cases.

Environmental factors may cause precipitation gauge measurements to be too high or too low. Among the most important factors are wind speed, precipitation type, temperature, ground cover and blowing snow. Since the disruption in air flow around a gauge grows as the wind increases, measurement inaccuracies increase as the wind speed rises. For rain, the WMO recommends the use of pit gauges to reduce wind effects on gauge catch (Sevruk and Hamon, 1984), but pit gauges are impractical at many GAW sites. Snow undercatch in high winds and low temperatures is a particularly well-documented problem. In a WMO publication on measurements of solid forms of precipitation, Goodison et al. (1998) report on snow undercatch from gauges in current use. Based on this seven-year multinational study, the GAW Precipitation Chemistry Programme makes the following recommendations:

- Avoid using heated automated (e.g., tipping bucket) gauges.
- Sheltered sites are preferred over open exposures. Locate gauges on level ground where vegetation offers a natural buffer from the direct force of the wind. Be careful to have sufficient separation from trees and other tall vegetation so that precipitation will not blow from the vegetation into the gauge nor will the vegetation interfere with the free fall of precipitation into the gauge. The precipitation chemistry sampler may require additional separation to avoid sample contamination (see Section 2.4.2).
- Where snow comprises at least 20% of annual precipitation, gauges must be equipped with a suitable wind shield (see Section 2.4.2) and wind speed and temperature should be measured at gauge height. These data can be used to correct for snow undercatch, although presently the GAW Precipitation Chemistry Programme does not recommend such corrections. Wind shields around precipitation chemistry samplers are discouraged because of the potential for contamination.
- NMHS personnel are encouraged to read the Goodison et al. (1998) report to avoid poorly performing gauges when selecting a model for wind-exposed locations. The Hellmann,

Belfort (shielded and unshielded), Tretyakov (unshielded and dual fence), and Nipher gauges were tested; some of these gauges exhibit very poor performance at high wind speeds.

3.2.1.3 Precipitation Chemistry Collection of Snow

Collecting a representative snow sample for precipitation chemistry measurements poses special problems. Most electronic sensors on precipitation chemistry samplers do not detect snow, particularly light, dry snow, as efficiently as rain. Light, dry snow also may fall into and then blow out of an open container or funnel. Snow may stick to sampler parts and later blow into the sample container. Ice may coat sampler parts and prevent proper operation. Heavy snow may even fill the container to overflowing and block sampler operation. Because winter conditions and ice and snow characteristics vary widely according to site location, elevation, and exposure, there is no standard snow chemistry sampler, and there is no universal way to address these problems.

Some samplers are especially adapted to improve snow collection. Heating the collector lid and other moving parts to about 4 to 5°C may help prevent snow and ice buildup from interfering with sample collection or sampler operation. For samplers with funnels, applying enough heat to melt snow and ice may be necessary, if the funnel depth is too shallow to accommodate the entire accumulation. Care should be taken when applying heat to avoid increased sample loss due to evaporation or sublimation. One way to preclude heating the sample is to use an open container instead of a funnel. In extremely cold regions, an open cylindrical polyethylene sample container (diameter of 20 to 30 cm) is recommended for use on wet-only samplers. The container height should be at least twice its diameter to reduce the potential for snow to blow out of the container.

3.2.1.4 Routine Instrument Checks and Maintenance

Standard operating procedures should include routine checks and maintenance of the precipitation chemistry samplers and standard precipitation gauges (and other meteorological instruments, when present). Routine checks include:

- Checking for proper precipitation chemistry sampler operation, especially sensor response and heating (i.e., that sensor activates sampler to collect precipitation and otherwise closes and seals precipitation sample container).
- Checking the precipitation gauge for leaks, damage, and proper operation.

Routine maintenance includes cleaning sampler and gauge parts essential to proper instrument operation. Cleaning all sampler surfaces that contact the sample (e.g., funnels, buckets, bottles, tubes, filters) is essential. Additional periodic or seasonal maintenance may be necessary to prepare the equipment for winter operations, e.g., installing/removing a precipitation gauge funnel, installing a wind shield, or charging the standard precipitation gauge with antifreeze or oil.

Operating manuals, including trouble-shooting guides, should be available for each instrument at each site.

3.2.2 Sampling Period

The sampling period is the time from installation to removal of the sample container in the precipitation chemistry sampler. Choice of the sampling period depends on network objectives, sample quality considerations, and operational costs. As sampling periods lengthen and the time between collection and analysis increases, the potential for sample deterioration increases.

The GAW Precipitation Chemistry Programme recommends 24-hour sampling periods with sample removal set at a fixed time each day, preferably 0900 local time. This requires a laboratory having adequate resources to analyze daily samples and support daily field operations, and it requires adequate personnel for daily site visits. Where the cost of site visits and large numbers of samples

makes daily sampling impractical, a multi-day sampling period, up to a maximum of 7 days (i.e., weekly sampling) is recommended. Weekly sampling that commences at 0900 local time on Tuesday is the 7-day sampling period of choice. Whether samples are collected daily or weekly, it is important to avoid removing samples during precipitation. This is done to reduce the high likelihood of contamination from handling a sample during rain or snow and is best accomplished by waiting for a pause in the event. If the precipitation has not paused after a few hours, the sample should be collected and a note made on its sample history form (see Section 3.5).

Sampling Period Specifications

Sampler Type	Duration	Start Time	Appropriateness for GAW	Note
Wet only	24 hour	0900 local time	Highly recommended	1
Wet only	Multi-day Not to exceed 7 days	0900 local time	Recommended	2
Wet only	>7 days 2 week or monthly	0900 local time	Not recommended	3
Wet only	Event or Storm Duration variable	Collection time variable	Not recommended	4
Bulk	24 hour	0900 local time	Discouraged	5
Bulk	Multi-day	0900 local time	Strongly discouraged	6

1. Requires daily visits to site, which may not be possible for some remote locations.
2. Provides a less costly option than daily sampling, with fewer samples and site visits.
3.   Greater chance that samples may be altered if they remain in the field for such long periods. Infiltration of dust or other materials is more likely than with daily or weekly sampling. A missing or invalid sample due to sampler malfunction or sample contamination may compromise or invalidate seasonal or annual averages.
4. Requires a full-time site operator and constant monitoring of precipitation. Labour-intensive and costly. Provides valuable research data but may not be practical for long-term monitoring.
5. While discouraged due to the possibility of sample contamination, 24-hour bulk data may be accepted for certain remote, harsh environments where dry deposition is minor and where wet-only sampler designs have been proven ineffective. Approval by the GAW Precipitation Chemistry Programme Science Advisory Group is required prior to the establishment of new bulk sampling sites.
6.   Bulk samples with a sampling period longer than 24 hours are assumed to be contaminated by dry deposition and/or other materials. Data from existing sites will be made available by the WDCPC only upon request. Acceptance of new bulk sampling sites is unlikely.

Two alternative weekly sampling protocols may be considered: 1) removing and analyzing samples that have accumulated in an automated wet-only sampler after one full week and 2) removing samples from an automated wet-only sampler after each day of precipitation, pouring the sample into a storage vessel kept in a dark and cool (possibly refrigerated) location, and analyzing the accumulated sample after one full week. Method 1 minimizes the cost of site visits and field operations; however, samples left in the collector at ambient conditions are subject to contamination, evaporation, and chemical degradation. Since the potential for chemical changes increases as the sampling period lengthens, the GAW Precipitation Chemistry Programme strongly discourages sampling periods that exceed one week. An additional concern of long-term sampling periods is that loss of just a few samples over the course of a year makes it difficult to calculate representative seasonal or annual deposition values.

Some GAW sites are equipped with automated wet-only samplers that offer daily sampling without requiring daily site visits. These samplers have the capacity to change sample containers every 24 hours at a fixed time (for consistency, preferably 0900 local time) and store the containers in a refrigeration unit. These collectors generally have higher power requirements than other automated collectors and require careful cleaning of the connecting tubes and other apparatus.

An alternative sampling protocol followed at some sites is sample removal on a storm-by-storm or precipitation event basis. This means that site operator must collect samples at all times of day or night. It also requires an unambiguous definition of an event and a method for operators to identify when an event has ended and a sample is to be removed. Weather radar, information on the storm track and intensity, and good communications are important elements in accurately following an event sampling schedule. The scheduling demands and information needs make event sampling especially costly and unless a rigorous sampling schedule can be met, the GAW Precipitation Chemistry Programme discourages event sampling.

3.2.3 Sample Preservation Practices

Regardless of the length of the sampling period, there is always the possibility of chemical degradation of the sample in the field during the course of sample collection, during shipment from the field to the laboratory, and prior to analysis at the laboratory. Sample preservation practices followed by most networks often do not completely stop chemical degradation. A recommended practice is refrigerating samples below 4°C in the laboratory before analysis. Refrigeration alone does not prevent partial or complete loss of labile species, such as formic and acetic acids, nitrite and sulfite. Fluoride and nutrients, such as orthophosphate and ammonium, may be compromised as well. Organic acid losses may result in an increase of a few tenths of a pH unit for samples between about pH 4.5 and 5.0. Ammonium losses can average up to 15 percent on an annual basis, depending on conditions of sample storage and shipment.

Various practices are used to reduce or eliminate chemical degradation. These practices are described briefly in the following sections. Whether or not biocides are used, the best practice is to minimize sample handling, keep storage times short, ship samples rapidly to the analytical laboratory, and analyze samples promptly.

3.2.3.1 Refrigeration

Refrigeration below 4°C is perhaps the most common preservation practice, and it slows most chemical and biological sample degradation. Ideally, collectors would be equipped to refrigerate samples during collection, although this is costly and places extra demands on collector power requirements in remote settings. Because most collectors are not equipped to refrigerate samples, it is desirable to refrigerate samples immediately upon removal from the field. For daily sample collection protocols, refrigeration immediately after collection and throughout sample storage and shipment reduces ammonium losses. For weekly sample collection protocols, refrigeration is effective if samples are removed from the precipitation chemistry sampler daily, poured into a refrigerated storage vessel that accumulates samples for one full week, and refrigerated throughout shipment and storage until

analysis. However, following these procedures does not preclude losses of organic acids and other labile species (e.g., sulfite and nitrite).

3.2.3.2 Use of Biocides

Another preservation practice is to prevent microbes from consuming the organic acids and nutrients in precipitation by adding chemical biocides to the collected samples. This requires strict quality control procedures that ensure these additives contain nothing that will contaminate samples. To date, biocides have been used primarily for research purposes and only on a limited basis in operational measurement programmes. Chloroform is a common biocide used for this purpose (Keene, et al., 1983, 2002, Keene and Galloway, 1984, 1986, 1988). Chloroform is toxic, volatile, and easily contaminated, but it is very effective in stopping microbiological activity, degradation of organic acids, and loss of ammonium. Adding approximately 0.5 mL of ultrapure chloroform to samples is typically adequate. Since chloroform is denser than water and immiscible, samples may be drawn for analysis from above the chloroform layer. This prevents chloroform from being a concern during sample analysis. This is an important consideration, because chloroform degrades ion chromatography columns, rendering them ineffective.

Another biocide that is added to precipitation is 2-isopropyl-5-methyl phenol or thymol (Gillet and Ayers, 1991, Ayers et al., 1998). Unlike chloroform, which is a volatile liquid, thymol is a solid at ambient temperatures. Although it sublimes (vapour pressure=1 mm Hg at 64ºC) under ambient conditions, the sublimation rate is sufficiently slow that it can be added directly to the sample container in the collector. Precipitation entering the container is "fixed" on contact with the thymol, effectively arresting biodegradation of the sample at the point of contact. Although it is an effective biocide, thymol is not immiscible and may interfere with some analytical procedures. Thymol may cause respiratory irritation and should be handled in a fume hood, and prolonged exposure may have other harmful health effects. Prior to using thymol, laboratory personnel must test its purity to ensure that it does not contain any of the chemicals being measured in precipitation and to ensure it does not interfere with the chromatographic, spectrophotometric, colorimetric, or other analyses.

In general, consider using a biocide where the NMHS objective is to measure accurately the organic acids and orthophosphate in precipitation or where refrigeration is not practical, such as in tropical areas. Rigorously follow special handling precautions that ensure the safety of field and laboratory personnel. If the central laboratory is near the site, the biocide should be added to the precipitation sample container by laboratory personnel. Before using biocides, carefully check for purity and interferences with all analytical procedures. Since biocide use requires extra sample handling, exercise regular quality control procedures that check the potential for sample and biocide handling contamination. While biocides may be used as a means to delay chemical analysis, particle dissolution and inorganic chemical reactions can continue to alter cation and anion concentrations and the free acidity of precipitation. See Keene and Galloway (1984, 1986, 1988), Keene et al. (1983), Herlihy et al., (1987), and Galloway et al. (1989, 1996) for studies on the use of chloroform in precipitation samples. See Ayers et al. (1998) and Gillet and Ayers (1991) for information on the use of thymol. Section 4.4.6 describes the laboratory analytical procedures and sample handling precautions that must be taken when samples that contain chloroform are analyzed for organic acids.

3.3 Sample Handling and Shipping

3.3.1 Cleaning and Preparation of Precipitation Sample Containers

Clean all surfaces that the sample may contact to a pre-specified level of cleanliness (conductivity below 1.5 µS cm^{-1}) before use. This applies to surfaces in the precipitation chemistry sampler and to other surfaces that contact the sample, such as funnels, tubing, syringes, or pipettes. For ease of description in this section, the term "precipitation sample containers" will refer to all of the surfaces that the sample may contact.

Precipitation sample containers must be cleaned with deionised water of known and assured quality. Since the quality of deionised water often limits container cleanliness, **the best and most consistent practice is to clean precipitation sample containers at a single central facility, such as the analytical laboratory, where the deionised water quality can be controlled most efficiently.** Where this is impractical or too costly, cleaning precipitation sample containers at field sites is an option. Field sites must have a supply of deionised water and, as a minimum, be equipped to measure conductivity, if precipitation sample containers are cleaned there. Whether containers are cleaned at a central facility or at the field sites, it is necessary to exercise routine quality control checks of the water. Conductivity of fresh deionised water (measured before any significant CO_2 uptake can occur) should be approximately 0.5 μS cm^{-1} (i.e., reagent-grade deionised water). A conductivity <1.0 μS cm^{-1} is essential for deionised water that has been in storage for any period of time.

Use of a detergent or acid solution to clean precipitation sample containers is typically unnecessary and is discouraged. If detergents or acids are used, special care must be taken to rinse away residues, which requires more time and water. An alternative to using detergents or acids is to allow the containers to soak in deionised water for 24 to 48 hours, leaching away soluble and exchangeable residues that may contaminate precipitation. Removing visible residues from precipitation sample container surfaces often requires wiping these surfaces with a sponge that is cleaned and soaked in deionised water. Wear rubber gloves when cleaning and handling precipitation sample containers and rinse surfaces repeatedly, until the conductivity of the rinse water falls below 1.5 μS cm^{-1}.

The GAW Precipitation Chemistry Programme recommends that precipitation sample containers be cleaned until the conductivity of the final rinse water (i.e., the rinsate) does not exceed 1.5 μS cm^{-1} whether cleaned in the field or the laboratory. Routinely checking that the rinsate conductivity does not exceed 1.5 μS cm^{-1} is a necessary quality control procedure. See Section 4.3.1.1 for discussions on cleaning of precipitation sample containers at the central analytical laboratory and for additional testing that is needed there to ensure sample quality.

After being cleaned, precipitation sample containers that are not used immediately must be dried by shaking off the excess water, and while still damp, sealed or covered in plastic and stored in a clean area. Air drying should be avoided as many contaminants are soluble in water and stick to dry surfaces.

It is strongly recommended that container blanks for precipitation sample containers, transfer bottles, funnels, and other containers be prepared and analyzed on a routine basis to ensure cleanliness. This can be done by adding 25 mL of deionised water (conductivity of 0.5 μS cm^{-1} if fresh or <1.0 μS cm^{-1} if stored) to the container and submitting to the laboratory for analysis.

3.3.2 Handling and Transporting Samples and Sample Containers

Every effort should be made to minimize sample handling and transfer between containers. Each surface that comes in contact with a sample is a potential source or sink for the dissolved constituents in precipitation. Soluble or exchangeable contaminants on container surfaces may introduce positive concentration biases. Similarly, container surfaces may adsorb dissolved ions, thereby introducing negative biases.

3.3.2.1 Handling and Transferring Samples

Because of the potential for chemical changes, the GAW-PC programme recommends that samples be transported to the laboratory in the precipitation sample container. This is not always practical, however, because of size, shape, or some other characteristic. If the sample must be transferred to another container, always do this in a laboratory or clean shelter, never in the open environment of the field site. Only transfer the sample by pouring it directly from one container to another, if at all possible, to avoid another contact surface. **High density polyethylene (HDPE) containers are recommended.** The use of pipettes, syringes, funnels, etc., is unacceptable.

An acceptable practice is to send samples from the field site to the analytical laboratory in clean shipping bottles provided by the laboratory. These bottles are often too small to accommodate the entire sample, particularly for very large volumes, and so only a portion of the sample is sent for analysis. Care must be exercised to ensure that frozen samples are completely thawed and well mixed before being poured into shipping bottles. When pouring, decant the liquid in an effort to leave insects, leaves, and other debris behind.

Always handle the precipitation sample with care and with a minimum of exposure to the atmosphere. These same considerations apply to precipitation sample containers before they are put to use. Once exposed, samples should be covered quickly, and then sealed tightly to minimize the potential for contaminating materials to fall into the sample, for evaporation, and for spillage. Never move any body part (hands, arms, or face) over an exposed sample. Wear disposable plastic gloves when transferring the sample between containers, even if your hands do not move over the sample. Never allow anything, even a gloved hand, to come in contact with a surface the sample may contact. As an added precaution, it is advisable to place sealed sample containers in clean plastic bags prior to use and after sample transfer. This additional layer of plastic protects the sample from exposure to soil, water, and other contaminants.

3.3.2.2 Sample Storage and Shipping

Containers used to store and ship samples should be unbreakable and also sealable against leakage of liquids or gases. During storing and shipping, steps should be taken to slow chemical change or biodegradation of samples. The recommended storage procedure is to refrigerate samples below 4ºC (see Section 3.2.3 for preservation practices). The best practice is to keep storage and shipment times short. Samples should be sent for analysis as soon after collection as practical. Rapid shipping services can speed sample delivery to the laboratory. Samples should be sent in insulated containers with "chill packs" that maintain the inside temperature below 4ºC.

Although rapid delivery of samples to the laboratory is recommended, cost and logistics may result in longer shipment times. An alternative is to send samples to the analytical laboratory weekly, using regular mail services. Before shipping samples to the laboratory, inspect each container to ensure it is properly sealed, labelled, and packed.

For refrigerated shipments, "chill packs" should be placed above and below the sample containers. There should be some way to check that sample temperatures do not exceed 4ºC. One way to do this is to include with the shipment a thermometer that records maximum temperatures. Another common practice is to include a container of water (not a sample) that is measured when the shipment arrives at the laboratory. Laboratory personnel should record the temperature when the sample is received and take corrective action when temperature limits are exceeded, e.g., add insulation or more "chill packs" to future shipments. If a sample history form (Section 3.5) accompanies the shipment, it should be protected against damage or destruction from possible sample leakage.

3.3.2.3 Field Blanks

A recommended practice for checking the cleanliness of sample collection and handling procedures is to collect field blanks. A field blank tests the total field measurement system, not just container cleanliness. (The container blank, described in Sections 3.3.1 and 4.3.1.3, uses a container selected randomly from the supply ready for use and it is limited to testing the cleanliness of container cleaning procedures.) It is recommended that for daily sampling, two to four blanks be collected randomly per month, and for weekly sampling, one to two blanks per month.

To collect a field blank, wait for a sampling period when there was no precipitation, add deionised water to the precipitation sample container and treat the container as a precipitation sample. Use a container that was installed in the precipitation chemistry sampler for a sampling period when no precipitation occurred. Handle the field blank by following the same stepwise procedures used to

handle a precipitation sample. For the test to be complete, it is important that the water come in contact with all of the same surfaces as precipitation. For funnel and bottle collectors, the field blank test should ensure that the water comes in contact with the funnel, connecting tubes, and bottle. With ambient temperatures above freezing, the water (or test solution) can be added to the sample container (funnel/ bottle etc.) while it is installed in the precipitation chemistry sampler. With ambient temperatures below freezing, remove the sample container from the sampler to a clean, warm room, where the test should be performed. Wait for a sampling period when there was no precipitation. It is important that the exact procedures for conducting the field blank test be followed and documented.

Field blank samples should be sent to the analytical laboratory, which measures the entire suite of anions and cations, just as for precipitation samples. Field blank analyses should be reported along with other quality assurance information, so that scientists have the data needed to evaluate the lower quantifiable limit of ion concentration measurements. This information should be provided to the WDCPC on an annual basis.

There is no universally correct volume of water to add to the precipitation sample container when preparing a field blank. The volume chosen should approximate the smallest volume required for a complete suite of laboratory measurements. This also represents the smallest amount of precipitation that the precipitation chemistry sampler can reliably collect for laboratory measurements. For example, if the laboratory requires 60 mL, choose a blank volume of 100 mL. If available, consider using simulated precipitation solutions, instead of deionised water, for field blank tests. The results of a programme that uses both deionised water and simulated precipitation can be a very effective means of quantifying the overall positive and negative biases in the precipitation chemistry measurement system.

3.4   On-Site Measurements

At least two measurements should be reported for every sampling period, the sample volume from the precipitation chemistry sampler and the precipitation amount from the standard precipitation gauge. These measurements should be compared with one another as a routine check of the performance of the precipitation chemistry sampler and gauge. Large differences may mean there is a measurement error or malfunction in one or both instruments. Because of aerodynamic differences in the sampler and gauge and because the sampler must first sense precipitation before opening, the sample depth is typically less than the gauge depth. For a properly functioning precipitation chemistry sampler, differences between and sampler and the gauge depths should be smaller than about 10 percent, except in high wind, blowing snow, or ice conditions.

Sample volumes must be measured gravimetrically, since this method is efficient, accurate, and less prone to contamination and spillage than volumetric measurements. Periodically (at least annually) the accuracy of the balance should be checked using a known reference weight. Volumetric measurements using graduated cylinders are strongly discouraged because of the potential for sample contamination and spillage.

Precipitation gauge measurements should be taken at the same time as the precipitation chemistry sample is collected. Gauge measurements should be reported for every sampling period, whether or not the precipitation chemistry sampler collected a sample. Beyond serving as a crosscheck of the efficiency and accuracy of precipitation sampler operation, gauge measurements are used to calculate annual wet deposition and wet deposition fluxes.

In addition to sample volume and precipitation gauge measurements, some programmes record field pH and conductivity measurements. These values are compared with laboratory measurements to evaluate chemical changes that can occur between the field and laboratory. The GAW Precipitation Chemistry Programme does not recommend field chemistry measurements unless supported by a comprehensive QA/QC programme that can verify the measurements. The WDCPC does not archive field pH and conductivity measurements, since they are not among the standard measurements.

If field chemistry measurements are made, they must never be done on the sample sent to the laboratory for analysis but rather on a portion that is removed from the sample sent for analysis. Measurements should be consistent with manufacturer's instructions and follow standard operational procedures. Any sample remaining after completion of field chemistry measurements must be discarded. Never return the portion removed for field chemistry to the portion sent to the laboratory for analysis.

3.5   Sample Documentation

Information about every sample must be recorded on a *sample history form*. This form documents quantitative and qualitative information and observations by the site operator. It provides information that affects laboratory decisions about the sequence and nature of the chemical analyses. It also provides information used in data screening and verification. Data from the sample history form are entered directly into the database management system. Required fields on the sample history form include:

1) Site name
2) Site identification number
3) Site operator name
4) Sample start date and time
5) Sample end date and time
6) Sample weight (including collection vessel weight)
7) Precipitation amount from gauge measurement
8) Precipitation type (snow, rain, freezing rain, hail, or mixed types)
9) Visible sample contamination (suspended particles, bird feces, insects, plant debris, etc.)
10) Instrument conditions (operating correctly/incorrectly)
11) Operator remarks (unusual circumstances, non-standard operating procedures, agricultural, industrial or vehicular activity at the site, other observations or problems)
12) Supply requirements (sample containers, deionised water, field chemistry supplies, chill packs)
13) An entry on the form to report dry or nearly dry conditions during the sampling period ("no precipitation" or "trace amount").

GAW Precipitation Chemistry Programme does not recommend a specific sample history form, since many sites already use forms as part of regional or international networks. Examples of two sample history forms used by GAW networks are shown in Figures 3.1 and 3.2. The sample history form should be a multi-copy form. At least one copy should accompany the sample shipment to the laboratory and another should be retained at the field site. Having copies at both locations helps to ensure that this valuable record is not lost, and it facilitates communication between field and laboratory personnel, should questions arise about the conditions of the site, the sample, or the equipment.

In addition to the sample history form, it is a good practice to maintain a field log book that records arrivals and departures from the field site, general weather conditions during the visit, and explanations of any unusual conditions, problems, or deviations from the normal routine. Any information that may bear on the sample quality or integrity should also be recorded on the sample history form.

ATMOSPHERIC INTEGRATED RESEARCH MONITORING NETWORK
FIELD OBSERVER FORM (FOF)

Send Completed Form with Each Sample
Problems? Call the CAL at 1-800-952-7353, or
e-mail: airmon@sws.uiuc.edu, or fax: 217-244-3054

* D51100 *

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
A Cooperative Research Support Program of the
State Agricultural Experiment Stations (NRSP-3)
Federal and State Agencies
and Private Research Organizations

FOR OFFICE USE ONLY

A

Temp (ºC) | . | | | Type
Leak | SP | SL

---

1. SITE

Name _____ ID

2. OBSERVER

Print name _____ Initials

3. SHIPMENT DATE

| MO | DAY | YR |

---

4. SAMPLE PERIOD

ON / OFF

| MO | DAY | YR | 0001-2400 |

5. SITE OPERATIONS

Check yes or no for all samples.
If no for Item 1 or 2, describe
in Block 11 and call CAL.

YES	NO
2	1
2	1
2	1

1. The **sensor heater** and **motor box** operated properly and the **event recorder** indicates the collector lid opened and closed promptly for each precipitation event.
2. **Raingage** operated properly during sampling period.
3. **Collector** opened and closed at least once during sampling period.

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6. SAMPLE CONDITION

Check yes or no for **all** samples. If yes, explain and quantify in Block 11.

YES	NO			YES	NO			YES	NO	
2	1	1. Bird droppings		2	1	3. Soot/ash/dirt particles		2	1	5. Leaves/twigs/pollen/plant matter
2	1	2. Cloudy or discolored		2	1	4. Insects/animal matter		2	1	6. Handling contamination
										7. Other

7. SAMPLE WEIGHT

Weigh all sample buckets.

Bucket + Lid + Sample

Bucket + Lid

−

= [ ] Sample Weight (grams)   X 0.00058 inches/gram = [ ] Sample Depth (inches)

8. PRECIPITATION RECORD *Circle all types that apply - for definition see Operator's Manual.*

Type | T | R | RW | S | SW | L | ZL | ZR | A | SP | SG | IC | IP | BS | E | F | K | H | D | BD | BN | + | −

Belfort gage depth (inches)

Do these values agree within ? 10%?   YES ☐   NO ☐ *(If no, reweigh)*

NWS gage depth (inches)

*DAY	00-01	01-02	02-03	03-04	04-05	05-06	06-07	07-08	08-09	09-10	10-11	11-12	12-13	13-14	14-15	15-16	16-17	17-18	18-19	19-20	20-21	21-22	22-23	23-24

Record hourly precipitation amounts to 0.01 inches (trace = T, missing = M). Top line is precipitation start date. Times are local (00-01 = 0001 through 0100 and 23-24 = 2301 through 2400 hours).

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9. SAMPLE CHEMISTRY

Only for Sample Weight greater than 50 grams

| MO | DAY | YR |

Distilled Water (µS/cm)

Specific Conductance (µS/cm)

| 7 | 5 | . | 0 | Standard Certified

Correction Factor

+ Standard Measured = Correction Factor

Correction Factor x Check Sample Measured = * Check Sample Corrected

Correction Factor x Precipitation Sample Measured = Precipitation Sample Corrected

pH

* Is check sample within range? *(If no, call CAL)*

* Check Sample pH

* Precipitation Sample pH

10. SUPPLIES

Circle if needed, until received.

Vials	Buckets	Dashpot Fluid
pH 4 Buffer	Bags	Raingage Charts
pH 7 Buffer	Tape	Raingage Ink
Check Sample	Ice Packs	Lid Seal Pad
75 µS/cm Std.	Field Forms	
pH Electrode		
Electrode Fill Solution		

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11. REMARKS

Rev. 11/00

Figure 3.1: Example of sample history form used in the Atmospheric Integrated Research Monitoring Network (AIRMoN).

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Figure 3.2: Example sample history form used in the Canadian Air and Precipitation Monitoring Network (CAPMoN).

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4. LABORATORY OPERATIONS

Concentrations of the main chemical constituents of precipitation are low and frequently at or near the detection limits of sensitive analytical instruments. High quality accurate results can only be obtained with adequate analytical chemical methods, sensitive instrumentation and strict QA/QC procedures throughout the analytical system. This chapter identifies the GAW precipitation chemistry analytes and the preferred methods for their analyses. It describes laboratory quality assurance and quality control objectives and activities; methods for sampling handling and chemical analyses; and laboratory data verification and reporting.

4.1 Overview of Laboratory Measurements

The following compounds are recommended for analysis in GAW precipitation samples: pH, conductivity, sulphate, nitrate, chloride, ammonium, sodium, potassium, magnesium and calcium. Analyses for formate and acetate are recommended for areas suspected of having high organic acid concentrations. Nitrite, phosphate and fluoride concentrations also may be important in certain areas, although their analyses are not required by GAW at this time. Preferred analytical methods are given below.

Analyte	Status	Preferred Methods[1]
pH	Required	Glass electrode
Conductivity	Required	Conductivity cell
Alkalinity	Optional	Titration
Cl^-, NO_3^-, SO_4^{2-}	Required	IC
NH_4^+	Required	IC, AC
Na^+, K^+, Ca^{2+}, Mg^{2+}	Required	IC, ICP, AAS/AES
Organic Acids[2]	Optional	IEC, IC
NO_2^-, F^-	Optional	IC
PO_4^{3-}	Optional	IC, AC

[1] IC = ion chromatography; AC = automated colorimetry; ICP = inductively coupled plasma spectrometry; IEC = ion exclusion chromatography; AAS = atomic absorption spectrometry; AES = atomic emission spectrometry.

[2] For areas with high organic acid concentrations, formate and acetate analyses are recommended.

The goal in the laboratory is to have all the required analytes measured for each sample. If small precipitation amounts frequently occur, then priorities for analysis in the laboratory must be set. Unless there are other regional priorities, typically the order is: first determine sulphate, nitrate and chloride ions, by ion chromatography, and secondly ammonium ion, sodium, potassium, calcium and magnesium ions by one of the preferred methods. The pH should be measured to facilitate the calculation of an ion balance. Many laboratories use their conductivity measurements to compare to calculated conductance. This comparison provides a complementary check for the ion balance calculation.

In addition to the analysis of actual precipitation chemistry samples, the laboratory is also responsible for the numerous quality control and quality assurance measurements and procedures that ensure the quality of the analytical results. These activities are described in the text that follows. Details about quality assurance in analytical chemistry may be found in Funk et al. (1995).

4.2 Laboratory Data Quality Objectives (DQOs)

The DQOs for the GAW Precipitation Chemistry Programme are given in Table 1.1, and discussed further in Chapter 6 and Appendix A. It is the responsibility of each laboratory to implement an appropriate set of operational and QA/QC activities to ensure that these objectives are met or exceeded. See the Glossary for definitions of quality control and quality assurance and U.S. EPA

(2002) for other related terminology.

> **Each laboratory should have a person responsible for implementing and managing a laboratory quality assurance program (QA manager).**

4.3   Quality Assurance and Quality Control Activities

Quality assurance (QA) and quality control (QC) activities for the laboratory can be divided into three distinct activities:

1) Setting laboratory data quality objectives
2) Carrying out QA/QC activities within the laboratory
3) Reporting the QA/QC information.

The details for conducting QC procedures should be described in the written *Standard Operating Procedures* (SOPs) for the laboratory. Details for QA activities are best described in a written *Quality Assurance Project Plan* (QAPjP) (U.S. EPA, 1998, Rothert et al., 2002). Both SOPs and QAPjPs must be updated at least annually and readily available to the laboratory staff. Laboratory staff should be active participants in the updating of these documents.

Specific quality control procedures include:

1) Documentation of and compliance with standard operational procedures (SOPs)
2) Preventive maintenance of laboratory equipment and instrumentation
3) Documentation of analyst training and upgrading
4) Provision of appropriate facilities, instrumentation and reagents
5) Inspections and/or reviews
6) Appropriate safety measures
7) Well-defined laboratory chain-of-custody
8) Traceability of calibration standards
9) Control charting
10) Accuracy checks (calibration checks, blinds, reagent blanks)
11) Precision checks (within-run and between-run duplicates).

4.3.1   Laboratory Sample Handling QA/QC

4.3.1.1 Sample Reception, Logging and Custody

Proper sample logging and *chain-of-custody* procedures must be implemented at the laboratory to ensure that samples are not lost, mixed up or misplaced. When samples are received at the laboratory, record the following information:

1) Date/time of reception
2) Site name
3) Sample numbers
4) Name of laboratory person who received the samples.

Store samples immediately in a refrigerator at 4°C until they enter the analysis stream. Follow the laboratory chain-of-custody procedures to ensure that samples can be tracked properly.

Summary of Laboratory QA/QC Activities

(Frequency of activities may vary slightly in different laboratories)

Daily
- Calibrate instruments and verify calibration curves using calibration check solutions
    - Analyze one or more calibration check solutions in each sample batch (or every 12 to 15 samples) that correspond to the 10th, 50th and 90th percentiles of the sample concentrations
    - Record and plot calibration check solutions on daily control charts that are inspected after every run
    - Repeat instrument calibration if control limits are exceeded
- Analyze DI water and reagent blanks in each sample batch
- Record details of standards preparation
- Update instrument maintenance records

Weekly
- Analyze blanks from
    - the laboratory's DI water
    - filter leachates using DI water
    - sample containers/bottles using DI water
    - any sampling containers that are sent to the field sites
    - any container blanks received from the field sites
- Analyze blind samples
- Split 2 to 5 % of precipitation samples for replicate analysis
- Split 1% of precipitation samples for a dilution check

Monthly
- Evaluate internal blind audit and replicate data from printouts/plots
- Select samples for reanalysis based on ion percent and conductivity percent differences
- Evaluate reanalysis data and suggest data changes to data manager
- Verify prior to shipment all quality control solutions that are sent to the field sites

Semi-annually
- Participate in laboratory intercomparisons

Annually
- Prepare laboratory QA report for publication

4.3.1.2 Sample Labelling, Transferring, and Storage

After reception and login, weigh the samples (to check for leakage during transit and to confirm the field weight) and inspect for visible contamination. Note any problems or inconsistencies in the weights, dates, times or other sample descriptions and send this information to the QA manager. Label all sample bottles or analytical vials with a laboratory identification number that can be cross-referenced to the field site and date. Note that in some laboratories, the transfer of samples from the collection vessel to analytical vials may involve filtering. Filtering is done to reduce particle dissolution effects on sample chemistry, to eliminate potential interferences from insoluble particles and to protect analytical systems. **Filters can be a source or sink for ions and must be tested periodically to ensure that precipitation chemistry is not altered during filtering. This requires periodic blank tests** (Rothert, 1999).

Every effort should be made to minimize sample handling and transfer between containers. Each surface that a sample contacts is a potential source or sink for the dissolved constituents in precipitation. Soluble or exchangeable contaminants on container surfaces may introduce positive concentration biases. Similarly, container surfaces may adsorb dissolved ions, thereby introducing negative biases.

Always handle the precipitation sample with care and with a minimum of exposure to the atmosphere. These same considerations apply to sample containers before they are put to use. Once exposed, samples should be covered quickly, and then sealed tightly to minimize the potential for matter to fall into the sample, or for evaporation or spillage. Never move any body part (hands, arms, or face) over an exposed sample. Never allow anything, even a gloved hand, to come in contact with a surface the sample may contact.

Containers used to store and ship samples should be unbreakable and also sealable against leakage of liquids or gases. **High density polyethylene (HDPE) containers are recommended.** HDPE is unbreakable, inexpensive and effective for collection and storage vessels. Glass containers are discouraged because they are prone to both positive and negative artefacts for cations. During storage and shipping, steps should be taken to slow chemical change or biodegradation of samples. The standard storage procedure is to refrigerate samples at 4°C (see Section 3.2.3 for field preservation practices). The best practice is to keep storage and shipment times short. Samples should be sent for analysis as soon after collection as practical.

While the standard methodology to control biological degradation is to refrigerate samples, there is ample evidence that chemical preservation, if done carefully, may be a superior control option. In general, consider using a biocide where the NMHS objective is to measure accurately the organic acids and orthophosphate in precipitation or where refrigeration is not practical. Rigorously follow special handling precautions that ensure the safety of field and laboratory personnel. Before using biocides, carefully check for purity and interferences with all analytical procedures. Since biocide use requires extra sample handling, exercise regular quality control procedures that check the potential for sample and biocide handling contamination. While biocides may be used as a means to delay chemical analysis, particle dissolution and inorganic chemical reactions can continue to alter cation and anion concentrations and the free acidity of precipitation.

At the present time two substances, chloroform and thymol, have been field tested and used successfully to chemically preserve samples (Section 3.2.3.2). Chloroform, being highly volatile, is added in small quantity to samples immediately upon collection. Thymol, being a solid, is placed in the sampler prior to sample collection. Thymol is not immiscible and may interfere with some analytical procedures. Both chloroform and thymol may cause respiratory irritation and should be handled in a fume hood, and prolonged exposure may have other harmful health effects. Prior to using chloroform or thymol, laboratory personnel must test their purity to ensure that they do not contain any of the chemicals being measured in precipitation and to ensure they do not interfere with the chromatographic, spectrophotometric, colorimetric, or other analyses. See Keene and Galloway (1984, 1986, 1988), Keene et al. (1983), Herlihy et al., (1987), and Galloway et al. (1989, 1996) for studies on the use of chloroform in precipitation samples. See Ayers et al. (1998) and Gillet and Ayers (1991) for information on the use of thymol. Section 4.4.6 describes the laboratory procedures and sample handling precautions necessary for organic acid analyses (where chloroform is used).

4.3.1.3 Cleaning and Preparation of Precipitation Sample Containers

Clean all surfaces that contact samples to a pre-specified level of cleanliness (conductivity of DI rinses below 1.5 μS cm^{-1}) before use. This applies to surfaces in the precipitation chemistry sampler and to other surfaces that the sample may contact at the field site or in the laboratory (such as funnels, tubing, syringes, or pipettes). For ease of description in this section, the term "sample containers" will refer to all of the surfaces that the sample may contact both in the laboratory and in the field.

Sample containers must be cleaned with deionised water of known and assured quality. Since the quality of deionised water often limits container cleanliness, **the best and most consistent practice is to clean sample containers at a single central facility, such as the analytical laboratory, where the deionised water quality can be controlled most efficiently and effectively.** Where this is impractical or too costly, cleaning sample collection containers at field sites is an option. See Section 3.3.1 for discussion on cleaning sample containers at field sites. Whether containers are cleaned at a central facility or at field sites, it is necessary to exercise routine quality control checks of

the water. Conductivity of fresh deionised water (measured before significant CO_2 uptake occurs) should be approximately 0.05 µS cm^{-1} (i.e., reagent-grade deionised water). A conductivity less than 1.5 µS cm^{-1} is essential for deionised water that has been in storage for any period of time.

Use of a detergent or acid solution to clean sample containers is typically unnecessary and is discouraged. If detergents or acids are used, special care must be taken to rinse away residues, which requires more time and water. An alternative to using detergents or acids is to allow the containers to soak in deionised water for 24 to 48 hours, leaching away soluble and exchangeable residues that may contaminate precipitation. Removing visible residues from sample container surfaces often requires wiping these surfaces with a sponge that is cleaned and soaked in deionised water. Wear rubber gloves when cleaning and handling sample containers and rinse surfaces repeatedly, until the conductivity falls below 1.5 µS cm^{-1}.

The GAW Precipitation Chemistry Programme recommends that sample containers be cleaned until the conductivity of the final rinse water (i.e., the rinsate) does not exceed 1.5 µS cm^{-1} whether cleaned in the field or the laboratory. Routinely checking that the rinsate conductivity does not exceed 1.5 µS cm^{-1} is a necessary quality control procedure. After being cleaned, shake water from sample containers and seal or cover them in plastic and store in a clean area. Air drying should be avoided, as many contaminants are soluble in water and stick to dry surfaces.

It is strongly recommended that container blanks, whether they are sample collection vessels and/or transfer bottles, should be prepared and analyzed on a routine basis to ensure cleanliness. This can be done by adding 25 mL of deionised water (conductivity less than 1.5 µS cm^{-1}) to the container and submitting to the laboratory for analysis.

4.3.2   Chemical Analyses QA/QC

Chemical laboratories involved in the analysis of GAW precipitation samples will achieve high quality performance levels only through adherence to strict QA/QC procedures in the analytical system. The following QA/QC activities are discussed in this section:

1) Calibration of analytical instruments
   a) Calibration standards – to assess accuracy of calibration
2) Use of *quality control samples*
   a) Replicate analyses – to calculate analytical precision; within and between run variability
   b) Blank samples – to look for background contamination
   c) Blind samples – to look for bias, sample contamination within the laboratory, or field and laboratory
   d) Dilution checks – assess accuracy of dilution methods for trace or high concentration samples
   e) Calibration check solutions – to assess accuracy of analytical methods for major ions
3) Use of certified reference materials – to assess laboratory bias
4) Interlaboratory Comparisons – to assess laboratory bias relative to other laboratories.

4.3.2.1 Calibration Control and Verification

Calibration of instruments is an integral part of every laboratory's standard operating procedures. Each laboratory must implement quality control procedures that guarantee the accuracy of calibrations. Recommended procedures include:

1) Using ultra-pure reagents traceable to Certified Reference Materials for the production of *calibration standards*
2) Checking that the calibration curve is within acceptable limits and that the correlation coefficient (r^2) is greater than or equal to 0.995(using 5 to 10 calibration standards per analytical run is recommended)

3) Ensuring that the concentrations of the calibration standards cover a range from 2% to 98% of all precipitation sample concentrations
4) Using extra calibration standards in non-linear portions of the calibration curves
5) Calibrating at the beginning and end of each analytical run
6) Analyzing and control-charting one or more *calibration check solutions* in each batch of samples, i.e., having calibration check solutions that correspond to the 20th, 50th and 80th percentiles of all sample concentrations for the NMHS
7) Reanalyzing the entire batch of samples when the calibration check solutions exceed the control limits.

4.3.2.2 Replicate Analyses

Replicate analyses (i.e., two aliquots of the same sample treated identically throughout the laboratory procedure) of precipitation samples provide a measure of analytical precision. There are two types of replicate analyses: within-run and between-run. Between-run replicates are more important than within-run because they capture the day-to-day variability of the analyses. Between-run replicates are the basis for estimating GAW laboratory precision.

…a word about Control Charting

Control charts are plots on which quality control data are plotted against pre-determined statistical limits; these limits indicate "in control", "warning", and "out of control" situations. Various types of control charts exist, including those that assess measurement variability and those that detect trends and biases. Example uses of control charts are: calibration check solutions; replicate analyses; deionised water; and reagent blanks. Control charts typically assume a normal distribution of the analytical data and the control limits are based on multiples of the standard deviation (S) of the results. A large number of control sample results (a minimum of 20) are needed to establish proper action and warning limits. Results outside 3 S away from the average or theoretical value should not occur (or more precisely, only 1 to 2 results of this type could be expected in every 1000 results). The 3 S value is therefore usually used as the corrective action limit, which requires that a new calibration be made and the analytical run repeated. The 2 S value is often used as a warning limit. When two consecutive analyses are outside 2 S, a new calibration should likewise be performed. The probability for this to occur is lower than 1 in 1000 results. Details of control charting can be found in Miller and Miller (1993), Taylor (1987) and ASTM (2002).

It is recommended that at least 2% and preferably 5% of the sample load be analyzed as between-run replicates. The replicate samples should be randomly selected from the sample stream. The between-run analysis results should be control charted immediately. Whenever control limits are exceeded, the entire batch of samples should be reanalyzed immediately.

Replicate data are used to estimate *laboratory precision*. The recommended method for calculating laboratory precision is given in Appendix A, Section A.3.

4.3.2.3 Blank Samples

"Blanks" or blank samples are quality control samples taken from reagents, deionised water supplies and rinses of laboratory glassware and apparatus. Chemical analysts are typically the individuals who prepare the blank samples for testing in the analytical system. The purpose of testing blanks is to ensure that unexpected background contamination does not exist in the analytical process.

Deionised water and reagent blanks undergo the same chemical analysis as the precipitation samples. One deionised water and one reagent blank should be analyzed per analytical batch. The analysis results should be control charted and corrective action taken when control limits are exceeded (i.e., replacement of the water and/or reagents).

4.3.2.4 Blind Samples

Blind sample checks provide another means of evaluating the quality of the laboratory data. These are quality control samples for which only the QA manager knows the concentrations. Blind samples assess the various effects of laboratory handling and analysis. They are used to test for bias and precision of the various analytes or to detect sample contamination. Blind samples may be placed anywhere in the sample queue (for example, immediately after calibration or prior to the next quality control sample) and are treated no differently than normal samples.

The blind samples may be composed of DI water, acidified DI water, simulated rainwater or certified reference materials. It is recommended that blind sample checks be conducted on a weekly basis. A more thorough discussion of blind samples may be found in Rothert (2002).

4.3.2.5 Dilution Checks

Dilutions are typically used on small volume samples to obtain a full set of chemical analyses, and on excessively high concentration samples to reduce concentrations to the normal operating range of the analytical instruments.

It is recommended that the dilution method be tested routinely on 1% of the sample load.

The accepted method for testing dilutions is to analyze aliquots from large samples both before and after dilution. Note that certified reference materials may also be used for testing dilutions but without simulating real sample matrix effects. The results should be compared and control charted. Before-and-after-differences, which exceed ±10% of the undiluted concentrations, should trigger a review of the dilution system. Dilutions of precipitation samples in the normal sampling stream should be halted until further checks have proven that the method can meet the ±10% criterion.

4.3.2.6 Calibration Check Solutions

A calibration check solution is a synthetic or real precipitation sample with known ion concentrations, which is analyzed in each analytical run in order to give an independent check of the analytical performance. Usually two or more calibration check solutions are prepared with concentrations that bracket the 20th to 80th percentile of expected precipitation values. Different compositions of calibration check solutions may therefore be required in different geographical regions.

Each analytical batch should include two or more calibration check solutions. The check solution results should be plotted immediately on control charts and inspected for values that exceed the warning limits and corrective action limits.

Some experienced laboratories use real precipitation as calibration check solutions. This approach requires a fairly large batch of precipitation that must be stored for one year in a refrigerated room in order to stabilize. The pH of the batch should be below 4.0, to slow the growth of algae and minimize sorption effects.

When synthetic calibration check solutions are used they must be prepared from different stock solutions than the ones used for calibration standards (Section 4.3.2.1). Whenever new calibration check solutions are made they should be analyzed and compared against the old ones to ensure that they give compatible results.

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┌─────────────────────────────────────────────────────────────────────────┐
│                  Preparing Calibration Check Solutions                    │
│                                                                           │
│   Set of Salts  ⇒                                                         │
│                  Concentrated Stock Solution ⇒                            │
│                     Use within 2 years                                    │
│                                   Secondary (dilute) Stock Solution ⇒     │
│                                   Use within 6 months                     │
│                                                 Calibration Check Solution│
│                                                 Prepare fresh solution weekly│
│                                                                           │
└─────────────────────────────────────────────────────────────────────────┘
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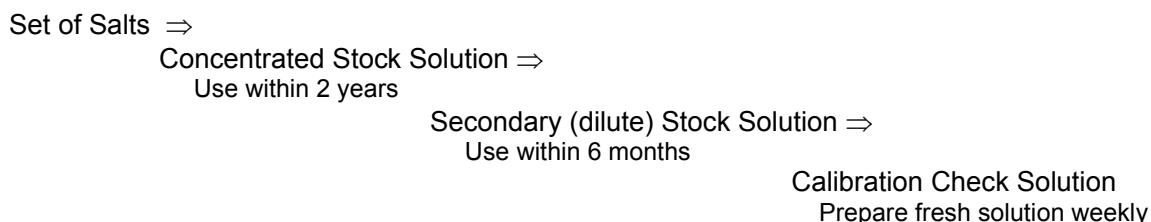
See Appendix C for an example detailing the preparation of calibration check solutions applicable to parts of Europe.

4.3.2.7 Certified Reference Materials

Bias within a single laboratory is defined as a systematic difference between the measured and expected values due to laboratory sample handling and analytical procedures. Potential bias can be evaluated using certified reference samples. Appendix D lists several sources for obtaining certified reference materials.

4.3.3   Laboratory Data Verification and Reporting

In addition to the quality control measures implemented during sample handling and processing, precipitation sample data must be verified by mathematical checks. Computerized programmes are best used to verify that all records (i.e., names, dates, times, locations, identification numbers, and analytical results) are free of typographical errors. Data entry procedures must include error checking. The GAW Precipitation Chemistry Programme recommends that data be transferred electronically between instrument and computer, as much as possible. This minimizes the need for manual data entry. The following error-checking procedure is recommended for data that must be entered manually:

1)   Data entry clerk enters the data record
2)   A second data entry clerk enters the data record
3)   Compare the two entries and identify differences
4)   Where there are differences in the data entries, correct the original data for any errors.

As an alternative, 5% to 10% of the data that have been entered by keyboard should be spot-checked by a second individual. As laboratories differ in the type of computer systems and amount of manually-entered versus computer-captured data, it is beyond the purview of this document to specify data merging procedures and basic statistical checks. However, if errors are found, the data entry process should be re-assessed. Any data error encountered must be returned to the originating party and be checked against laboratory and/or site records. Changes to the database must be authorized and confirmed by a designated quality control person.

4.3.3.1 Cation and Anion Balance

The ion balance of an individual sample is used to check and flag data. The principle of electroneutrality in precipitation requires that total anion equivalents equal total cation equivalents. A sample is flagged for reanalysis if the ion balance exceeds set limits (see WMO GAW Report No. 85, WMO GAW Report No. 102). For calculating the cation and anion balance the following equation should be used:

Ion Difference (%) = 100 · (CE - AE) / (CE + AE)   Eq. 4-1

where AE is the sum of anion equivalents (μe L^{-1}) calculated as:
    AE = 1000 · [Σ C_{Ai}/(Eq.Wt.)$_{Ai}$] + [5.1/10$^{(6-pH)}$]   Eq. 4-2
    C_{Ai} is the concentration of the ith anion in mg L^{-1}
    (Eq.Wt.)$_{Ai}$ is the equivalent weight of anion, i
    5.1/10$^{(6-pH)}$ is the calculated bicarbonate concentration at 25°C when pH >5.0
                                            (Stensland, 1998)

and   CE is the sum of cation equivalents (μe L^{-1}) calculated as:
    CE = 1000 · [Σ C_{Ci}/(Eq.Wt.)$_{Ci}$] + [10$^{(6-pH)}$]   Eq. 4-3
    C_{Ci} is the concentration of ith cation in mg L^{-1}
    (Eq.Wt.)$_{Ci}$ is the equivalent weight of cation, i
    10$^{(6-pH)}$ is the H^{+} concentration in μe L^{-1}

and the equivalent weights (Eq.Wt.) for the anions and cations are given in Table 4.1.

Table 4.1: The Equivalent Weights for Selected Anions and Cations.

Anion or Cation	Equivalent Weight
Cl^{-}	35.45
NO$_3^{-}$	62.01
SO$_4^{2-}$	48.03
NH$_4^{+}$	18.04
Na^{+}	22.99
K^{+}	39.10
Mg^{2+}	12.15
Ca^{2+}	20.04
F^{-}*	19.00
NO$_2^{-}$*	46.01
PO$_4^{3-}$*	94.97
H^{+}	1.01
HCOO^{-}*	45.02
CH$_3$COO^{-}*	59.04

*   Included in the calculation if measured.

    The GAW ion balance criteria are given in Table 4.2. **If the required criteria are not met, the chemical analyses should be repeated or a flag should be entered into the database indicating that the results did not meet the required criteria.**

Table 4.2: The Required Criteria for the Ion Balance.

Anions + Cations (μe L^{-1})	Acceptable Ion Difference (%)
$\leq$50	$\leq\pm$60
>50$\leq$100	$\leq\pm$30
>100$\leq$500	$\leq\pm$15
>500	$\leq\pm$10

NOTE: Some areas of the world are characterized by highly basic rain and the ion balance criteria described here may not be suitable because of problems with bicarbonate. Experience has shown that bicarbonate corrections at pHs greater than 6 have not always been successful. Each NMHS should review its ion balances in light of the range of sample acidities to determine suitable ion balance criteria for its location.

When the concentrations of all ions in a precipitation sample have been measured, a poor ion balance may indicate bad data quality. However, since this is not necessarily true at high pH or at low conductivity, EMEP has developed a system to flag precipitation data with poor ion balance using different criteria at various pH and ion concentrations. See Appendix E for this proposed alternative flagging system.

4.3.3.2 Comparison of Measured and Calculated Conductivity

For dilute solutions (e.g. below 10^{-3}M), the total conductivity (or specific conductance) can be calculated in μS cm^{-1} from the molar concentrations and molar ionic conductances (at infinite dilution) of the individual ions. The calculation is as follows:

$$\kappa = \sum c_i \bullet \Lambda_i^o \qquad\qquad\qquad \text{Eq. 4-4}$$

where κ denotes the calculated conductivity (or specific conductance) of the solution (in μS cm^{-1}), c_i the ionic concentration of the ith ion (in mmol L^{-1}), and Λ_i^o the molar ionic conductance of the ith ion (in S cm^2 mol^{-1}) at infinite dilution and 25°C (see Table 4.3).

Thus κ = 10$^{(3-pH)}$ ·349.7 + c[SO$_4^{2-}$]·160.0 + c[NO$_3^-$]·71.4 + c[Cl$^-$]·76.3 + c[NH$_4^+$]·73.5 + c[Na$^+$]·50.1 + c[K$^+$]·73.5 + c[Ca^{2+}]·119.0 + c[Mg^{2+}]·106.0 + c[F$^-$]·55.4 + c[NO$_2^-$]· 71.8 + c[PO$_4^{3-}$]·207.0 + c[HCO$_3^-$] ·44.5 + c[HCOO$^-$]·54.6 + c[CH$_3$COO$^-$]·40.9

where c[HCO$_3^-$] at 25°C = 5.1/c[H$^+$]   (i.e., 5.1/10^{9-pH}) for pH > 5.0.

The calculated conductivity (or specific conductance) values, κ, should be compared to the measured conductivity (or specific conductance) values for precipitation samples using the relation:

$$\Delta \kappa(\%) = 100 \cdot [(\kappa - \kappa_{meas}) / \kappa_{meas}] \qquad\qquad \text{Eq. 4-5}$$

The required comparison criteria between the measured and calculated conductivities are given in Table 4.4. If the required criteria are not met, the analysis should be repeated or the sample concentrations should be flagged in the database.

Table 4.3: Molar Ionic Conductances at Infinite Dilution and 25°C
(From CRC Handbook of Chemistry and Physics, 66th Edition, 1985-1986, pp. 167-168).

Ion	Molar Ionic Conductances, $\Lambda_i°$ (S cm^2 mol^{-1})
H^+	349.7
Cl^-	76.3
NO_3^-	71.4
SO_4^{2-}	160.0
NH_4^+	73.5
Na^+	50.1
K^+	73.5
Mg^{2+}	106.0
Ca^{2+}	119.0
F^-*	55.4
NO_2^-*	71.8
PO_4^{3-}*	207.0
$HCOO^-$*	54.6
CH_3COO^-*	40.9
HCO_3^-*	44.5

* Included in the calculation only when measured in significant concentrations.

Table 4.4: Required Conductivity Balance Criteria.

Measured Conductivity (µS cm^{-1})	Acceptable Conductivity Difference (%)
≤5	≤±50
>5≤30	≤±30
>30	≤±20

4.3.4 Laboratory Intercomparisons

It is mandatory that all laboratories doing chemical analyses of GAW precipitation chemistry samples participate in the WMO GAW Laboratory Intercomparison Studies. GAW personnel in every country must register their laboratory (or laboratories if more than one is involved) with the manager of the WMO GAW Laboratory Intercomparison Studies at the QA/SAC for the Americas. Twice per year, comparison samples are sent to each laboratory for analysis; the analytical results must be reported to the QA/SAC within the prescribed time interval. Each laboratory must also report the names of the GAW stations for which they perform chemical analysis.

Precipitation chemistry data from countries that do not participate in the WMO GAW Laboratory Intercomparison Studies will be sequestered within the World Data Centre for Precipitation Chemistry (WDCPC) in a separate data file.

It is the intention of the WDCPC to include in the data archive an indicator of laboratory performance (e.g., satisfactory, unsatisfactory) based upon the WMO GAW Laboratory Intercomparison Studies. Such measures ensure that the worldwide set of GAW data is accurate and comparable. See Chapter 6 for further discussions on assessing data quality.

4.3.4.1 Corrective Action for Unsatisfactory Performance

Unsatisfactory performance in one or more of the WMO GAW Laboratory Intercomparison Studies is an indicator of low data quality and questionable data acceptability. QA/QC procedures should be reviewed in light of this manual, especially Chapter 6. Corrective action must be taken immediately to upgrade the performance of the laboratory to a satisfactory level. Suggested actions include:

1) Upgrading the internal laboratory quality control programme
2) Implementing a routine system of analyzing and control charting Certified Reference Materials (CRMs)
3) Analyzing split samples provided by a collaborating 'in control' laboratory
4) Arranging for an external audit or expert visit by another GAW laboratory manager.

It is strongly recommended that GAW laboratories participate in other laboratory intercomparison studies to provide further evidence of analytical comparability. Such studies include:

1) EMEP Laboratory Intercomparison Studies operated by the Chemical Coordinating Centre of EMEP at the Norwegian Institute of Air Research
2) The Canadian Laboratory Intercomparison Studies
3) The Acid Deposition Monitoring Network in East Asia (EANET) Intercomparison Studies.

Details of these studies can be obtained by contacting the WMO Quality Assurance - Science Activity Centre for the Americas (see Chapter 1 for contact information).

4.3.5 Laboratory QA Reporting

Prior to analyzing each batch of samples, the analysts must prepare standards (and reagents) and evaluate the performance of the analytical instrumentation. Standards preparation and instrument maintenance information are recorded in notebooks that are kept in the individual laboratories.

Laboratories should prepare internal quality assurance reports annually, and make them available to GAW data users upon request (e.g., Rothert, 2002). These reports document the quality of the data generated by the laboratory and may include all types of QA information (e.g., statistical summaries of the various quality control samples, laboratory data verification checks, and laboratory intercomparison study results).

4.4 Analytical Measurements

The GAW Precipitation Chemistry Programme recommends certain analytical approaches but does not specify step-by-step analytical procedures (see Norwegian Institute for Air Research, 2001, Environment Canada, 2002, Rothert et al., 2002, Vet, 1991). The following sections should be used with more detailed, instrument-specific procedures. The newly developed formate and acetate determination (Section 4.4.6), however, is described here in more detail since it is not generally available in other literature.

4.4.1 pH Measurement

Past experience from regional networks and laboratory intercomparisons has shown that measuring pH in precipitation is difficult due mainly to the low ionic strength of the samples. Samples may also degrade due to biological activities and should therefore be kept refrigerated until the time of

analysis, when they are brought to room temperature. The pH measurements should be carried out within two days of sample arrival in the laboratory.

4.4.1.1 Background

The pH of precipitation varies between approximately 3.0 and 7.5 pH unit (the concentration of hydrogen ion normally from 1000 μe L^{-1} to <0.1 μe L^{-1}); lower or higher values are possible. The pH is related to the free acid activity as the negative logarithm of the hydrogen ion concentration by the equation:

$$pH = - \log [H^+] \qquad \qquad \text{Eq. 4-6}$$

where $[H^+]$ is the activity or concentration of free hydrogen ions. The pH of a precipitation sample is determined potentiometrically, using a standard pH meter with a glass (H^+) electrode in combination with a reference electrode. The glass electrode potential varies with the activity of H^+ ion in solution. In precipitation samples the difference between the actual hydrogen ion concentration and the hydrogen activity as measured with the pH meter, will typically be <0.02 pH unit.

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

4.4.1.2 Apparatus

Commercial pH meters are available with different specifications and options. A pH meter should have both an intercept and slope adjustment and should be capable of measuring to within ±0.01 pH unit. Combination electrodes containing both measuring and reference functions are often preferred since they require smaller amounts of sample, but a set of two electrodes may also be used with the pH meter. The measuring glass electrode is sensitive to hydrogen ions and the reference electrode can be calomel, or silver/silver chloride. Low ionic strength electrodes are now available commercially. Other reference electrodes can also be used as long as they have a constant potential. When selecting any electrode, confirm its ability to measure low ionic strength solutions by measuring a certified reference material. Response time should be less than one minute and addition of KCl should not be needed.

Measure DI water after buffers to thoroughly clean the semipermeable membrane. The pH of water should be about 5.65 pH unit. DI water measurements are slower than buffer measurements and precipitation samples and should read between 5.58 and 5.75 pH unit. Following DI water measure the 0.0001 N H_2SO_4 solution and the two calibration check samples to within ±0.05 pH unit.

Read the manual for the pH electrodes carefully. Store the electrodes in 0.1M KCl solution or as specified by the manufacturer. Prior to use, the pH electrode should be thoroughly rinsed with deionised water. One of the main problems with pH measurements is aging of the electrode. Old electrodes may give wrong pH results in low ion-strength solutions such as precipitation samples, even if they give a correct reading in a buffer solution. Use of quality control samples, including a 0.0001N H_2SO_4 solution, to check calibration and electrodes is therefore important. The 0.0001N H_2SO_4 solution check should be carried out once each hour during periods of measurement. Due to the activity difference between the buffer solutions and the 0.0001N H_2SO_4 solution, the pH will be slightly higher than the 4.00 value expected. If the reading is outside 4.05±0.03 pH unit, a new calibration should be carried out. Air bubbles in the electrodes give unstable readings. Quality control samples should be looked at following the 0.0001N H_2SO_4 check after the calibration. The pH value in the calibration check solutions should agree within ±0.05 pH unit of the expected value. If larger differences are observed, a new calibration should be performed and new calibration check solutions prepared if the results do not improve. If performance is still inadequate, the electrode must be replaced.

4.4.1.3 Reagents and Solutions

Use commercially available traceable standard buffer solutions of pH 4.01 (4.0) and 6.86 (7.0).

4.4.1.4 Calibration of pH Meter

Carry out the calibration as specified in the manual for the pH meter. Calibrate 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 to 7.5, commercially prepared 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 deionised 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. Measure the pH 6.86 buffer (first) and the pH 4.01 buffer (second) again to confirm that results are within ±0.02 pH unit. Rinse the electrode thoroughly with deionised water after each calibration. Precipitation samples have much lower concentrations than buffer solutions and incomplete rinsing will cause errors. The calibration should be followed by measurements with a 0.0001N H_2SO_4 solution and the two calibration check solutions, and be within ±0.05 pH unit.

4.4.1.5 Analytical Procedure

The procedure for measuring sample pH is as follows:

1) Calibrate the pH meter according to the procedure outlined in the previous section.
2) Keep the temperature of the samples at 25°C in the water bath if available or compensate for the difference between room temperature and 25°C. Maintain all solutions to be measured at the same temperature.
3) Place the sample solution in a clean polyethylene or borosilicate glass vessel with enough liquid to cover the sensing elements of the electrode.
4) Rinse the electrode with deionised water. Immerse the electrode in the sample vessel and swirl the sample gently for a few seconds (do not stir with rod or magnetic stirrer).
5) Allow the electrode to equilibrate and measure the pH of the sample until a constant value is obtained. This may be difficult for low ion strength solutions with pH in the range of 6 to 7. Record the pH value (to 0.01 unit).

Electrodes used for the wet deposition samples should not be used for other sample types.

4.4.2 Conductivity

4.4.2.1 Background

The conductivity of a solution is the reciprocal value of its specific resistance and can be directly measured using a conductivity bridge with a measuring cell. 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 microsiemens per centimetre ($\mu S\ cm^{-1}$), corrected to 25°C. The conductivity range of precipitation samples is 5 to 1000 $\mu S\ cm^{-1}$.

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

1) Conductivity meter (operating range of 0.1 to 1000 µS cm^{-1}; better 0.01 to 1000 µS cm^{-1}). Precision has to be within 0.5% of the range and accuracy at 1% of the range.
2) Conductivity cell (Use special conductivity cells, with a low cell constant, if the values in precipitation samples are expected to be mainly very low (<20 µS cm^{-1}).
3) Thermometer (0 to 40°C / 0.1°C).
4) Water bath 25°C.
5) Polyethylene or glass vessel corresponding to the diameter of the cell used.

4.4.2.3 Reagents and Solutions

1) Deionised water, conductivity <1.5 µS cm^{-1} (recommended quality of 0.5 µS cm^{-1}).
2) Potassium chloride, pro analysis (p.a.) quality.
3) Stock solution A, 0.1M KCl: 7.456 g of pre-dried (2 h at 105°C) KCl dissolved in deionised water, and diluted to 1000 mL at 25°C with deionised water.
4) Stock solution B, 0.01M KCl: 10 mL of 0.1M KCl, dilute to the mark of 100 mL at 25°C with deionised water.

Keep stock solutions in tightly closed high density polyethylene (HDPE) bottles. Their stability is 1 year at most.

4.4.2.4 Calibration

Calibration for conductivity measurement is multipoint. With each set of precipitation samples, prepare a set of 0.0001M, 0.0005M, and 0.001M KCl solutions from the 0.01M KCl stock solution by dilution with deionised water. The conductivity of the deionised water should also be measured. Plot the specific conductivity of known KCl solutions (Table 4.5) on a graph. If the measurements of the calibration solutions are outside the limits given in Table 4.5, check the instrument as specified in the manufacturers instrument manual. New measurements with the calibration solutions should then be carried out.   Read the precipitation sample conductivity directly from this plot of measured conductivities.

Table 4.5: Calibration Solutions for Conductivity, KCl Solutions at 25°C.

Concentration (M)	Conductivity (µS cm^{-1})		
	Theoretical	Upper limit	Lower limit
0.0001	14.94	16.5	13.5
0.0005	73.9	77.8	70.2
0.0010	147.0	149.0	145.0

4.4.2.5 Analytical Procedure

Follow the manufacturer's directions for operation, maintenance and storage of the measurement cell. Between each sample, rinse the cell thoroughly with deionised water and then rinse with the sample solution 2 or 3 times before taking a measurement. Clean the cell if contamination is discovered. Measure the value (to 0.1 µS cm^{-1}).

The conductivity of a solution depends upon its temperature. When the temperature of a solution rises one degree, the conductivity rises about 2 to 2.5% (depending upon its ionic composition) as a result of decreasing ion hydration and decreasing solution viscosity. To ensure consistent laboratory conductivity measurements, the GAW Precipitation Chemistry Programme recommends either of the following procedures:

1) Measure the conductivity of precipitation samples and quality control samples at 25°C using a water bath (care must be taken to avoid sample contamination), or
2) Measure at room temperature (within a temperature range from 18°C to 30°C) without any water bath, and then correct the measured value to 25°C using the coefficients given in Table 4.6.

Table 4.6: Correction Coefficients to Adjust Conductivity Values to 25°C.

Temperature (°C)	Correction coefficient	Temperature (°C)	Correction coefficient
18	0.865	**25**	**1.000**
19	0.884	26	1.020
20	0.904	27	1.041
21	0.923	28	1.061
22	0.940	29	1.080
23	0.961	30	1.100
24	0.980		

4.4.3   Anion Determination by Ion Chromatography

4.4.3.1 Background

Ion chromatography has been widely used in recent years to analyze major anions in precipitation, mainly in combination with electrochemical detection. Basic knowledge about ion chromatography is given in Weiss (1994). The ISO norm 10304-1 (1992) contains detailed information about ion chromatographic determination of anions in solution in lightly contaminated waters.

Sulphate, nitrate, chloride, as well as other anions 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 suppressor that exchanges all cations for H^+ ions. Instead of strong acid cation exchange columns, today micro membrane and self-regenerating suppressors with chemical or electrochemical regeneration are used. As the result of the suppression reaction, corresponding acids of the eluent ions and of chloride, nitrate and sulphate will reach the conductivity detector. A decreased basic conductivity and higher analytical signals now allow the detection of anions also in the lower µg L^{-1} range.

There are several anion exchangers with different properties available on the market. The time for one analysis and the quality of separation of single signals are dependent on the type of the column and the eluent, the concentration and the flow rate of the eluent.

Any anions with a retention time similar to that of the main anions in solution can cause an interference. For example, when NO_2^- is present, it elutes just after Cl^-, which can cause the peak to be asymmetric. In rare cases, when the concentration of Cl^- is very high compared with NO_3^-, it can also influence the determination of NO_3^-. The manual should be consulted to see how different integration programmes handle this problem.

With care, up to several thousand analyses can be performed with the same anion separator column. The most effective method of protecting the separator column is the use of a pre-column in front of it. Details are provided by the manufacturers in the manuals for the columns.

The ranges of measured anion concentrations in precipitation (deviations possible) and required detection limits (determined by the injection volume) are given in Table 4.7. Higher concentrations may sometimes occur in which case the samples must be diluted and reanalyzed.

Nitrite, phosphate and fluoride ions, which are not required GAW precipitation chemistry measurements, have been included in Table 4.7 for reference.

Table 4.7: Typical Range of Anion Concentrations in Precipitation and Recommended Detection Limits.

Anion	Range		Detection Limit (DL)	
	µmol L^{-1}	mg L^{-1}	µmol L^{-1}	mg L^{-1}
SO_4^{2-}	<1 to 300	<0.1 to 30	0.6	0.06
NO_3^-	<1 to 500	<0.1 to 30	1	0.09
Cl^-	<1 to 1400	0.02 to 50	1	0.04
NO_2^-	<0.2 to 10	0.01 to 0.5	0.2	0.01
PO_4^{3-}	<0.1 to 2	0.01 to 0.2	0.1	0.01
F^-	<1 to 30	0.01 to 0.5	0.5	0.01

4.4.3.2 Apparatus

Different commercial instruments are available using different columns and suppressor devices, including, for example Dionex and Waters. Two main types of instruments using different suppressor techniques, chemical and electrical suppression, are on the market. An integrator is recommended to process the chromatograms.

4.4.3.3 Reagents and Solutions

All reagents must be of recognized analytical grade. The purity of water used for dilution is highly important and should be filtered and deionised. The water should have a conductivity of <1.5 µS cm^{-1} (fresh water should be at 0.05 µS cm^{-1}) and not contain particles larger than 0.20 µm. The sample, calibration standards and reagent solution bottles should be made of high density polyethylene (HDPE).

Stock standard solution
Stock standard solution, for example 1000 mg L^{-1} (based on the element Cl, N, S), may be purchased as certified solutions from different manufacturers (e.g. Merck, see Appendix C and D for details) or prepared from salts dried in the prescribed way, dissolved and diluted to 1000 mL as listed in Table 4.8.

Table 4.8: Example of Stock Standard Solutions
(The salt amount indicated gives 1000 mg of the Cl, N, S per litre).

Salt	Weight (g)	Drying temp. (°C)	Drying time (hours)
NaCl	1.6485	150	1
Na NO$_3$	6.0679	105	2
Na$_2$SO$_4$	4.4299	105	24

Calibration solutions

Five calibration solutions and one zero standard (blank, normally water) are needed to generate a suitable calibration curve. The range to be used will depend on the concentration range for the samples. Experienced laboratories make use of two calibration curves; one linear covering most of the concentration range and additionally one non-linear in the low concentration, near the detection limit at the lower part of the range.

Typically, anion stock standards of 0.0, 0.5, 1.0, 2.5, 5.0 and 10.0 mL each are transferred with calibrated pipettes to 1000 mL volumetric flasks and diluted to volume with deionised water. These calibration standards will contain 0.0, 0.5, 1.0, 2.5, 5.0 and 10.0 mg L^{-1} respectively calculated on the basis of the elements Cl, N and S (note: not as NO_3^- and SO_4^{2-}).

The calibration standards, stored in acid-cleaned polyethylene containers in a refrigerator, may be stable up to one month but a weekly fresh preparation is recommended.

Calibration check solutions

Calibration check solutions should be used and should have a composition similar to the normal precipitation samples. It is important that they are made from a set of stock solutions different from the ones used for calibration standards.

Eluent solutions

The chemicals and concentrations to be used are normally given by the manufacturers of the different separation columns. Experienced laboratories optimize the separation by minor changes in the eluent concentrations. In practice it is useful to prepare 10 or 100-fold higher concentrated eluent solutions, which are stable for several months at 4°C and diluted when needed. Before use, eluent filtration through a 0.2 µm membrane filter is recommended for particle removal and degassing.

4.4.3.4 Analytical Procedure

In general operate the ion chromatograph according to the manufacturer's directions. Experience has shown that the best results are obtained when an IC is not turned off during workdays and operated with a reduced eluent flow during times with no analysis. If it is has been turned off, it may need two hours or more to warm up in order to obtain optimum conditions (depends on the equipment).

Samples for injection into the ion chromatograph must be free from particles to avoid blockage of the capillary connectors and of the inlet on the head of the separator column. Typically, one-way filters are used (0.2 to 0.45 µm) for filtration of precipitation samples. A periodic check of filter blanks is necessary.

One example of a measurement procedure is as follows:

1) Prepare new eluent and regenerator solutions.
2) Set up the chromatograph for most sensitive range.
3) Begin to pump the eluent and regenerant through the columns. If necessary, allow the IC to warm up.
4) Inject standard solutions through the loop injector (50 or 100 µL) and start analysis. Calibration curves should be made using the working standard solutions prior to each measurement of precipitation samples. The injection should start with the <u>highest</u> concentration standard followed by decreasing concentrations.
5) Run the calibration check solutions between the precipitation samples. The results should be plotted in control charts. At most, 30 precipitation samples should be injected before new calibration and calibration check solutions are injected. If the results of the calibration check solutions are not acceptable, reanalyze the last series of precipitation samples.

Calibration curves for the anions determined should be made by either peak area or peak height measurement (peak area measurement is preferable) prior to each measurement.

When an auto sampler is available:

1) Fill the auto sampler with calibration solutions, calibration check solutions, other quality control samples, and precipitation samples, starting with the highest standard concentration followed by decreasing concentrations.
2) Turn on the auto sampler to start analyzing samples. Check that the results of the quality control samples are acceptable by using the control chart.

4.4.4 Cation Determination by Ion Chromatography

4.4.4.1 Background

Ion chromatography has been widely used in recent years to analyze cations, as well as anions, in precipitation (Weiss, 1994). Simultaneity and sensitivity make the cation chromatography of today an alternative to the atomic spectroscopic methods. Details of ion chromatographic determination of soluted cations in water are given in ISO norm 14911 (1998).

The principle is the same as that of anion determination except that different column materials are used and the suppressor column is often omitted. The material commonly used for cation separation is a cation exchange resin with active surface groups. Sodium, ammonium, potassium, calcium and magnesium ions are detected by a conductivity detector, without changing the eluent when certain columns are used. In other columns monovalent cations (Na^+, NH_4^+, K^+) are determined using one eluent and divalent cations (Mg^{2+} and Ca^{2+}) with another eluent (because of their higher affinity to the resin).

Any cation with a retention time similar to that of the main cations may cause interference. For example, in samples with high concentrations of Na^+, the peak of NH_4^+ becomes asymmetrical and often causes significant error. In this case, measurement using more dilute eluent could improve the separation of peaks.

The ranges of measured cation concentrations in precipitation and required detection limits (determined by the injection volume) are given in Table 4.9. Higher concentrations may sometimes occur in which case the samples must be diluted and reanalyzed.

Table 4.9: Typical Range of Cation Concentrations in Precipitation and Recommended Detection Limits.

Cation	Range		Detection Limit (DL)	
	µmol L^{-1}	mg L^{-1}	µmol L^{-1}	mg L^{-1}
Na^+	1 to 900	0.01 to 20	1	0.02
NH_4^+	1 to 1000	0.01 to 20	1	0.02
K^+	<1 to 100	0.01 to 5	0.5	0.02
Ca^{2+}	<1 to 300	0.01 to 10	0.5	0.02
Mg^{2+}	<1 to 200	0.01 to 5	0.4	0.01

4.4.4.2 Apparatus

There are several manufacturers of ion chromatographs. The two most common are Dionex and Waters. An integrator is recommended to process the chromatograms.

4.4.4.3 Reagents and Solutions

Stock standard solution

Stock standard solutions for the most common metal ions may be purchased as certified solutions from different manufacturers in 2.5% HNO_3. A standard solution of NH_4^+ may be prepared from solid NH_4Cl in 0.01M HNO_3 (3.818 g salt amount gives 1000 mg of the element N per litre).

Calibration solutions

A set of calibration standards containing concentrations of cations in the range of 0.025 to 75 mg L^{-1} should be prepared from the stock standards. Five calibration solutions and one zero standard (blank, normally deionised water) are needed to generate a suitable calibration curve. The standards

to be used will depend on the expected concentration range for the different samples, e.g. 0.025, 0.050, 0.100, 0.250, and 0.500 mg L^{-1} should be selected when very low sample concentrations are foreseen.

The calibration standards should be stabilized with 0.01M HNO_3 and should not be stored for more than 1 month. Particular care should be taken with the NH_4^+ standard since it may absorb gaseous NH_3. The standards should be stored in polyethylene containers in a refrigerator.

Calibration check solutions

Cation calibration check solutions are similar to calibration check solutions for anions.

Eluent solutions

The chemicals and concentrations used are normally provided by the manufacturers of the different separation columns. Experienced laboratories may be able to optimise the separation by minor changes in the eluent concentrations.

4.4.4.4 Analytical Procedure

The measurement procedure for cations is similar to the example given for anions above.

4.4.5 Determination of Sodium, Potassium, Magnesium and Calcium in Precipitation by Flame Atomic Spectrometry (AAS or AES)

4.4.5.1 Background

Sodium, potassium, magnesium, and calcium in precipitation are often analyzed by atomic spectroscopic methods. Both flame (AAS and AES) and plasma (ICP-AES and ICP-MS) based methods can be used, but only the flame methods are described in this document. For these ions, ion chromatography has no special advantage concerning sensitivity, precision and accuracy over the spectroscopic methods, although analysis of all ions in one sample run is not possible with flame AAS or AES (single element methods). Details about theory and practice of atomic absorption spectrometry are given in Welz and Sperling (1998).

The method can normally be used for the determination of sodium, magnesium, potassium and calcium in precipitation within the range of 0.01 to 2 mg L^{-1}, but this will depend to a certain degree on the commercial instruments used.

The ions in the sample solution are transformed to neutral atoms in an air/acetylene flame. Light from a hollow cathode or an electrodeless discharge lamp (EDL) is passed through the flame. In

the AAS-mode, light absorption of the atoms in the flame is measured by a detector following a monochromator set at the appropriate wavelength. Light absorption is proportional to the ion concentration in the sample. In the AES-mode, the light emitted from the atoms excited in the flame is measured. Most commercial instruments can be run in both modes. AES is the preferred mode for sodium measurements.

In atomic absorption spectrometry, both ionisation and chemical interferences may occur. These interferences are caused by other ions in the sample, which reduce the number of neutral atoms in the flame. Ionisation interference is avoided by adding a relatively high amount of an easily ionised element to the samples and calibration solutions. For the determination of sodium and potassium, caesium is added. For the elimination of chemical interferences from aluminium and phosphate, lanthanum can be added to the samples and calibration solutions for calcium and magnesium.

4.4.5.2 Apparatus

1) Atomic absorption spectrophotometer with a digital readout, a suitable recorder or a personal computer. The wavelength range must be 200 to 800 nm. Preferably, the spectrophotometer should also be able to run in the emission mode.
2) EDL or hollow cathode lamps for Na, K, Mg and Ca. Single element lamps are preferred, but multi-element lamps may be used. EDLs are more intense than hollow cathode lamps, and are preferred for K and Na. When performing analyses in emission mode, no lamps are needed.
3) Pipettes and volumetric flasks in various sizes.

4.4.5.3 Reagents and Solutions

1) Deionised water.
2) Hydrochloric acid (HCl), suprapure, 37%.
3) Caesium chloride (CsCl), suprapure or Cs-solution specially produced for AAS.
4) Lanthanum oxide (La_2O_3), 99.99% or La-solution specially produced for AAS.
5) Sodium chloride (NaCl), spectrapure.
6) Potassium chloride (KCl), spectrapure.
7) Magnesium oxide (MgO), spectrapure.
8) Calcium carbonate ($CaCO_3$), spectrapure.

Compressed gas and pressure-reducing valves are necessary. Both acetylene and air are required. Air may be supplied from a compressor equipped with a cleaning unit.

Caesium-Lanthanum-solution, 100.000 mg Cs L^{-1} + 50.000 mg La L^{-1}
Transfer 5.865 g La_2O_3 and 12.67 g CsCl to a 100 mL volumetric flask. Add about 50 mL deionised water and 25 mL suprapure HCl, and dilute to the mark with deionised water.

Commercially available solutions specially produced for AAS may be used.

Calibration solutions and stock solutions
Na, 1000 mg L^{-1}:
Transfer 2.542 g NaCl, dried at 140°C for 1 hour before weighing, to a 1000 mL volumetric flask, add 50 mL of deionised water and 1 mL HCl and shake until all is dissolved. Dilute to the mark with deionised water. Store the solution in a polyethylene bottle.

K, 1000 mg L^{-1}:
Transfer 1.907 g KCl, dried at 110°C for 1 hour before weighing, to a 1000 mL volumetric flask. Add 50 mL of deionised water and 1 mL HCl and shake until all is dissolved. Dilute to the mark with deionised water. Store the solution in a polyethylene bottle.

_Mg, 1000 mg L^{-1}:_
Transfer 1.658 g MgO, dried at 180°C for 1 hour before weighing, to a 1000 mL volumetric flask. Add 10 mL HCl and shake until all is dissolved. Dilute to the mark with deionised water. Store the solution in a polyethylene bottle.

_Ca, 1000 mg L^{-1}:_
Transfer 2.497 g CaCO$_3$, dried at 180°C for 1 hour before weighing, to a 1000 mL volumetric flask. Add 50 mL of deionised water, and dissolve slowly with a minimum of HCl. Dilute to the mark with deionised water. Store the solution in a polyethylene bottle.

Working standard solution, Na, K, Mg and Ca 10 mg L^{-1}:
Pipette 10.0 mL of each of the 1000 mg L^{-1} stock solutions Na, K, Mg and Ca to a 1000 mL volumetric flask. Dilute to the mark with deionised water. Store the solution in a polyethylene bottle. The solution should be made fresh each time the calibration solutions are prepared.

Calibration solutions:
Pipette 1, 2, 5, 10, 15, 20, 40 and 50 mL of the 10 mg L^{-1} working standard solution to each of eight 100 mL volumetric flasks. Add 1 mL of the Cs-La-solution and dilute to the mark with deionised water. The concentrations in the solutions will be 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 4.0 and 5.0 mg L^{-1} respectively. A solution with 1 mL Cs-La- solution diluted to 100 mL is used as a blank.

The calibration solutions and the blank should be stored in polyethylene bottles and made fresh the day of analysis.

4.4.5.4 Calibration of the Instrument

After the instrument has warmed up, set the wavelength for the element to be analyzed as given in Table 4.10 or as recommended in the instrument manual, and adjust the slit width and the air/acetylene ratio as directed in the instrument instruction manual. Ignite the flame. Adjust the reading of the instrument to zero by spraying the blank into the flame. Run the calibration solutions and read the absorption (or emission) signals from the readout. Plot the calibration graph.

The instrument should be recalibrated after every 20 to 30 samples. A calibration check solution should also be run after each calibration.

Table 4.10: Wavelength Settings for the Analyses.

Element	Na	K	Mg	Ca
Wavelength (nm)	589.0	766.5	285.2	422.7

The detection limits (DL) are at least by a factor of ten lower than can be reached with ion chromatography.

4.4.5.5 Analytical Procedure

Transfer 10 mL of the sample to a test tube. Add with a micropipette 0.1 mL of the Cs-La solution and mix well. Run the samples and read the absorption (or emission) signal from the readout. Use the calibration graph to find the concentration in the sample.

NOTE: Read and follow the instructions for the instrument carefully. Standard methods of analysis (e.g., determination of K$^+$ in environmental liquid samples) are described in detail in application notes or special publications of the manufacturers.

4.4.6 Formate and Acetate Determination Using Ion Exclusion Chromatography

4.4.6.1 Background

Formic and acetic acids (HCOOH and CH_3COOH, respectively) are major chemical constituents of precipitation in both continental and marine regions. Available evidence suggests that these compounds originate primarily from natural biogenic sources; both direct emissions (over continents) and emissions of precursor compounds appear to be important. Biomass and fossil fuel combustion also result in the emission of carboxylic acids and/or their precursors to the atmosphere.

Carboxylic acids in precipitation are very unstable and rapidly disappear from unpreserved samples. To generate reliable data, precipitation must be sampled on a daily or event basis and immediately preserved with addition of a biocide such as chloroform ($CHCl_3$). Typically, 250 mL aliquots of sample (or less for low volume events) are treated with 0.5 mL of $CHCl_3$. Samples are then tightly sealed and refrigerated until analysis.

Carboxylic species can be analyzed by both ion chromatography (IC) (using a dilute eluent) and ion exclusion chromatography (ICE). However, acetate and propionate typically coelute when analyzed by IC and are thus impossible to resolve quantitatively. ICE exhibits fewer interferences associated with coeluting species and is thus preferred for analysis of precipitation samples.

For analysis by ICE, samples are added to an HCl eluent which then flows through a separator column, a suppressor column and a detector. Resin in the separator column partitions anions using the principle of Donnian exclusion; anions are retained and sequentially separated based on their respective pK_as and Van der Waals interactions with the resin. Anions of stronger acids with lower pK_as such as H_2SO_4, HNO_3 and HCl are effectively excluded and coelute early in the chromatogram; those of weaker acids with higher pK_as such as HCOOH and CH_3COOH elute later in the chromatogram. The suppressor column incorporates a cation exchange resin with silver added to the exchange sites; H^+ exchanges with the silver; the released silver subsequently reacts with Cl^- in the eluent to form AgCl, which precipitates within the column. Acid analytes exit the suppressor in a stream of deionised water. Detection is by conductivity.

Both ICE and IC measure the sum of dissociated (or ionised) and undissociated species. For instance, the measured total formate ($HCOO_t$) includes both formate ion ($HCOO^-$) and undissociated formic acid (HCOOH). The dissociated fraction ($RCOO^-$) is calculated as follows:

$$[RCOO^-] = [RCOO_t] \cdot (10^{\,pKa}/10^{\,pH}) \,/\, \{1 + (10^{\,pKa}/10^{\,pH})\} \qquad \text{Eq. 4-7}$$

where $RCOO_t$ is the measured concentration of total formate or total acetate, the corresponding pK_a for formic and acetic acids are 3.75 and 4.76, respectively, and pH is the measured free acidity of the sample. The dissociated fraction contributes to the sample's ionic strength and, therefore, must be included in ion balance analyses. This fraction also corresponds to the portion of each acid that contributes to the sample's free acidity.

Detection limits vary as a function of analytical ranges. The most sensitive range yields detection limits for $HCOO_t$ and CH_3COO_t of approximately 0.02 mg L^{-1} and 0.01 mg L^{-1}, respectively. Substantially lower detection limits can be achieved by IC but, as noted above, significant bias may be introduced by coeluting species.

Contamination represents a potentially serious problem, especially in the analysis of CH_3COO_t. Exposure of samples to laboratory air should be minimized. In addition, CH_3COO_t -containing reagents and cleaning solutions should not be exposed in the laboratory particularly during or preceding periods when samples are exposed. Table 4.11 gives an example of chromatographic operating conditions (other possibilities do exist).

Table 4.11: An Example of Chromatographic Conditions for Formate and Acetate Analyses.

Item	Operating Condition
Guard Column	None
Separator Column	HPICE-AS1 (Dionex)
Suppressor Column	ISC* (Dionex)
Detector	Conductivity
Eluent	1.0mM HCl
Injection Volume	0.5 mL
Flow Rate	0.8 mL min^{-1}
Sample Pretreatment	Spiked with HCl to match eluent**
Elution time	12 to 15 minutes

* Cut 50 mL suppressors in half and use 25mm lengths during each analytical run; this procedure minimizes peak tailing.

** Before injection, add 0.5 mL of 0.02N HCl to 5 mL of sample.

Optimal operating conditions vary somewhat between different columns, therefore, minor adjustment in flow rate or the ionic strength of the eluent may be required during initial setup to adequately resolve $HCOO_t$ and CH_3COO_t peaks. Lactate and/or glycolate peaks typically elute on the leading edge of the formate peak. Propionate typically elutes on the tailing edge of the CH_3COO_t peak.

Typical analytical ranges for $HCOO_t$ and CH_3COO_t and associated detection limits are summarized in Table 4.12.

Table 4.12: Typical Analytical Range and Detection Limits for Carboxylic Acids.

Species	Analytical Range (mg L^{-1})	Expected Detection Limit (mg L^{-1})
Low and Mid Latitude Continental Regions		
$HCOO_t$	0.0 to 2.0	0.04
CH_3COO_t	0.0 to 1.0	0.02
Marine and High Latitude Regions		
$HCOO_t$	0.0 to 1.0	0.02
CH_3COO_t	0.0 to 0.5	0.01

4.4.6.2 Apparatus and Supplies

1) Ion chromatograph with conductivity detector, autosampler (optional) and two-channel strip chart recorder.
2) Separator and suppressor columns specified above.
3) Volumetric glassware including 2000 mL, 1000 mL, and five 250 mL volumetric flasks; 10 mL and 20 mL volumetric pipettes; and 25 mL graduated burette with stand.
4) Two adjustable 1.0 mL redispensing pipettes.
5) Dessicator with dessicant and two low form, cylindrical weighing bottles (or other appropriate sealable storage container for dried standard salts).
6) Two 1 L, amber, high density polyethylene (HDPE), storage bottles.
7) 5.0 mL transfer pipette.
8) 50 mL HDPE beaker.
9) Autosampler vials with caps or, for manual injections, HDPE or glass sample tubes with caps.

4.4.6.3 Reagents and Solutions

1) 0.1N HCl and 2.0N HCl stock solutions (available from most chemical distributors).
2) Anhydrous NaHCOO and $NaCH_3COO$ ACS-grade (American Chemical Society) salts.
3) ACS-grade $CHCl_3$.

Working eluent 1.0mM HCl
Dilute 40 mL of 0.1N HCl to 4 L with fresh deionised water and transfer to collapsible cubitainer.

HCl-Spike solution 0.02N HCl
Dilute 10 mL of 2.0N HCl to 1 L with fresh deionised water and transfer to a clean, labelled redispensing pipette; set dispenser volume to 0.5 mL.

Chloroform
Transfer $CHCl_3$ to clean, labelled redispensing pipette; set dispenser volume to 0.5 mL.

NOTE: Chloroform is dangerous. Avoid contact with skin and do not inhale fumes. Treat waste as a hazardous material.

Stock solutions 1000 mg L^{-1} $HCOO_t$; 1000 mg L^{-1} CH_3COO_t
NOTE: Before weighing for the first time, transfer each reagent salt to a weighing bottle (or other appropriate container), dry at 105°C for 1 hour, and cool in desiccator (do not replace lid on bottle until salt has cooled). Thereafter, store weighing bottles containing salts in a desiccator. Use desiccant with colour indicator to monitor performance; redry desiccant as needed. Replace and redry reagent salts every 6 months or as needed.

Dissolve 1.5107 g of dry NaHCOO in fresh deionised water. Transfer to clean, labelled, amber, HDPE bottle. Add 0.5 mL $CHCl_3$ from redispensing pipette.

Dissolve 1.3894 g of dry $NaCH_3COO$ in fresh deionised water. Transfer to clean, labelled, amber, HDPE bottle. Add 0.5 mL $CHCl_3$ from redispensing pipette.

Flush dispenser several times before adding $CHCl_3$ to stock solutions; discard waste.

Refrigerate stock solution between uses; replace every 3 months or as needed.

NOTE: To ensure consistency between batches, a dilute standard solution should be prepared from the previous stock and analyzed as an unknown during the first analytical run calibrated with new stock.

Mixed working stock solution
Mix fresh for each run.

<u>*Low and mid latitude Continental: 20 mg L^{-1} $HCOO_t$; 10 mg L^{-1} CH_3COO_t:*</u>
Dilute 20 mL of 1000 mg L^{-1} $HCOO_t$ stock and 10 mL of 1000 mg L^{-1} CH_3COO_t stock to 1000 mL with fresh deionised water.

<u>*Marine and high latitude: 10 mg L^{-1} $HCOO_t$; 5 mg L^{-1} CH_3COO_t:*</u>
Dilute 20 mL of 1000 mg L^{-1} $HCOO_t$ stock and 10 mL of 1000 mg L^{-1} CH_3COO_t stock to 2000 mL with fresh deionised water.

Standard solutions
Mix fresh for each run.

Fill and flush burette several times with working stock (warm stock to room temperature before proceeding).

Add specified volumes of working stock (see Table 4.13 below) to labelled, 250 mL volumetric flasks, dilute to mark with fresh deionised water, and then add 0.5 mL CHCl$_3$ to each flask from redispensing pipette. Place stopper on flasks and mix thoroughly.

NOTE: To ensure consistency between runs, a standard solution from the each analytical run should be saved and analyzed as an unknown during the following analytical run.

Table 4.13: Standard Solutions.

mL of stock diluted to	Final concentrations (mg L^{-1}) from starting stocks of		
250 mL	5 mg L^{-1}	10 mg L^{-1}	20 mg L^{-1}
25	0.500	1.00	2.00
20	0.400	0.80	1.60
15	0.300	0.60	1.20
10	0.200	0.40	0.80
5	0.100	0.20	0.40

4.4.6.4 Analytical Procedure

1) Prepare run sheets. Each run should begin and end with a complete standard curve including a blank, starting with highest and decreasing to the lowest concentration. In addition, a mid range standard solution should be run between each group of five samples throughout the run to quantify variability in response.
2) Samples and standards should be poured as follows using the thoroughly cleaned and rinsed 50 mL HDPE beaker, 5 mL transfer pipette, and sample vials or tubes and caps:
   a) Rinse pipette and beaker with fresh deionised water; shake dry.
   b) Open sample or standard container, pour about 2 mL into beaker, swirl, discard, and shake beaker dry.
   c) Pour about 10 mL of sample or standard into beaker; immediately replace cap on container.
   d) Draw up about 2 mL of sample or standard from beakers into pipette, swirl and discard.
   e) Draw up 5 mL of sample or standard from beakers into pipette.
   f) Discard remainder of sample in beaker and shake dry.
   g) Dispense 5 mL sample from pipette into beaker.
   h) Dispense 0.5 mL of 0.02N HCl from redispensing pipette into beaker.
   i) Swirl to mix completely and pour spiked sample or standard into autosampler vial or sample tube; cap immediately.
   j) Repeat steps for remaining samples and standards.
3) The ICE suppressor is consumed during use and cannot be rejuvenated. The consumed portion darkens relative to the unused portion; a demarcation line migrates through the column as runs proceed. The suppressor should have sufficient capacity for about two days of use after which it must be replaced. Before starting the run, verify that the suppressor has sufficient capacity for the intended sample load.
4) Configure instrument with proper column loop, and eluent.
5) Open eluent line and adjust pump to specified flow rate.
6) After baseline stabilizes, adjust gain on each channel (one for HCOO$_t$ and the other for CH$_3$COO$_t$) of recorder to near full scale deflection based on response to the highest standard solution for the corresponding analyte. Recheck baseline; readjust baseline and gain as necessary to maximize resolution.
7) Inject standards and samples using the autosampler (if available) or manually.
8) Adjust baseline if necessary as run proceeds.
9) After run, measure peak heights from baseline for each analyte.
10) To maximize data quality, reduce data using quadratic or piece-wise linear calibration curves and linearly increment gain shifts between each set of midrange standards.

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5. DATA MANAGEMENT

Data management encompasses the entire process of collecting, quality assuring, reporting, archiving, analyzing and distributing the measurement data *and their supporting metadata*. While the measurement values are of interest to the data user community, the supporting metadata play an important role in establishing a level of confidence in the measurements. Whenever deviations occur from accepted field or laboratory protocols, or compromising events affect samples, the information must be reported and archived. This chapter describes all aspects of data management for the GAW Precipitation Chemistry Programme, including the required formats for data submission to the WMO Quality Assurance - Science Activity Centre for the Americas. Mandatory participation in the WMO GAW laboratory intercomparison programme is described.

Section 5 (Data Management) and Appendix F are being re-written. Please contact Van Bowersox (manager@qasac-americas.org) for further information or questions about data submission to the World Data Centre for Precipitation Chemistry or the Quality Assurance -- Science Activity Centre.

6. QUALITY ASSURANCE AND QUALITY CONTROL

This chapter describes the major Quality Assurance and Quality Control procedures that should be incorporated within the GAW Precipitation Chemistry Programme. Previous chapters on Siting, Standard Operating Procedures, Laboratory Procedures and Data Management contain many of the QA/QC procedures relevant to those activities, so this chapter summarizes the most important of these procedures and describes several overarching quality assurance activities not yet presented.

Quality assurance and quality control are now common terms that are understood by many in the precipitation chemistry measurement community. However, within the field of QA/QC, there is much terminology that might not be familiar to some readers. Those readers are referred to the following Web-based glossary of terminology called the *Terminology Reference System* operated by the United States Environmental Protection Agency (U.S. EPA, 2002) *http://www.epa.gov/trs/*.

Quality assurance and quality control are extremely important to the collection and reporting of high quality GAW data. For this reason, this chapter begins with a review of GAW Data Quality Objectives for precipitation chemistry measurements, thereby providing the measurement community with specific levels of measurement quality that must be achieved by every NMHS making GAW precipitation chemistry measurements. The following sections describe specific QA/QC procedures that should be instituted by NMHSs at their monitoring stations, laboratories and data centres in order to meet the prescribed Data Quality Objectives.

6.1 Quality Assurance Requirements

This section describes the specific Quality Assurance procedures recommended for adoption by the NMHSs involved in the GAW Precipitation Chemistry Programme. It includes subsections on Data Quality Objectives, the requirement for a Quality Assurance Officer, and the need for proper Quality Assurance documentation.

6.1.1 Data Quality Objectives

Data Quality Objectives (DQOs) are defined as follows:

> Qualitative and quantitative statements of the overall level of uncertainty that a decision-maker will accept in results or decisions based on environmental data. They provide the statistical framework for planning and managing environmental data operations consistent with user's needs (U.S. EPA, 1997).

> Quantitative Data Quality Objectives for the GAW Precipitation Chemistry Programme are shown in Table 1.1 and described in detail in Appendix A. These DQOs have been developed by the GAW Scientific Advisory Group for Precipitation Chemistry based on published achievable measures of data quality. The DQOs provide each NMHS with a specific set of objectives for bias, precision, completeness, detection limits, and calibrations. **It is the responsibility of each and every NMHS to review these DQOs and adjust their GAW precipitation chemistry measurements to meet the DQOs.**

6.1.2 Quality Assurance Project Plans

The Quality Assurance Project Plan (QAPjP) "integrates all technical and quality aspects of a project, including planning, implementation, and assessment. The purpose of the QA Project Plan is to document planning results for environmental data operations and to provide a project-specific "blueprint" for obtaining the type and quality of environmental data needed for a specific decision or use. The QA Project Plan documents how quality assurance (QA) and quality control (QC) are applied to an environmental data operation to assure that the results obtained are of the type and quality needed and expected." (U.S. EPA, 1998).

It is recommended that each NMHS prepare a Quality Assurance Project Plan for its GAW Precipitation Chemistry Programme. The QAPjP should describe in detail the QA/QC procedures incorporated into the measurement system. Guidelines for the preparation of QA Project Plans can be found in U.S. EPA (1998). Other public-domain guidelines for the preparation of QA Project Plans are equally acceptable. The QAPjPs should readily available to laboratory staff and updated at least annually.

6.1.3   Quality Assurance Reporting

Each NMHS is responsible for assessing the quality of its precipitation chemistry data against the Data Quality Objectives stated in Table 1.1. The process of analyzing the quality of the data is known as *Data Quality Assessment*, which is described in detail in a U.S. EPA (2000).

It is recommended that each NMHS prepare an annual or biannual Quality Assurance Report that includes a description of the QA/QC procedures used in the GAW precipitation chemistry measurement system and a formal assessment of data quality relative to the Data Quality Objectives. The report should focus, in particular, on the accuracy, precision, completeness, comparability and representativeness of the data. All QA Reports should be submitted to the GAW Quality Assurance - Science Activity Centre for the Americas for archiving. An outline of a QA Report suitable for adaptation to precipitation chemistry measurements can be found under the "Metadata details" worksheet at the following web site: *http://cdiac.esd.ornl.gov/programs/NARSTO /NARSTO_template_atmospheric_measurements.xls*. Statistical methods for the assessment of data quality are described in documents accessible from the following US Environmental Protection Agency web site: *http://www.epa.gov/quality/qa_docs.html*.

6.2   Quality Assurance and Quality Control for Field Operations

Described below are specific QA/QC activities and procedures recommended for use at GAW Precipitation Chemistry Programme measurement sites.

6.2.1   Siting and Instrument Placement

To ensure collection of spatially- and temporally-representative GAW data, all precipitation chemistry sites must satisfy the siting criteria presented in Chapter 2 for "Global" and "Regional" GAW sites. GAW sites should be assessed annually with respect to the siting criteria to determine whether they continue to meet the minimum GAW siting requirements. An independent audit of sites is recommended every five years. Changes to sites should be documented as indicated in Section 2.6.

6.2.2   Instrumentation

Described below are QA/QC procedures that ensure the correct installation and operation of GAW Precipitation Chemistry Programme monitoring instrumentation. Where appropriate, the methods are referenced back to specific sections in the Field and Laboratory Chapters.

6.2.2.1 Satisfying Minimum Operating Specifications

Precipitation chemistry collectors and standard precipitation gauges must meet the minimum operating specifications listed in Chapter 3, e.g., sensor sensitivity, chemical inertness. Only those precipitation chemistry samplers and standard precipitation gauges that meet the specifications should be purchased and used in the GAW Precipitation Chemistry Programme. **(Section 3.2.1)**

6.2.2.2 Instrument Pretesting

Repaired and newly-purchased instruments should be pre-tested in the laboratory or repair shop before being sent to GAW sites for operational use. Adherence to this principle will reduce unexpected instrumental down-time.

6.2.2.3 Spare Parts

Spare parts and/or spare collectors should be stored at GAW precipitation chemistry sites whenever possible to allow quick instrument repair/replacement, thereby reducing measurement down-time.

6.2.3 Sample Collection and Handling

A short summary of the most important QA/QC procedures related to field sample collection and handling is given below. Detailed procedures are described in Chapter 3.

6.2.3.1 Sample Container Testing

Precipitation sample containers (e.g., buckets, bags, funnel-and-bottles) used in precipitation chemistry samplers must be tested for chemical inertness before being deployed to the field. Specific testing must be done to ensure that the collection vessel material does not adversely affect precipitation through the adsorption/desorption of major ions to/from the vessel walls. Testing should be done with high and low volumes of deionised water and real rainwater samples of known concentrations or reference solutions (where reference solutions have known certified concentrations of the major ions within the normal range of real precipitation samples). The different volumes will indicate whether the material adsorbtion/desorbtion effects, if they exist, are volume-dependent and the different rainwater or reference solutions will indicate whether the effects are matrix- or concentration-dependent.

Old collection vessels should be tested in the foregoing manner at least every 5 years to ensure that absorption/desorption effects have not accumulated or changed with time and use.

6.2.3.2 Sample Container Cleaning

All sample containers (including funnels and bottles) must be cleaned with deionised water between uses – preferably at the analytical laboratory but, if necessary, at the field sites. At GAW sites where the collection vessels are cleaned on-site, the deionised water used in the cleaning process must be tested to ensure that it meets predetermined quality specifications, both before and after the sample containers are cleaned (see Section 3.3). Methods must include careful cleaning and rinsing of the bucket and/or funnel rims since they are in direct contact with the collector hood. After being cleaned, sample containers that are not used immediately must be air dried in a clean location, sealed or covered in plastic, and stored in a clean area before being placed in the precipitation chemistry collector. See Sections 3.3.1 and 4.3.1.3 for specific sample container cleaning procedures.

6.2.3.3 Sample Collection

Specific quality control procedures that prevent contamination from occurring during sample collection and handling include:

- Inspecting the collection vessels for visible signs of contamination **before they are placed in the collector**
- Standing on the downwind side of the precipitation chemistry samplers when collecting samples in order to reduce the potential for contamination
- Wearing disposable plastic gloves whenever handling precipitation sample containers and transferring samples
- Instructing operators never to touch the inside of sample containers
- Replacing dirty gaskets on the underside of the sampler hood at frequent and regular intervals (every few months depending on the dirtiness of the site)
- Checking for, and documenting, sample leaks in the field, during shipping, and upon receipt at the laboratory. **(Section 3.2.1)**

6.2.4 Sample Storage and Shipping

Proper storage and shipping methods must be used to preserve the chemical and physical integrity of the precipitation chemistry samples. Quality control procedures for this purpose include:

- Maintaining sample temperature at 4°C during periods of storage on-site, in the laboratory, and in shipment.
- Weighing samples to determine sample volume at the GAW precipitation chemistry station and at the laboratory in order to detect leaks in transit
- Instituting procedures to eliminate leaks during transit. **(Section 3.3)**

6.2.5 Blanks

Field blanks are to be collected on a regular basis to ensure that sampling methods and materials do not interfere with sample chemistry. It is recommended that, for daily sampling, 2 to 4 blanks be collected randomly per month and, for weekly sampling, 1 to 2 blanks per month. This should be done at every site. The blanks are to be collected by pouring an aliquot of deionised water into a dry sample container (e.g., bucket, bag, funnel-and-bottle) that was installed in the precipitation chemistry sampler for a sampling period during which no precipitation occurred (or for a short period which simulates the sampling period). The aliquot should be submitted to the laboratory in the same manner as precipitation samples. Blank sample data should be checked regularly for evidence of contamination and should be routinely control-charted. **(Section 3.3.2.3)**

IMPORTANT: Care must be taken to label all field blank samples. Blank data must be stored separately from precipitation sample data.

6.2.6 Data Reporting at the Field Sites

Sample History Forms must be filled out at GAW precipitation chemistry stations for every sampling period (see examples in Figures 3.1 and 3.2). Specific QA/QC items related to field data reporting are:

- Check for legible, accurate and thorough completion of sample history forms. Whenever problem entries are found, contact the station operator promptly to correct the problem and obtain accurate data.
- Based on information contained on the sample history forms, assess the quality of the sample data, for example, to identify problems with the operation of the sampling instruments and adherence or non-adherence to the standard operating procedures. **(Section 3.5)**

6.2.7 Routine Instrument Checks

When site operators collect precipitation chemistry samples, they must check that the precipitation chemistry samplers and standard gauges are operating correctly. Specific checks include:

- The sampler has electrical power and the switch is in the "on" position
- The sensor, upon being wetted or triggered, opens the hood
- The hood or cover returns to the 'closed' position when the sensor is no longer wet
- The hood makes a tight seal on the rim of the sample container with no visible gaps between the hood and the rim
- The standard precipitation gauge is mounted correctly and does not leak. **(Section 3.2.1.4)**

6.2.8 Preventive Maintenance

In order to reduce instrument breakdowns, preventive maintenance to the precipitation chemistry collectors should be performed at regular intervals. **(Section 3.2.1.4)**

6.2.9 Regular Site Inspections

Sites should be inspected once per year by NMHS staff to detect problems with the instrumentation and sample handling procedures as well as continued conformance to siting criteria. The inspector should check for the following:

- Proper precipitation chemistry sampler operation
- Lid moves properly and completely seals the precipitation sample container in dry weather
- Lid gasket is clean
- The sensor activates the sampler lid to open and close as designed
- The sample containers are clean
- The sample handling area is clean
- Correct adherence to Standard Operating Procedures (SOPs)
- Proper storage and shipping of samples
- Proper placement of instrumentation
- Confirmation that GAW siting criteria are satisfied. **(Section 2.6.)**

6.2.10 Corrective Action

Corrective action must be taken as quickly as possible after an instrument breaks down or sampling irregularities are detected. Such immediate response will ensure the site meets the GAW Precipitation Chemistry Programme annual data completeness objective of 95%. As mentioned in Section 6.2.2.3, corrective action times are reduced if spare parts or extra instruments are already on-site.

6.3   QA/QC for Laboratory Operations

Laboratory operations, as discussed in Chapter 4, cover a wide range of activities including sample reception, field sampling support, sample transfer, storage and analysis, quality assurance, quality control, and data reporting. QA/QC related to these laboratory operations can be broken down into 3 parts, namely:

1) Setting laboratory data quality objectives
2) Adopting good laboratory QA/QC practices
3) Regular QA/QC reporting.

Specific quality control procedures in the laboratory include:

- Good laboratory practice
- Good sample handling practice
- Documentation of analytical procedures
- Preventive maintenance of laboratory instrumentation
- Analyst training and upgrading
- Provision of appropriate facilities, instrumentation and reagents
- Inspections and/or audits
- Appropriate safety measures
- Well-defined sample chain-of-custody
- Traceability of calibration standards
- Control charting
- Accuracy checks (calibration controls, spikes, blinds, reagent blanks)

- Precision checks (within-run and between-run duplicates)

All of these activities must be considered when operating a well-controlled laboratory facility.

6.3.1 Laboratory Data Quality Objectives

The Data Quality Objectives of all GAW precipitation chemistry laboratories are presented in Table 1.1 and in Appendix A. It is the responsibility of each laboratory to implement an appropriate set of operational and QA/QC activities to ensure that these objectives are met or exceeded.

6.3.2 Laboratory Sample Handling QA/QC

Quality control procedures related to sample handling at the laboratory include the following:

- **Sample Reception, Logging and Custody**. Correct sample logging and chain-of-custody procedures must be implemented at the laboratory to ensure that no samples are lost, mixed up or misplaced. Samples should be stored at 4°C until they enter the analysis stream.
- **Sample Handling, Labelling, and Transferring**. After reception, logged samples should be weighed (to check for leakage during transit and to confirm the field weight) and inspected for visible contamination. Problem samples should be noted and the information verified.

6.3.3 Chemical Analyses QA/QC

Chemical laboratories involved in the analysis of precipitation samples are expected to meet the Data Quality Objectives. This can be done only through strict adherence to SOPs and QA/QC procedures within the analytical system. Specific QA/QC procedures are described below.

6.3.3.1 Calibration Control and Verification

All laboratories must implement quality control procedures that guarantee the accuracy of calibrations. Recommended procedures include:

- Using ultra-pure reagents traceable to Certified Reference Materials for the production of calibration *standards*
- Checking that the slope, intercept and correlation coefficient of each calibration curve are within acceptable ranges (the use of control charts is recommended)
- Using calibration standards that cover a range from 2% to 98% of all precipitation sample concentrations
- Using extra calibration standards in non-linear portions of the calibration curves;
- Calibrating at the beginning and end of each analytical run
- Analyzing and control-charting one or more *quality control check solutions* in each batch of samples. It is recommended that *calibration check solutions* correspond to the 10th, 50th and 90th percentiles of all sample concentrations for the NMHS. When a calibration check solution exceeds the control limits, the entire batch of samples should be reanalyzed.

6.3.3.2 Replicate Analyses

Replicate analyses of precipitation samples provide a measure of analytical precision. There are two types of replicate analyses: within-run and between-run. Here a "run" is defined as a set or batch of consecutive measurements with the analytical instrument operating within fixed calibration settings and within control limits. In general, between-run replicates are more important than within-run replicates because they capture the day-to-day and batch-to-batch variability of the analyses.

It is recommended that 2% to 5% of the sample load be analyzed as between-run replicates and that all replicate samples be randomly selected from the sample stream. The replicate analysis results should be control-charted immediately and, whenever the control limits are exceeded, the entire batch of samples should be reanalyzed. At the end of each year the replicate analysis data can be used to determine the analytical precision, which, in turn, can be compared against the Data Quality Objective for laboratory precision as stated in Table A.1 (see Appendix A for calculation methods). No less than 30 replicate samples should be used when calculating the analytical precision.

6.3.3.3 Laboratory Blanks

Deionised water and reagent blanks should undergo the same chemical analyses as the precipitation samples. One deionised water and one reagent blank should be analyzed per analytical batch. The analysis results should be control charted and corrective action taken when the control limits are exceeded, i.e., replacement of the deionised water and/or reagents.

6.3.3.4 Blind Samples

Blind samples composed of deionised water, acidified deionised water, simulated rainwater or certified reference materials should be inserted into the sample stream on a weekly basis. The results should be control charted to ensure that the system is in-control.

6.3.3.5 Dilution Checks

Dilution is often used to increase the volume of small precipitation samples (in order to obtain enough sample for full chemical analyses) and/or to reduce high concentration samples to the normal operating range of the analytical instruments. It is recommended that the dilution method be tested routinely on 1% of the samples. The accepted method for testing dilutions is to analyze aliquots of large precipitation samples both before and after dilution (certified reference materials are acceptable as well). Before- and after- differences that exceed 10% of the undiluted concentrations should trigger a review of the dilution system. Such checks should be carried out routinely and continuously control charted.

6.3.4 Control Charting

Quality control charts are statistical tools used to ensure that a measurement system is in control. Using control charts should be a standard practice in all GAW laboratories. See Section 4.3.2.2 for further discussion of control charts. Details on control chart methods can be found in Taylor (1987) and ASTM (2002).

6.3.5 Data Quality Control and Reporting

Data QA/QC procedures must be applied routinely to ensure that analytical results are accurate and complete. Specific QA/QC procedures include:

- Verification that all control limit exceedences on laboratory control charts have been dealt with in a timely and satisfactory manner (e.g., re-analysis)
- Verification that all extreme values and below detection limit values are correct
- Identification (flagging) of invalid or questionable analytical results, e.g., cases of laboratory contamination and instrument malfunctions
- Identification and re-analysis of samples that failed ion balance criteria.

6.3.6 Laboratory Intercomparison Studies

All laboratories that analyze GAW precipitation chemistry samples must participate in the WMO/GAW Laboratory Intercomparison Studies. NMHS personnel in every country are required to register their chemical laboratory (or laboratories if there is more than one involved) with

the manager of the GAW Precipitation Chemistry Programme Laboratory Intercomparison Studies at the QA SAC for the Americas (see laboratory registration form in Appendix G). Twice per year, intercomparison samples will be sent to each laboratory for analysis and the analytical results must be reported to the QA SAC within the prescribed time interval.

Precipitation chemistry data from countries that do not participate in the WMO/GAW Laboratory Intercomparison Studies will not be archived within the World Data Centre for Precipitation Chemistry. Such data will be sequestered in data files separate from the main archive. It is the intention of the WDCPC to include in the data archive an indicator of laboratory performance based upon the WMO/GAW Laboratory Intercomparison Studies.

Participation in laboratory intercomparisons outside of the WMO/GAW is encouraged. Such studies include the EMEP Laboratory Intercomparison Studies, the Canadian Laboratory Intercomparison Studies and the East Asian Network Intercomparison Studies. Details of these studies can be obtained by contacting the GAW Precipitation Chemistry Programme Quality Assurance Science Activity Centre in Albany, NY, USA.

Results of the WMO/GAW Laboratory Intercomparison studies should be used by each NMHS to assess its *Between Network Laboratory Bias.* A proposed methodology for calculating the Laboratory Bias is given in Appendix A. Once calculated, the laboratory bias values should be compared against the stated Data Quality Objectives for Inter-laboratory Bias in Table 1.1 (see Appendix A for details).

6.3.6.1 Corrective Action for Unsatisfactory Performance in One or More GAW Precipitation Chemistry Programme Laboratory Intercomparison Studies

Unsatisfactory performance by a GAW precipitation chemistry laboratory reduces the overall quality of the GAW Precipitation Chemistry Programme. Immediate corrective action must be taken to upgrade the performance of an under-performing laboratory to a satisfactory level. Suggested actions include:

- Improving the internal laboratory quality control programme
- Setting up a routine system of analyzing and control-charting Certified Reference Materials (CRMs)
- Analyzing split samples provided by a collaborating 'in-control' laboratory
- Arranging for an expert visit/audit by another GAW precipitation chemistry laboratory manager.

Laboratories with unsatisfactory performance that wish to arrange an expert visit should contact the WMO Secretariat or the QA SAC Americas.

6.3.7 Laboratory QA Reporting

It is recommended that all GAW precipitation chemistry laboratories produce an annual Laboratory Quality Assurance Report, which documents the quality of the data generated by the laboratory. Copies of the report should be made available to GAW data users upon request.

6.4   QA/QC for GAW Precipitation Chemistry Programme Data Management

Each NMHS should have a carefully designed and managed data handling system that encompasses site, laboratory and office data activities. Key elements of the QA system for data management are described in the following subsections.

6.4.1 The GAW Precipitation Chemistry Data Management Objective

The data management objective of the GAW Precipitation Chemistry Programme is as follows: **To submit final validated precipitation chemistry data in one year blocks to the GAW World Data Centre for Precipitation Chemistry (WDCPC) once per year, no later than 1 year after the year in which the data were collected**. For example, data for January 1 to December 31, 2002 should be submitted to the WDCPC by December 31, 2003.

It is a GAW requirement that each measured data value be accompanied by a "validity flag" which indicates whether the datum is valid (a "V" flag) or invalid (an "M2" flag). These flags must be assigned to the measurement data by the NMHS staff member responsible for the collection and reporting of the data. Details of the flagging system are given in Chapter 5 and Appendix F.

6.4.2 Data Custody / Data Flow

Data custody and data flow within each NMHS must be well-defined and carefully followed. Each person involved in the GAW Precipitation Chemistry Programme from the site operator to the laboratory analyst to the data manager, must understand and carry out data activities with great care and precision. All staff must be trained to detect data flow problems and initiate suitable corrective action.

6.4.3 QC of Field Data

Field data reported on Sample History Forms will consist of measurement data (e.g., rain gauge depth, sample weight/volume, etc.) and sampling information (e.g., comments on malfunctioning instrumentation, contamination, etc.). To ensure proper data management, the Sample History Forms must be reviewed immediately upon receipt from the field in order to: 1) identify inaccurate and/or missing data, 2) identify operational problems at the site and 3) initiate immediate corrective action. It is recommended that a designated individual be assigned the responsibility of inspecting the Sample History Forms as they arrive from the field sites for:

- transcription errors or missing entries
- evidence of poor collection efficiency of the sampler
- missing samples
- instrument malfunctions or problems.

It is the responsibility of this person to correct errors, collect missing information/samples and initiate corrective action.

6.4.4 QC of Laboratory Data

Laboratory data should be quality controlled to identify problems and inaccuracies. A laboratory staff member should be responsible for reviewing and releasing the data. Suggested quality control procedures are identified in Sections 4.3 and 6.3.5.

6.4.5 QC of Merged Field/Laboratory Data

Field and laboratory data must be merged into a single database. It is critical that the field and laboratory data match exactly, i.e., no mismatched samples and sampling dates. To ensure correct matching of field and laboratory data, both data sets should contain the same sampling date information and sample identification numbers. These numbers should then be used by a computer programme to do the matching.

6.4.6   Commenting and Flagging of Data

Each NMHS should flag the GAW Precipitation Chemistry Programme data in a manner that clearly identifies the data as *Valid* or *Invalid* (see Section 5.6.1)*.* A data quality control officer should review all data to ensure that measurement problems are identified and flagged in the data sets. When reporting data to the GAW World Data Centre for Precipitation Chemistry, care must be taken to conform to the GAW Precipitation Chemistry Programme data flagging system (see Section 5.6 and Appendix F).

6.4.7   Data Quality Assessment

Each NMHS should carry out a set of data validation, verification and assessment checks before signing off on the data for each year. These checks include outlier tests, ion balance checks, graphical time series plots and detection limit verification. Data that fail the assessment process should be flagged appropriately. Statistical methods for the assessment of environmental data are described in documents at the following U.S. Environmental Protection Agency web site*: http://www.epa.gov/quality/qa_docs.html*.

6.5   Documentation and Document Control

All elements of the GAW Precipitation Chemistry Programme must be documented and kept current. Each NMHS is responsible for producing a set of manuals including manuals for field, laboratory and data handling operations as well as for quality assurance. Ideally, this includes: Field Operators Manual, Instrumentation Manuals, Laboratory Manual, Data Management Manual, Quality Assurance Project Plan, annual Quality Assurance Reports, detailed job descriptions of personnel, Site Descriptions, and Data Reports. Each document should contain a document control system whereby pages are indexed properly and dates of new/updated pages are indicated.

6.6   Training and Upgrading

Staff training and upgrading are key to the success of the GAW Precipitation Chemistry Programme. All field and laboratory personnel should be trained and certified prior to the start of sampling at a GAW site. New operators must be trained immediately. Refresher training should be done routinely, e.g., every 2 years, to ensure that the field and lab personnel maintain correct up-to-date practices and procedures. Whenever new protocols are instituted, formal training should take place in the field and/or laboratory.

NOTE: Site operators should always be trained by certified training staff, not by other site operators.

6.7   Corrective Action

Speedy repair of malfunctioning wet deposition collectors is a necessity since failure to do so will result in unsatisfactory data completeness. NMHS personnel should ensure that corrective action is taken so that repairs to instruments (in the field and laboratory) are done within one to two days of detection. At remote GAW precipitation chemistry sites, spare parts and/or instruments should be kept on site so that faulty parts and instrumentation can be replaced immediately. Specialized training of on-site personnel may be required in such cases.

6.8   Calibration and Traceability

Proper calibration of field and laboratory equipment is essential. All calibrations should be traceable to accepted international standard organizations such as the U.S. National Institute of Standards and Technology and all calibration procedures should be documented in network manuals and quality assurance project plans.

At GAW precipitation chemistry sites, calibration methods should be followed for weighing balances (where applicable), recording rain gauges, and precipitation sensors. In the laboratory, calibrations must be applied to all analytical procedures.

6.9 Audits

Performance Audits and *System Audits* of the field, laboratory and data management systems are recommended every 5 years. *Performance audits* are defined as systematic checks that are quantitative in nature while *system audits* are systematic qualitative checks that usually consist of reviewing the measurement procedures to ensure that they are consistent with the standard operating procedures.

Performance audits include checks of the collector sensor sensitivity and operation, laboratory analysis of Certified Reference Materials, and computational checks (e.g., of the ion balance calculation) in the data centre. **Formal audits are ideally carried out by independent experts.** Where this is not possible, auditors from the NMHS can be used.

6.10 Routine and Non-Routine QA/QC Procedures for the Assessment of Measurement Accuracy, Precision, Comparability, Completeness and Representativeness

Five elements of quality assurance must be addressed by each NMHS in order to ensure high quality GAW precipitation measurements. The five QA elements are: accuracy, precision, completeness, representativeness and comparability. Specific quality assurance activities that address these issues are described below.

6.10.1 Accuracy

It is not possible to determine the absolute accuracy of precipitation chemistry measurements since there are no Standard Reference Materials falling from clouds at known rates. As a result, it is important that each NMHS: a) minimizes its measurement errors by adopting well-designed standard operating procedures and b) quantifies the accuracy of certain parts of the measurement system. Methods of minimizing measurement errors have already been discussed above. Methods of quantifying the accuracy of components of the measurement system include:

- Comparing the ion concentrations of dynamic field blanks against those of real precipitation samples. Ion concentrations in field blanks should generally be less than or equal to the 15th percentile of the ion concentrations in real precipitation samples.
- For weekly or monthly sampling periods, determining the amount of evaporation and dry deposition contamination to which samples are subject while sitting in the collectors. This can be done by setting a known amount of precipitation of known concentration in a closed collector and determining the lost volume and the increase in concentration by the end of a nominal sampling period.
- Analysis of certified reference materials by the laboratory.
- Audits of the field, laboratory and data management systems.

The results of these studies can be used to bracket the uncertainties of the overall data set. Further discussion of measurement uncertainties can be found at the following websites:
http://physics.nist.gov/cuu/Uncertainty/index.html
http://www.measurementuncertainty.org/.

6.10.2 Precision

Each NMHS can determine the overall precision of its precipitation chemistry measurements by operating two precipitation chemistry collectors and standard precipitation gauges simultaneously at the same site for at least one year. The two chemistry collectors must be operated independently but the samples should be analyzed by the same laboratory. Paired sample differences can be tested to

determine whether they are significantly different from zero and to estimate the magnitude of the differences (which is equal to the precision). Appendix A contains a recommended method for estimating precision based on this type of data. The calculation results should be compared against the Data Quality Objectives for Overall Precision as stated in Table 1.1. Publications that describe methods for estimating precision include NILU (1996), Sirois and Vet (1999) and Nilles et al. (1994).

6.10.3 Completeness

Completeness is defined as a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under correct normal conditions (U.S. EPA, 1976). There are two data completeness criteria adopted by the GAW Precipitation Chemistry Programme. These are documented in Olsen et al. (1990) (note that this reference identifies 4 additional completeness criteria which are not used in the GAW programme). The two completeness criteria are:

1) **The completeness of rain/snow gauge measurements of precipitation depth.** This is defined as the *Percent Precipitation Coverage Length* (%PCL) which is the percent of the summary period (e.g., month, season, year) for which information is available on whether precipitation occurred or not. In practice, this means the percentage of the time that a standard precipitation gauge was operating properly and reporting whether precipitation occurred or not. If precipitation was known to have occurred but no measurement of precipitation depth was available, then it is assumed that there was no knowledge of precipitation occurrence. Hence, if there were 365 sampling days in a year and a standard rain gauge reported data properly for only 300 of those days, then the %PCL = 82.2%.

2) **The completeness of precipitation depth associated with valid chemical analysis and valid sample collection.** This is defined as the *Percent Total Precipitation* (%TP). For a given summary period (e.g., month, season, year), it is the percentage of total precipitation depth measured by a standard gauge that was associated with valid precipitation chemistry data. For example, if a standard precipitation gauge measured 1000 mm in a year but the total standard gauge depth associated with valid precipitation chemistry samples was 782 mm, then the %TP = 78.2%. Note that the %TP should be calculated for each measured ion since some ion concentrations may be invalid or missing more than others.

For the GAW Precipitation Chemistry Programme, the acceptable data completeness levels are as follows (note that a site is required to meet both quarterly and annual completeness criteria to satisfy the annual completeness requirements):

GAW Acceptable Seasonal Data Completeness Measures
    %PCL $\geq$ 90%
    %TP $\geq$ 70%
GAW Acceptable Annual Data Completeness Measures
    %PCL
        Annual $\geq$ 90% and
        Each quarter $\geq$ 60%
    %TP
        Annual $\geq$ 70% and
        Each quarter $\geq$ 60%.

Methods of ensuring that the data completeness criteria are met include:

- repairing malfunctioning instruments as quickly as possible to minimize lost data
- making precipitation depth measurements every day, even if precipitation chemistry samples are not collected
- using large collection vessels so that sample volumes are sufficient for full chemical

analysis even with small precipitation events

- diluting low volume samples in the laboratory to maximize the number of chemical species analyzed
- minimizing the risk of sample contamination, leakage, breakage or loss through the implementation of good operating procedures.

6.10.4 Representativeness

Site representativeness can be assured by carrying out site inspections and audits on a regular basis to verify that the appropriate siting criteria are continually being met. *Sample representativeness* can be assured by minimizing all possible sources of sample contamination through good sampler design and proper standard operating procedures.

6.10.5 Comparability

Overall measurement comparability can be determined by collocating chemistry samplers and rain gauges of two or more GAW-member countries at a single site. The precipitation chemistry samples from each collector should be sent to their associated GAW precipitation chemistry laboratories (i.e., each collector should operate in the exact manner it would if it were located in its own country). The data from the different countries' samplers should be analyzed to determine their comparability and o*verall inter-network bias*. The inter-network bias should be compared against the Data Quality Objectives for Inter-Network Bias as stated in Table 1.1 (see Appendix A for a recommended method for estimating inter-network bias). Examples of published inter-network comparability studies include Sirois et al. (2000), and Areskoug (1988).

Multinational field comparisons are the best method of establishing overall measurement comparability between GAW countries. However, it is recognized that such studies are not feasible for all GAW countries.

6.11 Special Studies

Special studies should be carried out to investigate specific measurement problems or the impact of changing measurement methods. Examples include:

- studies to determine whether ions are adsorbed on or desorbed by sample collection vessels
- studies to assess the comparability of new and old sampling procedures and instrumentation
- studies to determine the suitability of various sample preservatives.

The results of these types of special studies should be used to select the best sampling methods and to estimate the uncertainty in the measurement system. Results should be reported in formal reports and made available to the international basis upon request.

6.12   References

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A DESCRIPTION OF HOW THE GAW PRECIPITATION CHEMISTRY DATA QUALITY OBJECTIVES WERE ESTABLISHED AND RECOMMENDED CALCULATIONS FOR DATA QUALITY ASSESSMENT

This appendix describes the methods by which the GAW Precipitation Chemistry Data Quality Objectives specified in Table A.1 were established, and provides details of recommended calculation methods for determining whether the Data Quality Objectives are being met by individual GAW countries (a process commonly referred to as *Data Quality Assessment*). Each of the following sections refers specifically to the Data Quality Objectives specified in Table A.1.

A.1   DETECTION LIMITS

The *Detection Limits* presented in Table A.1 were established from a review of the 2001 detection limits provided by all laboratories participating in the European Monitoring and Evaluation Programme (EMEP). The *Detection Limits* listed in Table A.1 are the median values of all of the participating EMEP laboratories. The DQOs should be achievable for all GAW laboratories; however, some may require improvements to their analytical and quality control methods.

Individual GAW laboratories can determine their *Detection Limits* by following one of the recommended procedures of the International Union of Pure and Applied Chemists (IUPAC). Readers are referred to the following Web site:

http://www.iupac.org/publications/analytical_compendium/Cha18sec437.pdf

for a full discussion of detection limits by IUPAC. The preferred method of determining *Detection Limits* in the GAW Precipitation Chemistry Programme requires making 30 or more (preferably many more than 30) repetitive chemical analyses of a low concentration ion solution. The solution must be stable and at a concentration level at or near the detection limit of the analytical technique. Ideally, this means that the concentration level should be between a blank level (pure deionised water) and the expected detection limit. In practice, the concentration level can be as high as, but not higher than 5 times the anticipated detection limit. For example, if the anticipated detection limit of a sulphate analysis is 0.04 mg L^{-1}, then the solution from which the actual detection limit is established should have a stable sulphate concentration of less than 0.20 mg L^{-1} and, ideally, between 0.01 and 0.04 mg L^{-1}. The 30 or more repetitive analyses can be done in either a single analytical batch or in a number of batches analyzed over a period of time, the latter being the preferred. The *Detection Limit* for each analyte is set equal to 3 times the standard deviation of the 30 or more repetitive analyses. When compared against the DQOs listed in Table A.1, those *Detection Limits* better than or equal to the DQOs are considered to have met the DQOs.

A.2   OVERALL PRECISION

Overall Precision is the precision of the complete precipitation chemistry measurement system including the field and laboratory components. The Data Quality Objectives for *Overall Precision* listed in Table A.1 were set at 1.5 times the precision values measured by one specific GAW network, that is, the Canadian Air and Precipitation Monitoring Network. The precision values for this network are published in Table I of Sirois and Vet (1999). Here, and in Sirois and Vet (1999), *Overall Precision* is expressed as the Modified Median Absolute Difference (M.MAD), which is described in detail below. The factor of 1.5 was chosen arbitrarily to broaden the precision allowed in the GAW Programme to account for the wide variation in measurement methods and capabilities across the GAW member countries. It is worth noting that for Mg^{2+}, Na^{+} and K^{+}, the *Overall Precision* as quantified by the Modified Median Absolute Difference in Sirois and Vet (1999) was less than the analytical detection limit for those ions, in which case the DQO values were set equal to the detection limit times the factor

of 1.5. The DQO for pH >5.0 was chosen arbitrarily since no precision estimates were available at the time of writing.

The estimation of *Overall Precision* by GAW member countries should be done by operating 2 identical precipitation chemistry collectors and standard gauges simultaneously at the same site for a period of one year or more. The paired concentration and depth data from the individual samples should be used to calculate the Modified Median Absolute Difference (M.MAD) where the M.MAD is a non-parametric estimator of the spread of the frequency distribution that is relatively insensitive to the presence of outliers and a consistent estimator of the standard deviation when the underlying frequency distribution is normal. The mathematical expression of the M.MAD is as follows:

$$M.MAD = \frac{1}{0.6745} Median(\,|\,x_i - Median(x_i)\,|\,) \qquad \text{Eq. A-1}$$

where x_i = variable of interest.

A description and sample calculation of the M.MAD are given below. Readers are referred to Sirois and Vet (1999) for complete details.

A.2.1 Calculation of the Modified Median Absolute Difference (M.MAD)

1) For each set of paired concentration data, *i*, from Sampler 1 and Sampler 2, calculate the between-sampler error, e_i, as

$$e_i = \frac{1}{\sqrt{2}} (C_{1i} - C_{2i}) \qquad \text{Eq. A-2}$$

where C_1 and C_2 represent the concentrations from Samplers 1 and 2 for the ith sample and the $\frac{1}{\sqrt{2}}$ term accounts for the fact that the errors in the two measurements are assumed to be drawn from the same distribution.

2) Calculate the Overall Precision (which is defined as the spread of the e_i values) equal to the Modified Median Absolute Difference (M.MAD) as follows:
    a) From all values of e_i collected from the paired values, calculate the median value of e_i or Median(e_i).
    b) For each value of e_i, subtract the Median(e_i) and take its absolute value, i.e., $|e_i -$ Median(e_i)|
    c) Determine the median of the $|e_i -$ Median(e_i)| values, i.e., Median $|(e_i -$ Median $e_i)|$
    d) Multiply the Median $|(e_i -$ Median $e_i)|$ value by 1/0.6745, a factor that sets the M.MAD as a consistent estimator of the standard deviation if the underlying distribution of $|e_i -$ Median(e_i)| values is normal.
3) Compare the calculated M.MAD value to the Data Quality Objective in Table A.1.

A.2.2 Example Calculation of the M.MAD

The following is a sample calculation of *Overall Precision* based on sulphate concentration data collected from duplicate samplers of the Canadian Air and Precipitation Monitoring Network.

Sampler 1	Sampler 2	e_i	Median(e_i)	$|e_i - \text{Median}(e_i)|$	Median $|e_i - \text{Median}(e_i)|$
5.234	5.453	-0.155	0.003	0.158	0.018
2.343	2.328	0.011		0.008	
2.359	2.335	0.017		0.014	
4.778	4.167	0.432		0.429	
0.736	0.733	0.002		0.001	
0.737	0.767	-0.021		0.024	
3.772	3.793	-0.015		0.018	
1.345	1.329	0.011		0.008	
11.787	11.426	0.255		0.252	
2.987	2.995	-0.006		0.009	
3.080	3.050	0.021		0.018	
1.095	1.098	-0.002		0.005	
1.636	1.631	0.004		0.001	
1.086	1.082	0.003		0.000	
3.207	3.314	-0.076		0.079	
1.756	1.788	-0.023		0.026	
1.772	1.778	-0.004		0.007	
3.118	3.102	0.011		0.008	
1.842	1.765	0.054		0.051	
2.719	2.677	0.030		0.027	
3.231	3.185	0.033		0.030	
1.239	1.289	-0.035		0.038	
4.392	4.354	0.027		0.024	
4.108	4.145	-0.026		0.029	
3.766	3.798	-0.023		0.026	
3.668	3.699	-0.022		0.025	
1.056	0.917	0.098		0.095	
2.560	3.580	-0.721		0.724	
0.863	0.870	-0.005		0.008	
1.202	1.207	-0.004		0.007	
2.812	2.809	0.002		0.001	
0.448	0.441	0.005		0.002	
15.412	14.285	0.797		0.794	
2.224	2.207	0.012		0.015	
2.621	2.631	-0.007		0.010	
0.920	0.928	-0.006		0.009	
1.642	1.601	0.023		0.020	
3.338	3.317	0.015		0.012	
5.910	5.839	0.050		0.047	

M.MAD = (1/0.6745) x 0.018 = 0.027 mg L^{-1}
DQO for *Overall Precision* from Table A.1 = 0.06 mg L^{-1}
Since the M.MAD < DQO, the *Overall Precision* for sulphate meets the DQO.

A.3 LABORATORY PRECISION

Laboratory Precision refers to the precision of the analytical measurements made by GAW laboratories responsible for measuring major ions in precipitation. The DQOs for *Laboratory Precision* specified in Table A.1 were set at 1.5 times the analytical precision of one of the highly precise GAW laboratories (i.e., the Environment Canada CAPMoN laboratory in Toronto, Canada) as published in Table II of Sirois and Vet (1999). The metric used for the analytical precision of the CAPMoN Laboratory was the Modified Median Absolute Difference (M.MAD) calculated from a large number of between-run replicate analyses. The factor of 1.5 was chosen to expand the tolerance of the DQOs beyond that of a single laboratory in order to account for the wide variety of laboratory methods and measurement capabilities within the GAW Programme.

Laboratories in the GAW Precipitation Chemistry Programme should estimate their *Laboratory Precision* by making between-run replicate analyses of 30 or more (preferably many more than 30) precipitation chemistry samples covering a broad range of ion concentrations. As with *Overall Precision*, the *Laboratory Precision* is calculated as the Modified Median Absolute Difference of the replicate data pairs. Laboratory personnel can use the same M.MAD methodology and sample calculation given in Section A.2 for calculating the *Laboratory Precision* by simply substituting the laboratory replicate data for the duplicate sampler data.

A.4   INTER-NETWORK BIAS

Inter-network Bias is a measure of relative accuracy or comparability between different networks that make the same measurements at the same time and place, under the same environmental conditions and near the *true value* of the measurements. *Inter-Network Bias* is only a partial measure of *Overall Accuracy* but it is a particularly useful one in that is readily quantifiable and easily understood.

Inter-Network Bias is quantified by making simultaneous side-by-side measurements of two or more networks at the same site. With this method, each network must use its own instrumentation, standard operating procedures, analytical laboratory and data management methods to produce its data. The multiple networks' data sets are then intercompared to determine the *Inter-Network Bias.* Collocated sampling must take place for at least one year in order to capture the full range of concentrations and environmental conditions that affect the measurements.

The Data Quality Objectives for *Inter-Network Bias* shown in Table A.1 were established based on a number of assumptions about collocated sampling, namely:

- Collocated collectors from different networks sample the same population of precipitation events.
- Each network's measurement system produces a unique distribution of sampling data that reflects that network's field and laboratory measurement methods.
- Perfectly comparable networks can theoretically produce identical data distributions but, in practice, are unlikely to do so. Even collocated samplers from the same network typically produce different data distributions.
- Highly comparable networks will typically produce data distributions that differ by at least as much as collocated collectors from a single network. In other words, two different networks will generally differ by more than the *Overall Precision* of an individual network.
- Networks that are significantly different from each other (to a given probability level) will typically have data distributions that differ from each other by as much as or more than the precision of the individual networks.

Based on these assumptions, the DQOs for *Inter-Network Bias* in Table A.1 were set at 1.5 times the inter-network biases measured in a network inter-comparison study that involved two highly precise GAW networks, namely, the United States National Atmospheric Deposition Programme/National Trends Network and the Canadian Air and Precipitation Monitoring Network. The *Inter-Network Biases* measured in this study were published as the Modified Median Absolute Differences in Table I of Sirois et al. (2000). The multiplicative factor of 1.5 was chosen arbitrarily as a way of expanding the tolerance in the GAW Programme to account for the wide variation of measurement methods and capabilities across GAW member countries. For Mg^{++} and K^+, the *Inter-Network Bias,* as quantified by the Modified Median Absolute Difference in Sirois et al. (2000), was less than the analytical detection limit so the DQO values in Table A.1 were set equal to the detection limit times 1.5. The DQO for pH >5.0 was chosen as 2 times the DQO for pH <5.0 since no quantitative bias estimates were available for that pH level at the time of writing.

The *Inter-Network Bias* DQOs for sample depth and standard gauge depth measurements were arbitrarily set at ±5% for rain, ±15% for snow, and ±10% for mixed rain/snow relative to the total annual precipitation depth for each type of precipitation. The DQOs were expressed in relative terms (i.e., percentages) because of the difficulty in establishing absolute values (in millimetres) for the 50 or

more national standard gauges (Sevruk and Klemm, 1989) and the more than 14 types of precipitation chemistry samplers in use today -- each having its own wind speed, exposure, wetting and evaporation errors (see Sevruk 1989 and Goodison et al., 1998 for a discussion of these errors).

GAW member countries can calculate *Inter-Network Bias* from collocated sampler data by following the method described in the next paragraph (it is assumed in this method that only two networks are collocated at the same site). Readers are referred to Sirois et al. (2000) for a more detailed description of the statistical model and methodology.

Calculation of *Inter-Network Bias* is best done by collocating a precipitation chemistry sampler and standard gauge from more than one network at the same site. After a minimum of one year of collocated sampler operation, tabulate the paired ion concentrations from the two samplers for all precipitation sampling periods, *i*. In cases where the sampling periods of the two networks are the same (e.g., daily-versus-daily, weekly-versus-weekly), the table can be simple and straightforward. For cases where the sampling periods are different (e.g., daily-versus-weekly sampling periods), the concentration values of the shorter sampling periods must be converted to precipitation-weighted mean concentrations of the longer sampling periods. For example, if a daily sampler is collocated with a weekly sampler, the daily concentrations must be converted into weekly precipitation-weighted mean concentrations for the same weekly periods as the weekly sampler. To do this, the standard gauge depth must be used as the weighting factor, <u>not the sample depth</u>. Weekly sample depths and standard gauge depths must also be calculated and tabulated.

1) For each pair of samples for each sampling period, calculate the between-network difference in concentration, sample depth and standard gauge depth as $\Delta C i = C_{1i} - C_{2i}$ where C_1 and C_2 represent the concentrations and depths measured by Networks 1 and 2 for sampling periods, i = 1 to n.

2) Test the frequency distribution of the between-network differences, $\Delta C i$, for normality (or non-normality). A test such as the Kolmogorov-Smirnov test can be used (see, for example, Gibbons, 1985).

3) <u>If the frequency distribution of the between-network differences is normal</u> (which is unlikely), use the *student-t test* to test whether the mean value of the between-network differences, $\Delta C i$, is significantly different from zero. <u>If the distribution is non-normal</u>, use the *sign test* to test whether the median value of the between-network differences is significantly different from zero. The result will determine whether a statistically significant *Inter-Network Bias* exists. Note that special multiple testing techniques must be used if more than two networks are being compared in order to establish significant differences between networks while at the same time preserving simultaneous confidence intervals across multiple tests. One such test is the Friedman Rank Sum Test described in Hollander and Wolfe (1973) and used in Vet et al. (1988).

4) <u>If the frequency distribution of the between-network differences is normal,</u> then calculate the mean value of the between-network differences. This value represents the *Inter-Network Bias* and should be compared against the DQO in Table A.1. If the mean value is found to be less than or equal to the DQO, then the two networks are considered to have met the Data Quality Objective for *Inter-Network Bias*. <u>If the frequency distribution of the between-network differences is not normal,</u> then calculate the median value of the between-network differences. This value then represents the *Inter-Network Bias* and should be compared against the DQO in Table A.1. If the median is found to be less than or equal to the DQO, then the two networks are considered to have met the Data Quality Objective.

5) For the sample depth and standard gauge depth measurements, calculate the annual totals of the rain, snow and mixed rain/snow events for each instrument. For each precipitation type, subtract the total depth measured by instrument 1 from the total depth measured by instrument 2 and divide by the average total depth of the two instruments. Compare this number to the DQOs specified in the table.

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A.5 INTER-LABORATORY BIAS

Inter-laboratory Bias is a measure of laboratory comparability. The Data Quality Objectives for *Inter-Laboratory Bias* in Table A.1 were determined using data from past precipitation chemistry laboratory intercomparison results, specifically the results of WMO/GAW Intercomparison Studies 23, 24, 25 and 26. Each of the 4 studies involved 65 to 70 laboratories that analyzed 3 samples with different ion concentrations. For each ion in each of the 12 samples, the frequency distribution of the 65-70 reported concentrations was determined and an *acceptable range* of reported concentrations established, as $\pm 0.5 \bullet (IQR)$ where IQR = the interquartile range of the frequency distribution of 65-70 laboratory results, i.e., the middle 50% of the reported values were used to determine the *acceptable range* for each sample. The calculated range for each ion in each sample was then expressed in relative terms by dividing by the median concentration of the particular sample and ion, i.e.,

$$\textit{Acceptable Concentration Range for each sample } = \pm \ [0.5 \bullet \frac{IQR}{Median} \bullet 100] \qquad \text{Eq. A-3}$$

The *acceptable ranges* of the 12 intercomparison samples were ranked from lowest to highest and the DQO for each analyte was set equal to the second highest value of the 12 (note that the highest value was avoided because of its potential to be an outlier). This value was considered to represent a reasonable and attainable DQO for all GAW laboratories in future GAW laboratory intercomparison studies.

Individual GAW laboratories can assess their WMO/GAW Laboratory Intercomparison results in light of the DQO for *Inter-Laboratory Bias* by using the following calculation:

1) For each ion in a each sample, calculate the laboratory's bias as:

$$Bias = 100 \bullet \frac{(C_{lab} - MedianC)}{MedianC} \qquad \text{Eq. A-4}$$

C_{lab} = the laboratory's reported concentration
$MedianC$ = Median concentration of all laboratories

2) Compare your laboratory's bias to the DQO for *Inter-Laboratory Bias* in Table A.1. If the bias value for a given ion is less than the tabulated value, then the laboratory is considered to have met the DQO for that ion in that sample.
3) Follow the same procedure for every ion in every sample.
4) If the calculated *Inter-Network Bias* value does not meet the DQO for a particular ion in one or more of the samples, then the laboratory is deemed not to have met the DQO for that ion in that study.

Example: Laboratory's reported sulphate value = 2.31 mg L^{-1}
Median sulphate value from all laboratories = 2.54 mg L^{-1}
Laboratory Bias = 100 • (2.31 – 2.54) / 2.54 = -9.1%
Laboratory Bias DQO for sulphate (Table A.1) = $\pm 7\%$
Since *Laboratory Bias* > DQO, the DQO for sulphate for that sample was not met by the laboratory.

The DQOs for *Inter-Laboratory Bias* are given in relative units (i.e., a percentage of the median concentration) rather than in absolute concentration units as was done for the other DQOs. Relative units were chosen here because there was a linear relationship between the inter-network bias and the ion concentrations in the samples analyzed by the 65-70 laboratories, i.e., the *Inter-Network Bias* was larger in samples with higher ion concentrations. Relative units (%) were therefore chosen as a simplest and direct way of compensating for this effect.

A.6 CALIBRATION LEVELS

Multi-point calibration curves are mandatory for all ion determinations in GAW laboratories. As a general rule, 5 to 10 calibration solutions should be used to formulate each calibration curve. Even more solutions should be used when the analytical range is large, when the calibration curves are not linear, or when many of the concentrations in an analytical run are at or near the analytical detection limit. The concentrations of the 5 to 10 calibration solutions should vary evenly between the 2nd to the 98th percentile values of the precipitation chemistry samples routinely analyzed by the laboratory. The exception to the foregoing is pH, for which two low-conductivity calibration solutions are recommended for calibration (pH = 4.0 and 7.0). To compensate for the paucity of calibration standards, several pH check solutions (i.e., stable low conductivity solutions with certified pH) should be included in each batch of samples to ensure that the pH meter is in control.

A.7 DATA COMPLETENESS

Data Completeness is an important data quality indicator when measurement data are summarized statistically over monthly, seasonal, quarterly or annual periods. This is because summary statistics (e.g., the mean, median, and standard deviation) can be highly misleading if large amounts of data are missing or deemed invalid during the summary period. It is therefore incumbent upon all reporting agencies to ensure that they have a sufficient amount of data before reporting their summary statistics. A detailed analysis of the effects of missing data on precipitation chemistry statistics can be found in Sirois (1990).

Two Data Quality Objectives for *Data Completeness* were selected for the GAW Precipitation Chemistry Programme, namely:

The *Percent Precipitation Coverage Length* (%PCL). %PCL is the percentage of a summary period (e.g., month, season, year) for which information is available on whether precipitation occurred or not. In practice, this refers to the percentage of the summary period that a standard precipitation gauge was operating properly and reporting precipitation depths. If precipitation was known to have occurred but no measurement of precipitation depth was made, then it is considered that there was no knowledge of precipitation occurrence. Example: if a standard rain gauge reported data properly for 300 of 365 days in a year (including both precipitation and non-precipitation days), then the %PCL = 300/365 = 82.2%.

The *Percent Total Precipitation* (%TP). %TP for a given summary period (e.g., month, season, year) is the percentage of the total precipitation depth measured by a standard gauge *that was associated with valid precipitation chemistry data*. Example: if a standard precipitation gauge measures a total of 1000 mm in a year but the total standard gauge depth associated with the valid precipitation chemistry samples is 782 mm, then the %TP = 78.2%. Note that the %TP must be calculated for each ion.

The Data Quality Objectives for *Data Completeness* as specified below and in Table A.1 were taken from Olsen et al. (1990):

GAW DQO for Annual Data Completeness

%PCL:	%TP
Annual ≥90%	Annual ≥70%
Every quarter ≥60%	Every quarter ≥60%

GAW DQO for Seasonal Data Completeness

%PCL ≥90%
%TP ≥70%

Each GAW site should calculate its data completeness values for seasonal, annual and quarterly periods as follows:

$$\%PCL = 100 \bullet \frac{M}{N}$$ Eq. A-5

where

M = Number of days during which the standard gauge worked properly and reported data

N = Total number of days in the year, season or quarter.

Note that a standard gauge that detects no precipitation on dry days is considered to be operating and reporting properly in this calculation.

$$\%TP = 100 \bullet \frac{M}{N}$$ Eq. A-6

where

M = Total precipitation depth during the summary period associated with samples having valid, non-missing ion concentrations

N = Total precipitation depth associated with all samples collected during the summary period.

The calculated values of *%PCL* and *%TP* should be compared against the Data Quality Objectives listed in Table A.1. Note that networks must satisfy both the annual and quarterly *Data Completeness* DQOs when reporting their summary statistics for annual periods. This prevents biases from occurring in the annual statistics caused by large amounts of missing data within one or more seasons of the year.

The *Data Completeness* DQO for the standard gauge depth measurements has been set at %PCL = 95% for a given annual period and %PCL = 90% for each of the calendar quarters with the annual period. This means that a standard gauge depth measurement must be made for every sampling period, with little to no tolerance for lost or missing data. The stricter requirement imposed for the standard gauge depth measurements is because the missing and lost data induce a direct negative bias into the deposition estimates derived by Equation 5-1, Chapter 5, Section 5.8 (Data Analysis).

A.8   REFERENCES

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Table A.1 : Data Quality Objectives (DQOs) for GAW Precipitation Chemistry Measurements.

Measurement Parameter	Detection Limits	Precision Overall	Precision Laboratory	Inter-Network Bias Overall	Inter-Network Bias Laboratory	Calibration Levels	Completeness
pH (pH units)	*	± 0.1 pH unit at pH > 5 ± 0.03 pH unit at pH < 5	± 0.04 pH unit at pH > 5 ± 0.02 pH unit at pH < 5	±0.24 pH unit at pH > 5 ±0.12 pH unit at pH < 5	± 0.07 pH unit	4.0 & 7.0 low ionic strength reference solution	90 %PCL[1] 70 %TP[2]
Conductivity (μS cm^{-1})	± 2	*	*	*	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Acidity/ Alkalinity (μmole L^{-1})	*	*	*	*	± 25%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
SO$_4^{2-}$ (mg L^{-1})	0.06	0.06	0.03	± 0.42	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
NO$_3^-$ (mg L^{-1})	0.09	0.06	0.03	± 0.36	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Cl$^-$ (mg L^{-1})	0.04	0.02	0.02	± 0.05	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
NH$_4^+$ (mg L^{-1})	0.02	0.02	0.01	± 0.08	± 7%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Ca^{++} (mg L^{-1})	0.02	0.02	0.01	± 0.05	± 15%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Mg^{++} (mg L^{-1})	0.01	0.01	0.01	± 0.02	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Na$^+$ (mg L^{-1})	0.02	0.01	0.01	± 0.03	± 10%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
K$^+$ (mg L^{-1})	0.02	0.01	0.01	± 0.02	± 20%	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Formate ((mg L^{-1})	*	*	*	*	*	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Acetate (mg L^{-1})	*	*	*	*	*	In a range between the 2nd & 98th percentile concentrations	90 %PCL[1] 70 %TP[2]
Standard Gauge Precipitation Depth (mm)	0.2	0.2 daily 0.3 weekly	n/a n/a	± 5% for rain ± 15% for snow ± 10% rain+snow	n/a n/a	In a range between the 2nd & 98th percentile depth values	95 %PCL - annual 90 %PCL - quarterly
Sample Depth (mm)	0.2	0.1 daily 0.3 weekly	n/a n/a	± 5% for rain ± 15% for snow ± 10% rain+snow	n/a n/a	In a range between the 2nd & 98th percentile depth values	90 %PCL[1] 70 %TP[2]

* -- Not Available

n/a -- Not Applicable

1) %PCL is Percent Precipitation Coverage Length (see Section 6.10.3). The 90%PCL completeness criterion applies to annual and seasonal summary periods. For annual summary periods, each quarter of the year must also meet a 60%PCL completeness criterion.

2) %TP is the Percent Total Precipitation (see Section 6.10.3). The 70% completeness criterion applies to annual and seasonal summary periods. For annual summary periods, each quarter of the year must also meet a 60%TP completeness criterion.

GAW PRECIPITATION CHEMISTRY PROGRAMME SITE
DESCRIPTION FORMS

This appendix contains a series of forms that may be used by the NMHS or site operators to describe their GAW precipitation chemistry field sites. These are not required forms for submission of data to the GAW precipitation chemistry programme or World Data Centre for Precipitation Chemistry (WDCPC).

The forms are intended as aids in selecting appropriate locations for new sites and in reviewing existing sites as to whether or not they meet siting criteria. They can be used to document important site information and through periodic review and updating they provide a chronology of site changes over time. They may also be used to assess whether a site is a regional or global GAW site. The forms are also a valuable tool for on-going internal site review or site auditing.

Each NMHS is encouraged to adopt these forms as part of their internal quality control programme or create similar ones tailored to their specific needs.

GAW PRECIPITATION CHEMISTRY PROGRAMME SITE DESCRIPTION FORM

Date (dd/mm/yyyy): _____   **(circle one) 1. New site   2. Site Change   3. Revision**

1.   GENERAL DESCRIPTION OF SITE

Site Identification	Name:	Site Code (assigned by GAW-PC):		
Site Address (include country)				
Site Classification	1. Global	2. Regional	3. Other (specify)	
Site Coordinates (in decimal degrees)	Latitude North/South		Longitude East/West	
Site Altitude (metres above or below sea level)				

2.   SITE ADMINISTRATION

Site Contact Person	
Site Mailing Address/Email	
Site Phone / Fax Number	
Laboratory Contact Person	
Lab Mailing Address/Email	
Lab Phone /Fax Number	
Site Ownership	
Operating Agency	
If site is part of another network, please name network	

3.   SITE INSTRUMENTATION

Instrument	Type/Model	Height of orifice above the ground (metres)
Precipitation Sampler		
Rain Gauge		

4. REGIONAL DESCRIPTION OF THE SITE

Regional scale (10km - 50km) Attach sketch map to this table.
Do not leave sections empty: indicate if "none" or "unknown."

Item	North Direction (NW-NE)	East Direction (NE-SE)	South Direction (SE-SW)	West Direction (SW-NW)
Main stationary air pollution sources >10 tonnes per year (SO_X, NO_X, NH_3, HCl etc.). For global site, include major emission sources >1,000 tonnes per year out to 150km				
Major roads with >5,000 vehicles per day (estimate traffic density)				
Cities with populations > 10,000 persons. For global site, include cities with populations > 100,000 out to 200km. Give approximate populations.				

5. LOCAL DESCRIPTION OF THE SITE

Local scale (150 m - 10 km) Attach sketch map to this table.
Do not leave sections empty: indicate if "none" or "unknown."

Item	North Direction (NW-NE)	East Direction (NE-SE)	South Direction (SE-SW)	West Direction (SW-NW)
Roads, with estimated traffic densities >1,000 vehicles per day.				
Airports, railways, or ship routes, with estimated traffic densities.				
Irrigated fields, farms or stock farms, and the name of crops and stocks.				
Stationary air pollution Sources >10 tonnes per year emissions (SO_X, NO_X, NH_3, HCl etc.).				
Cities or towns with > 1,000 persons, and their approximate populations.				

6. ON-SITE DESCRIPTION

On-site (within 150 m) Attach sketch map to this table.
Do not leave sections empty: indicate if "none" or "unknown."

Item	North Direction (NW-NE)	East Direction (NE-SE)	South Direction (SE-SW)	West Direction (SW-NW)
Trees, poles, fences and buildings, with heights indicated.				
Incinerators, domestic heating, parking lots, storage of fuel and agricultural products, dairy farm, or other livestock.				
Slope of the site (range of degrees)				
Ground cover type at the site (% gravel, grass covered, bare soil, rock, etc.).				
Type of environment at the site (presence of forests, rivers, lakes, marshes, farms or fields, tundra, desert, grassland, etc).				
Roads and their traffic densities*.				

*Describe roads with >100 vehicles per day for global sites, and roads with >1,000 vehicles per day for regional sites.

PREPARING CONTROL SOLUTIONS

Stock solutions and subsequent control solutions can be made from the salts NaCl, KNO_3 and NH_4NO_3, which should be dried overnight in a desiccator before weighing the proper amounts, and from $CaSO_4\cdot2H_2O$ and $MgSO_4\cdot7H_2O$, which should not be dried because they will loose some of the crystalline water. Sulphuric acid (H_2SO_4 e.g. from a Titrisol ampoule) may be used to acidify the solutions. The stock solutions in Table C.1 below should be stable for 2 years when kept in polypropylene bottles in a refrigerator.

The stock solutions in Table C.1 are used to prepare a set of the secondary, more diluted stock solutions in Table C.2. The secondary solutions should also be stored in polypropylene bottles in a refrigerator. New secondary stock solutions should be prepared every six months.

The control solutions in Table C.3 are prepared from the secondary stock solutions (Table C.2) by diluting 20.00 mL of the secondary solutions to 1000 mL. The control solutions should be kept in polypropylene bottles in a refrigerator. They are stable for no more than one month and it is recommended that fresh control solutions be made weekly.

Table C.1: Example of Stock Solutions for Synthetic Control Solutions, and of Products Used by Some Experienced Laboratories.

Compound	Producer	Quantity	Volume deionized water	Concentration in stock solution
NaCl	Merck, p.a. 6404	0.4770 g	500 mL	375.3 mg Na^+ mL^{-1} 578.7 mg Cl^- mL^{-1}
KNO_3	Merck, p.a. 5063	0.6585 g	500 mL	509.3 mg K^+ mL^{-1} 807.4 mg NO_3^- mL^{-1}
NH_4NO_3	Merck, p.a. 1188	1.1458 g	500 mL	516.4 mg NH_4^+ mL^{-1} 1775.1 mg NO_3^- mL^{-1}
$CaSO_4\cdot2H_2O$	Merck, p.a. 2161	0.4115 g	500 mL	191.6 mg Ca^{2+} mL^{-1} 459.3 mg SO_4^{2-} mL^{-1}
$MgSO_4\cdot7H_2O$	Merck, p.a. 5886	0.7850 g	500 mL	154.9 mg Mg^{2+} mL^{-1} 611.8 mg SO_4^{2-} mL^{-1}
H_2SO_4	Merck, Titrisol 9984 0.0500 mol	Contents of the ampoule	1000 mL	0.1000M H^+ L^{-1} 4802 mg SO_4^{2-} mL^{-1}

Table C.2: Example of Preparation of Secondary Stock Solutions. Volumes are of Stock Solutions to be Diluted to Generate 500 mL Solutions.

Secondary stock solution I (amount diluted to 500 mL)	Secondary stock solution II (amount diluted to 500 mL)
50.00 mL NaCl	20.00 mL NaCl
30.00 mL KNO_3	10.00 mL KNO_3
40.00 mL NH_4NO_3	20.00 mL NH_4NO_3
35.00 mL $CaSO_4$	20.00 mL $CaSO_4$
50.00 mL $MgSO_4$	30.00 mL $MgSO_4$
25.00 mL 0.1000N H_2SO_4	7.500 mL 0.1000N H_2SO_4

Table C.3: Control Solutions, Representative for Parts of Europe.

Component	Control solution C1	Control solution C2
SO_4^{2-}	6.669 µg SO_4^{2-} mL^{-1}	2.544 µg SO_4^{2-} mL^{-1}
NO_3^-	3.811 µg NO_3^- mL^{-1}	1.744 µg NO_3^- mL^{-1}
Cl^-	1.157 µg Cl^- mL^{-1}	0.463 µg Cl^- mL^{-1}
NH_4^+	0.827 µg NH_4^+ mL^{-1}	0.413 µg NH_4^+ mL^{-1}
Na^+	0.751 µg Na^+ mL^{-1}	0.300 µg Na^+ mL^{-1}
K^+	0.611 µg K^+ mL^{-1}	0.204 µg K^+ mL^{-1}
Ca^{2+}	0.268 µg Ca^{2+} mL^{-1}	0.153 µg Ca^{2+} mL^{-1}
Mg^{2+}	0.310 µg Mg^{2+} mL^{-1}	0.186 µg Mg^{2+} mL^{-1}
H^+	100 µe L^{-1} (pH 4.00)	30 µe L^{-1} (pH 4.52)
Conductivity (25°C)	61.2 µS cm^{-1}	21.7 µS cm^{-1}

Ion chromatography requires the constant use of calibration solutions. Several companies have a wide range of single and multi-element solutions for this purpose (See Appendix D). As an example, below is a list of standard solutions available from one such company (Merck):

- Chloride 1000 mg L^{-1}, prepared from sodium chloride in water, accurate value determined by argentometric titration and given on the product form
- Nitrate 1000 mg L^{-1}, prepared from sodium nitrate in water, accurate value determined by alkalimetric titration and given on the product form
- Sulphate 1000 mg L^{-1}, prepared from sodium sulphate in water, accurate value determined by precipitation titration and given on the product form
- Nitrite 1000 mg L^{-1}, prepared from sodium nitrite in water, accurate value determined by cerimetric titration and given on the product form
- Sodium 1000 mg L^{-1}, prepared from sodium nitrate in water, accurate value determined by acidimetric titration and given on the product form
- Potassium 1000 mg L^{-1}, prepared from potassium nitrate in water, accurate value determined by acidimetric titration and given on the product form
- Ammonium 1000 mg L^{-1}, prepared from ammonium chloride in water, accurate value determined by argentometric titration and given on the product form
- Calcium 1000 mg L^{-1}, prepared from calcium nitrate in nitric acid 0.5 mol L^{-1}, accurate value determined by complexometric titration and given on the product form
- Magnesium 1000 mg L^{-1}, prepared from magnesium nitrate in nitric acid 0.5 mol L^{-1}, accurate value determined by complexometric titration and given on the product form.

SOURCES FOR CERTIFIED REFERENCE MATERIALS

High-Purity Standards
P.O. Box 41727
Charleston, South Carolina 29243
USA

Tel: +1-843-767-7900
Fax: +1-843-767-7906
Web: *http://www.hps.net* or
        http://www.hps.net/simrain.html
Simulated Rainwater samples SR-I (low concentrations) and SR-II (high concentrations)
(Used by NADP, CASTNET, USGS)

Delta Scientific Lab Products Ltd.
1287 Matheson Blvd. East
Mississauga, Ontario L4W 2S7
Canada

Tel: +1-905-629-4545 or +1-800-387-3256
Fax: +1-905-629-7249
Email: *ken@deltascientific-labproducts.com*
(Used by CAPMoN. Not certified for NH4 or NO3)

Merck Headquarter
Frankfurter Str. 250
D-64293 Darmstadt
Germany

Tel.: +49-6151- 72-0
Fax: +49-6151- 72-2000
Web: *http://pb.merck.de*
Email: *service@merck.de*
Merck has a wide range of single and multi-ion or -element solutions for different purposes. These
include Certipure® and Titrisol® reference materials for calibration of IC, AAS, AES, GFAAS, ICP, pH
and conductivity measurements. The reference materials are traceable to NIST (National Institute of
Standards and Technology, Gaithersburg, USA) reference materials.

National Water Research Institute
Environment Canada
P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario L7R 4A6
Canada

Tel: +1-905-336-4653
Fax: +1-905-336-8914
Web: *http://www.nwri.ca/nlet/nlet.html*
Email: *crms.nwri@cciw.ca*
Rainwater samples (Catalogue #AES-02 and Rain-97)
(Used by various North American laboratories)

Community Bureau of Reference (BCR) – Certified Reference Materials
IRMM - Institute for Reference Materials and Measurements
Reference Materials Unit
Attn. BCR Sales
Retieseweg, B-2440 Geel
Belgium

Tel: +32-(0) 14-571 705
Fax: +32-(0) 14-590 406
Web: *http://www.irmm.jrc.be/mrm.html*
Email: *bcr.sales@irmm.jrc.be*
Simulated rainwater CRM 408 (low contents) and CRM 409 (high contents)
(Used by Waterworks' Testing and Research Institute (KIWA) Norway, and numerous European laboratories).

Wako Pure Chemical Industries, Ltd.
1-2, Dshomachi 3-Chome,
Chuo-ku, Osaka 540-8605
Japan:

Tel: +81-6-6203-3471
Fax: +81-6-6201-5964
Web: *http://www.wako-chem.co.jp*
This company provides simulated rainwater samples, and a wide range of single-ion, multi-ion, or multi-element solutions for various purposes. The reference materials for major ions in precipitation are traceable to JCSS (Japan Calibration Service System, *http://www.jcsslabo.or.jp*).
(Used by EANET and various Japanese laboratories).

Kanto Chemical Co. Inc.
Marusan Bldg, 11-5, Nihonbashi honcho 3-chome,
Chuo-ku, TOKYO 103
Japan

Tel: +81-3-3639-8301
Fax: +81-3-3639-9435
Web: *http://www.kanto.co.jp*
Email: *kida@gms.kanto.co.jp*
This company provides a wide range of single-ion, multi-ion, or multi-element solutions for various purposes. The reference materials for major ions in precipitation are traceable to JCSS (Japan Calibration Service System, *http://www.jcsslabo.or.jp*).
(Used by various Japanese laboratories).

FLAGGING PRECIPITATION RESULTS WITH POOR ION BALANCES AS VALID OR INVALID: A PROPOSED APPROACH FROM EMEP

Jan Schaug and Anne-Gunn Hjellbrekke
Chemical Coordinating Centre of EMEP

The ion balance (IB) gives an indication of precipitation data quality since the concentrations of all negatively charged ions in a sample necessarily will have to equal the sum of the positively charged ions. When the concentrations of all major ions in a precipitation sample have been measured, a poor IB *may* therefore indicate a poor data quality, and it is proposed that the sample results be flagged as described below.

This proposal aims at flagging data that are considered to have a quality less good than could be expected from EMEP's Data Quality Objectives (DQOs). The flagged data are divided into two groups; data that are considered to have a quality sufficiently high to be useful for EMEP and therefore are considered valid and should be used, and secondly data that are considered invalid. The criteria are summarised in Figure E.2.

A good IB is not a guarantee for good data quality. It is important to bear in mind that even though a good IB tends to indicate adequate sample handling and a good analytical skill in the laboratory, other factors may reduce the data applicability for EMEP and the overall data quality; e.g. local sources or sampling problems. Even sample contamination will not necessarily be detected through an ion balance calculation, i.e. when the contamination takes place before the analyses have been started.

It is proposed that the flags described below be linked to each result from a specific precipitation sample. Other information about the sample results may, however, override the IB flagging, and validate some of the results.

Random errors have been used below as a basis for the criteria. Systematic errors are considered either to be insignificant or already corrected for.

E.1   DEFINITIONS

C_i is the concentration of ion type *i* in a specific sample, expressed in $\mu e\ L^{-1}$. No index has been used for sample number below. IS is the sum of all ion concentrations, and ID is the difference between the sum of the cation concentrations and the sum of the anion concentrations. Both IS and ID are expressed in $\mu e\ L^{-1}$. ID would in ideal cases be zero. The ion balance, IB, expresses this difference ID in percent of the sum of all concentrations IS.

$$IS = \sum_{cations} C_i + \sum_{anions} C_i \qquad\qquad \text{Eq. E-1}$$

$$ID = \sum_{cations} C_i - \sum_{anions} C_i \qquad\qquad \text{Eq. E-2}$$

$$IB = (ID/IS) \bullet 10^2 \qquad\qquad \text{Eq. E-3}$$

All measurements have in reality some errors attached them, both systematic and random, and the ion difference ID and the balance IB will never be exactly zero. S_{ci} is defined as the standard uncertainty in the concentration of ion type *i* for a large number of samples or analyses at concentration C_i and is expressed in $\mu e\ L^{-1}$. S_{IB} is the corresponding standard uncertainty in IB that

can be calculated from the uncertainties S_{ci}. S_{IB}'s unit is as IB's percent, and is given by

$$S_{IB}^{2} = \left(1/IS^{2}\right)\left\{ \sum_{anions} \left[(IB+100)^{2} S_{ci}^{2}\right] + \sum_{cations} \left[(IB-100)^{2} S_{ci}^{2}\right] \right\}$$ Eq. E-4

The standard uncertainty in the concentrations, S_{ci}, normally increases with the concentrations themselves. S_{IB} will depend on the composition and concentrations in the sample and increases as IS decreases, i.e. S_{IB} will be high when concentrations are low.

Since it is assumed that all ions have been analyzed and all systematic errors removed, IB equals zero and equation E-4 is reduced to

$$S_{IB} = \sqrt{\sum_{all\_ions} S_{ci}^{2}} \bullet 10^{2}/IS$$ Eq. E-5

Normal distributions have been assumed below, and S_{ci} may be estimated from repeated analysis of the sample.

E.2 ION BALANCE IN DATA COMPLYING WITH THE DQO

Instead of estimating S_{ci} from analyses, S_{IB} can be estimated from the DQO if S_{ci} can be expressed by the DQO. The DQO, which give the maximum errors in the analytical chemical work, will therefore now be considered as 95% confidence limits for each chemical specie rather than strict upper limits. The DQO for a specific ion *i* will in this case span an interval of concentrations equal to ±1.96 S_{ci}, assuming normal distribution. This assumption obviously relaxes the requirements to analytical accuracy somewhat since 5% of the values will be outside the DQO.

The requirements given in the DQO (EMEP/CCC-Report 1/95) are that a concentration of component *i*, C_i, should be within $C_i \pm a \cdot C_i$ where a is either 0.10 or 0.15 (except for the very lowest concentrations).

When combining this with the assumptions in the preceding paragraph,

$$a \bullet C_i = 1.96 \bullet S_{ci} , \text{ or}$$ Eq. E-6

$$S_{ci} = \left(a/1.96\right) \bullet C_i$$ Eq. E-7

where a=0.10 for SO_4^{2-} and NO_3^-, and a=0.15 for all other ions.

Equations E-7 and E-5 can be used to estimate the expected uncertainty in IB, i.e. the limits for IB for measurements that comply with the DQO given the assumptions above.

E.3 CALCULATIONS OF ION BALANCE IN DATA COMPLYING WITH THE DQO

Estimations of S_{IB} have been carried out for a series of different concentrations and compositions from the DQO. The calculations demonstrate that S_{IB} depends on the composition of the sample as well as on the concentrations, and that S_{IB} obtains its highest values for two-component samples e.g. of ammonium sulphate with other components at the detection limit. The lowest S_{IB} occurs in samples with approximately equal concentrations of all ions (i.e. for EMEP, concentrations of sulphate, nitrate and chloride all being equal and twice the concentrations of ammonium, hydrogen ions, sodium, magnesium calcium, and potassium). Figure E.1 presents the approximate 95% confidence limits (i.e. ±2 S_{IB}), which can be expected from the DQO for two different sample types.

Assuming negligible systematic errors, the 95% confidence interval ($\approx 2 \cdot S_{IB}$) is expected to correspond to 7.1% to 10.8% for a sum of concentrations (IS) at 100 μe L^{-1} (Figure E.1) for the two compositions above. At IS equal to 1000 μe L^{-1}, the confidence interval correspond to ±4.6% to ±9.0%. For IS less than 100 μe L^{-1}, S_{IB}, increases strongly.

E.4   ION BALANCE IN SAMPLES WITH PH >5.5

It is well known that samples having pH values above 5.5 - 6.0 often have an apparent deficit of anions (e.g. EMEP/CCC-Report 8/97). This seems to differ from one measurement site to the next and is not yet well understood. Obviously this could be explained by components with weak acidic functional groups that are not analyzed, e.g. such as organic substances. The estimations above can therefore often not easily be applied to precipitation samples with pH above 5.5. Separate criteria for samples with and without pH >5.5 have therefore been proposed below.

E.5   CRITERIA FOR FLAGGING ION BALANCES IN PRECIPITATION SAMPLES WITH PH ≤5.5

The estimated standard uncertainties S_{IB} and confidence intervals making use of the two compositions in Figure E.1 have been used to set quality criteria for precipitation samples, a distinction was, however, made between samples with an ion sum IS higher and lower than 100 μe L^{-1}.

IS ≥100 μe L^{-1}

Samples with an ion balance within ±10% (Figure E.1) can be considered to contain valid data in accordance with the DQO. Valid, non-flagged precipitation data should therefore have an ion balance within ±10%.

Correspondingly it is suggested that samples within an ion balance twice the limits in Figure E.1 should be considered valid, but should be flagged to indicate that the quality is expected to be lower than targeted. Valid but flagged data should have an ion balance between –20% to –10% or +10% to +20%.

Results from samples outside 20% can be considered invalid. The 20% corresponds approximately to the confidence limits for data within 2 DQO.

IS <100 μe L^{-1}

When the sum of all ion concentrations is less than 100 μe L^{-1}, the criteria have been based on the ion difference ID (in μe L^{-1}) rather than IB due to the strong increase in IB with decreasing IS. When IS is exactly 100 μe L^{-1}, the IB limits 10% and 20% correspond exactly to ID equal to 10 and 20 μe L^{-1}, as seen from (3).

For IS <100 μe L^{-1} these limits at 10 and 20 μe L^{-1} are suggested to be kept unchanged, i.e., a sample with an ion difference within ±10 μe L^{-1} can be considered valid, and within ±20 μe L^{-1} as valid, but is to be flagged.

Samples with ion differences outside ±20 μe L^{-1} are considered to contain invalid data.

E.6   CRITERIA FOR FLAGGING ION BALANCES IN PRECIPITATION SAMPLES WITH PH >5.5

As mentioned above there is often an apparent anion deficit that is not well understood, and the size of the deficit may be different from one site to the next. Relaxed criteria should therefore be applied at present. The criteria have been based on the discussion above as well as on inspection of today's ion balances. They should take care of the ion balance differences EMEP has, and take care of major errors without excluding too much data.

<u>IS ≥100 μe L^{-1}</u>

Since there is an apparent deficit of anions ("too much cations"), the criterion for valid non-flagged data has been made less strict when this occurs. It is suggested that an upper limit for IB be set to +20% for valid non-flagged data. The corresponding limit at lower pH values (above) was 10%. It is suggested that the criteria for valid non-flagged data be kept at IB ≥-10% (as for pH <5.5) on the "negative IB side".

When the ion balance is larger than +20% and the data otherwise appear to be valid, they should be flagged. This means that data are not assumed to be invalid due to a high ion balance alone.

On the "negative IB side" it is proposed that the criterion be kept unchanged, i.e. if IB is between -10% and -20% data can be considered valid, but will be flagged.

If IB is larger than -20% the data are considered invalid.

<u>IS <100 μe L^{-1}</u>

For low concentration samples with IS <100 μe L^{-1} the criteria can be set similar to samples with IS ≥100 μe L^{-1}, but replacing the ion balance IB with the difference ID.

The criteria are summarised in Figure E.2.
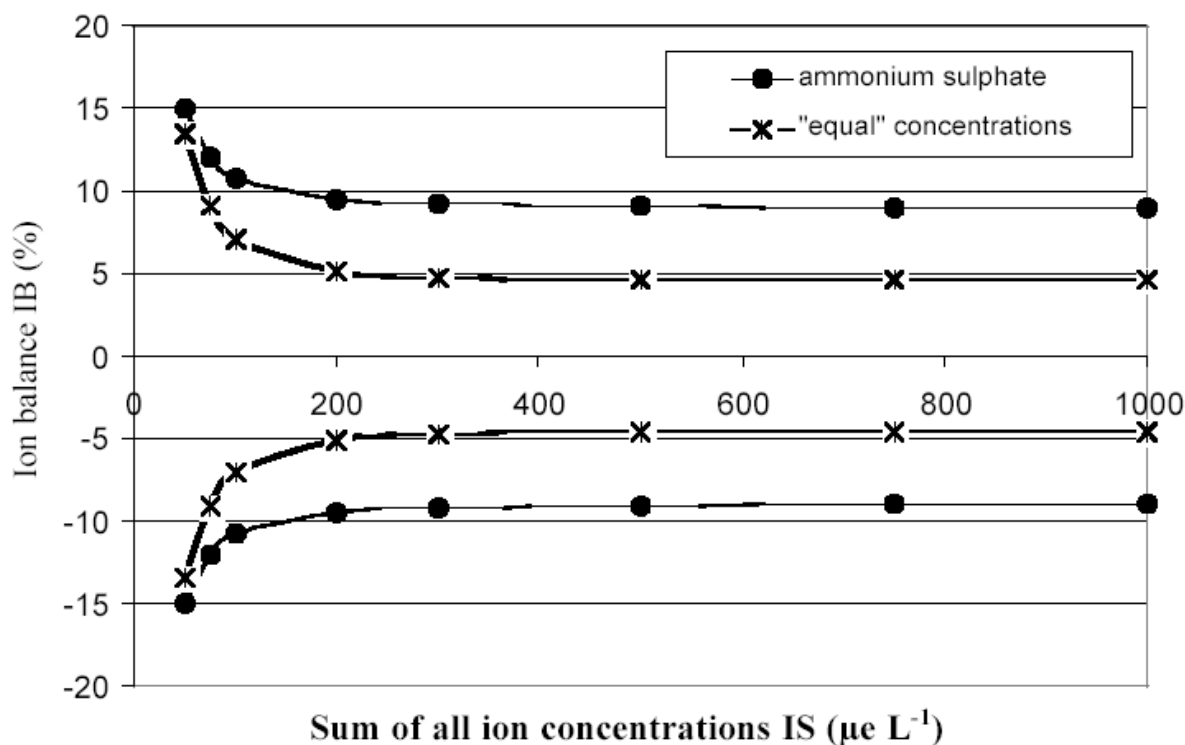
Figure E.1. Approximate 95% confidence interval for the ion balance for data complying with the DQO, calculated as ±2 S$_{IB}$. Upper and lower graphs are valid for a solution of ammonium sulphate with other components at the detection limit. The two other graphs are based on a solution with "equal" concentrations as defined above. It is assumed that all components have been measured and that bias of any significance has been removed.

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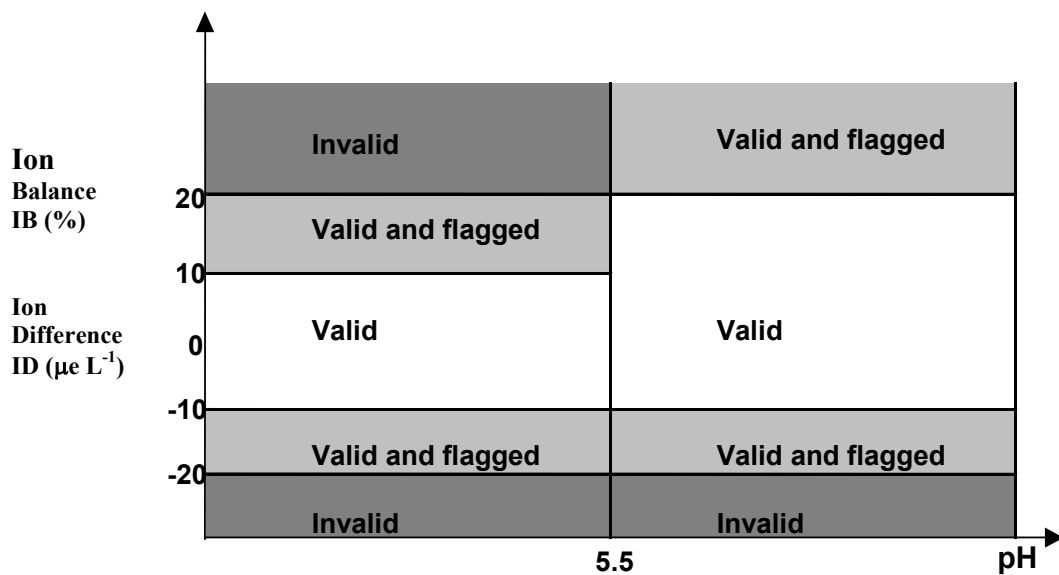
Figure E.2: *Criteria when the sum of ions IS $\geq$100 μe L^{-1} is based on the ion balance (IB) in percent. Criteria when the sum of ions IS <100 μe L^{-1} is based on the difference between cation and anion concentrations (ID) in μe L^{-1}.*

GUIDELINES FOR SUBMISSION OF GAW PRECIPITATION CHEMISTRY DATA TO QA/SAC AMERICAS

This appendix provides detailed information on the data format that must be used for submittal of GAW Precipitation Chemistry data to QA/SAC Americas. By using the data quality and data submittal information in Chapter 5 plus the detailed format descriptions in this appendix, a National Meteorological and Hydrological Service has all the information it needs to submit acceptable data.
·

Section 5 (Data Management) and Appendix F are being updated and re-written. Please contact Van Bowersox (manager@qasac-americas.org) for further information or questions about data submission to the World Data Centre for Precipitation Chemistry or the Quality Assurance -- Science Activity Centre.

LABORATORY AND STATION REGISTRATION FORMS FOR THE GAW PRECIPITATION CHEMISTRY PROGRAMME

This appendix contains two forms:

1) *The WMO/GAW Precipitation Chemistry Laboratory Registration Form.* This form can be used to register a new laboratory and precipitation chemistry network with the QA/SAC Americas or to update the information for an existing laboratory or network within the programme.

2) *The WMO/GAW Precipitation Chemistry Station Registration Form.* This form can be used to register a new precipitation chemistry station with the QA/SAC Americas or to update information on an existing station. The WMO/GAW is primarily interested in data that are globally or regionally representative. Please do not register stations that are only locally representative.
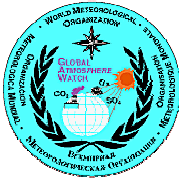
WMO/GAW
Precipitation Chemistry
Laboratory Registration Form

This form can be used to register a new laboratory and precipitation chemistry network to the QA/SAC Americas or to update the information for an existing programme. To make an update, the laboratory id MUST be filled in. When making an update, fields may be left blank if they have not changed.

Please print or type in the information.

1. Laboratory ID (if known)	**2. Primary Contact Person**	
	Circle one: Dr. Mr. Mrs. Ms.	(Please enter the Surname or Family name using uppercase letters)

Laboratory ID: 7 0 0 ☐ ☐ ☐

Name   _____

  _____

Title   _____

3a. Agency Name (in English)	**3b. Agency Name** (in the local language)

4a. Address (in English) (Please use a street address and avoid using a post office box number.)	**4b. Address** (in the local language) (Please use a street address and avoid using a post office box number.)

5a. Country (in English)	**5b. Country** (in the local language)

6. Telephone Number	**7. Fax Number**	**8. E-mail address**

9. Parameters Measured Circle all that apply:	**10. Web Site Address**
Major Ions (including pH and conductivity) Trace Metals Organic Acids Dry Deposition	**11. Additional Contacts** (List other contact people at the laboratory. Include titles, fax numbers and e-mail addresses. Continue on back, if needed.)

Send the completed form to: QA/SAC Americas, Atmospheric Sciences Research Centre, 251 Fuller Road, Albany, NY 12203 USA

Fax: +1 518 437 8758
email: qasac@qasac-americas.org

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WMO/GAW
Precipitation Chemistry
Station Registration Form

This form can be used to register a new precipitation chemistry station to the QA/SAC Americas or to update the information for an existing station. To make an update, the station id MUST be filled in. When making an update, fields may be left blank if they have not changed. If you have more than one station, then use a separate form for each station. *Please print or type in the information*.

1a. Station Name

1b. Station ID (if known)

| | | | | | | | | **Q** | **0** | **8** |

2. Is this an active GAW Station?
Circle one:

Yes   No

Former (explain)

3. GAWSIS ID
(for QA/SAC Use)

| | | | | | | |

4. Laboratory (that analyses the samples from this station.)

Laboratory ID   Laboratory Name

| **7** | **0** | **0** | | | |

5. Station Latitude*
(specify South latitudes as a negative value)

| | | | | . | | | |

+/-   (in decimal degrees)

6. Station Longitude*
(specify West longitudes as a negative value)

| | | | | | . | | | |

+/-   (in decimal degrees)

7. Station Elevation
(in metres)

_____

* Note: The latitude and longitude are the coordinates of the station where the station is centred on the precipitation sampler.

8. Date Station Began Operations

| | | | | - | | | - | | |
y   y   y   y   m   m   d   d

9. Date Station Ceased Operations
(if the station is still in operation, then leave blank)

| | | | | - | | | - | | |
y   y   y   y   m   m   d   d

10. Prevailing Climate
Circle one:

Temperate Wet

Temperate Arid

Tropical

Desert

Other (explain)

11. Is the site located within 100 km of an ocean?
Circle one:

Yes   No

12. What is the typical pH of the precipitation?
Circle one:

Acid (pH <5)   Basic (pH>7)

Neutral (5<pH<7)

13. Station Representativeness
(see Chapter 2 in *Manual for the GAW Precipitation Chemistry Programme* for the complete definitions) Circle one:

Global Scale (located in remote areas unaffected by local or regional pollution, volcanic eruptions, fires, dust, etc.)

Regional Scale (located in rural areas away from large population centres and industrial activity)

14. Comments and Deviations from Siting Criteria (see Chapter 2 in *Manual for the GAW Precipitation Chemistry Programme* for the criteria) (Continue on back if more space is needed)

Send the completed form to:

QA/SAC Americas
Atmospheric Sciences Research Centre
251 Fuller Road
Albany, NY 12203 USA

Fax: +1 518 437 8758
email: qasac@qasac-americas.org

Version 2003-04-11

THE WDCPC NON-SEA SALT SULPHATE CORRECTION ALGORITHM

H.1   OVERVIEW

Precipitation samples collected at stations influenced by oceanic air masses can contain sulphur from both marine and non-marine sources. Keene, et al. (1986) and Hawley et al. (1988) suggest that long term oceanic salinity is stable enough to estimate the sea salt sulphate (SS) and non-sea salt sulphate (NSS) based on the mass concentrations of the reference species sodium, and magnesium in seawater[1]. An algorithm consistent with the use of sea salt tracers has been implemented by the WDCPC to estimate the SS and NSS sulphate contributions to wet precipitation samples.

The algorithm employs a series of cascading range tests that compares the sample's ion ratios to those in seawater. Depending on which of the three ions, sodium, magnesium, or chloride, is selected as the best correcting method, one of these formulas is used:

$[NSS\_SO_4] = [SO_4] - (0.25 \times [Na])$ or

$[NSS\_SO_4] = [SO_4] - (2.09 \times [Mg])$ or

$[NSS\_SO_4] = [SO_4] - (0.14 \times [Cl])$

Note: Usually the sodium tracer is used. Because it is non-conservative, the chlorine tracer is used only when the sodium and magnesium sample concentrations are unavailable. The constants are derived from the seawater ratios of sulphate to the tracer species (Keene et al., 1986).

The measured sulphate concentration value is not altered by the algorithm. Instead, the algorithm creates and stores three generated values in the WDCPC database along with the measured total sulphate sulphur concentration, SO4_S:

- Calculated NSS sulphur component (Variable XSO4_S)
- NSS estimation method code (Variable XSO4MET)
- Calculated Below Detection Limit flag for NSS sulphur component (Variable XSO4_SB).

To obtain the SS sulphur from the measured sulphur concentrations in the original sample, data users are required to subtract the NSS amount from total measured SO4_S from the original sample.

Before the algorithm completes execution, it checks for negative values of $[NSS\_SO_4]$. Negative values indicate that the methodology is not sufficiently precise to indicate presence of non-sea salt sulphate. If a negative $[NSS\_SO_4]$ value is found, then it is replaced by +0.00.

H.2   DEFINITIONS

All concentrations are in mgL[-1].

NSS estimation method codes (xso4met)
:
     1: Calculation based upon [na]
     2: Calculation based upon [mg]
     3: Calculation based upon [cl]
     4: $[NSS\_SO_4]$ is set to [so4], because [so4] is BDL

---

[1] Both sets of authors make two important assumptions about the sea salt component in precipitation: 1) fractionation does not occur during either air mass formation or deposition, and 2) the conservative reference species found in the sample are comprised solely from sea salt. Because of both assumptions, sodium and magnesium are strongly preferred over chlorine as tracers of sea salt.

5: [NSS_ SO$_4$] is set to missing, because all the tracer ions are missing[2]
6: [NSS_ SO$_4$] is set to missing, because [so4] is missing
7: [NSS_ SO$_4$] is set to [so4], because all the tracer ions are BDL
8: [NSS_ SO$_4$] is set to [so4], because of unusual or non-standard conditions
9: [NSS_ SO$_4$] is set to [so4], because the station is not within 100km of the ocean.

NSS below detection limit (BDL) flag (xso4_sb):

0: [NSS_ SO$_4$] is above the detection limit
1: [NSS_ SO$_4$] is BDL, but is a positive value
2: [NSS_ SO$_4$] has been set to +0.00, after initially calculating a negative concentration.

H.3   DETAILED PSEUDO CODE

Convert sulphate as sulphur [so4_s] to sulphate [so4] /* the database stores sulphate as sulphur, not sulphate */

Assume that [NSS_ SO$_4$] is not BDL. (xso4b = 0)

The following constants were determined from the seawater concentrations of sulphate and its potential tracers (in mg L^{-1}):
so4_sw = 2700   -- the seawater sulphate concentration
mg_sw = 1290   -- the seawater magnesium concentration
na_sw = 10800   -- the seawater sodium concentration
cl_sw = 19374   -- the seawater chloride concentration.

na_corr = so4_sw/na_sw;   -- the sodium correction factor for seawater sulphate = 0.25
mg_corr = so4_sw/mg_sw;   -- the magnesium correction factor for seawater sulphate = 2.09
cl_corr = so4_sw/cl_sw;   -- the chloride correction factor for seawater sulphate = 0.14

IF the station IS NOT within 100km of the ocean THEN DO
        do not calculate Sea salt fraction, however set xso4 = so4
        set xso4met = 9   /* Station is not within 100km */
        END If
ELSE IF (NOT Oceanic derived salt) OR (Severe Weather Occurred) THEN DO
        do not calculate Sea salt fraction, however set xso4 = so4
        set xso4met = 8   /* Non-standard conditions */
        END Else If
ELSE DO   /* Process the stations that are within 100km under standard conditions */
        CASE when the sulphate concentration is missing DO
                set xso4met = 6 /* Sulphate is missing */
                set xso4 = to the 'missing' value
                END Case
        CASE when the sulphate concentration is BDL DO
                set xso4met = 4 /* Sulphate is BDL */
                set xso4b = 1   /* The NSS is BDL */
                set xso4 = [so4]   /* assume that all the sulphate is NSS */
                END Case
        CASE when [cl] is NOT (missing or BDL) AND
                [mg] is NOT (missing or BDL) AND
                [na] is NOT (missing or BDL) DO
                Compute the ratio of the tracer ions in the sample to the ratios of the tracer ions found
                in seawater. When the ratio of mg to na (ratio A) is close to one, the na correction

---

[2] Also, xso4net is set to 5 and [NSS_SO$_4$] is set to missing, when at least one tracer is missing while the remaining tracers are all BDL.

factor is selected. When A is not close to one, then the absolute value comparison in the next case has the effect of selecting the ratio of na to cl (ratio B) or the ratio of mg to cl (ratio C) that is closer to one.

$$A = ([mg]/[na]) / (mg\_sw/na\_sw)$$
$$B = ([na]/[cl]) / (na\_sw/cl\_sw)$$
$$C = ([mg]/[cl]) /(mg\_sw/cl\_sw)$$

```
CASE when (0.75 <= A <= 1.25)  DO
        set xso4 = [so4] – na_corr[na]
        set xso4met = 1
        END Case
CASE when (ABS(B-1) < ABS(C-1))  DO
        set xso4 = [so4] – na_corr[na]
        set xso4met = 1
        END Case
OTHERWISE DO
        set xso4 = [so4] – mg_corr[mg]
        set xso4met = 2
        END Otherwise
END Case
```

If we have reached these CASE statements, then at least one of the tracer ions, na, mg or cl is missing or is below the detection limit. Examine each tracer in the order na, mg and cl and choose the first one with a non-missing value above the detection limit.

```
CASE when [na] is NOT (missing or BDL) DO
        set xso4 = [so4] – na_corr[na]
        set xso4met = 1
        END Case
CASE when [mg] is NOT (missing or BDL) DO
        set xso4 = [so4] – mg_corr[mg]
        set xso4met = 2
        END Case
CASE when [cl] is NOT (missing or BDL) DO
        set xso4 = [so4] – cl_corr[cl]
        set xso4met = 3
        END Case
OTHERWISE DO       /*  [na], [mg], and [cl] are all missing or BDL */
        IF [na], [mg], and [cl] are all BDL THEN DO
        /* Treat the SS fraction as negligible */
                set xso4met = 7
                set xso4 = [so4]   /*  assume that all the sulphate is NSS */
                END If
        ELSE DO  /* at least one of the tracers is missing while the others are BDL */
                set xso4met = 5
                set xso4 = to the 'missing' value /*  NSS cannot be determined */
                END Else
        END Otherwise
END Else
```

Check if the formulas have produced a negative NSS value. If so then set it to 0.01.
(After conversion of sulphate back to sulphur and rounding off, the NSS value, xso4_s, becomes 0.00).

```
IF xso4met < 4 THEN   /* Was one of the NSS estimation formulas selected? */
      IF xso4 <= 0 THEN DO
              xso4 = 0.01
              xso4b = 2
              END IF
```

Convert xso4 to xso4_s /* convert sulphate to sulphate as sulphur */
Round xso4_s to the hundredths place

set xso4_sb = xso4b

/* End of Algorithm */

NOTE: At the WDCPC, this algorithm is implemented in the SAS Data language. SAS sequentially steps through the CASE structure, and executes the first CASE statement whose test is satisfied. Any remaining CASE statements in the same selection structure are ignored regardless if their tests would be satisfied or not.

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153.   WMO/GAW Aerosol Measurement Procedures: Guidelines and Recommendations. (WMO TD No. 1178).

154.   WMO/IMEP-15 Trace Elements in Water Laboratory Intercomparison. (WMO TD No. 1195).

155.   1st International Expert Meeting on Sources and Measurements of Natural Radionuclides Applied to Climate and Air Quality Studies (Gif sur Yvette, France, 3-5 June 2003) (WMO TD No. 1201).

156.   Addendum for the Period 2005-2007 to the Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007), GAW Report No. 142 (WMO TD No. 1209).

157.   JOSIE-1998 Performance of EEC Ozone Sondes of SPC-6A and ENSCI-Z Type (Prepared by Herman G.J. Smit and Wolfgang Straeter) (WMO TD No. 1218).

158.   JOSIE-2000 Jülich Ozone Sonde Intercomparison Experiment 2000. The 2000 WMO international intercomparison of operating procedures for ECC-ozone sondes at the environmental simulation facility at Jülich (Prepared by Herman G.J. Smit and Wolfgang Straeter) (WMO TD No. 1225).

159.   IGOS-IGACO Report - September 2004 (WMO TD No. 1235)