WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

No. 160

MANUAL FOR THE GAW PRECIPITATION CHEMISTRY PROGRAMME

Guidelines, Data Quality Objectives and Standard Operating Procedures

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WORLD METEOROLOGICAL ORGANIZATION
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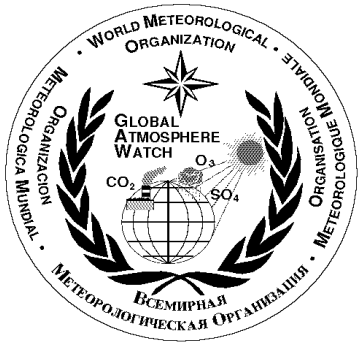

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MANUAL FOR THE GAW PRECIPITATION CHEMISTRY PROGRAMME

Guidelines, Data Quality Objectives and Standard Operating Procedures

Edited by Mary A. Allan

Prepared by

GAW Precipitation Chemistry Science Advisory Group

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NOTE

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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 x 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 (25^{th} and 75^{th} percentiles). For a normal population, the standard deviation can be estimated by dividing the interquartile range by 1.34898.
Kimwipes™	A trade name for a tissue used for cleaning sampler containers, laboratory instruments and other surfaces.

Kleenex™ 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:

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

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).