Malé Declaration on Control and Prevention of Air Pollution and its Likely Transboundary Effects for South Asia

Standard Operating Procedures (SOP)

Manual for Wet and Dry Deposition Monitoring

May 2013

NATIONAL IMPLEMENTING AGENCIES (NIAs) AND NATIONAL FOCAL POINTS (NFPs)

Bangladesh

NFP: Ministry of Environment and Forest

NIA: Department of Environment, Dhaka

Bhutan

NFP and NIA: National Environnent Commission

India

NFP: Ministry of Environment and Forests

NIA: Central Pollution Control Board, New Delhi

Iran

NFP and NIA: Department of the Environment, Tehran

Maldives

NFP and NIA: Ministry of Environment and Energy

Nepal

NFP: Ministry of Environment Science and Technology

NIA: International Centre for Integrated Mountain Development

Pakistan

NFP: Ministry of Climate Change

NIA: Pakistan Environment Protection Agency, Islamabad

Sri Lanka

NFP: Ministry of Environment and Natural Resources

NIA: Central Environmental Authority, Colombo

Foreword

The Malé Declaration on Control and Prevention of Air Pollution and Its Transboundary Effects for South Asia (Malé Declaration) monitoring programme started in 2001. Two manuals were made available to the network at the inception of the monitoring programme. The first manual, "Technical documents for wet and dry deposition monitoring" was adapted from the Acid Deposition Monitoring Network in East Asia (EANET) manual on the same subject as it was felt that rather than developing a manual afresh, it was best to adapt from an existing network in Asia with a manual that is being successfully implemented.

The second manual, "Training materials on monitoring for transboundary air pollution" was prepared from using contributions from Envirotech Instruments Pvt Ltd, Swedish Environmental Research Institute Ltd. (IVL) and Department of Meteorology at Stockholm University (MISU).

The first manual was reviewed and revised by the Monitoring Committee (MoC) in 2004. For the second revision made in 2008, it was decided to combine the material from both the earlier manuals to prepare an updated manual in several smaller volumes, as follows:

Volume 1:   Introduction to the Malé Network monitoring programme
Volume 2:   Basic concepts
Volume 3:   Instruments and analytical methods for the field
Volume 4:   Instruments and analytical methods for the laboratory
Volume 5:   Data management
Volume 6:   Quality assurance and quality control (QA/QC)

The idea was to create volumes that would be useful to specific user groups. It is expected that the different user would require the following volumes. The primary set of volumes is expected to be used regularly, whereas the secondary set of volumes is meant more as reference material.

	Primary vols. required	Secondary vols. required
Field data collectors	3, 5	1, 2, 6
Laboratory scientists	4, 5	1, 2, 6
NIA managers	1, 5, 6	2, 3, 4

To make it easy for the National Implementing Agency (NIA) personnel to perform their tasks proficiently, it was also decided to develop a Standard Operating Procedures (SOPs) manual. Accordingly, this manual has been written by Asian technical advisor on monitoring to the Malé Declaration, checked and reviewed by the MoC.

While this volume provides the basic procedures recommended for the Malé Network, it essentially provides a framework for NIAs to develop more detailed SOPs specific to their countries. NIAs are encouraged to use this volume for this purpose. A list of headings and guidance for developing country-specific SOPs is given in the Annex 1.

List of Abbreviations

A	Accuracy
AAS	Atomic Absorption Spectrometry
AES	Atomic Emission Spectroscopy
$AgNO_3$	Silver Nitrate
Al	Aluminum
$BaCl_2$	Barium Chloride
BDL	Below Detection Limit
Ca^{2+}	Calcium
$CaCO_3$	Calcium Carbonate
Cd	Cadmium
Cl^-	Chloride ion
$CoCl_2$	Cobalt (II) Chloride
DQO	Data Quality Objectives
EANET	Acid Deposition Monitoring Network for East Asia
EC	Electrical Conductivity
EDTA	Ethylenediaminetetraacetic acid
HCl	Hydrochloric acid
HCL	Hollow Cathode Lamp
HVS	High Volume Sampler
H_2SO_4	Sulphuric Acid
IC	Ion Chromatograph
IVL	Swedish Environmental Research Institute Limited
K^+	Potassium ion
K_2CrO_4	Potassium Chromate
La	Lanthanum
Malé Declaration	Malé Declaration On Control And Prevention Of Air Pollution And Its Likely Transboundary Effects For South Asia
MDA	Minimum Detectable Amount
Mg^{2+}	Magnesium ion
MgO	Magnesium Oxide
MISU	Department of Meteorology at Stockholm University
MoC	Monitoring Committee
MW	Megawatt
Na^+	Sodium ion
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NFP	National Focal Point
NH_3	Ammonia
NH_4^+	Ammonium ion

NIA	National Implementing Agency
NO_3^-	Nitrate ion
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NOx	Oxides of Nitrogen
OD	Outer diameter
P	Precipitation
pH	Activity of Hydrogen Ion in a solution
PM	Particulate Matter
PM_{10}	Particulate Matter of Particle size having 10 μm aerodynamic diameter
PO_4^{3-}	Phosphate ion
PVST	Percent Valid Sample Time
PVSV	Percent Valid Sample Volume
QA/QC	Quality Assurance / Quality Control
RH	Relative Humidity
R_1	QA requirement for Ion Balance
R_2	QA requirement for electrical conductivity measurement
Si	Silicon
S_i	Analytical Precision
SO_4^{2-}	Sulphate ion
SO_2	Sulphur Dioxide
Sr	Strontium
TDS	Total Dissolved Solid
TSPM	Total Suspended Particulate Matter
UNEP	United Nations Environment Programme
RRC.AP	Regional Resource Centre for Asia and the Pacific

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1.0 Objective of the Standard Operating Procedure Manual

This SOP manual has been written to ensure standardization in data collection and handling.   This is important as the Malé Declaration Network has eight member nations all with different levels of expertise and capacity.

The SOP manual will also ensure QA/QC in the acidic deposition monitoring programme so that it can yield high quality data that are robust enough for policy making.

2.0 SOP for monitoring acidic deposition

2.1 Scope

SOP is applied to a series of operations at monitoring stations and analytical laboratories, including sample collection and analysis, data reporting, and QA/QC.

2.2 Criteria for establishing regionally representative deposition monitoring sites

The following criteria are required for a regionally remote representative deposition monitoring site:

1. Vegetation can absorb significant amount of the pollutant/s that can cause erroneous results. Thus, samples in the determination of atmospheric pollutant concentration should not be collected in the forests.

2. Monitoring of transboundary air pollutants should be done at remote sites as close as is practically feasible to the international border. The monitoring sites should be at least 25 km away from the nearest town/ large industry and 10 km away from the nearest highway/ small industry.

3. To the extent possible, there should be no human habitation/ activity or other emission sources close to the sites. Population density around the sites should be low and should be expected to remain low in future.

4. The site should be representative of other remote areas in its proximity so that it can give valuable information on trends of air pollution in the region and the data can be used to verify results from models that operate at these regional scales (e.g. on 100 X 100km grids).

5. The sites should be predominantly downwind of major emission sources in neighboring countries and predominantly upwind of major emission sources in the country in which the monitoring is being done.

6. The sites should be sufficiently inland to avoid the influence of coastal breezes.

7. The terrain between the emission sources in the neighboring country and the monitoring sites is preferably flat.

8. The sites should be secured. They should be accessible to sample collectors. They should preferably have a power connection and be habitable for short periods, if necessary.

9. The sites should preferably have a meteorological station within about 50 km of them. The terrain between the monitoring site and the meteorological station should be flat.

10. The site should be within 12-15 hours travel time from the place where the samples (other than diffusive samplers) will be analyzed.

For best results, these criteria should be met to the extent possible. However, it is probable that all the above criteria will not be met at all the monitoring sites. A judicious choice must be made, and to the extent possible, the first six criteria should be met.

2.3 Data Quality Objective

Data quality objectives (DQOs) are introduced to ensure that the precision and accuracy of the data obtained are within acceptable limits. For the Malé Declaration Network, DQOs[*] have been defined as under:

Table 1. DQO values for wet and dry deposition monitoring

Accuracy	Precision	Precipitation	Completeness
$\leq\pm15\%$	$\leq\pm15\%$	$\geq90\%$	$\geq80\%$ - Precipitation & diffusive samples At least 4 valid $TSPM/PM_{10}$ samples/month

*TSP – Total Suspended Particulate Matter
 PM_{10} – Particulate Matter of 10 m particle size

Accuracy: Ratio of the difference between the certified and the analytical values to the certified value in QA/QC, expressed as a percent.

Precision: Relative standard deviation (Ratio of the standard deviation to average value in repeated measurements).

Precipitation: Ratio of the amount of precipitation collected by wet only/bulk collectors to that collected by a standard rain gauge.

Completeness: Ratio of the valid sample (measured as time or sample volume) to maximum sample that could have been collected.

See section 16, SOP on QA/QC for more explanation of above terms and how to calculate them.

2.4 Preparation of National SOPs

While this SOP manual provides a framework for SOP to be followed by the Malé Declaration NIAs, they are encouraged to write more detailed SOPs that are specific to their corresponding countries. A contents table for a country-specific SOP is given in Annex 1.

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[*] For definitions and description of each DQO, refer to Vol 6 of the Technical manual on QA/QC

SOP availability

This SOP and the country-specific SOP (when prepared) should be readily available to all persons working on the monitoring programme, and they should be aware of the existence of the SOPs.

Human resources

The NIA of each country should designate a manager for the Malé Declaration Network monitoring programme in that country and appropriate staff/s as required. Appointed Staff/s should possess adequate capacity to perform necessary monitoring tasks and ideally at least one member of the country team should have attended at least one of the Malé Declaration training events.

3.0   SOP for a bulk collector

3.1 Scope

This SOP describes the maintenance and control operations for a bulk collector.

A bulk collector should be installed either on the rooftop of the station or 1.5 m above the ground, away from any obstruction. Periodic maintenance checks should be done to ensure smooth operation of the instrument.

Figure 1. Bulk Collector

3.2 Source of maintenance and operational methods

Volume 3 of the Technical Manual.

3.3 Instrument placement and installation

The following guidelines should be followed while installing the instrument:

- The instrument should be installed in an open and flat area far enough from trees, hills, and other obstructions to avoid effects on sampling. No objects should be within a few meters from the instruments, and no object should shade the instruments.

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

- The instruments should be free from local emission and contamination sources such as waste disposal sites, incinerators, parking lots, open storage of agricultural products, and domestic heating. Regions within proximity of these emission and contamination sources should be excluded

- The horizontal distance between the collector and rain gauge, if provided, should be greater than 2 meters.

- Two bulk collectors should be used at a site. One of them should be placed close to the wet-only-collector (a few meters away). The other bulk collector should be placed about 100-200 meters away from the first collector.

- The site should have a sheltered hut equipped with electric power, a deep freezer (if possible, this is needed for sample preservation as an alternative to suitable preservatives), sink, water supply, deionised water (<0.15 mS/m), two balances set up on a stable work bench away from draughts and capable of measuring 1-15 kg and 0.1 mg-100 g, a telephone, working tables and chairs.

- The instrument should be placed on top of the hut or at least 50 m from it.

- Use wind shields around the instrument in very windy areas.

3.4 Maintenance checks

The following maintenance checks should be carried out as specified below:

Table 2. Maintenance checks for bulk collector

Subject	Item	Maintenance interval	
		Weekly	**Monthly**
Collection funnels and other water receiving parts	Rinse & clean	√	
No overflow of precipitation in collection bottle	Check	√	
No bird droppings on collector	Check	√	
Funnel is not cracked	Check		√

3.5 Operational procedures

The following operational procedures should be carried out:

Table 3. Operational Procedures for bulk collector

Subject	Item	Maintenance interval	
		Weekly	**Monthly**
Precipitation should be measured with a standard rain gauge either at the site or at the nearest meteorological station (see section 2 for siting requirements)	Measure	√	
Pre-weighing of receiving flask	Measure	√	
Water collected in the collector should be measured with a balance (weighed) and not a measuring cylinder	Measure	√	
Subject	**Item**	**Maintenance interval**	
		Weekly	**Monthly**

Retain 1 L of sample, or if less, total sample, for analysis after measuring sample quantity	Do	√	
Collected sample should be kept in a plastic bottle so that no contamination occurs	Do	√	
Check that collection bag if it is leak proof	Check	√	
After collection, refrigerate sample at 4^oC until analysis Ensure there is no ice formation in sample	Do	√	
If refrigerating the sample is not possible, add preservative, e.g. 400 mg of thymol to 1 L of sample	Do	√	
Use new disposable plastic gloves while handling sample and cleaning funnel	Do	√	
Rinse the funnel with deionised water; brush before collecting fresh sample; and wipe with clean paper	Do	√	
Keep proper documentation on all samples	Do	√	
Transport samples to the laboratory in ice-packed break-resistant containers, with in minimum possible time if preservative is not used	Do	√	
Collect rinse water and analyse	Do		√
Send the field blank to laboratory for analysis	Do		√

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well.

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

3.6 Manufacturer's contact

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karin.sjoberg@ivl.se

4.0 SOP for a wet only collector

4.1 Scope

This SOP describes the maintenance and control operations for wet-only-collector.

The wet only collector should be installed either on the rooftop of the station or 1.5 m above the ground, away from any obstructions. Periodic maintenance checks should be done to ensure smooth operation of the instruments.

4.2 Source of maintenance and operational methods

Volume 3 of the Technical Manual.

4.3 Instrument placement and installation

The following guidelines should be followed while installing the instrument:

- The instrument should be installed in an open and flat area far enough from trees, hills, and other obstructions to avoid effects on sampling. No objects should be within a few meters from the instruments, and no object should shade the instruments.

- The horizontal distance between a large obstruction and the instruments should be at least twice the obstruction height, or the top of an obstruction as viewed from the instruments should be less than 30º above the horizon.

- The instruments should be free from local emission and contamination sources such as waste disposal sites, incinerators, parking lots, open storage of agricultural products, and domestic heating. Regions within proximity of these emission and contamination sources should be excluded

- One of the bulk samplers should be placed close to the wet only collector (a few meters away). The other bulk collector should be placed about 200-300 meters away from the first collector.

- The horizontal distance between wet only collector and rain gauge, if provided, and bulk collector should be greater than 2 meters.

- The site should have a sheltered hut equipped with electric power, a refrigerator, sink, water supply, deionised water (<0.15mS/m), two balances set up on a stable work bench away from draughts and capable of measuring 1-15 kg and 0.1 mg-100 g, a telephone, working tables and chairs.

- The instruments should be placed on top of the hut, or at least 50 m from it.

- Use wind shields around the instrument in very windy areas.

4.4 Maintenance checks

The following maintenance checks should be carried out as specified below:

Table 4. Maintenance Checks for wet only collector

Subject	Item	Maintenance interval	
		Weekly	Monthly
Collection funnels and other water receiving parts	Rinse & clean	√	
No overflow of precipitation in collection bottle	Check	√	
No bird droppings on sensor	Check	√	
Satisfactory hood movement & hood sits tightly	Check		√
Overcharging of battery	Check		√
Proper heating of precipitation sensor	Check		√
Sensor sensitivity to rainfall of 0.5 mm/hr	Check		√
Hood opens within 1 minute of rain starting & closes within 3 minutes ending	Check		√
Hood is not cracked	Check		√
Battery and cables should be protected against rain	Check		√

4.5 Operational procedures

The following operational procedures should be carried out:

Table 5. Operational procedures for wet only collector

Subject	Item	Maintenance interval	
		Weekly	Monthly
Precipitation should be measured with a standard rain gauge either at the site or at the nearest meteorological station (See section 2 for siting)	Measure	√	
Pre-weighing of receiving flask	Measure	√	
Water collected in the collector should be measured with a balance and not with measuring cylinder	Measure	√	
Retain 1 L of sample, or if less, total sample, for analysis after measuring sample quantity	Do	√	
Collected sample should be kept in a plastic bottle so that no contamination occurs	Do	√	

Subject	Item	Maintenance interval	
		Weekly	Monthly
Check that collection bag if it is leak proof	Check	√	
After collection, refrigerate the sample at 4°C until analysis Ensure there is no ice formation in sample	Do	√	
If refrigerating the sample is not possible, add preservative, e.g. 400 mg of thymol to 1 L of sample	Do	√	
Use new disposable plastic gloves while handling sample and cleaning funnel	Do	√	
Rinse funnel with deionised water; brush before collecting fresh sample and wipe with clean paper	Do	√	
Keep proper documentation on all samples	Do	√	
Transport samples to the laboratory in ice-packed break-resistant containers, within minimum possible time if preservative is not used	Do	√	
Collect rinse water and analyse	Do		√
Send field blank to laboratory for analysis	Do		√

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

4.6   Manufacturer's contact
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5.0   SOP for passive (diffusive) sampler

5.1   Scope

This SOP describes the control operations for diffusive (passive) samplers.

Passive (diffusive) samplers should be installed on the rooftop of the station under a rain shade mounted on a hood.

5.2   Sources of maintenance and operational methods

Volume 3 of the Technical Manual

5.3   Instrument placement and installation

The following guidelines should be followed when installing the samplers:

* The samplers should be mounted under a rain shield with the grey screen facing downwards (see illustration below)

Figure 2. Samplers mounted under rain shield

* The samplers should be installed in an open, flat area, or on top of the roof of the monitoring station; far enough from trees, hills, and other obstructions to avoid effects on sampling. No objects should be within few meters from the samplers, and no object should shade the samplers.

* The instruments should be free from local emission and contamination sources such as waste disposal sites, incinerators, parking lots, open storage of agricultural products, and domestic heating. Regions within proximity of these emission and contamination sources should be excluded

* The samplers should be placed on top of the hut on a pole or mounted to the side of a wall.

* Samplers marked "Blank" should not be exposed, but kept at the site during the period the actual sampler is exposed.

- Send the samplers to the laboratory soon after exposure is over.

5.4 Operational procedures

The following operational procedures should be carried out:

Table 6. Operational Procedures for diffusive sampler

Subject	Item	Maintenance interval: Monthly
Check if the lid of box in which the sampler was sent, was tightly sealed when removing the sampler from the box	Check	√
Place the sampler under the rain shield for exposure	Check	√
When the sampler exposure has ended, place it back in the box from which it was taken and place the lid tightly, then in the box eventually in the plastic bag and seal	Check	√
Write the start and end date and time of exposure on box and fill protocol	Do	√
Send exposed samplers to the vendor within one month after the exposure	Do	√

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well.

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

5.5 Manufacturer's contact
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6.0   SOP for a High Volume Sampler for PM$_{10}$

6.1   Scope

This SOP describes the maintenance and control operations for a high volume sampler (HVS).

6.2   Sources of maintenance and operational methods

Volumes 3 of the Technical Manual (HVS section).

6.3   Instrument placement and installation

The following guidelines should be followed while installing the instrument:

- The HVS should be installed either on the rooftop of the station or 2-3 m above the ground, away from any obstruction. Periodic maintenance checks should be done to ensure smooth operation of the instrument.

- The instrument should be installed in an open, flat area far enough from trees, hills, and other obstructions to avoid effects on sampling. No objects should be within a few meters of the instruments, and no object should shade the instruments.

- The horizontal distance between a large obstruction and the instruments should be at least twice the obstruction height, or the top of an obstruction as viewed from the instruments should be less than 30º above the horizon.

- The instruments should be free from local emission and contamination sources such as waste disposal sites, incinerators, parking lots, open storage of agricultural products, and domestic heating. Regions within proximity of these emission and contamination sources should be excluded

- The site should have a sheltered hut equipped with electric power, a refrigerator, sink, water supply, deionised water (< 0.15 mS/m), a sensitive balance to do gravimetry, a desiccator, a telephone, working tables and chairs, a spectrophotometer (if gaseous monitoring is being done at the site), and a soap bubble meter.

6.4   Maintenance checks

The following maintenance checks should be carried out:

Table 7. Maintenance Checks for high volume sampler for PM$_{10}$

Subject	Item	Maintenance interval	
		Monthly	Other
Clean instrument regularly	Do	√	
Perform leak check on instrument	Check	√	

Subject	Item	Maintenance interval	
		Monthly	**Other**
If HVS is not to be used for >2 weeks, drain manometer water and flush manometer with fresh distilled water several times	Do	√	
Hose connecting blower is tight	Check	√	
Cyclone is clean	Check	√	
Check for deformity in silicon tube 'O' ring, and change if required	Check		Every 6 months
Do not clean blower with moisture-laden compressed air	Check		Every time preventive maintenance is done
Calibrate instrument	Do		At least once yearly

6.5 Operational procedures

The following operational procedures should be carried out:

Table 8. Operational procedures for HVS for PM$_{10}$

Subject	Item	Maintenance interval	
		Monthly	**Other**
Inspect filter paper for pinholes and stray PM	Check		Every time a fresh filter paper is put
Ensure that the rough side of the filter paper faces upwards	Check		Every time a fresh filter paper is put
Filter paper is conditioned in desiccator at 20-25ºC and RH <50% for at least 16 hrs prior to weighing	Do		Every time filter paper has to be used
Keep silica gel in perforated bottle in weighing chamber	Do		All the time
Install filter paper only when HVS is off	Check		Every time filter paper is loaded
Start sampler before replacing top cover	Do		Every time sampling is done
Do not over-tighten or under-tighten top cover	Do		Every time sampling is done
Apply talcum powder lightly on rubber gasket	Do		Every time new filter is placed
Ensure zero level of water in manometer, and there is no residue	Check		Every time sampling is done
Keep proper documentation on all samples	Do		For all samplings

Subject	Item	Maintenance interval	
		Monthly	**Other**
Use only distilled water to replace water in the manometer	Do	√	
Float must move freely in rotameter	Check	√	
Ensure that no solid particles are deposited in the rotameter nozzle	Check	√	
Note the time totalizer reading before and after each air sampling	Do		Every time sample is collected
Never fold filter paper completely	Check		Every time sample is collected
Handle filter paper with disposable plastic hand gloves only	Do		Every time filter is handled
Ensure stable power	Check		Every time HVS is used
Do not switch on or off the HVS with time totalizer set for operation	Do		Every time HVS is used
Take flow reading 5 minutes after the HVS has been switched on and the manometer reading has stabilized	Do		Every time HVS is used
Always attach a new weighed cyclone cup with every filter change	Do		Every time sample is collected
Do not switch on the HVS without a filter paper	Do		Every time sample is collected
Do not run the HVS during rainy days in an open atmosphere	Do		Every time HVS is used
Ice pack used to keep absorbing solutions for gaseous samples. The ice should be put in the ice tray	Check		Every time gaseous sampling is done
Float in rotameter is freely moving	Check		Every time HVS is used
Remove air bubbles from manometer water column	Do		Every time HVS is used

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well.

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

6.6 Manufacturer's contact

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7.0   SOP for Gravimetry

Gravimetry can only be used for PM. The parameters are TSPM and PM_{10}.

7.1 Scope

This SOP describes how to measure suspended particulate matter in ambient air.

7.2 Source of maintenance and operational methods

Volumes 3 and 4 of the technical manual (HVS and determination of SPM in the atmosphere section, respectively).

7.3 Range and sensitivity

Lower Quantifiable Limit: For a 24-h sample duration at 1132 L/min, the detection limit is determined by the reproducibility of the filter weight difference which shows a standard deviation (σ) of ~ +2 mg. The 3-σ detection limit is then ~3.5 µg/m^3. The 3-σ lower quantifiable limit depends on the filter used and may be as high as 5 µg/m^3.

Upper Quantifiable Limit: For 24-h sample duration at 1132 L/min, this limit is in the range of 400 to 1000 µg/m^3. The exact value depends on the nature of the aerosol being sampled: very small particles will clog the filter at a relatively low mass loading while larger particles will fall off during sample transport at high concentrations.

7.4 Interferences

Passive deposition occurs when windblown dust deposits on a filter both prior to and after sampling.

Inlet Loading and Re-Entrainment: Material collected in size-selective inlets can become re-entrained in the sample flow. It can be minimized by greasing or oiling inlet impaction surfaces, though this may change the size selective properties.

Re-circulation: Re-circulation occurs when the blower exhaust, which contains carbon and copper particles from the armature and brushes, is entrained in the samples air. Recirculation can be minimized by assuring a tight seal between the blower and the sampler housing or by ducting blower exhaust away from the sampler.

Filter Artifact Formation - Sulfur dioxide, nitrogen oxides, nitric acid and organic vapors can be absorbed on the filter medium along with the suspended particles thereby causing positive biases.

Filter Conditioning: Filter conditioning environments can result in different mass measurements as a function of relative humidity (RH). Twenty-four hours at a constant temperature and RH is considered adequate for sample equilibration.

Shipping Losses: Particle loss during transport occurs when filters are heavily loaded with large dry aerosols. Shipping losses are more prevalent on membrane than on glass fiber filters. Particle loss is minimized by shorter sample duration in heavily

polluted environments, use of fiber as opposed to membrane filters, folding the filter prior to transport, and careful shipping procedures.

7.5 Precision and accuracy

Mass of the filter deposit, flow rate through the filter, and sampling time have typical precision of $\pm$ 2 mg, $\pm$5%, and $\pm$ 1 min, respectively, as determined from performance tests. These uncertainties combine to yield a propagated precision of approximately + 13% at 10 µg/m^3 and approximately + 5% at 100 µg/m^3. The filter deposit mass measurement precision dominates at low concentrations while the flow rate precision dominates at high concentrations.

7.6 Procedure

- Calibration of HVS must be done prior to a monitoring campaign or after a major maintenance.

- PM collection:

1. Selection of Filter media: There is no single filter medium appropriate for all desired chemical analyses therefore it is necessary to design the filter media base on the target parameters before sampling. Several important characteristics for filter media selection of PM measurements are: Particle sampling efficiency (>99%), mechanical stability, chemical stability, temperature stability, low blank concentrations, flow resistance, loading capacity and cost.

2. Filter condition and weighing: The filter, before and after sampling, should be conditioned/ equilibrated in a temperature and relative humidity controlled environment. For TSPM, both blank and sample filter should be conditioned in a clean laboratory with temperature in the range of 15-30°C with $\pm$ 3°C variability and an RH of 20 to 45% with $\pm$ 5% variability for at least 16 hours prior to weighing. The balance must be equipped with an expanded weighing chamber to accommodate 20.3 x 25.4 cm (8 x 10 in) filters and must have a sensitivity of 0.1 mg.

3. Cup: a plastic cup fitted to the cyclone to collect PM is greater than 10 microns.

4. Field Logsheet: This is used to record required information during the start and end of the sampling; such as, sampling date, time, manometer reading, weather condition, incident that may cause changes in the value.

7.7 Computational method

Record initial and final readings of manometer, filter paper weight, cup weight and time totalizer.

$$Average\ flow\ rate = \frac{initial + final\ manometer\ reading}{2}\ \text{m}^3/\text{min}$$

$$Machine\ ontime = (final - initial\ time\ totalizer\ reading)x\ 60\ min$$

$$PM_{10}\ accumulated\ on\ filter\ paper$$
$$= (final - initial\ weight\ of\ filter\ paper)grams$$

$$Non - PM_{10}dust\ accumulated\ in\ cyclone\ cup$$
$$= (final - initial\ weight\ of\ cyclone\ cup)grams$$

$$Total\ air\ volume\ passed\ through\ cyclone/filter\ paper$$
$$= (average\ flow\ rate)\ x\ (machine\ actual\ run\ time)in\ \text{m}^3$$

$$PM_{10}concentration = \frac{(PM_{10}\ weight\ on\ filter\ in\ grams)\ x\ (10^6)}{\sum air\ volume\ passed\ through\ filter}\ \ \mu\text{g/m}^3$$

$$Non - PM_{10}concentration = \frac{non - PM_{10}\ weight\ on\ cup\ x\ 10^6}{\sum air\ volume\ passed\ through\ cup}\ \ \mu\text{g/m}^3$$

$$Total\ PM\ concentration\ in\ air = PM_{10}\ + non - PM_{10}\ concentration\ in\ air$$
$\mu\text{g/m}^3$

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well.

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

8.0 SOP for laboratory management

8.1 Scope

This SOP describes the procedures for managing equipment and handling standard reagents for analysis of acidic deposition.

8.2 Source of maintenance and operational methods

Volumes 3 and 4 of the Technical Manual.

8.3 General requirements for managing equipment

The following items are very important in every laboratory:

1. Technical manuals should be kept in a known secure location so that they can be retrieved whenever necessary.
2. Instructions for operation should be available for common uses (e.g. post on the wall near by the equipment location).
3. Logsheet used for recording daily instrument performance.
4. Regularly check the listing for maintenance.

8.4 Management of reagents

1. Deionised water: before using, ensure that the conductivity of deionised water is < 0.15 mS/m.

2. Chemicals and reagents: the opened and expiry date should be recorded and preserved according to manufacturer's instructions.

9.0   SOP for wet deposition sample treatment and analysis sequence

9.1 Sample treatment

Sample volume and weight, EC and pH should be measured immediately following sample collection or earliest possible time after sample collection at site and sample lists are checked and tagged with identification numbers, and prior to sample refrigeration or preservative addition. Repeat these labeling procedure after sample arrival at the laboratory. Subsequently, all samples should be filtered with clean membrane filters (pore size: 0.45μm). Filters should be well washed and be free from contamination. Samples should then be refrigerated at 4°C.

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

The ionic constituents can be measured after dilution with deionised water if the quantities of samples are fairly small (but concentration needs to remain within detection limit of equipment being used) or if the samples are of high concentration that is exceed the range of the analytical technique. Dilution may be done as follows: an aliquot of sample (e.g., 10 ml) is taken in a volumetric flask and deionised water is added 25 or 100 ml). It is also important to measure the ions in the used deionised water.

Note:
- Diluted samples are not to be used in measurement of pH and conductivity.
- The purity of water from target ions should be checked before dilution.
- The dilution flag must be marked in the reports.

9.2 Sample analysis sequence:

The sequence of analysis for wet deposition samples is illustrated in the following schematic diagram or flow chart:

In Lab:
Prepare and measure weight of sampling bottle (gr.)

On Site:
Collect precipitation and measure precipitation amount

In Lab:
Measure amount of wet deposition sample (gr.)

In Lab:
Sufficient sample amount for measurement of all items

Yes

No

In Lab:
1st portion: do not filter ⟶ measure EC
                    measure pH
2nd portion: filter ⟶ refrigerate at 4^oC
                    measure ions (within 1 week)

In Lab:
a)   After EC and pH measurement, sample volume is not sufficient for ion measurement

1st portion: DO NOT FILTER ⟶ measure EC ⟶ measure pH
2nd portion: FILTER ⟶ refrigerate at 4^oC ⟶ **dilute 2 to 10 times** ⟶ measure anions

In Lab:
b)   Sample volume not sufficient for pH, EC and ion measurement:

        Carry out measurement for ion only:
FILTER ⟶ refrigerate at 4^oC ⟶ **dilute 2 to 10 times** ⟶ measure ions
The order of measurement priority:
   1. NH_4^+,
   2. NO_3^-
   3. SO_4^{2-}, Cl^-
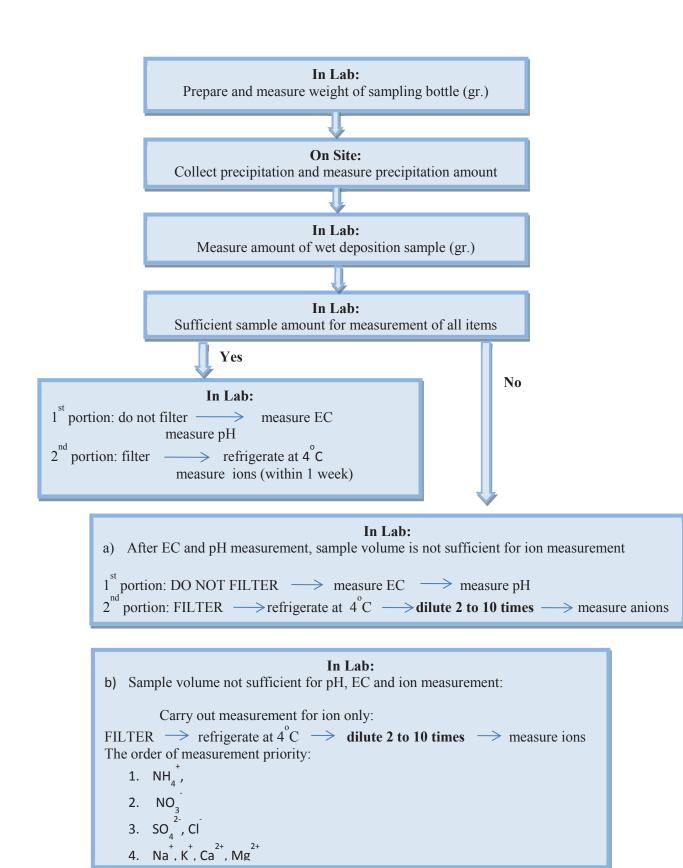   4. Na^+, K^+, Ca^{2+}, Mg^{2+}

Figure 3. Flowchart of sampling and management of samples

10.0   SOP for pH measurement

10.1 Scope

This SOP describes how to measure pH of wet deposition samples in the field and in the laboratory.

10.2 Reference for measurement

Volumes 3 and 4 of the Technical Manual (pH Meter section).

10.3 Reagents

pH standard buffer: Commercially available standard solutions (pH 6.86 and pH 4.01).
Deionised water: 0.15 mS/m.

10.4 Calibration

The pH meter should be calibrated prior to any set of measurements at $25\pm1^{o}C$ using the pH standard buffers.

10.5 Procedure

Instrument operation should follow specific manual as recommended by manufacturer.

An example for pH calibration and measurement with the use of pH 300i meter is shown below:

Calibration

1.   Set the temperature of the water bath at a constant level of $25\pm1^{o}C$.

2.   Press the <Cal> key repeatedly until the display Ct1 and the function display Auto Cal TEC appears. The sensor symbol displays the evaluation of the last calibration.

3.   Immerse the pH electrode into the first buffer solution (pH=7.0)

4.   Press <Run/Enter> key (the auto read measurement begins. If the measured value is stable, Ct2 appears.

Note: At this point, the auto cal TEC calibration can be terminated with <M>.

1.   Remove the electrode from the first buffer solution, rinse thoroughly with deionised water and dry it.

2.   Immerse the pH electrode into the second buffer (pH 4.01).

3.   Press <Run/Enter> key (the auto read measurement begins). If the measured value is stable, the instrument displays the value of the slope and the evaluation of the two point calibration.

4. Press<Run/Enter> key (the instrument displays the value of the asymmetry).

5. Switch to the measuring mode with <M>.

6. To set calibration interval, while pressing the <M> key, press <ON/OFF> key (display CAL disp).

7. Press <Run/Enter> key (display time of calibration display).

8. Set the interval of Calibration with <Δ> <∇>.

9. Report the result to the nearest 0.1 pH unit.

Measuring pH

1. Set the temperature of the water bath to $25\pm1^{\circ}C$. Keep the sample and the buffer in the bath and bring them to the same temperature.

2. Fully wash the detection part of the electrode with deionised water and remove the water on the electrode with clean tissue paper.

3. Connect the electrode and temperature sensor to the measuring instrument.

4. Press the on/off key (display test appears briefly on the display)

5. Select pH value or redox voltage (mv) with <M>.

6. Calibrate electrode using two buffers.

7. Rinse electrode with deionized water and remove the water.

8. Immerse the electrode in sample. Confirm that the water sample is at temperature of $25\pm1^{\circ}C$.

9. Press <AR> to switch on the drift control. Wait until measured value is stable and AR stops flashing.

10. Repeat measurement (Step 9 above) with a new aliquot of sample without rinsing between.

11. To cancel auto read at any time press <Run/Enter>.

Storing data (optional)

1. Press <STO> key in the measuring mode (display No. with the number of the next free memory location.

2. Press <Run/Enter>.Enter the Identification number with < ∇> <Δ>.

3. Terminate the save with <Run/Enter>.

4. Retrieving stored data (optional)

5. Press the <RCL> key in the measuring mode (display Sto disp)

6. Press <Run/Enter> key (display number at which data store)

7. Press <Run/Enter> key(display identification number)

8. Press <Run/Enter> key (display day, month)

9.   Press <Run/Enter> key (display time)

10. Press <M> key to return in measuring mode.

10.6 Precautions

1.   Always keep the electrode wet (with electrolyte in the cap of electrode) and clean from algal growth.

2.   Keep the electrode in deionised water if the instrument is used continuously.

3.   Rinse with appropriate solution (i.e., sample before measurement or deionised water after last measurement).

4.   Maintain the temperature at $25^{o}C$ during the measurement for both buffer and sample (or use a water bath).

5.   A part of the solution used for measuring EC can be used for measuring pH. EC should be measured first so as not to generate errors due to salt contamination from electrode.

6.   Rods of electrodes should not be rubbed when moisture is wiped from electrodes so that potential difference due to friction is not yielded.

7.   Deviation greater than 0.1 pH unit while cross checking with the two standard buffers indicates a faulty electrode.

10.7 Potential sources of errors

1.   Streaming current caused by sample stirring.

2.   Sample-keeping containers.

3.   Deterioration of electrodes.

4.   Temperature difference between sample and standard buffer solutions.

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well.

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

11.0   SOP for EC measurement

11.1 Scope

This SOP describes how to measure electrical conductivity of wet deposition samples in the field and the laboratory.

11.2 Source of maintenance and operational methods

Volumes 3 and 4 of the Technical Manual (EC meter section).

11.3 Reagents

Potassium chloride: Special grade
Deionised water: <0.15mS/m

11.4 Solution

0.05 M potassium chloride (KCl) standard solution: Weigh 3.719 g of KCl (either anhydrous or dried at $180^{o}C$ for 1 hour) and dissolve in deionised water. Transfer the solution to a 1000 ml volumetric flask and add deionised water to the line.

0.0005 M potassium chloride standard solution: Pipette 2 ml of 0.05 M KCl standard solution with a volumetric pipette to a 200 ml volumetric flask and add deionised water to the line.

11.5 Calibration
The instrument should be calibrated before each set of measurements at $25\pm1^{o}C$ using KCl standard solutions above.

11.6 Procedure
Instrument operation should follow specific manual as recommended by the manufacturer. An example for EC calibration and measurement using the EC meter model COND 330i is shown below:

Calibration

1.   Set the temperature of the constant temperature water bath to $25\pm1^{o}C$.

2.   Connect the conductivity electrode to the measuring instrument.

3.   Immerse the electrode into the electrolyte solution provided with the instrument.

4.   Press the <Cal> in the measuring mode (display Cell).

5.   Press <Run/Enter> key (display CAL and cell constant value, it should be 0.450-0.500 cm^{-1}).
Note : At this point, this procedure can be terminated with <M>.

Measuring EC

1. Set the temperature of the water bath to 25±1°C. Keep the sample and the potassium chloride standard solution in the bath and bring them to the same temperature

2. Wash the detector (cell) 2-3 times with deionized water, soak in a beaker with 0.0005 M potassium chloride standard solution.

4. Connect the conductivity electrode to the measuring instrument.

5. Press the < Φ> key (display test appears briefly on the display, after this, the measuring instrument automatically switches to the measuring mode).

6. Select the parameter (TDS, salinity, conductivity) by pressing <M> key.

7. Immerse the electrode in the water sample.

8. Press <AR> key to activate auto read.

9. Press <Run/Enter> key to start the auto read measurement, AR flashes on the display until a stable measured value is reached, this can be terminated at any time with <Run/Enter> key.

Storing data (optional)

1. Press the <STO> key in the measuring mode (display number with the number of the next free memory location).

2. Press <Run/Enter> key.

3. Enter the ID number with <∇ ><Δ>.

4. Terminate the save with <Run/Enter> key.

Retrieving stored data (optional)

1. Press <RCL> key (display SEr disp).

2. Press <Run/Enter> key (display number at which data store)

3. Press <Run/Enter> key (display identification number).

4. Press <Run/Enter> key (display day, month)

5. Press <Run/Enter> key (display time)

6. Press <M> key to return in measuring mode.

11.7   Precautions

3. Always keep the electrode dry (before and after use).

4. Measure the potassium chlorine standard solution at least once for every 20 samples measured at the same temperature, compare this EC data with the previous value, a precision of 0.5 % is acceptable, if not, the EC data for samples are rejected and an inspection is necessary.

5. Sample and standard solutions should be measured at the same temperature.

6. After samples with large EC are measured, soak the cell in deionised water for washing. Washing is sufficient when the EC of the water reaches about 0.8 μS/cm.

7. When the sample amount is small, one measurement is sufficient. 20 ml of sample is necessary for the perceptive parts of the electrodes to be fully immersed in the sample.

8. Be careful not to leave air in the measuring part of the glass cover of the cell. When air touches the cell, the indicating value decreases.

9. If a platinum electrode is being used, it should be rinsed thoroughly after use, and must be kept immersed in distilled water.

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well.

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

12.0   SOP for Anion determination

12.1 Scope

This SOP describes the procedures for the determination of water soluble anion concentration.

12.2 Source/s of maintenance and operational methods

Volumes 3 and 4 of the Technical Manual (Analytical methods and Spectrophotometer section, respectively).

12.3 Apparatus/Equipment

Suitable analytical procedures, which depend on the concentration range of samples, should be selected to obtain acceptable results. Several common methods/equipment for determining anion concentration in the solution are given below:

1. Titration: applicable range for chloride (Agentometric method) is 0.15 to 10 mg in the portion titrated (100 ml is recommended).

2. Spectrophotometer: applicable with sulfate concentration from 1 to 60 mg/L (by precipitation with $BaCl_2$), nitrate concentration from 0.01 to 1 mg/L (by Cd reduction method).

3. Ion chromatography: applicable with low anion concentrations (~1 mg/L) of SO_4^{2-} NO_3^-, Cl^-. Measured anion concentration and recommended Minimum Detectable amount (MDA) is given in Table 9.

Table 9. Recommended MDA for measured anion concentration

Anion	Measured concentration, mg/L	MDA, mg/L
SO_4^{2-}	19	0.1
NO_3^-	19	0.12
Cl^-	35.5	0.04

Source: Practical manual – Malé Declaration
Note: Care to eliminate possible interferences for each method.

12.4 Reagents
As required for analysis.

12.5 Calibration curve
General instruction for making a standard curve:

- Estimate the concentration range of the target ion.

- Prepare at least 3-5 points of standard concentrations covering the sample concentration range.
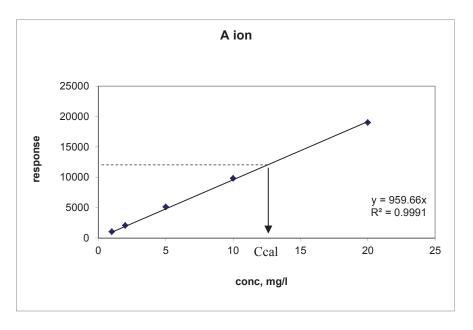
- Plot the standard curve.

Figure 4. Plot of a Calibration curve

Calculation the ionic concentration in the unknown sample from the standard curve:

- Determine the slope of the standard curve
- Determine the ionic concentration (C_{cal}):
  $$C_{cal} = Response/slope$$

- Determine the ionic concentration (A_{sample}) in the origin sample:
  $$A_{sample} = C_{cal} \times DF \text{ (dilution factor)}$$

Note:
- The calibration curve may be linear for a certain range of concentration. Thus, it may have a tendency to level off at higher concentrations.
- Checking of a mid-range standard should be taken at the beginning of a working day and every 10-20 samples afterward. A bias below 10-20% is acceptable, if this is not satisfied re-calibrate and re-measure the samples.

12.6 Procedure

1. **Determination of Chlorine by titration (Argentometric method):**

   Calculation :

   Chloride, mg/L $= (V_1 - V_2) \times 0.0141 \times 35450 /$ mL sample

   Where $V_1 =$ mL titration for sample
   $V_2 =$ mL titration for blank

   Chloride, μ mole/L $=$ Cl (mg/L) x 10^3 / 35.5
   35.5 is MW of Cl

```
┌─────────────────────────────────────────────┐
│  50 – 100 ml sample (pH 7 – 10) in 250 ml flask  │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│  Add 1 ml K₂Cr₂O₄ indicator                 │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│  Titrate with 0.0141 N AgNO₃                │
└─────────────────────────────────────────────┘
                      ↓
┌─────────────────────────────────────────────┐
│  Pinkish yellow at the end point            │
└─────────────────────────────────────────────┘
```
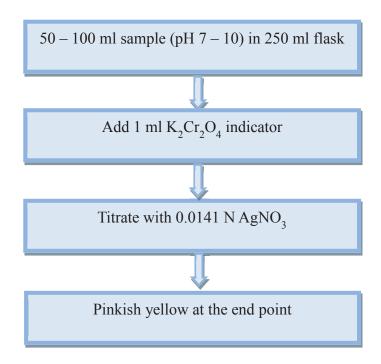
Figure 5. Flowchart for chlorine determination by argentometric method

2. Determination Sulfate using the Spectrometer Elico SL 171:

1. Checking spectrophotometer performance

Preparation of blank: Accurately measure 10 ml of "Anal R" quality HCl of 36-46% concentration. Add it slowly to 400 ml distilled water filled in one litre volumetric flask. Make it up to mark with distilled water and mix it up well.

Preparation of sample: Weigh exactly 22.2 g of "Anal R" quality Cobalt Chloride ($CoCl_2$). Transfer into one litre volumetric flask. Dissolve it in 1% Hydrochloric Acid (HCl) and make it up to the mark. Fill the blank (1%HCl) & sample ($CoCl_2$ Solution) solution in cuvettes.   Perform the steps as given in the operating instructions below to measure the transmittance/absorbance at wavelength 480 to 540 nm at 5 nm interval. Plot the graph of absorbance versus wavelength. The graph should be in increasing order up to 510-515 nm wavelength and then in decreasing order.

2. Operating procedures for the Spectrometer Elico SL 171:

* Turn the switch at 'ON" position. Warm up the instrument for 15 minutes. Press %T selector switch. Adjust the wavelength control to read the wavelength at which the test is desired.
* Open the sliding lid of the sample compartment. Turn the filter sliding control at filter position-1 to set zero adjustment. Close the sliding lid of the sample compartment.
* Turn the coarse and fine controls at their maximum and adjust %T control to get 0.00 displayed on the read out with the filter position-1.
* Now turn the filter sliding control at required position decided based on the wavelength selected.

Filter Position	Wavelength
	Below 395 nm
	395 to 600 nm
	Above 600nm

- Keep the blank cuvette at position 1 and the sample cuvette at position 2.
- Adjust 100%T (%T selector switch should be in pressed position) or 0.0 absorbance (O.D selector switch should be in pressed position) using coarse and fine controls knob with blank cuvette.
- Pull the cuvette position control at position 2.
- Read out the transmittance/absorbance of the sample.

Calculation:

SO_4, mg/L = Concentration obtained after calculated from the calibration curve x D

Where D = dilution factor

SO_4, µ mole/L = SO_4 (mg/L) x 10^3 / 96
96 is MW of SO_4

3. Precautions

- Always clean the cells thoroughly and rinse at least once with a portion of the sample, before filling the sample for measurement.
- Always wipe the exposed surface of the cells dry and free from finger prints, using tissue paper.
- Clean cells thoroughly immediately after use and prior to use. Do not leave solutions, particularly strong alkali, in the cells for periods more than an hour.
- Ensure no air bubbles the inner surfaces of the cells. Never use a brush or any tool for cleaning which may scratch the optical surfaces.

4. Cuvette Cleaning

Take 1g of Potassium dichromate, add a little distilled water and very slowly add approximately 100 ml of conc. H_2SO_4. Keep the cells in this acidic solution for a maximum period of 12 hrs. Wash the cells thoroughly with distilled water before use.

3. Determination of SO_4^{2-}, NO_3^- and Cl^- using an Ion Chromatograph (IC):

Instrument operation should follow specific manual recommended by the manufacturer.

An example for determination of the 3 above mentioned anions using the IC DIONEX-1000 is shown below.

Standard preparation: an individual or mixture of standard solution/s for the target ion can be purchased commercially. Working standard solutions are prepared from this stock standard.

Sample preparation: A volume of 2 ml of an aquatic sample is filtered using 0.45 um syringe filter before injecting into the IC.

Operation procedures:

1. Prepare the eluent (follow product manual).
2. Verify that amount of eluent in container if it is enough.
3. Switch on the nitrogen gas cylinder.
4. Switch on the PC and IC.
5. Open the software Server Monitor, click Star (wait until "idle" appears on the screen).
6. Open the software Chromeleon
7. Go to Panel, click twice on Traditional system and then Connected.
8. Attach the syringe to drain valve and lose the drain valve, click Open (eluent flow valve), click Close (eluent flow valve), close the drain valve and waste the eluent.
9. Loosen the prime valve, click Prime and wait until no air bubble in flow line.
10. Click Off (prime) and close the prime valve.
11. Check flow rate, suppressor: type and SRS current.
12. Click Start up.
13. Go to Control, select Acquisition On, click ECD_1 and OK.
14. Wait for baseline stable.
15. Inject sample.
16. To shutdown, go to Control and select Acquisition Off.
17. Click Shutdown and exit window.
18. Go to Server Monitor, click Stop (wait until "not running" appears on the screen) then close.
19. Switch off PC and IC.
20. Close gas cylinder.

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well.

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

12.7 Vendor's contact

S K Gupta
Envirotech Instruments Pvt Ltd
A-271 Okhla Industrial Area Phase 1, New Delhi 110 020
enviroteh@vsnl.com

13.0 SOP for Cation determination

13.1 Scope

This SOP describes the procedures for determining the cation concentration in the solution.

13.2 Source of maintenance and operational methods

Volumes 3 and 4 of the Technical Manual (Analytical methods section).

13.3 Apparatus/Equipment

As mentioned in the section 12.3, analytical procedures should be selected according to the concentration range of samples. Below are the common methods/equipments available as well as the method detection limits for detection of the cation concentrations in solution.

1. Titration: applicable range for Ca^{2+} (EDTA method) is about 25 mg in the portion titrated (100 ml is recommended). It is also applicable with NH_4^+ concentration > 5 mg/L (by distillation) or from 0.04 to 2 mg/L (by Phenate method).

2. IC or Atomic Absorption Spectrometer (AAS): applicable with low cation concentrations (~0.1 mg/L) of Na^+, K^+, Ca^{2+}, Mg^{2+}. Measured cation concentration and Recommended MDA is given in Table 10.

Table 10. Recommended MDA for measured cation concentration

Cation	Measured concentration, mg/L		MDA, mg/L	
	IC	AAS/AES	IC	AAS/AES
Na^+	21	2	0.05	0.01
NH_4^+	18	Na	0.05	na
K^+	3	1	0.03	0.03
Ca^{2+}	12	3	0.02	0.01
Mg^{2+}	5	0.5	0.02	0.005

Source: Practical manual – Malé Declaration
na: not applicable
Note: Eliminate possible interferences for each method.

13.4 Reagents

As required for analysis.

13.5 Calibration curve

Refer to section 12.5

13.6 Procedure

1. Determination NH_4^+ by distillation (for high concentrations):


```
┌─────────────────────────────────────────────────┐
│        Put 100 mL sample into 300 mL-test tube   │
└─────────────────────────────────────────────────┘
                        ↓
┌─────────────────────────────────────────────────┐
│              Add 5 mL borate buffer              │
│          (adjust pH > 9.5 with 6N NaOH)          │
└─────────────────────────────────────────────────┘
                        ↓
┌─────────────────────────────────────────────────┐
│     Connect to distillation apparatus, collecting│
│      distillate under 25 mL indicating boric acid│
└─────────────────────────────────────────────────┘
                        ↓
┌─────────────────────────────────────────────────┐
│     Collect at least 100 mL distillate (about 4 min)│
└─────────────────────────────────────────────────┘
                        ↓
┌─────────────────────────────────────────────────┐
│        Titrate distillate with 0.02N H₂SO₄       │
└─────────────────────────────────────────────────┘
                        ↓
┌─────────────────────────────────────────────────┐
│     Color change from **green** to **pale lavender**│
└─────────────────────────────────────────────────┘
```
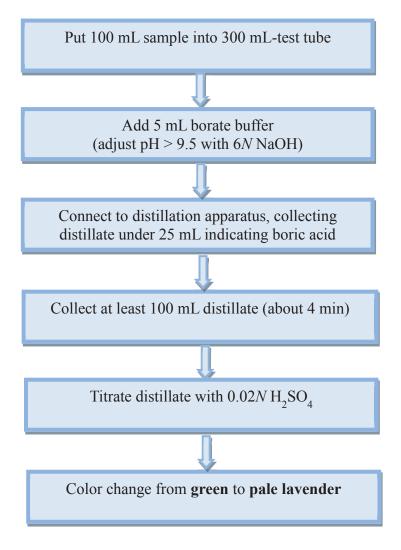
Figure 6. Flowchart for Determination NH4+

Calculation:

NH_4, mg/L = (A - B) x 280/ mL sample

Where A = mL titration for sample
      B = mL titration for blank

NH_4, μ mole/L = NH_4 (mg/L) x 10^3 / 18
      18 is MW of NH_4

2. Determination Na^+, K^+, Ca^{2+} and Mg^{2+} using the AAS

Preparation for Sodium measurement

- Stock Standard Solution- Na$^+$, 1000µg/ml. Dissolve 2.542g sodium chloride, NaCl (dried at 140^{0}C) in distilled/deionised water, add 10ml concentrated HNO$_3$ and make up to 1000 ml. 1ml=1000 µg Na.

- Wave length - 589.0 nm-589.6 nm
- Light source - Hollow cathode lamp
- Flame type   - Air-acetylene flame oxidising (lean, blue)
- Interferences - Na is partially ionised in the air-acetylene flame. The effect of ionisation may be substantially overcome by the addition of an excess (1000-2000 g/ml) of another alkali to standards and samples.
- Other flames - the slightly lower temperature air-hydrogen flame produces far less ionization than air-acetylene and may be preferred on that account. It also provides very little visible emission, giving it an advantage in signal-to-noise ratio (precision), particularly at the secondary line (330.2 nm).
- Flame emission - The most sensitive emission wavelength for Na is at 589.0 nm. An air-acetylene flame is recommended. Na$^+$ can also be determined at the 589.6, 330.2 and 819.5 nm wavelengths, but with reduced sensitivity.

Preparation for Potassium measurement

- Stock standard solution – K$^+$, 1000 ug/ml. Dissolve 1.907 g (dried at 110°C) of potassium chloride in 1 lit. distilled water
- Wavelength - 766.5 nm
- Light source - Hollow Cathode lamp
- Flame - Air –acetylene flame oxidizing (lean, blue)
- Interferences - K$^+$ is partially ionized in air-acetylene flame. The effect of ionization may be substantially overcome by addition of a large excess of other alkali salts to sample and standard solutions.
- Other flames - slightly lower temperature air-hydrogen flame produces far less ionization than air-acetylene and may be preferred on that account.
- Flame Emission - The most sensitive emission wavelength for K$^+$ is at 769.9 nm and 404.4 nm wavelength but with reduced sensitivity

Preparation for Calcium measurement

- Stock Standard Solution- Ca^{2+}, 500µg/ml. Suspend 1.2485g CaCO$_3$ (dried at 180^{0}C for 1 hour before weighing) in water and dissolve continuously with a minimum amount of 1+1 HNO$_3$. Add 10 ml concentrated HNO$_3$ and dilute to 1000 ml with distilled water. 1ml=500µg Ca^{2+}

- Stock standard solution – Ca^{2+} 500 ug/ml
- Wavelength - 422.7 nm, 239.9 nm
- Light source - Hollow cathode lamp
- Flame - Air–acetylene flame oxidizing (lean, blue)
- Flame adjustment - An oxidizing (fuel-lean) flame is recommended for optimum precision.

- Interferences – Silicon (Si), aluminum (Al), phosphate (H_2PO_4) and sulfate (H_2SO_4) depress the sensitivity for Ca^{2+}. Lanthanum (La) or strontium (Sr) at concentration of 0.1 to 1 % can be added to sample.
- Other flames - The nitrous oxide-acetylene flame will provide a better sensitivity ionization interferences should be controlled by adding a large amount of alkali-salt to the samples and standards.

Preparation for Magnesium measurement

- Stock Standard Solution- Mg^{2+}, 1000μg/ml. Dissolve 1.658g magnesium oxide, (MgO), in a minimum amount of 1+1HNO$_3$. Add 10 ml of concentrated HNO_3 and dilute to 1000 ml with distilled water. 1ml=1000μg/ml magnesium

- Stock std. Solution – Mg^{2+} 1000 ug/ml
- Wavelength - 285.2 nm
- Light source - Hollow Cathode lamp
- Flame - Air–acetylene flame oxidizing (lean, blue)
- Interferences - Si and Al depress Mg^{2+} absorption in the air-acetylene flame. The addition of La (0.1 to 1 %) will generally remove these interferences.
- Flame emission - A nitrous oxide-acetylene flame is recommended while air-acetylene flame can be used with reduced sensitivity.

Operating procedures for the AAS model (Spectra AA 220, True Double Beam Optics AAS)

1) Keep standards, samples and "Triple Distilled Water" and "Triple Distilled Water with 2% HNO$_3$" ready.
2) Switch "ON" the exhaust fan and the air-compressor. Ensure that the outlet pressure is set to "50 to 55" PSI. Always ensure to remove moisture from the Air-tank by loosening the "valve opening" at the bottom of the compressor before starting to use the air for lightening the flame.
3) Switch "ON" the AAS and computer systems.
4) Open the Software ("SpectrAA") from the desktop of computer. Open the "Method File" for the Element, which you wish to analyze. Select the page "Analyze" on the Method file.
5) Go to "Optimize". Go to "Optimize Lamp". Optimize the desired "Hollow Cathode Lamp (HCL)" through the screws on the base socket (on which HCL is mounted). The HCL optimisation is done to obtain 'Maximum Energy', which is displayed by a vertical bar (it changes its level as there is change in lamp energy). This should be done again & again until 'Maximum Energy Level - Peak' has reached and the 'energy' cannot be increased any further. (If the 'energy' level goes beyond the scale, it is brought within the scale range by pushing the "Rescale" Button on the same page - optimization page).
6) Ensure that the Burner is sitting properly & the HCl's Light Beam is passing over the burner slit throughout its length. This is to be checked with the "Alignment Card". Align the Burner (If it is not aligned or it has been misaligned). After proper optimisation of Lamp ensure to keep the

instrument ON and wait for about 20 to 30 minutes before starting the analysis (This is for warming up of electronics. It would give very good results and there are lesser variations in results).

7) Open the "Acetylene Cylinder" Regulator. Ensure that the Outlet Pressure is set to 10 psi which is equal to 0.7 kg/cm^2 or 0.7 Bar. (1 Bar = 14.7 psi).

8) Light the 'Flame' by pressing 'Flame ON' switch. (The switch must be kept pressed for few seconds until the flame is lit properly. The Fuel gas may take a few seconds to reach to burner). Ensure that the "Sample Inlet Capillary" remains dipped in to the "Triple Distilled Water" and there is enough "TDS" in the flask or beaker.

9) Now on the software page of "Optimize", select and click on "Optimize Signal". (Check the signal amount while TDS is being aspirated). Check the signal with any Standard Sample by aspirating it through the capillary inlet. Try to optimize the signal for "Maximum" by watching the display bar on the optimization page. (There are three main points, which can be adjusted for optimization of signal. (i) Burner's Vertical, Horizontal & Diagonal positions, (ii) Nebulizer and (iii) Fuel to Oxidant Ratio in flame). Please note that this optimization should not be touched unnecessarily if the signal is of proper desired level.

10) Remove the capillary input from the Standard Sample and Dip the capillary input into the "Triple Distilled Water with 2% HNO$_3$". (Wait for few seconds to ensure that all the standard sample has got flushed out of the Burner Chamber with the TDS).

11) Select and click on "Instrument Zero" after ensuring that there are no remains of Standard Sample in the Burner Chamber & Flame Stream. (This can be seen by observing the bar displaying signal intensity on the optimization page. The signal bar comes down to the original position, while there was no sample in the stream).

12) After completing the "Optimization" go to "Analysis". Here you should do "Standardization" before starting to analyze samples.

13) For Standardization first select "Blank" at the Standards list (It is the first item on the list). Aspirate "TDS with 2% HNO$_3$" (This is the solution with which all standards or samples have been diluted). After few seconds of aspirating of the "Blank" solution click "Analyze". The instrument will read the blank value & show it on screen.

14) "Standard 1" is selected automatically by the instrument. If it has not selected it automatically you may select it by clicking on it. Remove the capillary inlet from "Blank Solution" and put it into the "Standard 1" (This is the first standard of the element you are analyzing). Wait for few seconds to ensure that the standard has reached to the flame evenly and the reading becomes stable. Now click "Analyze". The instrument will read the Standard 1 value and display it on screen as well as it will show a graphical representation of the standard.

15) Do the sample steps for "Standard 2" and "Standard 3".

16) Now the instrument automatically goes to the 'Sample Analysis' – 'Sample 1'. Remove the capillary inlet from Standard 3 and dip into the "TDS" to ensure that all the standard solution has been washed away with TDS. Now dip the capillary tubing into the 'Sample1' (this is the sample you wish to analyze). Wait for few seconds to ensure that the

sample has reached to the flame evenly and the reading becomes stable. Now click "Analyze". The instrument will read the value of the sample and display it on screen.

17) Carry on analysing your samples one after the other in the same manner. (Please ensure that each time you are replacing your Standards or Samples, you must dip the capillary inlet into the "TDS" to ensure that there remains no 'Memory Effect' of the standard or samples).

18) After analysing all desired samples, ensure to aspirate at least 50 to 100 ml of pure "TDS" (without 2% HNO_3) through the capillary inlet in to the burner chamber and burner. (This will keep the burner chamber and burner safe from any salt deposits, which can occur if it is not done).

19) Now switch "OFF" the flame. Close the Acetylene Cylinder Main Valve. After closing Acetylene Cylinder Valve, try to empty the Acetylene line by switching the flame on switch. Thus Acetylene will get emptied from the tubing (which connects the cylinder and instrument). Shut down or close the Air Compressor. Close the Analysis page on computer by selecting "Stop" and Close. Shut down the computer. Shut "OFF" the instrument (Main AAS). Empty the Air-Compressor by opening the relieve valve at the bottom of the compressor. (Do not forget to close the valve after emptying it).

20) Switch "OFF" the Exhaust Fan.

21) Turn OFF or disconnect all electrical plugs from the outlets (such as of Computer, Printer, Compressor and Main Instrument).

Precautions

- Remember to switch on the Exhaust Fan first, it is very important! (This will ensure that all gases start getting exhausted whenever we are operating the AAS System).

- Handle all the chemicals with care! Always keep the Standard Bottles, Sample Bottles and Blanks etc. properly labeled with nos. and identification marks written with Marker Pen.

- Always crosscheck whether the HCl (Which you intend to use) is correctly placed on the "Base No." position, which you have fed (written) in the Method. Also, crosscheck in the program whether the lamp current has been written correctly for the lamp. (This would ensure correct selection of lamp and prevent lamps from operating at over current accidentally).

- Plan the analysis well ahead of time. Arrange for all items like "Triple Distilled Water" and "Triple Distilled Water with 2% HNO_3", All Standards and Samples before the analysis. Keep all these items in flasks or bottles and arrange these in line up positions as per the sequence of analysis. (This will ensure an easy availability of the samples etc. for analysis & you would not need to search for a particular sample during analysis).

- Always switch "ON" the Air-Compressor before switching on other Instruments and peripherals. (This would ensure that by the time you are

ready to switch on the flame, the Air pressure builds up inside the compressor tank. Further the fuel cannot be lit without the air accidentally).

- Always check whether there is enough water inside the Water Trap. (It is visible from outside. This will ensure that there is not a Backfire accidentally during lighting of flame).

- Always keep a watch on the vessel, which you have kept for drainage. It should be emptied with caution in a proper drain. (Please note that major portion of all standards and samples whatever you have analyzed gets collected into the drain vessel. The Standards and Samples may be of Toxic Nature).

- After each Standard Analysis or Sample Analysis, Pure TDS should be aspirated. In between the Standards or Samples aspirate TDS. (This will ensure that all traces of Standard or Samples are washed away. There will not be any memory effect due to this).

- Always use freshly prepared Standards for Standardization of Instrument (Calibration Curve). TDS with 2% HNO_3 can be used for 'Blank' or dilution purposes for some days say within the week of preparation.

- Every day for analysis perform new Calibration and draw new Calibration Curve. Do not use old Calibration Curve. (Old calibration curve can be used for general checking of sample concentrations but must not be used for actual analysis of samples).

- Every time you switch on the instrument for analysis, it is advised that Optimization of lamp is performed. (This will ensure that if at all the lamp alignment has been disturbed optimization corrects it).

- Always drain the Fuel Gas from the Tubing, which connects the cylinder to the instrument. (This ensures that no fuel gas remains in the system and there is absolutely no chance of getting the flame ignited accidentally).

- Always drain the Air Compressor. (This will ensure that there is no accumulation of water in the Air Tank. There will not remain any pressure on the Air carrying components of the instrument).

- Do not work on AAS without switching 'ON' the Exhaust Fan. (The Toxic gases from Standards or Samples may get spread in to the room and it may harm the persons present in the room).

- Do not use any Chemical, Standard, Sample, Blank or TDS etc., which are not properly marked. These may be of wrong family or concentrations. (Use of such Standards or Samples may have misleading results).

- Do not switch off any instrument while the fuel is burning. (This could lead to accidents).

- Do not try to switch on the burner without ensuring that air supply is on. (This could lead to accidents).

- Do not open the Flame Shield (Door in front of Burner) while the fuel is burning. (This will switch off the flame and it could be dangerous).

- Do not try to light the burner with very high fuel settings. Do not try to raise the fuel to very high level while doing optimisation. (Very high fuel setting could cause accidents).

- Do not try to raise the pressure of Acetylene by more than 12 psi or 0.8 bar. (It is dangerous to light the burner at higher pressures it could be accidental).

- Do not try to light the burner if there is a leakage of Fuel Gas. The leakage could be from any joint of Pressure Regulator or the tubing etc. (Lighting burner with a leaking fuel gas is extremely dangerous)

3. Determination Na^+, K^+, Ca^{2+}, Mg^{2+} using a IC:

Instrument operation should follow specific manual recommended by manufacturer.

To determine these 4 cations using the IC DIONEX-1000, please refer to section 12.

Record of observed problems and solutions preferred

Please make a note of problems that you have encountered with this equipment or procedure, their frequency, and the solutions you implemented to solve the problems. In the notes column, you may write anything significant that you wish to, including to what extent your solutions helped solve the problem. Such a record will help you and other NIAs as well.

Problem observed	Frequency	Solutions implemented	Notes
1.			
2.			

13.7 Vendor's contact

    S K Gupta
Envirotech Instruments Pvt Ltd
    A-271 Okhla Industrial Area Phase 1, New Delhi 110 020
    envirotech@vsnl.com

14.0 SOP for QA/QC

14.1 Scope

This SOP is for doing QA/QC to ensure the generation of good quality data.

14.2 References
Volumes 2 and 6 of the Technical Manual.

14.3 Data quality objectives
The required DQO values required by the monitoring programme are defined in the table below.

Table 11. DQO values for wet and dry deposition monitoring

Accuracy	Precision	Precipitation	Completeness
±15%	±15%	≥90%	≥80% - Precipitation & diffusive samples
			At least 4 valid TSPM/PM$_{10}$ samples/month

Accuracy

Accuracy is the ability of a measurement to produce results that are close to the "true" value. Lower systematic and random errors (refer to chapter on Basic Statistics) allow for higher accuracy. Accuracy (A) is computed for wet deposition and HVS samples (if used for gaseous sampling—no longer recommended) by the formula:

$$A = \frac{[(certified\ values) - (analytical\ values)]x\ 100}{certified\ values}$$

The accuracy of laboratory doing analysis for wet deposition samples and gaseous samples from an HVS can be assessed in an inter-laboratory comparison programme. Wet deposition samples (and if necessary SO_2 and NO_2 samples for urban monitoring sites) prepared artificially by the reference laboratory should be sent periodically to each of the participating national laboratory. The analytical values are the values obtained by the participating laboratory. The certified values are those obtained by the reference laboratory.

To assess accuracy of the results obtained by each laboratory, an inter-laboratory comparison should be done yearly with all participating laboratories receiving artificially prepared samples from the reference laboratory.

Precision

Precision is the ability of the measurement procedure to reproduce a result as closely as possible.

Sampling precision: Sampling precision should be established from time to time by duplicate sampling with co-located samplers or collectors. Identical procedures for sample collection, handling and storage.

Analytical precision: To estimate analytical variability, 5% of routinely analyzed samples should be analyzed twice. The sample should be divided into two portions; one portion being analyzed immediately after collection, and the other after 1 week. The latter portion should be refrigerated at 4°C until it is analyzed.

Analytical precision (S_i) is computed for wet deposition and the AAQ gaseous samples and is calculated with following formula:

$$S_i = \sqrt{\frac{\sum d_i^2}{2N_i}} \; x \; \frac{100}{A_v}$$

Where:

d_i = differences in the values of the duplicate analysis
N_i = number of sample pairs during duplicate analysis
A_v = mean of the duplicate analyzed samples

Precipitation

Precipitation (P) is computed for wet deposition measurement as the rainwater collected by the wet only and bulk collectors as a percent of water collected by a standard rain gauge.

P is computed monthly and annually as follows:

$$P = \frac{volume\ of\ precipitation\ measured\ by\ the\ collector\ x\ 100}{volume\ of\ precipitation\ measured\ by\ standard\ rain\ gauge}$$

Completeness

Completeness is measured as the ratio of valid sample time to the total sampling time required as per the sampling protocol for passive samplers and precipitation samples, expressed as a percent. Completeness for TSPM/ PM_{10} samples is defined a having collected at least four valid (14.5 hrs/collection time per sample) samples between the 10th and the 20th of each month. Completeness can also be measured as the ratio of the valid sample volume to the total sample that could have been collected as per the sampling protocol. Completeness can be measured as percent valid sample volume only for precipitation samples.

Percent valid sample time (PVST): Is the percent time for which a valid sample has been collected and which has a valid analysis. PVST can be used as a measure of completeness for samples obtained by using wet only and bulk collectors and diffusive samplers.

$$PVST = \frac{sampling\ time\ for\ which\ valid\ results\ are\ available\ x\ 100}{total\ time}$$

Precipitation samples: Completeness is the ratio of the valid sample actually obtained to a sample that could have been obtained, had the wet deposition monitoring been able to capture 100% of precipitation.

Percent valid sample volume (PVSV): Is the volume of valid precipitation sample, with valid analysis, expressed as a percent of total precipitation volume.

$$PVSV = \frac{volume\ of\ valid\ precipitation\ sample\ x\ 100}{total\ precipitation}$$

Precipitation samples must satisfy completeness DQO for both PVST and PVSV. It is sometimes possible that a precipitation sample may satisfy one of the completeness criteria but not the other. In such cases, it should be interpreted that completeness DQO was not satisfied.

Valid sample

A valid sample is one that falls within an expected range of values. An invalid sample is one where:

1. Sample contamination or error in sample collection, handling, storage or analysis, are very obvious.
2. For an HVS (only), the sample has been collected for ≤60% in a 24 hr sampling period, or less than 14.5 hrs.
3. The result is an outlier that is outside the expected range of values by a margin that is very large.

    Some outlier results cannot be immediately classed as invalid samples. In such cases, bias or systematic error of the analytical method and the laboratory use of the method should be assessed first. Bias is measured best in an inter-laboratory comparison study. However, if such a study is not on the horizon when a indeterminate outlier is obtained, it is possible to assess for laboratory bias by two methods: a) by measuring for recovery of known additions, or b) by analyzing duplicate samples and retaining the sign of the differences when calculating the average difference. From this value, subtract the method bias from the inter comparison study to determine the bias due to laboratory's practices as it interprets the method.

    If bias is within control, random error may have caused the outlier result. This should be checked using the Shewart's Control Chart. A control sample should be analyzed several times in quick succession and the Shewart's Control Chart used to determine whether the outlier is due to random error or whether the result is a true value.

    If after assessing for systematic and random error, there is still doubt about the validity of the sample, treat the sample as an invalid sample (when in doubt, discard the result).

14.4 Quality control

Monitoring site criteria: Representative monitoring sites must meet criteria laid down for them (see section 2 above).

Monitoring frequency: The sampling frequency for each sample should be as prescribed. Any deviations should be reported in the reporting formats. The monitoring protocol is:

- PM_{10} sampler 5 samples each of TSPM, PM_{10} per month; each of 24-hour collection time; collected between the 10th and the 20th of each month. A valid sample is one where the sample has been collected for $\geq 60\%$ time in one 24 hr sampling period, i.e., 14.5 hrs.

- Passive (Diffusive) samplers 12 samples each of SO_2, NO_2 and ozone per year; each sampler being exposed for 1 month from the first day to the last day of each month.

- Wet only collector   1 sample per week, i.e., 52 samples per year.

- Bulk collector   1 sample per week, i.e., 52 samples per year.

Registration of those working the programme: Those working on the programme should be registered with the NIA.

Monitoring schedules: Gantt charts for a work-time plan should be prepared and maintained.

Operational checks: All instruments and materials should undergo operational checks as required. For example, conductivity of deionised water used for rinsing, cleaning, dilution of samples, use in laboratory should be <0.15 mS m^{-1}. Only certified materials should be used. Instruments should be calibrated at the prescribed frequency.

- **Evaluation of reliability:** It should be ensured that instruments work within permissible sensitivity fluctuations. Repeat and parallel measurement should be done as prescribed.

- **Sample handling:** Handling, storage and transport of samples should be as prescribed.

- **Onsite inspections:** NIAs should conduct annual audits of sites and laboratories.

14.5   Quality assurance

An ion balance (R_1) should be within acceptable range. It should be computed as follows:

$$R_1 = \frac{(C_{eq} - A_{eq}) \; x \; 100}{(C_{eq} + A_{eq})}$$

Where C_{eq} and A_{eq} are the cation and anion equivalent concentrations in the sample expressed as µeq/L. The allowable ranges of R_1 in different concentrations are given below.

Table 12. Allowable ranges for R_1 in different concentrations

$C_{eq} + A_{eq}$ (µeq/L)	R_1 (%)
<50	±30
50-100	±15
>100	±8

R_2 should be within acceptable range: A comparison should be made between measured and computed EC of the sample, and R_2 computed as follows:

$$R_2 = 100 \; x \; \frac{(\Lambda_{calc} - \Lambda_{meas})}{(\Lambda_{calc} + \Lambda_{meas}} \qquad \text{expressed as a \%}$$

Where:

Λcalc (computed EC) = $\Sigma(C_i \bullet f_i)$, expressed in mS/m
C_i = concentration of ionic species i in solution, expressed in µmol/L
   at $25^{\circ}C$
And f_i = molar conductivity factor of ionic species I, expressed in Scm^2/mol
Λmeas = the measured EC, expressed in mS/m

The allowable ranges for R_2 in different concentration should be as given in the table below:

Table 13. Allowable ranges for R_2

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

- **Annual audits:** Annual audits should be conducted of the monitoring sites where samples are collected and the laboratory, where the samples are analyzed. Such audits may also be conducted an external agency, other than the NIA. The NIA may develop an audit format, which may be developed further by the auditor.

- **Inter-laboratory comparison:** An inter-laboratory comparison should be conducted annually.

15.0   SOP for data reporting and management

15.1 Scope

This SOP discusses data reporting and management

15.2 Data types

There are two types of data:

1. Monitoring setup data (site, instruments, equipment, human resources).
2. Monitoring data.   This consists of a) measured concentration of the parameter and flags explaining outliers or special circumstances explaining a data element and meteorological data; b) detailed data elements required for obtaining measured concentrations, eg, absorbance, rotameter/manometer and time totalizer readings.

15.3 Data reporting

Data elements 1 and 2b) need to be retained by the NIA and given to the Malé Declaration Network Secretariat only when required.

Data elements 2a) need to be given to the Malé Declaration Network Secretariat at the agreed frequency. Any statistical manipulation of this data and inferences drawn from them may also to be given to the Malé Declaration Network Secretariat.

15.4 Data reporting formats

15.5 Data storage

Data elements 1 may be updated as required and stored as hard/soft copy by the NIA.

Data elements 2b) may be retained by the NIA for 3 years after data elements 2a) have been published after approval by the Malé Declaration Network Secretariat.

Data elements 2a) need to be retained by the NIA and the Malé Declaration Network Secretariat.

<u>**Annex 1**</u>

Major Items to be included in national SOPs for wet deposition monitoring

To minimize differences between various monitoring site and laboratory staff, SOPs should be prepared for all elements of the monitoring and analysis process—from sampling through to data reporting. The SOP should be in accordance with the Malé Declaration wet and dry deposition monitoring manual.

It is important to ensure that SOPs are complied with reference to actual on site equipment and procedures. Even if samplers or analytical instruments conform to the monitoring manual, their manufacturers and/or types may be different in different institutions or analytical laboratories. SOPs should be prepared taking into account the condition of each organization/laboratory. Individual SOPs should clearly describe scope of application, designation of responsible staff and their supervisor, and reporting formats and so on. Every effort should be made to conform with the Malé Declaration manuals as closely as possible and any problems/issues apparent at the time of writing the country specific SOPs should be discussed with the Malé Declaration Secretariat and MoC.

In the following scheme, the fundamental items are listed regarding individual SOPs on wet and dry deposition monitoring. Additions and/or deletions may be needed, taking into account the actual condition of each laboratory in preparing SOPs.

1.0   Sampling

1.1   Appointment of sampling staff and their supervisors

1.2   Check of possible changes around the sampling sites
- Local situation (new construction of emission and contamination sources etc.)
- On-site situation

1.3   Check of sampling instruments apparatus
- Appearance of sampler (check for corrosion etc.)
- Operation of sampler (rain sensor, moving of lid, documentation of repair of sampler)
- Collection efficiency (comparison with standard rain gauge)
- Cleaning of sampling parts

1.4   Sampling methods
- Sampler (involving the documentation of checks and maintenance)
- Sampling interval (sampling dates)
- Change of sample vessels
- Addition of biocide

2.0   Sample transportation and storage

2.1   Transportation of samples

2.2   Sample storage
-        On-site storage
-        Laboratory storage

3.0   Measurement and chemical analysis

3.1   Appointment of analysis staff and their supervisors for each item

3.2   Development of training plan

3.3   Deionized water
-        Daily maintenance
-        Documentation of maintenance

3.4   Measurements with instruments
-        Measuring conditions of instruments
-        Calibration
-        Performance tests (sensitivity, stability, interference and its
         removal, documentation of repair)
-        Calculation of lowest detection limits and lowest determination
          limits
-        Documentation of maintenance

3.5   Operating procedures for measurements
-        Preparation of calibration curves
-        Measurement/analysis of samples
-        Repeated measurements/analyses
-        Check of sensitivity fluctuation

3.6   Treatment of measurement results
-        Calculation of concentrations
-        Measurement of sensitivity fluctuation
-        Repeat measurements/analyses
-        Calculation of ion balances
-        Comparison of measured and calculated conductivity

4.0   Quality assurance and quality control

4.1   Evaluation of sample collection
-        Comparison of precipitation amount with standard rain gauge
-        Evaluation of ion balance
-        Evaluation of conductivities

4.2   Evaluation of reliability
-     Evaluation of sensitivity fluctuations
-     Evaluation of repeated measurements/analyses
-     Evaluation of field blanks
-     Comparison between measured data and lowest detection and lowest determination limits

4.3   Evaluation of results
-     Representativeness of sampling sites
-     Evaluation of sample validity
-     Evaluation of completeness for the sampling period
-     Determination of total precision

5.0   Management of instruments, reagents and glassware

5.1   Management of sampling instruments
-     Appointment of management staff and their supervisors
-     Documentation of names of manufactures, types, manufacture dates and operation methods
-     Daily and regular maintenance and inspection methods (including troubleshooting, parts supply and recording)

5.2   Laboratory management
-     Appointment of management staff and their supervisors
-     Daily and regular maintenance and inspection methods (including items and recording format)

5.3   Management of measurement/analysis instruments
-     Appointment of responsible staff for each instrument, and overall measurement
-     Documentation of names of manufactures, types, manufacture dates and operation methods
-     Daily and regular maintenance and inspection methods (including troubleshooting, parts supply and recording)

5.4   Management of reagents, standard materials, etc
-     Appointment of management staff and their supervisors
-     Receiving and disposal of reagents (recording format of dates, manufacture names, dealers, purity, degree of standard and validity period)

5.5   Management of glassware and polyethylene vessels
-     Appointment of management staff and their supervisors
-     Cleaning methods
-     Storage
-     Confirmation of cleanness

6.0   **External audit**
-          Check of sampling sites
-          Measurement of field blank values
-          Operation check of samplers
-          Evaluation of the results of quality control
-          Evaluation of the measured results

Examples for Measurement and chemical analysis for several parameters

1. pH using pH meter

- Rinse the Probe with MiliQ water and dry with tissue paper
- Immerse the electrode in to well mixed sample
- Read the pH value and the Temp when it becomes stable

2. Conductivity using EC meter

- Rinse the electrode with MiliQ water and dry with tissue paper
- Immerse the electrode in to well mixed sample
- Read the EC value and the Temp when it becomes stable

3. Chloride (mg/L) – Titrimetry

- 50ml (Sample, Blank) (pH 7-10) into 250ml volumetric flask
- 1ml K_2CrO_4 (indicator)
- Titrate with 0.0141 N AgNO$_3$

Pinkish Yellow at the end

Chloride (mg/L) $\dfrac{(A-B)\times 0.0141\times 35450}{mL(sample)} = \dfrac{(7.25-0.4)x\ 0.0141\ x\ 35450}{50}$
= 68.47

50mL sample
A (mL titration for the Sample) = 7.25
B (mL titration for the Blank) = 0.4

4. Ca^{2+} (mg/L) – Titrimetry

- 100ml (Sample, Blank) in to 250ml volumetric flask
- Adjust pH to 12-13 by adding 5mL of 1N NaOH
- Add 0.2 - 0.4g Ca^{2+} hardness indicator
- Titrate with 0.01M EDTA

Light purple at the end

Ca^{2+} hardness (mg/L) = $\dfrac{(V1-V2)\times A\times 1000}{mL(sample)}$ = 63.00
100mL sample

$V1$ (vol of EDTA for the Sample) = 6.3
$V2$ (vol of EDTA for the Blank) = 0
A = the mg CaCO$_3$ equivalent to 1.0 mL EDTA = 1 for 0.01M EDTA
Ca^{2+} (mg/L) = Ca^{2+} hardness (mg/L) × 0.4 = 25.2

5. **Mg^{2+} (mg/L) = Mg^{2+} as CaCO$_3$ (mg/L) × 0.243**

Mg^{2+} as CaCO$_3$ (mg/L) = Total Hardness as CaCO$_3$ (mg/L) – Ca^{2+} Hardness as CaCO$_3$ (mg/L)

- 100ml (Sample, Blank) in to 250ml volumetric flask
- Add 2 mL buffer solution
- 0.2 - 0.4g Ca^{2+} hardness indicator
- Titrate with 0.01M EDTA

Blue at the end

Total hardness as CaCO$_3$ (mg/L) $= \dfrac{(V1-V2) \times A \times 1000}{mL(sample)} = 99.0$

100mL sample
$V1$ (vol of EDTA for the Sample) = 9.9
$V2$ (vol of EDTA for the Blank) = 0
A = the mg CaCO$_3$ equivalent to 1.0 mL EDTA = 1 for 0.01M EDTA
Ca^{2+} Hardness (mg/L) = 63.0 (taken from previous section)

Mg^{2+} (mg/L) = (99.0 – 63.0) x 0.243 = 8.75

6. **Ammonical Nitrogen – Distillation**

- 100ml (Sample, Blank) into 300ml Test tube
- 5mL borate buffer & few glass beads
- Adjust pH > 9.5 by adding 6N NaOH *(by using pH paper)*
- The samples change to green when distillation is over and blank remains blue
- Add absorbing solution of 25mL into Sample and Blank
- Titrate with 0.02N H$_2$SO$_4$

Pale lavender at the end

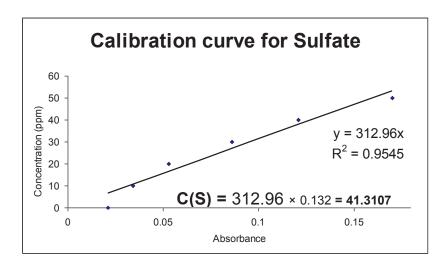NH$_3$-N (mg/L) $= \dfrac{(V1-V2) \times 280}{mL(sample)}$

100mL sample
$V1$ (vol of 0.02N H$_2$SO$_4$ for the Sample)
$V2$ (vol of 0.02N H$_2$SO$_4$ for the Blank)

7. **Sulphate – Spectrometry**

- 0, 10, 20,…50ml of SO_4^{2+} into 100mL volumetric flask
- Dilute up to the mark after adding 5mL of conditioning reagent into all 6 (Samples and Blank)
- Mixing in stirring apparatus
- Add a full spoon of $BaCl_2$ (Stirring at constant speed for 1 minute)
- Just after 1 minute pour into the curvet cell to measure the Absorbance at 420nm at 30 sec interval (for 4mins)
- Max Absorbance

Calibration curve for Sulfate

$y = 312.96x$

$R^2 = 0.9545$

C(S) = 312.96 × 0.132 **= 41.3107**

Concentration (ppm) vs Absorbance